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# Characterizations and Industrial Applications for Cement and Concrete Incorporated Natural Zeolite

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## Abstract

Zeolites have been widely used in various industries, leading to a high commercial value; this is mainly due to the wide diversity of naturally occurring species and the ability to synthesize new types. In the cement and concrete industry, natural zeolite is a popular natural pozzolanic material in some regions of the world owing to their economic, environmental, and technical advantages, among others, used pozzolanic materials. Many works have reported the use of natural zeolite as substituent material for cement in mortar and concrete. Generally, the use of natural zeolite can overcome environmental and economic problems associated with the use of high quantity of cement; furthermore, it is shown a strength enhancement and durability improvement properties of cement and concrete composites. In this context, this chapter strives to review the application of natural zeolite as pozzolan in cement and concrete composites, its characteristic, its proper incorporation, and each of the influencing parameters. In addition, the elaboration methods, textural and mechanical characterization, and applications of these composites will be treated.

**Keywords:** cement substitution, concrete, hydration, pozzolanic material, natural zeolite

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## 1. Introduction

The number of zeolites is constantly increasing; currently, the commission of structures of the International Zeolite Association (IZA) recognizes 232 unique structures that have been approved and have been assigned three letters of code [1]. The chemistry of zeolite has been

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a subject of significant interest due to the ion exchange properties of zeolite, crystallinity, thermal stability, and well-defined molecular size closed structures [2]. The code ASTM-618 (American Society for Testing Materials) defines pozzolans as siliceous or aluminum-siliceous materials, which by themselves have little to no cementing value, but when they are finely divided and in the presence of water and calcium hydroxide (Cal), they react chemically at room temperature to form cementitious agents [3].

Concrete made from Portland cement is the most widely used construction material today, mainly due to its cost-benefit ratio, in terms of compressive strength. Its manufacture involves the release of approximately 900 kg of carbon dioxide per 1000 kg of produced cements. Likewise, this amount of cement demands the use of 1693 kg of water and 4798 MJ in energy resources [4]. This is the importance of reducing the environmental impact that the manufacture of the same produces. The use of mineral additions in the production of concrete is a technologically possible alternative. However, its use requires high standards of assurance and quality assurance, similar to those of cement [5].

The extent of the benefits provided by the use of blended cements increases with increasing content of additives in blended Portland cements. However, the content of additives in blended Portland cements, especially for natural pozzolans, is limited by some factors, such as an increase in water requirement and a decrease in the rate of strength development of the cementitious systems. It has been found that the blended cements containing high volume (55% by weight) of natural pozzolans (volcanic tuff) possess lower 28-day compressive strength when compared to the reference Portland cement, although they show similar strength values at 91 days of age [6, 7]. Therefore, the production of high-volume natural pozzolan blended cements, which are able to compete against ordinary Portland cement, requires natural pozzolans exhibiting significantly high-strength activity.

In this chapter, we intend to review the literature available on these topics, addressing structural, mineralogical, and morphological properties, in the case of zeolites, and manufacturing processes, characterization, evaluation, and application, in the case of cement. As well each of the parameters influences the formation of cementing pastes, such as hydration, porosity, transport properties, durability, and carbonation, among others.

## **2. Properties of natural zeolite**

### **2.1. Pozzolanic activity surface area**

Pozzolans are materials with an amorphous and aluminous siliceous or siliceous content, which react with calcium hydroxide in the presence of water to form cementitious hydration products [8]. Among the most common natural pozzolanic materials, such as fly ash and silica fume, is zeolite, which is used in some regions of the world, due to its lower cost and accessibility [9, 10]. Zeolites generally show pozzolanic activity due to their structural characteristics, and their use as additions in cements provides additional technical advantages to construction materials [11].

The pozzolanic properties of natural zeolites are determined by their high sorption ability, ion exchange potential, and specific structure. Their action involves various steps, including

cation exchange; dissolution and/or breakdown of the zeolitic structure; possible formation of transient gel phases; and precipitation of hydrated calcium silicates and aluminates [12].

There are different methods of work for the evaluation of pozzolanic activity. In general, these methods are classified as indirect or direct, depending on the parameter to be studied [13]. Direct methods monitor the presence of  $\text{Ca(OH)}_2$  and its subsequent reduction in abundance over time, as the pozzolanic reaction proceeds, using analytical methods such as X-ray diffraction (XRD), thermogravimetric analysis (TGA), or assessment chemistry.

The Frattini test is a commonly used direct method involving chemical titration to determine the concentrations of  $\text{Ca}^{2+}$  and  $\text{OH}^-$  dissolved in a solution containing Portland cement and the test pozzolan. This method has been used to measure the pozzolanic activity of metakaolin [14], catalytic cracking residues [15], fly ash [16], and zeolites [17].

The saturated lime method is a simplified version of the Frattini test, in which pozzolan is mixed with a saturated solution of lime (slaked lime,  $\text{Ca(OH)}_2$ ) instead of Portland cement and water. The amount of lime set by the pozzolan is determined by measuring the residual dissolved calcium [18].

Indirect test methods measure a physical property of a test sample, which indicates the degree of pozzolanic activity. This may involve the measurement of properties such as compressive strength, electrical conductivity, or heat evolution by conduction calorimetry. The results of an indirect pozzolanic activity test are often corroborated by direct tests to confirm that pozzolanic reactions are occurring [19–22].

## 2.2. Ion exchange

Zeolites naturally occur from volcanic origin and belong to the family of hydrated aluminosilicates. Their microporous structures can accommodate a wide variety of cations, which compensate the negative charge created by the substitution of Si by Al. Therefore, natural zeolites appear as cation exchangers in many applications, thanks to this property. Some of the main applications of zeolites in this area include the selective treatment of wastewater, extraction of ammonia, odor control, extraction of heavy metals from nuclear, mining and industrial wastes, soil conditioning for agricultural use, and even as an additive for animal feedstock [23].

Among all identified zeolites, clinoptilolite is the most abundant natural zeolite. In the structure of the zeolite, there are three relatively independent components: the aluminosilicate system, the interchangeable cations, and the zeolitic water. The simplified empirical formula of zeolites is:



where  $x$  can vary from 0 to 0.5 and  $\text{M}^{n+}$  represents Alkali and alkaline earth metals. The structure of aluminosilicates is the most conserved and stable component and defines the type of structure water molecules that can be presented in voids of large cavities and joined between ion systems and ions interchangeable through aqueous bridges. Water can also serve as a bridge between interchangeable cations.

The channels of the natural zeolites are predominantly occupied by  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{H}_2\text{O}$ , as well as traces of  $\text{Mg}^{2+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Pd}^{2+}$ ,  $\text{K}^+$ , and  $\text{Ba}^{2+}$ . Among them,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  can be

exchanged with  $\text{NH}_4^+$  ions. The type and density of interchangeable cations influence the stability of the cavities and the thermal behavior of a zeolite [24–27].

### 2.3. Expansion at elevated temperatures

Concrete is more durable against elevated temperature and fire effects than many other construction materials. Although ordinary concrete is considered to have a satisfactory fire resistance, it can lose 40–60% of its original strength upon exposure to 500°C [28]. Bilim [29] reported mortars containing zeolite show generally better performance to high temperatures about 900°C.

Negative thermal expansion (NTE) is an unusual phenomenon in which materials shrink in volume when heated (or expand when cooled). It has only been observed in a small number of solids, including some metallic oxides, cyanide metal, polymers, and zeolites [30]. It is important to understand how zeolites behave as a function of temperature. In recent years, research has been carried out on NTE in purely siliceous zeolitic structures [31, 32] and with a little less attention [31, 33] to aluminum-containing zeolites, in which it is known that structures and properties are particularly sensitive to extra-structural charge balancing cations and host molecules in the pores.

Water is an important guest molecule in the pore system of natural and synthetic zeolites. Adsorbent and catalytic properties of zeolites are also strongly affected by their water content. Cations seek the most energy-stable positions, and these positions play an important role in the catalytic activity.

This subject was investigated by Ilić and Wettstein [34], who examined three distinct temperature ranges for volumetric thermal expansion. Associates with the dehydration of coordinated water molecules and with transverse vibrations of bridging oxygen atoms result in the reduction in the bonding angle.

### 2.4. Desorption of water at low humidities

As already mentioned, zeolite is a porous solid with a large capacity to house water molecules and can be used as a pozzolanic aggregate. The efficiency of porous aggregates as an internal curing agent in concrete depends on its water absorption and desorption characteristics. The desorption behavior of zeolite and other porous aggregates depends on the structure of their pores and mainly on the porosity size distribution. In general, a thick pore structure will lead to better desorption behavior [35–37].

Ghourchian et al. [38] were conducted a study of the performance of the porous aggregates and concluded that the water desorption of the zeolites is closely related to their microstructure. For a proper desorption, a thick-pored structure is needed with a high proportion of well-interconnected pores. While, in the case of zeolites, despite having a high-water adsorption capacity, they have a fine pore structure, which leads to retaining the water absorbed.

### 2.5. Re-adsorption of water at high humidities

Zeolites are selective adsorbents for the removal of carbon dioxide, water vapor, and other impurities from the mixtures. The impurities adversely affect the capacity of the adsorbents used for the separation or purification. Water is a strongly adsorbed component in zeolite [39].



Due to the nature of the cation exchange, natural zeolites show a high performance in the adsorption of cations in aqueous solution such as ammonium and heavy metals. However, zeolites show varied ion selectivity and competitive adsorption for multicomponent system [27]. In addition, these materials are not good adsorbents for the adsorption of anionic and organic ions. Surface modification with cationic surfactant can change the surface charge of the natural zeolite, making them applicable for adsorption of anions and organics. Most zeolites when heated give off water continuously rather than in separate stages at certain temperatures. The dehydrated zeolite can then reabsorb the original amount of water when exposed to water vapor. Recent investigation has shown that some zeolites such as phillipsite and gismondite lose and gain water in a stepwise manner. All-silica zeolites are chemically and hydrothermally more stable than aluminum containing ones and are therefore preferred for membrane application, including for dehydration, even though these types of membranes are hydrophobic [40].

The adsorption characteristics of any zeolite depend on the detailed chemical/structural composition of the adsorbent. The Si/Al ratio, the type of cation, the number, and the location are particularly influential in the adsorption. These properties can be modified by various chemical treatments to improve the separation efficiency of the natural raw zeolite. Acid/base treatment and impregnation with surfactant by ion exchange are commonly used to change the hydrophilic/hydrophobic properties for the adsorption of various ions or organic [27].

### **3. Effects of natural zeolite on the properties of cement and concrete composites**

#### **3.1. Mechanical properties**

In general, the higher the cement replacement by natural zeolite has the lower the compressive strength. However, the percentages of reduction in resistance generally decrease with increasing age in cement. This behavior may be related to the pozzolanic activity of the natural zeolite. In terms of compressive strength, it appears that natural zeolite performs better in mixed cement compounds with lower water-cementitious material (w/cm) ratio [41].

In term of compressive strength, it seems that natural zeolite performs better in blended cement composites with lower w/cm ratios. Ahmadi and Shekarchi [42] showed that the concretes containing natural zeolite with a w/cm ratio of 0.40 displayed higher compressive strength than the control mixture at the ages of 3, 7, 28, and 90 days, whereas contrary results were obtained for the concretes with a w/cm ratio of 0.5 in the present study. Markiv et al. [43] showed, recently, that the substitution of cement by zeolite resulted in some reduction in strength until 90 days of hardening, but after 180 days, compressive strength of concretes containing zeolite exceeds the strength of concrete without zeolite.

Uzal and Turanlı [44] reported the similar compressive strength of mortar with 55% zeolite in the binder to that of 100% Portland cement mortar, but this could only be achieved using superplasticizers. Karakurt and Topçu [45] found 30% replacement of Portland cement by zeolite in their blended cement mortars as optimum; the compressive strength was similar to the reference mortar. Valipour et al. [46] observed a fast decrease in the compressive strength

of concrete with the increasing amount of zeolite (10–30% of the mass of Portland cement) in the mix, even with an increasing superplasticizer dosage.

### 3.2. Alkali-silica reaction

It is generally recognized that the addition of pozzolan reduces the calcium hydroxide content in cement paste and improves the permeability of concrete [47]. The most important concerns in the design of durable concrete are the alkali-silica reaction (ASR) and sulfate attack.

ASR causes the premature deterioration in concrete. Alkali hydroxides present in the concrete pore solution react with amorphous or poorly crystalline silica phases in aggregates, forming a gel that imbibes water and expands [48]. The expansive pressure generated by the hydrated alkali silicate has been widely believed to induce cracking and deterioration of concrete. However, this notion may not be necessarily correct. Concrete is a porous material, and the hydrated alkali silicate is rheologically a fluid material that can slowly diffuse into the pores and preexisting cracks to lose its expansive pressure. The diffused alkali silicate has been proposed to generate an expansive pressure by reacting with  $\text{Ca}^{2+}$  ions [49].

### 3.3. Transport properties

The transport properties of concrete with the addition of zeolite have been studied by Ahmadi and Shekarchi [42] and Najimi et al. [41], who found a significant reduction in the penetration of water and chlorides, in the concrete with natural zeolite. On the other hand, Valipour et al. [50] reported that water sorptivity and gas permeability increase with the increase of zeolite in the mixture. Similar results were obtained for the oxygen permeability of Ahmadi and Shekarchi [42] but only for the dose of zeolite greater than 10%.

The liquid water transport parameters increase with the increasing addition of zeolite in the mixed binder. This is due to the pore distribution, that is, the volume of capillary pores, which is the most important factor, in the capacity of a porous medium to transport water in liquid form. In studies conducted by Vejmelková et al. [51], it was found that, for lower zeolitic contents, up to 20%, the values of water absorption coefficient and apparent moisture diffusivity were still acceptable. However, for high levels of cement replacement, the acceleration of water transport is so high that it could present a concrete durability risk.

Ahmadi et al. [52] reported that natural zeolitic addition in concrete results in better water absorption, water penetration, and electrical resistivity, and the ternary mixtures containing natural zeolite with silica fume or fly ash perform best in water permeability and chloride penetration tests.

### 3.4. Durability properties

#### 3.4.1. Sulfate and acid attack resistance

The durability of a concrete is a determining feature for its use, and this is due to the different corrosive environments to which it is exposed, including marine construction or hydraulic engineering. One of the important factors of this characteristic of concrete is the type of cement.

It has been shown that the use of pozzolanic additives for cements increases their resistance to corrosion, due to the high impermeability, the decrease in the content of  $\text{Ca(OH)}_2$ , and the reduction in the presence of capillary pores in the matrix. In fact, it hinders the penetration of aggressive media [53]. Concrete can be attacked by acids both internally and externally. The existence of different kinds of acid in the environment around the concrete causes a great reduction in the pH of the concrete, and the reaction between the acids and the hydrated and unhydrated cement finally leads to the deterioration of the concrete. The primary effect of any type of acid attack on concrete is the dissolution of the cement paste matrix [54].

Małolepszy and Grabowska [55] carried out a study dedicated to studying the sulfate resistance of a cementing paste with zeolitic addition. They confirmed the beneficial effect of the zeolitic additive for cement mortars because those containing zeolite did not show visible damage in the surface in an aggressive solution of sulfate, while in the mortar that did not possess it, I present surface microcracks pronounced. Exfoliation of corners and colors changes (yellow and gray incursions on the walls of the samples).

#### *3.4.2. Drying shrinkage*

The contraction is a phenomenon in which the concrete reduces its volume with time. The internal and external drying of the concrete is the main factor that causes the contraction. Internal drying, also known as self-desiccation, is caused by the consumption of water in the hydrating cement paste and the resulting creation of interfacial menisci between the pore fluid and the vapor in progressively smaller pores [56]. The creation of meniscus leads to the accumulation of capillary pressure that puts the solids under compression and causes a macroscopic contraction, called autogenous contraction [56, 57]. External drying takes place due to the evaporation of water from the surface of the concrete to the ambient air or due to the migration of water to adjacent members. The evaporation of moisture from the surface of the fresh concrete can cause cracking of the plastic shrinkage [58], and a greater moisture loss of the hardened concrete can cause shrinkage by drying [59].

Generally, the durability properties of concrete improved by partial replacement of cement with natural zeolite. However, the concrete that contains 15% of natural zeolite achieves a suitable drying shrinkage. The latter does not have a satisfactory performance in the acid environment [41].

#### *3.4.3. Freeze and thaw resistance*

The pores can have an effect on the properties of the material in different ways. The compressive strength is primarily related to the total porosity, the size of pores and their distribution, the size and form of the biggest pores, and the relation between the pores. Shrinking is the function of energy exchange on the surface of pore walls. Durability depends on freeze-thaw resistance and is controlled by the volume of air entrained in the pores and spaces between the pores [60].

Water absorption and freeze-thaw resistance of hardened cement paste depend on the size of pores and capillaries, their type and distribution, and the closing of the pores. Closed and small

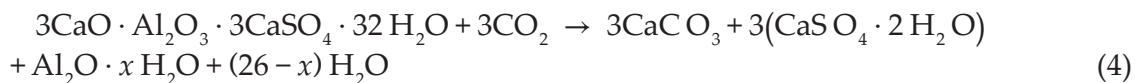
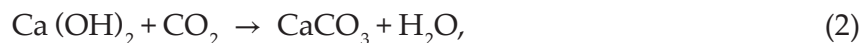


pores are not filled with water completely. Pores that are not filled up with water are called reserve pores. In freezing conditions, some water from fully filled pores may move to these reserve pores and thus create a space for ice expansion. The distance between filled and unfilled pores must be small, so that the freezing water would move from filled to unfilled pores [60].

Capillary pores in hardened cement paste are formed through the evaporation of excessive water used in producing the cement paste. Usually, the cement paste is made using more water, and it is necessary for chemical reactions that occur during the setting of concrete. According to A. K. Kallipi, capillary pores are open and easily fill with water. The destructive effect during freezing depends on the amount of water in hardened cement paste. Presumably, the bigger amount and size of the pores reduce the freeze-thaw resistance of concrete. Furthermore, it is important to mention that the concrete prepared with saturated and dry recycled aggregates exhibits poorer freeze-thaw resistance, whereas better results obtained from the concrete made with the semi-saturated aggregates [61].

#### 3.4.4. Carbonation

When a cementitious paste begins to harden with an air cure, and after the first minute of hydration, it is subjected to the action of carbon dioxide ions ( $\text{CO}_3^{2-}$ ) contained in the air, which reacts with  $\text{Ca}^{2+}$  ions of the portlandite, ettringite, and the silica gel of calcium in the form of Ca-carbonates ( $\text{CaCO}_3$ ). This carbonation of the hydrate products is provided in the following schemes [62]:



The air-curing conditions normally increase carbonation and cause incomplete hydration, self-neutralization, and drying shrinkage. These effects are most probably caused by decreasing the capacity for retaining sufficient water during the hydration and pozzolanic reactions. The depth of the carbonate layer formed depends on the contact time with  $\text{CO}_2$  and its concentration in the surrounding environment as well as the diffusion coefficient of the hardened cement paste [63–65]. As the air-curing conditions are more important for long-term reactions than for short-term ones, the C2S phase, which usually reacts after 21 days, is the most readily affected cement phase. The volume changes, which accompany the carbonation processes, lead to the filling of empty pore volumes with Ca carbonates and densify the structure of the hardened cement paste. Groves et al. [66], the microstructure of hardened pastes of  $\text{C}_3\text{S}$  and a smoke mixture of  $\text{C}_3\text{S}$ /silica by TEM, before and after partial carbonation in a pure  $\text{CO}_2$  atmosphere, concluded that calcium carbonate forms mainly in the outer product regions such as microcrystalline vaterite or calcite, which leads to a substantial level of carbonation of pulp in a day with a little additional carbonation in the coming days. The depth of penetration of  $\text{CaCO}_3$  in the cement matrix depends on the time of contact of carbon dioxide and its concentration in the medium and on the coefficient of diffusion [67].

Lilkov et al. [62] have studied the early hydration of the cement, mixed with additives of natural zeolite (clinoptilolite), and they concluded that the process of carbonation on the surface of the cement paste takes place directly between the calcium ions of the solution and the carbon dioxide of the air without the formation of portlandite and ettringite. The depth of the carbonate layer formed depends on the contact time with the  $\text{CO}_2$  and the rate of diffusion through the formed layer, where the crystallite size of the calcite is reduced overtime days.

#### 3.4.5. Corrosion of steel reinforcement

The main causes of reinforcing steel corrosion are reacted with various aggressive agents, such as atmospheric carbon dioxide and chloride ions, and chemical attack throughout the service life of the concrete [68]. In ordinary Portland cement, these harmful effects can be reduced by substitute pozzolans [69]. Under a corrosive environment, concrete properties can be improved by using pozzolans such as zeolite and diatomite [68].

Steel rebars are protected against corrosion by both chemical and physical mechanisms. The chemical protection is provided by the concrete high pH (12–13), which promotes the formation of a passive film on the steel surface. On the other hand, concrete acts as a physical barrier, hindering the access of aggressive agents. However, oxygen, water, chlorides, and/or carbon dioxide can be transported through concrete, reaching the rebars and inducing the corrosion attack. The chloride ions, when above a threshold value, provoke a local breakdown of the passive film and pitting corrosion. Carbon dioxide and its hydrolysis products react with the alkaline species present in concrete, leading to pH values as low as 9 [70].

Ahmadi and Shekarchi [42] found a positive effect of zeolite in cement mortar on the resistance to alkali-silica reaction. Janotka and Krajčí [71] reported an improvement of sulfate corrosion resistance of zeolite-containing concrete. Similar effects of zeolite on alkali-silica reaction and sulfate resistance were observed by Karakurt and Topçu [45]. On the other hand, Najimi et al. [41] reported a significant strength reduction of zeolitic concrete after exposure to sulfuric-acid environment, that is, ~20% after 356 days when compared with ~5% for reference Portland-cement concrete.

#### 3.4.6. Chloride-induced corrosion

Besides eco-friendly, concrete should be sustainable and durable due to its use in infrastructure applications, which are mostly in aggressive environments, such as harsh marine environments with highly possible chloride-induced corrosion. Valipour et al. [72] reported that natural zeolite from a durability point of view in harsh marine environments could be a good option for replacement of cement even comparing with metakaolin and silica fume, which would be beneficial even from environmentally friendly point of view. Because concrete containing 20% replacement level in splash exposure showed chloride diffusion resistance even better than metakaolin with 5% replacement level and silica fume with 5 and 7.5% replacement level.

Several studies have indicated that lowering the w/b ratio and adding different types of pozzolanic materials to the mix can improve the compressive strength, durability, and permeability of concrete. Lowering the w/b ratio reduces the porosity, which thereby reduces chloride

ingress during the exposure period by as much as 25% [46]. Moreover, pozzolanic materials are being used widely as mineral admixtures to enhance the mechanical properties of concrete and thereby improve the concrete's microstructure. These admixtures, either natural or artificial, reduce the  $\text{Ca(OH)}_2$  content produced during the cement hydration process and instead form C—S—H gel through the secondary reactions. This process retards the hydration process, significantly reducing the porosity and permeability of the concrete [73–75].

Valipour et al. [76] found that the partial replacement of cement by 10 and 20% natural zeolite drives a higher compressive strength at 28 days, while 30% zeolitic replacement decrease the compressive strength when compared with conventional concrete. Moreover, the use of natural zeolite to improve the durability of concrete in aggressive environments, such as the Persian Gulf, results in a concrete with appreciably low chloride permeability.

#### 3.4.7. Heat of hydration

Nowadays, there is a discussion concerning the role of natural zeolitic effects on the blended cement hydration during the time. During the early stage of hydration, the effects of zeolite are related to the critical role played by their structure and the large surface area of the particles determining the cation ability in the pore solution and the collateral effect on stimulation of Portland cement hydration due to the low reaction degree of the zeolite [77]. The later stage is the proper pozzolanic reaction between the CH liberated during the hydration of cement and the soluble  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  present in bulk zeolite occur after 2 weeks producing compounds with cementing properties [78, 79]. Some zeolites are thermally activated [80]. Özen et al. [10], Cornejo et al. [81], and García de Lomas et al. [82] studied the early-age hydration heat of Portland cement blended with a spent zeolite catalyst in an amount of up to 35% of the mass of cement, but the composition of the applied catalysts was significantly different from the natural zeolite. Caputo et al. [83] analyzed the hydration heat development in natural zeolite samples mixed with portlandite in a 1:1 ratio.

Furthermore, Tydlitát et al. [84] concluded that natural zeolite did not react during the early age, but it causes the acceleration of cement phase's hydration. Hence, the early effects of zeolitic addition depend on their physical and chemical characteristics, and it also depends on the Portland cement composition.

## 4. Application of natural zeolite as pozzolan in cement and concrete composites

### 4.1. Characteristic

Supplementary cementitious materials (SCMs) are natural or by-product materials, which react with  $\text{Ca(OH)}_2$ , (CH), and form hydraulic compounds, such as hydrated calcium silicate hydrate (C—S—H) and calcium aluminate hydrate (C—A—H) [1]. Natural zeolite belongs to the group of natural SCM, whose pozzolanic activity depends on several factors (chemical and mineralogical composition, particle size distribution, specific surface area, cation-exchange capacity, Si/Al ratio of the zeolite framework, etc.) [77]. Each of these factors provides unique characteristics to each cement mix.

In the previous studies concerning the use of zeolites in concrete production, one of the most frequent topics was their pozzolanic activity as a fundamental condition for their utilization as supplementary cementitious materials (SCMs). Perraki et al. [77] reported a good pozzolanic reactivity of zeolite, 0.555 g of  $\text{Ca}(\text{OH})_2$  per 1 g of zeolite according to the Chapelle test. Ahmadi and Shekarchi [42] found out that the pozzolanic activity of zeolite was lower than silica fume but higher than fly ash.

Many studies have promoted the use of the zeolite-bearing tuffs as SCMs due to their positive influence on the long-term compressive strength and durability. Nevertheless, the variability in tuff's mineralogical and physical properties results in limited understanding of pozzolanic activity of natural zeolites.

When zeolite is added to the cement, at a level of around 10%, some characteristics are modified, such as, an increase in compressive strength [43, 85], a decrease in pore size [86, 87], and an increase in corrosion resistance to the acid solution [55, 88].

#### 4.2. Proper incorporation

Many authors have talked about the appropriate amount of zeolite that must be incorporated into the cement, so that it improves its properties or it can maintain them. Najimi et al. [41] found out that incorporation of 15% natural zeolite in the blended binder improved compressive strength of concrete, but for concrete with 30% zeolitic content, they observed a 25% strength decrease even with adding a superplasticizer, which was not used in the reference mix; they concluded that concretes incorporating zeolite are characterized by the reduction in the heat of hydration and consequently of thermal cracking; and they also improved durability properties such as chloride ion penetration, corrosion rate, drying shrinkage, and water penetration. Ahmadi and Shekarchi [42] also reported that the incorporation of natural zeolite as a mineral admixture in concrete enhanced its durability properties. However, various types, structures, and purities of natural zeolites influence concrete strength and durability in different ways and can lead in some cases to contradictory results in experimental studies and observed an increase in compressive strength for up to 20% of natural zeolite used as Portland cement replacement, but this was achieved with an increasing amount of superplasticizer in the mixes containing zeolites. Uzal and Turanli [44] reported the similar compressive strength of mortar with 55% zeolite in the binder to that of 100% Portland cement mortar, but once again, this could only be achieved using superplasticizers; they describe that a lime reactivity of the clinoptilolite zeolite is comparable to silica fume, higher than fly ash and a non-zeolitic natural pozzolan. Therefore, calcium hydroxide as a cement hydration product combines with natural zeolite consisting of reactive  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  to form calcium hydrosilicates. Karakurt and Topçu [88] found 30% replacement of Portland cement by zeolite in their blended cement mortars as optimum; the compressive strength was similar to the reference mortar. Valipour et al. [50] observed a fast decrease in the compressive strength of concrete with the increasing amount of zeolite (10–30% of the mass of Portland cement) in the mix, even with an increasing superplasticizer dosage. Investigations of mechanical properties of concretes show that the substitution of cement by zeolite resulted in some reduction in strength until 90 days of hardening, but after 180 days, compressive strength of concretes containing zeolite exceeds the strength of concrete without zeolite. Introduction of zeolite and chemical admixtures in concrete permits the modifications of the phase composition of

cement hydration products with the formation of an extra amount of calcium hydrosilicates, hydrogelenite, and ettringite [43].

4.3. Influencing parameters

Najimi et al. [41] concluded that concretes incorporating zeolite are characterized by the reduction of the heat of hydration and consequently of thermal cracking and improved durability properties such as chloride ion penetration, corrosion rate, drying shrinkage, and water penetration. Sabet et al. [89] and Ahmadi and Shekarchi [42] also reported that the incorporation of natural zeolite as a mineral admixture in concrete enhanced its durability properties. However, various types, structures, and purities of natural zeolites influence concrete strength and durability in different ways and can lead in some cases to contradictory results in experimental studies.

Uzal and Turanli [44] reported that the type of major cation was found to be one of the probable factors governing the pozzolanic activity of clinoptilolite zeolites by affecting their degree of solubility in alkaline conditions. Experimentally demonstrated that pastes of blended cements containing a large amount of clinoptilolite tuff contain less amount of pores >50 nm when compared with Portland cement paste, which is beneficial in terms of mechanical strength and impermeability of the pastes.

4.4. Elaboration methods

The methods of preparation of cement mixtures with zeolite vary according to the type of study and parameter that is intended to know, and this is due to the constant search to improve their properties. However, there are regulations that help to delimit the use and management of pozzolans, this, if it is intended that the study has a commercial impact, or that meets the standards established for the development of mortars (Table 1).

Several authors have investigated how to improve the mechanical properties of cement with zeolite, and its resistance to compression is specific. Valipour et al. [50] and Chan [90] were agreed that, to improve this characteristic, cement mixtures should not exceed 45% of zeolitic addition. While if what is desired is to avoid the carbonation process of the cement, the additions should

Name	Scope
ASTM C-618	Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete
ASTM C-191	Standard test methods for time of setting of hydraulic cement by the Vicat needle
ASTM C-33	Standard specification for concrete aggregates
ASTM C-311	Standard test methods for sampling and testing fly ash or natural pozzolans for use in Portland-cement concrete
ASTM C-1202	Standard test method for electrical indication of concrete’s ability to resist chloride ion penetration
ASTM C-876	Standard test method for corrosion potentials of uncoated reinforcing steel in concrete
ASTM C150	Standard specification for Portland cement

Table 1. Standard specifications by ASTM.



not exceed 30% [62, 91, 92] because this process is more evident in the early hydration phase, but it reduces with the passage of time. It is necessary to consider that the hydration of the cement is perhaps the most important aspect because it will derive almost all the processes addressed in this article, besides being a determining factor in the cementing process of the mixture. Several researchers [84, 93, 94] concluded that the addition of zeolite to the cement paste greatly increases the early stage of hydration, and therefore, it is not recommended to exceed 40% of pozzolanic addition in the mixture. In this way, operational parameters that contribute to the development of a composite mix with the best features and operational performance can be established.

It is not enough to establish limits in the substitution of cement with pozzolans because the structure of the zeolite also plays a very important role in the interaction with the mixture; as already mentioned, there is a great variety of zeolites, each with its respective family and structure [95], and the treatment that each one must receive before its incorporation into the cementing pastes can be very different. First, it must be understood that the Si/Al ratio will define the homogeneity of the mixture and the setting process [96] with a higher percentage of alumina in their structure that will tend to have a weaker and slower setting, while those that have a very large pore diameter will facilitate the carbonation of the mixtures. There are many ways to incorporate zeolite to cement pastes, but they have in common the amorphization of the same, whether, by mechanical, chemical, or thermal methods, the main objective is to generate a correct balance between the Portland cement and the percentage of Si/Al content in the zeolite.

The dealumination is one of the most widespread methods for the control of the percentage Si/Al present in the zeolite and encompasses the aforementioned methods. In 1968, McDaniel and Maher prepared the ultra-stable Y zeolite by combining procedures for the exchange of sodium ions with ammonium and hydrothermal treatments at elevated temperatures ( $T \geq 600^\circ\text{C}$ ). Under the conditions of "deep bed," these treatments caused the removal of structural Al with the consequent decrease of the cell parameter. On the contrary, when the hydrothermal treatment was carried out in a "shallow bed," the protonated form of the zeolite was obtained without causing dealumination. It has been possible to dealuminate up to 98% Y zeolite by hydrothermal treatments without an appreciable loss of crystallinity.

In 1968, Kerr developed a method to dealuminate Y zeolites at low temperature (around  $100^\circ\text{C}$ ) by using a hydrolyzing and complexing agent of aluminum such as EDTA [97] with this method; however, you cannot dealuminate above 70% without drastic losses of crystallinity.

Subsequently, the use of  $\text{SiCl}_4$  at high temperatures was reported to dealuminate Y-type zeolites in a single step, quickly and with percentages of Al removal that could reach values above 90% [98].

Finally, Skeels and Breck reported a procedure in which ammonium hexafluorosilicate is used as a deadening agent, under mild conditions at low temperatures. It is a quick and simple method, but the superior level of dealumination, as with EDTA, is limited to 70% to avoid crystalline collapse.

#### **4.5. Textural and mechanical characterization**

The textural characterization of the zeolite-cement compound consists of measuring the pore size present in the element; the analysis of this porosity has as an objective to measure the surface of the pores and the volume of the same. It should be mentioned that the compound

may have microporosity or mesoporosity; as the study by Franus et al. [99], there are several ways to calculate the volume, distribution, and surface area of the pores among which are the general isotherm equation based on the combination of a modified Kelvin equation and a statistic thickness of the adsorbed film and the multilayer adsorption theory [100].

The mechanical characterization performed on cement pastes with zeolitic content does not differ from the typical mechanical compression tests (performed to see the maximum load before causing a fracture), which are carried out by means of a universal machine. However, both the size of the specimens and the laboratory conditions (temperature, pressure, and percentage of aggregates) depend on the author and the results that he intends to obtain. There is a lot of research on the mechanical state of the test tubes [41, 51, 99, 101], and it is important to mention that in most of them, the state of operation is evaluated after having been subjected to adverse media, such as chloride attack or exposure to acid media.

#### **4.6. Special applications of these composites**

At present, due to the many investigations that exist on cement with zeolitic addition, we can find large areas of opportunity for its application. However, its use as a cement for construction is the most researched application [9, 41, 93, 96], and this is obvious when the main function of this compound is to work as an alternative to ordinary cement (usually the Portland type) in the cement industry building. Although there are other applications of the same scope and not so obvious, which have not been given the same attention, among them we can find its use for the stabilization of sandy soils prior to the construction of roads [102, 103], agent for the reduction in pollutants and environmental conditions [76, 104], and its application in cementing operations carried out on the high seas and oil platforms [46, 105].

### **5. Concluding remarks**

The partial replacement of cement is a fact that every day becomes more important; it is an activity that is already carried out and that although there are few cement producers that commercialize with these compounds, it is a great step for the reduction in emissions of CO<sub>2</sub>. Many authors have contributed and are still investigating the properties that this mixture provides us in order to improve them and to be able to develop a mixed cement paste that is capable of equalizing the effectiveness of Portland cement, which although it is close to it, in the case of zeolite as a pozzolan, it has not yet been achieved that this represents 50% of the mixture. Fortunately, with the growing research and development of new methods for the synthesis and management of these minerals, achieving a balance between the costs of production and the effectiveness of the product can be a reality. It should be mentioned that the use of zeolite as a pozzolan is not a whim, and although it competes with other pozzolans that can deliver a better mechanical performance such as silica fume and volcanic ash, the possible production savings due to availability and improvement from other areas such as resistance to carbonation, transport properties, hydration of the mixture, and absorption of contaminants are concepts that are worth investigating and investing for their development and improvement.

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