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Natural zeolite and its application in concrete composite production

Yen Thi Tran[a,1], Jechan Lee[b,1], Pawan Kumar[a,c], Ki-Hyun Kim[a,*], Sang Soo Lee[d,**]

[a] Department of Civil and Environmental Engineering, Hanyang University, Seoul, 04763, Republic of Korea
[b] Department of Environmental and Safety Engineering, Ajou University, Suwon, 16499, Republic of Korea
[c] Department of Nano Sciences & Materials, Central University of Jammu, Jammu, 181143, J&K, India
[d] Department of Environmental Engineering, Yonsei University, Wonju, 26493, Republic of Korea

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ABSTRACT

Concrete is a composite material that is widely used in the construction industry due to its excellent mechanical and physical properties. Despite these benefits, concrete possesses several disadvantages including negative environmental impacts and mechanical durability (e.g., shrinkage, frost attack, and corrosion). To date, upgrading of concrete's properties to overcome such drawbacks has been one of the most challenging, but attractive, research topics for many researchers in this research field. As one of the effective means to meet such demand, the use of natural zeolites in the production of concrete has been made preferably to acquire the excellent performance along with improvement in terms of structure, durability, and mechanical properties. This review was designed to provide a comprehensive insight into the construction-related applications of natural zeolite. To this end, we discussed the structural and fundamental properties of natural zeolites and their applications to concrete production as natural pozzolans, internal curing agents, and lightweight aggregates. Also, through critical analysis of various researches made previously, we aim to offer a better understanding on the effect of zeolites' addition upon the performance of concrete in terms of workability, strength, durability, and permeability. Additionally, we describe the present challenges and future perspectives in the use of natural zeolites for concrete production.

1. Introduction

Concrete is by far the most commonly used building material for civil and military applications due to its mechanical stability and durability [1–4]. However, its production may have negative environmental impacts because a considerable amount of CO_2 (around 6% of total global CO_2 emissions [5]) is generated and released in the production of Portland cement, a hydraulic material used as a main component of concrete [3]. As concrete structures can deteriorate via several routes (e.g., shrinkage, frost attack, chloride attack, and sulfate attack), their durability tends to decline over time. Also, the cost of maintaining, protecting, repairing, and rehabilitating existing concrete structures cannot be neglected.

In order to resolve these issues, several solutions have been suggested in a practical context. The first one is to enhance mechanical structure and durability properties during the concrete manufacturing process. Another is to reduce the consumption of Portland cement in the process. These two concepts can be realized respectively by optimizing the particle packing density of the concrete [6] and by partially replacing the Portland cement with natural pozzolans and/or pozzolanic industrial byproducts such as ground granulated blast furnace slag (GGBFS), fly ash, or silica fume [7–10].

The addition of natural zeolites to concrete as pozzolans is found to highly efficient in strengthening the stability of the final concrete product. Natural zeolite is hydrated aluminosilicates with framework structure consisting of micropores, channels, and cavities. There are three major aspects of zeolite composition, namely extra framework cations, a porous framework, and a sorbed phase ($M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot nH_2O$) in which M is extra-framework cations such as K^+ Na^+, Ca^{2+}, and Mg^{2+}. Variables "n" and x are the number of H_2O molecules and the valence of M, respectively.

Natural zeolites have been used for various purposes in diverse fields including wastewater treatment [11–13]; gas purification [14,15]; and construction [16,17], particularly as a pozzolanic concrete additive. A zeolite additive with a high adsorption capacity (nearly 40% of its own weight [18]) can act as an internal water curing agent to help

* Corresponding author.
** Corresponding author.
E-mail addresses: kkim61@hanyang.ac.kr (K.-H. Kim), cons@yonsei.ac.kr (S.S. Lee).
[1] These authors are co-first authors because they contributed equally to this work.

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increase durability and permeability of the concrete with a low water/binder (w/b) ratio [19,20]. Additionally, natural zeolites are utilized as aggregate to make lightweight concrete [21]. Concrete containing a natural zeolite has also been shown to have increased resistance to sulfate attack [22,23] and freeze/thaw [24].

Considering the foregoing, in the present paper we will discuss the properties of natural zeolites and their applications to the production of concrete, based on a critical review of the most important recent literature. This review will also accelerate the present challenges of using natural zeolites as pozzolans for improving concrete properties and will present a number of possible options to overcome these challenges. Finally, we expand the discussion to include the future prospects of using natural zeolites as admixtures as well as lightweight aggregates in concrete. This article is thus expected to offer valuable insight into the promise of natural zeolites, based on in-depth evaluation of their potential use in the concrete industry.

2. Characteristics of natural zeolites

2.1. Structure

Natural zeolites are hydrated crystalline aluminosilicates having 3D honeycomb structures formed by tetrahedral TO_4 units (T: Si, Al) linked with other tetrahedrons by sharing of the four O atoms. Fig. 1 presents a model structure of natural zeolites.

Each AlO_4 tetrahedron carries a negative charge; thus, an extra-framework neutralizing cation is also present. The Si/Al ratio of zeolites (both natural and synthesis types) varies from 1 to ∞, representing various polymorphs of SiO_2 [25,26]. In general, natural zeolites have relatively low Si/Al ratios compared to synthetic zeolites, due to their lack of organic structure-directing agents. The zeolite structure contains channels and cages occupied by exchangeable charge-balancing cations and water molecules. Further, the zeolitic properties are not impacted by cations (e.g., K^+, Na^+, Ca^{2+}, and Mg^{2+}) that can be replaced by other extra-framework cations. At temperatures above 500 °C, the water molecules can be completely removed from the open cavities of the framework and the cations may be replaced by other ones, resulting in no change in zeolitic structure [27].

Zeolites are primarily made of tetrahedrons, the geometric arrangements of which are defined as secondary building units (SBUs). The types of zeolite structure are determined by the different ways to form polyhedra through linkages between SBUs. There are seven groups of SBUs [28] and around 40 types of natural zeolites [29]. Fig. 2 shows the types of SBUs that can be found in natural zeolites with regards to the positions of Si or Al.

Rings formed from 6, 8, 10, 12, and 14 oxygen atoms are interconnected with each other to create channels and pores in the zeolite structure of dimensions ranging from 3 to 10 Å. This size is affected by position, size, and coordination of the extra-framework cations [27].

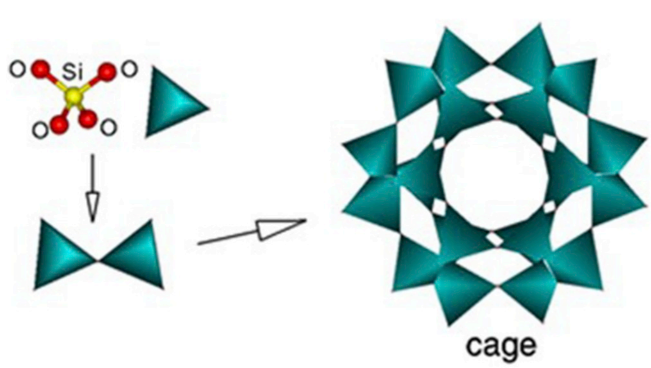


Fig. 1. Framework structure of natural zeolites. Reprinted from Moshoeshoe et al. [120]. This work is licensed under CC BY 4.

Therefore, control over pore opening can be exercised by replacing cations in the framework [25]. Table 1 summarizes structural properties, and Fig. 3 illustrates the structures of popularly used types of natural zeolites.

2.2. Properties

The ion exchange, adsorption, dehydration, and rehydration of a zeolite, which are related to its structure, framework, and composition, are important for determining zeolite properties [30,31]. Firstly, the large channel and cavity system within the zeolite structure and the existence of extra-framework cations make exchange of cations possible. The cation exchange capacities of natural zeolites are twice as high as those of bentonite clays, ranging from 2 to 4 milliequivalents per gram [31]. The substitution of Al^{3+} for some of Si^{4+} in the zeolite structure creates an inadequacy of positive charge in the framework. The net negative charge is neutralized by cations such as Na^+ and K^+ accommodated in cavities within the structure [32]. When a zeolite is exposed to a solution containing a high concentration of a cation, an ion exchange process can take place between Na^+ and the ion [31].

In terms of dehydration and rehydration, zeolites can be classified into two groups. Those of the first group, natural zeolites (e.g., clinoptilolite, chabazite, and mordenite), do not experience any change or collapse in framework structure during the dehydration process, while continuously losing weight with increasing temperature [31]. The second group exhibits no continuous weight loss under heat treatment but instead undergoes structural changes. In the latter case, zeolitic properties gradually disappear with increasing temperature owing to these structural changes [31,33].

2.3. Chemical composition

The regular formula of natural zeolites is $M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot nH_2O$, and the main components of natural zeolites are SiO_2 and Al_2O_3. To date, about 45 types of natural zeolites having various chemical properties have been discovered [32]. Among them, clinoptilolite ($[Na,K,Ca]_6[Si,Al]_{36}O_{72}\cdot 20H_2O$) and mordenite ($[Ca,Na_2,K_2]Al_2Si_{10}O_{24}\cdot 7H_2O$), which have high proportions of silica (approximately 70%) have been applied most widely for industrial purposes. For example, they are commonly used as odor control agents, water filters, and molecular sieves [34–36]. Natural zeolites tend to be of low purity due to impurities such as minerals other than Si, Al, and quartz. Thus, natural zeolites are inappropriate for applications requiring highly pure zeolite, such as petroleum refining and petrochemical production. Table 2 summarizes the chemical compositions of commonly used natural zeolites [32].

3. Application of natural zeolites to concrete production

3.1. As pozzolanic materials

A large amount of calcium hydroxide (CH) is known to be created when the hydration of cement takes place in concrete, apart from the formation of the main cementitious compounds, calcium silicate hydrate gel and calcium aluminate hydrate gel, which are responsible for concrete compressive strength. As the CH formed in the hydration has no cementitious property and can be dissolved in water (i.e., moisture), it can contribute to the formation of a highly porous cement paste that thus forms a highly vulnerable concrete. This problem can be alleviated by mixing cement with pozzolanic materials. A pozzolan usually contains a large proportion of SiO_2 and Al_2O_3, which can react with CH in the presence of water to create cementitious products (e.g., $3CaO\cdot 2SiO_2\cdot 3H_2O$ and $3CaO\cdot Al_2O_3\cdot 6H_2O$). These products can then form a dense microstructure of hardened cement paste and concrete [37]. Accordingly, pozzolanic reactions between SiO_2 and Al_2O_3 in natural zeolites and CH occur to form calcium silicate hydrate and

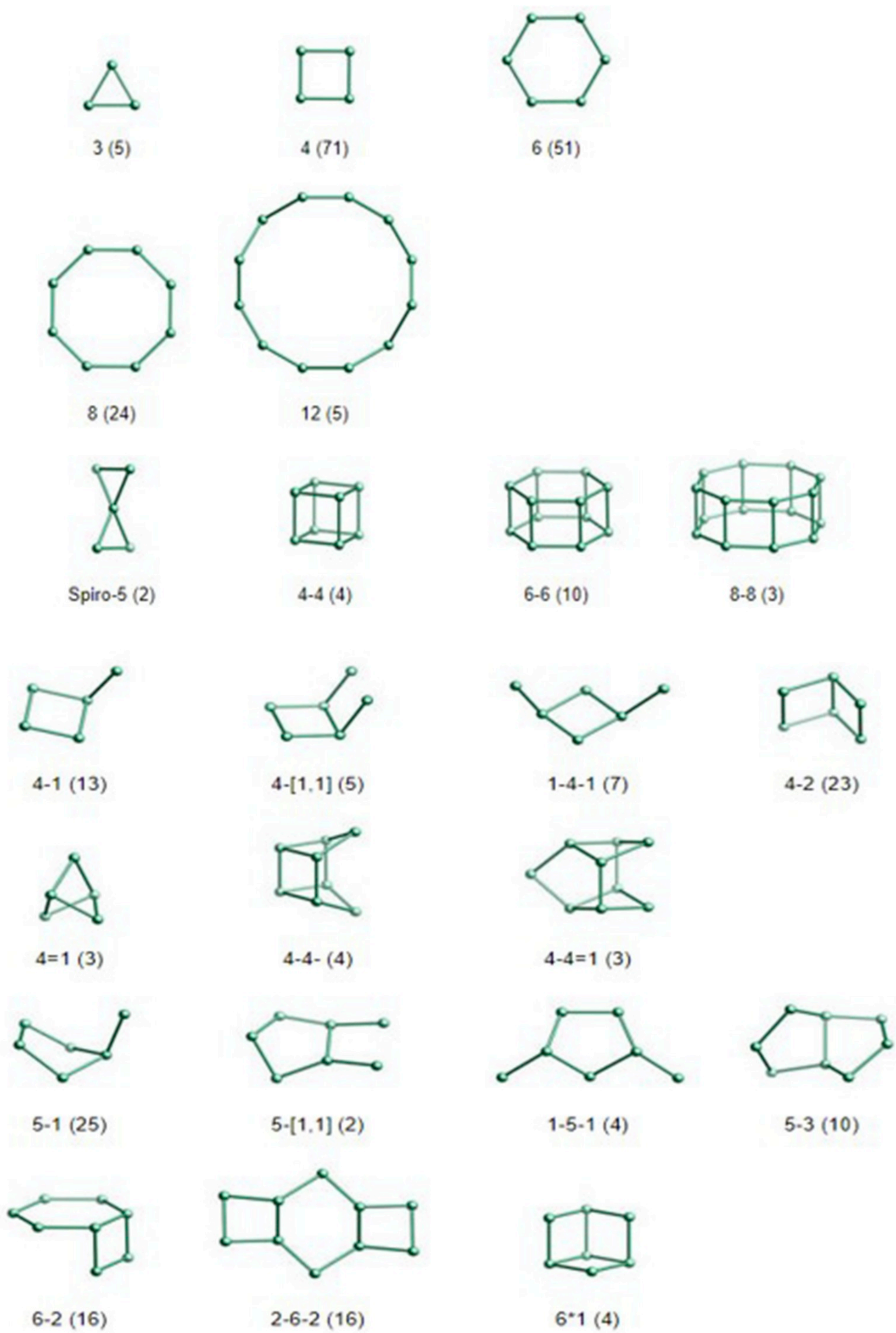


Fig. 2. Secondary building units (SBU) in zeolites (the spheres represent T atoms of TO_4 tetrahedras; the oxygen atoms are hidden for a more clarifying figure; the numbers in parentheses represent occurrence's frequency). Adapted from materials available in the public domain [121].

calcium aluminate hydrate gels which would further contribute to increasing the density of the concrete. Fig. 4 shows an example microstructure of a specimen using 100% Portland cement, showing contained microcracks and large size pores. In contrast, the microstructure of a sample incorporating GGBFS, a pozzolanic admixture contained a continuous network of small pores and a large number of small calcium silicate hydrate crystals created by means of cement hydration and pozzolanic reactions (Fig. 5). The pozzolanic reactions are as follows.

$$2SiO_2 + 3Ca(OH)_2 \rightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O$$

$$Al_2O_3 + 3Ca(OH)_2 + 3H_2O \rightarrow 3CaO{\cdot}Al_2O_3{\cdot}6H_2O$$

Besides, for concretes with low water/cement weight ratios (normally less than 0.25) [38,39] such as high- or ultrahigh-performance concrete, the available water is not sufficient to completely hydrate the large amount of cement used. The remaining unhydrated cement does not play a role in the strength development of the concrete. Hence, replacing this portion of the cement with pozzolanic material is a promising option to improve the microstructure of cement paste. In this

Table 1
Structural properties of common types of natural zeolites.

Order	Natural zeolite types (Code)	Chemical formula	SBU	Channels (Å)	Si/Al ratio	Ref.
1	Mordenite (MOR)	$(Ca,Na_2,K_2)Al_2Si_{10}O_{24}·7H_2O$	5–1	6.5 × 7 2.6 × 5.7	5.5	[112,113]
2	Clinoptilolite (CLI)	$(Na,K,Ca)_6(Si,Al)_{36}O_{72}·20H_2O$	4-4-1	3.6 × 4.6 3.1 × 7.5 2.8 × 4.7	6	[27,112,114,115]
3	Ferrierite (FER)	$(Na,K)_2MgAl_3Si_{15}O_{36}(OH)·9H_2O$	5–1	3.5 × 4.8 4.2 × 5.4	5–10	[27,112,116]
4	Chabazite (CHA)	$CaAl_2Si_4O_{12}·6H_2O$	6-6 or 6 or 4-2 or 4	3.8 × 3.8	1.0–4	[27,114,117]
5	Erionite (ERI)	$(K_2,Ca,Na_2)_2Al_4Si_{14}O_{36}·35H_2O$	6 or 4	3.6 × 5.1	2–4	[27,112,114]
6	Philipsite (PHI)	$(K,Na,Ca)_{1.2}(Si,Al)_8O_{16}·6H_2O$	8 or 4	3.8 × 3.8 3 × 4.3 3.2 × 3.3	1.5–4	[27,112,114,118]
7	Analcime (ANA)	$NaAlSi_2O_6·H_2O$	6-2 or 6 or 4- [1,1] or 1-4-1 or 4	1.6 × 4.2	2	[27,112]

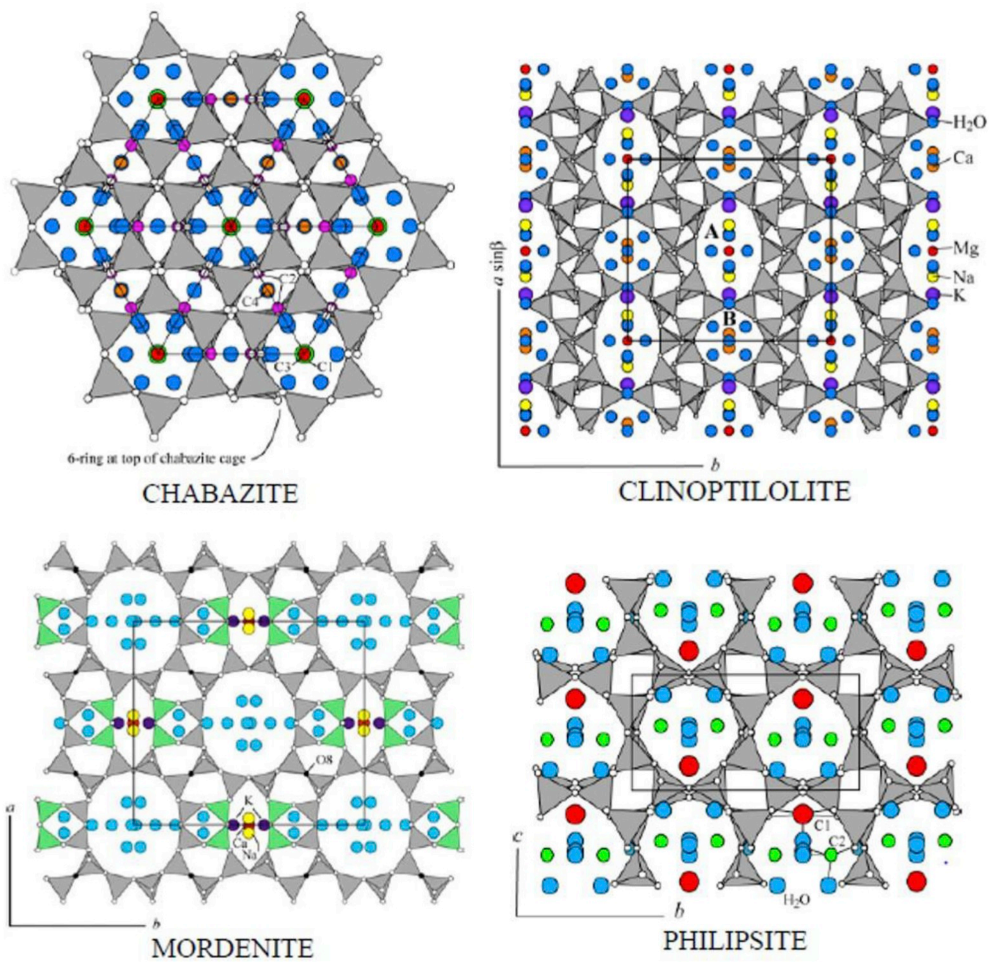


Fig. 3. Structures of some common natural zeolites. Adapted from materials available in the public domain [114].

respect, because natural zeolites having various porous structures and large active phases (SiO_2 and Al_2O_3) have pozzolanic properties, they have been utilized preferentially as pozzolanic materials in cement and concrete [40].

In a recent research made on high strength self-compacting concrete (HSCC), the behavior of concrete incorporating natural zeolite at 10 and 15 wt % of cement was assessed on comparative basis Samimi et al. [41]. They concluded that zeolite caused adverse impacts on the compressive strength (lower than that of conventional concrete by 1.18 and 1.55 times, respectively). Reductions in compressive strength were also noted in concrete incorporating natural zeolites (15% and 30% of cement mass) at every age studied, although these reductions decreased considerably with aging [42]. Although the similar effect was also observed previously [3,43], many researchers concluded that the use of natural zeolite had almost no negative effects [23,44] while showing even improved compressive strength of concrete [20,24,45–50]. These

Table 2
Chemical compositions of several types of natural zeolites [32,119].

Order	Mineral	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO	SrO	BaO	H_2O
1	Chabazite Ca	46.43	19.33	–	0.09	0.91	10.04	0.08	0.30	–	22.82
2	Chabazite K	47.62	20.29	–	0.61	5.60	3.33	0.16	–	–	21.42
3	Clinoptilolite	68.28	12.30	0.08	0.26	0.94	4.34	1.05	–	–	–
4	Paranatrolite	39.92	31.37	–	13.80	2.49	0.81	–	–	–	13.44
5	Mordenite	72.38	11.32	0.26	0.88	2.94	0.36	0.36	–	2.38	–

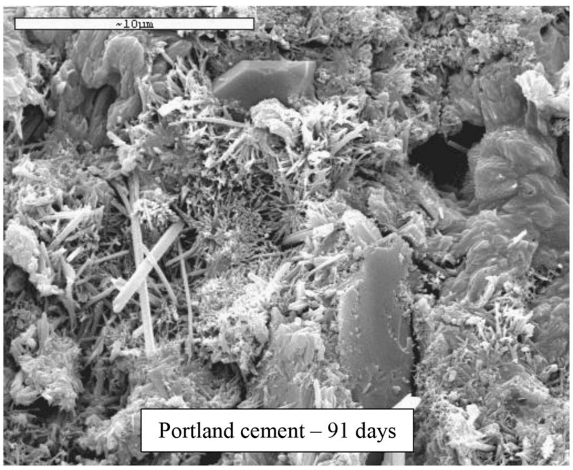


Fig. 4. Structure of specimen made from 100% Portland cement (Figure courtesy of Vietnam Institute for Building Materials).

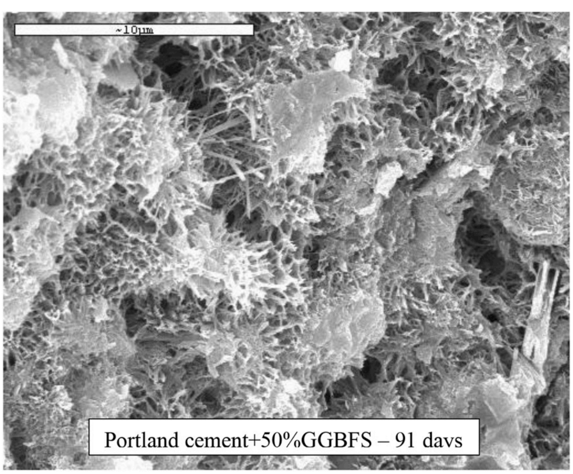


Fig. 5. Structure of specimen made from a mixture of 50% Portland cement and 50% GGBFS (Figure courtesy of Vietnam Institute for Building Materials).

conflicting observations can be attributed to a number of factors including the differences in water/cement (w/c) ratio and the amount of natural zeolite used. A rise in w/c ratio could lead to a lower compressive strength of concrete [51–54]. Besides, the higher zeolite content is suspected to increase porosity of hardened concrete to result in strength loss as well [55–59].

Clinoptilolite found in Iran has been investigated as a supplementary cementitious material at the concrete replacement ratios of 15 and 30 wt% [43]; the respective rapid chloride permeabilities of the resulting concretes after 28 days were 72.5 and 91.8% lower than those of a reference concrete using cement only. The results relating to chloride diffusion represented the ability of natural zeolites to increase the resistance of chloride ion penetration, especially at later ages of concrete (28–360 days after mixing). In the research on HSSC of Samimi et al. [41], the improvement of chloride penetration resistance was also observed. More specifically, the presence of natural zeolite (10% and 15%) in HSSC contributed to reductions of around 40 and 60% in the penetration levels of chloride ion at 28-day age, respectively. This desired effect of natural zeolites in reducing chloride ion penetration into concrete was also reported in other studies [5,44,49,50,60–62]. This improvement of chloride penetration could also be attributed to its pozzolanic reaction which consumes $Ca(OH)_2$ and leads to a decrease of $(OH)^-$ in the pore solution. Poon et al. [63] claimed that at the same water/cement ratio of 0.3 and age of 28 days, the pozzolanic reactivity index of natural zeolites is 13% higher than that of fly ash, whereas it is 6% lower than that of silica fume. The pozzolanic reaction has been found to occur most intensively in concrete aged for 28–360 days [23].

Apart from chloride penetration, adding natural zeolites to concrete also helps to enhance other durable properties in the environment with the presences of hazardous elements such as water, sulfate, CO_2, and extremely low temperature. The penetration of water into concrete system is considered as one of the most serious phenomena which can shorten the service life of concrete structures [64–67]. By using natural zeolite with the role of pozzolanic admixture, the microstructure of cement paste in concrete could be denser with the reduced porosity. These effects are extremely beneficial in promoting the resistance of water permeability. In a study conducted in 2016, Nagrockiene and Girskas investigated the effects on water permeability of concrete containing natural zeolite at the rates of 2.5%, 5%, 7.5%, and 10% of cement mass. The results indicated that this porous material can help reduce the penetration of water into concrete up to 57% [24]. Similar observations were noted in other studies [43,44,49]. In addition, an enhancement was reported in the sulfate resistance of concrete containing natural zeolites. According to Janotka and Krajči [22], after being cured in 5% $NaSO_4$ solution for 720 days, specimens containing natural zeolite (clinoptillolite) expanded only 0.6580%, in sharp contrast to 9.3296% for a reference sample. This implies that the incorporation of natural zeolites into concrete led to a considerable increase in its sulfate resistance. Similar results were observed by other researchers, e.g., Karakurt and Topçu [68] and Vejmelková et al. [23]. The improvement in the durability of concrete containing natural zeolite was also observed in its resistance to carbonation corrosion. According to Vejmelková et al., the increases in the ability of resisting to CO_2 environment stood at around 3% and 6% when adding 10% and 20% zeolite, respectively [23]. Additionally, it was reported that the incorporation of 10% of natural zeolites into concrete more than tripled the number of freeze/thaw cycles it endured, relative to a control concrete [24]. Vejmelková et al. [23] drew a similar conclusion after investigating the freeze/thaw resistance of concrete specimens containing 10% and 20% of natural zeolites (clinoptilolite). This result was also discovered by Markiv et al. [4].

3.2. As internal curing agents

Zeolites possess a high capacity for adsorbing and desorbing water as their porous structure made up of micro-, meso-, and macroscale pores [27]. Consequently, natural zeolites can be used as a medium to control the internal relative humidity of concrete. One of the most crucial phenomena appearing early in the aging of concrete is autogenous shrinkage, the main cause of concrete cracking [69–72]. In case of concrete with a very low water/cement ratio ($<$ 0.25) and high

Table 3
Evaluation of ratio of several key performance metrics between with and without addition of natural zeolites: Results are compared in terms of natural zeolite content in concrete.

A. Compressive strength of concrete

Order	Compressive strength of concrete with zeolite addition to those of concrete without zeolite ratio								Ref.
	Natural zeolite content (wt. % of cement mass)								
	2.5	5	7.5	10	12.5	15	20	30	
1	1.07	1.08	1.12	1.13					[24]
2		1.17		1.15	1.13				[20]
3		1.14		1.16		1.23	1.25		[48]
4		1.01		0.96					[3]
6				1.14					[45]
7	1.07	1.08	1.11	1.13					[46]
8		1.18		1.19		1.14		1.05	[47]
9				1.04			0.92		[49]
10				1.06		1.04			[44]
11				1.24			1.05	0.79	[5]
12					1.04				[79]
13						0.96		0.76	[43]
14				0.85		0.65			[41]
15				1.26		1.21			[50]
Average	1.07	1.11	1.12	1.109	1.09	1.04	1.07	0.87	

B. Chloride penetration of concrete

Order	Chloride penetration of concrete with zeolite addition to those of concrete without zeolite ratio					Ref.
	Natural zeolite content (wt. % of cement mass)					
	5	10	15	20	30	
1	0.98	0.44	0.41	0.35		[48]
2	1	0.71				[3]
4	0.56	0.38	0.31	0.25		[47]
5		0.5		0.33		[49]
6		0.6	0.4			[41]
7		0.57	0.49			[44]
8		0.18		0.19	0.27	[5]
9			0.15		0.06	[43]
10		0.46	0.36			[50]
11		0.53	0.42	0.5		[62]
Average	0.85	0.49	0.36	0.32	0.17	

C. Water penetration of concrete

Order	Water penetration of concrete with zeolite addition to those of concrete without zeolite ratio							Ref.
	Natural zeolite content (wt. % of cement mass)							
	2.5	5	7.5	10	15	20	30	
1	0.97	0.96	0.45	0.43				[24]
2		0.79		0.83	0.77	0.75		[48]
3				0.85				[4]
4	0.39	0.36		0.27				[46]
5				0.83		0.84		[49]
6				0.82	0.7			[44]
7					0.73		0.67	[43]

D. Frost resistance of concrete

Order	Frost resistance of concrete with zeolite addition to those of concrete without zeolite ratio							Ref.
	Natural zeolite content (wt. % of cement mass)							
	2.5	5	7.5	10	20	40	60	
1	2.37	2.49	2.89	3.32				[24]
2				1.32				[4]
3				1.14	1.07	0.72	0.5	[23]

(*continued on next page*)

Table 3 (*continued*)

E. Shrinkage of concrete							
Order	Shrinkage of concrete with zeolite addition to those of concrete without zeolite ratio						Ref.
	Natural zeolite content (wt. % of cement mass)						
	5	10	12.5	15	17	30	
1	0.36	0.26	0.23				[20]
2		0.62					[4]
3			0.59		0.97		[79]
4				0.84		0.64	[43]
5					0.64		[19]

cement content, the water content is inadequate for cement hydration. The internal relative humidity of concrete continuously declines during the cement hydration process, resulting in self-desiccation of the concrete [73]. The microstructure of self-desiccated concrete is dense with tiny capillaries at low water/cement ratios from 0.40 to 0.42 [74]. Autogenous shrinkage is then caused by surface tension in the capillary pores.

An efficient solution to prevent autogenous shrinkage is to maintain the humidity in the saturated capillaries [75]. Due to the dense microstructure, external water cannot move into the extremely small capillaries. Thus, internal curing is considered as a useful solution [76]. For internal curing, zeolite particles can play the role of water reservoirs distributed throughout the concrete due to their high adsorption capacity. Water adsorbed in these particles is drawn into the capillaries formed during the initial stage of concrete mixing process [77,78]. This helps prevent concrete from self-desiccating, thereby reducing autogenous shrinkage. Tuan et al. [20] evaluated the effects of natural zeolites upon the autogenous shrinkage of ultrahigh-performance concrete. The use of natural zeolites at 5%, 10%, and 12.5% yielded decreases in autogenous shrinkage values of ultrahigh-performance concrete of 64%, 74%, and 77%, respectively, after 28 days. According to Jun Zhang et al. [19], the autogenous shrinkage of concrete considerably decreased by employing prewetted zeolites as an ingredient; in a concrete with added natural zeolites they observed 42% of the shrinkage of a control mixture at the age of 28 days. This positive effect can be seen in another study of these authors in 2017 [79].

Drying shrinkage is another common shrinkage type occurring in concrete. This is caused by vaporization of water in the pore system of the concrete, reducing the volume of the concrete [80,81]. This leads to high tensile stress and subsequently to cracking [82,83]. Drying shrinkage predominates in concretes having high water/cement weight ratios of > 0.4. Najimi et al. [43] reported that mixing a natural zeolite (clinoptilolite) into cement at 15 wt% and 30 wt% resulted in sharp declines of drying shrinkage of 16% and 36%, respectively, at the age of 90 days. Markiv et al. [4] observed a similar result when replacing 10 wt% of cement with clinoptilolite. Concrete samples containing the natural zeolite experienced 2.6-fold decreases in drying shrinkage compared to control specimens.

3.3. As aggregates and air-generating agents in lightweight concrete

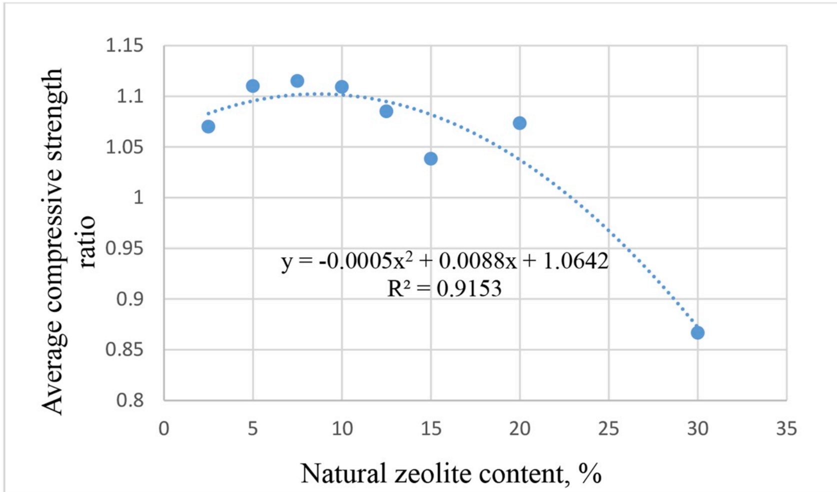
Natural zeolites have been utilized as lightweight aggregates and foaming agents in concrete production. The addition of natural zeolites to concrete can decrease unit weight [84,85] while improving thermal insulation ability. Karakurt et al. [21] investigated the utilization of natural zeolites as lightweight aggregates. They produced an autoclaved aerated concrete (AAC) using natural zeolites (clinoptilolite) at 25%, 50%, 75%, and 100% to replace silica sand. They found that the replacement of 50% of the cement with the natural zeolite is an optimum proportion overall in terms of compressive strength, lower unit weight, and higher thermal insulation capacity of the AAC. Otherwise, in the process of producing the AAC, a natural zeolite was calcined at 500 °C for 2 h to utilize it as a foaming agent. The pre-treatment of natural zeolite (i.e., calcination) provided the highest compressive strength, resulting from a high unit weight and low porosity of the AAC.

Fu et al. [86] invented a lightweight concrete using non-heat-treated and pre-heated natural zeolites. They produced concrete by combining 50–80 wt% of non-treated natural zeolites, 20–50 wt% of Portland cement, and 0–5 wt% of lime in a water/solid ratio greater than 0.7; the densities of these concretes varied from 1000 to 1300 $kg\,m^{-3}$ while their compressive strengths varied from 10 to 30 MPa. Fu et al. found that the surfaces of the natural zeolites became activated under heat treatment at 400–600 °C. After pre-wetting of the natural zeolites, air was generated and released due to water adsorption. This helped to create air bubbles in the concrete mix. Consequently, mixing 50–80% of pre-heated natural zeolites with 20–50% of Portland cement and 0–5% of lime yielded concrete products having density from 400 to 1000 $kg\,m^{-3}$ and compressive strength from 2 to 10 MPa.

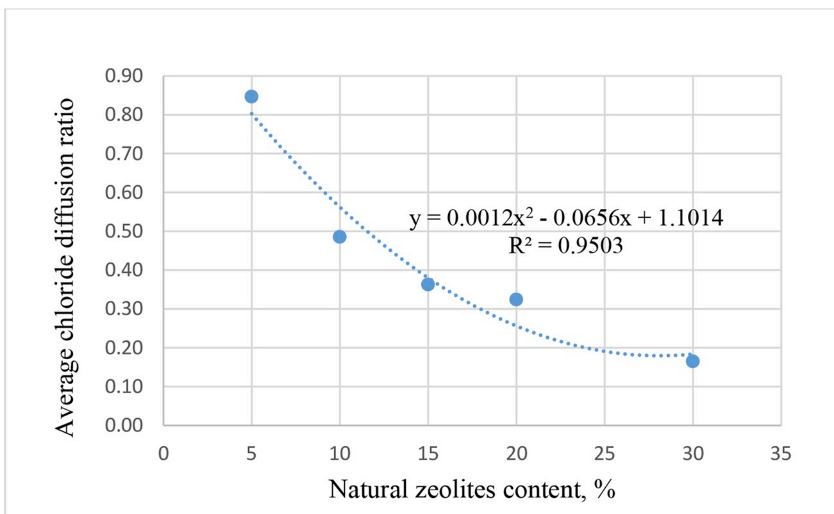
4. Assessment of the effectiveness of natural zeolites application to concrete

In the above section, we have discussed the effects of natural zeolites when added into concrete based on critical reviews made from various case studies. Accordingly, such incorporation was generally observed to have positive effects on enhancement of concrete properties. In this section, we conducted some quantitative analysis in an effort to derive the possible trend of natural zeolite application in relation to recognizable changes of some specific performance metrics for concrete (e.g., compressive strength, chloride permeability resistance, water penetration resistance, and shrinkage: Table 3). More specifically, the effects of such addition on concrete properties are assessed in terms of the ratio value of a given performance metric between zeolite-added concrete and reference concrete (i.e., without natural zeolites) or between after and before the addition of zeolite into concrete. The results summarized for each metric in Table 3 are hence all expressed in terms of ratio value between 0 and 1.

First, in case of compressive strength, the percentage of natural zeolites added into concrete products was seen to vary from 2.5 to 30 wt % of cement mass. In Table 3, the performance ratios for compressive strength are larger than 1 from almost all cases. This implies that the higher compressive strength was attained through the addition of natural zeolite. Likewise, in case of chloride permeability of concrete, the performance ratio also exhibited consistently a clear trend. With 5%–30% of the natural zeolite addition into concrete, the resistance to chloride diffusion increased very apparently. After 30% addition of natural zeolite, this positive trend however began to drop. In fact, such trend was seen consistently in other performance metrics like frost resistance and shrinkage (Table 3). Hence, it is found that natural zeolite addition is a highly useful option for the enhancement of concrete performance.



(a)



(b)

Fig. 6. The correlation between natural zeolite content and performance ratios of a given metrics between with and without addition of natural zeolite: (a) average compressive strength ratio and (b) average chloride diffusion ratio.

To meaningfully describe the effect of added zeolite content on performance metrics, the arithmetic mean values of the performance ratio were computed for some metrics and plotted against mixing rate of zeolite. Fig. 6a shows that the compressive strength of concrete is affected very systematically with the relative content of natural zeolite. Accordingly, the compressive strength of concrete could be controlled efficiently with the relative amount of natural zeolite added into concrete (2.5%–7.5%). The improvement in compressive strength gradually decreased as the added content exceeded 10% level. In this respect, 7.5% should be close to the optimal proportion for the addition of natural zeolite to optimize such metric. Likewise, chloride diffusion resistance was also explained similarly with the relative amount of natural zeolite added into concrete (Fig. 6b). Zeolite with its porous structure and high active phase (SiO_2 and Al_2O_3) thus appear to contribute effectively to the improvement of the microstructure of hardened cement paste. However, when the relative amount of natural zeolite keeps increasing, the porosity of concrete will increase remarkably. Those positive effects on microstructure of the paste then could not be large enough to mitigate the negative impacts.

5. Challenges and prospects of applying natural zeolites to concrete

Employing natural zeolites in concrete production decreases the workability of the concrete [20,43]. Therefore, the addition of a superplasticizer is necessary to maintain suitable workability in the resulting concrete mixture. It was concluded in several other studies that the incorporation of natural zeolite requires the high consumption of superplasticizer [41,48,61,87–91]. The decreased workability arises from natural zeolites' microporous structure, large specific surface area, and the rise of paste volume. Increasing the quantity of natural zeolites used increases the needed quantity of superplasticizer. Thus, although natural zeolites are not as expensive as Portland cement, the attendant need for expensive superplasticizer leads to high cost overall [11,43]. This might lead to difficulty in widely applying natural zeolites to the production of concrete.

When natural zeolites are added to concrete, the compressive strength of concrete can be reduced owing to the high amount of mixing water required by the porous structure and the high surface area of

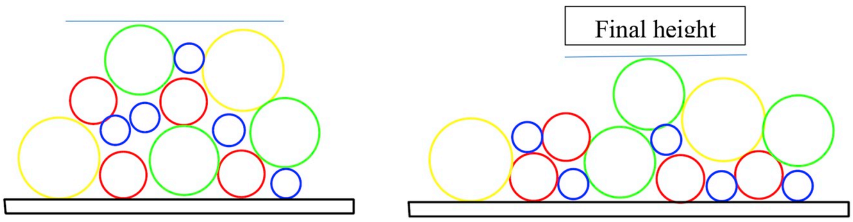


Fig. 7. Ball-bearing effect between spherical particles.

natural zeolites [20,21,41,43]. Furthermore, the reduction in compressive strength is also attributed to the water/cement (w/c) ratio. For example, it has been insisted that the compressive strengths of concrete samples containing natural zeolites would be lower than those of control samples when the w/c ratio is greater than 0.45 [47]. A similar result with the w/c ratio of 0.4 was also reported by Ahmadi and Shekarchi [48]. However, the advantages of applying natural zeolites can outweigh the disadvantages if an appropriate proportion of natural zeolites is selected for use in concrete production.

In order to resolve these limitations and to promote the application of zeolite in concrete production, several solutions can be taken into account in the future. In case of issues regarding the strength loss, we recommend that researchers could consider the approach of combining that admixture with other materials (e.g. silicafume [92–94], nano-silica [95–97], nano-titanium dioxide [98–100], and carbon nanotubes [101–103]). These materials are generally mixed into concrete mix to achieve two major roles. First, due to the presence of fine/superfine particles, these materials can serve as a filler, as they can be filled into the small or even tiny pores between large-size particles to improve the density of concrete mixture. Another role of them is to react with calcium hydroxyl ions (a hydration product) as they have pozzolanic activity. This process will contribute to the enhancement of the microstructure of hardened cement paste. Such combinations can thus be beneficial in increasing concrete strength and durability.

For the reduction of superplasticizer dosage, a potential solution could be to utilize materials with glass-like surface (e.g., ground granulated blast furnace slag) or spherical – shaped structure (e.g. silicafume and fly ash) along with natural zeolite in the production of zeolite incorporated concrete. By adopting this strategy, the "ball-bearing" effect (Fig. 7) can emerge between these spherical particles in the concrete mix to offer beneficial effects on the flow property of concrete [104–106]. Further, other approaches such as particle packing optimization [107] to obtain a high packing density for concrete containing natural zeolite mix or using different zeolites particle sizes could become a promising subject of research.

On the other hand, it is observed in many studies that the unique properties of natural zeolites such as porous honeycomb-like structure and high specific surface area allow them to work as a molecular sieve which can efficiently adsorb different contaminants such as heavy metals and CO_2 [108–111]. However, till date, the research focusing on the effects of concrete incorporating natural zeolites is limited with respect to the removal of pollutants. Such properties, if existing, can also contribute to the mitigation of the serious environmental pollution caused by the rapid development of industry. Thus, it could be a potential topic to study further in the future.

6. Conclusions

This article was organized to elucidate the feasibility of diverse forms of natural zeolites for their incorporation into the formation for concrete composite. A list of their advantageous properties (e.g., high SiO_2/Al_2O_3 contents, ion exchange, dehydration/rehydration, and adsorption) along with a porous framework structure allow natural zeolites to become a highly attractive material for potential application in construction fields. This review article thus accentuates a great potential of natural zeolites as additives to concrete in which they can greatly improve the mechanical properties and durability while helping reduce its permeability. Although the addition of natural zeolites to concrete can reduce concrete compressive strength and workability, their addition turns out to be highly beneficial overall. Most noticeably, it can considerably enhance other engineering properties such as shrinkage, chloride penetration, water permeability, carbonation resistance, and sulfate resistance.

A wide variety of studies have been conducted over a long time to learn more about the potential utility of natural zeolites in concrete. Nonetheless, we encounter a number of technical limitations that can lessen the advantages of using natural zeolites as concrete additives. To address these limitations and to help improve the applicability of natural zeolites in concrete, we suggest that researchers propose and develop strategies to increase compressive strength, decrease superplasticizer consumption, and include the use of other mineral admixtures.

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References

[1] O'Neil EF, Neeley BD, Cargile JD. Tensile properties of very-high-strength concrete for penetration-resistant structures. Shock Vib 1999;6:237–45.
[2] Jindal B. Concrete cloth: an innovative versatile construction material. 2018.
[3] Eskandari H, Vaghefi M, Kowsari K. Investigation of mechanical and durability properties of concrete influenced by hybrid nano silica and micro zeolite. Procedia Materials Science 2015;11:594–9.
[4] Markiv T, Sobol K, Franus M, Franus W. Mechanical and durability properties of concretes incorporating natural zeolite. Archives of Civil and Mechanical Engineering 2016;16(4):554–62.
[5] Valipour M, Yekkalar M, Shekarchi M, Panahi S. Environmental assessment of green concrete containing natural zeolite on the global warming index in marine environments. J Clean Prod 2014;65:418–23.
[6] Chen JJ, Li LG, Ng PL, Kwan AKH. Effects of superfine zeolite on strength, flowability and cohesiveness of cementitious paste. Cement Concr Compos 2017;83:101–10.
[7] Rajendran RR. Flexural behavior of concrete beam with GGBS and fly ash as supplementary cementitious material vol. 10. 2015. p. 32310.
[8] Hefni Y, Zaher YAE, Wahab MA. Influence of activation of fly ash on the mechanical properties of concrete. Constr Build Mater 2018;172:728–34.
[9] Kurda R, de Brito J, Silvestre JD. Water absorption and electrical resistivity of concrete with recycled concrete aggregates and fly ash. Cement Concr Compos 2019;95:169–82.
[10] Nuruddin MF, Chang KY, Mohd Azmee N. Workability and compressive strength of ductile self compacting concrete (DSCC) with various cement replacement materials. Constr Build Mater 2014;55:153–7.
[11] Wang S, Peng Y. Natural zeolites as effective adsorbents in water and wastewater treatment. Chem Eng J 2010;156(1):11–24.
[12] Markou G, Vandamme D, Muylaert K. Using natural zeolite for ammonia sorption from wastewater and as nitrogen releaser for the cultivation of Arthrospira platensis. Bioresour Technol 2014;155:373–8.
[13] Lin L, Wan C, Lee D-J, Lei Z, Liu X. Ammonium assists orthophosphate removal from high-strength wastewaters by natural zeolite. Separ Purif Technol 2014;133:351–6.
[14] Sircar S, Myers AL. Gas separation by zeolites. In: Auerbach SM, Carrado KA, Dutta PK, editors. Handbook of zeolite science and technology. 2003. p. 1063–104.
[15] Ackley MW, Rege SU, Saxena H. Application of natural zeolites in the purification and separation of gases. Microporous Mesoporous Mater 2003;61(1):25–42.

[16] Küçükyıldırım E, Uzal B. Characteristics of calcined natural zeolites for use in high-performance pozzolan blended cements. Constr Build Mater 2014;73:229–34.
[17] Farnood Ahmadi P, Ardeshir A, Ramezanianpour AM, Bayat H. Characteristics of heat insulating clay bricks made from zeolite, waste steel slag and expanded perlite. Ceram Int 2018;44(7):7588–98.
[18] Tatlier M, Munz G, Henninger SK. Relation of water adsorption capacities of zeolites with their structural properties. Microporous Mesoporous Mater 2018;264:70–5.
[19] Zhang J, Ding X, Wang Q, Zheng X. Effective solution for low shrinkage and low permeability of normal strength concrete using calcined zeolite particles. Constr Build Mater 2018;160:57–65.
[20] Tuan NV, Thang NC, Hanh PH, Yen TT. Effect of zeolite on autogenous shrinkage of ultra-high performance concrete. The 7th international conference of asian concrete federation: "sustainable concrete for now and the future". Vietnam: Hanoi; 2016.
[21] Karakurt C, Kurama H, Topçu İB. Utilization of natural zeolite in aerated concrete production. Cement Concr Compos 2010;32(1):1–8.
[22] Janotka I, Krajči L. Sulphate resistance and passivation ability of the mortar made from pozzolan cement with zeolite. J Therm Anal Calorim 2008;94(1):7–14.
[23] Vejmelková E, et al. Engineering properties of concrete containing natural zeolite as supplementary cementitious material: strength, toughness, durability, and hygrothermal performance. Cement Concr Compos 2015;55:259–67.
[24] Nagrockiene D, Girskas G. Research into the properties of concrete modified with natural zeolite addition. Constr Build Mater 2016;113:964–9.
[25] Payra P, Dutta PK. Zeolites: a primer. Handbook of zeolite science and technology. 2003. p. 1–24.
[26] Muraoka K, Chaikittisilp W, Okubo T. Energy analysis of aluminosilicate zeolites with comprehensive ranges of framework topologies. Chemical Compositions, and Aluminum Distributions 2016;138.
[27] Inglezakis VJ, Zorpas AA. Natural zeolites structure and porosity. In: Inglezakis VJ, Zorpas AA, editors. Handbook of natural zeolites. Bentham Science Publishers; 2012. p. 133–46.
[28] Breck D. Zeolite molecular sieves: structure, chemistry and use. 1st. New York: John Wiley & Sons Inc; 1974.
[29] Christie T, Brathwaite B, Thompson B. Mineral commodity report 23 – zeolites. N Z Min 2002;31:16–24.
[30] Mumpton FA. Natural zeolites. In: Mumpton FA, editor. Mineralogy and geology of natural zeolites. Mineralogical Society of America; 1981. p. 1–18.
[31] Ulmanu M. Mineralogy of natural zeolites. In: Inglezakis VJ, Zorpas AA, editors. Handbook of natural zeolites. Bentham Science Publishers; 2012. p. 52–69.
[32] Ulmanu M, Anger I. Physical and chemical properties. In: Inglezakis VJ, Zorpas AA, editors. Handbook of natural zeolites. Bentham Science Publishers; 2012. p. 70–102.
[33] Liebau F, Gies H, Gunawardane RP, Marler B. Classification of tectosilicates and systematic nomenclature of clathrate type tectosilicates: a proposal. Zeolites 1986;6(5):373–7.
[34] Wibowo E, Sutisna, Rokhmat M, Murniati R, Khairurrijal Abdullah M. Utilization of natural zeolite as sorbent material for seawater desalination. Procedia Engineering 2017;170:8–13.
[35] Adam MR, et al. The adsorptive removal of chromium (VI) in aqueous solution by novel natural zeolite based hollow fibre ceramic membrane. J Environ Manag 2018;224:252–62.
[36] Ates A, Akgül G. Modification of natural zeolite with NaOH for removal of manganese in drinking water. Powder Technol 2016;287:285–91.
[37] Mehta PK. Natural pozzolans: supplementary cementing materials in concrete. CANMET Spec Publ 1987;86:1–33.
[38] Schmidt M, Fehling E. Ultra-High-Performance Concrete: research, development and application in Europe. ACI Spec Publ 2005;228:51–78.
[39] Voort TV, S M, Sritharan S. Design and performance verification of ultra-high performance concrete piles for deep foundations. Center for Transportation Research and Education, Iowa State University; 2008. p. 224.
[40] Stanislao C, Rispoli C, Vola G, Cappelletti P, Morra V, Gennaro M. Contribution to the knowledge of ancient Roman seawater concretes: phlegrean pozzolan adopted in the construction of the harbour at Soli-Pompeiopolis (Mersin. Turkey). Period Mineral 2011;80:471–88.
[41] Samimi K, Kamali-Bernard S, Maghsoudi AA, Lgcgm SKB, Civil EAAM. Resistance to chloride penetration of high strength self-compacting concretes: pumice and zeolite effect. 2018.
[42] Givi AN, Rashid SA, Aziz FNA, Salleh MAM. Investigations on the development of the permeability properties of binary blended concrete with nano-SiO2 particles. J Compos Mater 2011;45(19):1931–8.
[43] Najimi M, Sobhani J, Ahmadi B, Shekarchi M. An experimental study on durability properties of concrete containing zeolite as a highly reactive natural pozzolan. Constr Build Mater 2012;35:1023–33.
[44] Ramezanianpour AA, Mousavi R, Kalhori M, Sobhani J, Najimi M. Micro and macro level properties of natural zeolite contained concretes. Constr Build Mater 2015;101:347–58.
[45] Ding J-T, Yan P-Y, Liu S-L, Zhu J-Q. Extreme vertices design of concrete with combined mineral admixtures. Cement Concr Res 1999;29(6):957–60.
[46] Nagrockienė D, Girskas G, Skripkiūnas G. Properties of concrete modified with mineral additives. Constr Build Mater 2017;135:37–42.
[47] Chan SYN, Ji X. Comparative study of the initial surface absorption and chloride diffusion of high performance zeolite, silica fume and PFA concretes. Cement Concr Compos 1999;21(4):293–300.
[48] Ahmadi B, Shekarchi M. Use of natural zeolite as a supplementary cementitious material. Cement Concr Compos 2010;32:134–41.
[49] Sabet FA, Libre NA, Shekarchi M. Mechanical and durability properties of self consolidating high performance concrete incorporating natural zeolite, silica fume and fly ash. Constr Build Mater 2013;44:175–84.
[50] Mohseni E, Tang W, Cui H. Chloride diffusion and acid resistance of concrete containing zeolite and tuff as partial replacements of cement and sand vol. 10. 2017. p. 372.
[51] Pp Y. Effect of sand fines and water/cement ratio on concrete properties vol. 4. 2018.
[52] Kolapo O, Babafemi AJ, Umoh A, Olawuyi B. Effect of batching methods on the fresh and hardened properties of concrete vol. 13. 2012. p. 773–9.
[53] Shamsai A, Rahmani K, Peroti S, Rahemi L. The effect of water-cement ratio in compressive and abrasion strength of the nano silica concretes vol. 12. 2012.
[54] Rahmani K, Rahmanzadeh B, Piroti S. Experimental study of the effect of water-cement ratio on compressive strength, abrasion resistance. Porosity and permeability of Nano silica concrete, vol. 12. 2018. p. 16–24.
[55] Lian C, Zhuge Y, Beecham S. The relationship between porosity and strength for porous concrete vol. 25. 2011. p. 4294–8.
[56] Kearsley EP, Wainwright PJ. The effect of porosity on the strength of foamed concrete. Cement Concr Res 2002;32(2):233–9.
[57] Kumar R, Bhattacharjee B. Porosity, pore size distribution and in situ strength of concrete. Cement Concr Res 2003;33(1):155–64.
[58] Burgoyne C, Amin MHG. The use of MRI to observe the structure of concrete vol. 57. 2005. p. 101–9.
[59] Menadi B, Kenai S, Khatib J, Aït-Mokhtar A. Strength and durability of concrete incorporating crushed limestone sand vol. 23. 2009.
[60] Feng N, Feng X, Hao T, Xing F. Effect of ultrafine mineral powder on the charge passed of the concrete. Cement Concr Res 2002;32(4):623–7.
[61] Uzal B, Turanli L, Mehta P. High-volume natural pozzolan concrete for structural applications. ACI Mater J 2007;104(5):535–8.
[62] Dousti A, Rashetnia R, Ahmadi B, Khatami D, Shekarchi M. Effect of natural zeolite and silica fume as a pozzolanic materials on the chloride diffusion of concrete. 2012.
[63] Poon C, Lam L, Kou S, Lin Z. A study on the hydration rate of natural zeolite blended cement pastes. Constr Build Mater 1999;13(8):427–32.
[64] Cui X, et al. Experimental study on the relationship between permeability and strength of Pervious Concrete. 2017;29(11):04017217.
[65] Wang L, Ueda T. Mesoscale modeling of water penetration into concrete by capillary absorption. Ocean Eng 2011;38(4):519–28.
[66] Smyl D, Ghasemzadeh F, Pour-Ghaz M. Modeling water absorption in concrete and mortar with distributed damage. Constr Build Mater 2016;125:438–49.
[67] Yoo J-H, Lee H-S, Ismail MA. An analytical study on the water penetration and diffusion into concrete under water pressure. Constr Build Mater 2011;25(1):99–108.
[68] Karakurt C, Topçu İB. Effect of blended cements produced with natural zeolite and industrial by-products on alkali-silica reaction and sulfate resistance of concrete. Constr Build Mater 2011;25(4):1789–95.
[69] Lura P, Mejlhede Jensen O, Weiss W. Cracking in cement paste induced by autogenous shrinkage vol. 42. 2009. p. 1089–99.
[70] Wu L, Farzadnia N, Shi C, Zhang Z, Wang H. Autogenous shrinkage of high performance concrete: a review. Constr Build Mater 2017;149:62–75.
[71] Yoo D-Y, Min K-H, Lee J-H, Yoon Y-S. Shrinkage and cracking of restrained ultra-high-performance fiber-reinforced concrete slabs at early age. Constr Build Mater 2014;73:357–65.
[72] Sobuz HR, Visintin P, Mohamed Ali MS, Singh M, Griffith MC, Sheikh AH. Manufacturing ultra-high performance concrete utilising conventional materials and production methods. Constr Build Mater 2016;111:251–61.
[73] Zheng-wu J, Zhen-ping S. Pei-ming WJJoWUoT-MSE. Self-desiccation effect of high performance concrete. vol. 19. 2004. p. 82–6. 4.
[74] Holt EE. Early age autogenous shrinkage of concrete. VTT Publ 2001;446:193.
[75] Liu F, Wang J, Qian X, Hollingsworth J. Internal curing of high performance concrete using cenospheres. Cement Concr Res 2017;95:39–46.
[76] Bentz DP, Jensen OM. Mitigation strategies for autogenous shrinkage cracking. Cement Concr Compos 2004;26:677–85.
[77] Lura P, Mejlhede Jensen O, Igarashi S-I. Experimental observation of internal water curing of concrete vol. 40. 2007. p. 211–20.
[78] Liu J, Shi C, Ma X, Khayat KH, Zhang J, Wang D. An overview on the effect of internal curing on shrinkage of high performance cement-based materials. Constr Build Mater 2017;146:702–12.
[79] Zhang J, Wang Q, Zhang J. Shrinkage of internal cured high strength engineered cementitious composite with pre-wetted sand-like zeolite. Constr Build Mater 2017;134:664–72.
[80] Mastali M, Kinnunen P, Dalvand A, Mohammadi Firouz R, Illikainen M. Drying shrinkage in alkali-activated binders – a critical review. Constr Build Mater 2018;190:533–50.
[81] Kim G, Kim J-Y, Kurtis KE, Jacobs LJ. Drying shrinkage in concrete assessed by nonlinear ultrasound. Cement Concr Res 2017;92:16–20.
[82] Shariq M, Prasad J, Abbas H. Creep and drying shrinkage of concrete containing GGBFS. Cement Concr Compos 2016;68:35–45.
[83] Hu X, et al. Drying shrinkage and cracking resistance of concrete made with ternary cementitious components. Constr Build Mater 2017;149:406–15.
[84] Emam E, Yehia S. Performance of concrete containing zeolite as a supplementary cementitious material. 2017.
[85] Mola-Abasi H, Shooshpasha I. Influence of zeolite and cement additions on mechanical behavior of sandy soil. Journal of Rock Mechanics and Geotechnical Engineering 2016;8(5):746–52.
[86] Fu Y, Ding J, Beaudoin JJ. Zeolite-based lightweight concrete products. Ottawa,

Canada: The United States: National Research Council of Canada; 1996.
[87] Feng N-Q, Peng G-F. Applications of natural zeolite to construction and building materials in China. Constr Build Mater 2005;19(8):579–84.
[88] Tokushige H, Kamehima H, Kawakami M, Bier T. Effect of use of natural zeolite as a mineraladmixture and an aggregate on physical properties of cement mortar and porous concrete. 2009. p. 1231–6.
[89] Jana D. A new look to an old pozzolan, clinoptilolite – a promising pozzolan in concrete. The 29th ICMA conference on cement microscopy. 2007. [Quebec, Canada].
[90] Bilim C. Properties of cement mortars containing clinoptilolite as a supplementary cementitious material. Constr Build Mater 2011;25(8):3175–80.
[91] Quanlin N, Naiqian F. Effect of modified zeolite on the expansion of alkaline silica reaction. Cement Concr Res 2005;35(9):1784–8.
[92] Srivastava V, Kumar R,C, Agarwal VK, Mehta P. Effect of silica fume on workability and compressive strength of OPC concrete vol. 3. 2015. p. 32–5.
[93] Limbachiya V, Ganjian E, Claisse P. Strength, durability and leaching properties of concrete paving blocks incorporating GGBS and SF. Constr Build Mater 2016;113:273–9.
[94] Xie J, Fang C, Lu Z, Li Z, Li L. Effects of the addition of silica fume and rubber particles on the compressive behaviour of recycled aggregate concrete with steel fibres. J Clean Prod 2018;197:656–67.
[95] Torabian Isfahani F, Redaelli E, Lollini F, Li W, Bertolini L. Effects of nanosilica on compressive strength and durability properties of concrete with different water to binder ratios %. J Advances in Materials Science and Engineering 2016;2016:16.
[96] Gopinath S, Mouli PC, Murthy A, Iyer N, Srinivasan M. Effect of nano silica on mechanical properties and durability of normal strength concrete LVIII. 2012. p. 433–44.
[97] Ibrahim M, Megat Johari MA, Rahman MK, Maslehuddin M, Mohamed HD. Enhancing the engineering properties and microstructure of room temperature cured alkali activated natural pozzolan based concrete utilizing nanosilica. Constr Build Mater 2018;189:352–65.
[98] Li Z, et al. Effect of nano-titanium dioxide on mechanical and electrical properties and microstructure of reactive powder concrete vol. 4. 2017.
[99] Sorathiya J, Shah S, Smit K. Effect on addition of nano " titanium dioxide " (TiO 2) on compressive strength of cementitious concrete. 2017.
[100] Zhang R, Cheng X, Hou P, Ye Z. Influences of nano-TiO2 on the properties of cement-based materials: hydration and drying shrinkage. Constr Build Mater 2015;81:35–41.
[101] Rashad AM. Effect of carbon nanotubes (CNTs) on the properties of traditional cementitious materials. Constr Build Mater 2017;153:81–101.
[102] Carriço A, Bogas JA, Hawreen A, Guedes M. Durability of multi-walled carbon nanotube reinforced concrete. Constr Build Mater 2018;164:121–33.
[103] VIDIVELLI B, ASHWINI B. A study on carbon nanotube (CNT) in concrete. International Research Journal of Engineering and Technology (IRJET) 2018;5(7):481–9.
[104] Thang N, Tuan N, Trung Thanh L, Huu Hanh P, Ye G. Ultra high performance concrete using a combination of silica fume and ground granulated blast-furnace slag in Vietnam. 2013.
[105] Saha AK. Effect of class F fly ash on the durability properties of concrete. Sustainable Environment Research 2018;28(1):25–31.
[106] Thang NC, Thang NT, Hanh PH, Tuan NV, Thanh LT, Lam NT. Nghiên cứu chế tạo bê tông chất lượng siêu cao sử dụng silica fume và xi lò cao hạt hóa nghiền mịn ở Việt Nam. Journal of Science and Technology in Civil Engineering 2013;15:83–92.
[107] de Larrard F, Sedran T. Optimization of ultra-high-performance concrete by the use of a packing model. Cement Concr Res 1994;24(6):997–1009.
[108] Motsi T, Rowson NA, Simmons MJH. Adsorption of heavy metals from acid mine drainage by natural zeolite. Int J Miner Process 2009;92(1):42–8.
[109] Egashira R, Tanabe S, Habaki H. Adsorption of heavy metals in mine wastewater by Mongolian natural zeolite. Procedia Engineering 2012;42:49–57.
[110] Wingenfelder U, Hansen C, Furrer G, Schulin R. Removal of heavy metals from mine waters by natural zeolites. Environ Sci Technol 2005;39(12):4606–13.
[111] Zendelska A, Golomeova M, Blazev K, Krstev B, Golomeov B, Krstev A. Adsorption of copper ions from aqueous solutions on natural zeolite vol. 41. 2015. p. 17–36.
[112] International Zeolites Association. IZA structure commision. www.izastructure.org/databases/.
[113] Meier WM. The crystal structure of mordenite (ptilolite)*. Z Kristallogr 2010;115(5–6):439–50.
[114] Index of Natural Zeolites Datasheets. cited 2018 Available from http://iza-online.org/natural/index.htm.
[115] B JR. Composition, optical properties, cell dimensions, and thermal stability of some heulandite group zeolites. Am Mineral 1972;57:1463–93.
[116] Vaughan PA. The crystal structure of the zeolite ferrierite. 1966;21(6):983–90.
[117] Dent LS, Smith JV. Crystal structure of chabazite, a molecular sieve. Nature 1958;181:1794.
[118] Steinfink H. The crystal structure of the zeolite. phillipsite 1962;15(7):644–51.
[119] Fragoulis D, Chaniotakis E, Stamatakis MG. Zeolitic tuffs of kimolos island, Aegean Sea, Greece and their industrial potential. Cement Concr Res 1997;27(6):889–905.
[120] Moshoeshoe M, Nadiye-Tabbiruka MS, Obuseng V. A review of the chemistry, structure, properties and applications of zeolites. Am. J. Mater. Sci. 2017;7(5):196–221.
[121] Secondary Building Units. cited 2018 Available from http://asia.iza-structure.org/IZA-SC/SBUList.html.