The effects of zeolite minerals as a partial substitute for cement on the strength properties of concrete

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ABSTRACT

Zeolites, commonly referred to as molecular sieves, are aluminosilicate minerals with an open structure and interconnecting holes that can be explored by molecular, atomic, and ionic components. Zeolites, called pozzolans, are hydrophilic aluminum silicates that contain alkali and alkaline earth elements. Their structure consists of a framework of SiO₄ and AlO₄ tetrahedrons with oxygen atoms at their corners. A pozzolan is a siliceous or aluminous substance that, when combined with cement, interacts with the resultant calcium hydroxide to generate a cementitious compound and eliminates inappropriate expansion induced by alkali-aggregate interactions. Furthermore, zeolites can reduce the porosity of the blended cement paste while improving the interfacial microstructure features since their structure offers distinct adsorptive properties that, when utilized with active acidic and polarizing sites, convey a catalytic abilities. This review focus on evaluating the improvement properties of concrete when replacing partial cement by zeolites.

Keywords: Zeolite, pozzolan, cement, concrete, improvement

1. INTRODUCTION

Concrete is one of the most commonly utilized building products in the world, and is also one of the products that has a great role in consuming non-renewable resources. Today, the vision based on sustainable development in the industrial business grows and increases; however, cement manufacturing emits a considerable amount of CO₂. Considering an estimated 0.9 kg of CO₂ emitted each kilogram of cement manufactured [1], the cement production accounts for approximately 5% of total greenhouse gas emissions [2]. It is necessary to employ sustainable building materials or processes to mitigate carbon dioxide emission and global warming. Converting to sustainable processes and materials is crucial for the construction business, since cement consumption and environmental impact continue to rise. The basic elements of concrete are cement, water (active components), fine particles, and coarse aggregates (inactive members). To mitigate CO₂ emissions, cement can be partially substituted by pozzolanic materials or industrial waste [3, 4].

There are many pozzolanic materials such as fly ash and micro-silica as admixtures in concrete is common, the effects of using natural zeolite as a pozzolanic material on the performance of self-compacting concrete (SCC) was shown that natural zeolite enhances the performance of SCC in its fresh state. Natural zeolite strengthens the viscosity and stability of concrete and prevents leakage. In extreme instances, it can produce compressive strength equivalent to or greater than that of reference concrete [5].

Therefore, research using extra cementing materials has consistently demonstrated the benefits of adding cement replacement materials. This review will focus on considering influences of zeolites as a partial replacement of cement to the strengthen properties of concrete production.

2. CHARACTERIZATION OF ZEOLITES Zeolites are microporous crystalline aluminum silicates having pore dimensions varying from 3-7Å. The most essential aspects of these solid materials are their well-defined structure, large surface area, selective sorption of tiny molecules (molecular sieves), and ion exchange. The zeolite composition can follow this formula [6]:

Table 1: The zeolite composition

Mm ⁺	Si ₁ -nAlnO ₂	nH ₂ O
Extra framework	Framework	Sorbed
cation		phase

Regardless of the synthesis conditions, the proportion of Al in the structure can range from Si/Al \approx 1 to ∞ . Enhancing the framework's Si/Al ratio can increase both hydrophobicity and hydrothermal stability.

The Structure Commission of the International Zeolite Association (IZA-SC) assigns a three-letter code to each framework type including:

Low-silica zeolites, also known as aluminum-rich zeolites, are nearly saturated in aluminum, with a Si/Al molar ratio of approximately 1. This feature offers them a high hydrophilic surface selectivity. Their pore volumes are the greatest among known zeolites, giving them a significant economic advantage in bulk separation and purification applications requiring high capacity.

Intermediate-Silica Zeolites: in the early 1950s, scientists at Union Carbide Laboratories

invented intermediate-silica zeolites with increased thermal, hydrothermal, and acid stability. When they were initially launched, they had a considerable commercial demand as both an adsorbent and a hydrocarbon conversion catalyst. These zeolites' surfaces remain heterogeneous and show remarkable selectivity for water and other polar molecules. Intermediate zeolites with Si/Al ratios < 5 include natural zeolites such mordenite, erionite, clinoptilolite, and Chabazite, as well as synthetic zeolites including omega, mordenite, Y, and L. In this Si/Al range, these materials maintain hydrophilic properties.

High-silica zeolites (Si/Al > 5) are hydrophobic and organophilic, with fewer strong Brønsted acidic sites. They also have superior thermal and hydrothermal stability. High silica zeolites can be generated directly during the synthesis phase by adding organic components to aluminosilicate and silicate gels, or through post-synthesis or modification methods such as hydrothermal steaming, the application of aqueous $(NH_4)_2SiF_6$, SiCl₄, or F₂ gas. De-alumination removes framework aluminum, which improves catalytic characteristics and thermal stability.

3. SOME APPLICATIONS OF ZEOLITES

Zeolites have numerous unique qualities as catalysts, including acidity, geometry selectivity, enormous surface area, and structural stability...

Inorganic reactions	Organic reactions	Hydrocarbon conversion
H ₂ S oxidation	Aromatisation (C4 hydrocarbons)	Alkylation
NO reduction of NH.	Alkylation (naphthalene, benzene	Cracking
	ethylbenzene, aniline, biphenyl,	Dehydration
CO oxidation,	polyaromatics, etc.)	Fischer-Tropsch synthesis
reduction	Aromatics (hydrogenation, oxidation,	Friedel-Crafts alkylation
Decomposition of H_2O	nitration, disproportionation,	Hydrocracking
	hydroalkylation, hydroxylation,	Hydrogenation,
	oxyhalogenation, etc.)	Dehydrogenation
	Chiral (enantioselective) hydrogenation	Hydrodealkylation
		Isomerisation
	Cyclohexane (oxidation, isomerisation, aromatisation, ring opening)	Methanol to gasoline
		Methanation
		Shape-selective reforming

Table 1: Application of zeolites as catalyst [6]

Zeolites' catalytic activities are owing to the presence of active areas (commonly referred to as bronsted acidic) on the OH bridging structure between the silicon and aluminum pathways. In aluminosilicatetype zeolites, neutral SiO_4 tetrahedra are formed by 4+ charges on framework silicon atoms at tetrahedral locations (T position) and 2⁻ charges on coordinating oxygen atoms. Substituting aluminum atoms for silicon atoms in the framework can shift the charges of the respective tetrahedra from neutral to negative. Extra-framework metal cations or hydroxyl protons balance negative framework charges, generating weak Lewis acid sites or strong Brønsted acid sites that catalyze zeolite compounds.



Figure 1. Different types of hydroxyl group and acid sites in zeolites [6].

Using zeolite A as a detergent builder is a notable success in the direct use of zeolites as ion exchangers to improve detergent cleaning efficiency by eliminating Ca^{2+} and Mg^{2+} ions from washing water and preventing their precipitation by surfactants [7].

In addition, zeolites, such as mordenite and clinoptilolite, are used to purify wastewater. For example, nuclear fuel elements from a nuclear reactor such as $^{137}Cs^+$, $^{90}Sr^{2+}...$ usually are stored in pond water [8] that is decontaminated by zeolites. Besides, waste water also contained many pollutants such as heavy metals, ammonia, ammoni nitrat,... These contaminants impact on plants, animals, and humans. Natural zeolites, clinoptilolite, phillipsite, and chabazite, are particularly useful to selectively eliminate ammonia [8, 9, 10] and heavy metals, such as Cd^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+} [8, 11], and partially Cr^{3+} [12].

Natural zeolites are ability to trap for harmful heavy metals, and effective carriers of herbicides, fungicides, and insecticides that usually use in agriculture [11].

Removal of sulfur-containing gaseous creatures such as H_2S/COS or CH_3SH from natural gas and biogas is of paramount significance. Zeolite treated with $CuSO_4$ desulfurizes liquid hydrocarbons.

Natural zeolites may be utilized to refresh

air in plane and vehicle refrigerators. Various zeolites are used to deodorize sewers, toilets, refrigerators, and others. Zeolites can adsorb methane (firedamp) in coal mines and carbon monoxide sealing systems.

Zeolites are also used in the food industry. CO_2 -saturated zeolite carbonizes aqueous solutions quickly. NaA and LiX degrade beer by adsorbing proteins [13]. Zeolites are also used as polymers protecting against degradation by ultraviolet radiation [13, 14].

Zeolites are also added in synthetic (polyesters, polyamides, polyacrylonitriles, etc.) fibres to prevent the degradation (Cuzeolite) or help fixation of dyes. Zeolites as fillers to make more density to paper [13]. Zeolites also support the adhesion of of polymers onto steel [15].

4. INFLUENCES OF ZEOLITES AS A PARTIAL REPLACEMENT OF CEMENT TO THE STRENGTHEN PROPERTIES OF CONCRETE PRODUCTION

Natural zeolites have the potential to be utilized for sustainable combined cement manufacture. Because of their beneficial properties, including silica-alumina content, pozzolanic reaction, low densities, high specific surfaces, glassy rock formations, and mineralogical shapes [16]. The specific surfaces of the pozzolans should be greater than 3000 cm²/gr. Meanwhile specific surfaces of zeolites can be larger than 100 m^2 / gr [17]. The specific surfaces of clinoptilolite and analcime are 4079 cm^2/gr and 4780 $cm^2/$ gr, respectively. These zeolites were prepared with lime-natural pozzolan mixture and the average compressive strength values for the lime-zeolite (pozzolan) mixture samples were determined as 9.02MPa and 6.30MPa, respectively after 7 days of curing time [16]. These results indicate that the zeolites used have potential for use as pozzolan. Using 10% natural zeolite as pozzolan increases the resistance to sulfate attack and chlorine penetration in zeolite-containing concrete. When zeolite was added, compressive strength increased by up to 20% compared to when no zeolite was used [18]. Furthermore, due to natural zeolites's pozzolanic properties, when adding zeolites to slag-based mortars that reduces the sulfate content in the mortar by about 22% as well as chloride content with time in all the tested mortars [19]. During the hydration of the cement binder, zeolite combines with calcium hydroxide to produce a C-S-H phase, thickening the mortar's microstructure and lowering its leachability. However, the pozzolanic activity of zeolite is determined by the hydration pattern of cement clinker [20]. One of the primary causes of delayed pozzolanic reaction is large particle size, which reduces zeolite solubility. Clinker hydration products precipitate on insoluble zeolite particles, replacing solubility with diffusion. As a result, the hydration of cement clinker components moves faster, while the pozzolanic processes of natural zeolite delay.

Utilizing zeolite substituted for cement increases the unconfined UCS of cemented soil [21]. The 30% substitution of cement with zeolite results in a significant boost in strength. A reduction in the porosity of a compacted mixture significantly enhances the strength of cemented soils and somewhat enhances the strength of zeolite-cemented combinations [21]. However, when tricalcium silicate is the main component of cement, adding 15% natural zeolites clinoptilolite (Si/Al = 5.8) as a partial replacement accelerates the early and late hydration reactions of tricalcium silicate, as seen by quicker initial and final setting periods and compressive strength values at 28 days [20].



Figure 2. Compressive strengths of cement mortars [20].

In addition to replacing a partial cement for conventional concrete, natural zeolites are also ultilized for recycled coarse aggregates concrete. Containing of 10% of natural zeolites in recycled coarse aggregates concrete indicated more 28-day compressive strength than conventional concrete [22]. Natural zeolites's properties are not only in the transient stage but also in the long term. A greater replacement (25%) reduced strength after 28 days of the curing time; nonetheless, a large positive change (83%) was detected over a three-year period [23].

This validates zeolite's long-term strengthenhancing potential. Silica fume, when combined with natural zeolite, considerably increased the strength.

Natural zeolites as additional substances can decrease the shrinkage without sacrificing the strength we use zeolite. 30% of zeolite with the maximum 28 days autogenous shrinkage shows that the shrinkage decreases [24]. When considering the tensile and flexural strengths of zeolite induced concrete, 10% replacement of cement by zeolite shows increasing trend of strength [25].









When adding natural zeolites as partial replacement of cement in crumbled rubber concrete that also improves the compressive strength and flexural strength associated to samples containing 5% rubber, 15% zeolite and 5% rubber, 10% zeolite respectively [26].

Concrete with zeolite as an additional ingredient can absorb a significant amount of CO_2 [27]. Embedding zeolite material into concrete absorbs CO_2 from the atmosphere, making it environmentally beneficial. Absorption of CO_2 and minimize air pollution, keeping the atmosphere clean and full of oxygen.

5. CONCLUSIONS

Experimental findings show that natural zeolite has a significant potential as an environmentally friendly material in concrete manufacturing, but its dosage should be cautiously chosen due to the deteriorating of mechanical characteristics with increasing zeolite concentrations.

All of the papers examined here show that natural zeolite's influence on cement hydration and the production of novel compounds has been extensively studied. However, the authors' findings differ since the effect of zeolites is dependent on a variety of characteristics, including particle size, specific surface area, Si/Al ratio, chemical and mineral compositions, solubility in alkaline mediums, and so on.

As above results, more in-depth researches are required to have a better knowledge of the impact of natural zeolites on the cement hydration process as well as cement-based pastes with different distributions of zeolite particle size.

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