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GREENING THE FUTURE OF CONSTRUCTION: UNLEASHING NATURAL ZEOLITE FOR ECO-FRIENDLY HIGH-PERFORMANCE CEMENT

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ABSTRACT: The design of blended cement with less clinker follows current construction material trends. This technique promotes energy efficiency, resource conservation, and CO_2 reduction. This study proposes e_{co}-friendly cement production methods that preserve concrete quality. To determine its potential for cement manufacture, Jordanian natural zeolite from almafrak (Amman, Jourdan) is tested for physical, chemical, and microstructural properties. Accordingly, the British standard mandates 6%, 10%, and 15% natural zeolite instead of clinker. The zeolite cement's chemical composition, physical properties, and microstructure were analyzed. With 6-15% natural zeolite replaced, zeolite cement has 23.29-25.99% silicon oxide, 4.92-6.22% aluminium oxide, 5.33-6.09% iron oxide, and 55.92-49.78% calcium oxide. The specific gravity of zeolite cement decreases by 5% when applied 15% natural zeolite. Zeolite cement had autoclave soundness of 0.1-0.17, fineness of 4930-5380 cm^2/kg, initial setting time of 125-130 minutes, final setting time of 225-285 minutes, specific gravity of 3.04-2.97, and loss on ignition of 3.71-5. The compressive strength of blended cement with 6%, 10%, and 15% natural zeolite replacement is 20.48, 14.24, and 11.25 MPa after 2 days, respectively. Compressive strength is 35.8 MPa, 36 MPa, and 37.6 MPa after 28 days. Zeocement's fibrous substance, created by zeolite minerals and calcium hydroxide during hydration, makes it compact and consistent. This fibro structure improves interfacial connections, reducing microcracks, strengthening structural integrity, and making Portland cement mixtures more durable.

Keywords: Blended cement, Mechanical aspects, Natural zeolite, Physicochemical properties, Zeocement.

1. INTRODUCTION

Ordinary Portland cement is common in the construction industry. Ordinary Portland Cement OPC has limitations that are difficult to overcome. These include its high energy consumption during manufacture, which reduces cost-effectiveness. OPC production uses scarce natural or artificial resources. Additionally, OPC production releases greenhouse gases like CO_2, contributing to around 6% - 8% of worldwide human-caused carbon dioxide emissions and 35% of industrial CO_2 emissions [1]. This category includes fly ash, silica fume, ground granulated blast furnace slag, rice husk ash, and metakaolin. In recent decades, substantial research has been done on replacing natural resources with by-products in cement-based composites.

Natural zeolite is a type of volcanic inorganic microporous mineral. It has a structure with pores and chambers that are arranged in a highly organized manner. This crystalline material comprises TO_4 tetrahedra (where T can be either Si or Al), and oxygen atoms act as bridges between these tetrahedra in a ring formation [2]. About 70 natural zeolite types have been identified, and more than 260 types have been synthesized. The largest producers of natural zeolites are China, South Korea, Jordan, Turkey, and Japan [3]. Using zeolites in construction materials became more popular in the late 1980s. This increase in popularity was driven by the growing recognition of their ability to absorb and exchange ions and their well-known pozzolanic characteristics [4]. Natural zeolites have a range of uses in fields, including treating wastewater [5, 6], purifying gases [7], and enhancing concrete as an additive [8].

Supplementary cementitious materials like natural zeolites can be used in concrete to improve its durability and permeability [9]. Adding a zeolite additive with high adsorption capacity can help internal water curing, especially when using a low water/binder ratio [10]. Additionally, using natural zeolites as aggregates in lightweight concrete is effective [11]. It's worth noting that incorporating it in concrete has also been found to increase its resistance to sulfate attack [12].

"Blended cement" is generally used for Portland cement blends with a pozzolanic or cementitious additive, such as volcanic ash like natural zeolite, fly ash, and granulated iron blast-furnace slag. Due to the cost and energy savings potential associated with their use, there is a worldwide interest in increasing the utilization of these additives. For that reason, researchers have extensively investigated the addition of natural pozzolans to form blended cement, thus demonstrating benefits in reducing energy consumption, greenhouse gas emissions, and cost [13,14]. Cement production is a significant source of CO_2 emissions due to using fossil fuels to power cement kilns. Therefore, [15] examined the efficacy of synthetic zeolite as a cement additive. They added 5-12% and 10-12% zeolite to cement clinker of the total weight produced in synthetic zeolite-containing and zeolite-kaolin-based cement samples. The second additive, kaolin, comprised 10-20% of the weight. The control sample and base cement samples were compared for compressive strength. The best compressive strength for zeolite-containing cement was 88% cement clinker, 5% Gypsum, and 7% synthetic zeolite. Consequently, replacing more than 25% cement clinker with 70% cement clinker, 5% Gypsum, 10% zeolite, and 15% kaolin yielded the best synthetic zeolite-kaolin-based cement.

Meanwhile, [16] investigated the properties of laboratory-produced blended cement with 55% volcanic tuffs from two Turkish locations compared to Portland cement. They found that blending cement with 55% natural pozzolans reduces alkali-silica expansion, thereby improving the durability of the cement. The study also found that blended cement with 55% pozzolan, ground for 90 minutes, exhibited slightly lower strength properties than Portland cement for up to 91 days, indicating the potential trade-off between durability and strength in blended cement formulations. Tydlitát et. al. [17] observed that the effectiveness of natural zeolite diminishes with increasing dosage in blended cement, with a discernible limit of 10% replacement of Portland cement, beyond which zeolite primarily serves as a fine filler rather than actively participating in hydration. Building upon this, Rahhal et. al. [18] emphasized the significance of using isothermal calorimetry to analyze its effect on early cement hydration. Natural zeolite (0-40%) was added to blended cement made with low and medium C3A content Portland cement. Results show that natural zeolite dilutes the heat release curve for low C3A cement and advances the C3S peak while intensifying the third peak attributed to C3A hydration for medium C3A cement, with flowability decreasing as zeolite replacement levels increase.

Researchers are developing new strategies to make the cement industry more sustainable by lowering its clinker content and CO_2 emissions, which makes the investigation relevant to this development. Hassan et. al. [19], studied how different proportions of synthetic zeolite catalysts (added to the kiln during clinker production) affect cement performance, focusing on clinker content and CO_2 emissions. The study showed that up to 10% synthetic zeolite could be seamlessly integrated into cement production without affecting mechanical properties, quality, or performance. Results indicate that using such additives to produce environmentally sustainable cement is beneficial.

The current research landscape within the cement industry predominantly focuses on utilizing clinoptilolite, the most common type of global zeolite, and synthetic zeolite. However, despite Jordan being the third-largest producer of zeolite worldwide, the unique properties of its zeolite remain primarily unstudied in terms of its potential impact on the cement industry. This research aims to address this gap by investigating the role of Jordanian zeolite within the cement industry, highlighting the significance of exploring its properties and potential contributions to cement production processes.

This study aims to thoroughly examine the physical, chemical, and microscopic properties of Jourdain natural zeolite, focusing on its appropriateness as a pozzolanic substance for the cement industry. The main goal is to ascertain the distinct mechanical qualities, enhancements in durability, and microstructural characteristics of zeolite cement compared to ordinary Portland cement. The study also aims to determine the optimum proportion of natural zeolite to boost cement performance while balancing improved characteristics and economic viability in cement production through a comprehensive examination.

2. RESEARCH SIGNIFICANCE

This research explores Jourdain's natural zeolite's physical, chemical, and microscopic characteristics, highlighting its suitability for the cement industry. Due to an absence of prior investigation, the impact of this particular type of zeolite within the realm of the cement industry still needs to be explored. The focus demonstrates why natural zeolite is chosen as a pozzolanic material to replace cement clinker without thermal processing. While it is evident that adding natural, unprocessed zeolite can enhance cement performance, the specific mechanical properties and durability improvements compared to ordinary Portland cement need to be identified. In addition to investigating the aspects mentioned above, the study will incorporate a microstructural analysis of zeolite cement. This analysis aims to provide insights into the internal structure of the cement incorporating natural zeolite, shedding light on its microscopic features and potential benefits for the overall cement matrix. The ultimate goal is to determine the optimal proportion of natural zeolite that can be effectively utilized as a substitute material in cement manufacturing, considering both performance enhancement and economic feasibility.

3. EXPERIMENTAL PROGRAM

3.1 Materials

The production of zeocement involves utilizing specific materials that play an essential role in achieving the desired properties. The following component materials were used:

- Clinker (Lafarge company-Iraq)

- Natural zeolite from a almafrak (Amman, Jourdan).
- Gypsum
- standard sand.
- Distilled water.
- OPC (Tasluja-Bazian Cement Factory/ CEM I 42.5 R)
- Coarse and fine aggregate.

3.1.1 Clinker

The sourcing of clinker is a critical step in the production of zeocement. This research analyzed clinker samples using X-ray fluorescence (XRF) spectroscopy to determine their chemical composition and properties. The test result is presented in Table (1). The visual representation of the clinker composition is provided in Figure (1/A).

3.1.2 Natural Zeolite (NZ)

The extent of NZ resources is not yet fully understood globally. Nevertheless, estimates suggest that approximately 120 million tons of clinoptilolite, chabazite, erionite, mordenite, and phillipsite can be found in near-surface deposits in the United States basin range province, with the potential for up to 10 trillion tons of zeolite-rich deposits in the country. In contrast, Jordan boasts abundant zeolite resources [2], making it an attractive option for sourcing NZ materials for research. Figure (1/C) shows a general view of the natural zeolite used in the experimental work.

Zeolite is not a singular mineral entity but a mineral group encompassing diverse mineral species. These zeolites exhibit distinctions primarily in their chemical compositions, particularly in the types of cations present, including potassium, sodium, calcium, and others. Therefore, X-ray Diffraction (XRD) analyses of the minerals were conducted for the Jordanian NZ used in this study to determine its chemical composition. The XRD test results in Table 2 indicate that the NZ comprises a group of minerals: Phillipsite, chabazite, and analcime. Despite the high-quality properties that characterize these minerals and this specific type of NZ, its role in cement and concrete production has not yet been studied. While most global NZ production is from the clinoptilolite mineral, this research stands out for its utilization of this particular type of NZ and the exploration of its impact on cement production. Table 1 shows Zeolite's XRF chemical property results, while Table 3 shows the NZ's physical tests result.

SEM was conducted to study natural zeolites' morphology, crystal structure, and chemical content. Fig. 2 shows how SEM analysis reveals zeolites' particle size distribution and shape, which affect surface area, packing density, and reactivity [20]. The SEM micrograph shows that NZ comprises phillipsite, chabazite, and analcime. Phillipsite is usually found in sedimentary zeolite deposits. However, pure phillipsite is rare. Fig. 2 shows robust prisms and short laths of phillipsite measuring 3 to 30 μm in length and 0.3 to 3 μm in thickness. Chabazite crystals are cubic. Analcime's cuboctahedra and trapezohedra are easily identifiable under the scanning electron microscope. These findings support prior studies [21] and align with the zeolite properties outlined in Table 2.

3.1.3 Gypsum

Adding Gypsum during cement production to control the setting according to British Standard 197 [22]. The chemical properties of Gypsum using X-ray fluorescence (XRF) analysis and their appearance are shown in Table (1) and Figure (1/B), respectively.

3.2 Zeocement Production

This research suggested substituting 6%, 10%, and 15% of the NZ with various amounts of ordinary Portland clinker and a fixed amount of Gypsum, as shown in Table 4. The reference used in this study was British Standard 197 [22]. This standard allows CEM II cement, often called Portland-composite cement, to be manufactured with a 6-20% natural pozzolanic component blend.

Fig.1 Shows: (A) clinker, (B) Gypsum, (C) natural zeolite, (D) ball mill used in grinding of zeocement.

Table 1 Shows the test results of X-ray fluorescence (XRF) of clinker, NZ, and Gypsum used in this research.

Symbol	Clinker (%)	NZ (%)	Gypsum (%)
CaO	66.6	14.12	32.62
SiO_2	20.3	40.12	2.77
Al_2O_3	3.078	11.38	0.62
Fe_2O_3	5.27	11.24	0.36
SO_3	0.367	1.439	38.75
MgO	1.388	5.119	1.2
K_2O	0.69	1.27	0.04
TiO_2	0.28	2.547	0.02

Table 2 XRD test results for minerals in the NZ selected in this research.

Zeolite Minerals%	Formula	Content (%)
Phillipsite	$(K, Na, Ca)1.2(Si,Al)_8O_{16} \cdot 6H_2O$	41.1
Chabazite	$CaAl_2Si_4O_{12} \cdot 6H_2O$	6.3
Analcime	$NaAlSi_2O_6 \cdot H_2O$	9.7

Table 3 Test results of the physical properties of NZ.

Parameter	Range
Colour	Reddish to dark brown, shown in Figure 1
Water absorption (%)	10.8
Unit weight (kg/m^3)	1010
Specific gravity	1.90
Void ratio (%)	30
Porosity (%)	35
Loss on ignition (%)	9
Soundness (%)	9

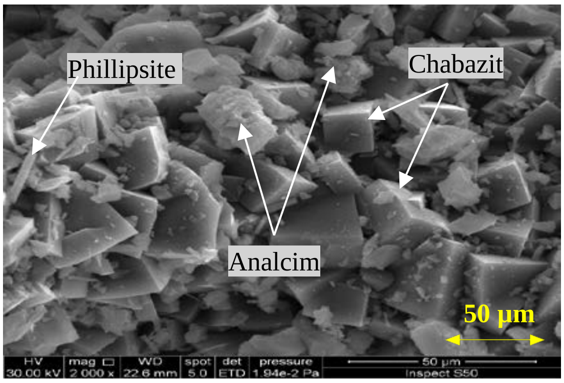


Fig. 2 Scan electron microscopic (SEM) of zeolite at 50 µm level.

The mill used in this research is a laboratory ball mill with a 25 kg raw mix capacity, as shown in Figure (1/D). Accurately weighed clinker, NZ, and Gypsum materials and mixed them thoroughly in a container. After grinding, the cement was passed through 100 µm and identified as the primary cement for subsequent chemical, physical, and mechanical evaluations to ascertain its characteristics. Coarser particles of size greater than 100 µm returned to the ball mill for further grinding. It should be noted here that the resulting mixture of zeocement was not smoothed similarly to ordinary cement, as the goal of this cement is to obtain the least energy required for its manufacturing. Figure 3 illustrates the three distinct types of zeocement (ZC1, ZC2, and ZC3). Notably, alterations in the quantity of NZ employed led to noticeable changes in the zeocement's color. Specifically, when NZ was replaced at a rate of 15%, the cement exhibited a red hue due to the inherent colour of the NZ used.

Table 4 Trial blending scenarios for blended cement.

Code for blending Scenario	Inputs quantity in the zeocement volume basis (%)			
	clinker	zeolite	Gypsum	Total input quantity (%)
ZC1	89	6	5	100
ZC2	85	10	5	100
ZC3	80	15	5	100

Fig. 3 Shows the colour and appearance of three types of zeocement.

3.3 Test Specimens

3.3.1 Physical properties of the zeocement.

The test of physical properties aims to investigate the composition of zeocement fineness, setting, hardening characteristics, and durability behavior. These aspects are essential in understanding the cement's fresh properties and handling during construction.

3.3.2 Fineness of zeocement

Cement particle fineness affects heat release during hydration. Higher cement fineness (lower particle size) increases heat production, especially during early hydration. Consequently, it significantly impacts cement compressive strength and durability. The British Standard (British Standards Institution 196-6) [23] specifies three cement fineness procedures. The sieving method, the air-jet sieving method, and the air permeability method (Blaine) are used to measure the specific surface area. In this study, the sieve method was used by sieving the produced cement from the sieve (90µm). This process is ideal for monitoring and regulating industrial processes and shows coarse cement particles. In addition, the air permeability method (Blaine) is conducted by determining its specific surface area. It involves examining the duration required for a particular air volume to pass through a compressed bed of zeocement with predetermined dimensions and porosity.

3.3.3 Setting time of zeocement

Using the Vicat Needle method, cement setting time was measured, which depends on fineness, water-cement ratio, Gypsum content, and chemicals. The time test includes starting and final setup timings that show the cement paste setting.

3.3.4 The specific gravity of zeocement

A Le Chatelier flask was used to determine the specific gravity of zeocement per (ASTM C188) [24]. The procedure involves immersing a weighed amount of cement in a liquid (kerosine) and measuring the displaced volume, allowing for calculating its specific gravity. The specific gravity test for zeocement was performed to assess the extent of density variation when incorporating NZ, which has a lower specific gravity compared to clinker.

3.3.5 Mechanical properties of zeocement

Samples of zeocement were subjected to the test following the method outlined in (British Standards Institution 196-1) [25] for mortar specimens and British Standard (BS EN 12390-2) [26] for concrete samples.

3.3.6 Microstructural analysis

SEMs employ a focussed electron beam to scan a specimen's surface to create images. Electrons interacting with sample atoms generate diverse signals that reveal the sample's composition and surface topography. Scoping electron microscopy uses high magnifications to obtain high-resolution images to assess tiny objects and characteristics. Al Khora Company in Baghdad used a Thermo Scientific Axia Chemi SEM for SEM analysis. A thin layer of gold alloy was put on specimen surfaces to prevent electron repulsion from the instrument. During SEM examinations, energy dispersive X-ray spectroscopy (EDS) was used to determine the sample's chemical composition.

3.3.7 Soundness (autoclaved test)

Soundness, in the context of cement paste specimens, refers to their ability to maintain structural integrity without developing cracks, disintegration, or other defects due to excessive volume changes; one of the primary contributors to such volume changes is the hydration of crystalline magnesia, specifically periclase (MgO). The maximum amount of MgO in cement is 6% according to American standards ASTM C151 [27].

In this study, we employed the autoclave expansion test to evaluate the soundness of cement paste specimens. The test involved 25 × 25 × 280 mm mortar bars with a 250 mm gauge length. Specimens were subjected to curing in steam inside an autoclave device under conditions of 20 kg/cm² and 216°C for 3 hours. ASTM C151 [27] specifies a limit of 0.8% for autoclave expansion as a criterion for soundness; if the expansion exceeds this limit, the cement is typically rejected. Table 5 illustrates the standard followed for zeocement chemical and physical properties testing.

Table 5 Test methods for zeocement and OPC.

Property	Test Method
Blaine specific surface (cm2/g)	BS EN 196-6 [23]
Fineness (wt.%), 90 µm	BS EN 196-6 [23]
Specific gravity	ASTM C188 [24]
Compressive strength (Mpa)	BS EN 196-1 [25]
Soundness—Autoclave expansion (%)	ASTM 151 [27]
Initial setting time (min)	BS EN 196-3 [28]
Finish setting time (min)	BS EN 196-3 [28]
Chemical analysis	BS EN 196-2 [29]

4. RESULTS AND DISCUSSIONS

4.1 Physical Analysis of Zeocement

Table 6 displays the proportion of particles passing the sieve (90 µm), specific gravity, and Blaine values for physically analyzed OPC and zeocement. OPC and zeocement have different particle sizes, specific surfaces (Blaine), and specific gravity. The particle size study reveals that blended cement types (ZC1, ZC2, ZC3) have retaining particle percentages of 5, 7, and 10% on sieve (90 µm) compared to OPC, which has no retention. ZC1, ZC2, and ZC3 have Blaine values of 4930, 5231, and 5380 cm^2/g, while OPC is 4590 cm^2/g, indicating a coarser zeocement composition than Portland cement. However, their Blaine fineness values are substantially higher. The coarse phase in blended cement may be linked to the larger particle size of the clinker phase, which makes grinding harder than the finer pozzolan phase.

Table 6 shows zeocement and Portland cement gravities. Specific gravities of cement range from 2.97 to 3.11 g/cm^3. The lowest value is for ZC3. The OPC was most valuable. NZ, used to make blended cement, causes specific gravity changes. NZ has 1.9 specific gravity. Specific gravity drops by 5% when applied by 15% (NZ). zeocement has a lower specific gravity due to the bulk replacement of cement clinker with NZ. When substituting different amounts of NZ, the paste volume rose, requiring more water to maintain a constant texture. The findings of this study were consistent with previous research conducted by [30, 31], which demonstrated that the use of natural pozzolanic materials with a lower specific gravity in the manufacturing of blended cement leads to a reduction in the specific gravity of the resulting cement. Reducing specific gravity is a valuable technique for decreasing the overall weight of a construction.

Figure 4 shows setting time test results. OPC mortar set longer than zeocement mortar. Initial settings for ZC1, ZC2, and ZC3 are 125, 129, and 130 min, respectively compared with 175 min for OPC. Zeolite particles' high water absorption may explain consistency loss to match OPC consistency; blended zeocement needs more water. According to some research, the first wetting of zeolite particles during mixing accelerates cement hydration. This suggests that NZ significantly affects hydration initiation. Absorption of water increases the solution's alkalinity, making clinker minerals soluble. In later phases, calcium hydroxide solution causes surface-controlled hydrolysis of zeolite, forming CSH gel on its surface [32].

For this reason, the initial setting time of the zeocement mixture is nearly comparable and wholly lower than the OPC mixture. Another logistical factor that may account for the lower initial setting time values of zeocement is the reduced clinker content. The minimum required initial setting time is 45 minutes. The zeocement successfully met the requirements outlined in EN 197 [22], considering all the different replacement levels for NZ.

Table 6 Physical specifications of zeocement.

Cement type	Passing from 90 µm (%)	Specific gravity	Blaine (cm^2/g)
PC	100	3.11	4590
ZC1	95	3.04	4930
ZC2	93	3.03	5231
ZC3	90	2.97	5380

The C3A content in zeolite-blended cement (ZC1, ZC2, and ZC3) differs significantly from that in ordinary Portland cement OPC. Specifically, the C3A content in ZC1, ZC2, and ZC3 is 4.03, 4.73, and 6.19, respectively, compared to 2.47 in OPC. This increase in C3A content corresponds to the more significant proportion of NZ added to zeocements. Due to this higher C3A content, the final setting time of zeocements tends to be longer as the zeolite blend ratio increases, in contrast to OPC. Even though the Blaine values for ZC1 and ZC2 are 5231 and 5380 cm^2/g, respectively, the dissolution of the C3A component in clinkers decelerates. This deceleration leads to an extended setting time, primarily due to a reduced rate of water diffusion, which is influenced by the decreasing Blaine values at higher blend ratios [33]. The maximum of 10 h (600 min.) final setting time requirements set by EN 197 [22] standards is satisfied.

4.2 Chemical Composition Result of Zeocement

The test results of the chemical composition of three types of zeocement and OPC are presented in Table 7. The test result indicated that all the zeocements types had higher SiO_2 and lower CaO content than the OPC. This aligns with the findings of [34]. The silica content of the blended cement increased from 23.29 % for 6% NZ replacement to 25.99 % for 15% NZ replacement. A similar trend was observed for the alumina and ferric oxide contents, which increased from 4.92% to 6.22% and 5.33% to 6.09%, respectively. The silica and alumina content is responsible for the formation of cementitious products (calcium silicate hydrates) and (calcium aluminate hydrates) when they react with lime $Ca(OH)_2$ in the presence of water [35]. Thus, as the NZ percentage increased, more silicate and alumina were available to react with the lime produced during cement hydration to produce additional cementitious products.

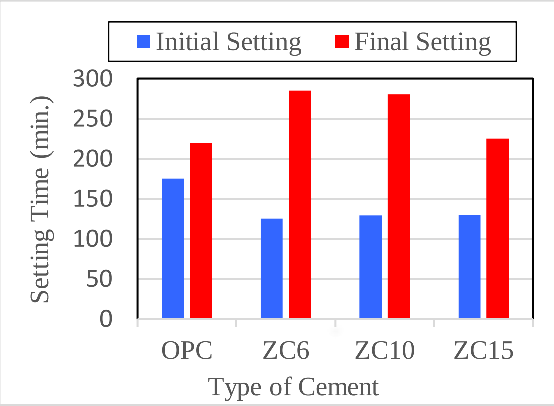


Fig.4 Setting time characteristics of zeocement and OPC.

Table 7 Chemical composition of OPC and zeocement.

Constituent	OPC %	ZC1%	ZC2%	ZC3%
SO_3	2.09	2.07	1.76	2.43
LOI	3.7	3.82	3.71	5.00
Fe_2O_3	5.56	5.33	5.56	6.09
SiO_2	19.66	23.29	24.27	25.99
CaO	60.44	55.92	54.30	49.78
MgO	3.49	2.35	2.50	3.19
AL_2O_3	4.1	4.92	5.33	6.22
C3A	1.47	4.03	4.73	6.19

Magnesium oxide (MgO) ranges from 2.35 to 3.19, while OPC is 3.49, representing minor oxides in the zeocement. High MgO is undesirable in cement because it causes unsoundness [36]. zeocement satisfied the maximum of 6.00% MgO content requirements for Type II and Type IIA Portland cement specified by ASTM 150 [37]. The SO_3 content in ZC2 and ZC1 is lower than that of the OPC. High SO_3 contributed to the higher setting time of the blended cement [38]. ZC satisfied the maximum of 3% SO_3 content requirement for Type II and Type IIA Portland cement specified by ASTM 150 [37]. The loss on ignition LOI of the ZC was higher than that of the OPC. The LOI ranges from 3.71% to 5% for the blended cement against 3.7% for the OPC. This indicates that the carbon content present in NZ furthermore contains organic matter. However, the requirements for the recommended limit of 5% by EN 197 [22] were satisfied.

4.3 Compressive Strength Result of Zeocement

Table 8 shows OPC and zeocement mortar and concrete compressive strength tests. The British Standard Institution EN 197 [22] defines ordinary Portland cement into three grades: 32.5, 42.5, and 52.5. The minimum compressive strength of regular Portland cement samples after 28 days of curing is estimated to be (32.5, 42.5, and 52.5 MPa).

Compressive strength test results in Table 8 showed that the three types of zeocement are considered (32,5) grade because concrete mortar compressive strength at 28 days is within 30 MPa compared to the three grades of ordinary cement. This research uniquely produces three blended cement models for the Iraqi market using clinker, NZ, and Gypsum. Ordinary Portland cement compressive strength relies on hydration speed. However, adding NZ to cement manufacturing causes three significant changes:

Table 8 Illustrates the compressive strength of three types of zeocement and OPC for mortar and concrete samples.

Cement type	compressive result of the mortar MPa		compressive result of concrete MPa		
	2 day	28day	Code	7 day	28 day
OPC	20.2	42.7	PC	20.6	45.54
ZC1	20.48	35.8	ZCC1	54.82	62.3
ZC2	14.24	36	ZCC2	35.9	49.7
ZC3	11.25	37.6	ZCC3	30.15	46.7

NZ has significant effects on early hydration, particularly in the early phases. It becomes pozzolanic when calcium hydroxide is produced. Calcium hydroxide reacts with zeolite's active ingredients, silica, and alumina, to generate another gel. Compared to normal cement hydration without pozzolanic components, this process dramatically increases compressive strength.

Reduced Hydration Rate and Heat: zeolite incorporation slows cement hydration. This reduces heat created during hydration, crucial to preventing heat-induced cracks. Decelerated hydration provides homogeneous hydration product dispersion in cement paste. This homogeneous distribution reduces cement voids. The current study examines the influence of natural zeolite on the compressive strength of blended cement mortar at different curing stages.

Mortar compressive strengths at two days exhibited variations. Specifically, the strength was lower for mixtures ZC2 and ZC3 compared to Ordinary Portland Cement mortar. Conversely, for ZC1, the strength matched that of OPC. This initial reduction can be attributed to the delayed pozzolanic properties of NZ, which become more apparent at later ages, and these properties' role in forming calcium hydroxide $Ca(OH)_2$. This finding complies with [39], demonstrating that natural zeolite-containing concretes (clinoptilolite type) have lower compressive strength than control concrete at all ages.

In contrast, all Zeocement combinations had virtually equal 28-day mortar strengths, showing the role of pozzolanic elements, which become active as cement hydrates. After 28 days of curing, substituting clinker with NZ at 6%, 10%, and 15% increased strength by 42%, 60%, and 70% compared to a 2-day compressive strength mortar, OPC increased 52%. NZ's more extended pozzolanic reaction and the creation of extra C–S–H gel boost strength. These findings align with [40], emphasizing that specimens with higher percentages of NZ exhibit higher confined and unconfined strength at later ages. It also aligns with [30], which showed that using NZ (clinoptilolite type) contributes to compressive strength development over time. However, it's worth noting that ZC3 showed a reduction of approximately 13% in compressive strength compared to the reference mortar at 28 days.

For the effect of NZ on blended cement concrete compressive strength at different curing stages, the rough qualities of (NZ) make concrete more cohesive and compact. Figure 5 shows the compressive strength development for the concrete sample compared with the reference OPC sample at 7 and 28 days. The compressive strength of the ZCC1, ZCC2, and ZCC3 concrete mixtures increased significantly compared to the OPC reference mixture. Natural zeolite combined cement and NZ's pozzolanic characteristics improved compressive strength significantly.

At seven days, the ZCC1 concrete mixture strengthened significantly throughout this time. This improvement is due to two main factors: a reduced water-to-cement (w/c) ratio, maintained at 0.26, and an optimal percentage of NZ replacement in ZC1 zeocement, which enhanced hydration product formation due to its homogeneous distribution. For 28-day concrete mixture results, as curing reached 28 days, NZ still affected concrete compressive strength. Similar to the 7-day results, the ZCC1, ZCC2, and ZCC3 concrete mixtures outperformed the OPC reference concrete mixture in strength development.

The rise in NZ cement production directly improved strength. However, ZCC2 and ZCC3, with higher w/c ratios (0.31 and 0.34, respectively), showed a different trend. Due to the higher amount of NZ in blended cement, more water was needed to maintain workability. These findings align with previous research [41, 42], which emphasizes that incorporating NZ in concrete mixtures invariably increases the overall water demand, influencing the compressive strength of the concrete.

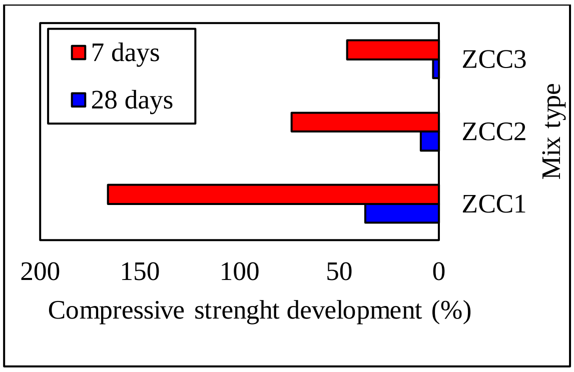


Fig. 5 The compressive strength development for concrete sample compared with reference OPC sample. Microcrack

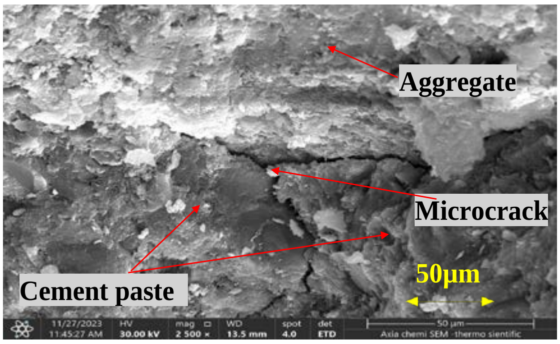
4.4 The Autoclave Expansion Result of Zeocement

Cement paste shouldn't shrink or expand after hardening. The hydration of free lime or free magnesia may be slow enough or other chemicals in the hardened cement paste, including calcium sulfate (Gypsum), may react differently. Free magnesium (MgO), which is diffuse and behaves like free lime, and Gypsum are added to the clinker before grinding to prevent abrupt setting and make cement paste unsound. If there is more Gypsum than reacts with the compound C3A during setting, it expands slowly and makes the cement paste unsound. The cement autoclave test examined the effect of magnesium oxide (MgO). Since ZC3 cement includes about 5% MgO, its effect on cement behavior had to be determined. All manufactured zeocement has stability values of autoclave soundness within the ASTM 151 [27] (0.1, 0.14, and 0.17 for ZC1, ZC2, and ZC3), and the high amount of free magnesia in ZC3 did not affect its soundness. All cement tests fall under the ASTM 151 [27] norm, which is less than 0.8%.

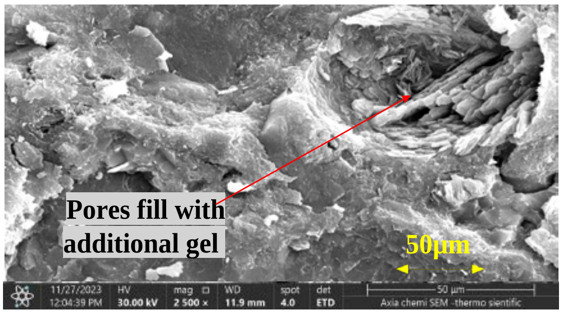
4.5 Microstructure Behaviour of Zeocement

Figures 6 and 7 show SEM pictures of cement paste for all mixes. During SEM examinations, samples were analyzed for phases using EDS shown in Fig. 8 and 9. SEM photos of Portland cement and zeocement with different natural zeolite percentages show distinct features. Ordinary concrete has microcracks, especially at the aggregate-cement paste contact and within the cement paste.

Close inspection reveals interlocking fibrous structures, especially in voids. These structures are extra compounds formed by interacting with natural zeolite silica and cement-hydration calcium hydroxide. This implies a unique interaction in zeocement mixture composition.

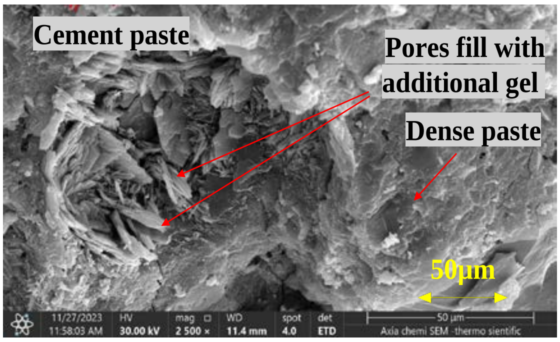


REF MIX

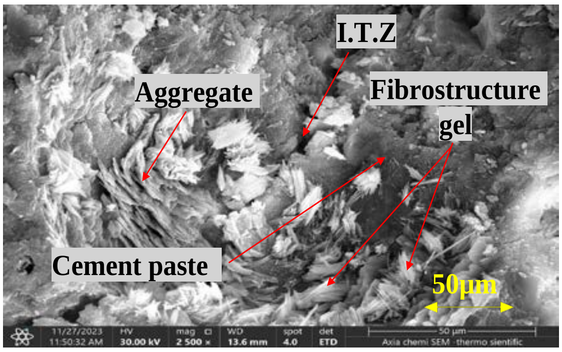


ZCC 1 MIX

Fig. 6 SEM image of reference mix and ZCC1 mix at 50 µm level at 90 days.

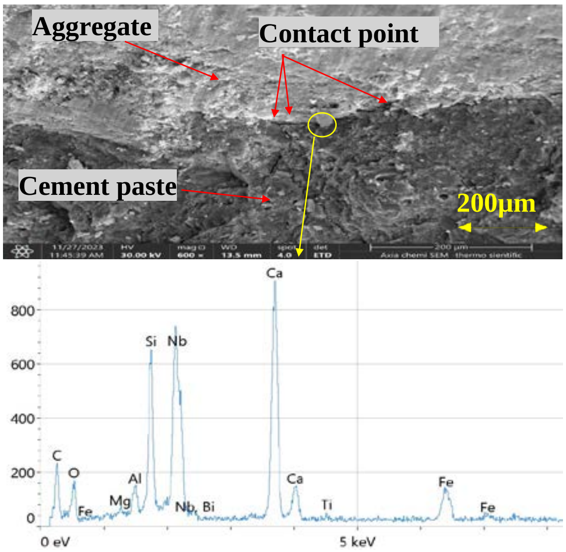


ZCC2 MIX



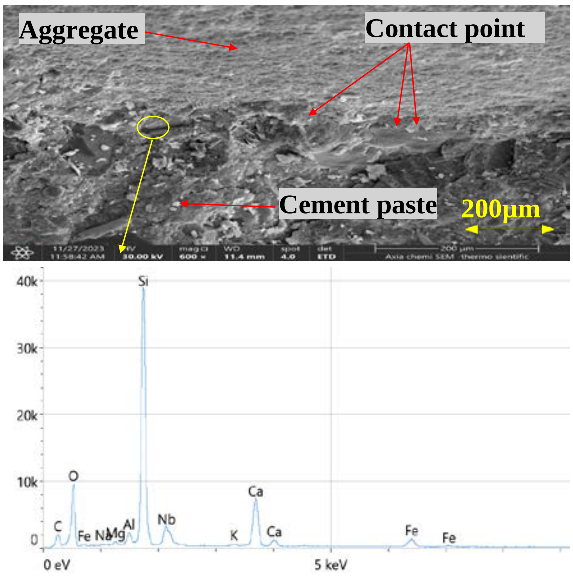
ZCC3 MIX

Fig. 7 SEM image of ZCC 2 and ZCC3 mix at (50 and 10 µm) level at 90 days age.



REF MIX

Fig. 8 SEM image and EDS analysis of reference mix at 200µm level.



ZCC 3 MIX

Fig. 9 SEM image and EDS analysis of ZCC3 mix at 200µm level.

SEM pictures show zeocement mixtures are compact and homogenous, unlike microcrack-filled concrete. Figures 6 and 7 show the SEM investigation of ZCC 1 and ZCC 2, focusing on cement matrix pore structure. Notably, pores are unique. They contain fibrostructures. This gel is formed when zeolite minerals (mainly silica) and calcium hydroxide (Ca(OH)2) combine during hydration. This fibrous gel fills pores, creating a more complex matrix.

A fibrous network in the pore spaces may prevent cracks and improve the material's stress resistance. This unusual fibrostructure is especially noticeable in ZCC3. SEM investigation of ZCC3 shows that fibrous elements fill pore gaps and connect cement and aggregate phases. This connectedness reduces microcracks in the interfacial region and improves structural integrity. Figures 8 and 9 illustrate the top aggregate connections with cement paste compared to the OPC mix with EDS analysis, demonstrating the fibrostructure's ability to connect cement and aggregate phases. It reinforces the cement paste-aggregate contact by establishing a network across both phases. This bridging process reduces microcracks, a vulnerability to concrete construction. Microcracks in interfacial zones must be minimized for numerous reasons. It increases structural durability and limits water and other hazardous agent penetration, reducing the chance of deterioration. The fibrous network is a barrier, preventing harmful substances from entering the concrete and extending its lifespan. The principal hydration products around the aggregate phase are more substantial due to cohesion. Thus, NZ improves the aggregate-cemented paste transition zone. This is due to the compact microstructure and increased compressive strength of ZCC3 mixes compared to reference mixes.

5. CONCLUSIONS

The research results show that the comprehensive study on Jordanian natural zeolite underscores its immense potential in zeocement production. The zeocement, incorporating up to 15% natural Zeolite, exhibited high-quality pozzolanic properties without compromising cement quality. The substitution of clinker with natural zeolite resulted in remarkable strength development, surpassing ordinary Portland cement (OPC 42.5 grade) in compressive strength by 42%, 60%, and 70% for substitution levels of 6%, 10%, and 15%, respectively, over two curing periods. All zeocement mixes met Iraqi and BSI standards for compressive strength and soundness while displaying setting times comparable to regular Portland cement. Additionally, zeocement production showcased lower energy demand due to the absence of the calcination process and reduced grinding energy requirements. The microstructural analysis revealed a distinct fibrous network formation, enhancing interfacial connections and minimizing microcracks, thereby improving structural integrity and promoting more excellent durability. Despite challenges such as increased water requirements, our findings collectively support the positive impact of Jordanian natural zeolite on zeocement properties, indicating a promising direction for further research and potential applications in the construction industry. Based on the results and conclusions, long-term durability studies will provide insights into the real-world performance for future investigations of zeocement, evaluating its resistance to environmental factors such as freeze-thaw cycles and chemical exposure. Additionally, investigating the compatibility of natural zeolite with other supplementary cementitious materials offers the potential to enhance zeocement properties while reducing its environmental footprint.

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Abbreviations

CO_2	Carbon dioxide
SO_3	Sulfur trioxide
AL_2O_3	Aluminum oxide
ASTM	American Society for Testing and Materials
OPC	Ordinary Portland cement
TO_4	T can be either Si or Al, and oxygen atoms
XRF	X-ray fluorescence
NZ.	Natural zeolite
XRD	X-ray diffraction
SEM	Scanning electron microscopy
CaO	Calcium Oxide
MgO	Magnesium oxide
K_2O	Potassium oxide
TiO_2	Titanium dioxide
Fe_2O_3	Iron Oxide
SiO_2	Silicon dioxide
LOI	loss on ignition
C3A	Tricalcium aluminate
CSH	Calcium Silicate Hydrate
EDS	Energy-dispersive X-ray spectroscopy