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An Experimental study on the Fundamental Properties of Zeolite Cement Mortar

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Abstract: As the cement industry not only consumes a large amount of energy but also uses limestone as the main as a raw material, emitting CO_2, the main culprit behind global warming, it is expected to face a serious setback in the near future caused by environmental problems. With the advent of today's cutting-edge technology and the public's increased awareness about global environmental issues, the cement industry is actively seeking ways to adopt a variety of technology as part of an effort to diversify its resources. This study is designed to assess the material properties of zeolite cement mortar which consists mainly of natural zeolite, which recently draws much attention for its possibility as an alternative material to cement. The paper found out the strength properties and the optimal mix proportions by using alkali activator (NaOH) instead of water (H_2O) and preparing hardened zeolite mortar samples through alkali-activated reaction. As a result, the 7 day compressive strength of natural zeolite cement mortar was measured to be 42MPa, when the optimal proportion of alkali activator and curing temperature were applied. The study concludes that zeolite shows higher strength than existing types of cement and has a great potential to replace current construction materials.

1 Introduction

When cement comprising of calcareous and argillaceous materials is calcinated at a high temperature of 1,500° calcium silicates (C_3S, C_2S) are created as a result of phase change and then hardened into hydrates such as Ettringite and C-S-H gel when they reacts with water. Cement is a hydraulic material which shows the tendency of drying shrinkage due to hydration and often develops defects like cracks [7-11]. It is vulnerable to harmful substances such as strong alkali and Cr^{6+}. Given these facts, it is time that further discussion should be made from a fresh new viewpoint about the development of a new concept of construction material.

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In order to develop a new concept of construction material which do not use portland cement which uses limestone as a major raw material, this study examined the material properties of zeolite cement mortar, which emits infrared ray in a natural state which is good for the human body and is also available for mass supply. To this end, this study compared the physical and chemical properties of natural zeolite with those of Portland cement. The objective of the study was to indentify the strength properties, reactive hydrates and hardening mechanism of zeolite cement mortar. In addition, the study presents basic data about the compressive strength development of zeolite cement mortar depending on methods, age and chemical reaction for its commercial use in civic engineering and structural engineering.

2 Experimental Procedure

2.1 Materials

2.1.1 Zeolite

This study used zeolite from Gampo, North Gyeongsang province, South Korea. Fig 1 indicates the results of grading analysis of natural zeolite using particle size analyzer. The average particle size of zeolite cement used for this study was 5.39 μm, which was smaller or similar compared to that of Portland cement. Zeolite cement's specific gravity was measured to be 2.16 and its specific surface area 885,500cm^2/g, which was 285times larger than that of Portland cement whose specific gravity and specific surface area were 3.15 and 3.112 cm^2/g.

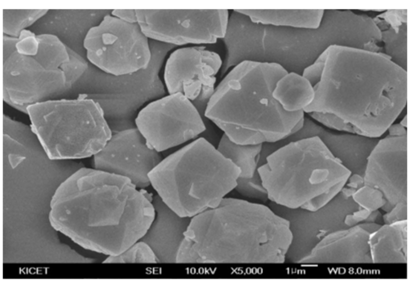

Figure 1: Image of Zeolite Size

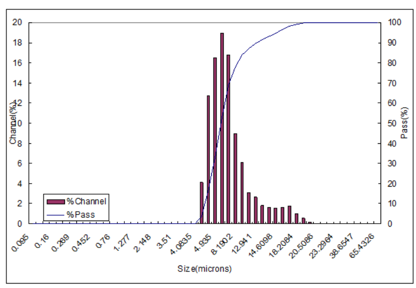

Figure 2: Size Distribution of Zeolite Cement

As the particle size of zeolite cement was smaller and its specific surface area became larger, more hydrates and hydration products around the specific surface area were created. As a result, void became smaller, forming more compact structures which in turn improved the compressive strength and structural properties. The disparity between the largest and smallest sizes of zeolite cement particles is smaller and its particle sizes are mostly of a similar size. As shown in Fig 2.

The chemical composition of zeolite cement consists mainly of O, followed by Si, Al, Ca and Na. In the meanwhile, its compound composition is comprised mostly of O_2, followed by Al_2O_3 and CaO. In comparison with a regular Portland cement, zeolite cement has a very small amount of CaO. In other words, the compound composition of Zeolite cement is made up largely of SiO_2 and Al_2O_3, which are known to contribute to pozzolanic activation. In addition, zeolite powder has the higher ratio of Al_2O_3 than Portland cement.

2.1.2 Alkali-Activator

This study found that the main ingredients of zeolite were SiO_2, Al_2O_3, which were chemically stable crystalline aluminosilicates with its micro-porous and well-aligned structures of a similar size. Such aluminosilicates vitreous bonded were so strong that the chemical bond needed to be dissolved in order to expose reactive materials kept inside them. Therefore, a strong alkali substance was used to dissolve the chemical bond of aluminosilicates

2.1.3 Fine Aggregate

This study used quartz as fine aggregate, which contained anhydrous silica (SiO_2), to prepare zeolite cement mortar for the experiment. A product of a Korean company with its maximum particle size of 0.6 mm was used as fine aggregate.

2.2 Test Plan of Zeolite Cement Mortar

This study used zeolite cement as a raw material and employed alkali activator for hardening unlike hydration.

This study has undergone 3 stages of the experiments to determine the optimal mix proportions. Different amounts of mixing water were added to the mixture of the same amount of binder, alkali activator and aggregate in order to determine its optimal proportions, according to testing method for compressive strength of hydraulic cement mortar. On the basis of the optimal proportion of mixing water, different amounts of alkali activator and aggregate were added in order to determine an optimal compressive strength during the first round of mix, as shown in Table 1

2.3 Physical Experiment

As shown in Table 1, 50x50x50 mm cubic-shaped test 12 pieces for each different mix proportion were used to conduct compressive strength tests of cement mortar according to KS F 5105 in order to determine an optimal mix proportion of zeolite

Table 1: Mix Proportion of Zeolite Cement Mortar Specimen

Mixture no.		Weight(wt%)			
		ZC	NaOH	Water	Aggregate
1	ZC-W1	180	90	22	565
	ZC-W2	180	90	29	565
	ZC-W3	180	90	36	565
	ZC-W4	180	90	44	565
	ZC-W5	180	90	52	565
	ZC-W6	180	90	72	565
	ZC-W7	180	90	90	565
2	ZC-N1	180	54	36	565
	ZC-N2	180	72	36	565
	ZC-N3	180	90	36	565
	ZC-N4	180	108	36	565
	ZC-N5	180	126	36	565
	ZC-N6	180	144	36	565
	ZC-N7	180	162	36	565
	ZC-N8	180	171	36	565
3	ZC-G1	180	90	36	360
	ZC-G2	180	90	36	441
	ZC-G3	180	90	36	540
	ZC-G4	180	90	36	720

cement mortar.; To determine an optimal curing temperature, the test used cement mortar samples of the optimal mix proportion of the highest compressive strength development, which were hardened at 4 different temperatures staring from 30°, 60°, 90° and 120°. To measure difference in the strength caused by temperature change, compressive strength tests were conducted after mixing at temperatures of 30° and 90° respectively. Then the results were compared and analyzed.

2.4 Results and analysis

2.4.1 Alkali Silica Reaction of Zeolite Cement Mortar

The 1st phase: the process of zeolite's surface anionizing when chemically stable aluminosilicates reacted with alkali activator (NaOH)

The 2nd phase: the dissolution process of inner vitreous parts of alkali silicate

$\equiv$Si - O - Si$\equiv$ + 3OH $\rightarrow$ [SiO(OH)$_3$]

$\equiv$Si - O - Al$\equiv$ + 7OH $\rightarrow$ $[SiO(OH)_3]$ +$[Al(OH)_4]$

The 3rd phase: the condensation-crystallization process and formation of hydrates through pozzolanic reaction A large amount of Si-Al was formed around zeolite due to the second phase. The dissolved $[SiO(OH)_3]$ and $[Al(OH)_4]$ (Ca^+) from particles of zeolite reacted to form zeolite A in the form of $Ca_{56}Al_{123}Si_{12}O_{48}$

The 4th phase: the development process of hydrates. A large quantity of Na-Si was formed outside zeolite particles due to the third phase. The surface of zeolite particles are comprised mainly of eluted Al-Si-Ca. It is determined that the alkali-activated zeolite reactant is zeolite A. The results of XRD analysis of zeolite cement's alkali hardening reactants are shown in Fig 3

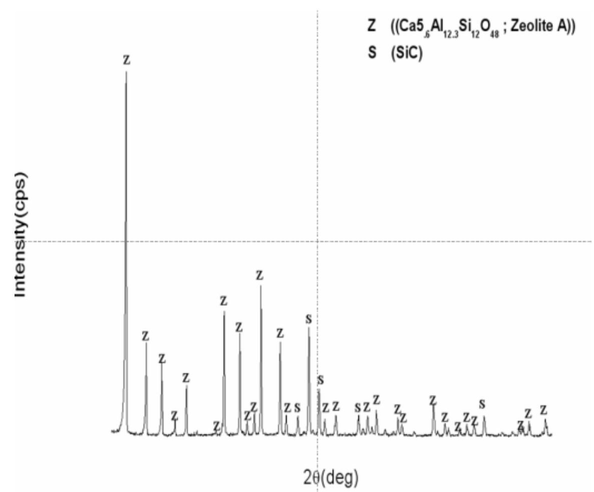

Figure 3: Analysis of Zeolite Cement Hardening using XRD

2.5 The Compressive Strength of Mortar

2.5.1 The Strength Properties depending on the amount of Mixing Water

To find out the optimum proportion of the maximum strength, compressive strength tests of zeolite cement mortar were conducted and measured by increasing the ratio of mixing water from 12% by 4% at a time until 50%, as shown in Table 4. The results of the compressive strength tests are as follows in Fig 8.

2.5.2 The Compressive Strength depending on the amount of Alkali Activator

The compressive strength of zeolite cement mortar was measured at 7 days. The results of the tests are shown in Fig 9. It was noted that as the amount of alkali activator, NaOH, increased, the compressive strength intensified. When the 95% ratio of alkali activator to zeolite powder was added in the mixture, it showed the highest compressive strength of 53.9 MPa. However, when a more-than-95% ratio of NaoH to zeolite was applied, excessive liquefaction took place, reaching a level where it was almost impossible to produce test pieces. Such phenomenon occurs as it does when mixing water increases because the total amount water used as a NaOH solvent increases which is considered to be detrimental to the strength development.

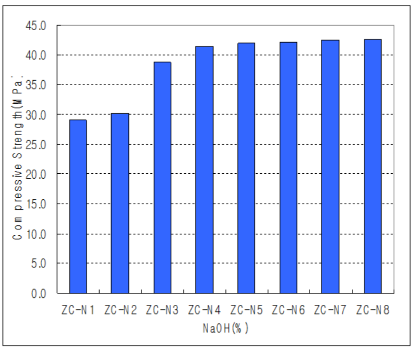

Figure 4: Compressive Strength with NaOH Ratio

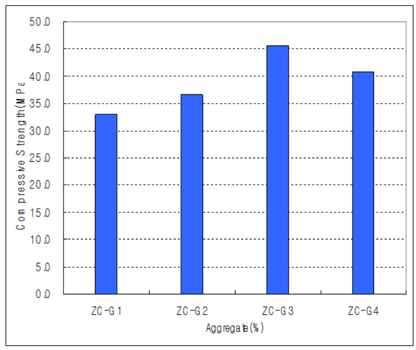

Figure 5: Compressive Strength with Aggregate Ratio

2.5.3 *The Optimal Compressive Strength Mix Proportions*

The highest compressive strength was determined after tests was done by adding different amounts of mixing water, alkali activator and aggregate to zeolite powder at various temperatures. The test determined the optimal compressive strength of zeolite cement mortar, as shown in Table 2. Additionally, the highest compressive strength appeared at over 90° curing temperature.

Table 2: Standard Mix Proportion of Zeolite Cement

Type	Weight(% per ZC)			
	ZC	NaOH(50%)	Aggregate	Water
ZC	180	171	565	0

With the ratio of alkali activator, aggregate and mixing water to zeolite powder were 95%, 314% and 0%, the 2 and 7 day compressive strength were 38.5 and 45.5 MPa respectively, showing an excellent performance. This study actually did not add any mixing water. However, NaOH used as alkali activator is 50% aqueous solution, meaning that since the moisture contained in alkali activator is equivalent to 47% of zeolite cement, the test samples have the same effects as the water-cement ratio of 47 and 53%. Therefore, the effect of boosting the compressive strength by adding more NaOH was limited to a certain degree as it added more moisture to the zeolite concrete mortar which in turn caused material problems such as bleeding.

2.5.4 The Strength depending on Curing Temperature

This study observed changes in the compressive strength relative to curing temperatures of the sample mixtures with the optimal proportion. As shown in Fig. 6, test pieces hardened at more than 90° showed higher compressive strength than any other. Test pieces hardened at 30° did not show an significant improvement in compressive strength development relative to age. It was determined that the higher the early curing temperature is, the better the early strength is. At over 90° curing temperature, there was not much difference in the compressive strength compared to 90°. The test results show that curing temperature is critical in alkali activation of zeolite cement, especially the early curing time. The study found the optimal curing temperature was 90°. As a result, there was little hydraulic heat inside mortar. Alkali activation reaction did take place actively at 30°

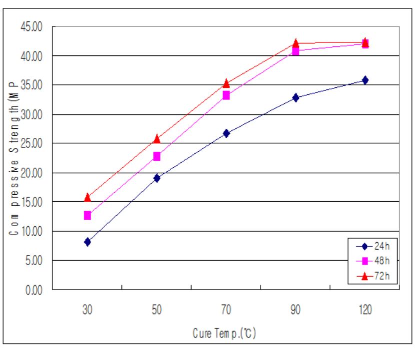

Figure 6: Compressive Strength with Cure Temperature

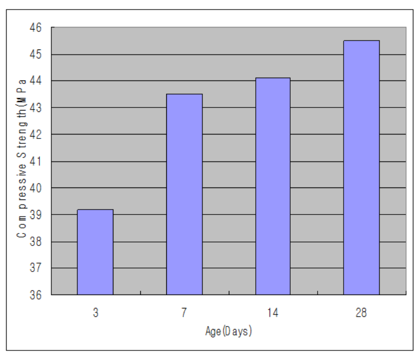

Figure 7: Compressive Strength with Age

2.5.5 The Compressive Strength depending on Age

Compressive strength tests were conducted on the zeolite cement samples which were mixed with an optimal proportion to develop the highest strength and hardening at 90°, as shown in Fig 7. The 3, 7, 14 and 28 day compressive strength of zeolite cement mortar was measured to be 39.2 MPa, 43.5 MPa, 44.1 MPa and 45.5 MPa respectively. The 3 day strength is 90% compared to that of the 27 day. The rate of increase in the compressive strength decreased as age grew, as opposed to early dramatic increases in the compressive strength. This study found that most hardening reaction of zeolite powder occurred at an early stage of reaction. Given the fact that the strength did not increase after 14 days of curing, most of hardening reaction occurred with 2 weeks, it can be utilized as high early strength cement which requires high strength at an early stage.

3 Conclusion

To tackle global warming triggered by CO_2 emissions by the cement industry and resolve problems such as hydration heat and drying shrinkage, this study examined a new concept of construction material using zeolite and alkali activator. After examining the physical and chemical properties of zeolite cement as well as mechanical properties of mortar, the study reached the conclusion as follows.

- This study used natural zeolite particle size was 5.39 μm with the specific gravity of 2.16 and the specific surface area of 885,500 cm^2/g. The chemical composition of zeolite consists of SiO_2 followed by Al_2O_3 and CaO. Although there are some irregular shapes of zeolite powder, most particles have round-shapes with different sizes.

Zeolite cement mortar was hardened through alkali activation instead of hydration. The study concludes that crystal hydration products in a combined form of zeolite and zeopolymer are found to form and develop the required strength.

Zeolite cement mortar's compressive strength changes depending on the amount of mixing water, alkali activator and aggregate. Through changes in the compressive strength caused by different proportions, the study identified the highest strength development mix proportions which were made of 180g of cement, 171g of NaOH (50%) and 565g of aggregate, and which show as much as 42.3 MPa. The alkali reaction becoming very active when alkali activator was over 50^{o}C, the highest compressive strength of the zeolite cement mortar was achieved at 90 ^{o}C dry curing(45.5MPa at 7days).

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