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An experimental study on the characteristics of chemically synthesized nano-cement for carbon dioxide reduction

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Portland cement is the essential binding agent in concrete. This cement is becoming a principal factor in air pollution because of the creation of CO_2 during its manufacture. The exhaustion of the natural resources needed for Portland cement production is also an issue. Therefore, a substitute material for this type of cement is needed. Nano-scale materials are of great interest due to their unique optical, electrical, and magnetic properties. These properties are strongly dependent on the sizes and shapes of the particles, and, therefore, it is important to be able to develop a construction route which retains the excellent properties of the nano-sized material. The purpose of this study was to synthesize nano-powder as a substitute for cement using a chemical method. Particle size, SEM, EDX, and porosity tests were conducted. This study investigated the compressive strengths of concretes with various compositions. Specimens were tested for compressive strength three, seven, 14, and 28 days after manufacture. In the results of this study, the medium-sized (50% by weight) nano-cement particles created via chemical synthesis were less than 168 nm in size, and the compressive strength of the mortar prepared using these nanoparticles was 53.9 MPa.

Key words: CO_2 reduction, Chemical synthesis, Alkali activation, Compressive strength, Highly functional construction material.

Introduction

In 1814, England's Joseph Aspidin first introduced the Portland cement that is being used universally in the current construction field. Since then, Korea has come to be known as a worldwide expert in the production of Portland cement. However, the cement industry is based on consumption, and it results in the discharge of 700 kg-800 kg of CO_2 per 1 ton of cement.

Since the beginning of the 21st century, the concrete cement environment has been constantly changing at a rate that has become critical to the fields of science and business. First of all, based on the selection of the "Kyoto protocol" to reduce greenhouse gases in order to prevent global warming, a practical plan for the reduction of CO_2 and greenhouse gases is urgent, as the results are still insufficient.

Also, a solution for the environmental destruction resulting from the depletion of natural resources is also an immediate concern. In addition, due to the nation's rapid economical development, citizens are demanding better technological and energy-producing materials that could further their qualities of life in order to accomodate the country's standard of advancement.

Based on these needs, some developed countries have combined either nano-size silica or small particles of iron oxide with cement to improve its strength. Other reports have stated that a few developed countries have actually succeeded in producing a detailed structure of cement through the milling or use of small particles of these additive materials [1, 10-12].

This paper will be based on the use of these small particles to reduce the formation of CO_2 during cement production and will rely on a more detailed chemical synthesis method to produce small, nearly nano-sized particles that will be hardened into cement to maintain its detailed structure.

Then, powerful and advantageous construction materials will be developed and, through a chemical synthesis method that uses natural compounds, a new nano-size cement material will be manufactured. Also, the use of the minute particles to maintain the cement's basic physical and chemical features will be analyzed, and a plan for the practical implementation of this new cement formulation will be developed.

Research Significance

The nano-scaling of particles can result in dramatically improved or different properties from those of conventional grain-size materials of the same chemical composition [2, 3, 9] Accordingly, the use of nano-SiO_2 in particle form was considered in this paper in order to analyze the influences of the silica fume on the micro scale in the cement mortar. The authors believe that this study researching cementitious materials on a nano-scale will be useful for concrete technology [4, 13].

Experimental Procedure

Materials

Raw materials

The raw materials for preparing nano-scale particles were nano-silica, sodium aluminate, and sodium hydroxide.

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The nano-silica had a mean particle size of 12 nm and a specific gravity of 0.13. The physical features of these particles are shown in Table 1.

Fine aggregate

To prepare the nano-cement mortar, a fine aggregate with a maximum particle diameter of 0.6 mm and a specific gravity of 2.63 was used. The physical features of the aggregate are shown in Table 2.

Active alkali agent

In this study, because the silica-alumina glassy chain of the manufactured nano-cement was firm and sturdy, the internal reaction materials were exposed by dismantling the compound to allow the reaction to occur. NaOH diluted with 50% water was used as an active alkali agent to dismantle the silica-alumina compound. The physical features of this agent are shown in Table 3.

Manufacturing process of the nano-cement Al-source

After adding the prepared reaction materials according to the composite ratio into two 2 Pyrex flasks, the raw materials for the Al-source were agitated at 90 °C using a heating mantle and agitator until melting was complete. When the completely melted solution cooled, tri-ethanol amine (TEA) was added, and the Al-source material was formed after 24 hours of ripening in an air-sealed container. The mole ratio of the composite compound for the Al-source is shown in Table 4.

Manufacturing process of the nano-cement Si-source

Silica was gradually added to distilled water until a gel status was reached. Then, the Si-source material was prepared through a 24-hour ripening process. The mole ratio of the composite compound for the Si-source material is shown in Table 5.

Table 1. Physical properties of nano-silica

Type	Average particle size	BET	Specific gravity
Nano-silica	12 nm	200 m^2/g	0.13

Table 2. Physical properties of sand

Size	Specific gravity	Unit weight	Fineness modulus	Absorption
≤ 0.6 mm	2.63	16,121 N/cm^2	2.48	0.1

Table 3. Chemical properties of NaOH (50%)

Type	Density	Boiling point	Melting point
NaOH (50%)	1.525	145 °C	12 °C

Table 4. Al-source composition

Deionized water	Sodium aluminate	Sodium hydroxide	Triethanolamine (TEA)
1360 g	52 g	92 g	120 g

Table 5. Si-source composition

Deionized water	Nano-silica
320 g	16 g

Solidification

After ripening the mixed nano-silica gel and alumina gel for about one day, 15.468 g of alumina gel were gradually added to 100 g of silica gel at a rate of 100 g/minute^{-1} and agitated using a turbine mixer until a soft gel was formed. Nano-cement was obtained by drying this gel in a 100 °C oven for 24 hours.

Mortar combination

The developed minute particles of cement in this study were produced to solidify the silica-alumina or the glassy chains of Si, Al, and Ca and to stimulate their responses. In order to carry out this experiment, the compounds had to be disassembled so that the inner reacting substances could be exposed. The purpose of this test was to harden the substances through the use of an alkali-activator [5, 10].

The sizes of the particles used in this experiment were extremely small and the use of the alkali-activator for stiffening was conducted in order to determine a new combination preference. Thus, using the mixture value (NC-N3) determined in a previous test as a standard, and in order to deduce a proper test mixture value, a three-stage experimental process was developed [6-8, 12].

At a 90 °C dry curing status, variations in the amounts

Table 6. Mix proportions of the specimens

	Mixture no.	Weight (% per NC)			
		NC	NaOH	Water	Aggregate
1	NC-N1	100	30	20	314
	NC-N2	100	40	20	314
	NC-N3	100	50	20	314
	NC-N4	100	60	20	314
	NC-N5	100	70	20	314
	NC-N6	100	80	20	314
	NC-N7	100	90	20	314
	NC-N8	100	95	20	314
2	NC-W1	100	50	12	314
	NC-W2	100	50	16	314
	NC-W3	100	50	20	314
	NC-W4	100	50	24	314
	NC-W5	100	50	29	314
	NC-W6	100	50	40	314
	NC-W7	100	50	50	314
3	NC-G1	100	50	20	200
	NC-G2	100	50	20	245
	NC-G3	100	50	20	300
	NC-G4	100	50	20	400

of NaOH, water, and aggregate contributed to the production of a mixture like that shown in Table 6.

Preparation of the nano-cement mortar

The nano-cement had a sturdy silica-alumina glassy chain composed of Si, Al, and Ca. It was necessary to expose the internal reaction materials by dismantling these chains in order to allow the reaction to occur. In addition to the existing hydration reaction, an alkali activation method was used for hardening.

Therefore, considering the particle sizes and the new hardening method using an alkali active agent, the tests were conducted by varying the quantities of NaOH and aggregate under a 90 °C dry curing temperature to introduce an appropriate mix ratio, as shown in Table 7. To evaluate the compressive strength of the nano-cement mortar, cubic specimens of 50 × 50 × 50 mm were manufactured.

Experimental Results and Discussion

Nano-cement

The specific gravity and specific surface area of the nano-cement were measured as 2.11 and 3,582,400 cm^2/g, respectively. The specific surface area increased 1,150 times compared to that of the 3,112 cm^2/g of the normal Portland cement. The specific gravity of the normal Portland cement was 3.15. It was estimated that the hydration or hardening materials were created in higher concentrations around the aggregates as the specific surface area increased because the composed particles of nano-cement became smaller. The compressive strength and dynamic characteristics improved as the void size decreased, and the cement became denser. The chemical components of the nano-cement are presented in Fig. 1.

Compared to the normal Portland cement, the amount of CaO in the nano-cement was extremely small. Reviewing

Table 7. Standard mix proportion of nano-cement (wt% per NC)

NC	Alkali activator	Aggregate	Water
100	95	314	0

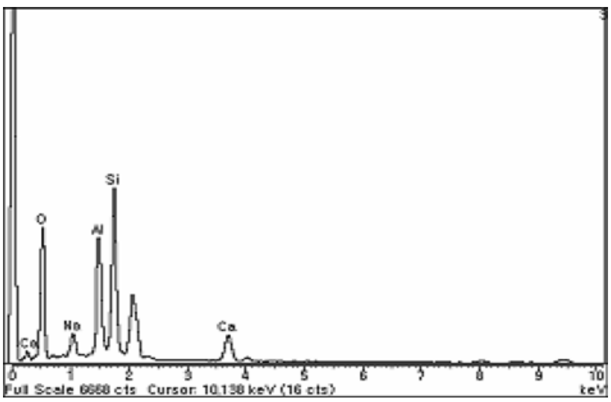

Fig. 1. Chemical composition of the ingredients as determined by EDX.

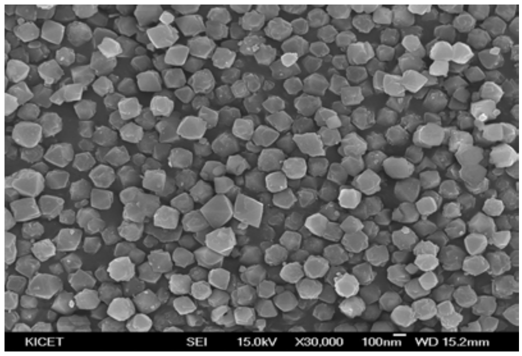

Fig. 2. FE-SEM image of nano-cement.

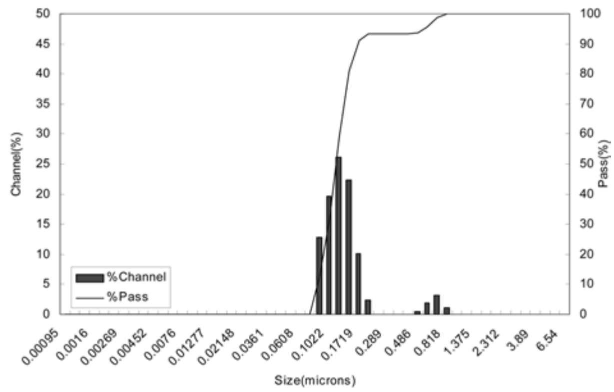

Fig. 3. Size distribution of nano-cement.

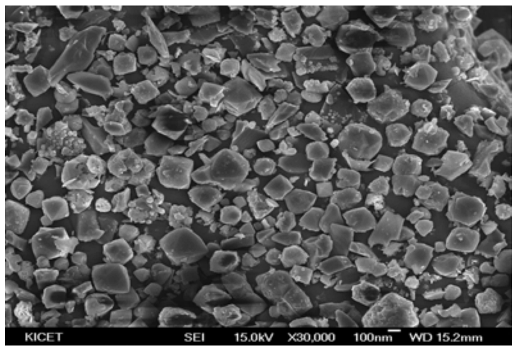

Fig. 4. FE-SEM images of cement mixtures.

the chemical component ratio of the nano-cement, the composition mainly consists of SiO_2 and Al_2O_3, components contributing to the pozzolan reaction. It is estimated that C_3A is generated in some amount, judging from the fact that the content of Al_2O_3 in the manufactured powder was higher than that in the normal Portland cement.

A JSM-6700F SEM *(of JEOL Company)* was used for the SEM measurements.

As shown in Fig. 2 and Fig. 3, the average potential size (D50) of a minute particle of cement that was produced and fostered for two weeks was 168 nm, with most of the particles having sizes of 120-170 nm. The combination time for the cement particle powder, the powder particle size, and the amount of powder being produced are all closely related to one other. To acquire a precise amount

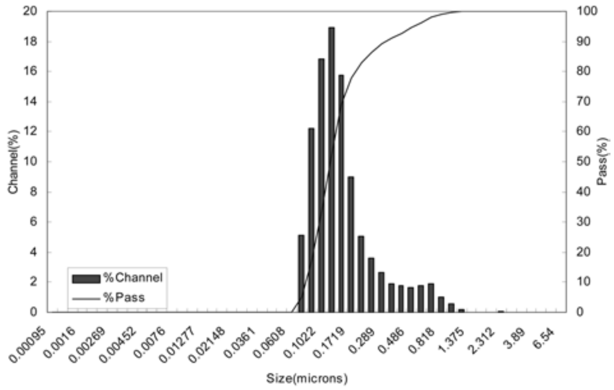

Fig. 5. Size distribution of nano-cement mixtures.

of powder at a specific size, if the combining time is deviated, a powder consisting of particle sizes like those in Fig. 4 and Fig. 5 can be achieved. These nano-sized minute particle cement compounds have very small aperture spaces, which, as they are further decreased, will allow for a more detailed design of nano-cement.

Compressive strength

The compressive strength of the nano-cement mortar according to NaOH concentration was measured seven days after production. The results of the compressive strength tests are shown in Fig. 6. As the amount of NaOH increased, the compressive strength increased. The highest compressive strength of 53.9 MPa was achieved when the active alkali agent was added at an amount of 95% of the nano-cement's weight. However, when NaOH was more than 95% of the nano-cement's weight, the workability was very poor because of the high viscosity.

Compressive strength according to the quantity of aggregate

Fig. 7 shows the compressive strengths at seven days with different amounts of aggregate. The highest compressive strength was found when the ratio of nano-cement to aggregate was 1 : 3, the same ratio used in Portland cement mortar.

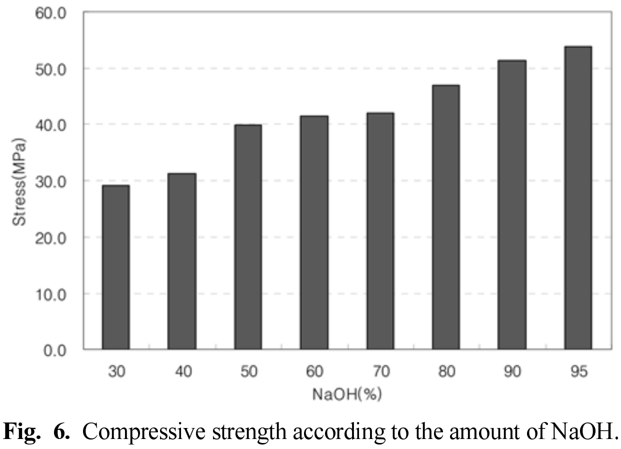

Fig. 6. Compressive strength according to the amount of NaOH.

Compressive strength according to age

Compressive strength was measured at 3-28 days. The results are shown in Fig. 8. The specimens were conditioned at room temperature for one day prior to the compressive strength tests. The rate of compressive strength increase was high during the first several days, with 90% of the hardening of the nano-cement mortar occurring in the first seven days. The proposed formula resulting from the regression analysis of the relationship between age and compressive strength was (1):

$$f = 53.35D^{0.115}, \quad (1)$$

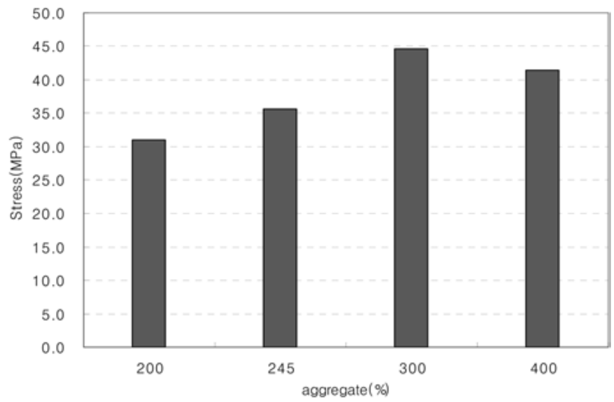

Fig. 7. Compressive strength according to the amount of aggregate.

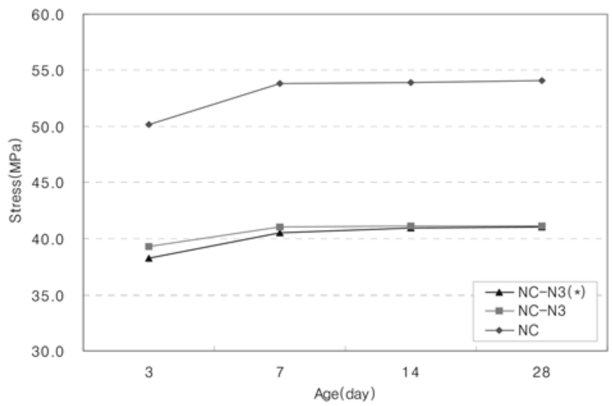

Fig. 8. Compressive strength according to age.

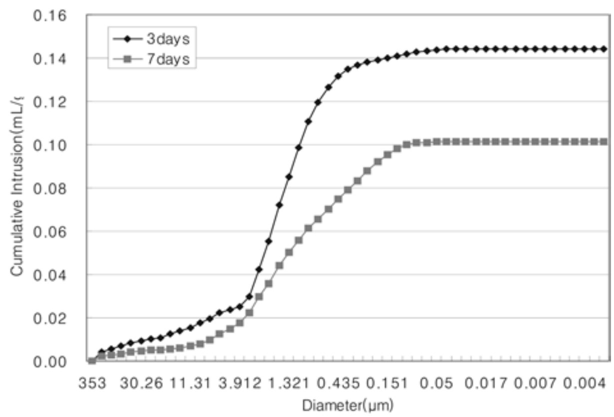

Fig. 9. Nano-cement mortar voids.

where f is compressive strength (MPa), and D is age (day).

Void and void rate

Void measurements were performed using an Auto Pore IV 9500 from Micromeritics Instrument Co. The cumulative void rate curve is presented in Fig. 9. The void and void rate at three days were measured as 490 nm and 26.4%, respectively. At seven days, the void was 223 nm and the void rate was 19.3%, illustrating that the void and void rate decreasedz as the age progressed. These results imply that the strength increased as the hydration materials created by the alkali reaction became denser.

Further Research

The strength of the cement mortar produced with nano-particles was improved compared to that of normal Portland cement. Furthermore, it can be predicted that the strengthening effect of the nano-particles would be further enhanced in concrete because the nano-particles improve not only the cement paste but also the interface between the paste and the aggregate.

Conclusions

This research was conducted to develop a cement with superior capabilities in order to address the arising problems from the current cement production process. After analyzing this new cement, the following conclusions have been made.

1. The average particle size in the proposed cement-production method was about 168 nm, and the final cement product had a specific gravity of 2.11 and a specific surface area of 3,582,400 cm^2/g. Some of the combined small elements of the powder had irregular shapes, but most of the particles were octahedrally-shaped.
2. To deduce the most suitable mixture, variations in the amounts of water/binder, fine aggregate, and alkali activators were used to measure the compressive strength. The measured results showed that constant amounts of water/binder and fine aggregate were advantageous to the strength of the final cement, and, as the concentration of the alkali activator increased, the hardening rate increased.
3. After measuring the compressive strengths of the combined test objects, dry curing at 90 °C resulted in the highest compressive strength due to the fact that the NaOH alkali reaction is very active at temperatures greater than 50 °C. As a result, it is suggested that curing should take place in an environment above 50 °C in order to optimize the strength.
4. The average compressive pressure for the minute particles of the cement mortar specimen after seven days was 53.9 MPa.
5. An analysis of the nano-sized cemented elements and a comparison of the results with those of normal mortar cement features through a compressive strength assessment resulted in a conclusion that this new nano-cement can be used as a precast product.

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