

An Experimental Study of Chemical Synthesis Cement for CO₂ Free

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ABSTRACT: Portland cement is the essential binding agent in concrete. The cement is becoming a principal factor in air pollution because of the creation of CO₂ during manufacturing. Besides because of the exhaustion of the natural resources, Portland cement will also become a crisis. So a substitute material for the cement is needed. Nanoscale materials become great interest due to their unique optical, electrical and magnetic properties. These properties are strongly dependent on the size and shape of the particles and therefore it is important to be able to develop the construction part, in spite of excellent properties of nano-sized material. The purpose of this study is 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 strength of concrete with various compositions. Specimens were tested for compressive strength at 3, 7, 14 and 28days. The medium-sized (50% by weight) cement particles created by chemical synthesis were less than 168 nm. The compressive strength of the mortar prepared using this cement was 53.9 MPa.

Keywords: CO₂ reduction, Chemical synthesis, alkali activation, compressive strength, highly functional construction material

1. INTRODUCTION

The portland cement that is being used universally in construction field was first introduced by England's Joseph Aspidin in 1824. Since that moment it has helped Korea to become a great country by experting a cement. However, all of the cement industry is consumption type and it gives off 700kg of CO₂ per 1 ton.

After the 21st century, the environment that is related to cement concrete has been constantly changing in all sorts of form and changing has also become so serious the world of science and business are starting to face new challenges. First of all, after selecting "Kyoto protocol" for the purpose of reducing greenhouse gases in order to prevent global warming, it is necessary for us to work out a new counter measure about

reducing CO₂ and greenhouse gas but the result is still insufficient.

Also, a solution for environmental destruction resulting from drying up natural resources is also necessary at this minute. In addition, owing to a nation rapid economy development, citizens are speaking out for better materials that could increase their life to meet up the country's standard advancement.

On this, it has been reported that some developed countries have combined either a nano-size silica or small particles of iron oxide with previous cement to improve its strength. Other case has been reported, that is couple of developed countries have actually succeeded in producing a detailed structure of cement through milling or using small particles of the materials.

This thesis will take the small success account which prevents the development of CO₂ during the cement production procedure and by relying on a more detailed chemical synthesis method while producing, particles will be produced into small sizes that is close to nano compared to the previous small particles of cement and they will be hardened into cement to maintain its detailed structure.

Then, powerful and advantageous construction materials for the interior will be invented and considering the growth motivation of high value-added industry, through a chemical synthesis method that uses natural resources, a new theory of nano-size cement material is planned to be made construction materials. Also, basic, physical and chemical features of the invented minute cement particles have been seized and a plan to put it into practical use has also been looked into.

2. EXPERIMENTAL PROCEDURE

Materials

- Raw materials

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

silica with mean particle size of 12nm, specific gravity of 0.13 was used.

The physical features are shown in Table 1.

Table 1: Physical properties of nano-silica

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

- Fine aggregate

To prepare nano cement mortar, fine aggregate with maximum particle diameters of 0.6 mm, specific gravity of 2.63 was used.

The physical features are shown in Table 2.

Table 2: Physical properties of sand

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

- Alkali active agent

In this study, because the silica-alumina glassy chain of the manufactured nano cement is firm and sturdy, the internal reaction materials must be exposed by dismantling the combination to make the reaction occur. NaOH diluted with 50% water was used as an alkali active agent to dismantle the silica-alumina combination

The physical features are shown in Table 3.

Table 3. Chemical properties of NaOH(50%)

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

Manufacturing process of nano cement

- Al-source

After pouring prepared reaction materials according to the composite ratio into 2

Pyrex flasks of 2 liter capacity, 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 decreased in temperature, tri-ethanol amine(TEA) was added, and the Al-source was manufactured through 24 hours of ripening in an air-sealed container.

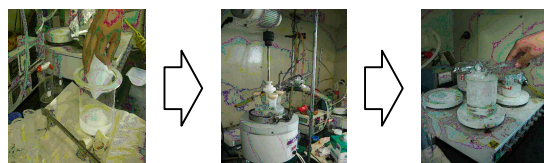


Figure 1: Manufacture process of Al-source

The mole ratio of composite compound for Al-source is shown in Table 4.

Table 4: Al-Source composition

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

- Si-source

As shown Fig.2, silica was gradually added to distilled water with a magnetic bar until gel status was reached. Then, the Si-source was prepared though a ripening process for about 24 hours.

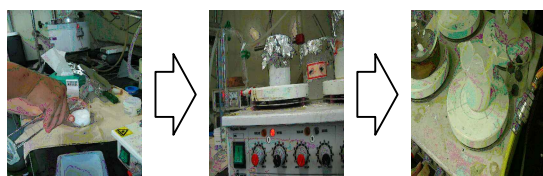


Figure 2: Manufacture process of Si-source

The mole ratio of composite compound for Si-source is shown in Table 5.

Table 5: Si-Source composition

Deionized water	Nano-silica
320g	16g

- 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 the speed of 100 g/min and agitated using a turbine mixer until a soft gel formed. Nano cement was obtained by drying this gel in a 100 °C oven for 24 hours.

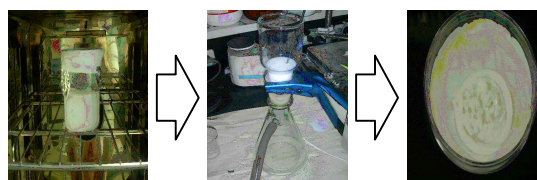


Figure 3: Solidification process of nano cement

- Combination for Mortar

The developed minute particles of cement in this study were made first, to solidify the silica-alumina or glassy chain of Si, Al, and Ca and to stimulate their response. Second, in order to carry out this experiment, the combination had to be disassembled so that the inner reacting substances could be exposed. A different method was used so that compared to the previous hydration, the purpose of this test was to harden the substances through alkali-activator.

As a result, the point that the size of the particles that was used in this experiment was extremely small and using alkali-activator for stiffening was carried out to set an appropriate standard for mixture was performed, because a new preference for combination was necessary. Thus, by using the mixture value (NC-N3) that was designed from a previous test as a standard, in order to deduct a proper test mixture value, this research had to conduct a 3 stage experimental process.

At 90°C of dry curing status, giving variations to the amount of NaOH, water, and aggregate contributed to planning out a mixture like seen in Table 6

Table 6: Mix proportion 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

Preperation of nano cement mortar

The nano cement developed had a sturdy silica-alumina glassy chain of Si, Al, and Ca. It was necessary to expose the internal reaction materials by dismantling this combination in order to make the reaction occur. An alkali activation method was used for hardening apart from the existing hydration reaction.

Therefore, considering particle sizes and the new hardening method by an alkali active agent. The test by changing the quantity of NaOH and aggregate under 90 °C dry curing were conducted to introduce an appropriate mix ratio of the test on the basis of the mix ratio as shown in table.7. To evaluate the compressive strength of the nano cement mortar, cubic specimens of 50×50×50mm were manufactured.

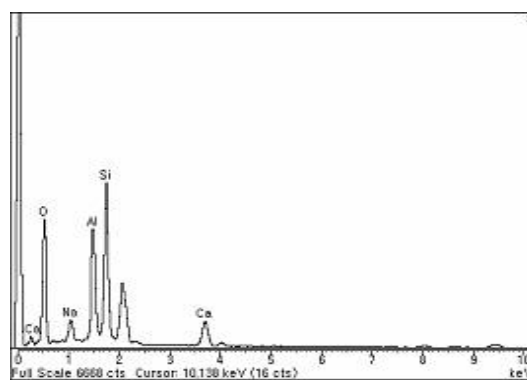
Table 7: Standard Mix Proportion of Nano Cement (wt% per NC)

NC	Alkali activator	Aggregate	Water
100	95	314	0

3. RESULTS AND ANALYSIS

Nano cement

Gravity and specific surface area of the nano cement was measured as 2.11 and 358.24 m²/g, respectively. The specific surface area increased 1,150 times compared to the 3,112 cm²/g of general Portland cement. The gravity of general Portland cement was 3.15. It was estimated that hydration or hardening materials are created more around the aggregates as the specific surface area increases because the composed particles of nano cement became smaller. Compressive strength and dynamic characteristics improve as void size shrinks and the cement becomes denser. Chemical components are found in Fig 4.

**Figure 4:**Chemical composition ingredient using EDX

Compared to general Portland cement, the amount of CaO in the nano cement was extremely small. Reviewing the chemical component ratio, the composition mainly consists of SiO₂ and Al₂O₃, components contributing to pozzolan reaction. It is estimated that C3A is generated in some amount, judging from the fact that the content of Al₂O₃ in the manufactured powder is higher than in Portland cements.

JSM-6700F measurement equipment of JEOL Company was used for the SEM measurements at $\times 30,000$ magnifications.

Like shown in Fig 5, and Fig 6, the average potential size (D50) of a minute particle of cement that has been produced and fostered for 2 weeks measured out to be 168nm while most of the size showed 120~170nm. The combination time for cement particle powder, powder particle's size, and the amount of the powder being produced are all deeply related to each other. At this moment, with the intention of acquiring the precise amount of the powder and potential size, if the combining time is deviated by the user, it is proved that the user can achieve powder of particles for the size like in Fig 7 and Fig 8. These minute particle cements that are the size of nano have very small space of aperture and as the space narrows down, it will be designed in a more detailed way.

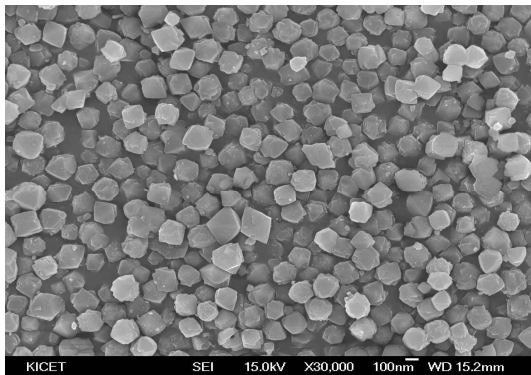


Figure 5: FE-SEM image of nano cement

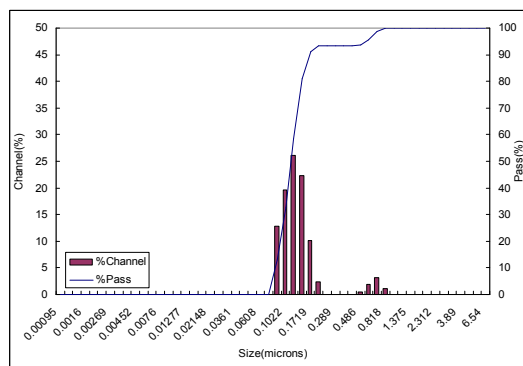


Figure 6: Size distribution of nano cement

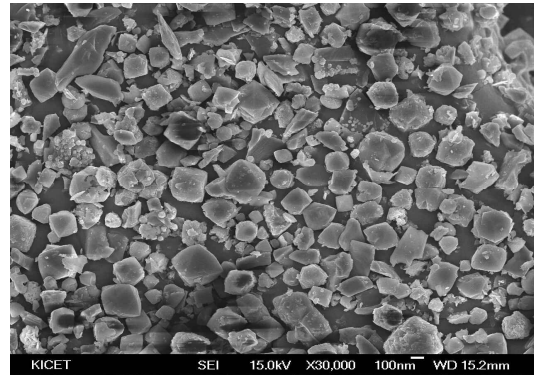


Figure 7: FE-SEM image (Mix each synthesis cements)

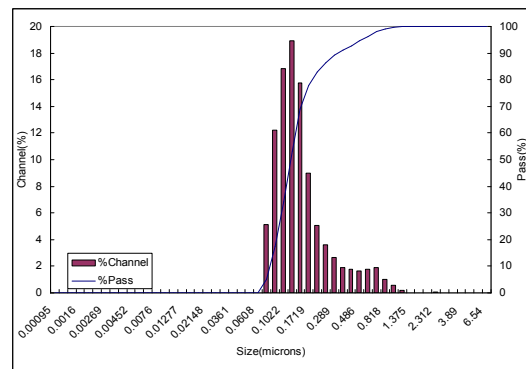


Figure 8: Size distribution of nano cement (Mix each synthesis cements)

Compressive strength

- Compressive strength according to the quantity of alkali active agent

Compressive strength of the nano cement mortar according to NaOH was measured at 7 days. Results of compressive strength are shown in Fig 9. As the amount of NaOH increased, compressive strength increased. The highest compressive strength of 53.9 MPa was achieved when alkali active agent was put into 95% of the weight of the nano cement. However, when NaOH was more than 95% of the weight of the nano cement, workability was very poor because of high viscosity.

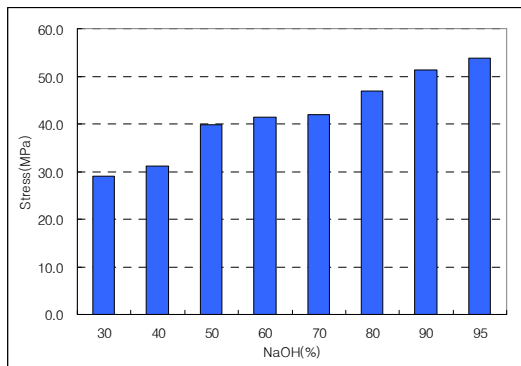


Figure 9: Compressive strength with NaOH rates

- Compressive strength according to the quantity of aggregate

Fig 10 shows compressive strengths at 7 days with different amounts of aggregate. The highest compressive strength was when the ratio of nano cement to aggregate was 1:3. This was the same ratio for aggregate and Portland cement mortar.

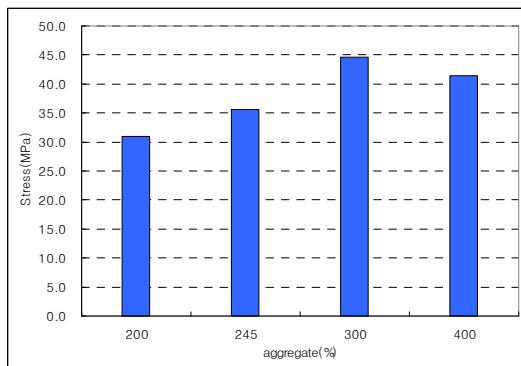


Figure 10: Compressive strength with aggregate rates

- Compressive strength according to age

Compressive strength was measured at 2 ~ 28 days. Results are shown in Fig 11. Specimens were kept at a normal temperature for one day before the compressive strength measurement was taken. The increased rate of the compressive strength was high at early ages. The hardening reaction of the nano cement mortar occurred mostly over 90% at early ages (7 days). The proposed formula created by the result of the regression analysis of the relationship between the age and compressive strength of the mix ratio was:

$$f = 53.35D^{0.115}$$

f : compressive strength(MPa)

D : age (day)

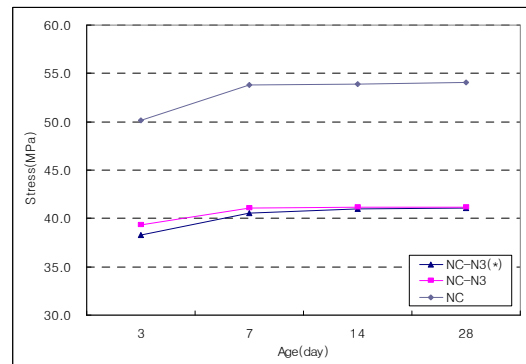


Figure 11: Compressive strength with ages

- Void and void rate

Void measurements were performed using Auto Pore IV 9500 of Micromeritics Instrument Co. The cumulative curve of the void rate is in Fig. 12. The void and void rate at the age of 3 days were measured as 490 nm and 26.4%, respectively. At the age of 7 days, void was 223 nm and void rate was 19.3%. Void and void rate decreased as age progressed from 3 to 7 days. Strength increased as the hydration materials created by the alkali reaction became denser.

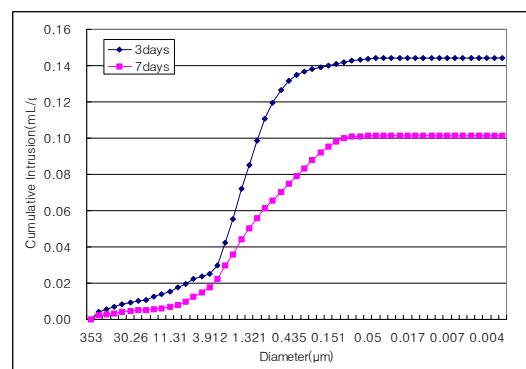


Figure 12: Void of nano cement mortar

4. CONCLUSION

This research was done for the purpose of inventing a cement that would have superior capabilities in order to solve the arising problems (CO₂) from the previous progress of making cement and after

acquiring the values of its characteristics, and it is judged that developed nano cement will contribute to solve the problems of Portland cement - air pollution, exhaustion of the natural resources.

1. The average size for the hydrothermal method one of the chemical methods was about 168nm, specific gravity 2.11, and with the rate of the powder being 358.24m₂/g, small particles of cement were made. Some of the combined small elements of the powder had lopsided shapes for the size, but it was clear that most of the shapes were octahedron.
2. To deduce the most suitable mixture, variations was the amount of water/binder, fine aggregate, and alkali-activators to measure the compressive strength. The measured results showed that the constant amount of water/binder and fine aggregate was advantageous to the manifestation degree and as the alkali-activator increased, manifestation progressed with a positive tendency as well.
3. After measuring the compressive strength of the combined test objects, dry curing at 90°C gave off the highest compressive strength and this was due to the reason that NaOH alkali reaction is very active when the temperature is above 50°C. As a result, it can be suggested that the curing being in an environment above 50°C would be better for the increase.
4. The average compressive pressure for the minute particles of the cement mortar specimen for 7 days turned out to be 53.9MPa.
5. Unlike the previous producing method of cement, through the chemical reactions, the material character is understood with the nano-sized cemented elements and after analyzing and comparing the results between those of this and the usual mortar cement features through the compressive strength assessment, a conclusion was reached that it can be used as a precast product.

REFERENCES

- [1] Samia Ferchiche, Juiusz Warzywoda, Albert Ascco Jr. 2001. "Direct synthesis of zeolite Y with large particle size" *International Journal of Inorganic Material* Vol.3. pp773-780.
- [2] Elena Alcanara Ortega, Chris Cheeseman, Jonathan Knight, Maria Loizidou, "Properties of alkali-activated clinoptilolite" *Cement and Concrete Reach* Vol.30, pp.1641-1646.
- [3] Hui Li, Hui-gang Xiao, Jie Yuan, Jinping Ou 2004. "Microstructure of cement mortar with nano-particles" *Composites. Part B, Engineering*, Vol.35 No.2, pp185-189.
- [4] Ye Qing, Zhang Zenan, Kong Deyu, Chen Rongshen 2005. "Influence of nano-SiO₂ addition on properties of hardened cement paste as compared with silica fume" *Construction and Building Materials*, Available online
- [5] C.Y.LEE, H.K.LEE, K.M.Lee 2003. "Strength and microstructural characteristics of chemically activated fly ash-cement systems" *Cement and Concrete Research* Vol.33. pp425-431.
- [6] Vasant R. Choudhary, Anil K. Kinage 1998. "Hydrothermal Synthesis of Gallosilicate (MFI) Zeolite" *J. Chem. Technol. Biotechnol.* Vol.72, pp.176-182.