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## Evaluation of Petroleum Coke Ash Mortar Compressive Strength Blended with Nano-Bubble Water

Évaluation de la force de compression du mortier aux cendres de coke de pétrole mélangé avec l'eau à nano-bulles

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ABSTRACT: Greenhouse gas is one of the main causes of environmental problems, and many attempts have been made to reduce greenhouse gases in many different ways around the world since the Kyoto Protocol in 1997. Since industrialization, the use of cement in the construction industry has been unavoidable, yet a large volume of greenhouse gases generated from producing cement is released into the atmosphere annually. Therefore, ash from refining crude oil is used in this study as an alternative material to cement, with the aim of assisting in the reduction of greenhouse gases. In addition, functional water within bubbles is used to address the increasing of material strength. In this study, the nano-bubble water used as functional water has a long life span and is able to maintain a sustainable gas concentration. In order to determine the degree to which the nano-bubble water, which is able to maintain a constant gas, can increase strength as a functional water, a general tap water was used to the compare it. The compressive strength of the nano-bubble was compared with that of the tap water.

RÉSUMÉ: Le gaz à effet de serre est l'une des principales causes des problèmes environnementaux. Depuis le protocole de Kyoto, le monde déploie tous ses efforts pour réduire les gaz à effet de serre. Toutefois, il est inévitable d'utiliser le ciment dans la construction depuis l'industrialisation. Lors de la production du ciment, un grand volume de gaz à effet de serre sont toujours émis. A été donc utilisée pour cette étude la méthode selon laquelle les cendres produites lors du raffinage du pétrole brut sont utilisées comme matière alternative du ciment pour réduire les gaz à effet de serre. De plus, pour résoudre le problème dont la solidité baisse lors de la réutilisation, l'eau fonctionnelle respectueuse de l'environnement a été utilisée. L'eau à nano-bulles utilisée comme eau fonctionnelle dans cette étude a une longue durée de vie et maintient la concentration de gaz durable. Afin de vérifier combien l'eau à nano-bulles qui maintient une certaine concentration de gaz augmente la solidité en tant qu'eau fonctionnelle, l'eau du robinet normale a été utilisée pour groupe contrôle et la solidité à la compression a été comparée et revue pour 3, 7, 14 et 28 jours.

KEYWORDS: Nano-bubble, Petro-cokes ash, compression strength

### 1 INTRODUCTION.

Due to rapid industry development, the earth is undergoing many environmental problems such as global warming caused by greenhouse gases. Among the greenhouse gases, carbon dioxide most significantly affects climate change.

Since the Kyoto Protocol in 1997, many countries have been making a effort towards reducing carbon dioxide emissions. Espicially, this is closely related to the cement manufacturing processm because cement has been used as an important material in the construction industry. About a ton of carbon dioxide gas is emitted per ton of cement in the cement buring process (Bang, 2003) and carbon dioxide gas is emitted during the firing process.

It is difficult to find a cement substitute material to reduce these carbon dioxide emissions to then reduce greenhouse gases.

Therefore, in order to develop an cement substitute material, we evaluated the strength of ash-mortar using petro-coke ash as a substitute for cement.

It also investigated that the difference in the strength of concrete using cement and petro-coke ash mortar using nanobubble water.

### 1.1 Petro-Coke Ash

Petro-coke ash is made by decomposing the remaining bitumen after refining crude oil. Petroleum coke generates sulfur oxides upon heating, thereby increasing greenhouse gas emissions. However, petroleum cokes can now be produced through a desulfurization facility that declared the Kyoto Protocol standards for  $CO_2$  emissions.

As petro-cokes convert bitumen into solid state fuel, it is more economical and efficient than other types of fuel.

Moreover, this method produces less ash accumulation and slag at high temperature and allows easier maintenance. By using petro-coke powder of ultrafine particles as fuel, combustion efficiency can be improved.

### 1.2 Nano-Bubble

### 1.2.1. FEATURES OF BUBBLE

A bubble is a circular cavity filled with air or other gases inside a liquid. Bubbles are classified by their diameter. A macro-bubble has a diameter of 50  $\mu$ m or more, a micro-bubble has a diameter of 10~

50  $\,\mu m,$  and a nano-bubble has a diameter of 0.2  $\,\mu m$  (=200nm) or less (Agarwal et al., 2011).

A macro-bubble bursts at the surface of the water due to its rapidly increasing velocity accelerated by the buoyant force. Micro-bubbles, however, have a small volume and thus exist in water for a long time. A bubble contracts and transforms into a nano-bubble due to the self-pressurization of the internal gas; alternatively, the inner gas diffuses into the water and the bubble disappears according to Henry's law.

The strong hydrogen bonding keeps the internal gas of nanobubble from diffusing. The bonding force builds an equilibrium state that helps to withstand high internal gas pressure and eventually makes it exist for a long time (Han, 2012).

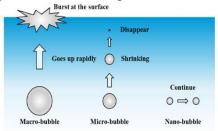


Fig. 1 Persistence according to bubble size type.(Song, 2014)

The resulting microbubbles have a long lifetime. The reasons for such a long service life are as follows; (1) the charging phenomenon of the Nano bubble surface; (2) the supersaturation state of the gas; (3)the strong hydrogen bonding force; (and (4) the Zetapotential and finally the pH

Second, Ushikubo et al. reported that the diffusion of gas, by the Hen ry Law, is caused by the concentration gradient due to the concentration difference from the high concentration to the low concentration. And th en, when the repulsive forces acting in the fine bubbles are generated, s o that the stable state can be maintained

Third, the strong hydrogen bonding force of the surface tension prevents the diffusion of gas inside the bubble and maintains a high internal pressure, so that the fine bubble can be maintained.

Fourth, the factor by Zeta potential. The Zeta potential consists of a stern layer and a diffuse layer. Stern layer refers to the electron layer and the diffuse layer refers to the ion diffusion layer. The diffuse layer is the theoretical interface where particles and ions are stably present. The potential of this boundary is the Zeta potential.

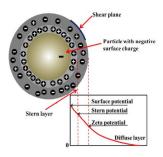


Fig. 2 Zeta potential in fine bubbles.(Song, 2014)

The reference value of stability for zeta potential is 30mV. When a fine bubble has a large zeta potential, it does not make bond because of the repulsive force between the fine bubbles. However, when the zeta potential is low, fine bubbles are coupled due to small repelling force between them. The diameter of the fine bubbles becomes larger and unstable.

The zeta potential is affected by pH, and the zeta potential has a value o f 0 at pH3.0~3.5, and the potential gets more negative as pH increases.

### 1.2.2 Principle of fine bubble generation.

When the gas is continuously injected in a supersaturated state to mai

ntain bubbles for a long period, the, the dissolution cannot proceed furth er. Undissolved gases are likely to exist as bubbles.

When the gas is injected into a porous membrane, an interface between the liquid and the gas is formed. At the interface, the surfaces of the liquid and gas form a spherical shape by the same principle as that of blowing a balloon through the hole of a porous membrane by hydrogen bonding causing surface tension.

In this process, the bubble is separated when the drag force of the wat er acting on the bubble becomes larger than the surface tension between the liquid and water near the hole

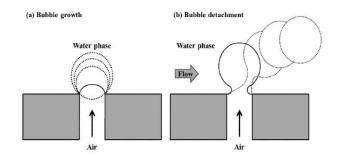


Fig. 3 Principle of fine bubble generation.(Song, 2014)

### 1.2.3 Analysis method of fine bubbles (NTA: Nano Particle Tracking Analysis)

As shown in Fig. 4, a laser is irradiated on the particles in Brownian motion in the dispersion, and the light scattered from the particles is observed through a microscope. At this time, the distance between two moving particles for a certain time is traced, and the particle conversion factor is measured. The particle size and distribution are then measured by substituting them into the STOKES-EINSTEIN equation.

The STOKES-EINSTEIN equation has the following formula. The dispersion coefficient D is related to the average value radius R of the STOKES-EINSTEIN equation of the particles

$$D = \frac{K_B T}{6\pi \eta R} \tag{1}$$

 $K_{R}$ : BOLTZMANN-CONSTANT

T : TEMPERATURE

η : VISCOSITY

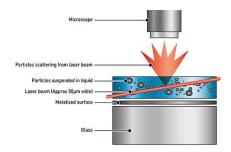


Fig 4. Nano-particle tracking analysis principle

### 1.3. Contents of research and range

Among the materials used for cement mortar, with fly ash (FA), it is one of the most difficult to develop strength without special treatment. However, in this study, the aim was to increase strength of the cement mortar without special treatments.

To evaluate the applicability of petro-coke ash mortar, the strength of cement mortar using petro-coke ash mortar made with nano-bubble water as the functional water was compared with that of the experimental group of mortar made with tap water.

### 2 RESEARCH CONTENT

### 2.1. EXPERIMENTAL OBJECTIVES AND OUTLINE

The aim of this study is to evaluate the strength characteristics of cemen t substitute materials by using the Petro-cokes ash and nano-bubble wat er.

The nano-bubbles applied in this study are a material that has a long lif etime and can maintain a constant gas concentration (Han, 2012).

### 2.2. EXPERIMENTAL CONDITIONS AND METHODS.

### 2.2.1. HOW TO CREATE NANO-BUBBLE WATER

As shown in Fig. 5, the pressure of the hydrogen gas from the hydrogen is set to 5 bar, the external pressure of the hydrogen gas acting on the s urface of the third distilled water for 24 hours is 0.15MPa, and the hydrogen gas pressure acting on the porous ceramic filter is 0.5MPA.

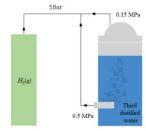


Fig. 5. Production of the hydrogen nano bubble water

### 2.2.2 Production of the test piece and compression strength test 1) Petro-coke Ash mortar mix proportioning

The compounding ratio was calculated according to KS L 5105 (2007). The weight of cement was replaced with the weight of Petro-cokes ash of 510g. In addition, 1250g of sand was used, and the amount of mixed water was applied at 48.5% of the weight of Petro-cokes ash to calculat e the mixture water of tap water and nano-bubble, respectively. The curing periods were 3 days (CASE 1), 7 days (CASE 2), 14 days (CASE 3), and 28 days (CASE 4).

### 2) Petro-coke Ash mortar combination and specimen molding.

Petro-cokes ash and sand were mixed in a mixing vessel in accordance with the mixing ratio, and the mixing water was placed into the vessel a nd mixed.

Thereafter, the thickness of the mold was divided into three equal parts, and compaction was performed 32 times using a compaction rod for ea ch part. After each layer was compacted in this manner, the surface of the mold was planarized, and the moisture was then maintained. According to the method described, twenty-four cubic specimens were produced. And this twenty-four cubic specimens were classified as a test specimen using tap water and nano-bubble water.

### 2.2.2.3. Curing and compression strength measurement

The water was cured until the required curing period and maintained at a temperature of 22  $^{\circ}$  C. The cured specimens were dried outside the water tank for 24 hours. The strength of the specimens thus formed was measured by using a Universal Testing Machines (UTM) according to the curing period, and the average compressive strengths of three specimens were determined.

### 2.2.3. Experimental equipment

2.2.3.1. Nano-particle Tracking Analysis (NTA)





Fig. 6. NTA Measuring equipment

### 2.3. Experiment result

2.3.1 Concentration according to the diameter of nano-bubble water.

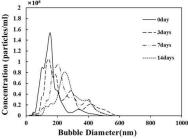


Fig. 7 Size distributions of nano-bubbles (Jung, 2017)

### 2.3.2 Stability of nano-bubble

When the self-made fine bubble generator is filled with the third distilled water and the hydrogen gas is maintained at a pressure of 5 bar for 24 hours, a bubble with the size of 1 nm or less in diameter used in the study can make 120 to 170 million nano-bubbles in 1 ml of water.

The concentration of the fine bubbles produced by this method after 3 days is higher than that immediately after the production. This is becaus e, when a nano-bubble is made, a micro-bubble is also produced. By He nry's law, the micro bubble is destroyed immediately after the formatio n, but it is in an unstable state, through which it changes into a nano-bu bble by self-pressurization.

However, after three days, the concentration of fine bubbles remains st able over the long period.

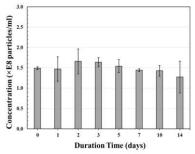


Fig. 8 Concentration of nano-bubbles (Jung, 2017)

### 2.3.2 compression strength measurement result of the Petrocokes mortar

In the previous study, Table 1 shows the comparison of the compressive strength of cement mortar on the 7th day according to the compounding ratio. As a result, the strength of cement mortar using nano-bubble water was improved by 20.24% on average (Han, 2012).

The results of the test for compressive strength of petro-cokes ash-mortar are shown in Table 2. The table shows the four cases classified according to the curing period. As shown in Table 2, the strength of Petro-cokes ash-mortar using nano-bubble water is higher than that of cement made up with tap water.

Using nano-bubble water, Petro-cokes ash mortar has a distinct improvement of the compression strength from at least 60.1% to a maximum of 114.7% compared with mortar using tap water.

Table 1 Comparison of compressive strength of cement mortar after 7 days(Han 2012)

mortal arter / days(rian, 2012)								
	Case No.(7days, MPa)							
	1	2	3	4	5	AVE		
Tap water	23.23	21.53	22.94	21.26	21.70	22.13		
nano-bubble	26.13	25.43	28.44	25.04	28.03	26.61		
water								

Table. 2 Comparison of Petro-cokes ash-mortar compressive strength with mixed water (MPa)

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	Case No.						
	1	2	3	4			
	3days	7days	14days	28days			
Tap water	2.88	4.44	4.20	6.00			
nano-bubble water	4.87	9.74	12.05	12.88			
Compression	60.1	119.4	186.9	114.7			
Strength Increment							
(%)							

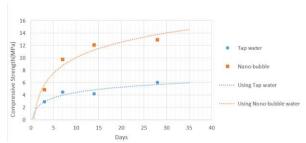


Fig. 9 Compression of petro-cokes ash mortar compressive strength in using Nano-bubble water and Tap water

### 3 CONCLUSION

### 3.1. conclusion

Petro-coke ash is produced when petro-coke is used for thermal power generation, and is deemed a remnant produced in the refining silo. An e xperimental study was conducted to evaluate the increased strength of a sh mortar when petro-coke ash is mixed with nano-bubbles.

In the previous study by Han, Jung-Keun et al. (2012), it was found that the compressive strength of cement mortar increases regardless of the n umber of nano-bubbles. In this study, it was confirmed that the compres sive strength of nano-bubble water was higher than that of petro-cokes a sh-mortar. This is because the nano-bubble reacts chemically when mix ed with the petro-cokes ash, and is denser than when it is applied with t an water

Petro-coke ash and nano-bubbles are new materials that have not yet b een fully studied. However, as can be seen in this study, the improveme nt of the strength of the petro-cokes ash-mortar due to the use of nano-bubble water was confirmed. To understand the reason for this phenome non, research needs to be carried out and an analysis performed of the chemical structure of the interaction between the nano-bubble and the pet ro-coke.

Petro-coke ash is a renewable resource for environmentally friendly thermal power generation, which can facilitate future technological and economic development. In the future, petro-coke ash is expected to be generated at a higher volume than is currently generated. Moreover, environment-friendly treatment methods should be considered.

### **4 ACKNOWLEDGEMENTS**

This research was supported by the Korea Agency for Infrastructure Technology Advancement under the Ministry of Land, Infrastructure and Transport of the Korean government (Project Number: 16SCIP-B108153-02).

This research was also supported by the Chung-Ang University Graduate Research Scholarship in 2016 and by a grant from the National Research Foundation (NRF) of Korea, funded by the Korea government (MSIP) (NRF-2015R1A2A2A01008372).

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