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# Physical and chemical properties of new ecological concrete reducing $CO_2$ emissions below zero level by carbonation curing

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## ABSTRACT

A new ecological concrete was developed which can achieve $CO_2$ emission levels below zero by capturing $CO_2$ emitted from thermal power stations. This concrete is based on two typical features: one is the use of a special additive (dicalcium silicate γ phase: $\gamma$-$2CaO\cdot SiO_2$) and coal-ash instead of cement. These materials have very low level of $CO_2$ emissions, and $\gamma$-$2CaO\cdot SiO_2$ hardens concrete by reaction with $CO_2$. Another feature of this concrete is the capture of $CO_2$ contained in exhaust gas from thermal power stations. After this concrete is manufactured, it is placed into a curing chamber. The chamber is filled with exhaust gas, and $CO_2$ contained in the exhaust gas is captured in the concrete. The authors introduce materials and method of manufacturing and show the physical and chemical properties of this concrete in this paper.

**Keywords:** $CO_2$ emission, Carbonation curing, $\gamma$-$2CaO\cdot SiO_2$, Exhaust gas

## 1. INTRODUCTION

The reduction of greenhouse gases has become a priority issue in various industries. According to the Kyoto Protocol, Japan is obligated to reduce greenhouse gas emissions estimated at 1,260 million tons in 1990 by 6% before 2012. As shown in Figure 1, $CO_2$ emissions in Japan have decreased gradually from 2007 (Ministry of the Environment, 2012). However, after the occurrence of the Great East Japan Earthquake in 2011, the tendency of this graph may change considerably. The electric industry accounts for

*value of 11' is preliminary figures

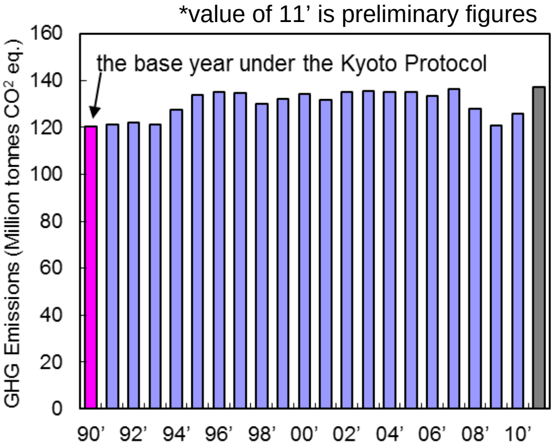

**Figure 1. Greenhouse Gases emissions in Japan**

approximately 30% of the $CO_2$ emissions generated in Japan. Enhancement of thermal efficiency in power stations and expansion and diffusion of recyclable energies such as hydro power, solar power and wind power are being promoted vigorously.

On the other hand, some efforts are being made to reduce $CO_2$ emissions even in the concrete fields in Japan. (Sakai, 2010) “Optimization of structural types and construction methods” and “Effective use of by-products” were introduced in the “Recommendation of environmental performance verification for concrete structures (draft),” (JSCE, 2005).

A large amount of $CO_2$ is generated during the manufacturing process of cement. For this reason, using by-products such as fly ash or blast-furnace slag with a small amount of $CO_2$ emissions instead of cement is the main method of reducing $CO_2$ emissions in the concrete fields. For instance, according to the Japan Society of Civil Engineers (JSCE), the $CO_2$ emissions can be reduced about 15% by using fly-ash cement type B and approximately 40% by using blast-furnace cement type B.

Under these circumstances, the authors confirmed from past studies that a very dense matrix could be obtained by mixing in concrete a special additive called $\gamma$-$2CaO \cdot SiO_2$ (hereafter “$\gamma$-$C_2S$”) as a major component, followed by carbonating the mixture forcibly (Watanabe, 2004). The authors have developed a new ecological concrete by using $\gamma$-$C_2S$ instead of cement and by carbonation curing. $\gamma$-$C_2S$ has a very low level of $CO_2$ emissions. Moreover, the new ecological concrete uses coal-ash instead of cement. As a result, $CO_2$ emissions of this concrete were reduced by half compared to ordinary concrete.

The authors have also developed a new ecological concrete by applying this “carbonation” technique to “$CO_2$ capture and storage to concrete” (Torichigai, 2010). When the concrete is manufactured, exhaust gas from thermal power stations is used as the source of supply of $CO_2$ for carbonation curing. It is considered that capturing $CO_2$ to concrete by carbonation curing leads to reduced $CO_2$ emissions from thermal power stations. More $CO_2$ is captured during the hardening process than $CO_2$ emission amounts originating from materials during the production of the ecological concrete. The total $CO_2$ emissions of the newly developed concrete could be brought down to below zero.

Materials used and the manufacturing method of new ecological concrete are introduced in this paper, and the physical properties of the concrete such as compressive strength, resistance to abrasion, and chemical properties are reported.

## 2. MATERIALS AND METHODS OF MANUFACTURING

### 2.1 Special additives $\gamma$-$C_2S$

Table 1. shows the chemical and physical properties of $\gamma$-$C_2S$. $\gamma$-$C_2S$ consists of CaO and $SiO_2$ as the principal components, and the main mineral composition is gamma type calcium silicate. It is manufactured using by-product containing mainly $Ca(OH)_2$ and $SiO_2$ powder. $\gamma$-$C_2S$ is a powdery material. Specific surface is a little bit coarser than portland cement. $CO_2$ emissions of $\gamma$-$C_2S$ have been estimated in past studies (Morioka, 2010). There are many manufacturing methods, but the quantity of $CO_2$ generated during manufacture of the special

**Table 1. Chemical and physical properties of $\gamma$-$C_2S$**

| Chemical composition (%) | | | | | | | Mineral composition (%) | | Density (g/cm$^3$) | Specific surface (cm$^2$/g) |
|---|---|---|---|---|---|---|---|---|---|---|
| LOI | CaO | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Na_2O$ | $K_2O$ | $\gamma$-$C_2S$ | $\beta$-$C_2S$ | | |
| 0.05 | 64.58 | 33.50 | 1.16 | 0.33 | 0.01 | 0.00 | 93.7 | 1.4 | 3.00 | 2010 |

**Table 2. Properties of materials used**

| Type | Materials | Summary |
|---|---|---|
| Concrete | HPC | High early strength Portland cement, density:3.15 g/cm$^3$ |
| | BFS | Blast furnace slag, density:2.92 g/cm$^3$ |
| | $\gamma$-$C_2S$ | $\gamma$-$C_2S$, density:2.85g/cm$^3$ |
| | F | Coal ash, density:2.20g/cm$^3$ |
| | S1 | Crushed sand, density:2.57g/cm$^3$, fineness modulus: 2.76 |
| | G | Crushed stone, density:2.61g/cm$^3$ |
| | AD1 | Air-entraining and water reducing admixture |
| Mortar | BB | Blast-furnace cement type B, density: 3.04 g/cm$^3$ |
| | $\gamma$-$C_2S$ | $\gamma$-$C_2S$, density:2.85g/cm$^3$ |
| | F | Coal ash, density:2.20g/cm$^3$ |
| | S2 | Hill sand, density: 2.56 g/cm$^3$, fineness modulus: 2.47 |
| | AD2 | Non-ionic detergent |

additive can be reduced by using by-product containing $Ca(OH)_2$ that generates smaller quantities of $CO_2$. The quantity of $CO_2$ emitted during manufacture of $\gamma$-$C_2S$ is about one-fifth that of ordinary portland cement.

### 2.2 Materials and mix proportion

Properties of materials used in the new ecological concrete are shown in Table 2. In this paper, two types of mix proportion for the new ecological concrete are studied. One of the mix proportion type is concrete which is used for precast concrete blocks as shown in Fig.2 (left) Various examinations were conducted so that $CO_2$ emissions of used materials could be reduced as far as possible while required strength was satisfied, and the following conditions were adopted for mix proportion: Water binder (binder= HPC + BFS + $\gamma$-$C_2S$ + F) ratio is 48%, component ratio of binder is set at [OPC: BFS: $\gamma$-$C_2S$: F = 24: 32: 24: 20], slump of the concrete is 8 cm, and the air content of the concrete is 4.5%.

Another mix proportion type is mortar which is used for interlocking blocks as shown in Fig. 2(right), and the following conditions were adopted as mix proportion: Water binder (binder= BB + $\gamma$-$C_2S$ + F) ratio is 30%, component ratio of binder set at [BB: $\gamma$-$C_2S$: F = 67: 8: 25], slump of the mortar is 0 cm, and air content of the mortar is 8.0%. This mortar can de-molded after casting immediately.

**Figure 2. Appearance of new ecological concrete (left) and mortar (right)**

### 2.3 Manufacturing method of this concrete

After this concrete was mixed by concrete mixer, it was cast in forms. When the compressive strength reached 3.0 N/mm$^2$, the sample was de-molded, and carried to the carbonation curing chamber shown in Fig. 3. For quality control, a cylindrical specimen of φ10 cm × 20 cm in size was prepared, and the same curing method was applied. Exhaust gas from a thermal power station was supplied into the curing chamber for sealing after adjusting the temperature to 50°C and the relative humidity to 40%.

A phenomenon called "neutralization" occurs during reaction with $CO_2$ in the air in ordinary concrete. However, neutralization depth after 20-30 years may be only about 10 mm from the surface. In the new ecological concrete, a large quantity of $CO_2$ is absorbed immediately by controlling curing temperature and humidity, and by supplying $CO_2$ of high concentration contained in exhaust gas.

Moreover, temperature and humidity control system shown in Fig.3 can control the temperature and humidity of the curing chamber without electricity energy by using industrial steam or industrial water to heat exchanger. By using this system, $CO_2$ emissions during the manufacturing process of the new ecological concrete are reduced sharply.

The concentration of $CO_2$ was measured and found to be between 15 and 20%. Sulfur oxides (SOx), and nitrogen oxides (NOx) is contained in the exhaust gas, and the concentration of SOx and NOx in the exhaust gas were several 10 ppm.

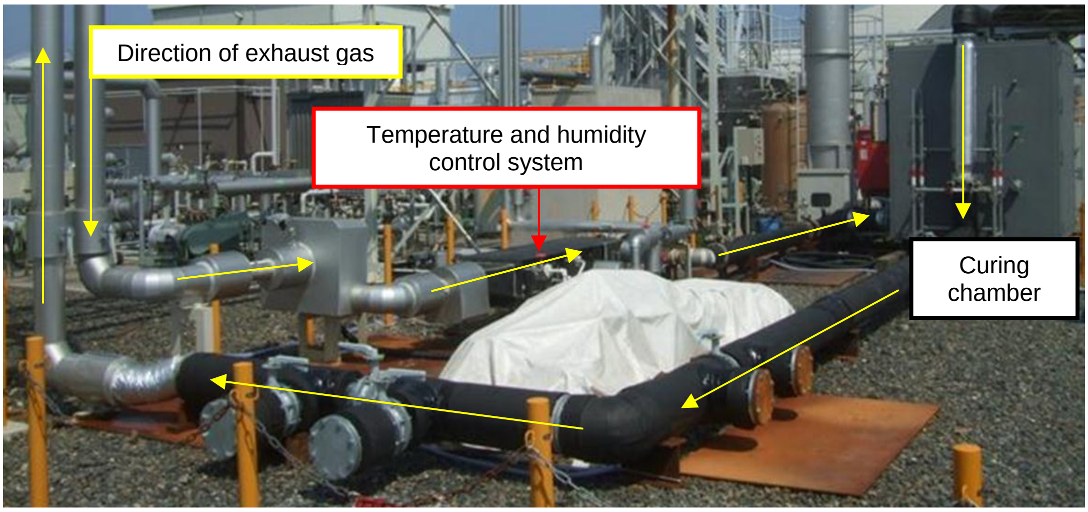

Figure 3. Carbonation curing equipment

### 2.4 Experimental method

After the carbonation curing, some experimental tests were carried out. Carbonation depth, $CO_2$ contents, $CO_2$ emissions, and phase analysis of the new ecological concrete were measured to clarify the chemical characteristics of the concrete, and compressive strength was measured to clarify the physical characteristics of the concrete. Moreover, to show the feature of new ecological concrete, resistance to abrasion and leaching tests were carried out for the new ecological mortar blocks.

## 3. EXPERIMENTAL RESULTS FOR CONCRETE

### 3.1 Carbonation depth

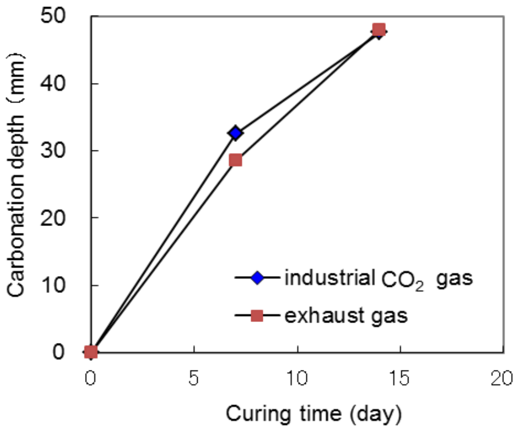

**Figure 4. Relationship between curing time and carbonation depth of concrete**

Relationship between curing time and carbonation depth is shown in Fig. 4. Carbonation depth is measured based on JIS A 1152 “Method for measuring carbonation depth of concrete.” Carbonation depth of concrete which is cured with the same temperature, same humidity, and pure $CO_2$ gas of 20% concentration which is industrially manufactured, is also shown in this figure. Concrete cylindrical specimens of φ10 cm × 20 cm were fully carbonated in about 14 days regardless of the gas used, and carbonation speed was equivalent to that obtained using exhaust gas and industrial $CO_2$ gas. This figure shows that neither several 10 ppm NOx nor SOx included in exhaust gas influences carbonation depth and speed of this concrete.

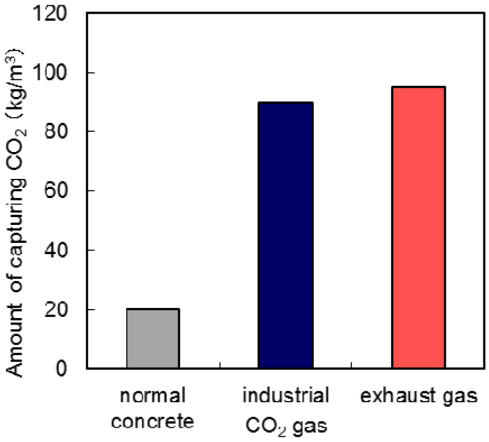

**Figure 5. Amount of capturing $CO_2$**

**Table 3. $CO_2$ emission of raw materials (kg-$CO_2$/ton)**

| | |
|---|---|
| Ordinary Portland Cement | 766.6 |
| Blast Furnace Slag | 26.5 |
| Coal Ash | 0 |
| γ-$C_2S$ | 159.3 |
| River sand | 3.7 |
| Coarse Aggregate | 2.9 |

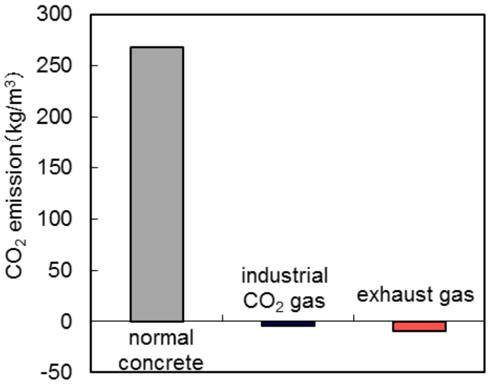

**Figure 6. Amount of $CO_2$ emission**

### 3.2 $CO_2$ emission

The amount of captured $CO_2$ of the new ecological concrete after carbonation curing is shown in the Fig. 5. In this study, an inorganic carbon analyzer “*coulometer*” made in Japan by Ans Corporation was used as the analytical instrument, where $CO_2$ generated by dropping hydrochloric acid in a sample is collected into an absorbing liquid and $CO_2$ amount is quantified through a titration method. This device enables measurement of only inorganic carbon gasified due to decomposition with the acid (Higuchi, 2013). The amount of captured $CO_2$ in concrete, which is cured with the same temperature, same humidity, and pure $CO_2$ gas of 20% concentration which is industrially manufactured, is also shown in this figure. Moreover, the amount of captured $CO_2$ in normal concrete (Water binder ratio is 47%, using ordinary portland cement) cured in air for 6 months are shown in this figure.

Amount of captured $CO_2$ in concrete which is cured in 20% industrial $CO_2$ gas and cured in exhaust gas is equivalent, and the amount of captured $CO_2$ of these concretes increased as compaerd with normal concrete. It seems that normal concrete captured $CO_2$ in air, and the new ecological concrete captured $CO_2$ contained in industrial $CO_2$ gas or exhaust gas. This fact was verified when carbonation curing is applied using exhaust gas from thermal power stations, it is possible to capture a large amount of $CO_2$ contained in exhaust gas in concrete.
The $CO_2$ emission intensity values originated from materials used in this study are shown in Table 3. Based on these values, $CO_2$ emissions originating from materials during the production of these concretes were calculated. The calculated result was 85.7 kg/m$^3$. The value obtained by subtracting the amount of captured $CO_2$ shown in Fig. 5 from the calculated $CO_2$ emissions based on Table 3, is shown in Fig. 6. According to this figure, $CO_2$ emission of the ecological concretes cured in industrial $CO_2$ gas or exhaust gas were reduced sharply compaerd with normal concrete. Moreover, it was clarified that when carbonation curing was performed using exhaust gas, the amount of captured $CO_2$ surpassed the $CO_2$ emission amount originating from the materials.
It has been verified that by choosing a combination of materials giving small amount of $CO_2$ emissions, and by applying carbonation curing through an appropriate method, a large amount of $CO_2$ can be captured in concrete, and the total $CO_2$ emissions including that originating from materials can be reduced to a negative value.

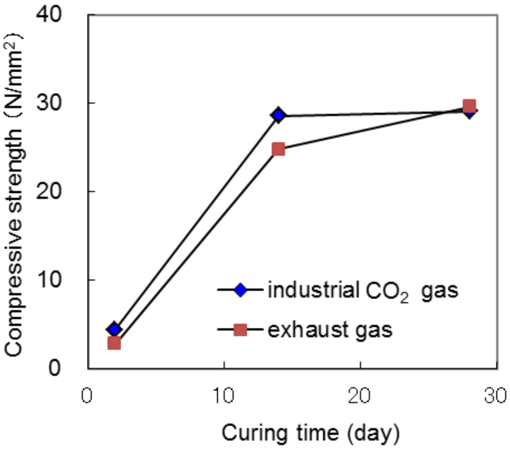

Figure 7. Compressive strength

## 3.3 Compressive strength

The relationship between curing time and compressive strength is shown in Fig.7. Compressive strength is measured based on JIS A 1108. The compressive strength of the concrete cured at the same temperature, same humidity, and $CO_2$ gas of 20% concentration which contains neither NOx nor SOx instead of exhaust gas, is also shown in this figure. Compressive strength of concrete which is cured with exhaust gas at 14 days is slightly lower compared to concrete cured with industrial $CO_2$ gas. But compressive strength at 28 days of concrete cured with exhaust gas is equivalent to the compressive strength of concrete cured with industrial $CO_2$ gas. This figure shows that neither several 10 ppm NOx nor SOx in exhaust gas influences compressive strength of this concrete.

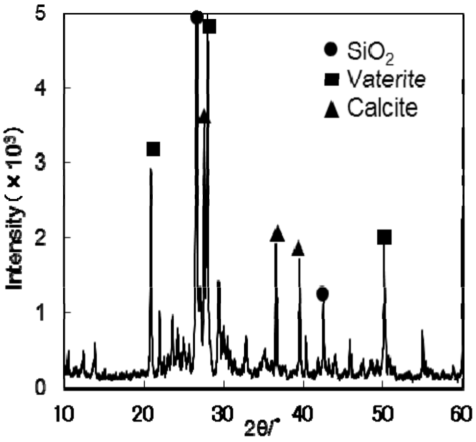

Figure 8. XRD patterns of the concrete cured with exhaust gas for 14days

## 3.4 Phase analysis

The fractured samples of concrete cylindrical specimens which were cured with exhaust gas for 28 days, were subjected to XRD analysis. XRD-patterns of the concrete cured with exhaust gas for

14 days are shown in Fig.8. The main minerals of this concrete are calcite, vaterite and $SiO_2$. It is considered that calcite and vaterite are precipitated by carbonation curing. Generally, it is known that calcite is precipitated when $Ca(OH)_2$ which is the main hydrate of concrete reacts with $CO_2$. In past studies, it was also known that vaterite precipitated alternatively when $\gamma$-$C_2S$ reacted with $CO_2$ (Saito, 2008). This figure shows that $\gamma$-$C_2S$ reacted with $CO_2$ satisfactorily. This figure also shows that $Ca(OH)_2$ does not exist in this concrete. It is seen that all $Ca(OH)_2$ of this concrete reacted with $CO_2$ by carbonation curing. Moreover, no mineral containing NOx or SOx was not found in this concrete. It is shown that NOx and SOx contained in exhaust gas do not affect the reaction of $Ca(OH)_2$ or $\gamma$-$C_2S$, which is included in this concrete with $CO_2$.

## 4. EXPERIMENTAL RESULTS FOR MORTAR BLOCK

### 4.1 Resistance to abrasion

Interlocking block is usually used for roads, such as driveways and sidewalks. Therefore, high resistance to abrasion is required in interlocking blocks. The resistance to abrasion of mortar was estimated by the abrasion test. Abrasion test was done based on ISO 9352:1995 “Plastics - Determination of resistance to wear by abrasive wheels”. Results of abrasion test are shown in Fig. 9. In this figure, the test results of normal interlocking block (water binder ratio is 30%, using blast-furnace cement type B) are also shown. This figure shows that the resistance to abrasion of the new ecological mortar is greater than that of the normal interlocking block. It is considered that calcite and vaterite are precipitated in this mortar by carbonation curing and the mortar become dense.

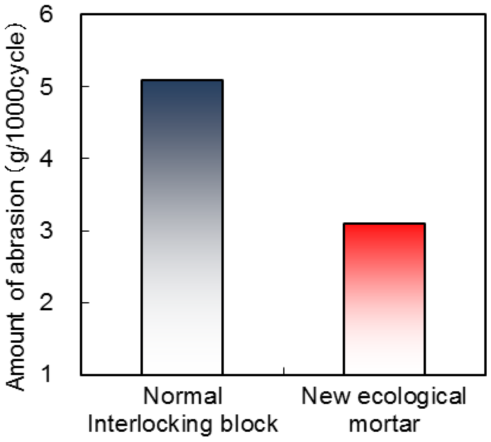

**Figure 9. Amount of abrasion at 1000cycle**

### 4.2 Leaching (efflorescence)

When manufacturing interlocking blocks, efflorescence occurs frequently. Since the appearance of the surface become worse when efflorscences are occred, occurence of efflorescence must be reduced as much as possible. The incidence of efflorescence when manufacturing normal interlocking blocks or new ecological mortar blocks is shown in Fig,10. Appearances of both blocks are also shown in Fig. 10. It is seen that the incidence of efflorescence is small in the new ecological mortar compared to normal interlocking blocks. It is known that $Ca(OH)_2$ included in concrete and $CO_2$ in air react and efflorescence occurs. In the new ecological mortar, since all $Ca(OH)_2$ is changed to $CaCO_3$ by carbonation curing, it is considered that efflorescence has not occurred. Moreover, the pH value of this concrete is close to neutral (7-8) because this concrete is fully carbonated and $Ca(OH)_2$ does not exist. This concrete has high resistance to leaching of Calcium from concrete.

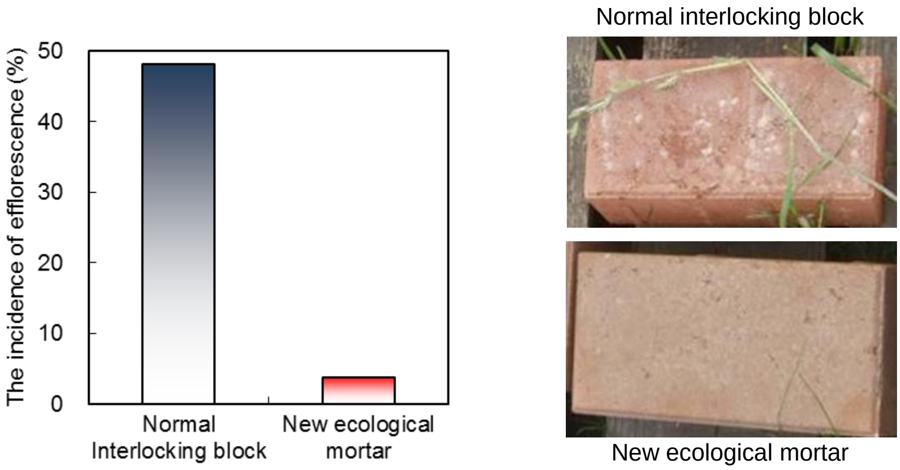

**Figure 10. Incidence of efflorescence (left) and appearance of the surface of mortar (right)**

## 5. CONCLUSIONS

Materials and manufacturing method of new ecological concrete are introduced, and physical, chemical properties of this concrete are reported in this paper. In concluding, I should note that shown below.

(1) Carbonation speed, the amount of captured $CO_2$, and compressive strength of the new ecological concrete cured with exhaust gas were equivalent to those of the concrete cured with industrial $CO_2$ gas. It was clarified that neither several 10 ppm NOx nor SOx contained in exhaust gas influence carbonation speed, the amount of captured $CO_2$, and the compressive strength of new ecological concrete.

(2) After calculating $CO_2$ emission amount originated from raw materials, $CO_2$ balance related to concrete production was evaluated. As a result, by choosing powder compositions, and by applying the proper method of carbonation curing, the $CO_2$ emission amount including that originated from raw materials can be reduced to negative value.

(3) Resistance to abrasion of the new ecological mortar is greater than that of the general interlocking block. It is considered that calcite is precipitated in this mortar by carbonation curing and the mortar become dense.

(4) The incidence of efflorescence is small in the new ecological mortar compared to general interlocking block. In this mortar, since all $Ca(OH)_2$ has changed to $CaCO_3$ by carbonation curing, it is considered that efflorescence has not occurred.

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