

Utilization of Concrete Waste to Capture CO₂ with Zeolite

by

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Abstract

Attention has focused on carbon dioxide capture and storage (CCS) in recent years, which is considered to be a key technology for controlling global warming and achieving sustainable development. This study examined CO₂ capture using concrete waste. Usually, it is not favorable for reinforced concrete to be exposed to CO₂ because the resultant neutralization of concrete deteriorates its strength. However, such concrete can still be used for exterior covering and pavement. It can also be used to absorb CO₂ mainly by reacting with the CaO, that is contained in the concrete. This paper discusses the effects of zeolite addition and porosity on these materials. It is found that as much as 30% of CO₂ can be recovered into the material based on the total CO₂ emission during cement production.

Keywords: Carbon dioxide capture and storage, Concrete recycle, Zeolite addition

1. Introduction

"Heat island phenomena" have become significant in the large cities all over the world with the decrease in the green spaces (or open space reserve), which implies the annual average temperature is steadily increasing. Along with the progress in the global warming, the average temperature in Tokyo, Japan, has risen by about 3°C for the past 100 years while the normal temperature rises by 1.1°C for the entire Japan¹⁾ and the increase in the average temperature all over the world by about 0.85°C/year.²⁾ Especially, the warming in the large cities has been remarkable.

The cause of warming of the large cities includes the increase of absorption and the thermal storage of heat because of the increase in asphalt paving and concrete surfaces and the decrease in the reflectivity of construction materials. Therefore, the pavement that can suppress the rise road surface temperature has been introduced to improve in the thermal environment in the large cities. The water retentive concrete block pavement where a lot of excessive water can be absorbed with the plain concrete can decrease the road surface temperature. It can not only drain water to the roadbed under the block but also disperse the heat of vaporization of water. This kind of concrete can be used as roadbed and pavement materials where strength is not an essential matter. Among these activities, a number of studies should be mentioned on green concrete.^{3,4,5)}

On the other hand, if absorption and the fixation of CO₂ (one of

the main greenhouse gases) are accomplished with this kind of water retentive concrete and even with the reproduced concrete scraps, one can attain two purposes at the same time, i.e., both the capture of CO₂ and the lower temperature in the urban area can be obtained.

Generally speaking, the acidification and neutralization of concrete with CO₂ have been problematic because these reactions deteriorate the strength of concrete. However, strength of concrete is not a major concern if it is used as pavement block.

Addition of artificial zeolite to concrete has been attempted in order to adsorb harmful substances chiefly contained in the automotive exhaust emission and to improve water quality.

It can be said that the evaluation concerning with CO₂ absorption of concrete with additional zeolite has not been done, though zeolite shows a very good adsorption characteristic for CO₂ as well as for NO_x.

In the present study, keeping the porous concrete in mind, the authors prepare various kinds of concrete blocks. The purpose of this study is to measure the CO₂ absorption by the neutralization reaction and to examine the effect of artificial zeolite addition. Based on the experimental results, the effects of void ratio and the addition of artificial zeolite will be discussed.

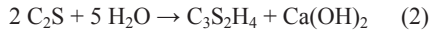
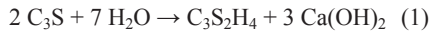
2. Principle

The principal products of the hydration reactions, which are primarily responsible for the strength of concrete, are the calcium silicate hydrates that make up most of the hydrated cement. They are formed from the reaction between the two calcium silicates

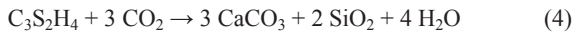
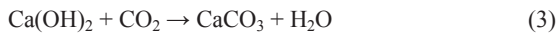
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and water. These reactions may be written as



where C_3S , C_2S and $C_3S_2H_4$ stand for $3 CaO \cdot SiO_2$, $2 CaO \cdot SiO_2$, and $3 CaO \cdot 2 SiO_2 \cdot 4 H_2O$ if we follow the industrial tradition. Calcium silicate hydrate is a basically amorphous material that does not have the precise stoichiometric composition indicated in the above equations.⁶⁾ During weathering and neutralization of concrete, major elements of hydration products such as calcium hydroxide and calcium silicate hydrate may react with carbon dioxide to generate calcium carbonate, which reaction can be expressed by the following:



Thus, carbon dioxide capture and storage (CCS) may be carried out through these reactions.

3. Experiment

3.1 Preparation of specimen

Preparation of mortar (plain concrete) specimen was accomplished following JIS (Japan Industrial Standards) A 1132-2006⁷⁾: "Method of making and curing concrete specimens," which is equivalent to ISO 1920-3:2004. Three identical specimens were prepared at a time. Mortar pieces were chosen in order to simplify the experiment for CO_2 absorption observation. Cement mostly used was ordinary Portland cement. Water/cement ratio was 50 %. Porosity of the pieces was prepared at 0, 25 and 50 % void with using a foaming agent (Fine foam 707, BASF). For all specimens, the amounts of aggregate and water were 1350 and 225 grams, respectively. Cure was done for 20 days in water at temperature $7 \pm 1^\circ C$ and drying under atmosphere at temperature $20 \pm 1^\circ C$ with relative humidity 65 %. The configuration of the piece was $40mm \times 40mm \times 160mm$. Two samples were used in the bending and compression tests and the other one was tested for a CO_2 absorption process.

3.2 Experimental procedure

Pure carbon dioxide gas was introduced into a container of $300 mm \times 300 mm \times 500 mm$ to establish the atmosphere that contained CO_2 at 3 volumetric %. The concentration was measured with a digital carbon dioxide checker (CD-1, Fuso Co. Ltd., Tokyo, Japan). Then a mortar test piece was set in the container and the CO_2 content was continuously measured until the concentration became below the detection limit of 0.04 %. The experiment was repeated until total experimental time reached 100

hours. The experimental setup is shown in Fig. 1.

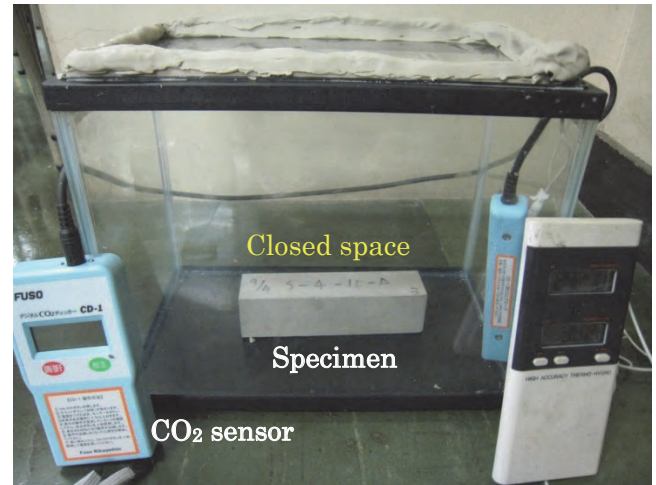


Fig. 1 The experimental setup of the CO_2 exposure runs.

4. Results and Discussion

Figs. 2 and 3 are the typical example of variation in relative CO_2 concentration as a function of time. The vertical axis shows logarithm of the ratio C/C_0 : the real time concentration C over the initial concentration C_0 . The slope in the graph stands for reduction rate of CO_2 . Here, the measured CO_2 content is the one inside the experimental container where the sample specimen is placed. Based on these readings, the amount of absorbed CO_2 can be calculated for unit volume of mortar. The rate of absorption or the capture of CO_2 changes with the sample mortar specimen.

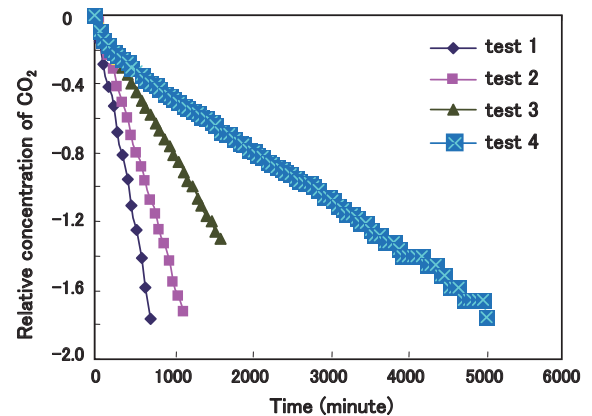


Fig. 2 Variation in CO_2 content inside the sample container; Sample 0 void – 0 zeolite

Fig. 2 shows the variation without any void or zeolite

addition, where the total experimental time exceeded 100 hours only after the fourth repeat. On the other hand, CO₂ absorption runs in Fig. 3 were repeated twelve times for the sample with 50 % void ratio, even without zeolite addition, that implies the void ratio is one of the key factors for CO₂ capture, for the absorption of CO₂ has to be enhanced with the larger surface area of the absorbent material.

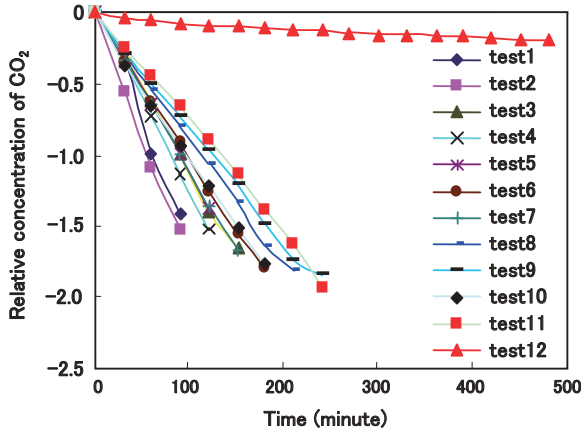


Fig. 3 Variation in CO₂ content inside the sample container; Sample 50 % void – 0 zeolite

Table 1 lists the tested specimen with cumulated CO₂ per unit mortar volume (kg/m³). Figs. 4 to 6 show the increase in the cumulated CO₂ as a function of time, where Figs. 4, 5 and 6 correspond to the void ratios of 0, 25 and 50 %, respectively. In cases for normal mortar with no void (0 % void), additional zeolite up to 90 kg/m³ increased CO₂ absorption. However, it seems that the excessive zeolite even gives a negative effect. A 180 kg/m³ addition case is even worse than that without any addition. In general, CO₂ absorption is not quite good; less than 5 g per specimen within 100 hours.

Table 1 Calculated CO₂ recovery for each mortar specimen (to a volume of 1 m³)

| Void ratio (%) | Zeolite addition (kg/m ³) | Captured CO ₂ (kg/m ³) | CO ₂ emission during cement production (kg/m ³)(*) | CO ₂ recovery (%) |
|----------------|---------------------------------------|---|---|------------------------------|
| 0 | 0 | 8.5 | 412.6 | 2.05 |
| 0 | 45 | 13.6 | 409.3 | 3.32 |
| 0 | 90 | 18.6 | 402.1 | 4.62 |
| 0 | 180 | 6.5 | 390.9 | 1.67 |
| 25 | 0 | 20.6 | 325.0 | 6.35 |
| 25 | 45 | 40.4 | 327.9 | 12.32 |
| 25 | 90 | 47.6 | 322.1 | 14.78 |
| 25 | 180 | 68.2 | 313.8 | 21.74 |
| 50 | 0 | 28.8 | 276.1 | 10.43 |
| 50 | 45 | 54.4 | 272.0 | 19.99 |
| 50 | 90 | 71.7 | 268.0 | 26.74 |
| 50 | 180 | 76.2 | 260.4 | 29.27 |

*The value of CO₂ emission per 1 kg cement production: 0.812 kg-CO₂ per kg-cement has been taken from the database of Architectural Institute of Japan⁸⁾.

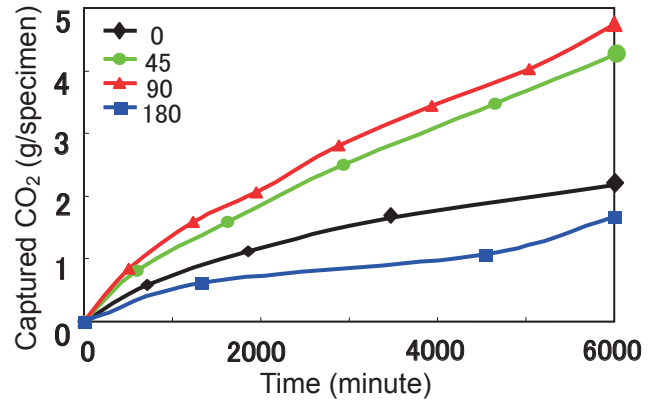


Fig. 4 CO₂ capture as a function of time for mortar specimen with no void and zeolite addition: 0, 45, 90 and 180 kg/m³

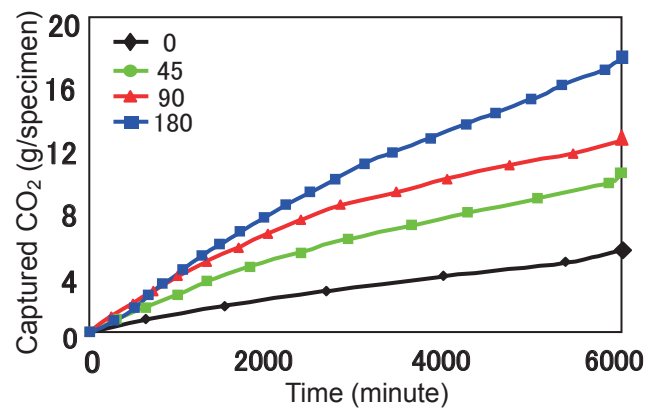


Fig. 5 CO₂ capture as a function of time for mortar specimen with 25 % void and zeolite addition: 0, 45, 90 and 180 kg/m³

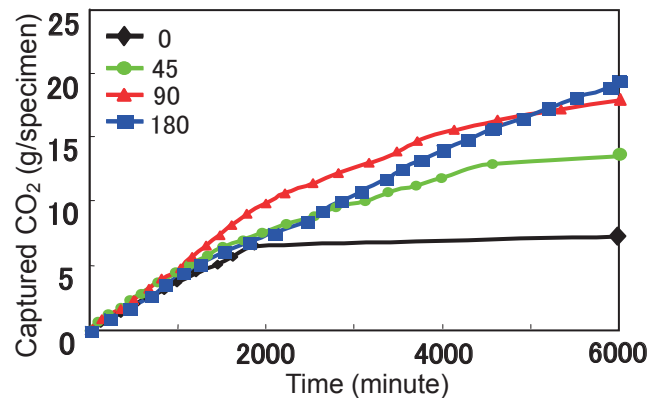


Fig. 6 CO₂ capture as a function of time for mortar specimen with 50 % void and zeolite addition: 0, 45, 90 and 180 kg/m³

Cases for 25% void ratio actively improve the absorption reaction. The more is the zeolite addition, the larger the captured CO₂ becomes. Moreover, in cases for 50 % void ratio, more than 45 kg/m³ addition gives a substantial effect on CO₂ capture, though a 180 kg/m³ addition case does not remarkably

enhance the absorption reaction compared with the case for 90 kg/m³ addition. From these findings, it is concluded that there should be an effective addition and the void ratio that maximize the rate of CO₂ absorption and its cumulated amount. Calculated CO₂ emission data per unit mortar volume are also listed in Table 1. They can be derived from the cement production emission data (kg- CO₂/kg-cement) based on LCCO₂ value taken from Architectural Institute of Japan.⁸⁾ From these data, it can be seen

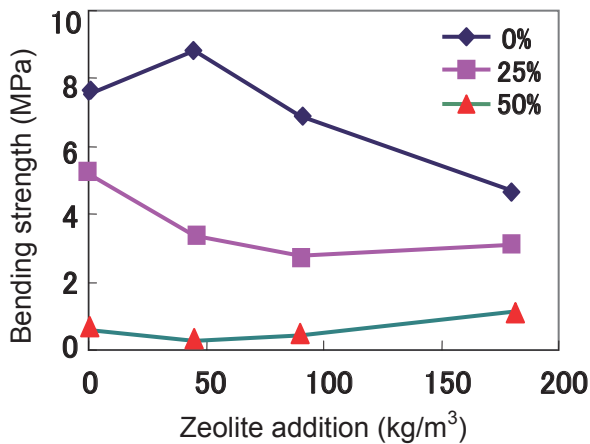


Fig. 7 Bending strength as function of additional artificial zeolite for void ratios of 0, 25 and 50 %

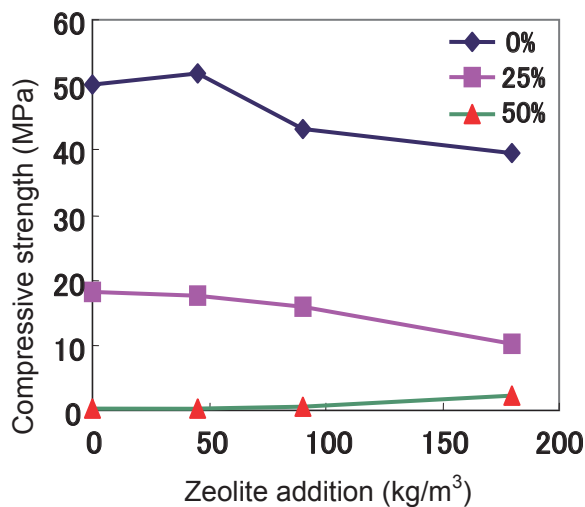


Fig. 8 Compressive strength as function of additional artificial zeolite for void ratios of 0, 25 and 50 %

that as much as 30 % of CO₂ can be recovered with a combination of 50 % void and 180 kg zeolite addition to a 1 m³ mortar. Artificial zeolite addition can enhance the absorption.

Weakening of the concrete with zeolite addition is an unfavorable result. Figs. 7 and 8 show the variation of bending and compressive strength of the mortar specimens, respectively. The sample specimen used in the strength test is an identical one that was used in the CO₂ absorption experiment. The variation among the same void ratio group is shown against the zeolite addition in these figures. It can be seen in Fig. 7 that, though

zeolite addition to the specimen without void (0% void) happened to strengthen the mortar, the bending strength of 0 and 25 % void decreased at the end. In case of 25 % void, the strength can be recovered to some extent, though the extent is very small. In case for the 50 % void, the strength of this group is very low, zeolite addition can increase the strength at the end. On the other hand, compressive strength of the mortar specimens in Fig. 8 decreased for the groups of 0 and 25 % voids. The extents of the decrease are found to be 20 % and 43 % for 0 and 25 % voids groups, respectively. For the case of 50 % void, which is basically fragile mortar, the strength can be substantially recovered. In any case, this kind of strength cannot be applicable to the construction as a structural material. However, the material becomes usable if it is set in the area where extensive strength is not required, i.e., patching on the exterior walls, the pavement tiles and roadbed applications, etc.

Experiment was also done using high-early-strength Portland cement other than ordinary cement. This kind of cement contains 40 % more CS₃ than ordinary Portland cement in order to promote hydration and enhance strength in the early stage, which in turn, produces more Ca(OH)₂ in the concrete. However, its CO₂ adsorption ability found to be quickly reduced after several repeats of observation.

5. Closing Remarks

If one can make concrete and mortar porous to some extent, the CO₂ absorbent like artificial zeolite will be utilized as an extremely effective material. It is very important if one can utilize waste concrete components such as CaO, Ca(OH)₂ and its related compounds to absorb CO₂ and form CaCO₃. Concrete wastes have been getting more and more problematic in case where this kind of architectural wastes cannot be dumped because of the shortage of the local dumping site. If such wastes can be reused towards environmentally benign purposes, it should be one of the most attractive impacts to suppress CO₂ emission and global warming.

Acknowledgment

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References

- 1) Japan Meteorological Agency: http://www.data.jma.go.jp/cpdinfo/chishiki_ondanka/p08.html
- 2) Intergovernmental Panel on Climate Change: Synthesis

- Report (2014).
- 3) Janez Turk, et al.: Environmental evaluation of green concretes versus conventional concretes by means of LCA, *Waste Management*, 45 (2015), p.194-205. DOI 10.1016/j.wasman.2015.06.035.
 - 4) Evi Aprianti: *J. Cleaner Product* (2016) DOI 10.1016/j.jclepro.2015.12.115.
 - 5) N. Otsu and K. Watanabe: "Experimental Study on Composite Cement Materials with High Fluidity and Toughness Containing Fine Aggregates from Natural and Recycled Sources," *Proceedings of the School of Engineering, Tokai University*, 55, (2015), pp. 43-49. (Japanese).
 - 6) *Concrete construction engineering handbook*; Edward G. Nawy, ed., CRC Press, New York, (1997), p.1-5.
 - 7) JIS (Japan Industrial Standards) A 1132-2006: "Method of making and curing concrete specimens," (2006).
 - 8) *LCA Database*, Architectural Institute of Japan, (2006).