

# DEVELOPMENT OF N<sub>2</sub> AND H<sub>2</sub>O BET SURFACE AREA OF LOW HEAT PORTLAND CEMENT

Hiroki SUGIMOTO<sup>\*1</sup>, Ryo KURIHARA<sup>\*1</sup>, Ippei MARUYAMA<sup>\*2</sup>

## ABSTRACT

Low heat Portland cement shows larger drying shrinkage than ordinary cement. To elucidate the mechanism of large shrinkage, fundamental property of low heat Portland cement paste was investigated. The results of N<sub>2</sub> sorption measurement show that the amount of total sorption amount does not increase after 28 days of age. On the other hand, from water vapor sorption measurement and TGA, total sorption of water vapor molecules and amount of CBW increase after 28 days of age. It was suggested that the generation mechanism of C-S-H was different from ordinary Portland cement.

**Keywords:** low heat Portland cement, C-S-H, nitrogen sorption, water vapor sorption

## 1. INTRODUCTION

Shrinkage of hardened cement paste (hcp) in concrete cause alteration of concrete property through micro-cracking around aggregate [1, 2, 3]. In addition, it causes large drying shrinkage of concrete and if it is restrained, cracking occurs. This cracking has large influence on stiffness change of structural response against earthquake [4, 5].

On the contrary, in our previous research, shrinkage of hcp depends on mineral composition of original cement clinker [6, 7]. But such mechanism is not clarified.

For the long-term use of concrete structure, fundamental knowledge of cement chemistry is necessary, such as aging management of predicting the structural performance during in-service period.

In the present contribution, microstructure development of low-heat Portland cement paste system is investigated by considering the difference in density of C-S-H using the nitrogen sorption measurement and the water vapor sorption measurement [8, 9, 10], and some new findings are reported.

## 2. EXPERIMENT

### 2.1 Materials

Low heat Portland cement, whose chemical composition and mineral composition are shown in Table1 and Table2, was used to produce the specimens.

The water to cement ratios of the specimen was set as 0.40 and 0.55 (noted as L40 and L55 respectively). The paste was mixed in a planetary centrifugal mixer (the rotation/revolution speed are 980 rpm, 1000 rpm, respectively.) for 1.5 min firstly to w/c = 0.40, in case of w/c = 0.55, water was added and it was mixed for further 1.5 min. Fresh cement paste was scrapped from the inside of the mixing container. All the materials were stored in a thermostatic room at 20 ± 1 °C for 1 day prior to mixing. The mixing was performed at room temperature and the specimens were then immediately moved to a thermostatic room 20 ± 1 °C. To minimize segregation, the paste was remixed using spoon every 30 min for 6 hours. After remixing, the specimens were casted into mold with sealed condition. They were kept for 3, 7, 28 and 91 days at 20 °C. After each curing period, the nitrogen sorption

Table1 Chemical composition of low heat Portland cement

LOI (%)	Blaine (m <sup>2</sup> /g)	Chemical composition (mass%)									
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O <sub>eq</sub>	Cl <sup>-</sup>
0.73	3710	25.85	3.32	3.08	62.28	0.76	2.84	0.19	0.25	0.35	0.003

Table2 Mineral composition of low heat Portland cement

Mineral composition (mass%)						
Alite	Belite	Aluminate phase	Ferrite phase	Periclase	Bassanite	Gypsum
20.37	62.21	2.29	11.30	0.52	2.17	1.14
± 1.48	± 3.14	± 0.26	± 0.56	± 0.18	± 0.57	± 0.41

\*1 Graduate student, Dept. of Environmental Engineering and architecture Nagaya Univ., JCI Student Member

\*2 Prof. Dept. of Environmental Engineering and architecture Nagaya Univ., Dr. Eng., JCI Member

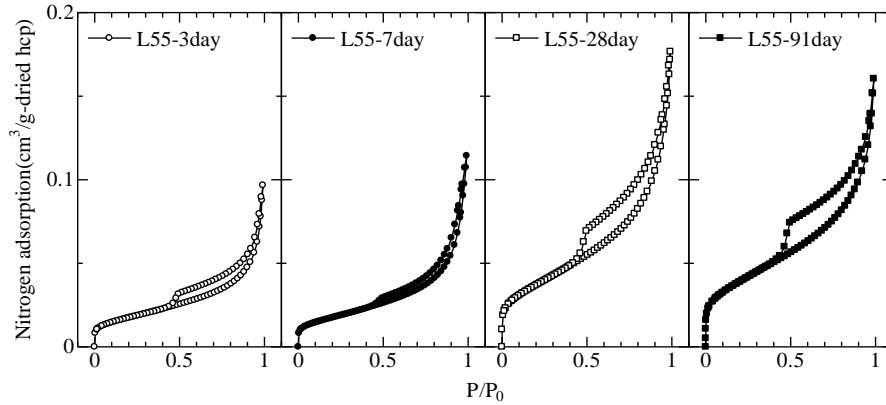


Fig.1 Nitrogen sorption isotherm at each material age of L55

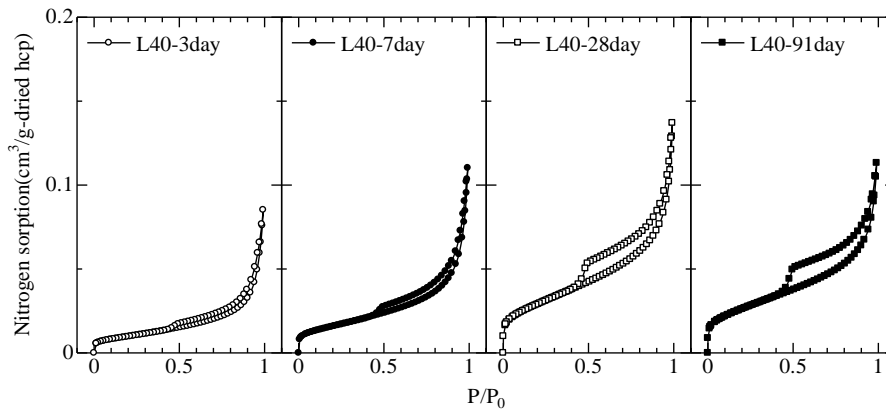


Fig.2 Nitrogen sorption isotherm at each material age of L40

measurement, water vapor sorption measurement and thermogravimetry were conducted.

## 2.2 Nitrogen sorption measurement

The nitrogen sorption measurements were conducted using the volumetric method. A sample (~100 mg) was used for each measurement at 77.4 K, with an adsorption amount increase/decrease tolerance of  $5.00 \text{ cm}^3 (\text{STP}) \text{ g}^{-1}$  and a time tolerance of 180 s. The measurement points on the adsorption and desorption branches were at intervals of  $p/p_0 = 0.05$  up to 0.95, and ended at 0.99. The Brunauer-Emmett-Teller (BET) surface area ( $S_{N_2}$ ) [11] of the adsorption branch was calculated with a nitrogen molecule cross-sectional area of  $0.162 \text{ nm}^2$  [12]. The samples were ground in a mortar, and sample powder with diameter of 25-75  $\mu\text{m}$  was used for this analysis. For pre-treatment, the samples were dried using a vacuum pump and heated to  $105 \text{ }^\circ\text{C}$  with a heating mantle for 30 min.

## 2.3 Water vapor sorption measurement

Water vapor sorption of the samples was measured using the same sample condition (~20 mg) as those for the nitrogen sorption isotherm at room temperature ( $20 \text{ }^\circ\text{C}$ ), with a pressure tolerance of 0.05 mmHg and a time tolerance of 120 s. The measurement points on adsorption branches were at intervals of  $p/p_0 = 0.05$  up to 0.95, and ended at 0.98. The BET surface area ( $S_{H_2O}$ ) of the adsorption branch was calculated using BET theory with a water molecule cross-sectional area of  $0.114 \text{ nm}^2$  [13].

## 2.4 TGA

Thermogravimetry analysis (TGA) was conducted for powder sample (~20 mg) with a diameter under 100  $\mu\text{m}$  for each measurement. The results were evaluated using differential thermogravimetry (DTG). The temperature range was from room temperature to  $1000 \text{ }^\circ\text{C}$  and the rate of temperature increase was  $10 \text{ }^\circ\text{C}/\text{min}$ . Nitrogen was used as a carrier gas. For pre-treatment, the samples were dried using a vacuum pump for 24 hours at  $20 \text{ }^\circ\text{C}$ .

A chemically bound water (CBW) was calculated from the mass difference before and after measurement. The difference between the original weight and CBW takes into account of mass loss of water molecules. DTG results per unit weight of cement were calculated. Assuming that the mass change from  $20 \text{ }^\circ\text{C}$  to the vicinity of  $200 \text{ }^\circ\text{C}$  is evaporable water, a mass subtracting the mass of evaporable water from the mass difference up to  $1000 \text{ }^\circ\text{C}$  is considered as CBW. During these calculations, since the abrupt decrease in mass around  $600 \text{ }^\circ\text{C}$  [14] is caused by decarbonation of calcium carbonate, this impact was taken into consideration.

## 3. EXPERIMENTAL RESULTS

### 3.1 Nitrogen sorption measurement

#### (1) L55

Fig.1 shows the nitrogen sorption isotherm for L55 at each material age.

Here, a sharp decrease in the sorption isotherm

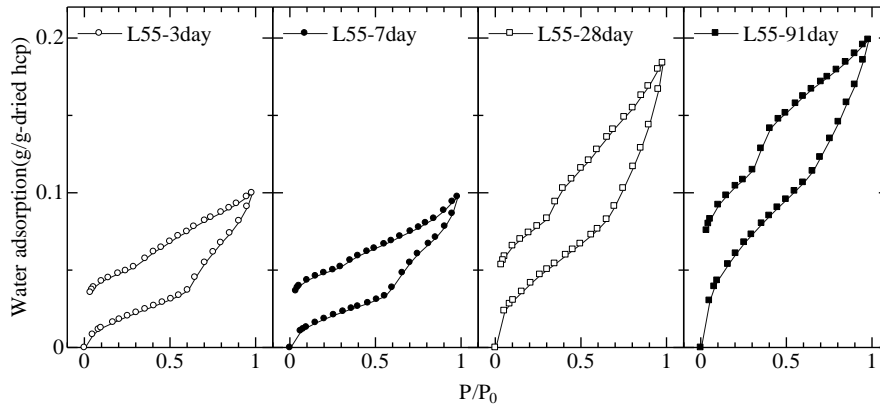


Fig.3 Water vapor sorption isotherm at each material age of L55

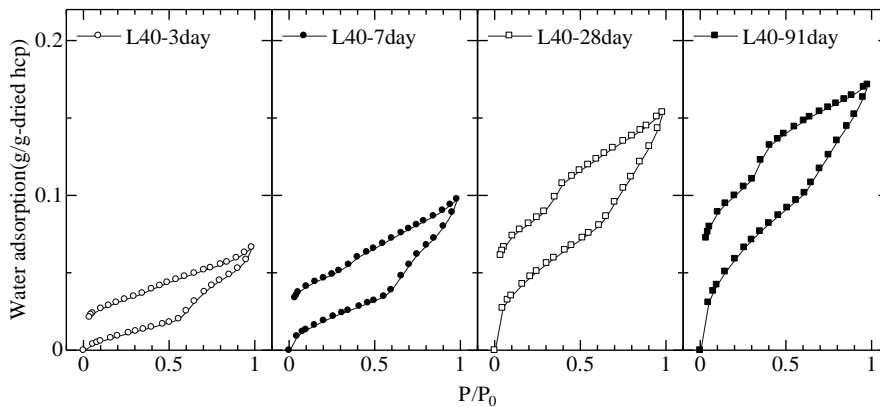


Fig.4 Water vapor sorption isotherm at each material age of L40

as seen in  $p/p_0 = 0.3-0.4$  in the desorption branch is called kink [15]. This behavior is originated from the cavitation. It has been found that evaporation of the condensed pore fluid from the spherical cavities occurs by cavitation if the width of the connecting pores is smaller than a critical value (e.g., 5 nm for nitrogen adsorption) [15]. The larger the kink, the larger the volume of the meso-pores with connecting pores whose size is less than 5 nm.

Paying attention to the kink between  $p/p_0 = 0.3-0.4$ , the increase between the measurement results of 7 days of age and the result of 28 days of age is pronounced. The amount of desorption associated with kink increased by about 30%.

Focusing on the maximum adsorption amount in the vicinity of  $p/p_0 = 0.99$ , it was confirmed that the increase was observed from 3 days to 28 days of age, but no increase (or slight decrease) from 28 days to 91 days was observed.

#### (2) L40

Fig.2 shows the nitrogen sorption isotherm for L40 at each material age. Focusing on the kink  $p/p_0 = 0.3-0.4$ , it is similar to L55, the increase in kink is significant from 7 to 28 days of age, and the slight increase also occurs from 28 to 91 days of the age. Focusing on the maximum adsorption amount in the vicinity of  $p/p_0 = 0.99$ , an increase was confirmed from 3 to 28 days of age, and a decrease in the maximum adsorption amount between 28 days and 91 days of age

was confirmed. This trend is the same as that of L55.

### 3.2 Water vapor sorption measurement

#### (1) L55

Fig.3 shows the water vapor sorption isotherm of L55 at each material age. It was confirmed that the sorption isotherm of 3 days and 7 days of age generally draw the same isotherm.

About the kink between  $p/p_0 = 0.3-0.4$  in the desorption process in the water vapor sorption isotherm, kink was not confirmed in the measurement results of 3 days and 7 days of age. On the other hand, kinks were confirmed in the measurement results on the age of 28 days and 91 days.

Regarding the maximum adsorption amount in the vicinity of  $p/p_0 = 0.98$ , the maximum adsorption amount of 3 days and 7 days of age are almost the same. It can be confirmed that it increases from 7 days to 91 days of age. The maximum adsorption increases markedly between 7 and 28 days of age, which is similar to the nitrogen sorption measurement. On the other hand, in the nitrogen sorption measurement, it decreased between 28 days and 91 days of age, and the opposite tendency was confirmed for water vapor sorption measurement.

#### (2) L40

Fig.4 shows the water vapor adsorption isotherm for L40 at each material age. Unlike the result of L55, it was confirmed that the adsorption isotherm was

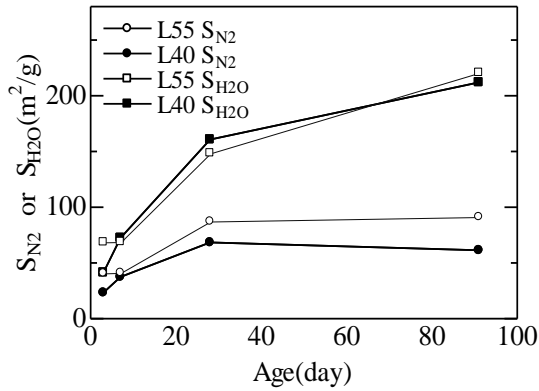


Fig.5 BET specific surface area of L55 and L40

changed between 3 days and 7 days of age. As for the kink between  $p/p_0 = 0.3-0.4$ , the kink was not confirmed on 3 days and 7 days of age.

Regarding to the maximum adsorption amount in the vicinity of  $p/p_0 = 0.98$ . It was confirmed that the maximum adsorption amount increased as the material age increased between 3 days and 91 days of age. It was confirmed that the nitrogen sorption isotherm decreased between 28 and 91 days of age, and the water vapor sorption isotherm increased, which is similar to L55.

### 3.3 BET specific surface area

The change in the nitrogen BET surface area ( $S_{N_2}$ ) and water vapor specific BET area ( $S_{H_2O}$ ) with the material age calculated from the sorption measurement of L55 and L40 summarized in Fig.5. From 3 to 7 days of age, L55 has not changed both  $S_{N_2}$  and  $S_{H_2O}$ . On the other hand, at L40, it was confirmed that both  $S_{N_2}$  and  $S_{H_2O}$  increased. It was confirmed that  $S_{N_2}$  was almost constant, and  $S_{H_2O}$  increased in both L55 and L40 between 28 days and 91 days in the age range.

### 3.4 TGA

Fig.6 shows the results of DTG of L55. Here, the graph of DTG is shown shifted by 100 ng/s/ $\mu$ g for each measurement result for a clarity. It can be confirmed that the baseline (which was confirmed as gradual decrease line from 200 to 600 °C) of DTG increases as the material age of the specimen becomes larger. From this, it is considered that the amount of CBW increases between 3 days and 91 days of age. The peak between 400 °C and 500 °C is a decrease caused by dehydration of calcium hydroxide [16].

Fig.7 shows the results of DTG of L40. An increase in baseline of DTG can be confirmed between 3 days and 28 days of age. On the other hand, there is no significant difference between 28 days and 91 days.

### 3.5 Chemical bound water

The change in the CBW with the material age for L55 and L40 summarized in Fig.8. At the age of 3 days, L55 and L40 showed almost the same amount of CBW. Between 7 and 28 days of age, the amount of CBW of L40 is larger than those of L55. It was confirmed that

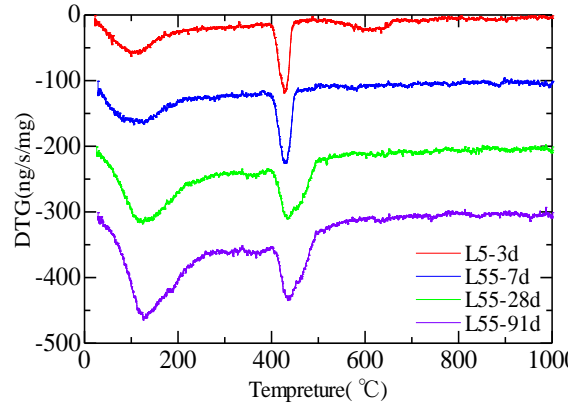


Fig.6 DTG at each material age of L55

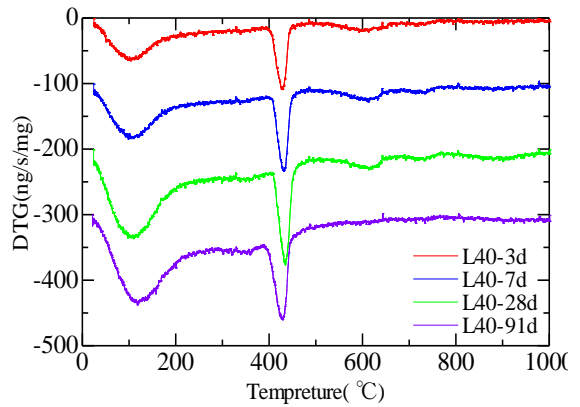


Fig.7 DTG at each material age of L40

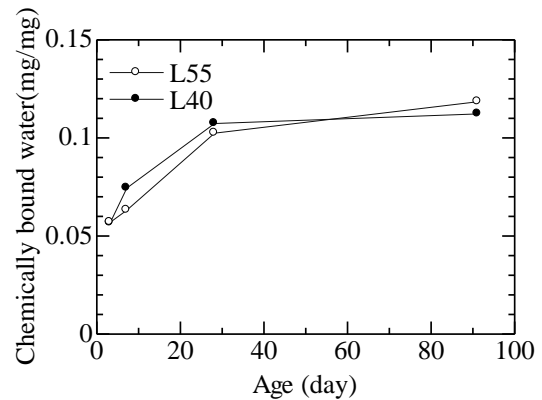


Fig.8 The change in the material age of chemical bound water of L55 and L40

the amount of CBW of L55 exceeds L40 between age of 28 and 91 days. Generally, during the early age, rate of hydration of cement is quite similar. Only when the available water and precipitation space are limited, the rate of hydration is changed. Based on the current data, slight increase in rate of hydration of L40 might be explained by the higher amount of precipitation sites (or volume of super saturation) due to large number of cement surface per unit volume of hcp. And continuous increase of L55 can be explained by the larger precipitation space due to larger water to cement ratio.

#### 4. DISCUSSION

Experimental results of nitrogen sorption measurement, water vapor sorption measurement and thermogravimetric analysis confirmed the following in the hardened cement paste using low heat Portland cement.

- (1) The microstructure hardly changes until 7 days of age because there is small change in the nitrogen sorption isotherms and the water vapor sorption isotherms and kink is also small.
- (2) The microstructure greatly changes after 7 days of age.
- (3) Between 28 days and 91 days of age, the pores capable of adsorbing nitrogen do not increase, but the pores to which water vapor can adsorb increase.
- (4) Up to 28 days of age, regardless of the water cement ratio, the amount of chemical bound water increases roughly in proportion to the age. But from 28 to 91 days of age, the amount of chemical bound water increases in case of L55 but no increase was observed in case of L40.

##### 4.1 The microstructure of low heat Portland cement

Calcium silicate hydrate (C-S-H), which accounts for the majority of hardened cement paste, can be divided into high density parts (HD C-S-H) and low density parts (LD C-S-H) [8]. In the nitrogen sorption measurement, information on the cavity structure of LD C-S-H is obtained. And in the water vapor sorption measurement, information on the microstructure of entire C-S-H including LD C-S-H and HD C-S-H is obtained [9].

In this experiment, the nitrogen adsorption amount and the  $S_{N_2}$  did not increase from 28 days to 91 days of age, and this tendency is not influenced by the water cement ratio. In the experiments by Jennings et al. [10], it was confirmed that the nitrogen sorption measurement was carried out using ordinary Portland cement, and the material age and the  $S_{N_2}$  were proportional. But it is not reproduced here. The large discrepancy can be explained by the belite reaction, which must be strongly visible in our case.

It should be, however, emphasized that the water vapor adsorption amount and water vapor specific surface area increased. That indicates that only HD C-S-H is increased during this period which corresponds to the main belite reaction period commenced after the end phase of alite reaction [17, 18]. To explain the sorption behavior, there are two possibilities; 1) belite hydration only forms HD C-S-H in original boundary of cement grains (as inner C-S-H), 2) the reaction of belite creates HD C-S-H by precipitation-filling the spaces between C-S-H sheets of LD C-S-H, in addition to the mechanism of 1). The mechanism 2) will well explain reduction of  $S_{N_2}$  of L40 in later ages. It is unlikely that only HD C-S-H will increase in the process of hydration of cement. However, deterministic experimental results have not

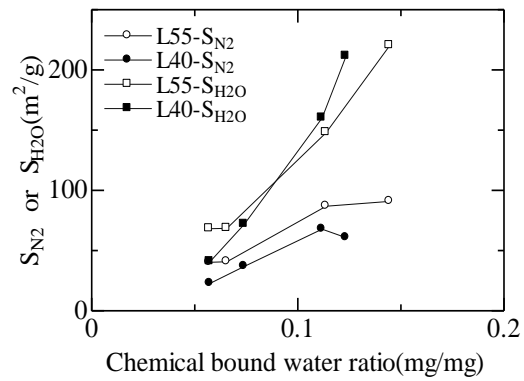


Fig.9 Relationship between BET specific surface area and chemically bound water of L55 and L40

been obtained in the present study. In the future, it is necessary to clarify the mechanism of C-S-H precipitation of belite by powder X-ray diffraction and other techniques.

##### 4.2 Relationship between BET surface area and CBW

Fig.9 shows the relationship between  $S_{N_2} / S_{H_2O}$  and CBW of L55 and L40. It was confirmed that the relationship between  $S_{N_2}$  and CBW is roughly proportional from 3 days to 28 days of age. However, it was confirmed that L55 increased and L40 decreased from 28 days to 91 days of age. It was confirmed that  $S_{H_2O}$  became larger as CBW increases. And the tangent of  $S_{H_2O}$  is increased as hydration proceeded. This phenomenon also suggested that the mechanism 2), because increasing of number or interlayer spaces where the surface potential from each C-S-H mono-layer overlapped and water molecules are easily adsorbed in, cause increase the  $S_{H_2O}$  efficiently from a view point of increase in CBW, as an index of cement hydration.

#### 5. CONCLUSION

The findings obtained on hardened cement pastes prepared using low heat Portland cement in this experiment are as follows:

- (1) When the low heat Portland cement paste is used, there is small change in the microstructure from 3 days to 7 days of material age, and the microstructure greatly changes after 7 days of age.
- (2) Pores capable of adsorbing nitrogen molecules did not increase from 28 days to 91 days of material age. It is highly possible that this tendency is attributable to belite which is contained in low heat Portland cement.
- (3) It was confirmed that space where water molecules can be adsorbed increases between 7 days and 91 days of material age. In other words, it is considered that microstructure derived from HD C-S-H and LD C-S-H has developed between 7 days and 91 days of age.
- (4) Above (2), (3) and previous studies suggested that the mechanism of formation of calcium silicate

hydrate is different between alite and belite.

#### ACKNOWLEDGEMENT

This research is supported by Chubu Electric Power Co. Inc., and JSPS Kakenhi 16H06363. Authors express their acknowledgements.

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