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Influence of Silicone Oil on Durability of Portland Blast Furnace Slag Cement Mortar

Gota Kishimoto¹, Junho Kim², Hyeonggil Choi³ and Yukio Hama^{4*}

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Abstract

In this study, the development of carbonation resistance in blast furnace slag (BFS) mortar when using silicone oil (SO) is investigated. Moreover, the influence of SO on drying shrinkage and frost resistance are investigated. The results indicate that SO tends to improve the carbonation resistance of BFS blended mortar and reduces drying shrinkage; however, it decreases frost resistance. The water repellency of SO has a positive effect on carbonation and drying shrinkage. Furthermore, there is a possibility that SO prevents the consumption of calcium hydroxide (CH) by carbonation and hydration in portland blast furnace slag cement type B (BB) samples. SO exists in the form of oil droplets in hardened cement pastes and inhibits the relaxation of water pressure at freezing. This is a probable cause for why SO decreases frost resistance.

1. Introduction

Recently, the use of industrial by-products, such as blast furnace slag (BFS), has increased in the construction industry, due to their potential to reduce CO₂ emissions (Miyasawa *et al.* 2010; Chen *et al.* 2012; Kumar *et al.* 2008). Although BFS blended cement has greater long-term compressive strength and a smaller heat of hydration, it can also have lower compressive strength at early stages of curing and lower carbonation resistance (Gu *et al.* 2014, 2015; Cetin *et al.* 2016; Rakhimova *et al.* 2014, 2015; Matsuka *et al.* 2010). Previous studies have attempted to find methods of improving carbonation resistance.

In the existing literature, it has been reported that decreasing air permeability by reducing the water to cement ratio, or by applying a finishing material, was effective in preventing carbonation (Kasai 1983). Moreover, these studies found that incorporating and applying silane water repellent to a concrete mixture using recycled aggregate (Zhu *et al.* 2013), using polymers as admixtures (Takahashi *et al.* 2013), and using Silicone Oil (SO) (Saito *et al.* 2004, 2005) were all effective for

increasing the carbonation resistance.

In Matsushita's study, it was revealed that using SO improved the carbonation resistance of autoclaved lightweight concrete (ALC) (Matsushita *et al.* 1999, 2004). In addition, Saito *et al.* discovered that SO improves carbonation resistance, reduces the drying shrinkage, and decreases the frost resistance of ordinary Portland cement (OPC) concrete (Saito *et al.* 2005).

In this study, the influence of silicone oil on improving the carbonation resistance of BFS blended cement mortar is investigated. In addition, experimental evaluation of the influence that the addition method of SO (external vs. internal) has on the mixture properties is performed. Moreover, the shrinkage reduction effect of SO was compared with a shrinkage reducing agent (SR), and its performance was evaluated. Finally, the impact on frost damage resistance due to the addition of SO was also studied.

2. Experimental method

The experiments consist of three series, Series 1, 2, and 3, which are shown in **Table 1**, **Table 2**, and **Table 3**, respectively. In series 1, the influence of SO on carbonation resistance and frost damage resistance are investigated. The water-to-binder ratio (W/B) is 0.55, and the binder-to-sand ratio (B:S) is 1:3. Only two types of binding agent are tested, one composed solely of OPC, and the other with a BFS replacement ratio of 45 wt% (BB). Thus, the most important experimental variable is the SO addition ratio (0, 0.5, 1, 2, 3, and 5 wt%), the influence of which is described herein.

Based on the experimental results of Series 1, Series 2 is aimed at investigating the influence of BFS replacement ratio and SO addition ratio on carbonation resistance. The four types of binder used are: OPC, BA (OPC 85%, BFS 15%), BB (OPC 55%, BFS 45%) and BC (OPC 35%, BFS 65%), and the seven SO addition

¹Graduate student, Division of Sustainable and Environmental Engineering, Muroran Institute of Technology, Muroran, Japan.

²Postdoctoral Researcher, College of Environmental Technology, Graduate School of Engineering, Muroran Institute of Technology, Muroran, Japan.

³Assistant Professor, College of Environmental Technology, Graduate School of Engineering, Muroran Institute of Technology, Muroran, Japan.

⁴Professor, College of Environmental Technology, Graduate School of Engineering, Muroran Institute of Technology, Muroran, Japan. *Corresponding author, E-mail: hama@mmm.muroran-it.ac.jp

Table 1 Experimental composition (Series 1).

Series 1	Mark	Binder [%]		W/B	B:S	SO	AE	Measured Properties
		OPC	BFS			B×wt. [%]		
	N	100	0	0.55	1:3	- 0.1 0.5 1 2 3 5	- 0.01	<ul style="list-style-type: none">• Air content• Flow• Compressive strength• Carbonation depth• Pore structure• CaCO₃ content• Ca(OH)₂ content• Durability Factor• Bubble spacing factor
BB	55	45						

Table 2 Experimental composition (Series 2).

	Mark	Binder [%]		W/B	B:S	SO	Measured Properties
		OPC	BFS			B×wt. [%]	
Series 2	N	100	0	0.55	1:3	-	<ul style="list-style-type: none"> • Air content • Flow • Compressive strength • Carbonation depth • Water absorption ratio • Water vapor adsorption properties
	BA	85	15			0.5	
	BB	55	45			1	
	BC	35	65			3	
						5	

Table 3 Experimental composition (Series 3).

Series 3	Mark	Binder [%]		W/B	B:S	SO	SR	Measured Properties
		OPC	BFS			B×wt. [%]		
	N	100	0	0.50	1:3	-	-	<div>• Air content</div> <div>• Flow</div> <div>• Compressive strength</div> <div>• Drying shrinkage</div>
						5	5	
BB	55	45	-			-		
			5			5		

ratios are 0, 0.5, 1, 3, 5, 7 and 10 wt%. Although the addition ratio of SO is in accordance with the weight of the binder, we also consider the influence of the method of SO addition. In Series 1, the total amount of mixing water is calculated excluding SO mass (External Addition); in Series 2, the total amount of mixing water is calculated including SO mass (Internal Addition).

In series 3, SO and SR are compared based on the resulting reduction of drying shrinkage. The water-to-binder ratio (W/B) is 0.50, and the binder-to-sand ratio (B:S) is 1:3. SO addition amount are 0, 1 and 5 wt%, and the SR addition amount is 5 wt%.

2.1 Materials

Tables 4 to 8 shows the properties of the materials used in this study. OPC and BFS are used for the binding materials and Shiraishi sand is used as the fine aggregate. For the four different mixtures under investigation, the BFS replacement ratios are set at 0%, 15%, 45%, and 65%. SO is commercially available as an internally added silicone water absorption inhibitor for building materials and has a characteristic of fixing to hydrates

without heat treatment. The SO is added after the mortar is mixed. The air-entraining (AE) agent uses is an alkyl ether-type anionic surfactant, and the shrinkage reducing agent uses is a mineral oil-type shrinkage reducing agent, which improves freezing resistance.

2.2 Measured properties and methods

2.2.1 Fresh properties

The flow and air content of the fresh mortar were measured according to JIS R 520 and JIS A 1128, respectively.

2.2.2 Compressive strength

The compressive strength test was conducted in accordance with JIS A 1108. The mortar was cured in $\phi 5 \text{ cm} \times 10 \text{ cm}$ cylindrical plastic molds. Curing of the compressive strength test samples took place in water for 4 weeks at 20 °C.

2.2.3 Accelerated carbonation test

The accelerated carbonation test was conducted according to JIS A 1153. The carbonation depth was measured

Table 4 Binding materials properties.

Classification	Kind	Mark	Density [g/cm ³]	Specific surface area [cm ² /g]	Chemical composition [%]								Alkali content
					SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	CaSO ₄	Ig.loss	
Cement	Ordinary Portland Cement	OPC	3.16	3500	21.4	5.5	2.8	64.3	2.1	1.9	-	0.56	Total alkali amount
Admixture	Blast Furnace Slag	BFS	2.91	3930	34.0	14.4	0.83	43.3	6.5	-	-	0.1	0.25
													Basicity
													1.89

Table 5 Fine aggregate properties.

Surface dry density [g/cm ³]	Absolute dry density [g/cm ³]	Water absorption ratio [%]	Unit volumetric mass [kg/L]	Actual ratio [%]
2.67	2.63	1.57	1.75	66.5

Table 6 Properties of silicone oil (SO).

Density [g/cm ³]	Viscosity (25°C) [cSt]	Refractive index	Flash temperature [°C]
0.96	20	1.42	160

Table 7 Properties of air entraining agent (AE).

Density [g/cm ³]	Total alkali amount (%)	Chloride ion amount (%)
1.04~1.08	3.7	0.00

Table 8 Properties of shrinkage reduction agent (SR).

Density [g/cm ³]	Viscosity (mPa · s)	pH	Solubility
0.90~0.95	5~15	6.0~9.0	Dissolved in water

by spraying a phenolphthalein solution on the fracture surface after 13 weeks of exposure to accelerate carbonation conditions (temperature: 20 ± 2 °C; relative humidity (RH): $60 \pm 5\%$; CO₂ concentration $5 \pm 0.2\%$).

2.2.4 Mercury intrusion porosimetry test

The pore structure was determined by mercury intrusion porosimetry (MIP). Test samples were cured in water for 4 weeks at 20 °C. Next, they were cut into 5 mm cubes and immersed in ethanol for 1 week to stop the hydration of cementitious material. Finally, they were vacuum freeze-dried for 24 hours before conducting the MIP test. There are multiple drying methods for cement-based materials, but freeze-drying is additionally suitable for MIP (Galle 2001) because this method is a less damaging method for cement based materials, so freeze-drying was the selected approach.

2.2.5 CaCO₃ and Ca(OH)₂ contents

The CaCO₃ (CC) and Ca(OH)₂ (CH) content was investigated using thermogravimetry - differential thermal analysis (TG-DTA). Test samples were made from hardened cement paste powder with a W/B of 0.5, water cured at 20 °C for 1 week, then air cured at 20 °C 60% RH for 1 week. After curing, the non-carbonated samples were vacuum dried for 1 day, and the carbonated samples were put in a chamber at 20 ± 2 °C, $60 \pm 5\%$ RH, and a CO₂ concentration of $5 \pm 0.2\%$. CC content was determined by the mass reduction at 500-800 °C and

CH content was determined by the mass reduction at 400-500 °C.

2.2.6 Freeze and thaw test

The freeze and thaw test was carried out for 300 cycles under a freezing temperature of -18 °C and a melting temperature of 5 °C. The freezing time was 2.5 hours and the melting time was 1 hour and half. The size of test specimens were used 4 cm × 4 cm × 16 cm prisms which were cured in water at 20 °C for 4 weeks.

2.2.7 Bubble spacing factor

The bubble spacing factor was measured using a microscope equipped with a CCD camera and a magnification factor of 175, according to the linear traverse method. The sample was prepared by cutting a prism specimen of 4 cm × 4 cm × 16 cm with a concrete cutter, then sequentially grinding the cut surface with polishing sand # 80, # 320, and # 800. Traverse length was determined according to ASTM C 457.

2.2.8 Water absorption test

For the water absorption test, 4 cm × 4 cm × 16 cm prism specimens were used. Test samples were water cured for 4 weeks, then air cured in a constant temperature, constant humidity room at 20 °C and 60% RH for another 4 weeks. For the actual test, all but one surface was covered with butyl tape, and the specimen was submerged for 21 days.

2.2.9 Water vapor adsorption test

In the water vapor adsorption test, a 5 mm cubic sample (water cured for 4 weeks at 20 °C) was vacuum-dried for 3 days, then subject to changes in relative humidity from 5% to 95% at intervals of 5% using the Hydro-sorb1000 (Quantachrome Instruments). Kishimoto *et al.* (2010) stated that when using mortar samples, sample size should be larger than a 5 mm cube to get reproducible data. Furthermore, Maruyama *et al.* (2013) stated that the Brunauer-Emmett-Teller (BET) specific surface area changes according to the drying process of the sample. The test conditions described above were decided upon as a result of this finding. The change in mass at each level of relative humidity was measured until the pressure change fluctuation in the cell was ± 0.05 mmHg for 300 seconds.

Moreover, specific surface area was obtained from the water vapor adsorption test by excess surface work (ESW) theory (Matsushita *et al.* 2004; Aono *et al.* 2009; Adolphs *et al.* 1998; Adolphs 2007). In general, BET theory is often used for this objective. (Brunauer *et al.* 1938). Although BET theory is applicable between relative humidity values of 0.35-0.50, ESW theory is applicable for all ranges of relative humidity. Thus, ESW theory was chosen to determine the specific surface area.

2.2.10 Drying shrinkage test

The drying shrinkage test was carried out according to JIS A 1129-3. The specimen used was 4 cm $\times$ 4 cm $\times$ 16 cm prism, which was placed in a constant temperature and humidity chamber at 20 °C and 60% RH after 1 week of curing in water at 20 °C.

Fig. 1 Change in flow vs. SO addition ratio (Series 1).

Fig. 2 Change in air content vs. SO addition ratio (Series 1).

3. Results and discussion

3.1 Basic properties (Fresh properties, Compressive strength)

3.1.1 Fresh properties

Figures 1 and 2 show the relationship between SO addition ratio and flow or air content, respectively, for externally added SO (Series 1). The flow and air content were not significantly affected by SO.

Figures 3 and 4 show the relationship between SO addition ratio and flow or air content, respectively, for internally added SO (Series 2). As the SO addition ratio increases, the flow tends to decrease. It is thought that this is caused by the reduced quantity of mixing water due to the internal method of SO addition. Furthermore, the addition of SO tends to increase the air content. This is thought to be because the decrease in fluidity caused by addition of SO increases the entrapped air. However, when the SO addition ratio is about 5 to 7%, the air volume reaches a maximum, with no clear explanation.

3.1.2 Compressive strength

Figures 5 and 6 show the relationship between SO addition ratio and compressive strength in Series 1 and Series 2. In Series 1, SO is introduced via external addition, separately from the defined quantity of mixing water. When considering that the amount of SO is equivalent to the amount of mixing water, the W/B increases substantially as the SO addition ratio increases, so it can be expected that the compressive strength will decrease. However, a slight decrease in compressive strength was observed in N non-AE, and in the other cases almost no

Fig. 3 Change in flow vs. SO addition ratio (Series 2).

Fig. 4 Change in air content vs. SO addition ratio (Series 2).

change in compressive strength occurred with increasing SO addition ratio; thus, the influence of SO on the compressive strength is small. In Series 2 (Internal Addition of SO), considering the results of Series 1, compressive strength may increase because the actual W/B decreases; however, again almost no change is observed with SO addition ratio. This may be because of the increased air content. Generally, the compressive strength decreases as the air-void level increases (Chindaprasirt *et al.* 2008). Therefore, considering the air content, it can be concluded that the actual compressive strength increases as SO is added.

From these measurements of basic properties, it appears that SO does not greatly affect the basic properties of mortar when the External Addition method is used.

3.2 Carbonation

Figure 7 shows the relationship between SO addition ratio and carbonation rate coefficient in Series 1. For the N specimens, there was little change in the carbonation rate coefficient up to an SO addition ratio of 3% and a slight decrease at 5%. For the BB specimens, the carbonation rate coefficient decreased constantly up to an SO addition ratio of 2%, and dropped to nearly 0 at 3% and 5%. It was found that the carbonation rate coefficient of BB specimens was significantly lower than that of N specimens when the SO addition ratio is 3% or more, and the carbonation inhibiting effect of SO is higher in BB than in N.

Fig. 5 Change in compressive strength vs. SO addition ratio (Series 1).

Fig. 6 Change in compressive strength vs. SO addition ratio (Series 2).

Figure 8 shows the relationship between SO addition ratio and carbonation rate coefficient in Series 2. For the N specimens, the carbonation rate coefficient did not change significantly before the SO addition ratio reached 0.5%, and in the case of the BA specimens, it did not change before reaching an SO addition ratio of 1%. The difference in degree of carbonation was not confirmed, but in the other specimens the carbonation was suppressed as the SO addition ratio increases regardless of the BFS replacement ratio. In contrast to the N specimens, in the BFS cement, the carbonation rate coefficient for an SO addition ratio of 0% increases with increasing BFS replacement ratio, so the decline in the carbonation rate coefficient can be attributed to the SO. Furthermore, carbonation resistance of BA specimens improved more than that of N specimens when the SO addition ratio was 5%, and that of BA and BB specimens improved more than N specimens when the SO addition ratio was 7%.

Here, the degree of carbonation suppression is different between **Figs. 7** and **8** because the method of adding SO is different. In series 1, the method of SO addition is 'External Addition' that is the mass of SO is not included in the mixing water. On the other hand, in series 2, the method of SO addition is 'Internal Addition' that is the mass of adding SO is included in mixing water. So, when SO is added by 'Internal Addition', actual W/B decreases with increasing of SO addition ratio and degree of carbonation suppression is increase.

Fig. 7 Change in carbonation rate coefficient vs. SO addition ratio (Series 1).

Fig. 8 Change in carbonation rate coefficient vs. SO addition ratio (Series 2).

Table 9 Progress of carbonation (accelerated carbonation test 13 weeks).

Binder	SO-0%	SO-0.5%	SO-1%	SO-3%	SO-5%	SO-7%	SO-10%
N							
BA							
BB							
BC							

Table 9 shows the state of carbonation after an accelerated carbonation test period of 13 weeks. The difference in the progress of carbonation due to BFS replacement ratio and SO addition ratio is notable. Also, a blackish-brown discolored area appeared at the central area of the specimen with a high BFS replacement ratio and high SO addition rate. This discoloration is thought to be due to iron sulfide contained in BFS. In previous literature it has been said that this discoloration in BFS cement occurs because of the influence of moisture in the material, and it disappears when it is oxidized by air. (Sioulas *et al.* 2001) It seems that the reason the specimens with a high BFS replacement ratio and a high SO addition ratio have blackish-brown portions is the change in moisture content due to the addition of SO.

It is well known that pore structure affects the durability of concrete (John *et al.* 1990; Kamada *et al.* 1996; Gonen *et al.* 2007). As in the current study, a previous study (Saito *et al.* 2005) showing the carbonation inhibiting effect of SO stated that one of the causes of improving carbonation resistance is the reduction in the number of pores with a diameter greater than 10 nm due to SO addition. Therefore, we considered influence of pore structure on carbonation. **Figures 9 and 10** shows pore size distribution per SO addition ratio. There was no consistent tendency of pore size distribution due to SO addition. Then **Fig. 11** shows experimental results giving the relationship between the number of pores

with a diameter greater than 10 nm and the carbonation rate coefficient. Contrary to the previous study, this study saw no correlation between the two variables.

It is also conceivable that the change in moisture condition in the material due to the addition of SO influences the carbonation. The progression of carbonation is a reaction which greatly influences the moisture condition of a material (Ota *et al.* 2011), so it is thought that the water repellency effect of SO changes the moisture state inside the material, leading to suppressed carbonation. **Figure 12** shows the relationship between the water absorption rate and the carbonation rate coefficient. The carbonation rate coefficient decreases as the water absorption rate decreases due to the increase in the SO addition ratio. Specifically, when the water adsorption rate is under 1%, the carbonation resistance decreases remarkably. **Figure 13** shows the results of the water vapor adsorption test. The amount of water vapor adsorbed decreased with SO addition. Carbonation is a reaction that occurs in the adsorbed water within the material, and since the addition of SO reduced the amount of adsorbed water, it also suppressed carbonation. Furthermore, **Table 10** shows the ESW specific surface area from the water vapor adsorption test. ESW specific surface area decreases when SO is added. A smaller surface area for water adsorption means that there are fewer places for carbonation reactions to occur, which explains why SO prevents car-

bonation.

Figure 14 shows the thermal analysis results of TG-

DTA. The CC content was determined by the mass reduction at 500-800 °C, and the CH content was deter-

Fig. 9 Pore size distribution per SO addition ratio (OPC).

Fig. 10 Pore size distribution per SO addition ratio (BB).

Fig. 11 Relationship between pore area and carbonation rate coefficient.

Fig. 12 Relationship between water absorption rate and carbonation rate coefficient.

Table 10 ESW specific surface area from water vapor adsorption test.

Binder	ESW specific surface area [m ² /g]	
N	SO-0%	104.3
	SO-5%	98.1
	SO-10%	46.3
BB	SO-0%	118.0
	SO-5%	87.0
	SO-10%	49.8

mined by the mass reduction at 400-500 °C. **Figure 15** shows the calculated results of the quantitative determination of CC content. Although the CC content was increased due to accelerated carbonation, the results show that this increase was suppressed in samples with greater SO addition. **Figure 16** shows the calculated results of the quantitative determination of CH content. When the SO addition ratio is 0 wt%, the amount of CH decreases with carbonation regardless of the binder, but it decreases more in the N samples than in the BB samples. This is thought to be a result of the high CH content in the N samples. In the case of 5 wt% SO addition, the amount of CH decreases due to carbonation in the N samples, but there is almost no change in the BB samples. From this result, it follows that the production of CC in BB occurs not from CH, but from C-S-H. Ishida *et al.* (2009) stated that the carbonation of C-S-H was slower than that of CH, but in the case of BB samples, the carbonation of C-S-H may be faster than in the N samples. In the existing literature, cement pastes containing high amounts of BFS (BFS: OPC =3:1, or 9:1) tend to have carbonation rates of C-S-H that are higher

than those of CH (Borges *et al.* 2010). Furthermore, although it is stated that BFS cement consumes CH during hydration (Kwak *et al.* 2004; Harasawa *et al.* 2015) this occurrence may be prevented by adding SO. These results suggest that the addition of SO suppresses the formation of CC and consumption of CH by carbonation, and in the particular case for BB samples, consumption of CH by carbonation is nearly absent. This is also perhaps one of the reasons that, when adding SO, BB samples had higher carbonation resistances than N samples.

3.3 Drying shrinkage

Figures 17 and 18 show the level of drying shrinkage as the test progresses. For an SO addition ratio of 1 wt%, the shrinkage was equivalent to that for 0 wt% SO in the case of the N samples, while for the BB samples, the shrinkage was greater than for 0 wt% SO. However, regardless of the composition of the binder, adding 5 wt% SO showed a shrinkage reduction effect of the same degree as when 5 wt% SR was added. **Figures 19 and 20** show the change in mass over the course of the test. When SR was used, the mass loss was the largest, 5 wt% SO addition resulted in a smaller reduction, and 1 wt% SO addition or without additives had the smallest mass change rates. Generally, it is thought that when mass change is small, the change in length is also small, but the opposite trend was shown in these results. The shrinkage reduction mechanism by SR is generally attributed to a decrease in the surface tension of the pore solution. In future studies it will be beneficial to study the change of surface tension due to SO.

It is well known that the pore structure of a cement

Fig. 13 Results of water vapor adsorption tests.

affects its drying shrinkage characteristics. It is said that smaller pore diameter and larger capillary tension cause larger shrinkage (Kurihara *et al.* 2015). When pores with different diameters are continuous, capillary water moves to the smaller diameter side, due to the capillary phenomenon (Study group on anti-shrink design *et al.* 2004). However, because the pore walls are water repellent because of the addition of SO, there is a possibility that the movement of capillary water to the smaller diameter side will be inhibited. This occurrence suggests that when adding SO, the moisture shifts to the coarse diameter side, the capillary tension decreases, and drying shrinkage is reduced. However, verification of this theory is necessary in future studies.

Maruyama *et al.* (2009) proposed the hydration pres-

sure theory as a mechanism of drying shrinkage based on disjoining pressure theory proposed by Derjaguin (Derjaguin *et al.* 1976). According to the theory of hydration pressure, disjoining pressure due to hydration forces appearing on a surface with high hydrophilicity is a dominant factor in drying shrinkage, and it is said that when the surface of the material has high hydrophilicity, the amount of drying shrinkage increases (Maruyama *et al.* 2010). As shown in Fig. 13, adsorption decreases with SO addition, and the interior of the material becomes hydrophobic. Thus, based on the viewpoint of hydration pressure theory, it is conceivable that the hydrophobicity of the material due to the inclusion of SO is one of the reasons for the reduction in drying shrinkage. Furthermore, it was stated that, when using SR, the

Fig. 14 Results of TG-DTA.

Fig. 15 Results of calculation of CaCO_3 content.

Fig. 16 Results of calculation of Ca(OH)_2 content.

specific surface area from the water vapor adsorption test decreases (Maruyama *et al.* 2009). Table 10 shows the ESW specific surface area obtained from the water vapor adsorption test. When using SO, the specific surface area found during the water vapor adsorption test decreases, as it does with SR. Therefore, it can be said

that water repellency greatly alters the shrinkage reduction effect of SO.

3.4 Frost resistance

Figures 21 and 22 show the change in durability factor of cement depending on the SO addition ratio. Although

Fig. 17 Relationship between change in length and testing age (OPC).

Fig. 18 Relationship between change in length and testing age (BB).

Fig. 19 Relationship between change in mass and testing age (OPC).

Fig. 20 Relationship between change in mass and testing age (BB).

Fig. 21 Changes in durability factor vs. SO addition ratio (OPC).

Fig. 22 Changes in durability factor vs. SO addition ratio (BB).

improvement in the durability factor by air entrainment was observed, the durability factor tended to decrease as the SO addition ratio increased for both N and BB specimens. In addition, when the SO addition ratio was effective for suppressing carbonation (3 wt% or more), the durability factor dropped under any condition, requiring consideration of a new measure against frost damage, other than air entrainment. **Figure 23** shows the change in the bubble spacing factor at SO addition ratios of 0 wt% and 5 wt%, and **Fig. 24** shows the relationship between the bubble spacing factor and the durability factor. The addition of SO decreases the bubble spacing factor, and although the bubble spacing factor is under 250 μm , the durability factor is decreased. This is an unusual result as it is generally said that, when the bubble spacing factor is under 250 μm , frost resistance prevents a decrease in durability (Powers 1949). **Figures 25** and **26** show the quantity of bubbles and hardened air contents for SO addition ratios of 0 wt% and 5 wt%. **Figure 27** shows the bubble distribution on the observation surface by the linear traverse method. Many small bubbles are distributed due to the addition of SO, and such a change in the bubble distribution causes the bubble spacing coefficient to decrease. However, there

is a possibility that small bubbles observed in the sample with added SO are not air bubbles. Instead, SO may have separated from the mixing water and diffused in the form of oil droplets, which were then counted as bubbles during observation by the linear traverse method. Similar phenomena have been reported in the current literature where shrinkage reducing agents which is not adverse effect frost resistance have been used (Narumi *et al.* 2014).

In the current literature, the use of hydrophobic compounds in cement improves the frost resistance (Nishi *et al.* 2014; Narumi *et al.* 2012). However, in these studies, the amount of hydrophobic compound is less than the SO quantity studied in this paper. Here, frost resistance has been improved with a lower SO addition ratio, such as 0.1 wt% or 0.5 wt%. Narumi *et al.* stated that when using a higher quantity of SR which is not adverse effect frost resistance, frost resistance decreases markedly (Nishi *et al.* 2014).

Here, if SO exists in the form of oil droplets within the material, the cause of the low frost resistance due to the addition of SO can be considered as such: the movement of unfrozen water from the coarse diameter capillary is inhibited by SO oil droplets, preventing the

Fig. 23 Changes in bubble spacing factor by SO addition.

Fig. 24 Relationship between bubble spacing factor and durability factor.

Fig. 25 Changes in bubble quantity by SO addition.

Fig. 26 Changes in hardened air contents by SO addition.

Fig. 27 Observation surface of linear traverse method.

water pressure relaxation mechanism by air from working.

Moreover, it can be hypothesized that capillary water moves to larger diameter pores due to water repellency, and the frozen water volume increases. As previously mentioned in this paper, there is a possibility that capillary water moves to larger diameter pores because of SO. It is said that the capillary water freezing temperature decreases as the pore diameter becomes smaller (Katsura *et al.* 1996), so if capillary water moves to large diameter pores, the frozen water volume increases. This is perhaps the reason SO decreases the frost resistance of mortar.

Nonetheless, there are some reports of concretes with water repellency (not using silicone oil) having high resistance to freezing and thawing (Revilla *et al.* 2001; Nunes *et al.* 2016). In these studies, the drying process is included in the freeze and thaw test. In the case of SO, if the drying process is included in the freeze and thaw test, there may also be a possibility that the frost resistance increases.

Furthermore, in this experiment, the freeze and thaw test was conducted using 4 cm × 4 cm × 16 cm mortar samples. It is stated that specimen size affects the results of freeze and thaw tests and in the case of the current mortar samples, the durability factor could be 70% less than for a 10 cm × 10 cm × 20 cm concrete samples (Nakamura *et al.* 2013). Thus, sample size must be considered to evaluate freezing and thawing properties.

4. Conclusion

In this study, the influence of SO on carbonation, drying shrinkage, and frost resistance were investigated. A summary of the results obtained in this study is given below.

- 1) The influence of SO on the basic properties (flow, air, and compressive strength) varies depending on the method of SO addition. In the case of external addition, the influence on basic properties is small.
- 2) Carbonation is suppressed as SO addition ratio increases, regardless of BFS replacement ratio. Compared with N, the carbonation suppressing effect of

SO in portland blast furnace slag cement was larger in BA and BB. SO decreases the amount of adsorbed water, thereby preventing carbonation. Moreover, SO may prevent the consumption of CH by carbonation and hydration.

- 3) When the SO addition ratio is 5 wt%, the shrinkage reduction effect is to the same degree as for 5 wt% SR addition. Based on hydration pressure theory, the water repellency from SO and the decrease of specific surface area are reasons for why SO reduces drying shrinkage.
- 4) Both N and BB have significantly lower frost resistance as the SO addition ratio increases. At the SO addition ratio that is expected to have a carbonation inhibiting effect (over 3 wt%), the improvement of frost resistance by entrained air is not recognized and other measures must be considered for improving frost damage. SO exists in the form of oil droplets in cement hardened pastes and inhibit the relaxation of water pressure at freezing, which may be the reason SO decreases frost resistance.

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