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Sulfate Resistance of Cement Matrix Containing Limestone Powder

Han-Young Moon[1)*], Ho-Seop Jung[1)], Seung-Tae Lee[2)], and Jong-Pil Kim[1)]

[1)]*Dept. Civil Engineering, Hanyang University, Seoul, Korea*
[2)]*Dept. of Civil Engineering, University of Toronto, Canada*

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Abstract

In order to improve the performance of concrete, generally, modern cements often incorporate several mineral admixtures. In this study, the experimental included the flow value, air content of mortar containing limestone powder and length change and compressive strength of mortar specimen immersed in sulfate solutions. From the experimental results, the limestone powder cement matrices improved the physical properties and sulfate resistance of cement matrices at 10% replacement ratio of limestone powder. The 30% replacement ratio of limestone powder was significantly deteriorated in sodium sulfate solution. Irrespective of fineness levels of limestone powder, length change and SDF of mortar specimens with only 10% replacement was much superior to the other replacements.

Keywords : limestone powder, sulfate attack, length change, strength deterioration factor(SDF)

1. Introduction

To improve the properties of cement concrete of aggressive environment, many researchers studied blended cement. In order to improve the performance of concrete, generally, modern cements often incorporate several mineral admixtures. On the other hand, limestone is important material for cement manufacture. The addition of limestone to Portland cement may significantly improve several cement properties such as compressive strength, water demand, workability, durability and several effects on the mechanism and kinetics of cement hydration. Nehdi et al.[11] investigated the effect of limestone microfiller replacement of cement on the mechanical performance and cost effectiveness of low water-binder ratio superplasticizer Portland cement mortars.

Sulfate deterioration of concrete is commonly observed in structures exposed to soil or groundwater containing a high concentration of sulfate ions. During the previous few decades, it has been reported that the proper initial curing of blended cement concrete, mixtures with low water-cementitious ratio, and using Type V cement with low C_3A content were recommended as the methods to resist sulfate attack. However, significant changes in cement chemistry have resulted in cement with a low silicate ratio (C_3S/C_2S) for sulfate environments.[9] This is because higher silicate ratio cement results in increased calcium hydroxide content in the hardened cement matrix, thereby enhancing the susceptibility of such cements to the softening type of sulfate attack.[10,12]

The objectives of this study were to monitor the physical deterioration of mortar specimen with different fineness levels and replacement ratio of limestone powder, and to analyze the possible products formed by sulfate attack.

2. Experimental details

2.1 Materials and specimen preparation

2.1.1 Cement

In this study, KS L 5201 Type I cement was used for all mixtures. The cement, ordinary portland cement (hereinafter OPC), was provided by S-company Cement Ltd. The blaine fineness of this cement was 328m^2/kg. This cement had 42.8% C_3S content and 9.7% C_3A content, respectively. The physical properties and chemical composition of the cement are given in Table 1.

* *Corresponding author*
Tel.: +82-2-2290-0323 Fax : +82-2-2293-9977
E-mail address: moon77@hanyang.ac.kr

Table 1 Physical properties and chemical composition of OPC

Physical properties	
Specific gravity	3.15
Specific surface area (m^2/kg)	328
Setting time (hr. : min.)	
Initial	3 : 41
Final	6 : 01
Compressive strength (MPa)	
3 days	22.6
7 days	31.6
28 days	38.7
Chemical composition (%)	
Silicon dioxide	21.7
Aluminum dioxide	5.7
Ferric oxide	3.2
Calcium oxide	63.1
Magnesium oxide	2.8
Sulfur trioxide	2.2
Loss on ignition	1.3

Table 2 Properties of fine aggregate

Specific gravity	Absorption, %	Fineness modulus
2.60	0.8	2.80

Table 3 Physical properties of superplasticizer

Main component	Polycarbonic acid based compound
Appearance	Dark brown liquid
Solid content	20%
Specific gravity	1.04 ± 0.02
pH	2.5 ± 1.0

2.1.2 Aggregate

The fine aggregate, river sand, which is a fine aggregate immune to most chemical agent and has little organic compounds, is employed for manufacturing cement matrix specimens. The fine aggregate was entirely passed from the sieve of 5 mm. The properties of fine aggregate are listed in Table 2.

2.1.3 Admixtures

(1) Superplasticizer: In order to obtain a suitable workability, superplasticizer (hereinfafter SP) selected from several available products after an evaluation of their workability, is a polycarbonic acid based chemical admixture. Table 3 showed that physical properties of superplasticizer used in this study. It was added to the mixing water as 1.8% of weight of cementitious materials.

(2) Limestone powder: The limestone powders were provided by W-Chemical Ltd. In this work, two kinds of limestone powders were used; their mean diameters are 3.11㎛ (hereinafter LSA) and 18.62㎛ (hereinafter LSB), respectively. There are physical properties and chemical composition of limestone powders given in Table 4. Also, particle size distribution of limestone powder LSA and LSB present in Fig. 1.

Table 4 Physical properties and chemical composition of limestone powder

Items	LSA	LSB
Mean particle size (㎛)	3.11	18.62
Moisture (%)	0.5	0.03
Whiteness (%)	96.5	91.9
Specific gravity	2.71	2.71
Specific surface area (m^2/kg)	2,650	1,010
Silicon dioxide (%)	0.51	0.93
Aluminum dioxide (%)	0.22	0.28
Ferric oxide (%)	0.09	0.15
Calcium oxide (%)	54.4	53.1
Magnesium oxide (%)	0.62	0.88
Loss on ignition (%)	43.44	43.35

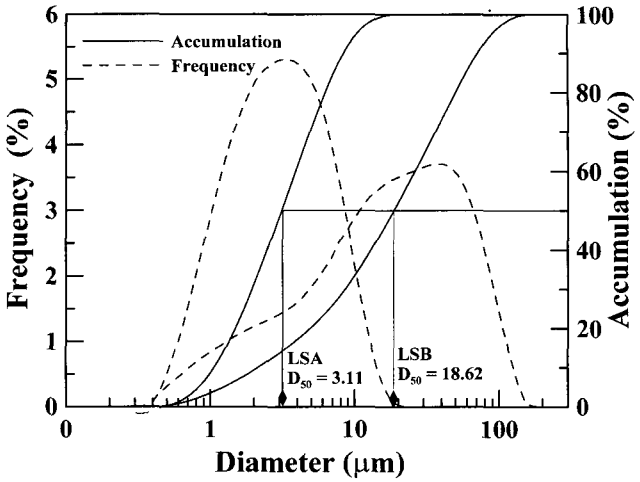

Fig.1 Particle size distribution of LSA and LSB

2.1.4 Test solutions

The exposure solution used to provide sulfate attack to the specimens was by dissolving reagent grade chemical in water. According to ASTM C 1012, the concentration of sulfate solution for immersion test is 33,800 ppm of SO_4^{2-} ions. Thus, the chemical used to conform this concentration was the 5% sodium sulfate solution (hereinafter NS solution) and the 4.24% magnesium sulfate solution (hereinafter MS solution). All specimens were initially cured in water for 7 days and then immersed in test solutions for periods of exposure. Water and solutions temperature were kept 20±1□ during the test period. Before immersion, mortar specimens were tested to determine the initial compressive strength and length change. These solutions were renewed every 4 weeks.

2.2 Methodologies

All of the specimens were manufactured by mortar mix of 5 liter capacity accordance with KS L 5105. Air content

of mortar was measured in accordance with KS L 3136. The procedure of this method is as follow; mortar mixing, weight of mortar is measured, and then, air content was calculated with the weight of cement, sand, water, limestone powder from the mixture proportion of mortar.

The length change was conducted on accordance with ASTM C 1012 at each immersion period. All length change values were compared with the initial length of prism mortar after 7 days of curing in tap water. The deterioration of cube mortar specimens is also investigated by measuring the strength deterioration factor (hereinafter referred to as SDF), which is given by following Eq. (1).

$$SDF = \frac{S_t - S_s}{S_t} \times 100(\%) \quad (1)$$

where, St = the average compressive strength of mortar cured in tap water, Ss = the average compressive strength of mortar immersed in test solutions

The compressive strength measurements were conducted on 50mm cube mortar specimens. All specimens, those mortar specimens were de-molded after 1 day of mixing and cured in tap water at room temperature for an additional 6 days. Then, some of the specimens were moved to test solutions and were continuously immersed during predetermined periods. The compressive strength tests were performed on each mixture at 0, 28, 56, 91, 180, and 270 days of immersion. At each interval, the compressive strengths of mortar specimens drawn from tap water and test solutions were measured and then their values were averaged. The X-Ray diffraction (XRD) is conducted using the RINT D/max 2500 X-ray diffractometer. The source of radiation is CuKα with a wavelength of 1.54□ at a voltage of 30 kV. The 2 theta angle range covered for each paste specimen is from 5° to 40°. The scanning speed is 2min. In order to determine the solid phases in the paste specimens qualitatively, X-ray diffraction analysis technique is used.

2.3 Mixture proportion

The paste samples were made using 100g of total binder and 45g of diluted water. Water-binder ratio of paste specimens was fixed at 0.45.

All pastes were cast into 10×10×285mm prism mold for microstructural analysis. Mixture proportions of cement mortar containing limestone powders are water binder ratio of 0.45. The limestone powders can be classified into two types: LSA and LSB (Table 5).

Table 5 Mixture proportions of cement mortar

Symbol	Replacement ratio (%)	W (g)	C (g)	S (g)	Limestone powder(g)
Control	0	405	900	1,800	0
LSA10	10	405	810	1,800	90
LSA20	20	405	720	1,800	180
LSA30	30	405	630	1,800	270
LSB10	10	405	810	1,800	90
LSB20	20	405	720	1,800	180
LSB30	30	405	630	1,800	270

3. Results and discussion

3.1 Physical properties

Fig. 2 and 3 show the flow value and air content of cement mortar containing limestone powders, respectively. The thick solid line indicates the results of control mortar in Fig. 2. In all mortar mixtures, the flow values are higher than that of control mortar. The air contents, however, are lower than that of control mortar. The flow value of LSA and LSB mortars with 30% replacement ratio show the 157.6% and 137.6%, respectively.

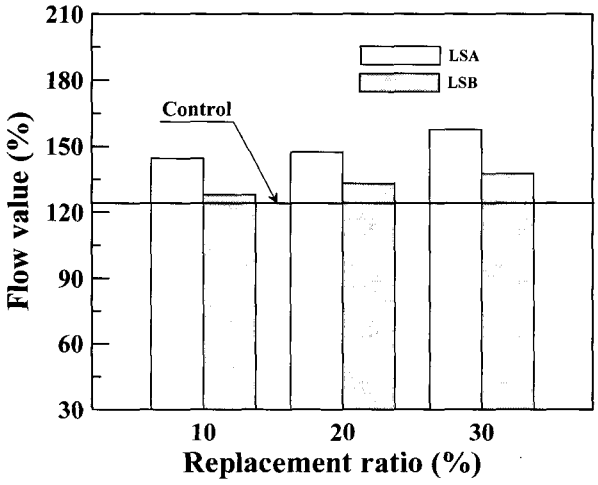

Fig. 2 Flow value of mortar according to replacement ratio

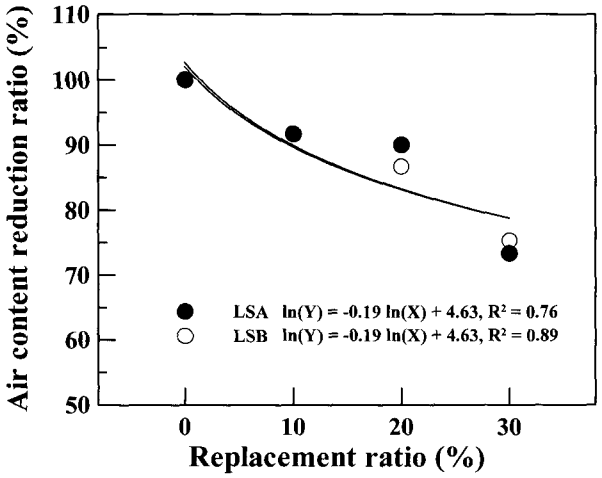

Fig. 3 Air content reduction ratio of mortar according to replacement ratio

Therefore, the rate of increase of LSA and LSB mortars were exhibited 25.3% and 9.4% of the control mortar, respectively. The relationship between replacement ratio and flow value is a proportional relation.

For evaluating to the fineness levels and replacement ratio, the flow value appeared greatly as the large fineness and replacement ratio. Moreover, the air content of all mortars decreased with increase the replacement ratio irrespective of fineness levels by micro-filler effect of limestone powders. At 30% replacement ratio, air content of LSA and LSB mortars decrease of 73.3% and 75.3% compared with control mortar, respectively. Because of their extremely small particle size, the limestone powder occupy the voids between the cement grains, acting as a filler, reducing the porosity of the bulk cement matrix and resulting in a densified structure. This trend is similar to a work carried out by Cho et al.[4)]

The compressive strength of mortar containing limestone powder with different fineness levels was measured. Table 6 indicates the compressive strength ratio of mortar specimen with limestone powder. From this table, it can be found that as the replacement ratio of limestone increases, the compressive strength decreases. This is why that the cement content in mortar decreased with replacement of limestone powder, as mentioned previously.

In addition, regarding compressive strength after 28 days, several factors, such as the influence of limestone powder on the alite and aluminate hydration rate and the change of pore solution, are probably involved, but a discussion of this is beyond the scope of this study.

3.2 Sodium sulfate attack

3.2.1 Strength deterioration factor

The strength deterioration factor values of mortar specimens with different fineness levels of limestone powders exposed to NS solution were presented in Figures 4 and 5, respectively. The SDF values were calculated at the 28, 56, 91, 180 and 270 days of exposure. Fig. 4 shows the SDF values of mortar specimens with different replacement ratios of LSA immersed in NS solution for 270 days. All mortar specimens showed negative values of SDF at 28 days of exposure. These negative values of SDF signify an increase in compressive strength, which is attributable to the filling up of the pores by reaction products, densifying the mortar matrix in early period of exposure.[1,3,7)]

Table 6 Compressive strength ratio of cement mortar

Symbols	3 days	7 days	28 days
Control	100	100	100
LSA10	92.9	91.5	94.3
LSA20	77.5	77.5	82.9
LSA30	67.2	62.5	66.0
LSB10	88.1	91.4	99.6
LSB20	73.7	80.4	82.7
LSB30	54.9	66.0	70.1

After 56 days of exposure, the SDF of control, LSA20 and LSA30 mortar specimens increased with immersion period. However, for LSA10 mortar specimen, the SDF was somewhat stable with increase of immersion period. After 270 days of exposure, the SDF values, indicating about 26% to 29%, of control, LSA20 and LSA30 mortar specimens were similar, whereas LSA10 mortar specimen showed about 12.6% in SDF value at the same immersion period.

The SDF in LSB mortar specimens with different replacement ratios was shown in Fig. 5. The variation of SDF values related to LSB mortar specimens with different replacement ratios was presented in Fig. 5. The LSB10, LSB20 and LSB30 mortar specimens placed in NS solution for 270 days recorded about 13.9%, 22.8% and 23.0% in SDF values, respectively.

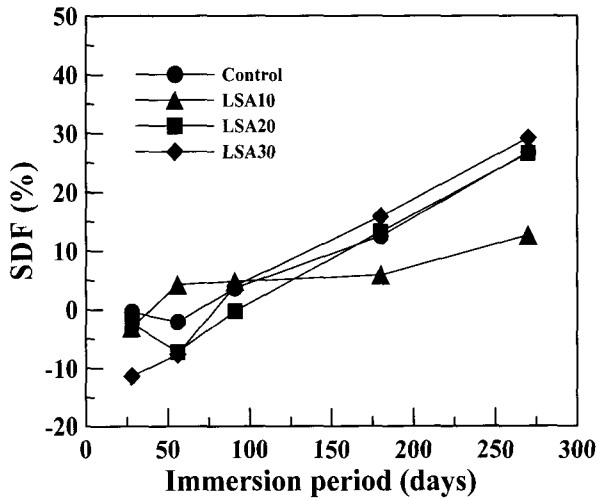

Fig. 4 SDF of LSA mortar (NS solution)

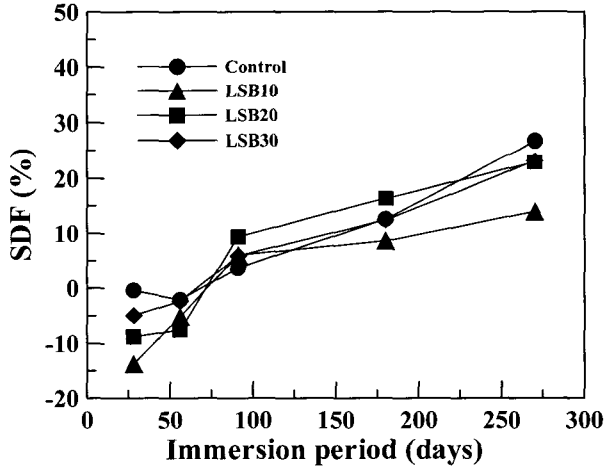

Fig. 5 SDF of LSB mortar (NS solution)

From the results of this test, it was revealed that mortar specimen with replacement ratio of 10% by cement mass, irrespective of fineness levels of limestone powder, showed a good sulfate resistance with respect to strength reduction.

3.2.2 Length change

Length change of mortar specimens tested in present study was measured on the basis of ASTM C 1012. Length change of LSA mortar specimens with different replacement ratio levels immersed in NS solution is presented in Fig. 6. It was clearly evident that mortar specimens replaced with 20 and 30% of LSA showed a significant expansion in the solution. On the other hand, the mortar specimen with 10% of LSA showed a better sulfate resistance against expansion. The length change value of LSA10 mortar specimen was 0.118% after 270 days of sulfate exposure, whereas length change values of LSA20 and LSA30 mortar specimens were 0.595% and 0.692% at the same exposure period.

The tendency of length change of LSB mortar specimens is shown in Fig. 7. A remarkable observation of length change was the relatively excessive expansion of LSB mortar specimen with 30% replacement. Furthermore, comparing to that of control mortar specimen, a better sulfate resistance of LSB mortar specimen with 20% replacement was also investigated. After 270 days of exposure, the length change values were about 0.192%, 0.049%, 0.097% and 0.498% for mixtures with 0, 10, 20 and 30% replacement with LSB. Therefore, it is concluded that approximately 10% replacement for LSA mortar specimen was more effective on sulfate resistance, whereas up to 20% replacement for LSB mortar specimen.

This conclusion suggests that the thaumasite formation formed in mortar specimens incorporating limestone powder affects more reduction in compressive strength, compared to length change. This is why the lack of cohesiveness and the mushy effect of thaumasite formed in mortar specimen system. In other words, as more cement is replace by limestone powder, the increased amount of thaumasite led to the more pronounced degradation of mortar specimens.

3.2.3 XRD analysis

Deteriorated parts of paste specimens containing limestone powders were examined by XRD after 270 days of exposure. The x-ray curves of the LSA paste specimens exposed to NS solution are presented in Fig. 8. The XRD of control paste specimen is also compared to investigate the influence of limestone powder on the products formed by sulfate attack. For XRD trace of control paste specimen, the presence of thaumasite and ettringite was obvious at around

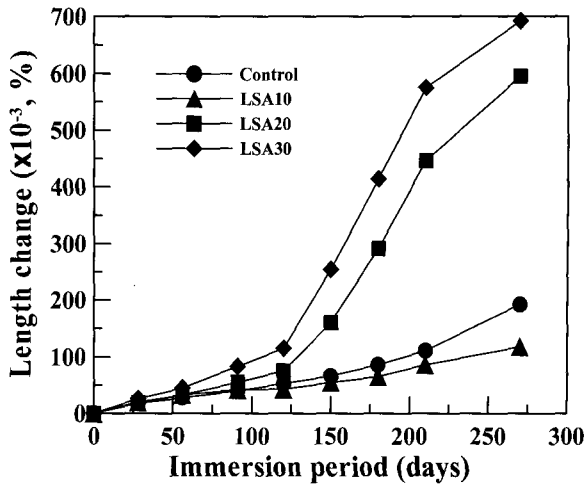

Fig. 6 Length change of LSA mortar (NS solution)

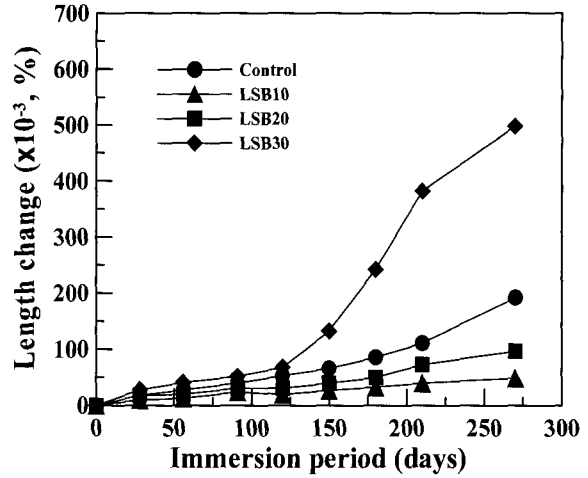

Fig. 7 Length change of LSB mortar (NS solution)

9.1° 2θ. Furthermore, the two major peaks are also present in both minerals at 16.0°and 32.3°2θ. Actually, it is difficult to distinguish thaumasite formation from ettringite formation, when only small amount are present in cement matrix system, because of their structural similarities.

In Fig. 8, it was clear that the intensity peaks for calcite were increased with increase of LSA replacement. On the contrary, intensity peaks for portlandite showed a reverse tendency with increase of LSA replacement. From the XRD result, it was found that the main factor causing deterioration of cement matrix with LSA was the thaumasite formation. Another important observation in these XRD traces was the absence of gypsum formation. The XRD trace corresponding to control paste specimen did not show a symptom of the product even at 11.7°2θ, which is the main peak intensity. Fig. 9 shows XRD curves of powders obtained from LSB paste specimens exposed to NS solution for 270 days. The XRD analysis results related to LSB paste specimens were very similar those of LSA paste specimens, as shown in Fig. 8.

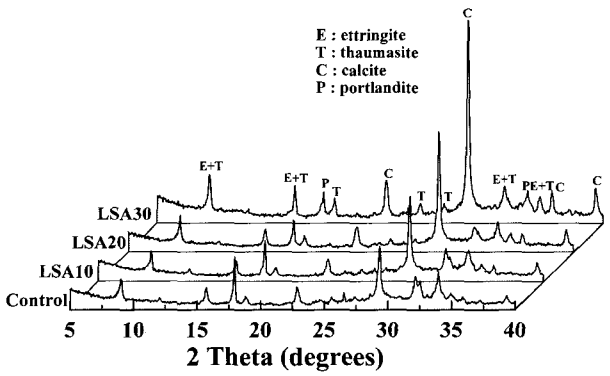

Fig. 8 XRD patterns of LSA paste immersed in NS solution for 270 days

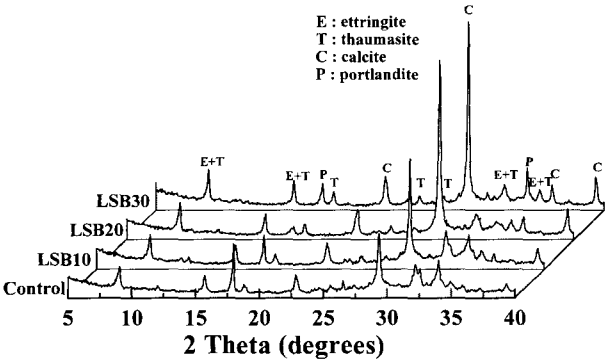

Fig. 9 XRD patterns of LSB paste immersed in NS solution for 270 days

3.3 Magnesium sulfate attack

3.3.1 Strength deterioration factor

The data on SDF in LSA mortar specimens immersed in MS solution for 270 days were plotted in Fig. 10. For LSA10 mortar specimen, the stable trend was observed during test period, whereas LAS20 and LSA30 mortar specimens showed relatively sharp increase. After 270 days of exposure, the SDF values were about 14.4%, 29.0% and 37.7% for LSA10, LSA20 and LSA30 mortar specimens, respectively. In this figure, there was no negative value in SDF even at early immersion period. Fig. 11 present the data on SDF of LSB mortar specimens immersed in MS solution for 270 days. The poor resistance of LSB30 mortar specimen was displayed after 56 days of exposure. Similarly, a stable increase in SDF was observed in LSB10 mortar specimen. The LSB20 mortar specimen had a similar trend with control mortar specimen in strength reduction after 91 days.

In magnesium sulfate environment, it is widely accepted that magnesium sulfate attack is primarily determined by the diffusion characteristics of both hydroxide and sulfate ions. Hydroxide ions diffuse from the paste outward to form brucite, and sulfate ions diffuse inward to produce

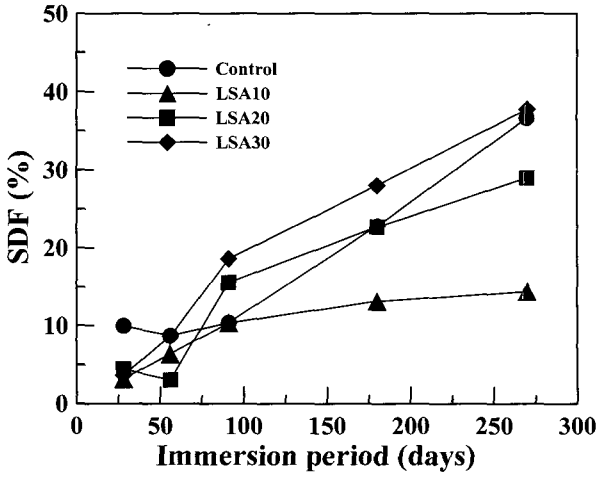

Fig. 10 SDF of LSA mortar (MS solution)

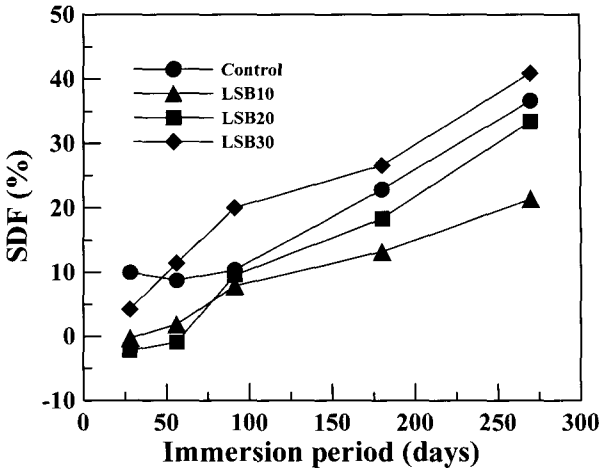

Fig. 11 SDF of LSB mortar (MS solution)

gypsum. The combined surface double-layer (brucite and gypsum) in early age protects the hardened cement matrix from magnesium sulfate attack. However, in later age, once this protective surface skin peels off, C-S-H and calcium hydroxide in paste are attacked by aggressive ions, and therefore the deterioration accelerates with age.[2] The previous discussion[13] suggested that brucite would retard the deleterious effect of magnesium sulfate attack at the early age of deterioration, however, at later age, sulfate solution could diffuse more easily into the hardened cement matrix due to the decomposition of C-S-H to M-S-H. This alteration is probably the major process of magnesium sulfate attack as stated by Cohen and Mather.[5] Magnesium sulfate attack on cement matrix with limestone powder has been reported by Hartshorn et al.[6]

3.3.2 Length change

Fig. 12 shows that the length change value of LSA mortar specimen with 10% replacement was very similar to that of control mortar specimen stored in MS solution up to 270 days. As expected, the length change values of LSA mortar

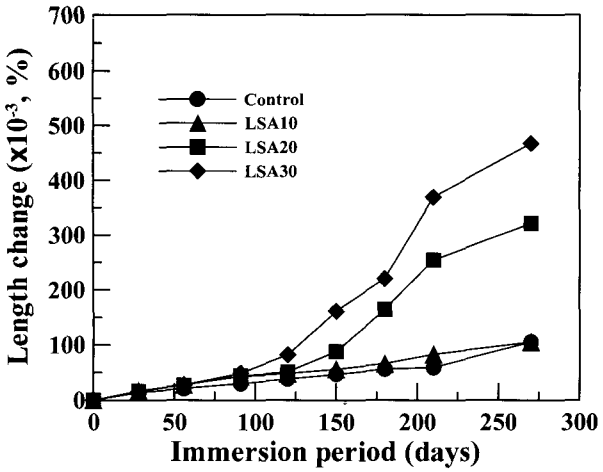

Fig. 12 Length change of LSA mortar (MS solution)

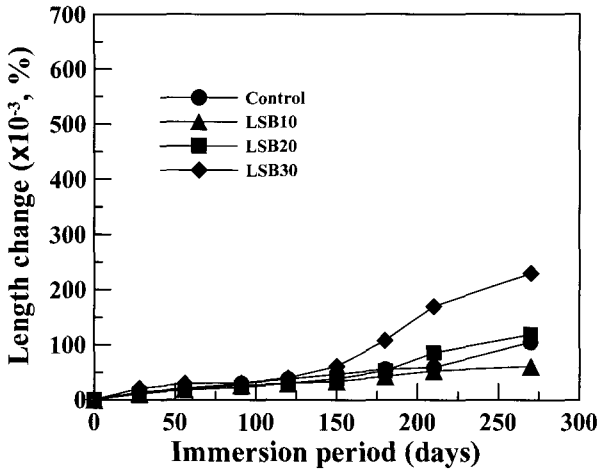

Fig. 13 Length change of LSB mortar (MS solution)

specimens were greatly increased with increase of replacement ratio. However, the length change was observed to be lower in LSA mortar specimens placed in MS environment compared to those placed in NS environment, except mortar specimen with 10% replacement. After 120 days of exposure, the drastic increase of length change of LSA mortar specimens with 20% and 30% replacement was observed.

Fig. 13 presents the data on length change of LSB mortar specimens with different replacement ratios under MS solution for 270 days. All mortar mixtures except LSB30 mortar specimen had similar values in length change during test period. Furthermore, mortar specimen with even 30% replacement of LSB recorded about 0.23% in length change at 270 days of exposure.

3.3.3 XRD analysis

Fig. 14 presents the XRD traces for the sample of control and LSA pastes exposed to MS solution. Unlike XRD patterns of control and LSA paste exposed to NS solution, maximum intensity peak for gypsum at 11.7°2θ was obviously observed. These XRD analyses suggest that the main

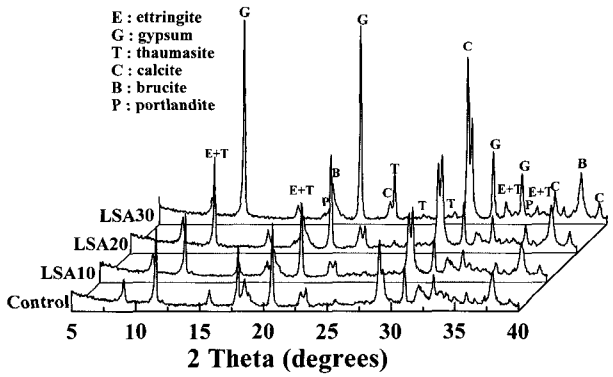

Fig. 14 XRD patterns of LSA paste immersed in MS solution for 270 days

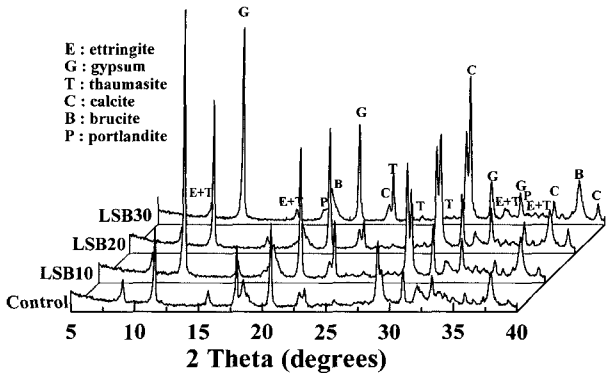

Fig. 15 XRD patterns of LSB paste immersed in MS solution for 270 days

deterioration caused under MS solution is the formation of gypsum. Also, the existence of brucite peaks in the samples supports the possibility that magnesium ions react with calcium hydroxide at surface part of the samples.

The intensity peak for gypsum was increased with increase of replacement ratio of LSA. For XRD trace of control paste sample, it was observed that the intensity peaks for portlandite were present at 18.1 and 34.1°2θ. However, for XRD traces of LSA10 and LSA20 paste samples, there were no evidence on the presence of portlandite. Fig. 15 shows the XRD traces of LSB paste samples exposed to MS solution for 270 days of immersion, respectively. The deterioration mode of LSB paste sample was also the formation of gypsum. Moreover, no portlandite peaks were observed in the samples with LSB.

4. Conclusions

It has been generally reported that the engineering properties and durability of cement matrix incorporating limestone, as either filler or aggregate, show different behaviors depending on the sources and particle shapes of it. Thus, it should be noted that the results of this study is only associated with materials produced from a local supplier.

Based on the results performed in this study, the following conclusions can be drawn.

(1) The workability of cement mortar containing limestone powder is higher than that of control mortar, and air content is lower than that of control mortar. The compressive strength of cement mortar with limestone powder uniformly decreased with increase replacement ratio regardless of the fineness levels.

(2) In sodium sulfate solution, cement mortar with 10% replacement of limestone powder showed a good sulfate resistance indicating small ratio of SDF and length change irrespective of fineness levels of limestone powder. The main factor causing deterioration of cement matrix with limestone powder was the thaumasite formation.

(3) In magnesium sulfate solution, irrespective of fineness levels of limestone powder, length change in mortar specimens with only 10% replacement was much lower than that in mortar specimens with 20% or more replacement. It was found through XRD analyses that the main deterioration caused by magnesium sulfate attack was the formation of gypsum.

As stated above, although limestone powders led to the less development of compressive strength compared with control, a good resistance to sulfate attack at 10% replacement level was exhibited.

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