

The Effect of Limestone Powder Addition on the Optimum Sulfate Levels of Cements Having Various Al_2O_3 Contents

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1. Introduction

The main objective of the addition of calcium sulfate (SO_3) in the grinding process of cement clinker is the control of rapid hydration of C_3A . In addition, the quantity of SO_3 affects the other properties of cement such as strength development and length change, etc. Therefore, the optimum SO_3 content is considered to be the quantity that allows the maximum compressive strength and the minimum length change [1]. Many researchers including Lerch [2] have reported the relationships between the optimum SO_3 content and the characteristics of cement such as a chemical composition and fineness. Almost of all researchers agree that the optimum SO_3 content tends to increase with an increase in Al_2O_3 and alkali contents and fineness of cement. As a result, the SO_3 limitation of ordinary Portland cement, OPC in ASTM is up to 3.5 mass% depending on the C_3A content.

The recent Japanese cement industry is expected to be the key industry to organize a resource recycling society because it utilizes about 2800 million tons of waste materials and by-products every year. Generally these waste materials and by-products contain more Al_2O_3 than OPC [3]. If it is possible to increase the Al_2O_3 content, the cement industry can contribute environments more. The change of Al_2O_3 content surely affects the optimum SO_3 content. Also, not every but many cement standards allow some types of additives including limestone powder, LSP, below 5.0 mass% in OPC. Hawkins *et al.* reviewed technical information on the use of LSP in Portland cement for the permission of LSP addition in ASTM C 150 [4]. It is well known that in hydrated cement, with C_3A , LSP produces calcium aluminate carbonate hydrates [5]. The reaction ratio of their process is greatly affected by SO_3 content [6]. Bobrowski *et al.* [7] reported that LSP could replace some of the calcium sulfate. Therefore, the optimum SO_3 content can also vary with LSP content.

It seems to be difficult to apply previous studies directly to the recent cement because the chemical compositions or the finenesses of cements have been changed and there are few studies discussing the effect of LSP. Also, the influence of SO_3 and LSP on hydration process of cement has not been fully analyzed quantitatively. Therefore, it is meaningful to investigate the effect of LSP addition on the optimum SO_3 content and hydration of present cement with various Al_2O_3 contents.

In this study, the relationships between SO₃ content and properties such as setting time, expansion in water, compressive strength, and drying shrinkage of recent Japanese commercial cement were examined. The effects of LSP addition on these properties were also examined. In order to investigate the affecting mechanism of SO₃ content and LSP addition on the properties, the hydration was characterized by porosimetry and XRD/Rietveld method.

2. Experimental Conditions

2.1 Materials used

The characteristics of materials used are shown in Table 1. Three types of cement used had different Al₂O₃ contents from 3.5 to 7.2 mass%. The fundamental point of the effect of Al₂O₃ is the contribution for the hydration. Al₂O₃ mainly exists as C₃A and C₄AF but the reactivity of C₃A is expected higher than that of C₄AF. Therefore, the amount of C₃A and C₄AF may be more important than the amount of Al₂O₃. Mineral compositions by Bogue calculation and by XRD/Rietveld analysis were also shown in Table 1. There are significant differences in mineral compositions. C₃A content varies from 1.6 to 9.6 mass%. Cement 3 is the most rich in Al₂O₃ but is not in C₃A because the amount of C₄AF is relatively high.

SO₃ content in cement was adjusted from 2.0 to 6.0 mass% by reagent grade calcium sulfate hemi-hydrate with 758 m²/g of Blaine specific surface area. When the SO₃ contents to show the maximum compressive strength was investigated, the SO₃ content was modified by every 0.2 mass% around the optimum. The LSP content of cement was adjusted at 0 and 4 mass% by replacing a part of OPC.

2.2 Experimental methods

(1) Setting time and compressive strength

Setting time and compressive strength were evaluated according to JIS R5201. The setting time was measured using cement paste with standard consistence. The compressive strength was measured by rectangular mortar bars having 4*4*16 cm dimension, 3.0 of sand/ cement ratio, 0.50 of water/ cement ratio. No chemical admixture was added. Specimens were cured in water at 20°C. The experimental error of setting time is ±14 min for initial setting and ±18 min for final setting. The experimental errors of compressive strength at 3, 7 and 28 days are ±1.0, ±1.4 and ±1.6 MPa,

Table 1 Characteristics of cement used

L.O.I.	BL*	Mineral composition (mass%)										Chemical composition						Setting time**			
		Bogue					XRD/Rietveld					SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Initial	Final
		m ² /kg	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	mass%						hr:min				
Cement1	0.70	333	48.6	29.5	2.5	12.0	51.2	32.1	1.6	13.0	23.1	3.5	4.0	63.6	1.6	2.1	0.1	0.4	3:15	4:45	
Cement2	0.85	287	56.5	19.3	8.8	9.3	62.3	17.2	9.3	9.6	21.6	5.3	3.1	65.2	0.9	1.8	0.2	0.3	3:20	5:00	
Cement3	0.55	301	59.0	8.9	12.1	12.8	56.6	15.0	8.8	17.6	18.6	7.2	4.2	63.4	1.9	1.1	0.4	0.0	3:55	7:30	
Limestone	43.57	1000	-	-	-	-	-	-	-	-	0.0	0.0	0.0	51.4	1.6	0.0	0.0	0.0	-	-	

*BL: Blaine specific surface area **Setting time: SO₃ = 2.0mass%

respectively.

(2) Expansion in water and drying shrinkage

Mortar specimens of 4*4*16 cm dimension were prepared according to JIS R5201. Opal glasses were mounted on the both edges of specimens. The length of mortar cured at 20 °C for 7 days measured by a comparator was defined as the initial length of the mortar. After that, mortar specimens that were cured in water were applied for the measurement of the expansion in water at the ages of 14, 35 and 98 days. Mortar specimens at the same ages and were cured at 20 °C under relative humidity of 60% were used for the measurement of drying shrinkage. The experimental errors of expansion in water at 7 days, 28 days and 91 days are ± 0.0008 , ± 0.0009 and ± 0.0012 %, respectively. Those of drying shrinkage at 7 days, 28 days and 91 days are ± 0.0014 , ± 0.0024 and ± 0.0008 %, respectively.

(3) XRD/Rietveld analysis

Sealed cylindrical specimens of cement pastes of $\phi 5 \times H 4$ cm dimension having 0.50 of W/C were cured at 20 °C until a given age and then immersed into acetone to stop the hydration. After that, pastes dried at relative humidity of 11% for 7 days were subjected for analysis. As an internal standard, 10 mass% of α -alumina was added and ground with cement paste. The measurement condition by XRD was 50 kV and 350 mA using Cu-K α radiation, the scan range of $2\theta = 5 - 65^\circ$, the step width of 0.0234° , and the scan speed of 0.13 s/step. The Rietveld analysis was performed using TOPAS (BrukerAXS) software. The Rietveld analysis was carried out by following a previous study [8]. In this study, the amount of amorphous phase quantified by Rietveld analysis was defined as an amount of calcium silicate hydrate (C-S-H). The maximum difference from the true value of the quantified amount of C₂S was 2.2 mass% and that of C₃S, C₃A and C₄AF was 1.2 mass%. That of ettringite, monosulfate hydrate, monocarbonate hydrate and hemicarbonate hydrate was 1.0, 1.2, 0.6 and 1.0 mass%, respectively. The accuracy of quantification of the amorphous phase was ± 2 mass% [8].

(4) Porosity

The cement paste used for the measurement of porosity was prepared as the same manner with XRD measurement. The paste was immersed into acetone to stop the hydration at a given age and applied for the measurement after D-drying for 7 days. The pores of diameter from 3.0×10^{-3} to 3.8×10^2 μm of cement pastes were quantified by mercury intrusion porosimetry, MIP.

3. Result and discussions

3.1 Relationship between SO₃ content and properties of cement

(1) Setting time and the minimum SO₃ content

When the SO_3 content of cement is not high enough, the cement shows a flash setting. Therefore, the minimum SO_3 content is the SO_3 content required to control the setting time within an adequate time range (initial ≥ 60 min, final ≤ 10 hr by JIS). Usually this value is smaller than the optimum SO_3 content for other properties. The setting time of cements with 2.0 mass% of SO_3 used in this study satisfies the JIS. Therefore, the minimum SO_3 content of these cements is less than 2.0 mass%. The effect of SO_3 content on the setting time of cement 2 with and without LSP is shown in Fig. 1. The setting time was delayed with the increase of SO_3 content higher than 4.0 mass%. This is thought to be caused by the increase of the water requirement for standard consistence of the paste prepared with high SO_3 cement as shown in Table 2 because of the high content of calcium sulfate hemi-hydrate. The cement containing LSP also shows a similar trend to the results of the cement without LSP except 6.0 mass% of SO_3 . It is thought that the final setting time of cement without LSP was longer than that with LSP due to the higher W/C ratio.

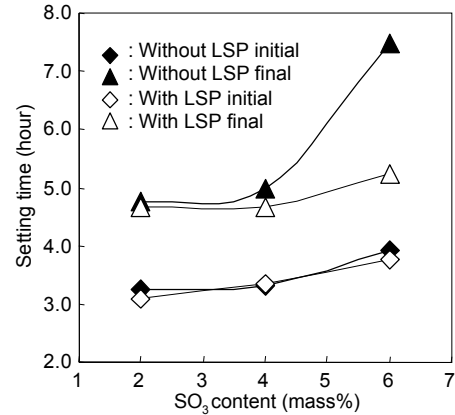


Fig. 1 SO_3 content and setting time of cement 2

Table 2 W/C of cement paste

Cement	SO_3 content (mass%)	W/C
Cement 2	2.0	28
	4.0	29
	6.0	35
Cement 2 with LSP	2.0	28
	4.0	29
	6.0	33

(2) Expansion in water and the maximum SO_3 content

The most important reason why the maximum SO_3 content in cement was specified in standards is to restrain an excessive expansion in water. This expansion is thought to be caused by the expansive pressure with the growth of ettringite crystals from the reaction between SO_3 and C_3A and C_4AF . However, the ettringite produced during the initial stage of hydration before setting does not contribute to the expansion. The expansion depends on the amount of ettringite produced after setting and hardening

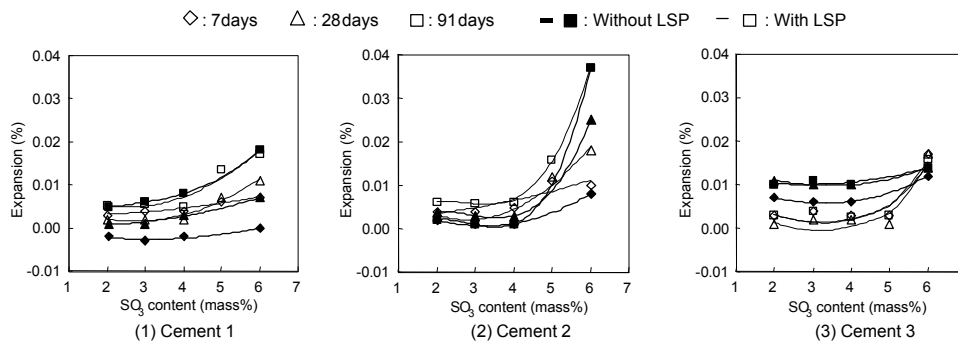


Fig. 2 SO_3 content and expansion in water

[9]. When the SO_3 content is more than a specific value, the expansion increases drastically with the increase of SO_3 content [10,11,12]. In addition when SO_3 content is constant, expansion becomes smaller with the increase of fineness of cement [12]. This attributes to the more quantity of initially produced ettringite, which does not contribute to the expansion in water but reduces the quantity produced later.

In Fig. 2, the relationships between the expansion in water and the SO_3 content for cements 1, 2 and 3 with and without LSP are shown. Depending on the SO_3 contents, the expansion behavior was different. When the SO_3 content was more than around 4.0 mass%, the expansion in water significantly increased with the SO_3 content. The expansion in cement 2 was the largest at 6 mass% of SO_3 . The expansion of mortar is considered to be influenced not only by ettringite formation, but also by strength and pore structure of mortar, etc. The expansion in water of cements with LSP showed the almost same trend with cements without LSP. However, the expansions of cement 3 became smaller by the LSP addition at lower SO_3 contents. This is partly because the hydration is relatively accelerated by the addition of LSP at low SO_3 content as discussed later in 3.2 and 3.3.

(3) Compressive strength

The compressive strength is the most important property considering the optimum SO_3 content in cement. Cements have a specific SO_3 content showing the maximum compressive strength [1,11,13,14]. Also, the specific SO_3 content varies with age even for identical cements and generally increases at longer ages [11].

In Fig. 3, the relationships between the SO_3 content and the compressive strength of cements 1, 2 and 3 with and without LSP are shown. The optimum SO_3 content for compressive strength is defined as the limit SO_3 content beyond that value the compressive strength decreases more than a measurement error. Regarding cement without LSP, as with previous studies, the compressive strength increases with the increase in SO_3

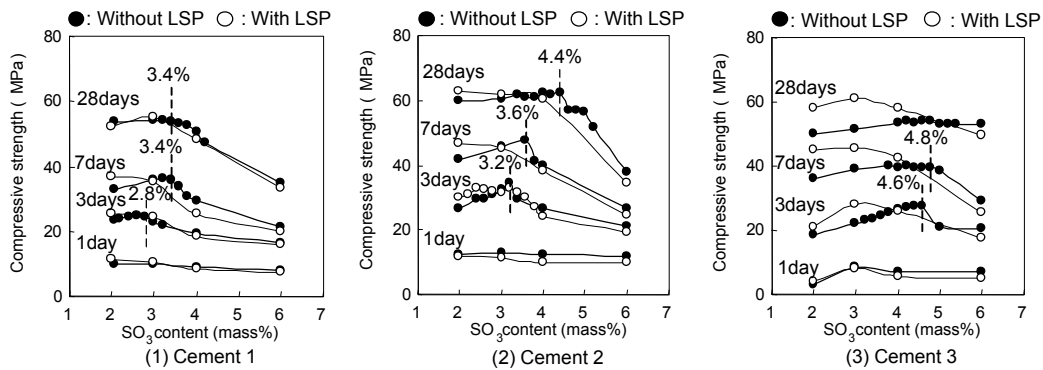


Fig. 3 SO_3 content and the mortar strength of cements 1, 2 and 3 (Dashed lines indicate the optimum SO_3 content for compressive strength)

content for all cements and decreases in excess of a given SO_3 content. Also, the optimum SO_3 content giving the maximum compressive strength for a cement type tends to increase at longer ages. In Fig. 4, the relationships between the Al_2O_3 content and the optimum SO_3 contents for compressive strength of cements 1, 2 and 3 with and without LSP are shown. Further investigation considering Al_2O_3 and Fe_2O_3 content will be shown in the later section but here the simple Al_2O_3 content is discussed. With an increase of Al_2O_3 content, the optimum SO_3 content for compressive strength increased. These results support Lerch's study [2] mentioned above. In this study, with increase of 1 mass% of Al_2O_3 , the optimum SO_3 content for compressive strength without LPS increased 0.52 mass% on average.

When significant amount of LSP is added, the compressive strength of cement decreases. This is caused by the increase in the actual W/C by the LSP addition. On the other hand, some researchers have reported that the compressive strength increased with the addition of small amount of LSP [15]. This is explained as the micro filler effect, which is the hydration acceleration by LSP acting as crystal nuclei. Usually these effects are significant during early ages.

Campitelli *et al.* reported that the optimum SO_3 according to ASTM C 563 decreases with the increase in the LSP content [16].

Although the optimum SO_3 content for the maximum compressive strength of cement without LSP was relatively easy to identify, that of cement containing LSP was not clear. When the SO_3 content of cement is less than that required for the maximum compressive strength of cement without LSP, the compressive strength of cement with LSP tends to be higher than that without LSP. This trend is the most noticeable in cement 3 with high Al_2O_3 content, especially after 7 days. On the other hand, when the SO_3 content of cement is higher than that showing the maximum compressive strength of cement without LSP, the compressive strength of cement with LSP tends to be slightly lower. These effects of LSP will be discussed later in 3.3. In this study, the SO_3 content where the curve of compressive strength of cement with LSP crosses that of cement without LSP in Fig. 3 was defined as the optimum SO_3 content for compressive strength of cement with LSP. As shown in Fig. 4, the optimum SO_3 contents for compressive strength of cement with LSP were 0.2 to 1.0 mass% lower than those of cement without LSP.

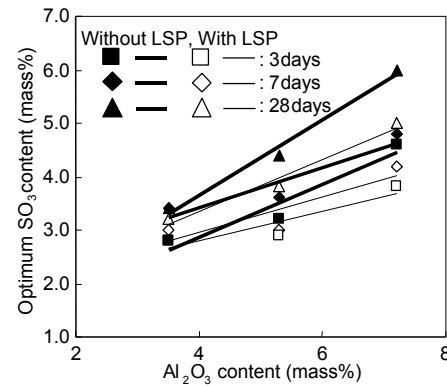


Fig. 4 Al_2O_3 content and the optimum SO_3 content for mortar strength

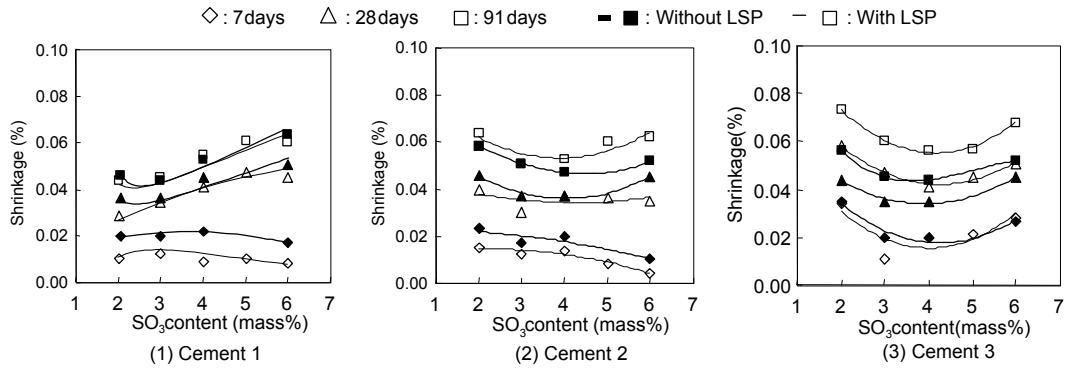


Fig. 5 SO₃ content and drying shrinkage

(4) Drying shrinkage

Drying shrinkage is also important when considering the optimum SO₃ content. It is well known that for a given cement type, there is a specific SO₃ content showing the minimum drying shrinkage. This SO₃ content increases with age and/or C₃A content in the same way with the maximum compressive strength [17]. There are various opinions about the influence of LSP addition on the drying shrinkage of hardened cement. However, the influence of small amounts of LSP addition (such as 5 mass% or less) on the drying shrinkage is reported to be negligible [18].

In Fig. 5, the relationships between the SO₃ content and the drying shrinkage of cements 1, 2 and 3 with and without LSP are shown. Each type of cement has a specific SO₃ content showing the minimum drying shrinkage. However, the differences between the minimum and maximum values of the drying shrinkage ratio were much smaller than those of the expansion ratio in water. The SO₃ content showing the minimum drying shrinkage was not clear compared to that of the compressive strength. However those of cements 1, 2 and 3 were approximately 2-3, 4 and 4 mass% of SO₃ content, respectively regardless of LSP content. Therefore, the SO₃ content giving the maximum compressive strength of each type of cement mentioned above could also make the drying shrinkage minimum.

The addition of LSP did not affect the optimum SO₃ content showing the minimum shrinkage but did the value of shrinkage. At earlier ages and lower Al₂O₃ contents, LSP decreases the shrinkage. At later ages and for higher Al₂O₃ contents, LSP increases the shrinkage. Although this is thought to be the influence of LSP on the type of hydrates, strength development and porosity, further investigation is required.

Table 3 Optimum SO₃ content (%)

	Cement1 Al ₂ O ₃ =3.5%	Cement2 Al ₂ O ₃ =5.3%	Cement3 Al ₂ O ₃ =7.2%
Setting	>2	>2	>2
Strength*+	3.0-3.8	3.2-4.4	4.6(-6.0)
Strength**+	2.8-3.2	2.9-3.8	3.8-5.0
Shrinkage**	2-3	4	4
Expansion**	<3-4	<4	<5

*Age: 3-28days **Age: 91days

+: Without LSP ++: With LSP

(5) Optimum SO₃ content

The optimum SO₃ contents of cement considering setting time, expansion in water, compressive strength and drying shrinkage are shown in Table 3. The SO₃ content giving the maximum compressive strength also satisfies the optimum range of SO₃ contents for other properties regardless of Al₂O₃ content and LSP addition. The optimum compressive strength of cement with LSP can be obtained at lower SO₃ contents than cement without LSP as much as 0.2-1.0 mass% depending on Al₂O₃ contents.

3.2 Porosity measurement and hydration analysis

The main reason why compressive strength increases with the increase of SO₃ content is thought due to the hydration acceleration of C₃S [17,19]. In addition, Bensted *et al.* reported that decrease in compressive strength with more SO₃ content is the influence of the expansion due to the excess formation of ettringite [20]. However, other researchers have reported that a decrease in compressive strength is caused by the inhibiting effect of SO₃ for the hydration [10]. The definitive explanation has not been concluded. In order to investigate the working mechanisms of the SO₃ content and LSP addition on the compressive strength, porosimetric and phase analyses were carried out.

(1) Porosity

In Fig. 6, the relationship between the compressive strength and the porosity of cement 2 at the ages from 1 to 91 days are shown. It is well known that compressive strength of hardened cement correlates with its porosity [13]. There is a negative correlation between porosity and compressive strength also in this study. This result indicates that the change in compressive strength by the change of SO₃ content was caused by the change of porosity of hardened mortar.

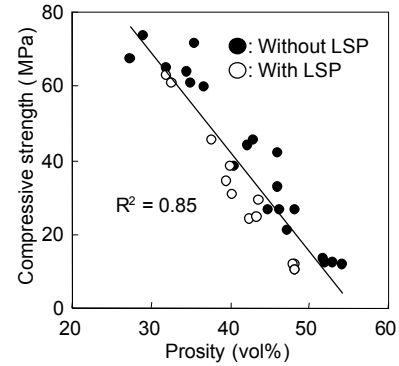


Fig. 6 Porosity and mortar strength of cement 2

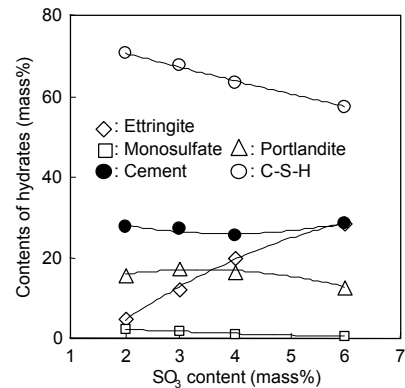


Fig. 7 SO₃ content and phase composition (Cement 2 without LSP, 28 days)

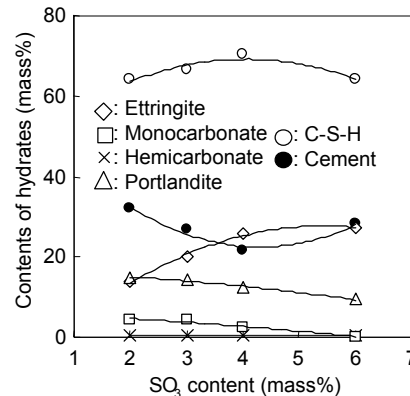


Fig. 8 SO₃ content and phase composition (Cement 2 with LSP, 28 days)

(2) Quantification of cement hydration by XRD/Rietveld analysis

In order to investigate the mechanism of the change of porosity by SO_3 content, the hydration were analyzed by XRD/Rietveld method. In Fig. 7, the relationships between the phase composition and the SO_3 content of cement 2 without LSP at 28 days are shown. The amount of ettringite increased with the increasing of SO_3 content. Although the amount of C-S-H decreased with the increase of SO_3 content, except for ettringite, the amount of monosulfate and portlandite remains roughly constant regardless of SO_3 content. These results suggest that the decrease in porosity was caused by the increase in ettringite.

The relationships between the phase composition and SO_3 content of cement 2 with LSP at 28 days are shown in Fig. 8. The amount of unhydrated cement decreased in the range from 2.0 to 4.0 mass% of SO_3 . However, at 6.0 mass% of SO_3 the amount of unhydrated cement was more than that at 4.0 mass% of SO_3 . By the addition of LSP, the effects of SO_3 content on the hydration were changed for the formation amount of C-S-H and ettringite. The formation amount of C-S-H became constant independent of the SO_3 content. The amount of ettringite at lower SO_3 contents increased by the LSP although it was the same with that without LSP at higher SO_3 contents.

The results of hydrates analysis suggest that the increase in the amount of ettringite contributed to the decrease in porosity. However, the amount of ettringite formed is also reported to correlate with the expansion in water [21]. Therefore, it is considered that the porosity is decreased by the ettringite formation up to a specific value of SO_3 content, thereafter further addition of SO_3 resulted in the increase of porosity caused by excess ettringite formation. In order to investigate the specific value of SO_3 , the relationships between SO_3 content and porosities measured are examined and shown in Fig. 9 for cement 2 without LSP at the age of 28 days.

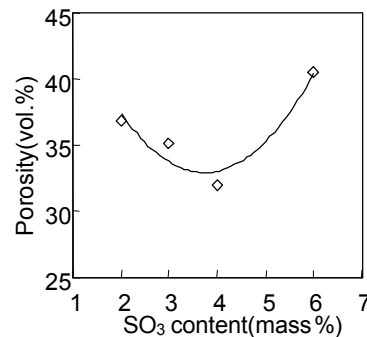


Fig. 9 SO_3 content and porosities by MIP of cement 2 without LSP at 28 days

MIP measurement indicates that the porosity decreased from 2.0 to 4.0 mass% and increased again at 6.0 mass% of SO_3 . This is contradictory to the degree of hydration shown in Fig. 7. There is no indication showing the decrease in the degree of hydration at 6.0 mass% of SO_3 . This result suggests that at lower SO_3 contents, the porosity was decreased by the volume increase in hydrates. However, at 6.0 mass% of SO_3 , ettringite formation caused the increase in porosity. This result indicates that the decrease in compressive strength in the range over the optimum SO_3

value for compressive strength is caused by the increase in the porosity by the excess formation of ettringite.

3.3 Discussions

(1) Optimum SO_3 content

In this section, the reason why the optimum SO_3 content for compressive strength is different depending on cement type is discussed. The amount of ettringite formation affects significantly the optimum SO_3 content for compressive strength as mentioned in 3.2. Because Al_2O_3 and Fe_2O_3 can be sources of ettringite, the relationship between optimum SO_3 content for compressive strength and Al_2O_3 and Fe_2O_3 contents are examined and are shown in Fig. 10. With the increase in Al_2O_3 and Fe_2O_3 content, the optimum SO_3 content for compressive strength increased. This result suggests that Al_2O_3 and Fe_2O_3 content has a close correlation with ettringite formation. The amount of SO_3 addition consisting with Al_2O_3 and Fe_2O_3 content in cement is important.

Next question is the reason why the optimum SO_3 content for compressive strength increases with the increase in Al_2O_3 and Fe_2O_3 content. Ettringite formation can increase the compressive strength by decreasing of porosity. Therefore, the effect is considered to be most significant at early ages when much amount of pore is remained. On the other

hand, ettringite formation at later ages is considered to increase the porosity and to result in the decrease of compressive strength. In Fig. 11, the amount variations of ettringite with age elapse in cements without LSP having 2.0 and 4.0 mass% of SO_3 are shown. At the age of 1 day, for 2.0 mass% of SO_3 , the amount of ettringite was more in the order of cement 3, cement 2 and cement 1. The amounts of ettringite in cements 2 and 3 decreased after 1 day. However, that in cement 1 was almost constant until 28 days. For cements having 4.0 mass% of SO_3 , although the amount of ettringite in cement 3 was the most from 1 to 7 days, it was the

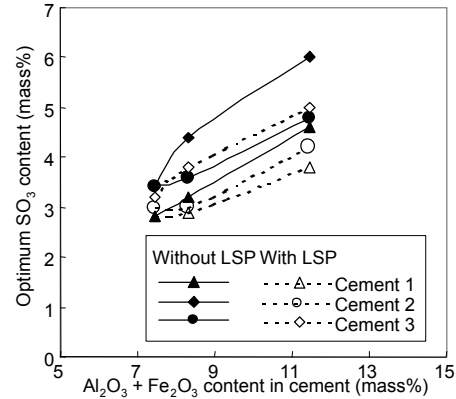


Fig. 10 The optimum SO_3 for compressive strength and $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content in cement

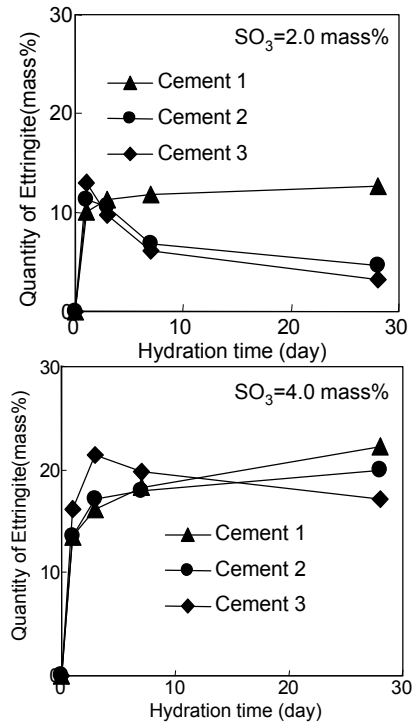


Fig.11 The amount of ettringite in cement without LSP

least of all at 28 days. On the other hand, that in cement 1 increased and became the most of all at 28 days.

From these results, the amount of ettringite in cement 1 didn't decrease for long term even at the low SO_3 content because the Al_2O_3 and Fe_2O_3 content was relatively low. Therefore, at high SO_3 content, the amount of ettringite increased for long term and this increased the porosity and inhibited the increase of compressive strength. On the other hand, the amount of ettringite in cement 3 was significantly high in the case of high SO_3 content at early ages. Consequently, the porosity decreased to increase the compressive strength. The more amount of ettringite is considered not to decrease the compressive strength for long term even at high SO_3 content because the amount of ettringite in cement 3 didn't increase in later ages.

These results suggest that the influence of ettringite on porosity is different depending on the type of cement because the amount and age of ettringite formation is different depending on the contents of Al_2O_3 and Fe_2O_3 even at the same SO_3 content. This is considered to be one of the reasons why the optimum SO_3 content for compressive strength is various for each type of cement. The reason why the optimum SO_3 content for compressive strength increases with age elapse is considered that the pores generated by the crystal growth of ettringite were then filled gradually by the other hydrates formation such as C-S-H.

(2) Effect of LSP

As shown in Fig. 10, with the increase in Al_2O_3 and Fe_2O_3 contents of cements with LSP, the optimum SO_3 content for compressive strength increased similar to the case without LSP. At the low contents of Al_2O_3 and Fe_2O_3 , the optimum SO_3 content for compressive strength in the cement with LSP is similar to that without LSP. However, with the increase in Al_2O_3 and Fe_2O_3 content in the cement with LSP, the optimum SO_3 content for compressive strength was lower than those without LSP. At the lower SO_3 contents, LSP significantly enhanced the compressive strength of cement with high Al_2O_3 and Fe_2O_3 .

In order to investigate the effect of LSP addition on the reduction of optimum SO_3 content for compressive strength, the hydration analysis was performed by XRD/Rietveld method. In Fig. 12, the volumetric amount of

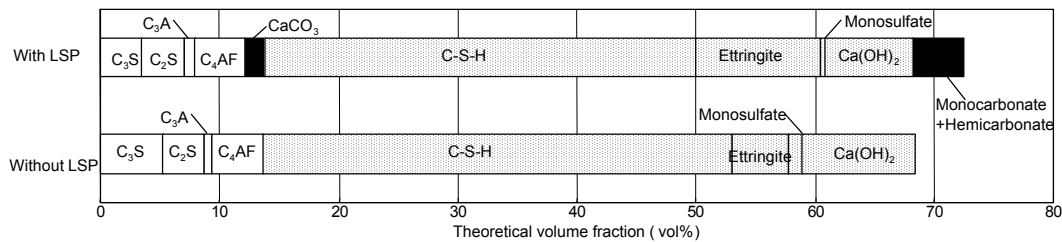


Fig. 12 The volume ratio of minerals and hydrates in cement 3 at 7 days

hydrates in cement 3 with 2.0 mass% of SO_3 at the age of 7 days is shown. In the condition, significant increase in compressive strength was observed. The volume of each mineral and hydrate was calculated by using the quantification results of each phase by XRD/Rietveld analysis and the density data [22]. With the addition of LSP, the amount of unhydrated C_3S decreased. The acceleration of hydration of C_3S in the presence of LSP especially at early age has been reported by researchers [23]. This effect of LSP is considered to be most significant in cement 2 with the highest C_3S .

Although the amount of unhydrated aluminate minerals did not change by presence of LSP, the quantities of aluminate hydrates (ettringite, monosulfate hydrate, and calcium aluminate carbonate hydrate) increased as shown in Fig. 12. C_3A and C_4AF generally produce monosulfate hydrates by the reaction with ettringite after gypsum is consumed. When cement contains LSP, however, C_3A and C_4AF do not react with ettringite but in fact reacts with LSP instead after the consumption of gypsum. From this reaction, calcium aluminate carbonate hydrates are produced. In this case, the total volume of aluminate hydrates doesn't decrease even after the consumption of gypsum because ettringite is not consumed [8]. Therefore, by presence of LSP, the amount of ettringite increases at given SO_3 content.

In Fig.13, the variation of the amount of ettringite with age elapse in cements having 2.0 and 4.0 mass% of SO_3 and LSP are shown. The amounts of ettringite in cement 2 and 3 at 2.0 mass% of SO_3 became higher by the LSP addition and were almost constant until 28 day. On the other hand, although the amount of ettringite in cement 1 became more by the LSP addition, it was less than that in cement 2 and 3 with LSP. At 4.0 mass% of SO_3 , the amount of ettringite in cement 1 and 2 with LSP increased until 28 days accompanied by the progress of hydration of C_3A and C_4AF . Therefore, the increase in compressive strength was restrained by the ettringite formation. However, since that in cement 3 with LSP decreased after 7 days, the increase in compressive strength was observed. These differences in the amount of ettringite by LSP addition can be explained by the result in Fig.12. These results are attributed to be

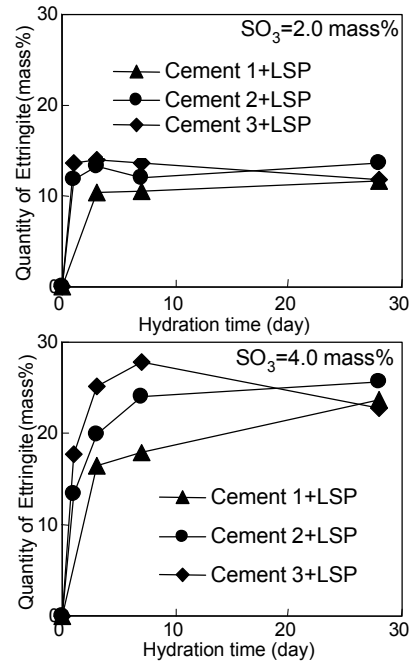


Fig. 13 The amount of ettringite in cement with LSP

the reason of the effect of LSP addition in cement with high Al_2O_3 and Fe_2O_3 content at low SO_3 content.

When cement contains high amounts of SO_3 , the reaction of LSP is limited. When LSP does not contribute to the hydration, the addition of it causes the increase of the actual W/C ratio. Consequently, the addition of LSP tends to slightly decrease the compressive strength of mortar prepared with cement with a high SO_3 content.

4. Conclusions

In order to clarify the effects of LSP addition on the optimum SO_3 content, by using cements having Al_2O_3 content from 3.5 to 7.2 mass%, SO_3 content from 2.0 to 6.0 mass% and LSP content of 0 and 4 mass%, the setting time, the expansion in water, the compressive strength, and the drying shrinkage were evaluated. The effect of LSP addition on the relationships between SO_3 content and various properties are discussed with the analytical results of porosimetry and phase analysis.

- 1) Without LSP addition, the setting time was constant in the SO_3 range from 2.0 to 4.0 mass% but it delayed in the range more than 4.0 mass%. The expansion in water was almost constant in the range of SO_3 from 2.0 to 4.0 mass%, but it increased in the range more than 4.0 mass%. The drying shrinkage of cement with 3.5 mass% of Al_2O_3 was minimized at 2.0 to 3.0 mass% of SO_3 . Those with more Al_2O_3 were minimized at approximately 4.0 mass% of SO_3 .
- 2) With the addition of LSP, compressive strength increased at lower SO_3 contents and slightly decreased at higher SO_3 contents. The optimum SO_3 content for compressive strength tends to decrease by LSP addition. The increasing effect of LSP in the compressive strength is eminent for the cement having higher Al_2O_3 and Fe_2O_3 contents.
- 3) The SO_3 content ranges showing the maximum compressive strength satisfied the optimum SO_3 content for other properties regardless of LSP content. When these results are applied to cement production, the influence of alkali content and fineness also should be considered.
- 4) Regarding the influence of SO_3 content on compressive strength, the porosimetry and hydration analysis clarified that the compressive strength increased by the increase in hydrates mainly ettringite caused by increased amounts of SO_3 . However, beyond the optimum value for compressive strength such as 6.0 mass%, excess amounts of ettringite formed to increase the porosity resulting in the decrease in the compressive strength.
- 5) Although the ettringite produced at early age contributes decreasing porosity to increase the compressive strength, that produced for long term increases the porosity to decrease the compressive strength. This is considered to be the reason why cement with high Al_2O_3 and Fe_2O_3 requires higher amount of SO_3 . By the addition of LSP, the amount of ettringite increases. Therefore, it increases the compressive strength of

cement especially with high Al_2O_3 and Fe_2O_3 and lower SO_3 contents than the optimum value for compressive strength at early age.

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