

Structure Analysis of Glass of CaO-Al₂O₃-SiO₂ System by Means of NMR

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1. Introduction

The glassy materials such as slag and fly ash have been widely used as hydraulic materials, because of their properties of low heat liberation of hydration and some chemical durability. Although there are many reports on the reactivity of granulated blast furnace slag, they had been done mainly from the point of view of chemical composition, alkalinity and degree of vitrification[1,2]. Of course, there are many reports on the glass structure but a very few concerning with reactivity, but many had interests in the glass structure of calcium aluminosilicate glass concerning with the dynamics in geology and with the glass manufacturing industry. They discussed the relationship between structure and properties such as glass transition temperature, viscosity and so on.

Diamond[3] had been reported the relation between CaO content and halo position in the XRD pattern, in which they reported there are two groups, one is less than 20 mass % of CaO and another is 20 to 30 % of CaO. Authors had also been reported on the relationship over the range of 30% of CaO[4]. Wang et al.[5] had reported about the effects of heat treatment on the slag hydration, where they said that the glass structure did not change by heat treatment but reactivity was affected very much.

Neuville et.al [6] had measured the Al/Si tetrahedral distribution in the glass network in different Qⁿ species in very wide range of the CaO-Al₂O₃-SiO₂ system using ²⁷Al MQ-MAS NMR and Raman spectroscopy. They concluded that, in CaO/Al₂O₃ = 1, Al and Si are mainly in Q⁴ species and at higher CaO/Al₂O₃ joins of 1.57 and 3, they depolymerize to Q² and Q³. In the peraluminous glasses (R<1), five- and six- fold coordinated aluminum (⁵Al and ⁶Al) had been detected. They also discussed the effects of ⁵Al on the viscosity of glasses.

Siwadamrongpong, et al.[7,8] had investigated on the structure of ternary alumino-silicate glasses. They discussed the conditions of the existence of triclusters with the composition, such as the molar ratio of [MO, M₂O]/[Al₂O₃], [SiO₂]/[Al₂O₃] and non-bridging oxygen (NBO). The Al-O-Al linkage is thermodynamically unfavorable but exists as triclusters. They concluded as the existence of the triclusters conditions could be defined stoichiometrically as either [MO, M₂O]<[Al₂O₃] or 2[SiO₂]<3[Al₂O₃]+ [MO,

M₂O]. And the amount of NBO (non-bridging oxygen; Si-O-not Si) can be calculated as $[NBO]=2\{[CaO]-[Al_2O_3]\}$. In these discussion, the role of each composition for the microstructure of the system of CaO-Al₂O₃-SiO₂ had been assumed as follows; First, the silicate ion and aluminate ion are constituted as (SiO₄)⁴⁻, (AlO₄)⁵⁻. Second, the Ca²⁺ is preferably coordinated to (AlO₄)⁵⁻ as (AlO₄)⁴⁻---M⁺. Third, the residue of Ca²⁺ should be preferably coordinated to (SiO₄)⁴⁻. And the relation between chemical composition and n or N of Qn(AlN) in the analysis of NMR are expressed as $N=2[Al_2O_3]/[SiO_2]$ and $n=4\{1-2([CaO]-[Al_2O_3])/([SiO_2]+2[Al_2O_3])\}$

Allwardt et.al [9] had also reported that there is a strong preference in the bonding for Si-NBO in the CaO-Al₂O₃-SiO₂ system than Al-NBO from the results of ²⁷Al NMR and ¹⁷O MAS and 3QMAS NMR.

Authors had already reported about the relation between hydration properties and composition in the system of CaO-SiO₂-Al₂O₃ glass, gypsum and lime with excess amount of gypsum[4]. A distinguished feature of the hydration reaction in this system, that is the rate of hydration of glass or the rate of heat liberation, is that there is a period with a constant rate of reaction. The constant rate of hydration and the time for consuming the lime added had closely related with the composition of glass. During the constant rate of hydration, there is enough amount of CaO, SO₄²⁻ to produce ettringite with ideal formula and C-S-H- with CaO/SiO₂ mole ratio of 1.425. The reactivity is not in one relation for all region but two which are divided by the composition of $CaO/(Al_2O_3+SiO_2)=0.6$.

On the other hand, NMR spectroscopy had already been applied to cement chemistry[10], in which Wieker et.al. introduced the investigation of the silicate structure of C-S-H by using ²⁹Si NMR spectroscopy. P.Faucon et.al. [11] also reported about the investigation of surface degradation of cement paste by water leaching using with ²⁹Si MAS-NMR and ⁵⁷Fe Mossbauer.

Here we had studied the structure of glasses by using with a high resolution solid state NMR and discussed the relation between the glass structure and hydration reactivity.

2 Experimental

2-1 Synthesis of glasses in the system of CaO-Al₂O₃-SiO₂

Glasses with targeted composition were prepared in the same way reported in literature 4. They are 8 glasses shown in (Table 1). The mixtures of chemical reagents of CaCO₃, Al₂O₃ and SiO₂ (Wako

Chemicals Co. Ltd. Japan) were melted in electrical furnace with MoSi₂ heater at 1600 degree C for 1 h. Then they were quenched into water.. Samples of A,B,C and D were located in the lower [CaO] region, that is [CaO] was about 33 mass%, and that of E, F, G and H are located in higher [CaO] region, that is [CaO] was in the range of 41 to 46 mass%.

2-2 XRD measurements

XRD measurement was performed for confirmation of glassy state of synthesized samples with Rigaku Geiger Flex 2027. X-ray was Cu-K α , 30kV-40mA. Scanning speed was 2 degree/min.

Table 1 Chemical composition (mass %) of synthesized glasses

Sample	CaO	Al ₂ O ₃	SiO ₂
A	33.5	0	66.5
B	32.6	14.1	53.5
C	32.6	23.7	43.7
D	32.3	34.7	32.3
E	44.3	0	55.7
F	40.7	14.1	45.2
G	46.1	21.0	32.9
H	44.0	29.5	26.5

2-3 High resolution solid state NMR measurements

²⁷Al MAS NMR and ²⁹Si MAS NMR were measured by using FT-NMR for solid state (Chemagnetics, CMX-300). The resonance frequencies used were 78.3 MHz and 59.7 MHz for ²⁷Al and ²⁹Si, respectively. Magic Angle was set before insertion of the sample, by optimizing the response of the ⁷⁹Br signal of the spinning side band of KBr (Maciel's method). The diameter of probe tube and the rate of sample spin for ²⁷Al and ²⁹Si were 4 mm ϕ 9 kHz and 7.5 mm ϕ 4 kHz, respectively. Chemical shifts were compensated by using AlCl₃ and silicone rubber (poly-di-methylsiloxane) for references of Al and Si, respectively.

3 Results and discussion

3-1 Results of XRD measurements

XRD patterns for each synthesized sample were shown in (Fig.1). All samples were confirmed as just glassy phase because their patterns showed only halo. The halo peak positions (2θ in degree) were shifted to higher degree with the concentration of CaO. Relation between the halo peak position (2θ in degree) and calcium content ($[\text{CaO}]$ in mass %)[3,4] were shown in (Fig.2). They were plotted on the previous results[4]. The halo peak position for glass B,C and D located very near the main relationship line, $2\theta=0.094[\text{CaO}]+25.3$, and that of glass A,E,F,G and H something diffused from the line, but all had good relationship as previous results. The relationship between the CaO contents of glasses and the position of halo in XRD pattern for fly ash was reported by Diamond[3]. They reported that there are two parts, one is the range less than 20 mass % of CaO (Range I), where the peak shifts with the content of CaO, and another is more than 20 mass %, where the peak does not shift as $2\theta=\text{ca.}32^\circ$ (Range II). In this and previous experiment, all of the CaO contents for the samples were higher than 28 mass % (Range III) and the halo shifted as $2\theta=0.24[\text{CaO}]+22.7$ with the CaO content. There is some shift gap between that for the Range I and Range II, and between Range II and Range III.

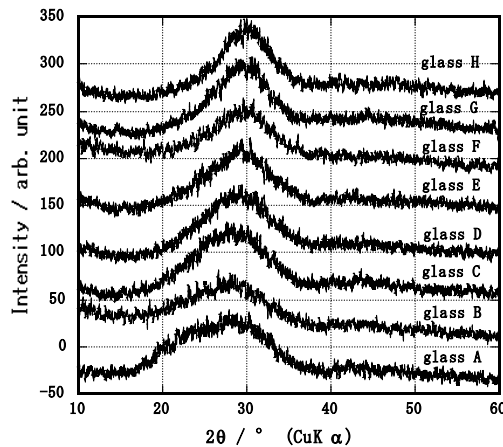


Fig.1 XRD pattern for synthesized halo position and CaO content.

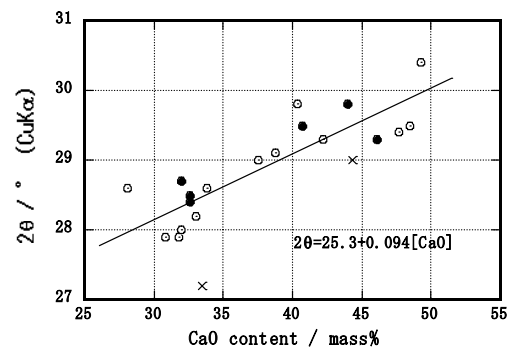


Fig.2 The relationship between halo position and CaO content.

3-2 Results of ^{27}Al MAS NMR measurements

The MAS NMR patterns of ^{27}Al for synthesized glasses of B, C, D, F, G and H were shown in (Fig.3), which were measured by MAS NMR using with $\text{Al}(\text{NO}_3)_3$ solution as standard material. All shifts located between 50 to 70 ppm, and their symmetry is not so good. Somewhat tailed towards

lower frequency. This means that coordination number of Al for all samples is almost 4, but with some amount of 5 coordinated Al ion. Generally, 4 coordinated Al ion shifts +50 to +80 ppm, and 6 coordinated Al shifts -10 to +20 ppm, by using $\text{Al}(\text{NO}_3)_3$ solution as standard material. 5 coordinated Al, which is observed in andalusite and some amorphous or gel phases, has a shift of +30 to +50 ppm[12].

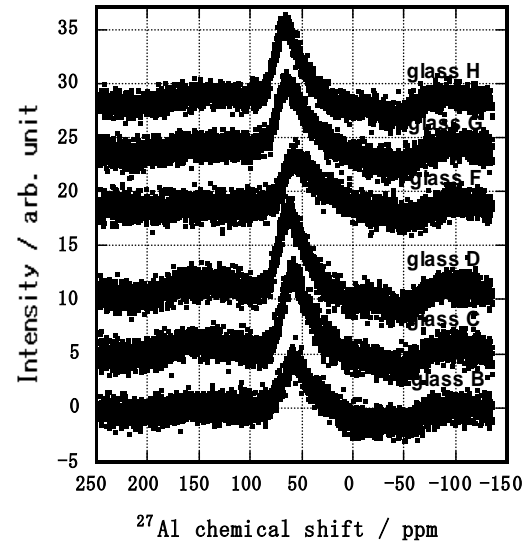


Fig.3 MAS NMR patterns of ^{27}Al for synthesized glasses.

3-3 Results of ^{29}Si MAS NMR measurements

The MAS NMR patterns of ^{29}Si for synthesized glasses of A, B, C, D, E, F, G and H were shown in (Fig.4), which were measured by MAS NMR using with silicone rubber as standard material. These chemical shifts were plotted with alumina content as shown in (Fig.5). These glasses were classified in two groups. Group I is consisted of A~D and group II is E~H, as like as previous report[4]. In group I, the chemical shift was changed from -88 ppm to -82 ppm with Al_2O_3 content of 0 to 34 mass%, and in group II they were changed from -84 ppm to -76 ppm with Al_2O_3 content of 0 to 30 mass%. The CaO content for each group was ca.33 mass% and 44 mass%, respectively. From this figure, the effects of Al_2O_3 content on the chemical shift of ^{29}Si were in the same tendency for both groups, except A.

These spectra for each sample were automatically decomposed to three spectra by using Origin 6.1 with Gaussian function. The results are shown in (Fig.6) and (Fig.7). The spectra for A and E, which do not have Al component at all, was deduced for one spectrum. The spectra of B, C, D, F, G and H were deduced for two or three spectra, that is, B(B1 and B2), C(C1, C2 and C3), D(D1, D2 and D3), F(F1, F2 and F3), G(G1, G2 and G3) and H(H1, H2 and H3). The spectra denoted as peak1 seemed to belong to spectrum A or E, those of peak2 seemed to be somewhat shifted to lower frequency and those of peak3 seemed to be shifted to higher frequency.

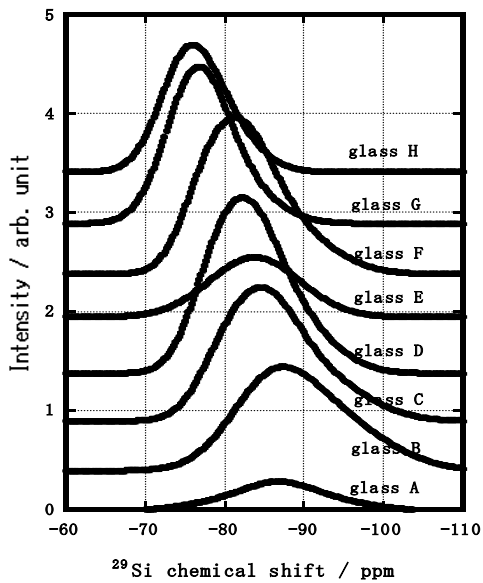


Fig.4 MAS NMR patterns of ^{29}Si for synthesized glasses.

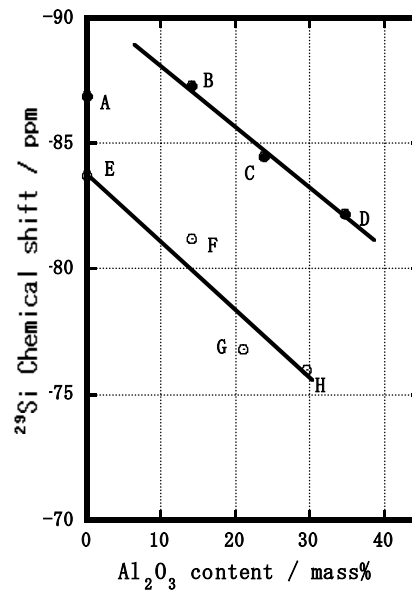


Fig.5 ^{29}Si chemical shift and Al_2O_3 content.

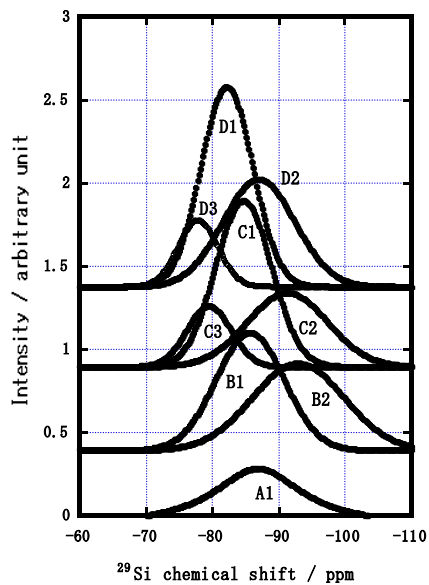


Fig.6 The decomposed spectra of ^{29}Si NMR for glasses of A, B, C and D.

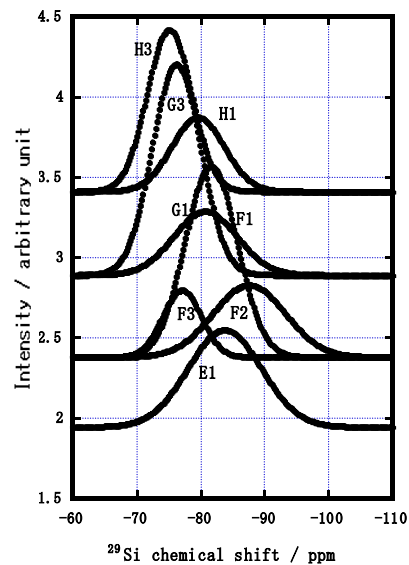


Fig.7 The decomposed spectra of ^{29}Si NMR for glasses of E, F, G and H.

The relationship between ^{29}Si chemical shift and the Al_2O_3 content for the shifts of each isolated spectra were shown in (Fig.8). The ^{29}Si chemical shift ranges are also shown in Fig.8 for each Qn[13]. They were classified into several groups as shown with lines. When the ranges of (F3,G3,H3), (E1, F1, G1, H1, C3, D3), (A1, B1, C1, D1) and (B2, C2, D2) lines were compared with the ranges of quoted ^{29}Si chemical shift ranges, they can be assigned as Q^0 , Q^1 , Q^2 and Q^3 , respectively. The δ_{ppm} with n of Qn(NAI) was 5~10 ppm. These were somewhat smaller than the reported values [13]. From these results, spectra in each group were affected in same way by the content of Al_2O_3 (in mass %), with a relation of $\delta_{\text{ppm}} = + 15*[\text{Al}_2\text{O}_3]$.

On the relationship between chemical shift and local structure or chemical component, there are lots of reports. It is said that the chemical shift is affected by the coordinated chemical group, the bond strength or the bonding length of Si-O, the bonding angle of Si-O- M^+ and so on. Kirkpatrick et al.[13], Plee et al.[14], Kinsey et al.[15], Sanz et al.[16] and Alma et al.[17] were reported on the effects of the degree of condensation, Qn, and coordinated number of Al, Qn(N), on the ^{29}Si chemical shift. From their reports, $\delta_{\text{ppm}} = -10*n$ for Qn and $\delta_{\text{ppm}} = 5\sim 7*N$ for Qn(N). Engelhardt et al.[18] had also reported that the bonding length of 10^{-4} nm long affects 1 ppm for ^{29}Si chemical shift.

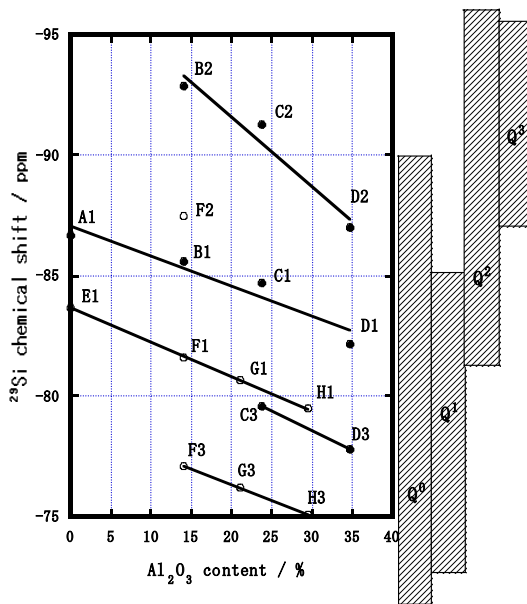


Fig.8 ^{29}Si chemical shift for each decomposed spectrum via Al_2O_3 content and the ^{29}Si chemical shift ranges [11].

On the other hand, although Allwardt et.al [9] had said that there is a strong preference in the bonding for Si-NBO in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system than Al-NBO from the results of ^{27}Al NMR and ^{17}O MAS and 3QMAS NMR, the n and N in Qn(NAI) for a glass in the system of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ can be calculated from the composition with the following assumption[7]. That is, 1) Si(IV) and Al(III) should exist as tetrahedron of SiO_4^{4-} and AlO_4^{5-} . 2) Ca^{2+} should preferentially coordinate to AlO_4^{5-} tetrahedron to make $(\text{AlO}_4)^{4-} \text{---} M^+$, and the remaining CaO should

coordinate to SiO_4^{4-} tetrahedron and AlO_4^{5-} tetrahedron. 3) AlO_4^{5-} tetrahedron should also coordinate to SiO_4^{4-} tetrahedron. So, if the value of $2[\text{Al}_2\text{O}_3]/[\text{SiO}_2]$ is 1, N is 1. if the value is 2, N is 2, and if the value is 0.7, N=0 should be 30% and N=1 should be 70%. On the other hand, if the value of $(2*([\text{CaO}]-[\text{Al}_2\text{O}_3])/([\text{SiO}_2]+2*[\text{Al}_2\text{O}_3]))$ is 4/4, n is 0. If the value is 3/4, n is 1. If the value is 2/4, n is 2. Calculated values of Qn(N) for each sample by this method were shown in (Table 2). For the value of n, group I distributed from Q^1 to Q^3 , but Group II was almost Q^1 . For that of N, both of groups similarly distributed.

For the chemical shift of ^{29}Si , increase in $[\text{Al}_2\text{O}_3]$ makes n and N to increase. When the n increases, chemical shift will be in lower frequency and when the N increases chemical shift will be in higher frequency. For all synthesized glasses, main ^{29}Si chemical shifts were changed to higher frequency with the content of Al_2O_3 , as shown in (Fig.4). It seems that they obey to the value of N. The effects of increase of n seems to be appeared in the fact that the ratios of peak area between decomposed peak2 and peak1 were increased and those of decomposed peak3 and peak1 were decreased with the content of Al_2O_3 , as shown in (Fig.6 and 7).

Table 2 Calculated values (%) of Qn(N) for synthesized glasses.

Sample	Chemical composition/mol%					Probability of each n				Probability of each N		
				*1	*2							
	Al_2O_3	CaO	SiO_2			n=1	n=2	n=3	n=4	N=0	N=1	N=2
A	0	35.1	64.9	0	4.32	1				1		
B	8.6	36.2	55.2	0.31	3.05	0.05	0.95			0.69	0.31	
C	15.1	37.7	47.2	0.64	2.35		0.35	0.65		0.36	0.64	
D	23.2	39.3	37.5	1.24	1.54			0.54	0.46		0.76	0.24
E	0	46.0	54.0	0	6.82	1				1		
F	8.5	44.9	46.5	0.37	4.57	1				0.63	0.37	
G	13.1	52.2	34.8	0.75	5.14	1				0.25	0.75	
H	19.1	51.8	29.1	1.31	3.89	0.89	0.11				0.69	0.31

*1: $2[\text{Al}_2\text{O}_3]/[\text{SiO}_2]$

2: $(2([\text{CaO}]-[\text{Al}_2\text{O}_3])/([\text{SiO}_2]+2*[\text{Al}_2\text{O}_3]))$

3-4 The relationship between hydraulic reactivity and ^{29}Si chemical shift

The relationship between hydraulic reactivity and chemical composition, especially with Al_2O_3 content had been already mentioned in previous report[4]. Rate of hydration of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glasses and gypsum with

lime were investigated, especially for the system of excess lime. Conclusively authors were reported as the time (T3) for consuming the mass of lime added were related to the amount of Al_2O_3 in glasses, and the glasses were classified in two groups. Here authors thought T3 as one of indices of hydraulic reactivity.

In (Figure 9), the relationship between T3[4] and ^{29}Si chemical shift was plotted. With lowering the frequency of resonance, T3 increased. The lowering infrequency means that the silicate is highly condensed, and highly condensed silicate loses reactivity. Still they are classified in two groups, but it can be said that the ^{29}Si chemical shifts express the hydraulic reactivity of glasses in almost one linear relation.

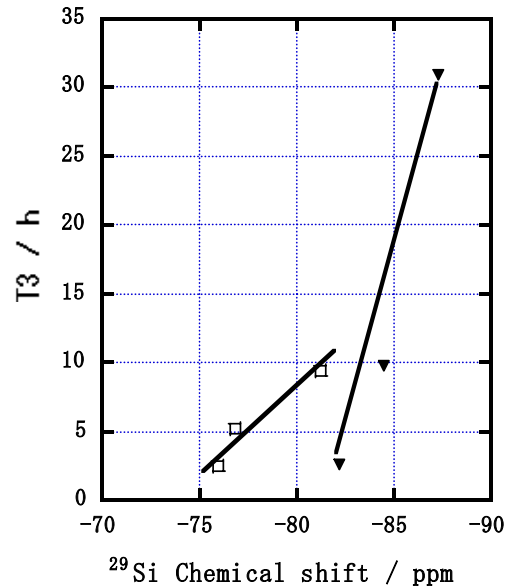


Fig.9 T3 [4] and ^{29}Si chemical shift.

4 Conclusion

Synthesized glasses of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system were investigated microstructure by XRD and a high resolution solid state NMR. Local structure of Al(III) and Si(IV), especially the effects of Al_2O_3 content on the chemical shifts of ^{29}Si were discussed. Finally the relationship between the hydraulic reactivity and microstructure (Qn(N)) of glasses was also discussed. These are concluded as follows;

- 1) The halo peaks of XRD for glasses were located in the relation of $2\theta = 0.094[\text{CaO}] + 25.3$, $[\text{CaO}] > 28$ mass%.
- 2) Almost all Al(III) should be coordinated with 4 oxygen, but the profile of ^{27}Al NMR spectra were somewhat tailing towards lower frequency.
- 3) For the chemical shift of ^{29}Si NMR, the increase in $[\text{Al}_2\text{O}_3]$ makes both of n and N increase. When the increases in n, chemical shift will be in lower frequency and when the increases in N, chemical shift will be in

- higher frequency. For all synthesized glasses, main chemical shifts were changed to higher frequency with the content of Al_2O_3 . It seems that they obey to the value of N. The effects of increase of n seem to appear in the fact that the ratios between each peak area of decomposed peak2 and peak1 were increased and that of decomposed peak3 and peak1 were decreased with the content of Al_2O_3 .
- 4) The ^{29}Si chemical shifts are still classified in two groups, but it can be said that the ^{29}Si chemical shifts express the hydraulic reactivity of glasses in almost one linear relation.

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