

Effects of components on the rate of heat liberation of the hydration in the system of glass/gypsum/lime

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Abstract

Slag-simulated glasses in the system of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ were prepared. Their rates of heat liberation were measured in the system with gypsum and lime, especially in the excess gypsum system. They have a period with constant rate of heat liberation. These rates depend on the components of the glass. The effects of the components on the rate of heat liberation were discussed.

The rates of constant heat liberation depend on the composition of glass especially the contents of CaO and Al_2O_3 . The period of this process was controlled by the amount of lime addition. During this stage, the solid Ca(OH)_2 was completely consumed. In this sulfate-excess system, the reaction equation, during Ca(OH)_2 consumption, should be written as; glass + gypsum + lime \Rightarrow C–S–H with a C/S ratio of 1.42 and Ettringite.

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1. Introduction

The glassy materials such as slag and fly ash has been used as hydraulic materials. They have properties of low heat liberation of hydration and some chemical durability. Their hydraulic reactivity has been discussed with basicity and vitrified ratio as the chemical components and the structure of glass, respectively. It has already been reported that the 28 days compressive strength of JIS mortar of slag-50%-containing blastfurnace slag cement changes about 1 MPa with 0.1% changes in basicity or with 10% change in vitrified ratio.¹ From the phase diagram in the system of gehlenite and melillite,² it can be understood that the basicity of remaining glassy phase changes 0.1% as vitrified ratio changes 10%. The researches in the relation between component and glass structure is still small, but Diamond³ 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 20–30% of CaO . Wang et al.⁴ 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.

The granulated blast furnace slag (GBFS) are well known as a latent hydraulic material, that is, GBFS reacts and hardens in high alkalinity solution and/or in a liquid with Ca(OH)_2 . In the hydration of GBFS at room temperature we can recognize the formation of C–S–H, but not the crystallized C–A–H. Of course crystallized C_3AH_6 is usually found in products formed in an autoclave treatment. On the other hand, hardened materials of slag-OPC with small amount of SO_4^{2-} are sometimes broken by the attack of sea water with SO_4^{2-} by the formation of ettringite. Authors had already reported about the hydration of fly ash that the hydration will stop by the lack of lime and/or gypsum.⁵ In the hydration of glass of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system, there are very important meanings in the ratio of glass, lime and gypsum.

In this report, glasses with different components were synthesized and the rate of heat liberation and products were measured. The effect of the components and the

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amount of lime added were discussed in the excess gypsum system.

2. Experimental

2.1. Synthesis of glasses

Glasses with targeted composition were prepared from mixtures of chemical reagents of CaCO_3 , Al_2O_3 and SiO_2 (Wako Chemicals Co. Ltd., Japan). These 13 mixtures (G1–G13) were melted in electrical furnace with SiC heater at 1600°C for 1 h. Then they were quenched into water. These processes were repeated. No crystalline phase was confirmed by XRD (MINIFLEX CN2005, Rigaku Co. Ltd., Japan), and the peak of halo of XRD was also measured. The chemical composition was measured by atomic adsorption spectroscopy (AAS 107-50A, Hitachi Co. Ltd., Japan). The chemical composition, density and Blaine's specific surface area were shown in Table 1 and Fig. 6. The specific surface areas for these samples were around $3600\text{ cm}^2\text{ g}^{-1}$.

2.2. Measurement of heat liberation of hydration

The hydraulic reactivity for these glasses was measured in the system of glass/gypsum/lime with conduction calorimeter (TCC-2, Tokyo Riko Co. Ltd., Japan) at 20°C . Glass, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ were mixed with the contents of 90 parts, 10 parts and 1–3 parts, respectively. Water/solid ratio was 1.0.

2.3. Analysis of solid state components

Changes in the amount of glass, gypsum, lime and hydration products were measured by XRD and DTA (TG/DTA 32, Seiko Electrical Industry Co. Ltd., Japan). Mixtures of glass, gypsum and lime were hydrated with $w/c = 1.0$ at 20°C for intended periods. After the period, samples were immediately washed by acetone and were supplied for XRD and/or TG/DTA measurement.

Table 1

Chemical composition and physical properties of synthesized glasses

Sample name	CaO	Al_2O_3 (mass%)	SiO_2	Density (g/cm^3)	Specific surface area (cm^2/g)
G1	33.0	14.0	53.0	2.83	3890
G2	33.8	20.9	45.3	2.83	3520
G3	30.8	25.6	43.6	2.87	3670
G4	31.8	28.8	39.9	2.82	3740
G5	32.0	31.0	36.8	2.96	3650
G6	28.1	35.8	36.1	2.87	3620
G7	42.2	13.6	44.2	2.88	3650
G8	38.8	17.9	43.0	2.89	3780
G9	40.4	23.6	35.8	2.95	3260
G10	37.5	30.1	31.5	2.81	3620
G11	49.3	7.4	43.3	2.95	3850
G12	47.7	10.5	41.6	2.97	3530
G13	48.5	15.3	36.0	3.09	3550

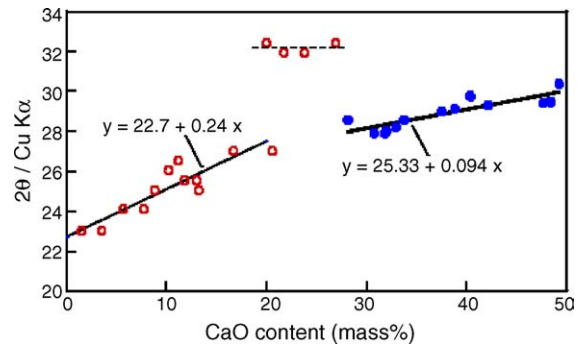


Fig. 1. Effects on the Halo position of XRD pattern for synthesized glasses. (○) is after Diamond³ and (●) is obtained in this experiment.

2.4. Analysis of chemical composition of liquid phase

After an intended hydration period, hydrated mixture was filtered with 5 C filter paper and the concentration of Ca, Al and Si for the filtrate was measured by AAS. That of S was measured with the method of JIS R 5202, in this method SO_4^{2-} was precipitated by BaCl_2 as BaSO_4 .

3. Results and discussions

3.1. Chemical composition and halo position of XRD pattern

The relationship between the CaO contents of glasses and the position of halo in XRD pattern for fly ash was reported by Diamond.¹ 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). The results in this experiment were added in the figure as shown in Fig. 1. Almost all of the CaO contents in this experiment were higher than 28 mass% (Range III) and the halo shift changed with the CaO content but the position were less than 32° . There are shift gap between that for the Range I and that of the Range II, and between Ranges II and III.

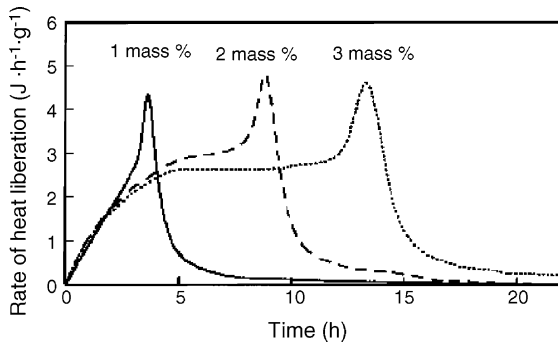


Fig. 2. Pattern of rate of heat liberation of G4 with 1–3% $\text{Ca}(\text{OH})_2$.

3.2. Rate of heat liberation of hydration

3.2.1. Effects of the amount of lime added

The effects of the amount of $\text{Ca}(\text{OH})_2$ were shown in Fig. 2, which sample was G4 (CaO : 31.8, Al_2O_3 : 28.8, SiO_2 : 39.9). In the initial stage of hydration, the rate of heat liberation gradually increased and then the rate became constant if there was still $\text{Ca}(\text{OH})_2$, if not, the rate had suddenly increased and decreased in a short period.

Consequently we can characterize the heat liberation curve into four stages as shown in Fig. 3. They are stage I of the initial acceleration period, stage II of the constant rate of heat liberation period, stage III of the second acceleration period and stage IV of the final decreasing rate period. They are divided in time with T1–T3. T4 is the time when the hydration is almost ended. The constant rate of heat liberation (H_c) and the total heat liberations until the peak (Q_T) were defined as the magnitude of the rate of heat liberation in stage II, and the summation of heat liberation up to time T3, respectively.

The patterns of heat liberation for glass samples of G10, G11, G12 and G13 were very diffused from typical pattern as shown in Fig. 3. But T3 for most of all samples were almost proportional to the amount of lime added in each glass sample and H_c for each glass sample were not affected by the amount of lime added.

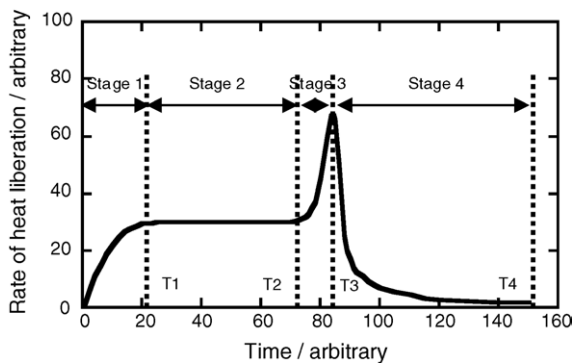


Fig. 3. Illustration of the typical pattern of heat liberation.

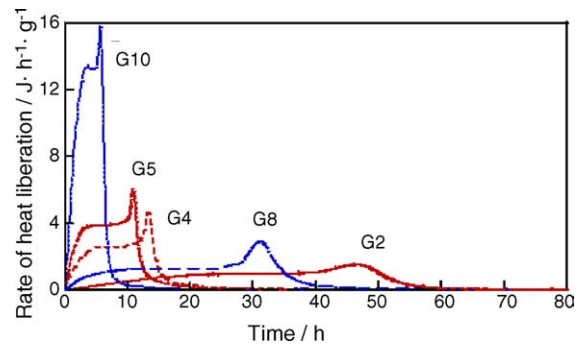


Fig. 4. Effect of the composition of glasses on the heat liberation curves.

3.2.2. Effects of the chemical composition of glasses

The effects of the chemical composition of glasses on the rate of heat liberation were shown in Fig. 4. The constant rate of heat liberation (H_c) were affected by the chemical composition of the glass. It was found that H_c has a close relationship with the content of Al_2O_3 ($C_{\text{Al}_2\text{O}_3}$) in the glass as shown in Fig. 5. It was found that there are two groups in the relation. Group I has lower H_c than group II. Group I includes the glass samples of G1–G7 and group II includes those of G8–G13. These groups are shown in Fig. 6. A borderline between these two groups exists at about 37.5 mass% of CaO . On the other hand, when these H_c were plotted versus the basicity which is calculated by the equation of $(\text{CaO} + \text{Al}_2\text{O}_3)/\text{SiO}_2$, all were gathered into one relation as shown in Fig. 7.

3.3. Changes in the chemical composition in liquid phase and the mineral composition during hydration

Changes in the mineral composition during hydration of mixes of glass, gypsum and lime was shown in Fig. 8. The results were obtained for the sample G2 (90 parts), gypsum (10 parts) and lime (3 parts) by XRD. In stage I, gypsum and lime gradually decreased and till the end of stage II, lime has been consumed. Gypsum decreased until T3 and it became constant after T3. Hydration product of ettringite could be identified after period T1 and it increased until T4. C–S–H

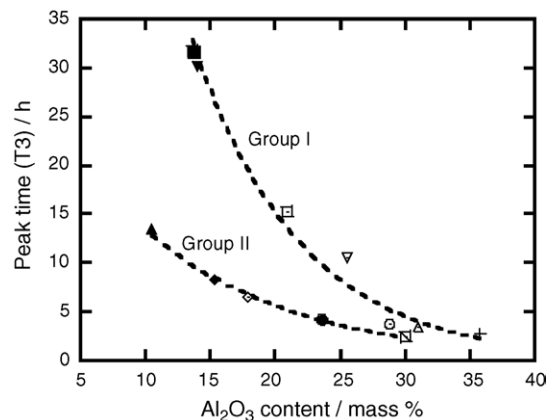


Fig. 5. Relationship between T3 and Al_2O_3 content in glass.

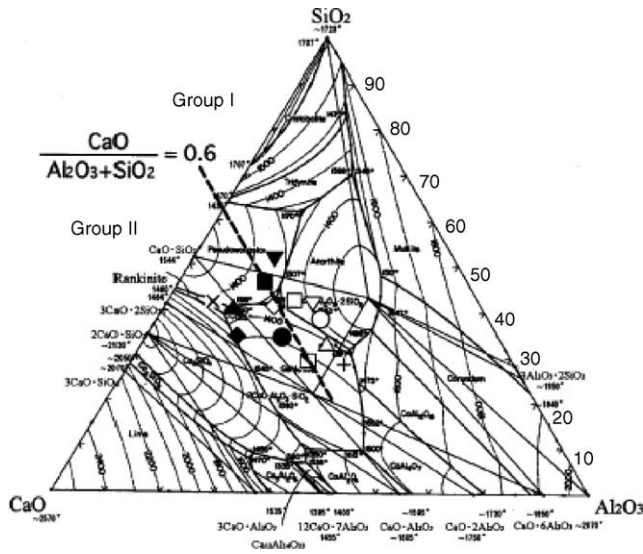


Fig. 6. Sample position on the CaO–Al₂O₃–SiO₂ system.

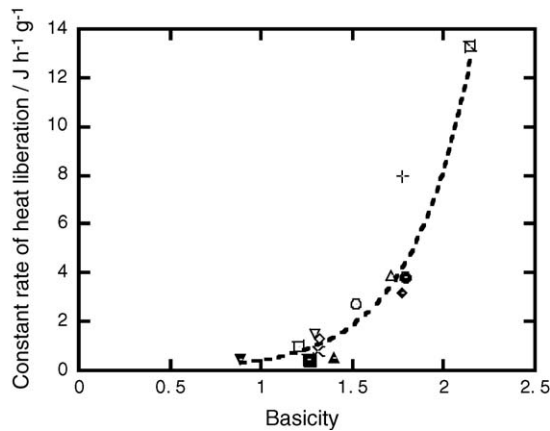


Fig. 7. Relationship between constant rate of heat liberation and basicity.

had to expect to be produced from many experimental results but it was not identified by XRD.

On the other hand, here, the changes in chemical composition in liquid phase were shown in Fig. 9. The concentration of Si⁴⁺, Ca²⁺ and Al³⁺ in the liquid phase did not change up

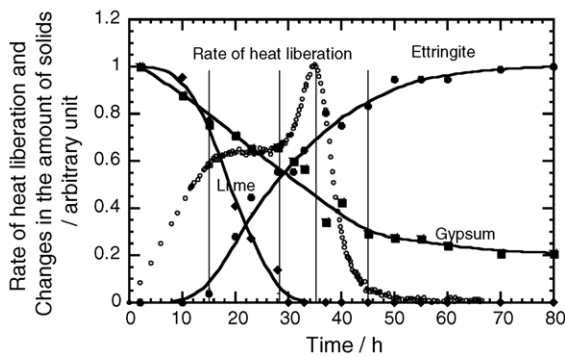


Fig. 8. Changes in the amount of solid phases during hydration.

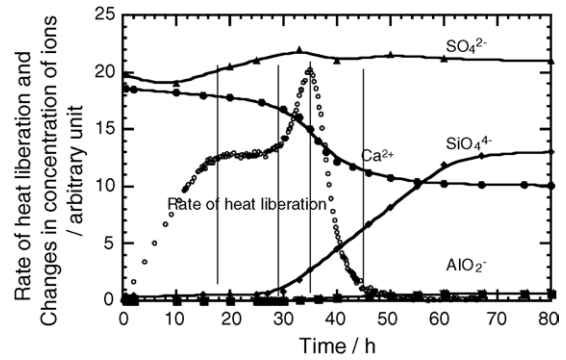
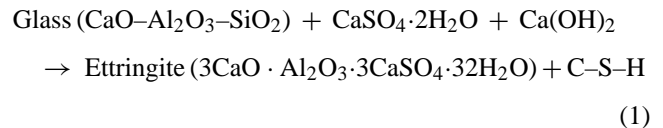


Fig. 9. Changes in the composition of liquid phase during hydration.

to the end of stage II. After that, the concentration of Ca²⁺ decreased gradually from about 900 to 550 ppm. That of Si⁴⁺ increased from 1 to 20 ppm and that of Al³⁺ was 0 to 0.7 ppm. About the SO₄²⁻, there was a little change after the end of stage II, but it was almost constant of 1000 ppm.

3.4. Hydration equation of glass/gypsum/lime system

According to Figs. 8 and 9, the crystalline phase of Ca(OH)₂ added were consumed before T2 and then after the Ca(OH)₂ in liquid phase reacted slightly until T3. So, Q_T should be controlled by the amount of Ca(OH)₂. From these results, it was assumed that the reaction equation of glass, gypsum and lime should be as follows;



Moreover, the mole ratio of CaO/SiO₂ for the C–S–H produced in this system can be estimated as 1.425. Because the hydration products should be only C–S–H and ettringite in this gypsum excess system of glass/gypsum/lime. In this equation, the mole ratio of CaO/SiO₂ for C–S–H strongly affects the amount of ettringite produced and it also affects the heat of hydration. When we analyzed the relationship among Q_T and the amount of ettringite formation using 360 J g⁻¹ for the heat of formation of ettringite, the relation coefficient among them was the highest in the mole ratio of CaO/SiO₂ of C–S–H as 1.425. Then when the mole ratio of CaO, Al₂O₃ and SiO₂ in glass and Ca(OH)₂ added are expressed as M_{CaO} , $M_{\text{Al}_2\text{O}_3}$, M_{SiO_2} and $M_{\text{Ca(OH)}_2}$, respectively, the reaction ratio can be calculated from the following equation.

$$3^* a^* M_{\text{Al}_2\text{O}_3} + 1.425^* a^* M_{\text{SiO}_2} = a^* M_{\text{CaO}} + M_{\text{Ca(OH)}_2} \quad (2)$$

3.5. The relationship between the chemical composition and the characteristics of heat liberation behavior

From the point of view of Eq. (2), the reaction ratio of glass at T3 can be calculated. Fig. 10 shows the relation-

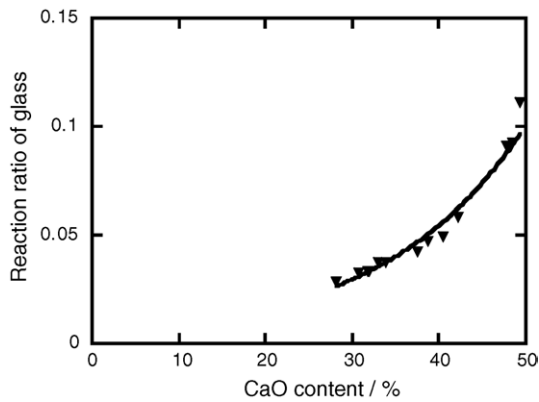


Fig. 10. Relationship between reaction ratio of glasses with 3% Ca(OH)_2 at T3 and CaO content in glass.

ship between the reaction ratio of glass and CaO content. All glasses falls in a unique relation, although T3 was classified in two groups. Fig. 11 also shows a relationship between the thickness of reacted glasses at T3 and CaO content. Of course this shows almost the same relation than in Fig. 10, because all samples have almost same specific surface area.

The heat liberation curves have a unique pattern as shown in Fig. 3. Here we try to calculate total heat of liberation by using an equation as;

$$Q_{\text{Tcalc}} = H_c T_3.$$

Results were shown in Fig. 12. Except G10, (G11), G12 and G13, all (G1–G9) had fallen near the values of Q_T measured.

The amounts of ettringite formation were also calculated with Eq. (2). Total heat liberation has a linear relation to the amount of ettringite (calculated) as shown in Fig. 13. From this coefficient in the relationship, 355 J g^{-1} is very similar to that of literature⁶ of 360 J g^{-1} . It was found that the most of all heat liberation were controlled by the ettringite formation, although this hydration system C–S–H was also produced.

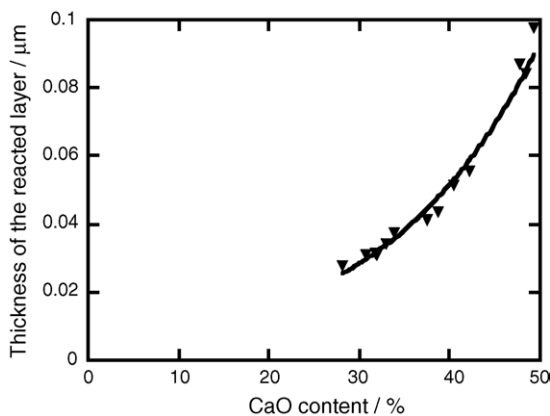


Fig. 11. Relationship between reacted thickness of glasses at T3 with 3% Ca(OH)_2 and CaO content in glass.

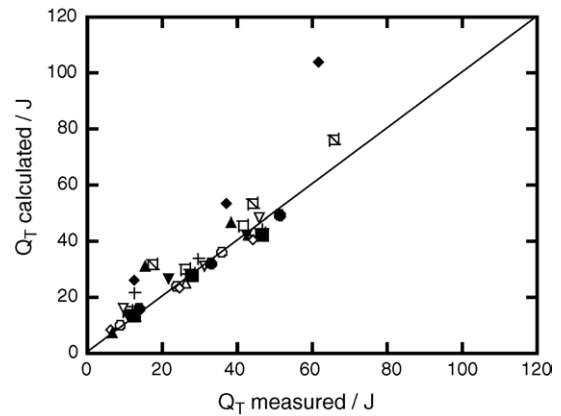


Fig. 12. Calculated Q_T and measured Q_T .

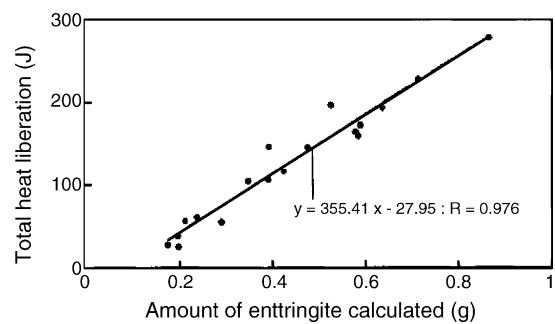


Fig. 13. Relationship between total heat liberation (Q_T) measured and the amount of ettringite calculated using the CaO/SiO_2 ratio of 1.425 for C–S–H.

Finally we calculated the rate of hydration thickness of glasses, which were calculated as;

reaction ratio \times mass of sample/density/specific surface area

Results were shown in Fig. 14 as the relation to the Al_2O_3 content. It was found that there are two groups (Groups I' and II') as like as Fig. 5. In Fig. 5, Group I consisted with G1–G7 and Group II did with G8–G13, but in the relationship

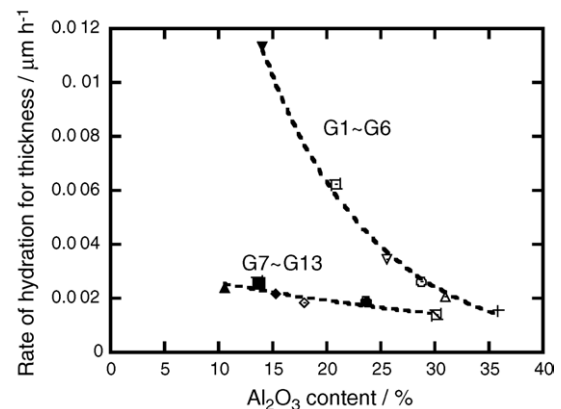


Fig. 14. Relationship between rate of hydration for thickness and CaO content.

between Al_2O_3 content and the rate of hydration in thickness, Group I' was G1–G6 and Group II' was G7–G13.

4. Conclusions

The hydration behavior in the system of glass/gypsum/lime was reported. These experiments were simulated to the hydration of high sulphonated slag cement. The effects of glass components and the amount of lime added on the rate of hydration, the rate of heat liberation and hydration equation were discussed and concluded as follows;

1. There were periods with constant rate of hydration, as shown in Fig. 3, whose periods were proportional to the amounts of lime added in each glass system. The rates of heat liberation in constant rate were related to the basicity of glasses.
2. The times for consuming the mass of lime added (T3) were related to the amount of Al_2O_3 contents in glass, and they were classified in two groups.
3. The products in this system were estimated as ettringite with ideal formula and C–S–H with CaO/SiO₂ ratio of 1.425.
4. Most of all heat of liberation were controlled by the ettringite formation.
5. The rates of hydration for thickness were related to the amount of Al_2O_3 contents and they were classified into two groups. In this classification, one member of G7 behaved differently in the relationship of the times for consuming the mass of lime and in that of the rates of hydration for thickness.

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