Third International Conference on Sustainable Construction Materials and Technologies http://www.claisse.info/Proceedings.htm

Study on Cement Recycling System Using Sodium Gluconate

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ABSTRACT

Most ready-mixed concrete plants have the problem of construction waste sludge, which causes environmental pollution and economic loss. A system for recycling sludge water is therefore needed. This paper discusses the adsorption and action mechanisms of sodium gluconate set-retarder, along with recycling of sludge water, especially hydration control using sodium gluconate.

The delayed time of hydration depends on the concentration of residual sodium gluconate. When the residual concentration of sodium gluconate was over 0.018–0.020 mass%, the hydration of cement did not proceed.

Relationship between the heat liberation at 1day and non hydrated alite amount calculated by XRD method is linear. We can estimate the amount of non-hydrated alite in sludge water by using $Mg(NO_3)_2 \cdot 6H_2O$ and calorimetric data.

Keywords. Sludge water, Sodium gluconate, Set retarder, Rate of heat liberation, Heat liberation

INTRODUCTION

Most ready-mixed concrete plants have a problem of construction waste sludge, which causes environmental pollution and economic loss. A sludge water recycling system is therefore highly desirable.

In Japan, Japanese Industrial Standard (JIS) A 5308 permits the addition of 3% sludge water (as solid state) to cement in concrete. However, it is pointed out that a reduction of fluidity and increase in water demand occur upon use of sludge water.

A set-retarder can delay the hydration of cement within the sludge water. However, there are few studies of the action mechanism of set-retarders effect on cement hydration. To achieve more widespread recycling of sludge by using set-retarders, we have to clarify the action mechanism of hydration control from the point of view of cement hydration.and we also have to establish the evaluation method of residual cement content of sludge.

This paper discusses the adsorption of sodium gluconate and its set-retarding mechanisms. And this paper also discusses recycling of cement sludge, especially hydration control by sodium gluconate and the evaluation method of residual cement content of sludge.

Table-1 Chemical and mineral compositions and properties of ordinary portland cement

	Chemical compositions (mass %)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Cl	SO_3
OPC	21.6	5.3	2.3	64.5	2.11	0.25	0.55	0.11	1.8

	Mineral compositions* (mass %)				Blaine (cm^2/g)	Density (g/cm^3)
	C_3S	C_2S	C_3A	C_4AF		
	64.4	11.6	9.5	8.0	3090	3.17

*Calculated by Bogue's equation

EXPERIMENTAL PROCEDURE

Materials

Alite was synthesized in the laboratory from industrial raw materials and reagents using an electric furnace.

The chemical composition and mineral composition of the ordinary portland cement used as calculated from Bogue's equation are shown in Table 1. The contents of C_3S, C_2S, C_3A and C_4AF are 64.4%, 11.6%, 9.5% and 8.0%, respectively.

Sodium gluconate was used as a set-retarder in this study.

Measurement

(1) Sample preparation

The water to powder (limestone powder, synthesized alite and ordinary portland cement) ratio was 0.5 and the mixing time was 10 minutes. The dosages of sodium gluconate were 0, 0.1, 0.2, 0.4, 1.0, and 2.0 %.

(2) Hydration reaction of cement

The hydration ratio of alite or C_3A was calculated by XRD internal standard method.

(3) Adsorption and residual concentration of sodium gluconate in the liquid phase

The liquid phase in paste was obtained by centrifugal suspension. The residual concentration of sodium gluconate in the liquid phase was measured by a total organic carbon analyzer (TOC -5050A, Shimadzu). The adsorbed amounts of sodium gluconate were then calculated from the concentration of sodium gluconate in the initial solution and the liquid phase after adsorption testing. A 10 minute adsorption time was adopted to reach equilibrium conditions of system.

(4) Measurement of heat liberation

Cumulative heat liberation and rates of heat liberation of ordinary portland cement with or without sodium gluconate were measured using a multi-channel conduction (sandwich-type) calorimeter (Tokyo Riko co.ltd). The time of maximum heat liberation rate (T1) was estimated and used to characterize the hydration of cement.

(5) Measurement of BET specific surface area

After 10 minutes, hydration was stopped by adding a large amount of acetone and the samples were dried on an aspirator (1.0×10^4 Pa). The specific surface area of hydrated cement with various concentrations of sodium gluconate was then measured using N_2 gas adsorption.

EXPERIMENTAL RESULTS AND DISCUSSION

Hydration of cement minerals

Fig. 1 indicates the hydration reaction ratio of alite and C_3A in the initial hydrated cement.

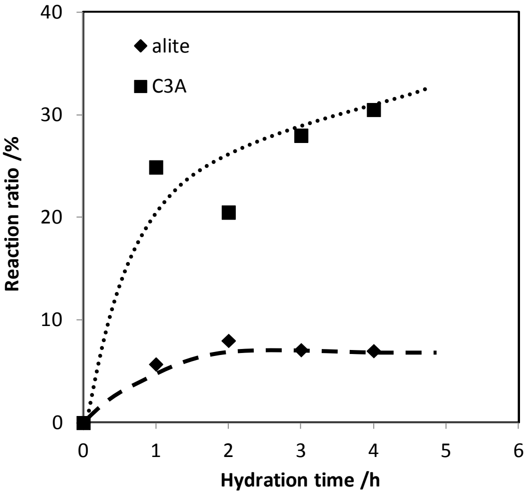

Fig. 1 Reaction ratio of alite and C_3A during initial cement hydration

The hydration ratio of alite is 6~8% at 1hour and no drastically change was observed from 1hour to 4hours. This phenomenon is explained by induced mechanism of alite. C_3A has higher hydration activity and the reaction ratio of C_3A was about 30% at 1hour.

After 4 hours of hydration, the hydration reaction ratios of C_3A and alite were about 30% and 10%, respectively. In other words, 70% of C_3A and 90% of alite still remain as hydration active cement. We could reuse this cement effectively for the environmental loading reduction

Adsorption of sodium gluconate on alite

Fig. 2 shows the isotherm of sodium gluconate on alite.

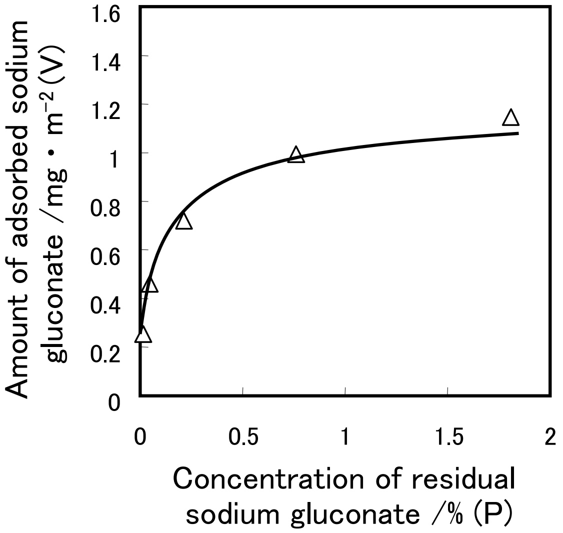

Fig. 2 Adsorption isotherm of sodium gluconate on alite

The amount of adsorbed sodium gluconate on alite (V) gradually increased and adsorption became saturation at about 0.8mass% of sodium gluconate residual concentration. The relationship between P/V and concentration of residual sodium gluconate (P) is linear (Here we omitted this Figure). It is considered that the adsorption of sodium gluconate on alite is Langmuir type adsorption and the cross sectional area of a sodium gluconate molecule calculated from the experimental results was 0.303 nm^2 under saturation.

Hydration control of alite with sodium gluconate

Fig. 3 indicates the relation between the concentration of residual sodium gluconate and the time of maximum heat liberation rate (T1).

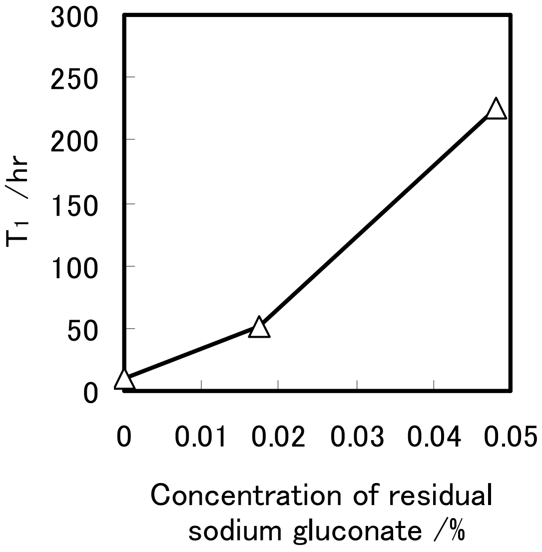

Fig. 3 Comparison of T_1 of sodium gluconate on alite

The retarded time of hydration also depended on the concentration of residual sodium gluconate. This result indicates that we can control retardation time by controlling of the residual sodium gluconate concentration. Hydration was retarded for 220h with 0.05% residual concentration of sodium gluconate in liquid phase. And the hydration of alite was retarded for 40h with 0.019% residual concentration of sodium gluconate in liquid phase.

Hydration control of OPC with sodium gluconate

The relationship between concentration of residual sodium gluconate and specific surface area of hydrated cement after 4 hours hydration is shown in Fig. 4.

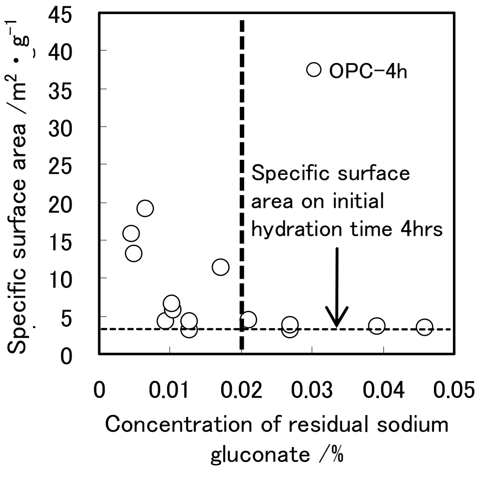

Fig. 4 Relation between concentration of residual sodium gluconate and specific surface area of hydrated cement after elapsed time of 4 hours

Specific surface area of OPC did not change when the residual sodium gluconate in liquid phase was increased. When the residual concentration of sodium gluconate was over 0.018–0.020 mass%, the hydration of cement did not proceed.

Estimation of residual C_3S amount by heat liberation

Table 2 shows the relationship between residual alite amount by XRD internal standard method and cumulative heat liberation of OPC.

Table 2 Relation between residual amount of Alite and heat liberation

Hydration time	0h	1h	2h	3h	4h
Residual amount of Alite[%](XRD)	100	94.3	92.0	92.9	93.0
Heat liberation for 1day[J/g]	167.3	156.2	157.7	159.3	160.3
Relative Heat liberation[%]	100	93.3	94.3	95.2	95.8

There is a linear relation between the cumulative heat liberation at 1day and non hydrated alite amount calculated by XRD method. We can estimate the amount of non-hydrated alite by using calorimetric data.

The swift method of estimation of non-reacted alite amount is needed for practical usage of sludge water.

The influence of $Mg(NO_3)$ ・ $6H_2O$ on the rate of heat liberation of cement paste with or without sodium gluconate after 1hour hydration is shown in Fig. 5.

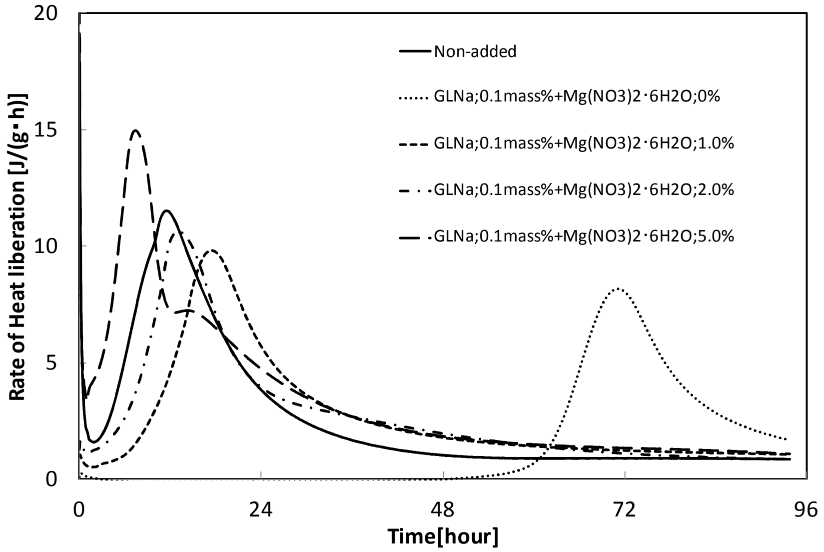

Fig.5 Influence of sodium gluconate and $Mg(NO_3)_2$ ・ $6H_2O$ on the rate of heat liberation

The time of maximum heat liberation rate (T1) of cement paste after 1hour hydration was 11.3 hours without sodium gluconate. T1 was drastically increased from 11.3 to 71.3 hours by adding of 0.1mass% sodium gluconate. And when $Mg(NO_3)_2 \cdot 6H_2O$ was added for cement with sodium gluconate, T1 was decreased. When the dosage of $Mg(NO_3)_2 \cdot 6H_2O$ was 1.0mass%, T1 was 18hours and the dosage was 2.0mass%, T1 was 12.3hours. In the case of 2.0mass% of $Mg(NO_3)_2 \cdot 6H_2O$, the T1 was same as that without sodium gluconate.

Table 3 shows the relation between the dosage of $Mg(NO_3)_2 \cdot 6H_2O$ and the heat liberation of cement paste at 24hours.

Table 3 Relation between dosage of $Mg(NO_3)_2 \cdot 6H_2O$ and heat liberation of cement paste at 24hours

	Non-added	GLNa 0.1mass%			
$Mg(NO_3)_2 \cdot 6H_2O$	0%	0%	1%	2%	5%
T1	11.3	71.3	18	12.3	7.2
Relative Heat liberation[%]	100	2	77.3	90.1	117.5

When the dosage of $Mg(NO_3)_2 \cdot 6H_2O$ is 2.0mass%, the relative heat liberation of cement paste was 90% compared with non-added cement paste. As shown in Table 2, the amount of non-reacted alite was about 90% at 1hour hydration. From these results, we can estimate the amount of non-hydrated alite in sludge water by using calorimetric data.

CONCLUSIONS

This paper discussed the adsorption of sodium gluconate and its set-retarding mechanisms. And this paper also discussed the recycling of sludge water system, which may enable recycling of cement sludge, especially hydration control by sodium gluconate and the evaluation method of residual cement content of sludge water.

The results are as follows.

The adsorption behavior of sodium gluconate on cementitious materials was clarified in this study. The saturated absorption behavior between the sodium gluconate and alite follows a Langmuir adsorption isotherm.

Hydration of alite was retarded for 220h with 0.05% residual concentration of sodium gluconate in liquid phase. And the hydration of alite was retarded for 40h with 0.019% residual concentration of sodium gluconate in liquid phase. The degree of hydration of cement can be controlled by adding sodium gluconate.

The delayed time of hydration depended on the concentration of residual sodium gluconate. When the residual concentration of sodium gluconate was over 0.018–0.020 mass%, the hydration of cement did not proceed.

Relationship between the heat liberation at 1day and non hydrated alite amount calculated by XRD method is linear. We can estimate the amount of non-hydrated alite by using calorimetric data.

Finally, we can swiftly estimate the amount of non-hydrated alite in sludge water by using $Mg(NO_3)_2 \cdot 6H_2O$ and calorimetric data.

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