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Scientific paper

Method for Estimating Quantity of Non-Hydrated Cement in a Cement Recycling System

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Abstract

The objective of this research was to develop a method for the rapid estimation of the quantity of residual cement in sludge water and to control its hydration reaction using sodium gluconate in order to enable the residual cement in sludge water to be effectively utilized. The quantity of residual cement in sludge water can be estimated by measuring the heat of hydration liberated in 24 h using a conduction calorimeter. It is possible to recommence sodium gluconate-controlled cement hydration using magnesium nitrate. A method was developed to simulate the rate of the hydration reaction, which makes it possible to estimate the quantity of residual cement in sludge water by measuring the rate of heat liberation of hydration over 10 h.

1. Introduction

In today's society, where there is a need to implement low carbon recycling systems, the reduction and reuse of waste sludge water from the production of ready-mixed concrete at factories is an important issue. Data from 2006 indicate that about 1 million tons of sludge are generated annually in Japan.

Sludge is a mixture of cement and very fine aggregate that occurs as waste at construction sites or forms when residual recycled concrete is sieved to remove aggregates. Cleaning water that contains a sludge component, which is referred to as sludge water, is formed when water is used to clean equipment such as ready-mixed-concrete mixers and agitators.

To reduce the quantity of sludge formation at ready-mixed-concrete factories, Japanese Industrial Standard A 5308 "Ready-mixed Concrete" prescribes a method of using mortar that adheres to the inside of truck agitator drums. This allows for a solid sludge component of up to 3% (the mass of the solid sludge component as a percentage of the unit cement quantity in the concrete mix) to exist in sludge water when it is used as concrete

mixing water. However, if sludge water is added, the concrete fluidity is reduced and the quantity of water required to produce the concrete increases. This method is not used widely because of its high cost and complicated management of sludge water. The number of ready-mixed-concrete factories that use sludge water as concrete mixing water is low and the amount of industrial waste that they generate after the dewatering process is large.

Sludge water contains fine particles that originate from cement that has already been hydrated, and from non-hydrated cement and aggregates. By using a set retarder such as sodium gluconate (GLNa) or similar, the hydration reaction of the unhydrated cement in the sludge water can be controlled (Atarashi *et al.* 2012a). The sludge water can then be reused effectively to replace a portion of the new cement when producing ready-mixed concrete. This could reduce the required cement production quantity, which would contribute significantly to reductions in CO₂ emissions.

It is necessary to establish a method to determine the amount of non-hydrated cement in the sludge water so that this non-hydrated cement can be used as cement. To date, the authors have found that there is a correlation between the percentage of reacted alite, which contributes to the generation of early strength in cement, and the liberated heat of hydration as obtained from a conduction calorimeter (Atarashi *et al.* 2012b). A prototype conduction calorimeter that is capable of measuring the heat of hydration of cement has been produced jointly with Tokyo Riko, a calorimeter-manufacturing company (Sakai *et al.* 1997). It is suggested that the measurement of heat using a calorimeter can be utilized effectively in cement quality control and inspection (Sakai *et al.* 2010).

The objective of this research was to formulate a method for the rapid evaluation of the quantity of cement remaining in sludge water whose hydration reaction has been suppressed using GLNa. This could enable the effective reuse of residual cement in sludge water. In the

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method, the amount of non-reacted cement remaining in the sludge water is determined using a conduction calorimeter. Furthermore, a method for the rapid evaluation of the quantity of non-reacted cement in sludge water, for which the hydration has been suppressed, was developed using a metallic salt and computer simulation. The objective was to integrate these research results to establish a new cement recycling system to use the cement contained in sludge water effectively.

2. Test outline

2.1 Test materials

The cement used in this study was ordinary Portland cement (OPC) with the properties listed in **Tables 1** and **2**. The chemical composition of OPC was measured in accordance with JIS R5204, and the mineral composition of OPC was calculated from the chemical composition using Bogue's equation. GLNa was used as the set retarder, and magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), which has an accelerating effect on the retarded cement, was used as the metallic salt (Harada 1995, 1996).

2.2 Determining the residual quantity of cement in sludge water

Simulated sludge was produced with a water cement ratio (W/C) of 4.0 without the addition of GLNa and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. It was mixed manually for 3 min at 20°C. After allowing the hydration reaction to proceed for 1 to 24 h at 20°C, the hydration was stopped with a large amount of acetone, and the quantity of residual cement (C_3S) was determined by comparing the areas under the peaks at 51.78 (2theta) obtained from x-ray diffractometry (XRD). The effect of the amount of hydrates was canceled by using weight loss on ignition (Imoto *et al.* 2002).

Sample hydration was stopped with a large amount of acetone for samples that had been hydrated between 0 and 24 h. After drying the acetone by aspirator, the hydration of this cement was recommenced for 24 h at 20°C. The integrated quantity of the heat of hydration liberated from the cement paste was measured using a twin conduction calorimeter (Tokyo Riko, Tokyo, Japan). By comparing the XRD quantitative method and calorimetric data, the validity of the method for determining the quantity of residual alite in the residual cement was investigated.

2.3 Rapid evaluation of the quantity of residual cement in sludge water using metallic salt and a conduction calorimeter

The cement paste (produced using ordinary Portland cement for research purposes) had a W/C of 4.0, and a GLNa content of 0–0.2 mass%. Mixing was carried out manually for 3 min at 20°C. GLNa was added after hydration for 1 h at 20°C to produce simulated sludge water in which the hydration was suppressed. Then, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added at 0 to 8.0 mass% with respect to the cement, and the mixture was sampled. The heat of hydration properties of this simulated sludge water were determined using a conduction calorimeter.

2.4 Liquid phase concentration of GLNa

Centrifugal separation was carried out at 10,000 rpm (3400G) for 10 min on simulated sludge prepared in the same manner as described in Section 2.3. The supernatant water obtained was filtered using a membrane filter with 0.20 μm diameter holes. The residual concentration of GLNa in the liquid phase was calculated using a total organic carbon analyzer (TOC5050A, Shimadzu, Kyoto, Japan).

3. Test results and discussion

3.1 Development of method for determining the quantity of residual cement in sludge water using calorimetric measurement

An investigation was carried out with the objective of establishing a method to determine quantitatively the amount of residual cement in sludge water using a conduction calorimeter.

Figure 1 shows the relationship between the quantity of residual cement (C_3S) in the sludge water and the cumulative heat of hydration liberated during the 24 h period after recommencing the hydration. The cumulative heat of hydration of the non-hydrated cement is expressed as a relative heat of hydration with the cumulative heat of hydration in 24 h being 100.

As the quantity of residual cement in the sludge water increased, the relative heat of hydration in 24 h increased. However the regression curve does not cross the origin because of the background noise of the calorimetric data, a correlation was found between the quantity of residual cement (C_3S) in the sludge water and the cumulative heat of hydration liberated during the 24 h period after recommencing the hydration.

The conventional quantitative determination of the

Table 1 Chemical composition of ordinary Portland cement (mass%) (Measured with JIS R5204).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Other	Total
21.56	4.68	2.98	65.63	1.30	1.90	0.33	0.39	1.23	100.00

Table 2 Physical properties and mineral composition of ordinary Portland cement (mass%) (Calculated with Bogue's equation).

Density (g/cm^3)	Blaine (cm^2/g)	C_3S	C_2S	C_3A	C_4AF	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
3.16	3310	62	15	7	9	3.2

amount of non-hydrated cement remaining in cement must be measured using an XRD internal reference method, which requires skill in measurement and time. The measurement of the heat of hydration as proposed in this research enables the quantity of residual cement in sludge water to be estimated simply and in 24 h.

3.2 Investigation of rapid method to determine the quantity of cement in sludge water using magnesium nitrate

If it were possible to estimate the quantity of residual cement in sludge water rapidly, it would be possible to use the cement in the sludge water occurring in ready-mixed-concrete factories effectively and this could reduce the environmental load.

Figure 2 shows the effect of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on the heat of hydration properties of sludge water to which GLNa has been added.

Time T_1 , which indicates the maximum rate of heat liberation of plain paste, is 11 h as shown by the dashed line on the graph. T_1 for plain paste increases significantly with the addition of GLNa. As reported previously (Song *et al.* 2004, 2008), this occurs because GLNa is absorbed onto the cement surface, thereby suppressing hydration and making it possible to control the reaction of the cement by controlling the GLNa dosage. For example, when this dosage is 0.05 and 0.1 mass%, T_1 is 14 and 29 h, respectively, and at 0.15 and 0.20 mass%, T_1 is more than 50 h. With the addition of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, T_1 decreases as the dosage increases. For example, at a GLNa dosage of 0.1 mass%, when 1.0 and 2.0 mass% $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are added, T_1 is 15 and 11 h, respectively. The latter value is almost the same as the T_1 value of the plain paste without the addition of GLNa and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

It has therefore been shown that by sampling a portion of sludge water in which hydration has been prevented by GLNa and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ addition, it is possible to eliminate the suppression of cement hydration.

3.3 Mechanism of recommencing hydration reaction using magnesium nitrate

The mechanism for recommencing hydration using $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was then investigated.

Figure 3 shows the specific surface area of the solid component of the sludge water and the concentration of GLNa in the liquid phase of the sludge water to which 0.1 mass% GLNa and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at dosage of 0 to 4.0 mass% were added.

As the dosage of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ increases, the concentration of GLNa in the liquid phase decreases rapidly, and the specific surface area of the solid component of the sludge water increases significantly. Also, when the dosage of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is 1.0 mass% or higher, the concentration of GLNa in the liquid phase and the specific surface area of the solid component of the sludge water become almost constant.

The authors have reported that the GLNa is in equi-

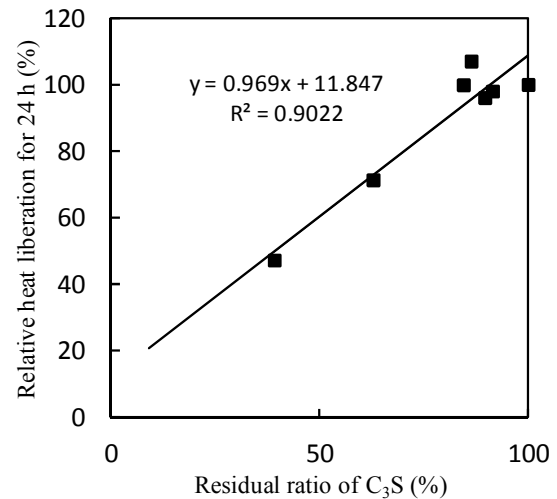


Fig. 1 Relationship between residual ratio of C_3S and relative heat liberation in 24 h.

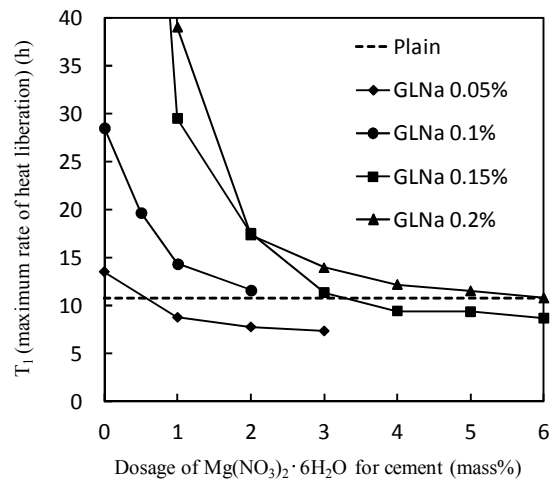


Fig. 2 Influence of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on T_1 .

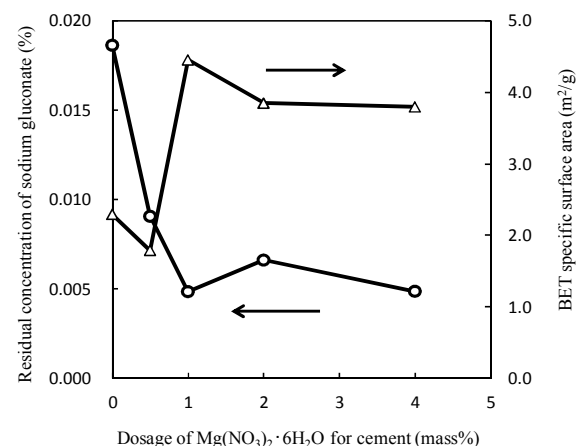


Fig. 3 Relationship between $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dosage and residual concentration of GLNa.

librium Langmuir adsorption on the alite in the cement; that there is a correlation between the concentration in the liquid phase and T_1 ; and as the concentration in the liquid phase decreases, T_1 also decreases (Song *et al.*

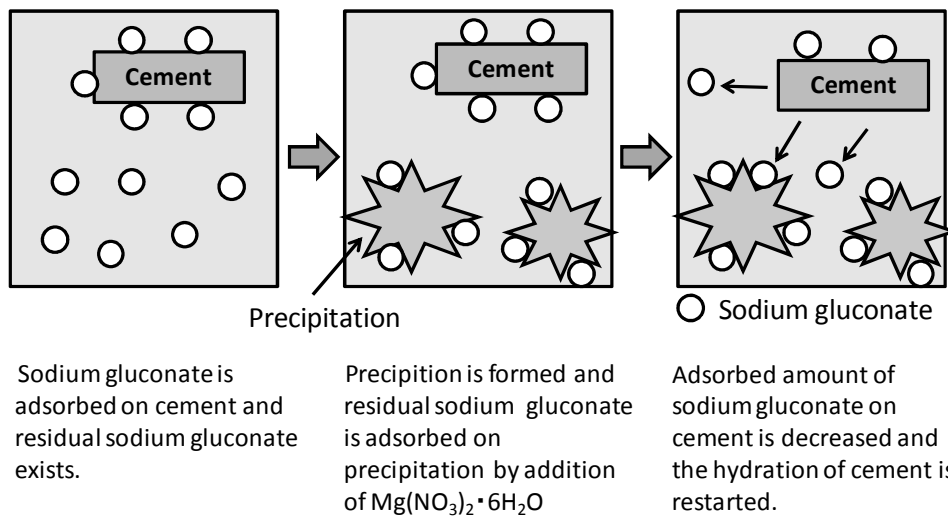


Fig. 4 Schematic illustration of $Mg(NO_3)_2 \cdot 6H_2O$ effect on retardation of cement hydration.

2008). From these results, the mechanism for recommending hydration using $Mg(NO_3)_2 \cdot 6H_2O$ is assumed to be as shown schematically in Fig. 4.

Precipitation was caused by the addition of $Mg(NO_3)_2 \cdot 6H_2O$ so that the specific surface area of the solid component of the sludge water increases significantly, and the residual concentration of GLNa in the liquid phase is reduced accordingly. It is thought that the GLNa that is absorbed onto the alite in the cement is released as a result. The reduction in quantity of absorbed GLNa eliminates the hydration retardation affect, and as a result, hydration recommences.

3.4 Development of a rapid method to estimate the residual cement by predicting the heat liberation curve

A model that is capable of simulating all of the extremely complex compound reaction processes of hydration, including the initial reaction, the latent period, and the rate of heat liberation from the exothermic reaction until the end of the reaction, based on engineering knowledge, has been proposed by Tomosawa (1974). This model uses the following equation to represent the rate of the hydration reaction and the percentage completion:

$$-\frac{d\alpha}{dt} = \frac{3C_{w0}}{r_0^2 v \rho_c} \frac{1}{\frac{1}{k_d \alpha^{2/3} r_0} + \frac{\alpha^{-1/3} - (2-\alpha)^{-1/3}}{D_e} + \frac{1}{k_r \alpha^{2/3} r_0}} \quad (1)$$

where r_0 is the radius of the unreacted cement particles in the initial period, ρ_c is the density of the unreacted cement, k_r is the coefficient of the rate of reaction at the reaction surface, v is the stoichiometric proportion for the reaction between water and cement (mass standard), and C_{w0} is the concentration of water at the surface of the hydration compounds.

It is assumed that the hydration compounds are double the volume of the unreacted cement. Mass transfer coefficient k_d in the initial reaction stage and effective diffusion coefficient D_e of water in the gel are expressed as

functions of the percentage unreacted cement particles, as follows:

$$k_d = \frac{B_d}{1-\alpha} + C_d(1-\alpha)^2, \quad (2)$$

$$D_e = D_E \left(\ln \frac{1}{1-\alpha} \right)^2, \quad (3)$$

By carrying out a simulation of the rate of heat liberation from various types of Portland cement using Eq. (1), it is possible to determine each of the parameters.

By analyzing the amount of change of peak position of the rate of heat liberation by adding GLNa as shown in Fig. 5, the parameters of the Tomosawa model are simulated as shown by Table 3. It reveals that the delay of the reaction by adding GLNa is caused by decreasing mass transfer coefficient k_d . As a result, it is possible to simulate the quantity of additional material such as GLNa in accordance with the peak position.

As shown in Fig. 6, the quantity of residual cement in sludge water can be determined by sampling a portion of the sludge water whose hydration initiation time has been retarded by the addition of GLNa. The metallic salt

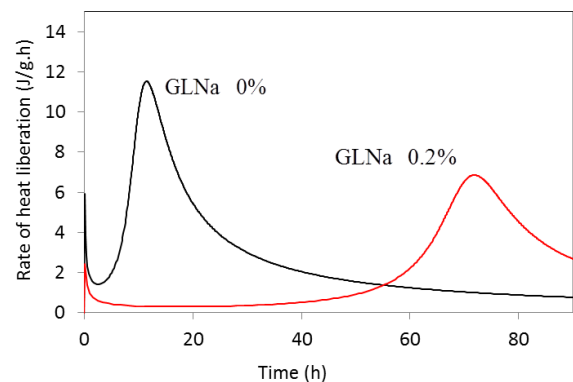


Fig. 5 Simulation results of rate of heat liberation of Portland cement that contains GLNa.

$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ can then be added to obtain a test specimen in which the retarded hydration is restored to the original state, and the rate of heat liberation of hydration from this test specimen can be measured to evaluate the residual quantity of cement in the sludge water.

Approximately 50 h of measurement time are required to simulate this rate of heat liberation. However, by using the properties of the heat liberation curve derived from Eq. (1), it is possible to reduce the measurement time significantly. The process from the initial latent period to the accelerating period in the hydration reaction corresponds to the process from the curve to express a local minimum to the maximum peak in the rate of liberation. Experience has shown that if simulation is carried out up to this peak, the measurement values after the peak can also be described by the simulation. Therefore, by simulating the measurement values for 12 h up to the peak value of the rate of heat liberation, it is possible to predict the entire rate of heat liberation. The results are shown in Fig. 7.

The simulation can be carried out for the heat liberation curve using measurements in 10 h, which is expected to reduce the evaluation time significantly. If it is possible to carry out such a rapid evaluation, then sludge water whose hydration has been suppressed the previous day can be used to produce concrete the following day.

4. Conclusions

The objective of this research was to develop a rapid method for evaluating the quantity of residual cement in sludge water whose hydration reaction has been retarded using GLNa, so that the residual cement contained in the sludge water can be used effectively. A method for determining the quantity of non-hydrated cement in the sludge water (whose hydration has been retarded using GLNa) has been developed using a conduction calorimeter or a computer simulation method. The results are as follows.

- 1) It is possible to estimate the quantity of residual cement in sludge water by measuring the quantity of heat liberated in 24 h using a conduction calorimeter.
- 2) A method to simulate the rate of the hydration reaction was developed. This method enables the quantity of residual cement in sludge water to be estimated by measuring the rate of heat liberation of hydration up to 10 h.

As a result of this research, it is possible to effectively use sludge water that has been inadequately used in the past. Further, the possibility of reusing the cement component in sludge water effectively would allow the cement and concrete industry to increase the use of industrial waste and contribute to the development of a recycling and low carbon society. Therefore, the social and secondary effects of this research are significant.

Japanese cement industry CO_2 emissions are large, next to those of the electrical power and iron and steel

Table 3 Fitting parameters in Eq.(1) simulated at GLNa 0% (Plane) and GLNa 0.2%.

	GLNa 0%	GLNa 0.2%
k_r [cm/h]	6.3×10^{-6}	5.0×10^{-5}
B_d [cm/h]	3.0×10^{-9}	9.0×10^{-10}
C_d [cm/h]	1.2×10^{-3}	1.0×10^{-4}
D_e [cm ² /h]	1.0×10^{-10}	1.0×10^{-10}

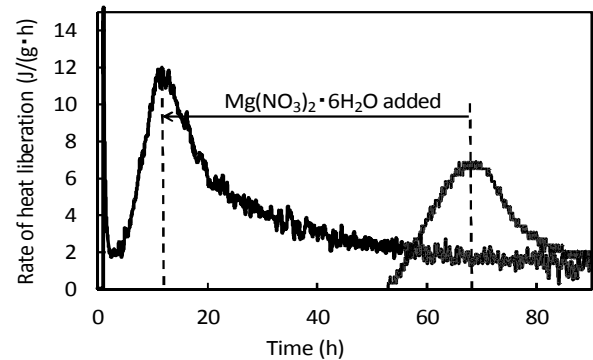


Fig. 6 Influence of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on cement hydration.

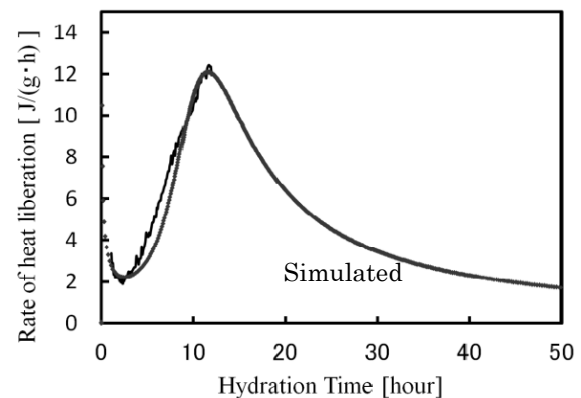


Fig. 7 Result of heat liberation curve by simulation method.

industries. The results from this research are expected to contribute to the achievement of Japan's CO_2 emission targets by further reducing these emissions in cement production.

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