

Hydration Mechanism of Alkali Activated Slag Cement

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(Received February 3, 1999)

For many years, alkali activated blast furnace slag cement containing no ordinary portland cement has received much attention in the view of energy saving and its many excellent properties. We examined the structural change of slag glass which was activated by alkali metal compounds using IR spectroscopy. The properties of hydrated products and unhydrated slag grains was characterized by XRD and micro-conduction calorimeter. Ion concentration change in the liquid during the hydration of blast furnace slag was also studied to investigate the hydration mechanism.

Key words : Hydration, Mechanism, Alkali, Activation, Slag, Cement

I. Introduction

Ground blast furnace slag has a latent hydraulic reactivity, which can be activated by proper activators. The hydration process of slag is very slow without activator. One of the widely used activators is an ordinary portland cement(OPC). Many researchers have investigated the hydration of slags using different activatoers such as gypsum, $\text{Ca}(\text{OH})_2$, NaOH , Na_2CO_3 and so on.¹⁻¹⁰ Among these activators, Na compounds have many advantages in terms of slag activation and mechanical strength development. Alkali activated slag exhibits the different properties depending on the kinds of activators, composition, and atomic coordination state of cations in the slag. The objective of this paper is to investigate the hydration process of alkali activated slag by two Na compounds as slag activators.

II. Experimental Procedure

The chemical composition and fineness of blast furnace

Table 1. Chemical Composition and Fineness of Slag (wt.%)

CaO	MgO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Na ₂ O	Fineness (cm ² /g)
41.9	5.5	16.3	34.8	0.5	0.75	4000

slag used in this study were shown in Table 1. Reagent grade NaOH (abb. NH) and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (abb. NS) were used as activators in this study. XRD analysis showed that blast furnace slag was consisted of mellilite and merwinite. The glass ratio of blast furnace slag was measured by optical microscope after grinding blast furnace slag into powders and the glass ratio of blast furnace slag was 98.1%.

In this research, several tests such as heat liberation during hydration, ion concentration in liquid phase, and microstructure of hydrates were conducted. The conditions of tests are shown in Table 2.

III. Results and Discussion

1. Heat Liberation Test

Table 2. Test Conditions

Experiment	Instrument	Conditions
Heat Liberaton Test	Micro-Conduction Calorimeter	Water/solid: 0.4 Concentration of Activator(Na_2O base): 2, 4, 6 wt. % of Activator (Na_2O base) Temperature: 20°C
Liquid Analysis	Ca, Na-AAS Si, Al, Mg- ICP/MASS	Concentration of solution: 0.3N (NaOH , Na_2SiO_2) Water/solid: 10 Temperature: 20°C
Hydrate Analysis	Infrared Spectroscopy DTA-TG SEM/EDS XRD	Paste Water/solid 0.4 Concentration of each activator (4 wt.%, Na_2O base) Temperature: 20°C (80% RH)

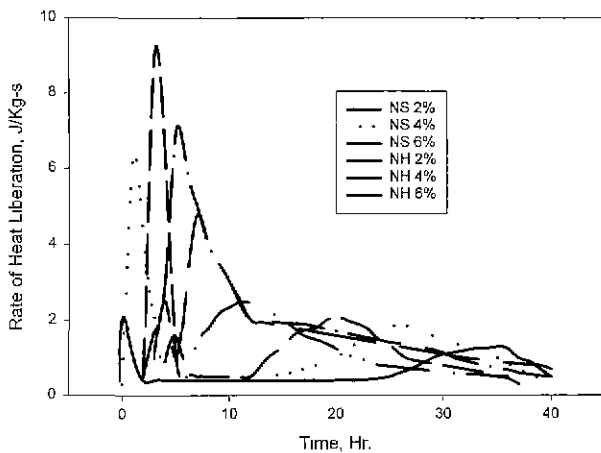


Fig. 1. Heat liberation curves of hydration with time.

The heat liberation curves of NH-slag and NS-slag system were shown in Fig. 1. NH-slag system did not show any dormant period but NS-slag system showed a dormant period. The difference in heat liberation curves between two systems is due to their different hydration mechanism, which will be discussed later. Slag dissolution rate was found to increase with increasing NaOH content, but the amount of Na_2SiO_3 did not affect slag dissolution rate. The heat liberation curve of NS system was similar to that of OPC except the time interval of dormant period.

2. Liquid Analysis

The ion concentration change in liquid phase was shown in Fig. 2. In NH-slag system, the quantities of eluted aluminum, silicon, calcium, and magnesium are as follows:

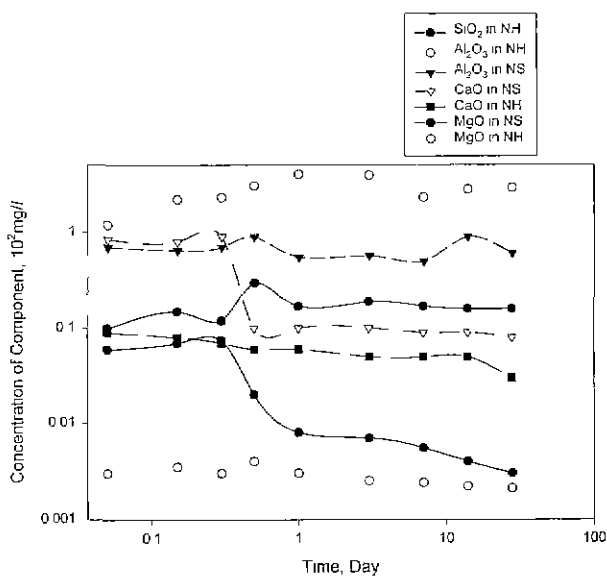
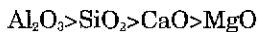


Fig. 2. Ion concentration change of liquid phase with activation time. (0.3N Na base)

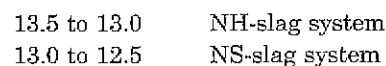
These results agreed well with earlier studies. There is a period of remarkable $\text{Al}(\text{OH})_4^-$ elution in NaOH solution between 1 and 3 days. This phenomenon is a peculiar elution of $\text{Al}(\text{OH})_4^-$, which was proposed by Tsuyuki.²¹ Generally in NaOH solution, it is known that C_2ASH_8 was formed at first as a gel state on the particle surface. After this process, $\text{Al}(\text{OH})_4^-$ was eluted remarkably to the liquid phase. During this process, crystalline C_2ASH_8 was formed, where Si and Ca components on solid-liquid interface reacted with Al components in liquid phase. The surface of slag particles became Al poor structure after elution of $\text{Al}(\text{OH})_4^-$ and C-S-H was formed by topochemical reaction. The strengthening mechanism of slag in NaOH solution is due to this C-S-H formation. Contrary to $\text{Al}(\text{OH})_4^-$, CaO elution was restricted due to the formation of gel film on the particle surface and the elution of MgO hardly occurred. This is due to the fact that MgO containing mineral were not activated by NaOH.

In NS-slag system, the quantities of eluted calcium, aluminum and magnesium up to 6 hrs. was as follows;



Especially, the elution of CaO in glassy phase was remarkably increased up to 6 hrs. and decreased abruptly after that. This period corresponds to the formation of calcium silicate hydrate(C-S-H) and calcium aluminosilicate hydrate(C-A-S-H). The reason for the remarkable elution of CaO was due to the weak formation of gel film by Na^+ ion, which was retained in glassy phase. Unlike the NH-slag system, the quantities of $\text{Al}(\text{OH})_4^-$ kept a certain level during the hydration process without any peculiar elution of $\text{Al}(\text{OH})_4^-$. From this result, we confirmed that the change of C_2ASH_8 from gel to crystalline state did not occur actively in NS-slag system. MgO was remarkably eluted until 6 hrs. and then abruptly decreased similar to the case of CaO. It was concluded from this result that MgO containing mineral was well activated by NS.

In general, slag hydration is accompanied by breaking the network of Si-O-Si or Al-O-Si and liberating network modifier Ca^{2+} at the same time. The early hydration of NS-slag system is controlled by the reaction between the eluted Ca^{2+} and the anion group of activator in liquid phase. The pH change and the quantity of Na^+ remained in solution were shown in Fig. 3. The pH change during hydration period was minor. The pH values of NH-slag and NS-slag system were as follows;



In NH-slag system, the quantity of Na^+ in solution decreased slightly with hydration time. The quantity of Na^+ in NS-slag system was nearly constant. Above results indicate the possibility of Na^+ incorporation into the slag hydrate, especially in NH slag system.

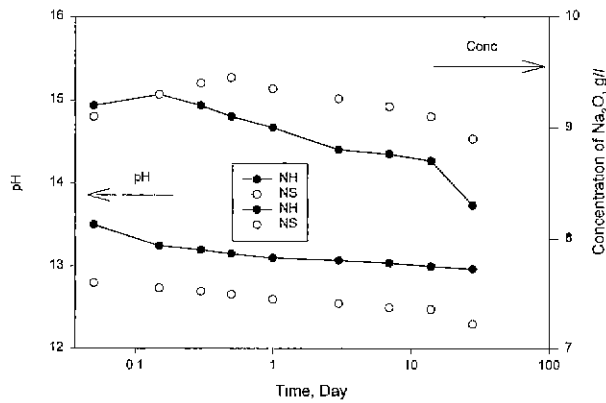


Fig. 3. Change in pH and Na⁺ with time.

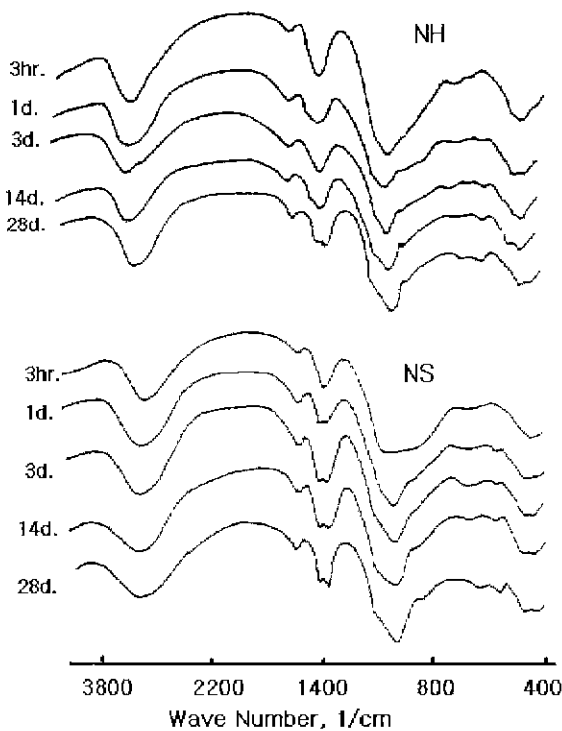


Fig. 4. IR transmission spectra with hydration time in each system.

3. Hydrate Analysis

3.1. Infrared spectroscopy(IR)

IR patterns of hydrated products with hydration time were shown in Fig. 4. The slag glass structure which is consisted of SiO₂ network has a strong absorption band at 1100 cm⁻¹ (Si -O- Si stretching vibration). When Al₂O₃ is added to this structure, Si-O-Si linkages will be inevitably broken and Al-O-Si bonding will be formed. The occurrence of non-bridging oxygen is accompanied by the incorporation of network modifier Ca²⁺ as shown in Fig. 5 and the absorption band of silicon ion shifts to the lower wave number.(spectrum broadening)¹⁰ Slag hydration is accompanied by the breaking Si-O-Si and Al-O-Si network of glassy slag. Many absorption bands are observed

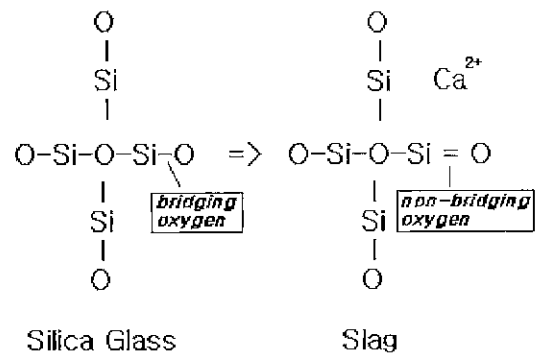
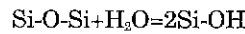


Fig. 5. Schematic diagram of CaO-Al₂O₃-SiO₂ glass system.

at 3300, 1650, 1450, 950, 870, and 600 cm⁻¹. The absorption band at 3300 cm⁻¹ and 1650 cm⁻¹ are the stretching vibrations of Si-OH and H-OH, respectively. The absorption band near at 1450 cm⁻¹ is related to the formation of Na-Al-Si-H₂O hydrate. The band at 950 cm⁻¹ is related to the stretching of Si-O-Si. The intensity of this band is increased with hydration time. The band at 870 cm⁻¹ was due to the stretching vibrations of Si-OH groups according to the following equation;



In NH-slag system, the intensity increase at 870 cm⁻¹ was more clearly revealed. Usually, blast furnace slag contains solid solutions which were made of akermanite (Ca₂MgSi₂O₇)-gehlenite(CaAl(SiAl)O₇) system. Akermanite (Ca₂MgSi₂O₇)-gehlenite (CaAl(SiAl)O₇) solid solution is produced when Al³⁺ is substituted for Mg²⁺ or Si⁴⁺ in akermanite.

From the literature related to the structural analysis of blast furnace slag, it was confirmed that the coordination number of Al³⁺ by O²⁻ changed from 4 to 6 or vice versa depending on the manufacturing process. The absorption band of Al-O vibration is very different depending on the coordination number of Al³⁺, where 700-720 cm⁻¹ is due to the absorption of fourfold-coordinated Al³⁺ and 500-600 cm⁻¹ is due to the sixfold-coordinated Al³⁺.¹⁰ It is very difficult to confirm both bands in the IR spectra of unhydrated glass structure. In this study, the absorption band near 600 cm⁻¹ was observed in all systems and this absorption is related to the sixfold-coordinated Al³⁺ but absorption band at 700-720 cm⁻¹ was not observed. There is a difference in the appearance of absorption peaks between different activator-slag system. The beginning of absorption is faster in NH-slag system than that in NS-slag system until 3 hr. This fact corresponds to the results of heat liberation and liquid analysis although IR spectra were similar in all systems after that.

3.2. Differential thermal analysis(DTA)

DTA curves of the hydrates were shown in Fig. 6. The endothermic peak at 100-130°C represents the hydrates of tobermolite gel. The exothermic peak at 800-900°C represents the slag devitrification, that is, the formation

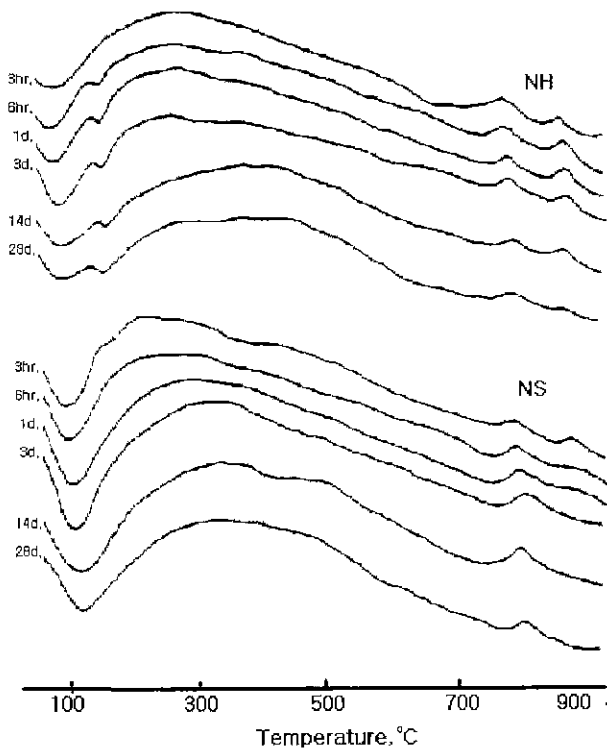


Fig. 6. DTA curves of hydrates with hydration time in each system.

of crystalline minerals; mellilite and merwinite. In NH-slag system, the exothermic peak at 870°C remained until 28 days, which represents a crystallization of merwinite. From this result, it can be considered that merwinite (MgO contained mineral) is not well activated by NH. In NS+slag system, exothermic peak at 870°C did not appear after 6 hours. It corresponds to the result of liquid analysis.

3.3. XRD analysis

SEM/EDS observation on the fracture surface was reported elsewhere.¹³ It showed a wide range of gel character and dense structure in NS-slag system. In NH-slag system, the microstructure was not well developed. EDS analysis was done to confirm Na component remaining on hydrate surface. Na component within the hydrates was detected but it is not obvious whether Na component was incorporated into hydrate or simply adsorbed on the hydrated surface. It is very difficult to identify the incorporation of Na within the hydrates. The unhydrated grain in NH-slag system is a MgO containing mineral. This corresponds to the results of liquid analysis.

XRD patterns of 28 days hydrates were shown in Fig. 7. From XRD analysis, the existence of CSH, C_4AH_{13} , $CaCO_3$ and akermanite was confirmed. The zeolite type minerals were found for all alkali-activated slag. From the fact that the synthesis of zeolite is very difficult at room temperature because its formation is controlled by temperature, zeolites produced in this system were metastable and crystalline zeolites were not found in this

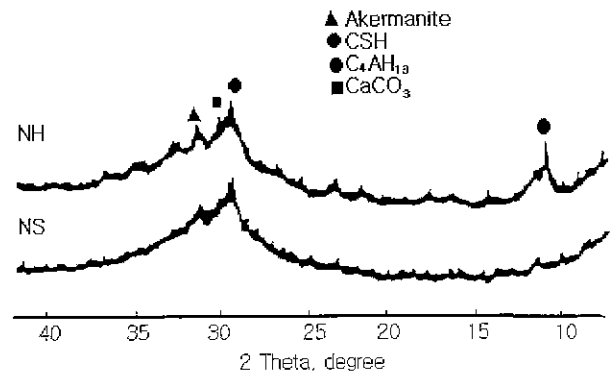


Fig. 7. XRD patterns of hydrates (28 days) in each system.

study.

IV. Conclusions

NH-slag system did not show a dormant period but NS-slag system showed dormant period longer than that of OPC. The ion concentration change of liquid phase was different depending on the activator and the hydration time, which was as follows.

Activator	Quantity of Eluted Ions	
	NH	$Al_2O_3 > SiO_2 > CaO > MgO$
NS	6 hr.	$CaO > Al_2O_3 > MgO$
	6 hr. to 28d.	$Al_2O_3 > CaO > MgO$

In NH system, early hydration process is attributed to the formation of calcium aluminate hydrates (C_3AH_6 , C_4AH_{13}) in solid-liquid interphase. The early hydration process in NS system is attributed to the formation of CSH in solution as gel state. MgO containing mineral was well activated by NS and Na^+ component was remained in CSH but it was not obvious whether Na^+ is incorporated into CSH or not.

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