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Characteristics of Alkali-activated Natural Hwangtoh Paste Utilizing Microwave Heating

Kim, Baek-Joong Yi, Chong-Ku* Kang, Kyung-In
School of Civil, Environmental and Architectural Engineering, Korea University, Seongbuk-Gu, Seoul, 136-713, Korea

Abstract

In this study, the potential use of indigenous natural loess(Hwangtoh) as a new construction material, via alkali activation in conjunction with microwave heating, was investigated. Hwangtoh pastes with three different mix proportions of varying alkali liquid concentrations at a constant liquid-to-Hwangtoh ratio of 0.55 were prepared. Through the investigation it was found that it is possible to prepare Hwangtoh paste with 19.02 N/㎟ at the age of 4 hours with the alkali solution of 8M NaOH and 1:4.5 mass ratio of liquefied Na_2SiO_3 at the curing temperature of 60℃ by microwave heating. The strength development at early age of the alkali activated Hwangtoh paste specimens may be attributed to both a higher rate of reaction and moisture evaporation due to microwave heating

Keywords : microwave, heating system, geopolymerization, hwangtoh

1. Introduction

With interest in environmental issues on the rise, there is an urgent demand to reduce the quantity of cement currently used, and to apply new construction materials that can replace cement, which is known to consume a lot of energy in the manufacturing process, and emit a large quantity of CO_2. To reduce the volume of cement currently used, industrial by–products with latent reactivity such as fly ash, blast furnace slag, and silica fume are being used as supplementary cement materials, and efforts have been made to develop new eco–friendly substitutes for cement, by applying alkali activation process to raw materials, which contain a large quantity of reactive oxides such as quartz sand, aluminum silicate in combination with caustic lime. Recently, it has been reported that kaolin–like material can be solidified using the alkali–activated geopolymerization process.

Studies on the geopolymerization process fall into two main categories depending on the properties of the raw material used[1,2]. One involves the activation using a low–alkali activator, in which blast furnace slag (BFS), mainly composed of Si and Ca, is commonly used [3,4,5,6,7]. It has been reported that a compressive strength of 40MPa or higher can be reached through room temperature curing, but the decline in constructability and drying shrinkage caused by the rapid solidification are reported as disadvantages in this method. The other is a method that activates the materials mainly composed of Si and Al, such as fly ash (FA), silica fume (SF), and metakaolin (MK), using high concentration of alkali activator[8,9,10,11,12,13]. Although the second method requires a curing temperature of 50° C or higher, it is known to offer the advantages of a compressive strength of 60MPa or greater and

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* Corresponding author : Yi, Chong-Ku
[Tel: 02-3290-3329 , E-mail: chongku@korea.ac.kr]

enhanced durability.

With the recent interest in using eco-friendly materials, the geopolymerization process has been applied to studies on the utilization of natural resources such as kaolin, which contains a large quantity of Si and Al[14]. A previous study showed that kaolin can be adequately activated to satisfy the conditions stipulated in the Korean Industrial Standard (KS) for the manufacture of bricks, including the requirements for compressive strength and absorption rate. However, the mixture required curing at a high temperature of 50° C or higher[15], resulting in a energy-inefficient production, when a conventional oven was used.

This study was carried out in an attempt to seek an efficient curing method that could serve as an alternative to the conventional heating oven and to improve the productivity of kaolin-based geopolymers. Herein, a geopolymerization process using microwave heating was applied to indigenous Korean natural loess (Hwangtoh), and the characteristics of the alkali-activated natural Hwangtoh paste were analyzed and reported.

2. Experiment

Hwangtoh, a material similar to kaolin, was solidified through the geopolymerization process under different curing methods to evaluate the differences in the productivity, based on the curing period in the manufacturing process. The test specimens were prepared using pastes of natural Hwangtoh and varying alkali activators. Specimens in A series were cured using the conventional thermal method (conduction and convection), while B series were cured by microwave heating.

2.1 Test Material

2.1.1 Natural Hwangtoh

The Hwangtoh used in this study was produced in Gyeongsangbuk-do, Korea., The elemental analysis of the Hwangtoh (Table 1) shows that it is mostly composed of silica, aluminum, and iron with the presence of relatively small amounts of titanium, calcium, magnesium.

Table 1. Chemical properties of Hwangtoh(mass%)

SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2	CaO	MgO
48.8	31.9	14.4	1.3	0.79	0.71	1.40

The Hwangtoh produced in Gyeonggsangbuk-do was compounds of aspheric and amorphous particles 2 mm in diameter or smaller. In order to improve the reaction with alkali activator, the Hwangtoh was crushed to particles, 200 ㎛ or smaller in diameter before use. The final particle size distribution is shown in table 2.

Table 2. Particle size distribution of Hwangtoh(mass%)

Smaller than particle size(㎛)	5	10	50	100	150	200
Cumulative rate(%)	12.56	28.45	55.79	87.31	97.68	100

2.1.2 Alkali activator

6M and 8M sodium hydroxide solution (NaOH) and liquefied sodium silicate (Na_2SiO_3) were used as the activator. The chemical composition of the liquefied Na_2SiO_3 is presented in Table 3.

Table 3. Chemical composition of liquefied Na_2SiO_3

SiO_2	Na_2O	Water(H_2O)
28.1%	9.2%	62.7%

Table 4. Mix proportions of Hwangtoh paste

No.	Liquid/Binder ratio	Hwangtoh	NaOH solution			Liquefied Na_2SiO_3		
No.	Liquid/Binder ratio	Hwangtoh	Molarity	NaOH	Water	Na_2O	SiO_2	Water
I	0.55	100	6M	10.20	39.80	0.46	1.405	3.135
II	0.55	100	8M	13.10	36.90	0.46	1.405	3.135
III	0.55	100	8M	11.79	33.21	0.92	2.81	6.27

2.2 Mix and experiment method

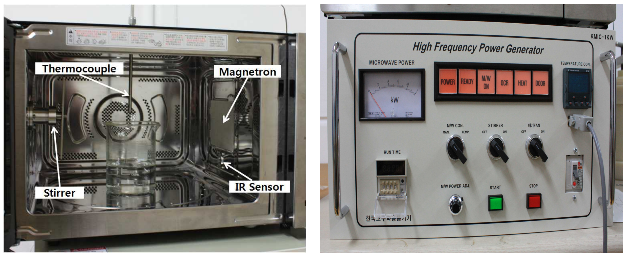
Table 4 shows the mix proportions and experiment parameters considered in this study. Hwangtoh pastes were prepared by thoroughly hand mixing the Hwangtoh and theliquid activator at the liquid to binder ratio of 0.55, which was chosen based on the previous fluidity test results[15].

The dimensions of the specimens were 50 mm × 50 mm × 50 mm in compliance with KS L 5105. Before the specimens were removed from the molds, all specimens had been cured at 60±1℃ for 6 hours. The specimens were then classified by curing method into A and B series; where A series were cured for 7 days in an environmental chamber at 60±1 ° C and 40±1 % relative humidity, while B series were cured for 4 hours using a microwave heating machine. Compressive strength and weight changes of the specimens were measured at different curing age for both series.

2.3 Microwave curing

The alkali activation of Hwangtoh paste requires a certain level of temperature for stable reactivity. To maintain a desired activation temperature, conventional heating via conduction or convection is often used though, the method yields a low energy efficiency. On the other hand, microwave heating vibrates the water particles within a body, causing friction between molecules and efficiently generating heat. It is evaluated to be energy efficient and is not affected by the shape of the specimen.

The microwave heating system consists of a) microwave generator, b) microwave power control system, and c) monitoring system. The microwave generator is composed of a magnetron that converts electric energy into microwaves, and a stirrer that evenly distributes the microwave within the cavity of 250 mm × 300 mm × 230 mm. The control system is designed to control the power of the magnetron in two modes: one is to maintain a constant temperature of the specimen according to the readings from IR sensors or thermocouple, the other is to maintain an assigned power level (power priority control). In addition, the monitoring system includes an auto tuning function that prevents any rapid changes in an actual test based on the monitoring results of the temperature change of the specimen and power used for the magnetron that generates microwave, and the preliminary test results. Figure 1 shows the prototype microwave heating system used for this research.



(a) Cavity (b) Controller

Figure 1. Prototype Microwave Heating System

Power priority control was tried first to determine an appropriate power level for the curing of the specimen. Temperature change of the natural Hwangtoh paste specimens were recorded at the magnetron power level ranging from 40W to 80W with an increment of 20W. The average temperature change recorded at the core of specimens I, II and III is illustrated in Figure 2.

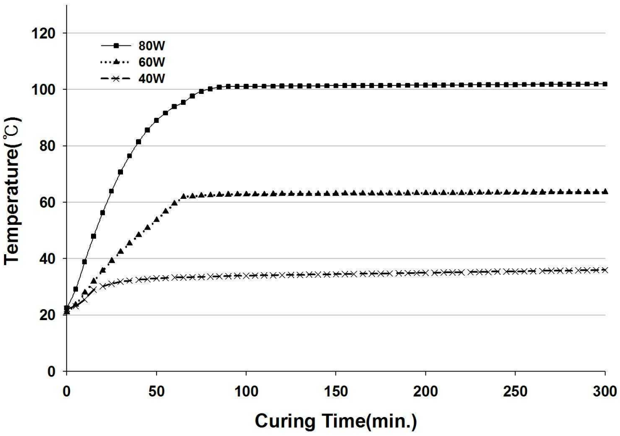


Figure 2. Temperature versus curing time curves at different magnetron power levels

As the power of the magnetron increased gradually, the temperature at the core of the specimen increased accordingly. For the series B, the magnetron was set at 60W based on the result shown in Figure 2 to obtain the temperature level similar to that of A series cured in a constant temperature and humidity chamber.

3. Experiment results and analysis

3.1 Compressive strength of natural Hwangtoh paste

The compressive strengths of the specimens at different curing ages are shown in Table 5. At 7 days, the compressive strength of specimens I and II with 0.046 mass ratio of Na_2O were 12.39N/mm^2 and 13.79N/mm^2, respectively. For specimen III, with 0.092 mass ratio of Na_2O with identical NaOH mol concentration to that of specimen II, the compressive strength of 18.66 N/mm^2 was measured at 7 days. From these results, it can be deduced that Na_2SiO_3 has a greater impact on the development of compressive strength of Hwangtoh paste than NaOH. In addition, specimens I and II, which had a relatively small amount of Na_2SiO_3, showed a lower rate of increase in compressive strength after 5 days, while specimen III slowed in its incremental rise in compressive strength after 3 days. It seems that the presence of Na_2SiO_3 is conducive to a higher rate of reaction, and the development of compressive strength at initial setting can be attributed to moisture evaporation.

Table 5. Compressive strength of Hwangtoh paste(A series)

Specimen		Compressive strength (N/mm^2)			
Specimen		1day	3day	5day	7day
I	a	4.24	6.74	9.88	12.54
I	b	4.31	6.17	10.48	12.28
I	c	4.12	6.24	10.67	12.36
II	a	4.32	7.65	12.63	14.21
II	b	4.82	8.38	12.30	14.13
II	c	4.64	8.32	12.53	13.04
III	a	5.45	14.62	17.45	18.45
III	b	5.82	15.16	18.01	18.89
III	c	5.76	14.73	17.83	18.65

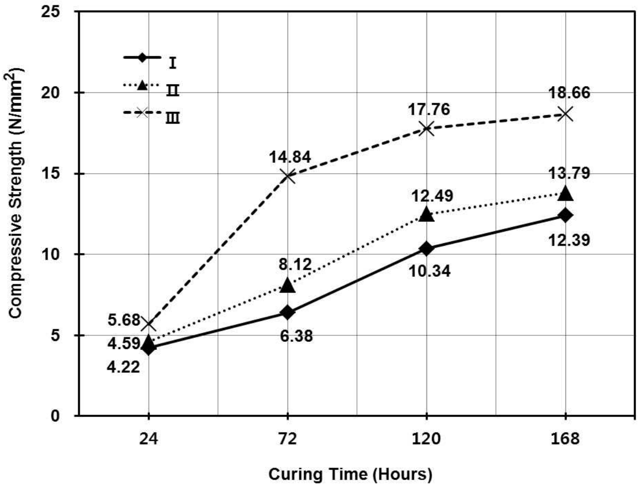


Figure 3. Compressive strength development versus curing time (A Series)

Table 6 shows the compressive strength of all specimens in B series by age, and Figure 4 shows the average compressive strength of B series, which were cured at the magnetron power of 60W which yielded a specimen temperature of 60℃ at the core. The compressive strength of B series was developed earlier than that of A series. In terms of compressive strength of the specimens, with 0.0046 mass ratio of Na_2O in liquefied Na_2SiO_3 to binder, 16.24 N/mm^2 and 17.36 N/mm^2 were the measures taken at 4 hours for specimen I with 6M NaOH and specimen II with 8M NaOH, respectively. In the case of specimen III, with 0.092 mass ratio of Na_2O at NaOH mol concentration identical to specimen II, the compressive strength of 19.02 N/mm^2 was measured at 4 hours. As in A series, the compressive strength of B series increased as the NaOH mol concentration increased and the higher volume of Na_2SiO_3 was used.

Table 6. Compressive strength of Hwangtoh paste(B series)

Specimen		Compressive strength (N/mm^2)			
Specimen		1h	2h	3h	4h
I	a	7.54	11.88	15.37	16.25
I	b	7.27	13.2	15.89	16.23
II	a	8.13	14.28	17.23	17.5
II	b	8.39	14.15	16.67	17.22
III	a	8.91	16.88	18.56	18.95
III	b	9.26	17.09	18.86	19.09

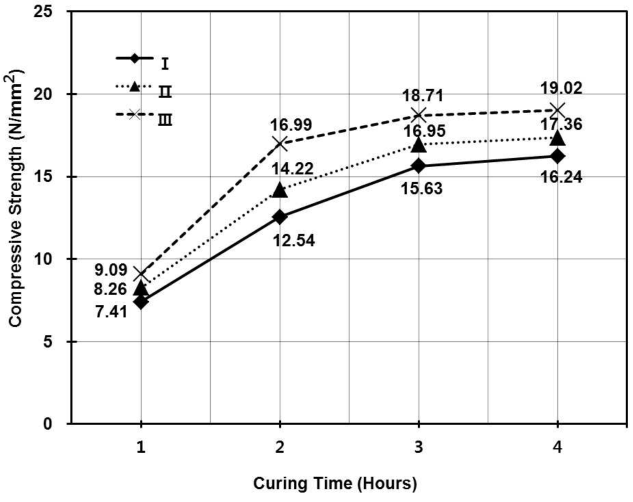


Figure 4. Compressive strength development versus curing time(B Series)

3.2 Compressive strength development versus degree of moisture evaporation

The moisture evaporation was monitored by measuring the weight of specimens in both A and B series by age, to evaluate its relation with the development of compressive strength. Specimen III, which showed the highest compressive strength in A and B series, was chosen for this purpose. Specimen III contained 25.47% moisture by total weight of the specimen when manufactured. The weight loss of the specimen was caused by moisture evaporation during curing. A relatively high rate of weight loss was found at an initial setting. In fact, 98.4% and 98.8% of moisture were evaporated at 7 days in A series and at 4 hours in B series, respectively. Figure 5 illustrates the development of compressive strength with the moisture evaporation over curing time. It was found that there was a gradual increase in compressive strength as more moisture evaporated over time. In comparison with A series, the total curing period needed for equal degree of moisture evaporation was greatly reduced in B series, and the compressive strength of B series at the same degree of moisture evaporation was higher as well.

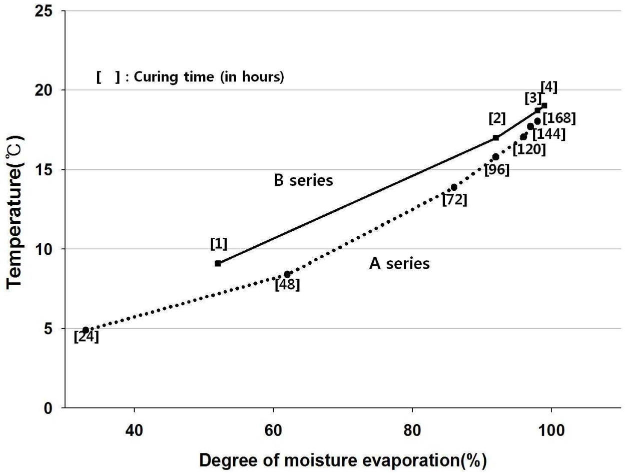


Figure 5. Compressive strength development versus degree of moisture evaporation

3 Review of appropriateness as a construction material

In the production of natural Hwangtoh–based alkali–activated binder through the geopolymerization process, only 1/40 of the curing time is required compared to that of the existing method of conduction or convection at 60℃, greatly improving productivity. To verify the appropriateness of the binder cured by microwave heating as a construction material, the quality standard of representative construction materials stipulated in KS was reviewed, and the summary of related information is shown in Table 7.

Table 7. Quality standard of construction Materials

Items		air dried gravity	Compressive Strength (N/mm^2)	absorption ratio (%)	standards
Concrete Brick	A	less than 1.7	more than 8	–	KS L 4004
Concrete Brick	B	less than 1.9	more than 12	–	KS L 4004
Concrete Brick	C–1	–	more than 16	less than 7	KS L 4004
Concrete Brick	C–2	–	more than 8	less than 10	KS L 4004
Ash Brick		–	more than 8	less than 15	KS L 8520
Clay Brick	1	–	more than 22.54	less than 10	KS L 4201
Clay Brick	2	–	more than 20.59	less than 13	KS L 4201
Clay Brick	3	–	more than 10.78	less than 15	KS L 4201

The compressive strength of natural Hwangtoh–based alkali activated binder (16.24~19.02 N/mm^2) is slightly lower than the requirement for the first class KS clay bricks of 22.54 N/mm^2, but satisfies the requirement for unburned concrete bricks of 16 N/mm^2. In addition, the absorption ratio of the binder (7.8–8.0%) is slightly higher than the requirement for C type 1st class concrete bricks (7%) indicated in Table 7, but it is below 10%, which is the standard for construction materials made of clay, which shares similar properties with Hwangtoh. Thus, there are possible uses of natural Hwangtoh–based alkali activated binder as a construction material , and it is believed that its use will include a greater number of applications with future research.

Table 8. Characteristics of alkali-activated natural Hwangtoh paste utilizing microwave heating(Curing time: 4 hours)

No.	Compressive Strength (N/mm^2)	absorption ratio (%)
I	16.24	8.0
II	17.36	8.0
III	19.02	7.8

4. Conclusion

The effect of microwave heating on the productivity of kaolin–based geopolymers was studied in this research by comparing the characteristics of alkali–activated Hwangtoh pastes cured by conventional method and microwave heating. Based on the results obtained in the study, the following conclusions were drawn:

1) For Hwangtoh paste produced through the geopolymerization process at liquid binder ratio of 0.55, Na_2SiO_3 seems to have a greater impact on the development of compressive strength than NaOH.
2) When using microwave heating, the time was reduced to 1/40 of the time required to develop a given compressive strength compared to that when using a conduction or convention method. Thus, microwave heating seems to be a promising alternative to the conventional method.
3) It was found, through the experiment, that Hwangtoh binder with compressive strength of 18MPa with absorption ratio of 8% can be

prepared in 4 hours of curing when using the mix proportion and microwave heating presented in this study. Furthermore, the aforementioned compressive strength and absorption ratio of the Hwangtoh binder were found to be in accordance with the construction materials requirements for concrete bricks per the quality standard of representative construction materials stipulated in the related Korean Standards.

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