Kinetics and Mechanisms of Hydrothermal Reaction of Granulated Blast Furnace Slag

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Kinetics and mechanisms of hydrothermal reactions of the systems slag-lime-water (I) and slag-quartz-lime-water (II) have been studied. In the initial stage of reaction in system (I), nearly amorphous calcium silicate hydrate with low lime content was formed and continued to grow in strength. Formation of hydrogarnet ($3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$) accompanied by the crystallization of calcium silicate hydrate caused a reduction in strength. In the reaction in system (II), a product with high lime content was formed which was then changed into a low lime product after complete consumption of free lime. Slag was highly reactive but inhibited reaction of quartz, especially during the initial stage of the hydrothermal solidification process. The rate of hydrothermal reaction as well as the characteristics of the products change considerably with temperature.

The reactivity of granulated blast furnace slag subjected to hydrothermal reaction for a long time was compared with that of quartz, silica glass[1] and other silicates.[2] However, the composition and physical state of the compounds obtained by the hydration of slag has not been clarified. Blast furnace slag, especially granulated one, has been used as a raw material for cement.[3] Advantages attained by the use of slags are: (1) omission of the process of combining CaO and SiO_2, and (2) economization of limestone and fuel. The hydraulic properties of slag are dependent on composition included in the quaturnary system SiO_2–Al_2O_3–CaO–MgO, the presence of constituents other than those main components and the amount of crystalline material in the quenched slag.

Kondo and Ohsawa[4] reported a method to determine the amount of granulated blast furnace slag as well as the rate of hydration of slag in cements. However, the kinetics and mechanisms of the hydrothermal reaction have not yet been studied.

Kondo and Daimon[5] analyzed the hydration of tricalcium silicate as an example of solid reactions having induction and acceleration periods. The first product, which may have a structure similar to the reactant, forms on the surfaces of reactant grains. The nuclei of the stable product are produced in the first product layer and act as reaction centers; the main reaction to form a stable product occurs rapidly in the acceleration period. In the hydration of calcium silicates, hydrates produced in this stage are poorly crystalline and metastable, turning gradually to more stable form.

In the present paper, we give the kinetics and mechanisms of two hydrothermal reactions: (I) slag-lime reaction; and (II) slag-quartz-lime reaction. Slag and quartz having narrow particle size distribution were used in order to obtain better results.

Experimental

Starting Materials. Granulated blast furnace slag consisting of calcium oxide, 44.0%; silica, 34.3%; alumina, 15.5%; and magnesia, 3.4% was used. These contents are approximately the average of compositions of slags produced in Japan. Slag was first ground and particles of radii 5—10 μ were then isolated by methanol elutriation. Quartz with particle radii 3.5—5 μ and very fine powder of highly purified, special grade calcium hydroxide were used.

Autoclaving. Two mixtures were prepared. (1) Slag (80 wt.%) and calcium hydroxide (20 wt.%) were mixed for 1 hr with use of ethanol to attain homogeneity. Ethanol was evaporated and 20 wt.% of water was then added to the dry mixture which was stirred for 3 min. From the paste produced, cylindrical specimens of 3.14 cm^2 in cross-sectional area and 1 cm in height were moulded at a pressure of 50 kg/cm^2 (157 kg/3.14 cm^2). (2) Slag (50 wt.%), quartz (30 wt.%) and calcium hydroxide (20 wt.%) were mixed and moulded according to the same procedure. The moulds were placed in containers at 100% humidity for 4 hr in order to attain initial setting, then D-dried for 24 hr and kept in vacuum desiccators.

The specimens were autoclaved; temperature was raised at a rate of 2 °C/min and then kept at 180.5 ± 0.8 or 213.1 ± 0.4 °C, each for 0.5, 2, 6, 12 and 24 hr. Steam was then released for cooling. Specimens were transferred to a desiccator, and then dried in CO_2 free nitrogen atmosphere at 105 °C for 24 hr in order to remove free water (saturated steam pressure, 10.0 and 20.0 atm at 180.5 and 213.1 °C, respectively).

Examination of Specimens. After being dried, the specimens were tested for compressive strength. Free CaO, uncombined slag, free silica and combined (non-evaporable) water contents were determined with crushed samples. A mineralogical examination was also made by means of X-ray diffraction, the hydrates formed being identified.

The free CaO content was determined as follows. The sample (0.5 g) was dispersed in a glycerol/ethanol mixture (1 : 5 v/v, 40 cm^3), together with a small amount of barium chloride (0.5 g) as a catalyst, and phenolphthalein as an indicator. This mixture was kept boiling while being titrated with a standard ammonium acetate solution. Boiling and titration were continued until pink coloring no longer appeared.

The amount of free silica was estimated from the amount of insoluble residue. The sample (0.5 g) was treated first with 2 M-hydrochloric acid (30 cm^3) at 60 °C. The residue was treated with 5% sodium carbonate solution (50 cm^3) at 100 °C for 15 min, ignited and weighed.

Combined water was regarded as being equal to the ignition loss with correction as regards the free lime, taking into consideration the fact that each one mole of free CaO is accompanied by one mole of non-evaporable water.

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The uncombined (free) slag was determined by means of X-ray diffraction with calcium fluoride as an internal standard. Conversion of amorphous granulated slag into the crystalline form was carried out by heating at 900 °C for 5 min. The calibration curve was obtained with binary mixtures of crystalline slag and quartz with various weight ratios. The diffraction lines were selected to be those at 2.85 A (31.4° 2θ) and 3.153 A (18.3° 2θ) for crystalline slag (melilite) and CaF_2, respectively. Each sample was ground, heated at 900 °C on a platinum sheet for 5 min and then mixed with CaF_2 (10 wt.%) with the use of ethanol to ensure the homogeneous mixing. After being dried, diffraction pattern was obtained between 35° and 25° in 2θ, using Cu $K\alpha$. The percentage of uncombined slag was regarded as the average of the closest four determinations.

For the determination of free slag, the method by Kondo and Ohsawa[4] is applicable only to reactions at lower temperature provided that the hydration products are nearly amorphous. The method cannot be applied under hydrothermal conditions due to the fact that the crystalline hydration products remain insoluble.

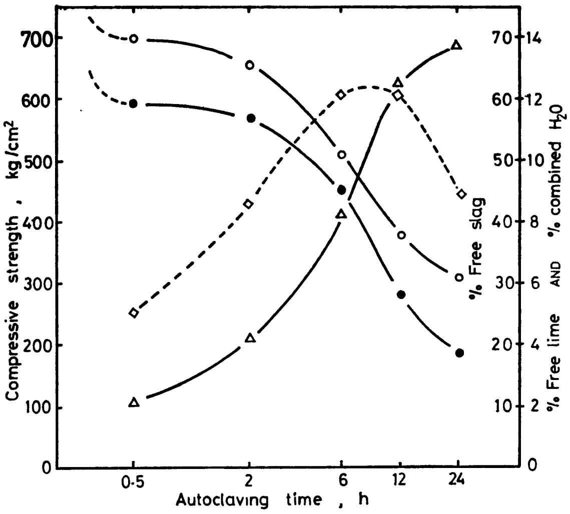

Fig. 1. Slag–lime–water system at 181 °C.
◇: strength, ○: free lime, ●: free slag,
△: combined H_2O.

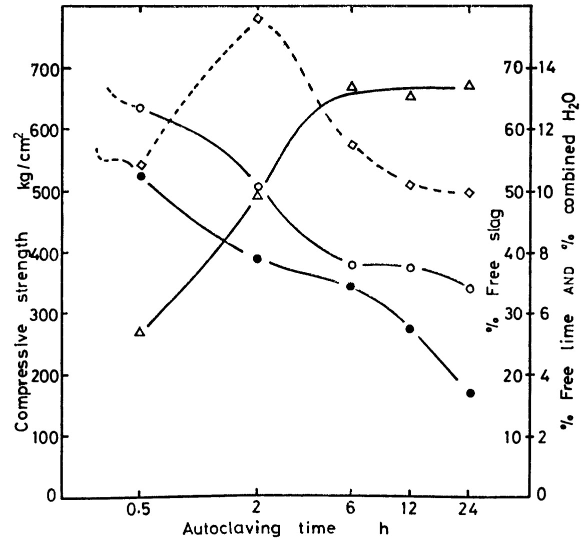

Fig. 2. Slag–lime–water system at 213 °C.
◇: strength, ○: free lime, ●: free slag,
△: combined H_2O.

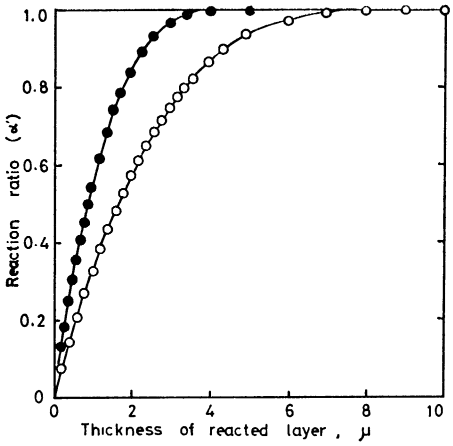

Fig. 3. Relation between reaction ratio and thickness of the reacted layer.
○: particle size 5—10 μ radius
●: particle size 3.5—5 μ radius

Results and Discussion

(I) Slag–Lime–Water System. The free CaO, combined water and uncombined slag contents together with the compressive strength of the specimens autoclaved at 181 and 213 °C are shown in Figs. 1 and 2, respectively. These values were calculated on the basis of the ignited weights of specimens. The molar compositions of the formed hydrates as well as some other data are given in Tables 1 and 2. The reaction ratio of CaO was defined as the ratio of combined CaO to the total CaO concerned with added $Ca(OH)_2$. The thickness of the reacted layer on surfaces as a function of the reaction ratio (reacted slag/total slag) is shown in Fig. 3. The experimental values of α' were used to calculate q, the depth of the reacted layer. It was assumed that $\alpha' = 1-(r_0-q)^3/r_0^3$, where r_0 is the radius of a particle before the reaction takes place. If we assume that the proportion of the particles having a radius r is constant, and the minimum and maximum sizes are a and b respectively, the relationship between α' and q can be calculated by

$$1-\alpha' = \frac{\int_a^b (r-q)^3 \mathrm{d}r}{\int_a^b r^3 \mathrm{d}r} = \frac{1}{(b^4-a^4)}[(b-q)^4-(a-q)^4]$$

for $q<a$, and

$$1-\alpha' = \frac{\int_a^b (r-q)^3 \mathrm{d}r}{\int_a^b r^3 \mathrm{d}r} = \frac{1}{(b^4-a^4)}(b-q)^4$$

for $q \geq a$. For slag with particle radii 5—10 μ, the values of a and b are 5 and 10 μ, respectively. The depth of the reacted layer on the particles for all the specimens can be estimated from Fig. 3.

Reaction at 181 °C (10 atm): Nearly amorphous calcium silicate hydrates were formed as the initial product. X-ray diffraction study showed that during the first 6 hr the only phase identified was calcium silicate hydrates. Subsequent crystallization of calcium hydrosilicate led to the continuous growth of strength.

TABLE 1. CHARACTERISTICS OF SLAG–LIME–WATER SYSTEM AT 181 °C

Autoclaving time	0.5h	2h	6h	12h	24h
% Ingited hydration products	26.7	30.2	44.8	64.5	75.6
Reaction ratio of CaO	12.3	17.8	36.1	52.8	61.4
Reaction ratio of slag	29.9	32.5	46.5	66.7	78.4
Depth of reacted layer on slag particles	0.90μ	0.99μ	1.55μ	2.50μ	3.30μ
Molar compositions of the formed hydrates referred to one mole of ($SiO_2+Al_2O_3$):					
CaO	1.28	1.34	1.45	1.46	1.45
SiO_2	0.79	0.79	0.79	0.79	0.79
Al_2O_3	0.21	0.21	0.21	0.21	0.21
H_2O	0.66	1.18	1.63	1.71	1.60

TABLE 2. CHARACTERISTICS OF SLAG–LIME–WATER SYSTEM AT 213 °C

Autoclaving time	0.5h	2h	6h	12h	24h
% Ignited hydration products	34.9	50.9	58.1	65.3	76.3
Reaction ratio of CaO	20.8	36.5	52.8	53.0	57.5
Reaction ratio of slag	37.5	53.6	59.1	67.6	79.9
Depth of reacted layer on slag particles	1.18μ	1.83μ	2.10μ	2.55μ	3.41μ
Molar compositions of the formed hydrates referred to one mole of ($SiO_2+Al_2O_3$):					
CaO	1.34	1.40	1.50	1.45	1.42
SiO_2	0.79	0.79	0.79	0.79	0.79
Al_2O_3	0.21	0.21	0.21	0.21	0.21
H_2O	1.30	1.69	2.07	1.76	1.53

Hydrogarnet ($3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$) was also formed after 6 hr. Accumulation of hydrogarnet besides the crystallization of calcium silicate hydrate might reduce the strength.

Reaction at 213 °C (20 atm): By autoclaving for 30 min, nearly crystalline calcium silicate hydrates were formed as confirmed by X-ray diffraction. After 2 hr (Fig. 4) cubic crystals of hydrogarnet were formed, calcium silicate hydrate being crystallized in the form of interlocking fibres and rods. Continuous decrease in strength took place during the first 2 hr of autoclaving. This is also attributed to the accumulation of hydrogarnet and crystallization of calcium silicate hydrate.

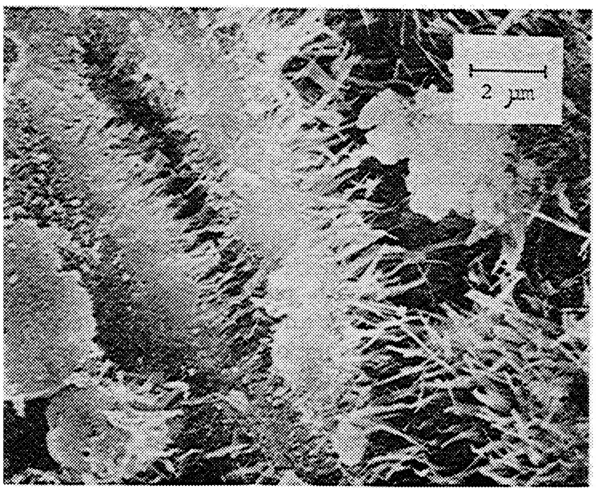

Fig. 4. The microstructure of slag-lime paste at 20 atm, 2 h autoclaving, interlocking fibres and rods of calcium silicate hydrates, beside cubic hydrogarnet.

Reaction Mechanism: It is suggested that a rapid hydrothermal change takes place until 20—25% of slag is hydrated. This stage corresponds to stage I in the induction period.[5]

A very slow hydrothermal reaction follows as a result of the formation of an almost impervious coating on the slag particles during the first stage; a dormant period which corresponds to stage II in the induction period.[5] The dormant period starts when about 25% of reactant is hydrated and lasts until about 30% is hydrated. The beginning and duration of the dormant period change with autoclaving temperature. At 181 °C, the percentage of ignited hydration product formed is 26.7% in 0.5 hr and 30.2% in 2 hr, so that the initial fast reaction is almost completed after 0.5 hr and the dormant period after about 2 hr. At 213 °C, the percentage of ignited hydration product is 34.9% in 0.5 hr, which is after the dormant period.

In the third stage crystallization of the initial products occurs. Diffusion through the crystallized product becomes free and a very fast interaction of water with the unhydrated part starts, lasting until about 80% of slag is hydrated. This leads to the formation of an "inner" product.

Hydration is retarded by accumulation of products. The diffusion through the pores of products becomes the rate determining factor. The mechanism is in line with that obtained by Brunauer and his co-workers[7] on low porosity cement pastes at 5—50 °C.

(II) Slag–Quartz–Lime–Water System. The experimental results are shown in Figs. 5 and 6 and Tables 3 and 4. Thickness of the reacted layer on the surfaces of the slag and quartz particles can be estimated by means of the relation given in Fig. 4.

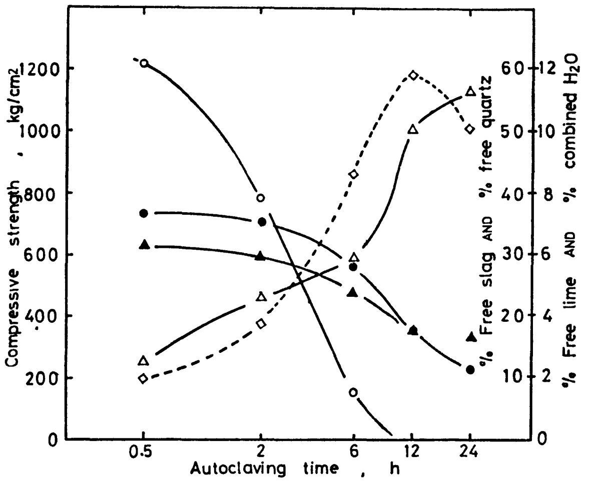

Fig. 5. Slag–quartz–lime–water system at 181 °C. ◇: strength, ○: free lime, ●: free slag, △: combined H_2O, ▲: free quartz.

It was found that determination of uncombined slag by means of X-ray becomes difficult since the reaction products can also be converted into melilite when heated at 900 °C. The reaction ratio of slag obtained in system (I) are used.

Interaction of Slag and Quartz: The reaction ratios of both slag and quartz (Tables 3 and 4) indicate that the hydrothermal reactivity of granulated slag is greater than that of quartz, particularly in the initial stage of the reaction. The high reactivity of slag inhibits the reaction of quartz in the early stage of hydrothermal solidification. The reactivity of quartz in lime-quartz hydrothermal reaction given by Kondo[1] was higher than that we obtained. Evidence for the high reactivity of slag was obtained by comparison of the

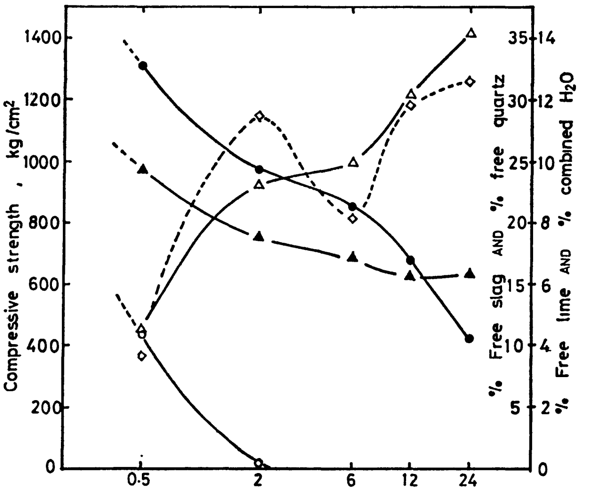

Fig. 6. Slag–quartz–lime–water system at 213 °C. ◇: strength, ○: free lime, ●: free slag, △: combined H_2O, ▲: free quartz.

Table 3. Characteristics of slag–quartz–lime–water system at 181 °C

Autoclaving time	0.5h	2h	6h	12h	24h
% Ignited hydration products	19.8	27.1	46.5	65.3	72.3
Reaction ratio of CaO	23.5	50.9	90.4	100.0	100.0
Reaction ratio of slag	29.9	32.5	46.5	66.7	78.4
Reaction ratio of quartz	0.9	6.0	24.3	45.5	48.1
Depth of reacted layer on slag particles	0.90μ	0.99μ	1.55μ	2.50μ	3.30μ
Depth of reacted layer on quartz particles	0.01μ	0.08μ	0.39μ	0.79μ	0.85μ
Molar compositions of the formed hydrates referred to one mole of ($SiO_2+Al_2O_3$):					
CaO	1.61	1.80	1.48	1.14	1.10
SiO_2	0.80	0.83	0.88	0.89	0.89
Al_2O_3	0.20	0.17	0.12	0.11	0.11
H_2O	1.16	1.64	1.07	1.13	1.13

Table 4. Characteristics of slag–quartz–lime–water system at 213 °C

Autoclaving time	0.5h	2h	6h	12h	24h
% Ignited hydration products	38.4	56.9	61.3	67.3	73.6
Reaction ratio of CaO	72.6	98.9	100.0	100.0	100.0
Reaction ratio of slag	37.5	53.6	59.1	67.6	79.9
Reaction ratio of quartz	22.5	41.0	45.5	50.2	49.8
Depth of reacted layer on slag particles	1.18μ	1.83μ	2.10μ	2.55μ	3.41μ
Depth of reacted layer on quartz particles	0.35μ	0.70μ	0.79μ	0.90μ	0.89μ
Molar compositions of the formed hydrates referred to one mole of ($SiO_2+Al_2O_3$):					
CaO	1.39	1.20	1.14	1.08	1.09
SiO_2	0.89	0.90	0.90	0.90	0.89
Al_2O_3	0.11	0.10	0.10	0.10	0.11
H_2O	0.95	1.22	1.19	1.30	1.39

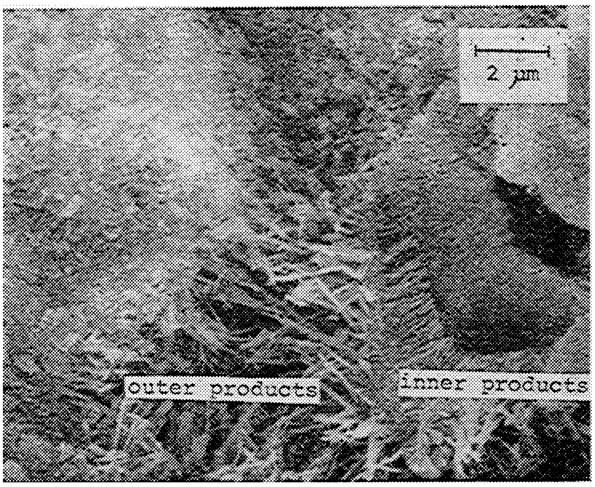

Fig. 7. The microstructure of slag–quartz–lime paste at 10 atm, 6 h autoclaving.

compressive strengths obtained in the two systems in the present study. The strength attained in the early stage was greater in system (I) than in system (II) (Figs. 1, 2, 5, and 6). However, in the latter system, growth of strength reaching a maximum of about 1200 kg/cm^2 was obtained due to the formation of much calcium silicate hydrate and lesser hydrogarnet.

Reaction at 181 °C: Nearly amorphous high lime calcium silicate hydrates were formed during the first 2 hr of hydration (Table 3). X-ray diffraction revealed only the formation of ill-crystallized calcium silicate hydrate. The accumulation and later crystallization of the high lime product account for the continuous development of strength during the first 12 hr. Scanning electron microscope observation (Fig. 7) obtained after autoclaving for 6 hr indicates the unhydrated part of the grain was directly attached to an "inner product" 1.5 μ in depth, the "outer product" with loose structure and about 2 μ in thickness being observed outside the original grains as acicular and interlocking fibres. After consumption of all free CaO during a period of 12 hr, the maximum strength of the specimens was attained. The high lime product then started to transform into a low lime product in the form of fibres and rod like crystals. Crystallization results in a reduction of strength because of its low surface area.

Reaction at 213 °C: A high lime product was formed and crystallized during the first 2 hr of autoclaving. At that time all the free CaO was consumed, high lime product changed into low lime product, and a part of the previously bound CaO was released and then bound to a new part of the unhydrated reactants. This resulted in an increases of the total contents of binding centers in the specimens. The creation of new binding centers caused an increase of strength after 6 hr autoclaving.

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