

Hardening Properties of Activated Calcium Dialuminate Clinker with Phosphoric Acid Solution

Tae-Woong Song and Sei-Gi Kim*

Dept. of Inorg. Mat. Engineering, Kyungnam Univ., Masan 631-701, Korea

*Research and Development Department, Hyundai Cement Co., Ltd. Youngwol, 230-840, Korea

(Received September 9, 1997)

Basic properties of new cement pastes based on the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ were studied. Phosphoric acid solutions and calcium dialuminate clinkers synthesized by the hydration-burning method were used for liquid and powder components of the paste, respectively. Variation in the compositions of the paste was achieved by changing the liquid/powder ratio and the concentration of phosphoric acid solution. The hardening rate of the paste was so largely affected by the amount of phosphoric acid that hardening was inhibited with the low-concentrated solution but was explosively accelerated with the high-concentrated solution. The phosphoric acid solutions of concentration of 45~50% and the liquid/powder ratio of 0.5~1.5 were favoured for the high early-strength cement paste with the reasonable hardening rate and high strength. The binding phase of hardened paste was the dense amorphous gel of the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$, in which the unreacted calcium dialuminate grains were embedded.

Key words : Calcium dialuminate, Hydration-burning method, Phosphoric acid, High early-strength cement paste

I. Introduction

$\text{CaO}\cdot 2\text{Al}_2\text{O}_3(\text{CA}_2)$ has been recognized to have the largest alumina content and the lowest hydraulicity among the known hydraulic calcium aluminates. However, CA_2 -based clinker with highly activated surface and good hydraulic properties has been reported. It could be synthesized by the "hydration-burning method" which consists of calcining a mixture of limestone and Bayer alumina, hydrating the calcined mixture, and reburning the hydrated paste.¹⁻⁴⁾ The microstructure of the clinker revealed to be a solid agglomerate⁵⁾ composed of CA_2 and showed very high surface area which is favorable to dissolution during hydration by the dissolution-precipitation mechanism. The reactivity of the activated CA_2 clinker with water has been found to be superior to that of $\text{CaO}\cdot\text{Al}_2\text{O}_3(\text{CA})$ synthesized by the conventional clinkering method.³⁾

Chemically bonded ceramics in the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ were studied^{6,7)} using the reactions between the high alumina cement (main phase: CA) and the phosphoric acid solution under the hydrothermal condition. Similarly, the activated CA_2 clinker, even under the normal condition, reacted easily with phosphoric acid, which gives more alumina-rich materials and a possibility of some special uses including the high early strength cements and the refractory cements.

In the present study, neat paste was prepared by using the activated CA_2 clinker and the phosphoric acid solutions of various concentrations. Basic hardening properties, microstructures, mineralogical changes, and

mechanical strengths of the paste were investigated.

II. Experimental Procedure

The phosphoric acid solutions of various concentrations were used for the source of P_2O_5 component of the paste. The activated CA_2 clinker was used for the source of CaO and Al_2O_3 components. The activated clinker was prepared as follows; the mixture of relatively pure limestone and alumina of a molar ratio of CA_2 was pelletized and fired at 1300°C for an hour. Slightly sintered pellets were then ground and hydrated with the weight ratio of solution to powder (S/P ratio) of 0.7 at 35°C for a day. Finally, the activated CA_2 clinker was obtained by reburning and quenching the crushed hydrates at 1250°C. The mineral phase and the microstructure of the clinker were confirmed by X-ray diffractometry (XRD) and scanning electron microscopy (SEM) respectively. The clinker was then ground to 74 μm for the powder component of the various pastes.

The actual compositions (wt.%) of the paste in the present study lie on $\text{CaO}\cdot 2\text{Al}_2\text{O}_3\text{-H}_2\text{O-P}_2\text{O}_5$ compositional plane in the system $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O-P}_2\text{O}_5$. Variation in compositions within this plane was achieved by changing the S/P ratio and the concentration (wt.%) of phosphoric acid solution. Mixed paste was cured in an end-sealed cylindrical mould with a diameter of 3 cm and a height of 4 cm for various periods of time.

The hardening rate was assessed by a laboratory method that measures the time taken until Gilmore needle (final) falling to the surface of sample from constant

distance over the surface makes no traces. The data are *not absolute value* but may give useful information on the relative hardening rate. For the compressive strength test, hardened pastes with a diameter of 3 cm and a height of 3 cm were used. The phase and microstructure of the hardened paste were studied by XRD and SEM.

III. Results and Discussion

1. Miscibility and hardening rate of pastes

From the sample observations during mixing and the hardening rate tests, the compositional plane could be divided into five distinguished areas as shown in Fig. 1. The characteristics of each area can be summarized as follows; in area A, the S/P ratio of the sample was too low to prepare homogeneous mixture by usual mixing method while the S/P ratio of area B was too high to obtain reasonably dense structure after hardening. In most cases the workability of the pastes in area C was high enough to mix homogeneously but these pastes scarcely set until several days probably due to the retarding action of the polymerized Al-P-O-OH film^{5,9} covering the surface of the CA₂ grains. The reaction between the CA₂ clinker and the phosphoric acid solution in the pastes of area D was so violent that mixtures overflowed explosively, which gave very porous and brittle materials after instantaneous setting. Finally, in area E only, the paste showed the adequate mixing, forming, setting, and hardening properties for the high early strength cement paste.

The hardening rates of pastes of various compositions within area E is also shown in Fig. 1. The effect of the S/P ratio and the content of phosphoric acid on hardening can be summarized as follows; when the concentration of phosphoric acid solution exceeded 45%, the hardening rate increased linearly with the S/P ratio and/or the con-

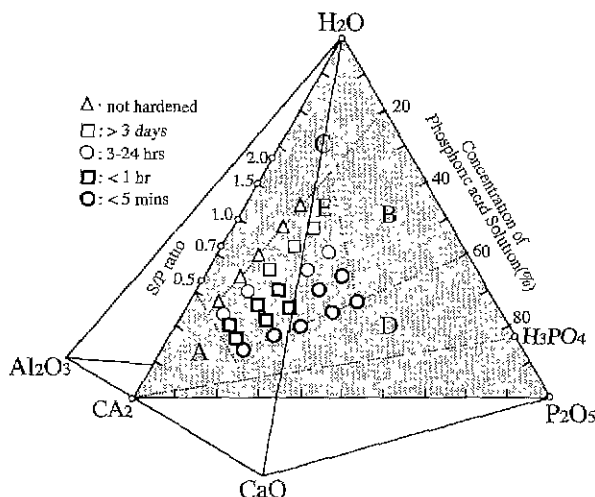


Fig. 1. Compositional areas (A-E) and compositions of pastes of different miscibility and hardening rate.

centration of the solution. This means that the hardening is accelerated with total amount of the phosphoric acid added to the paste. On the other hand, when the concentration of the phosphoric acid of the solution was lower than about 40%, the hardening rate decreased with the S/P ratio probably due to the retarding action of the low-concentrated solution. It is suggested that the hardening time of a certain paste could be controlled easily by adjusting the S/P ratio and the concentration of liquid component.

2. Mineralogical and microstructural properties

The activated CA₂ clinker, the raw material used in this study as a powder component of the pastes, was revealed to be consisted mainly of CA₂ with small amount of CA and unreacted alumina by XRD. The microstructure of the clinker was highly microporous as shown in Fig. 2. After the clinker was ground to 74 μm, its specific surface area measured by BET method was more than 4 m²/g.

In general, all calcium aluminates and alumina cements produce AH gel, CAH₁₀, C₂AH₅, C₃AH₆, and AH₃ (C: CaO, A: Al₂O₃, H: H₂O) as the hydration products in different proportion according to the mixing and curing temperature. The activated CA₂ clinker used in this study hydrated with water in the same way. But with the addition of phosphoric acid, quite different phases were produced after hardening as shown in Fig. 3. The only unreacted CA₂ clinker was found in the hardened paste. However, there were neither any calcium aluminate hydrates nor aluminium hydrates. The binding phase was found out to be an amorphous phase by XRD and remained without any changes in mineral phase at room temperature.

By increasing the quantity of the phosphoric acid, the amount of the binding phase increased and the unreacted CA₂ decreased proportionally in the paste. So the remaining of unreacted CA₂ in all samples of area E means insufficiency of P₂O₅ component for complete reaction. But more phosphoric acid may not be useful to im-

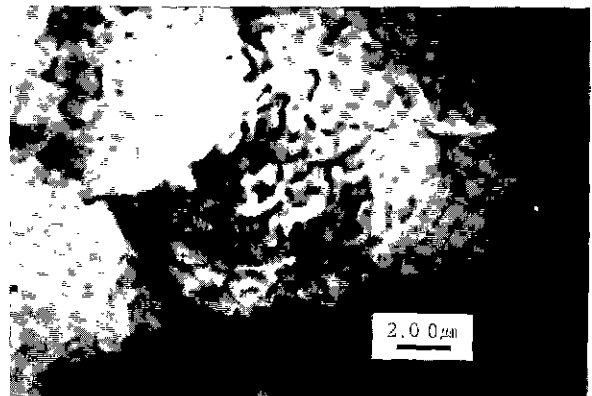


Fig. 2. SEM micrograph of CA₂-based clinker activated by the hydration-burning method.

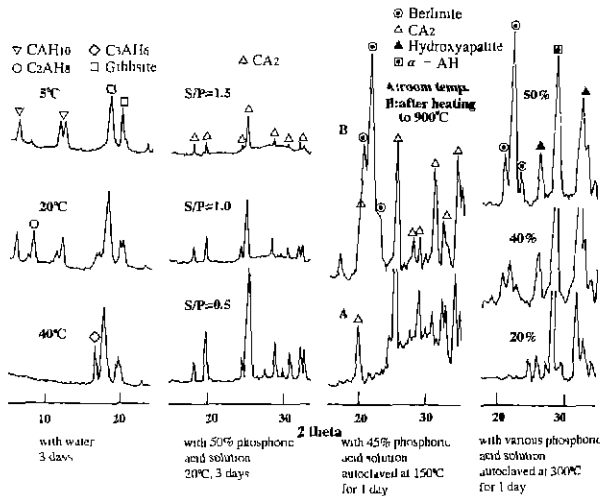


Fig. 3. XRD patterns of pastes prepared from the activated CA₂ clinker with various phosphoric acid concentrations under the different conditions.

prove a performance of the paste because increasing the concentration of phosphoric acid may move the paste composition to area D, and increasing the S/P ratio may move it to area B, causing the mixing trouble and the strength reduction in the paste, respectively.

When the hardened paste was heated to a temperature of 600°C or above, the crystalline phases of α-AH₃ (boehmite), AlPO₄ (berlinit), and Ca₁₀(PO₄)₆(OH)₂ (hydroxyapatite) were produced by the expense of amorphous binding phase. However, when the paste was prepared under the hydrothermal condition at the temperature above 250°C, the crystalline phases were produced directly without formation of amorphous phase. These results suggest that the binding phase consist of amorphous gel of the system CaO-Al₂O₃-P₂O₅-H₂O. The phase is presumed to be an amorphous gel with P-O-Al linkage that might have formed from Al and PO₄ ions, and fixed by Ca ion.

SEM micrographs of the fractured surface of the hardened paste were shown in Fig. 4. The morphology of hardened paste was much denser and more homogeneous than that of the commercial high alumina cement paste composed of normal crystalline calcium aluminate hydrates. Once the paste was hardened, there was nearly no changes in morphology of the binding phase. It was consistent with the results of XRD which showed no changes in mineral phase with the passage of time.

3. Mechanical strength of hardened pastes

Somiya *et al*³¹ reported that the strength development of a paste of CA₂ prepared by the conventional clinkering method begins at 3 days after mixing CA₂ with 50%-phosphoric acid solution. In the present research using activated CA₂ clinker, however, considerably high compressive strength (up to 250 kgf/cm²) developed within

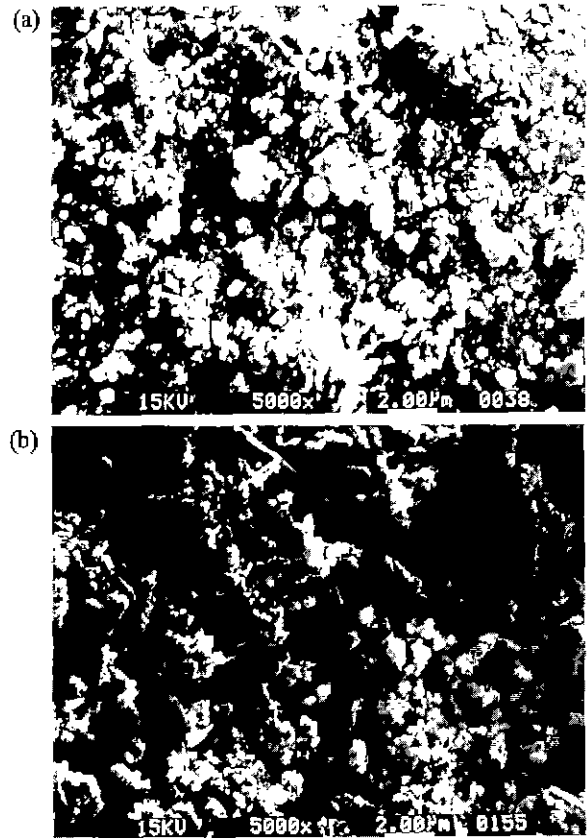


Fig. 4. SEM micrograph of the fractured surface of the hardened paste prepared with (A) CA₂-based clinker and 50%-phosphoric acid solution and (B) water and commercial high alumina cement.

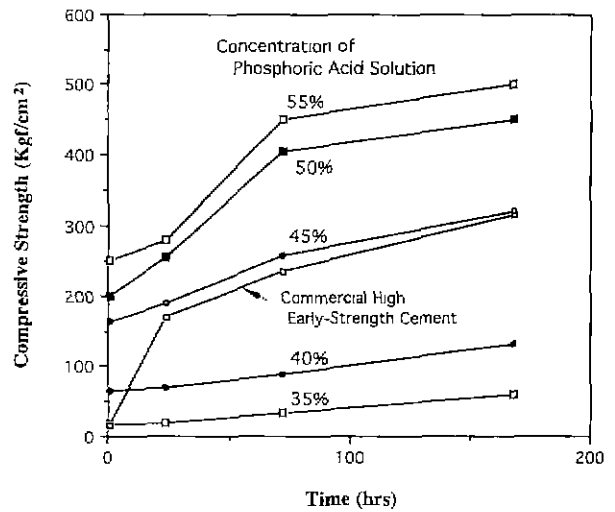


Fig. 5. Strength development of the paste prepared with various concentrations of phosphoric acid solution (20°C, S/P =0.5).

an hour and then about 90% of 7-days strength developed within 3 days as shown in Fig. 5. The results show that the amount of phosphoric acid added to the paste is an important factor affecting the mode of the strength development. The compressive strength in-

creased linearly with the concentration of the phosphoric acid solution used. But increasing the total amount of the phosphoric acid by increasing S/P ratio was less effective for the strength improvement in the fully hardened body of the composition of area E, as is usual with other cementitious materials.

IV. Conclusions

The basic hardening properties of the new cement paste prepared from the activated CA_2 -based clinker and phosphoric acid solution were as follows;

The hardening rate and the mechanical strength of the paste were largely affected and were adjustable by the concentration of the phosphoric acid solution and the S/P ratio. Hardening was inhibited with the low-concentrated solution while it was explosively quick with the high-concentrated solution. Adequate mixing, forming, and hardening properties could be obtained with the phosphoric acid solution of concentration of 45~50% and with the S/P ratio of 0.5~1.5.

The final binding phase was the dense amorphous gel of the system $CaO-Al_2O_3-P_2O_5-H_2O$, in which the unreacted CA_2 grains were embedded.

The strength development of the paste prepared with a proper composition was very faster and higher than that of a high early-strength cement paste for normal use.

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