

ENVIRONMENT-PROTECTING UNBAKED CEMENT AND ITS HYDRATE MECHANISM

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Abstract

This experiment was carried out to make cement with a strength of 42.5 MPa using blast-furnace water-hardened slag and two active agents. The authors probed the hydrate mechanism of the cement based on the measurements of pH value and heat of hydration and XRD patterns. They also observed hydrate production through an electron scanner. This research found that the cement hydrate process includes several stages, such as an inducement prophase, inducement phase, accelerating phase, the second inducement phase and the second accelerating phase. The main hydrate products were C-S-H gelatin, C_3AH_{13} , AFt, AFm, albite, and micro plagioclase.

1. Introduction

China increases its cement production each year. It is estimated that cement production will be 800-850 million tons by the year 2010, equaling nearly half of the world total cement output. One ton of cement needs about 0.8 ton of portland cement clinker, which requires one ton of CO_2 . From 1995 to 2010, the cement industry in China will add 7.5 billion tons of CO_2 to the earth's atmospheric layer, about half of the world discharge amount. With this amount of CO_2 production, we can see how the Chinese cement industry influences the environment. We must find a way to strictly

limit the output of portland cement clinker in the future. One of the goals of this research is to research and develop an environment-protecting binding material.

Low activity water-hardened slag and heavy slag have not been used efficiently. The current method for discharging and stacking the slag pollutes the environment. So compounding non-clinker or little-clinker environment-protecting unbaked cement by stimulating the activity of slag it would be a significant innovation.

The purpose of this research is to compound 42.5 environment-protecting unbaked cement with the water-hardened slag, the primary raw material, and the compound activated agent by simple grinding-mix technology (i.e., omitting calcinations process) and to explore the hydrate mechanism of the environment-protecting unbaked cement.

2. Raw Materials and the Main Properties of the Environment-protecting Unbaked Cement

Water-hardened slag from the Hancheng iron factory was used for this research and its chemical composition is listed in Table 1. The basicity coefficient and mass coefficient were found by calculating the chemical component by 0.930 and 1.795, respectively. The slag is acidic. The fineness of the selected slag was 0.08 mm, and the sieve residue was 2%.

Table 1: Chemical component for water-hardened slag

| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | MnO | Alkalescence coefficient | Quality coefficient |
|-----------|------------------|--------------------------------|--------------------------------|-------|------|------|--------------------------|---------------------|
| Ratio (%) | 32.40 | 15.24 | 2.41 | 40.26 | 4.76 | 0.98 | 0.930 | 1.795 |

X-ray diffraction of the slag is shown in Fig. 1. Analysis shows that 65% of the slag is noncrystalline, with significant amounts of active SiO_2 and active Al_2O_3 present. In addition, there is about 35% gehlenite $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and 4% hemative in water-hardened slag, so it is a type of low-activity slag.

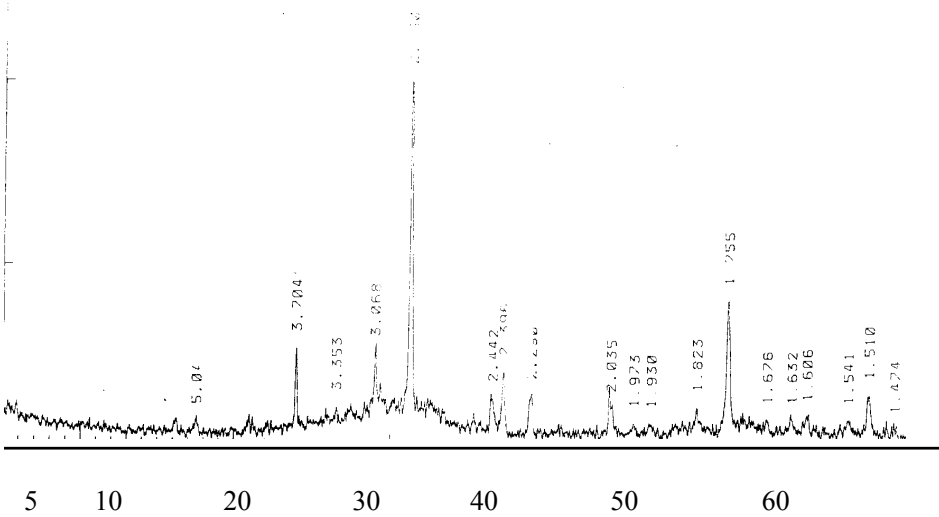


Fig. 1: XRD patterns of water-hardened slag

According to experiments, the authors chose active booster B and C. Different components of fines are mixed for 8 minutes in a ball crusher. The mortar strength test for environment-protecting unbaked cement is detailed in specification ISO679. The standard quality for sand and water used as cementing material are 450g, 1350g, and 225 g. The result of the experiment is shown in Table 2. We can see that the optimum proportion of active booster B is 3.5% and active booster C 2.5%, the compressive strength of 3d and 28d is 26.6 and 44.9 MPa, respectively; the bending strength of 3d and 28d is 5.1 and 6.6 MPa. The cement conforms the national strength grade standard (GB1344-1999) for portland cement.

Table 2: Paste strength under different mix proportion

| Serial number | Water-hardened slag (g) | Component B (g) | Component C (g) | Compression stress (MPa) | | Folding stress (MPa) | |
|---------------|-------------------------|-----------------|-----------------|--------------------------|------|----------------------|-----|
| | | | | 3d | 28d | 3d | 28d |
| 1 | 433.1 | 9.8 | 7.1 | 8.4 | 20.1 | 2.9 | 4.4 |
| 2 | 429.6 | 11.8 | 8.6 | 17.1 | 28.7 | 4.0 | 4.8 |
| 3 | 426.4 | 13.7 | 9.9 | 22.0 | 35.7 | 4.9 | 6.1 |
| 4 | 422.7 | 15.9 | 11.4 | 26.6 | 44.9 | 5.1 | 6.6 |

The other technological properties measured by Chinese national standard GB/T1346-1989 indicate that water consumption for standard consistency is 152 ml, higher than water consumption for ordinary portland cement. Initial set time is 78 minutes and final set time is 135 minutes, both a little longer than ordinary Portland cement set times. Volume stability passes the pat test. Overall, properties of this cement conform completely to the demands of Chinese national standards.

3. Hydrate Reaction and Mechanism Analysis of Environment-protecting Unbaked Cement

The activity level of water-hardened slag depends on its chemical composition and internal structure (noncrystalline content). The slag demonstrates a rapid-cool effect when mucked out. It forms a loosely netted glass structure with many apertures. It can be described by the Zachariasen three-dimensional distorted netted structure.

Water-hardened slag is hydrated when the sharp reaction of active agent and OH^{-1} ions is initiated by the agent when OH^{-1} enters the aperture of the netted glass structure. The hydration mechanism of cement can be analyzed by determining the change in

OH^- density (pH value) in the cement-water system and the hydrate heat-releasing speed.

The x-ray diffraction experiment indicates that the main hydrates of the 28-day-old cement include C-S-H, Aft, C_3AH_3 , Alite, and microplagioclase, etc. As seen in Fig. 2, the main hydrates are C-S-H and Aft. In addition, the cement-water system pH value and the cement heat of hydration are determined by studying the cement hydrate and water (1:50) solution, which indicates the curve of the pH value change as seen in Figure 3. The heat of hydration for the cement is determined using the method formulated by the Chinese national standard board. When environment-protecting unbaked cement is mixed with water, the excitation medicament acts rapidly in water and releases ions such as OH^- , Na^+ , and SO_4^{2-} . The pH value of the system increases rapidly and the hydration reaction occurs at the same time. The OH^- ions in the solution get into the reticular formation gap of the water-hardened slag's vitreous body, acts with the activity silica-alumina positive ions, scatters, and dissolves the slag's reticular formation, dissolving out Ca^{2+} and forming C-S-H, Aft, C_3AH_3 , alite, and micro plagioclase.

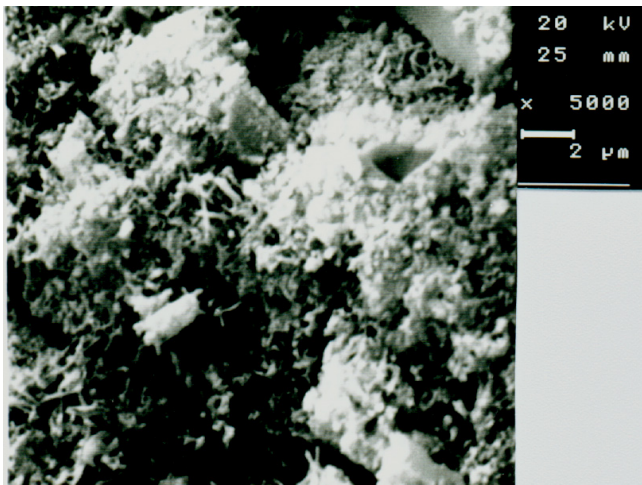


Fig. 2: Scanning electrical-mirror photo of 28-day age

Meanwhile, the Ca^{2+} ions in solution increase, causing over-saturation of the C-S-H and hydration calcium aluminate, making the hydrate condense and increase. In slag, $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ reacts with the SO_4^{2-} Ca^{2+} Na^+ ions and forms AFt and C-S-H (part of Ca^{2+} is substituted by Na^+).

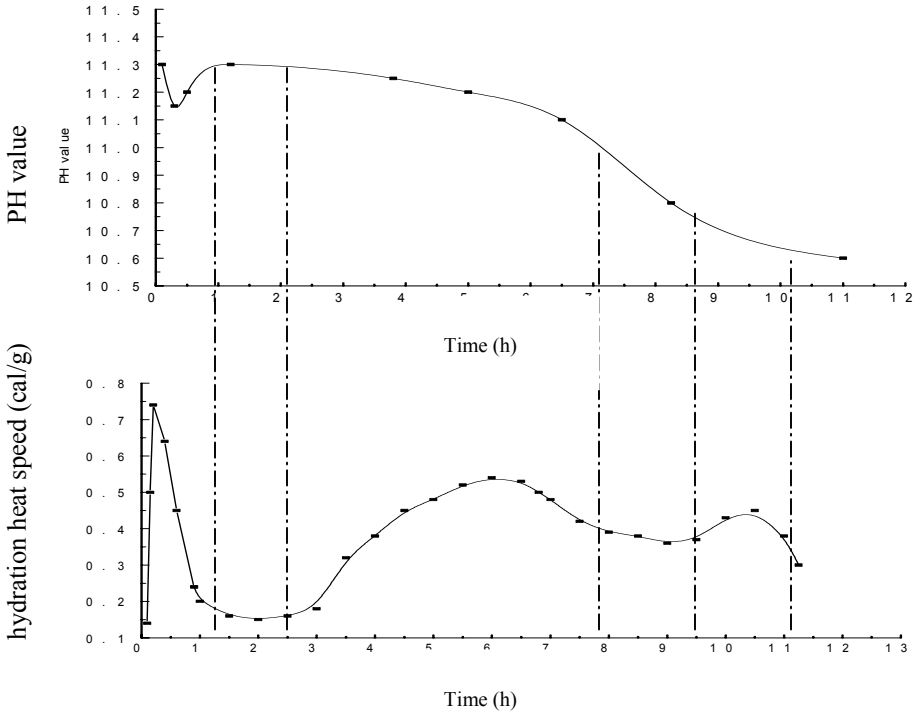


Fig. 3: PH value and hydrating heat speed curve of cement

When the hydration reaction reaches a certain point, Ca^{2+} and SO_4^{2-} ions are not enough because of excessive consumption. At this point, AFt forms sulphuric hydration calcium aluminate sulfate (AFm). The final products are C_3AH_6 , AFt, AFm, albite and C-S-H (in which a part of Ca^{2+} is substituted by Na^+).

It can be seen from the reaction mechanism of the cement that the solution and reaction of B and C creates AFt deposits when the cement is mixed with water. It separates the slag from solution and controls the hydration process. At the beginning of the hydration reaction, the pH value of the solution increases rapidly, the hydration of cement is very fast, and the hydration process moves into the pre-induction period. As seen in Fig. 3, as the pH value increases to 11.3 or so, the slag reacts quickly with Ca^{2+} OH^- SO_4^{2-} Na^+ ions of the medium and forms a hydrate of AFt C-S-H (a part of Ca^{2+} is substituted by Na^+). At this point, the pH value of the solution drops to 11.1 and the cement's hydration rate increases rapidly. The main product of this phase is AFt. After 20 minutes, AFt and C-S-H adhered to the slag grain surface as it increases, impeding the diffusion of OH^- Ca^{2+} SO_4^{2-} ions in the slag reticular formation, postponing the hydration velocity of the cement. This process lasted about an hour until the hydration reached the induction period.

As the speed of hydration in the induction period decreases, the pH value of the solution continued to be high. Extensive hydration makes AFt and C-S-H on the surface of slag grain become thick and crystal stress is produced. Crystal stress is increases with increased thickness. When the crystal stress reaches a certain threshold, AFt and C-S-H burst locally, exposing the fresh surface of slag grain that is not hydrated. The slag's fresh surface forms the hydrate of AFt at the reaction of OH^- Ca^{2+} SO_4^{2-} Na^+ etc, helping the exploded surface recover. The hydrated surface of the slag grain produces the process of "warp-crack," and meanwhile the hydrate scatters to the surrounding slag grain gradually and fills up the space occupied by the solution between slag grains. The pre-induction and induction periods consume a great number of SO_4^{2-} ions as the density of SO_4^{2-} ions in solution drops. Then the system hydration accelerates. We can see from Fig. 3 that the pH value of the solution starts to drop for 2.5 hours before beginning the hydration acceleration period.

The observed hydration of the acceleration period is mainly the reaction between Ca^{2+} OH^- Na^+ ions and active SiO_2 Al_2O_3 . The main hydrate is C-S-H and C_3AH_13 albite and micro plagioclase. The hydration velocity of cement in this stage accelerates as the pH value of the solution gradually decreases. After the acceleration period, the slag

hydration is violent and the velocity of hydrate heat-release is fast, resulting in a heat-release velocity peak of about 6 hours. Heat-release velocity has been very slow, about 7.5 hours, and the curve of heat-release velocity tends to be smooth, ending with the hydrate acceleration period before the stable period.

The stable period of the hydrate continues for 9.5 hours. At this point, the second hydrate period begins, and the lack of SO_4^{2-} in the system leads to a reaction between hydrate AFt and Al_2O_3 in the slag and forms AFm, releasing a large amount of hydration heat in the process. As the hydrate heat-release velocity increases, the second hydrate heat-release peak appears at about 10.5 hours. The second hydrate acceleration period ends after about 1 hour. When the cement hydration gets into the second stable period, there is not an obvious hydrate heat-release velocity peak and the hydrate velocity of slag is slow. This process continues until the end of cement hydration.

During this process, the paste of environment-protecting unbaked cement completes the process of interlace conjunction and loses its working plasticity, forming a rigid-brittle material.

4. Conclusions

As low activity water-hardened slag is processed to increase the activity level, using up to 94% slag, the researchers found that is possible to make environment-protecting unbaked cement could that meets the standard 42.5 slag cement in strength condensing time and cubic stability.

X-ray diffraction and scanning electrical-mirror experiments indicate that the main hydrate of this cement is C-S-H amorphous gel C_3AH_{13} AFt Afm, albite, and microplagioclase. According to the change in pH values and the determination of heat hydrate, an analysis of the hydrate process of this cement, includes the pre-induction period, induction period, acceleration period, stable period, the second acceleration period, and the second stable period.

References

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