Hydration of blended cement with high alite content

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We have produced a trial high alite cement in a cement plant and have researched the hydration reaction of the high alite cement with blended materials. The high alite blended cement has a higher heat of reaction and produces a more hydrated product than ordinary Portland cement, as confirmed by heat liberation from a calorimeter. The amount of Ca(OH)2 (or CH) was confirmed to be higher than that of ordinary Portland cement. In this research, we focused on measuring the properties of blended high alite cement in the early hydration period. Results were obtained for hydrated samples at up to 28 days to ascertain the possibility of using high alite cement and its potential improvement in blending.

Key-words : Blended cement, Blast-furnace slag, Fly ash, Cement hydration, Calorimeter, Heat liberation, High alite cement

1. Introduction

Blended cement is a cement type with less than 95% clinker in the powder.1) Cement is usually blended with other background materials in a suitable ratio. The most common ingredients for blending with Portland cement clinker are pozzolanas and latent hydraulic materials, such as ground granulated blast-furnace slag (BFS).2,3 Other materials such as ground limestone and fly ash (FA) may also be used. The types of blended cement are separated and specified by chemical composition and physical properties. Hydrated blended cement products should meet certain requirements, especially the compressive strength after 28 days. Blended cement types can be classified according to the ratio of clinker and blending material. The specifications for BFS-blended cement and FA-blended cement are listed in JIS R5211 and JIS R5212.

Global environmental situations have forced major industries to increase energy savings and reduce CO2 emissions in recent decades. To achieve this aim in the cement and construction industries, blended cement is needed, as it can play a significant role in improving waste management and is environmentally friendly. Total CO2 emissions can be reduced significantly as can be seen from a comparison of emissions from the cement production line with emissions from blending materials, such as BFS and FA.3,4) The mechanical properties of blended cements differ from normal cement because the cement powder in blended cement is replaced by mineral additives or blending materials. A reduction in the cement particle content results in a reduced early stage reaction and reduced early strength development in the hardened structure. This occurrence can be observed and compared in calorimetric studies of the heat of hydration reaction. By adjusting the phase content in cement as related to early hydration, we should be able to change the early reaction properties of blended cement.

The alite (C3S) phase is known to be the main reactive cement phase in the early stages of hydration and is the main component in clinker. This phase is important in terms of the setting time, hardening and more importantly, the mechanical strength of the hardened cement paste or concrete during early hydration (~7 days). It can be produced by the sintering at high temperature of calcium oxide (CaO) and silica (SiO2) with a flux additive such as an alumina (Al2O3) phase and felite (Fe2O3).5) The product from the hydration of C3S is CH, which is important for strength development, durability of the hardened paste and the reactivity with blending materials.

Because of the importance of the mechanical properties during the early hydration stages, it should be possible to improve on the reaction in blended cement by increasing the amount of C3S in cement powder or in clinker before it is mixed with the blending materials.

The main purpose of this research is to improve on the early performance of blended cement by using higher C3S content clinker compared with ordinary Portland cement (OPC). High C3S content clinker was produced in the laboratory to ensure that this type of cement can be synthesized and manufactured. It has also been confirmed that this cement can be produced on an industrial scale. The heat of hydration and the hydrated products were studied compared with normal OPC paste or blended mixtures.

2. Experimental

2.1 Materials preparation

Six batches of raw materials powder (DC Corporation, Kanagawa, Japan), were mixed with a small amount of water to improve the packing ability of the powder. Pellets were created using a hand-operated hydraulic pump (Riken P-16B, Riken Seiki co., LTD. Hiroshima, Japan) and a polymer mud pressure. Pressure was applied slowly to the powder-containing mold in the molding stage up to 17 MPa, stabilized at the selected pressure for 2 min, and then the pressure was released slowly. Pellets with no visual cracks on the outer surface were placed on a platinum plate.

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The sintering process was conducted using an electric furnace (SSFT-1520, Yamada Denki co., LTD. Tokyo, Japan) at a maximum temperature of 1450°C and with a soaking time of 3 h at a 10°C/min heating rate. After reaching the expected condition, sintered pellets (clinker) were removed quickly for rapid quenching by an air blower (at room temperature) for 30 min. Thereafter the clinker was stored in a humidity-controlled atmosphere, before the grindability tests were conducted. Grinded clinker samples were sent to the DC Corporation research facilities for X-ray fluorescence analysis.

The chemical and phase composition of the cement used in first synthesized clinker process is shown in Tables 1 and 2 (where HM is the hydraulic module, AI is the activity index, IM is the iron module and SM is the silica module). These cements were made in order to confirm the possibility of producing high C3S cement. After a test in laboratory scale, trial products were made from actual cement plant that are supported by the DC Corporation. Two types of high C3S cement were chosen, together with OPC for hydration study. The chemical composition and phase content of chosen cement are shown in Table 3 and Table 4, respectively (where HAC is high C3S cement). Blending materials used in this research is FA (class F) and BFS with a specific surface area of ~4000 cm²/g, as shown in Table 5.

### 2.2 Experimental process

#### (1) Clinker grindability

An alumina ball mill was used in the grinding process. An alumina mortar was used to crush the hardened clinker (<600-μm sieve), before it was placed in a ball mill for grinding using a planetary pot mill machine (LA-PO.4, ITOH co., LTD. Tokyo, Japan). Blaine’s surface area was measured at 10, 20, 40 and 60 min to assess the clinker grindability. After grinding, the clinker (powder) was collected and sieved using a 90-μm sieve.

#### (2) Calorimetric study

The calorimeter that was used in this experiment is a multi-channel twin conduction type calorimeter (SCM-12L, Tokyo Rico Co., LTD Tokyo, Japan). According to Sakai et al. this calorimeter can be used to measure the heat of hydration that...
should be related to reactions in the cement paste and can indicate the cement quality. Unblended samples were studied before blending conditions were applied. The FA and BFS ratio ranged from 20–50% with a water-powder ratio (W/P) of 0.4.  

(3) Thermogravimetric/differential thermal analysis (TG/DTA)  
Hydrated samples were produced to measure the hydrated products at different hydration times (1, 3, 7 and 28 days) with W/P = 0.4. All samples were cured at 20°C in sealed plastic bottles. The hydration was stopped by using acetone. After being ground with acetone, powder samples were analyzed by TG/DTA (NETZSCH TG/DTA 2000S, Kanagawa, Japan). Data obtained from this analysis were used to calculate the loss on ignition and the amount of CH present.

(4) Reaction ratio of C3S  
Samples that had already stopped hydrating were prepared for quantitative X-ray diffractometry analysis by mixing with 10% MgO. The MgO and C3S peaks at 42.9081 and 51.7828° (2θ), respectively, were used. Plane indices or Bragg reflection index of MgO and C3S are (200) and (22-6), respectively, while Cu Kα1 wavelength is at 1.5418 Å. The peak area was calculated using the ‘xcurve fit’ program and the MgO peaks were averaged and used for normalization of the C3S peak area. Thereafter, the normalized C3S peak area was used to calculate the reaction ratio of the C3S phase.

3. Results and discussion

3.1 Manufacture of HAC  
HAC synthesis was conducted successfully at laboratory scale. After the clinker mineral compositions had been obtained (Table 1), the cement phase composition in the clinker was calculated using Bogue’s equation. The calculated phase composition of the synthesized clinker is shown in Table 2. Based on these results, we chose No. 1, 3 and 5 (see Table 2) to continue trial production and termed these OPC, HAC-2 and HAC-1, respectively. The chemical and phase content of trial cement are shown in Table 3 and Table 4.

3.2 Grindability of raw clinker  
The time required to grind the clinkers to the optimal point in an alumina ball mill was different for each clinker. We decided to use raw data to determine the calculated time required for the clinker to reach a 3000 cm² Blaine specific surface area and compared this with the phase content in each clinker.

The relationships between clinker grindability and belite (C2S) and C3S contents are shown in Figs. 1 and 2, respectively. The high surface area in the product results from the related amount of C2S phase, which is relatively low compared with OPC. The hardness of the C2S phase is known to be greater than that of C3S.  

We concluded that a higher C3S content will result in better grindability because a higher C3S phase content results in the formation of a lower C2S phase content (compared with OPC).
Therefore, HAC will have a better grindability compared with OPC. This means that a HAC will require less energy to grind, which contributes to energy savings and CO₂ reduction.

### 3.3 Heat liberation

The first result from the calorimetric study is the heat liberation of each sample, which shows the development of heat per specific time. A pure HAC sample shows faster and higher heat development compared with OPC, as shown in Fig. 3. The additives also affect the rate of heat generation and change the rate of heat liberation pattern completely compared with the non-blended cement. These different rates of heat liberation patterns of the BFS- and FA-blend are shown in Fig. 4. This indicates the different reactions between the additives and the cement particles.

We assume T₁ and K₁ as the time needed for the reaction to reach the first highest peak and the height of that peak, respectively, in the heat evolution graph (as shown in Fig. 3). The difference in reaction according to the different amounts of additives and types is shown in Table 6.

**Fig. 4.** Heat evolution rate of pure HAC-1 and results from FA blending conditions.

| Cement type | Blending condition | T₁ (h) | K₁ (J/h) |
|-------------|--------------------|--------|---------|
| HAC-1 (none) | 7.42               | 15.35  |
| HAC-2 (none) | 6.75               | 17.87  |
| OPC (none)  | 9.25               | 11.52  |
| HAC-1 BFS 20% | 10.17             | 13.44  |
| HAC-1 BFS 30% | 9.25              | 12.20  |
| HAC-1 BFS 40% | 8.58              | 11.11  |
| HAC-1 BFS 50% | 8.17              | 10.01  |
| FA 20%      | 11.17             | 12.06  |
| FA 30%      | 10.17             | 10.65  |
| FA 40%      | 10.33             | 9.27   |
| FA 50%      | 10.00             | 7.64   |
| HAC-2 BFS 20% | 7.58              | 13.74  |
| HAC-2 BFS 30% | 6.83              | 12.60  |
| HAC-2 BFS 40% | 6.50              | 11.03  |
| HAC-2 BFS 50% | 6.25              | 10.27  |
| FA 20%      | 7.83              | 12.87  |
| FA 30%      | 7.17              | 11.53  |
| FA 40%      | 7.58              | 9.86   |
| FA 50%      | 7.75              | 8.03   |

Figures 5 and 6 show the heat liberation of the samples blended with FA and BFS, respectively. The results of the non-blended cement are also shown at 0% replacement. The influence of the C₃S phase content in the cement also causes a change in heat liberation. Both types of high C₃S samples showed a greater heat liberation than those of OPC. This excess heat may be problematic in HAC without blending. However, this excess amount of heat should improve the hydration reaction for the blended cement.

The heat liberation of FA-blended samples decreased gradually when the replacement ratio increased. A 20% FA replacement showed the same level of heat liberation as the OPC at 1 and 3 days. At 7 days, 20 and 30% FA replacement resulted in the same level as that of the OPC. This indicates that FA may not influence the hydration reaction in the early stages (1–7 days). However, FA is known to be hydrated in the long term. The heat liberation of BFS-blended samples is different from that of FA. A 20–40% replacement of BFS resulted in the same level of heat liberation compared with that of OPC at 1 and 3 days of hydration. Therefore, all BFS-blended samples showed a higher level of heat liberation compared with that of 7 days hydration of OPC. This indicates that BFS influences the early hydration reaction and the increasing heat liberation level means that BFS reacted during hydration.

Based on the heat liberation results, we selected the BFS replacement ratio as 20–50% and the FA replacement ratio at 10–30% for the next study.

### 3.4 Amount of CH in hydrated product

The amount of CH increased rapidly during 1 and 3 days of hydration, after which the incremental rate became lower towards 28 days. The calculated amount of CH in the HAC samples (HAC-1 and HAC-2) was significantly higher than that of OPC. This higher amount of CH generated from the hydration reaction can be related to the hydration rate and also to the heat liberation level, as measured using a calorimeter. The higher C₃S phase in HAC-1 and HAC-2 should be the main cause of the higher amount of CH and the free lime content in the cement is also considered to be related.

Blended sample conditions were determined for the blended HAC samples. Results from the HAC blended samples have been indicated by theoretical (dashed) lines. This was done assuming
that there was no influence between the blending materials and clinker or hydrated product from the clinker and that the CH was generated only from the OPC. Graphs of the blended cement samples of HAC-1 at 1 and 28 days hydration are shown in Figs. 7 and 8. The amount of CH in the hydrated product decreased when the replacement ratio increased. For both types of HAC, only blended cement samples with 10 and 20% FA replacement showed higher amounts of CH compared with OPC while 30% FA and 20% BFS replacement showed similar levels to the OPC. The other replacement ratios resulted in a lower amount of CH than in OPC. We can assume from the theoretical line comparison that FA and BFS affect the amount of generated
This effect has already been studied and has been reported as the effect of fine particle additives. However, CH amount in BFS was lower than those of FA blended cement because BFS consumes CH for reaction. While FA is pozzolanic materials, its reaction in cement is slower compared with BFS. Therefore we can only observed the different of CH in BFS blended samples in this early reaction experiment but long term curing experiment is needed in the future.

Given that the amount of the CH phase is related to the strength properties and carbonation resistance in the hydrated cement product, which is related to the durability of the hardened product, this higher amount of CH in both the HAC-1 and HAC-2 should make this type of cement more suitable for use in a blended-type cement.

3.5 Reaction ratio of C₃S

The reaction ratio calculation from the area under the C₃S peak of the blended cement was difficult to observe from normal XRD measurements. Some of the results from the XRD analysis show that the C₃S peak area did not differ significantly when the hydrated time increased at 7 and 28 days. Therefore, the result should be confirmed by other methods, such as the ‘selective dissolution method’, to study the reaction of replacement materials in future studies. However, even if the results for the C₃S reaction ratio of the blended cement sample show an analytical error, the approximate results of the reaction ratio in early hydration is related to the previous study.

Figure 9 shows the reaction ratio of the C₃S phase in the blended HAC-1 system (both FA and BFS). The graph shows that the C₃S phase reacted faster than the non-blended system. This should confirm the effect of the fine particle additives.

4. Conclusions

(1) HAC can be produced at the laboratory- and cement production-scale.
(2) The grindability of HAC is better than OPC because of the difference in phase content. Therefore, HAC should require less energy and time to be ground and reduce environmental concerns.
(3) Mineral additives affect the hydration reaction in the blended cement system, as observed from the results of the heat liberation rate (calorimeter test). The introduction of an additive will reduce the heat liberation rate of the cement. An increased proportion of additive will accelerate the C₃S phase reaction slightly.
(4) BFS reacts in the blended cement matrix faster than FA, as observed from the heat liberation results. The amount of CH reduced over the curing time also endorses the use of CH in the pozzolanic reaction of CH.
(5) HAC produces more CH in the hydration reaction than OPC. This allows for a replacement of up to 20% BFS or FA to maintain the same CH content as OPC. This high level of CH can also be used to indicate the higher resistance to carbonation in the structure.
(6) Based on the heat liberation and carbonation resistance, HAC is suitable for use as a blended cement at 10–30% FA replacement and ~20–30% BFS replacement. However, since the heat liberation of HAC is higher than OPC, this cement is not suitable for use in an unblended state.

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Fig. 9. Reaction ratio of C₃S at different curing times in blended HAC-1 samples.