Effect of temperature on the physico-mechanical and microstructure properties of cement pastes containing fly ash and silica fume

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Abstract. This study aimed to investigate the effect of heat treatment on the physico-mechanical and microstructure properties of cement pastes containing fly ash (FA) and silica fume (SF). Portland cement (OPC) has been partially replaced by 5% SF and 20, 30, 40 and 50 wt.% FA. After curing, the hardened cement pastes were dried at 100°C for 24 hours, subjected to thermal treatment at the rate of 5°C/min, and heated at temperature of 200, 400, 600, 800, 1000°C for 2 hours, then cooled to room temperature in air. Finally, their bulk density and compressive strength were determined. X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods and were used for identification of the changes in the microstructure of the cement matrices. The results showed that the cement pastes containing 80% OPC + 5% SF + 15% FA is the optimum mix which gives a higher compressive strength and lower bulk density loss. Moreover, this optimum binder has the formation of inner fibers and crystalline needle like Wollastonite, Gehlenite which is responsible for the reduction in compressive strength loss from 800 up to 1000°C.

1. Introduction

Concrete working at high temperatures often deteriorates in properties affecting structural strength. The aggregate, cement used in concrete, mix design and thermal expansion properties greatly affect the ability of concrete to work at high temperatures. The influence of high temperatures on concrete properties can be minimized by the use of mineral additives and thermally stabilized aggregates. The benefit of mineral additives with heat resistance is to create a pozzolanic reaction between the Silicon dioxide in mineral additives and the Calcium hydroxide (CH) in cement. At high temperatures, microstructure changes occur that affect the quality of concrete. First of all, CH cause microscopic cracks around its surrounding area at about 300°C [1]. Then the dehydration of CH occurs strongly in the temperature range of 500 – 550°C. The destruction of CH explains the reason why the content of free CaO in hardened cement paste increases significantly at about 550°C [2]. The second hydration of free CaO when cooling the sample will cause the volume expansion and destroy the inner the structure of hardened cement paste [3].

There have been many reports outlining the effect of fine mineral additives on the properties and structure of cement stone at high temperatures. The introduction of finely ground mineral additives in cement plays a necessary role when exposed to high temperatures due to the association of mineral additives with free CaO. These additives need to be required: easily combined with CaO, not melting, resistant to high temperatures, reducing shrinkage of cement hydration products, increasing the
strength of cement at high temperatures, not making reducing the activity of binder. The additives including SiO$_2$ and Al$_2$O$_3$ are mostly used as heat-resistant additives for cement. Some additives were investigated such as chamotte, alumina brick powder, kaolin, and blast furnace slag. Fly ash (FA) is a type of industrial waste that has also been studied as a binder component at high temperatures.

Dias WP S. et al believe that binder including cement replaced by 10% FA by weight can eliminate all surface cracks in the samples when cooled after preheat at 600°C [4]. Rehsi SS and Garg SK conclude that binder with a content of 20 ÷ 30% FA provides good heat resistance and dimensional stability when subjected to high temperatures and then cooled in high humidity [5]. The impact of high temperatures on the properties of cement and concrete using SF has also been investigated recently. Ghandehari M et al. concluded that replacing OPC by 10% SF improved concrete microstructure and mechanical properties of concrete when subjected to high temperatures and then cooled in high humidity [6]. Meanwhile in the study of Morsy M S et al showed that 5% SF replaced OPC gives cement mortar samples the higher strength at 800°C [7].

Some studies also mention the use of mixed additives to enhance the heat resistance of OPC. Chan Y N et al used a mixture of 15.4% SF and 38.5% FA (by weight, to replace cement) to make concrete that could work up to 800°C [8]. Heikal M's research shows that OPCs replaced by 10% FA and 10% SF have best improved the properties and structure of binder at 450°C [9].

In this paper, the authors studied the effect of temperature on the properties and structure of ternary binder composing OPC, FA and SF when heated to a temperature of 1000°C.

2. Materials and experimental program

Materials used for making heat – resistant binder in this study compose of Song Gianh Portland cement PC40 meeting TCVN 2682:2009. Fly ash from Vinh Tan Thermal Power Plant, has an activity index of 89.8%, according to TCVN 10302: 2014 and is classified as Type F according to TCVN 10302:2014. Silicafume from Sika meet all the requirements of TCVN 8827: 2011 as mineral additives for mortar and concrete. Chemical composition and some properties of materials are shown in tables 1 and 2.

| Materials | Oxides (%) | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | SO$_3$ | K$_2$O | Na$_2$O | LOI |
|-----------|------------|--------|-------------|-------------|-----|-----|-------|-------|-------|-----|
| OPC       |            | 21.12  | 12.09       | 1.44        | 60.73 | 0.86 | -     | 2.93  | -     | 0.84|
| FA        |            | 55.20  | 20.97       | 6.27        | 0.95 | 1.54 | 0.13  | 3.39  | 0.54  | 11.0|
| SF        |            | 89.00  | 1.03        | 1.01        | 1.21 | 1.39 | 0.02  | 2.00  | 0.90  | 3.43|

| Property | Unit | OPC | FA | SF | Methods |
|----------|------|-----|----|----|---------|
| Specific density | g/cm$^3$ | 3.11 | 2.29 | 2.22 | TVCN 4030:2003 |
| Bulk density     | kg/m$^3$ | 973.2 | 982.1 | 699.1 | TVCN 4030:2003 |
| Water content    | %    | - | 0.40 | 1.25 | TVCN 6016:2011 |
| Compressive strength at 28 days | MPa | 51.86 | - | - | TVCN 6016:2011 |
| Standard water   | %    | 32.2 | - | - | TVCN 6016:2015 |
| Initial setting time | min | 110 | - | - | TVCN 6016:2015 |
| Final setting time | min | 160 | - | - | TVCN 6016:2015 |
| Soundness        | mm   | 0.22 | - | - | TVCN 6016:2015 |
| Surface area     | m$^2$/g | 1.3881 | 0.4538 | 17.6596 | BET |
| Strength activity index | % | 89.9 | 109.2 | - | TVCN 6016:2011 |

The binder samples were prepared in the proportions shown in Table 3. The amount of OPC replaced by additives was 20, 30, 40 and 50%. The FA content was fix at 5%, the remaining additives is FA. The binder samples were manufactured in the moulds 20x20x20 mm. After curing, the samples were dried at 100°C for 24 hours and put into the furnace for heating to temperature levels of 200, 400, 600,
800 and 1000°C with a heating rate of not more than 5°C/min, then followed by constant heat process for 2 hours. After heating, the samples were cooled to room temperature and the volume density (bulk density) and the compressive strength of binder were determined. For microstructure analysis, the paper used the method of X-ray powder diffraction analysis (XRD) and scanning electron microscope (SEM).

Table 3. Materials proportion of heat-resistant binder, wt.%

| Sample Name          | OPC | FA | SF | Water of consistency |
|----------------------|-----|----|----|----------------------|
| OPC (Control sample) | 100 | 0  | 0  | 32.2                 |
| S5F15                | 80  | 15 | 5  | 31                   |
| S5F25                | 70  | 25 | 5  | 30.2                 |
| S5F35                | 60  | 35 | 5  | 29.4                 |
| S5F45                | 50  | 45 | 5  | 28.8                 |

3. Results and discussion

3.1. Bulk density

The results of the bulk density of the binder samples at high temperatures are shown in Figures 1 and 2.

![Figure 1](image1.png) ![Figure 2](image2.png)

**Figure 1.** Bulk density of binders at high temperature

**Figure 2.** The loss of bulk density of binders at high temperature

As the temperature increased to 200°C, the amount of free water and physical water evaporated [1-2], resulting in a reduction in the volume change from 2.01 to 3.01% when compared with the value at 100°C. From 200-400°C, there is a loss of physical and chemical bonding of CSH, CAH and calcium sulphaaluminate as well as calcium aluminosilicate hydrates [10], causing a drastic reduction of bulk density from 5.50 to 6.27%. From 400-600°C, dehydration of CH occurs, especially at about 550°C, leading to the most significant decrease of bulk density from 9.39 to 10.41%. When heating up binder samples to 600-800°C, formation of $\beta$-C$_2$S is observed due to the decomposition of C-S-H, bulk density continue to decrease from 10.69-12.06%.

At 800-1000°C there was a decomposition of CaCO$_3$, OPC samples were completely destroyed and the remaining samples had bulk density reduced from 11.48-11.79%. At the same temperature level, the OPC sample has a higher bulk density when compared to the sample containing additives because of the smaller specific density of additives, but the OPC sample has the largest decline in bulk density. This result indicate that there were a strong dehydration of CH and decomposition of CaCO$_3$ [10]. In the samples containing additives, the S5F15 sample gives the highest bulk density value and the
smallest bulk density depletion. An appropriate additive content helps limiting some harmful processes such as dehydration, decomposition, and shrinkage occurring in binder at high temperature.

3.2. Compressive strength

The results of compressive strength of the binder samples are shown in Figure 3 and Figure 4. At room temperature (25°C), the greater the rate of cement replacement by additives, the less compressive strength of the sample when compared to control sample (OPC). This can be explained by the lower FA activity of cement, causing the dilution effect of cement. By drying and heating the binder samples to 100 ÷ 200°C, the strength of the binders gradually increases. At this temperature range, the dehydration of free and physical water causes the binder to contract decreasing the volume while free water evaporates to promote the continuous hydration of OPC and increase the strength of binder (like the "steam vapour curing" process) [11]. The compressive strength at 200°C was increased by 23.7% to 34% when compared to the compressive strength at 100°C.

Heating the sample to 400°C, the compressive strength of the samples in general decreases when compared to that of 200 ° C but it is still higher than the strength of 100°C. In particular, OPC samples experienced a drastic strength reduction of 23.3% while samples containing additives have compressive strength increased from 5.8% to 13.8% when compared to that at 100°C. The reason may be due to the high decomposition of CSH and CAH minerals in OPC samples [10], while in samples containing additives there are new minerals generated due to pozzolanic reaction. This results in the formation of hydrothermal products including tobermorite minerals (5CaO.6SiO₂.xH₂O) more durable than CSH minerals 2 to 3 times [12].

When heating the sample to 600 ° C, the compressive strength of the samples is greatly reduced. OPC samples had a drastic reduction of 48.3% in compressive strength while samples containing additives only had a compressive strength reduction of 1.4% to 7% compared to compressive strength at 100°C. During this period, the decomposition of CH into free CaO and the reaction of moisture in the air during cooling causes the micro-cracks, increases the sample volume, reduces strongly the sample strength [3].

When heating samples to 800°C, the compressive strength of the samples sharply decreases. The OPC sample had the lowest compressive strength due to the second phase of the C-S-H decomposition formation of β-C₃S [2], the strength decreased by 70.6% compared to the value of compressive

Figure 3. Strength compressive of binders at high temperature

Figure 4. The loss of strength compressive of binders at high temperature
strength at 100°C. The strength of the samples containing additives decreased from 15.9% to 47.3% when compared to the compressive strength value at 100°C. When heating the sample up to 1000 °C, a strong reduction of the compressive strength of the samples was observed. OPC samples were completely cracked due to the strong decomposition of CSH and CaCO$_3$. The samples containing additives had a decrease in strength from 67.54% to 79.93% compared to the compressive strength at 100°C. The samples containing additives had a lower attenuation strength than the OPC sample because the pores of binders were filled with additional hydration products as a result of the pozzolanic reaction, especially with the appearance of SF. At 800-1000°C, the decomposition of CSH gels is the basis for the solid reaction in binders to form new minerals with structures similar to C$_2$S, which are wollastonite and gehlenite crystals [9].

The combination of FA and SF additives in binder samples significantly improved the compressive strength values of binder samples at high temperatures. In binder containing additives, the samples containing 5% SF and 15% FA give the highest compressive strength values in the temperature range of 400-1000°C. At 800°C, the sample gives the highest compressive strength value of 51.7 MPa, it means more 2.75 times higher than the OPC sample. In another study, binder samples only used FA additives with a content of 25% (weight compared to cement) has compressive strength of 39 MPa (1.4 times higher than the control sample OPC) at 800°C [13]. The effects of mixed additives FA and SF compared with FA were also shown in the study of Ibrahim R Kh [14].

3.3. XRD analysis

XRD was performed to detect changes in the hydration products of binder samples in the presence of FA and SF at high temperatures. Figure 5 shows the results of XRD analysis of OPC and S5F15 samples before and after heating. At a temperature of 25°C, OPC samples have CH, C$_2$S, C$_3$S, CaCO$_3$, CSH minerals. The appearance of these minerals in the OPC is similar to that previous research by Heikal M [15]. When the sample had additives, it led to a reduction of CH peaks compared to the control samples (OPC), some peaks disappeared due to the pozzolanic reaction of SF to produce CSH. At 800°C, OPC samples have the appearance of CH, C$_2$S, C$_3$S, CaO and CaCO$_3$ minerals. At this temperature, CSH gel completely disappeared [2], mainly replaced by crystal phase with structure similar to C$_3$S. CH peaks were decreased due to CH decomposition to create free CaO is one of the

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**Figure 5. XRD analysis of OPC and S5F15 before and after exposure to high temperature**
causes to destroy the samples by the moisture absorption of CaO causing volume expansion. For the sample containing additives S5F15, CH peaks are significantly reduced, the solid reaction occurs between CaO and SiO₂, Al₂O₃ in the binder composition promoted the new mineral formation such as CA and wollastonite (CS) [16]. The wollastonite is a ceramic product that enhances the compressive strength. Research on Heikal M's CKD using SF also showed the occurrence of this mineral, C₂S and C₃S at 800°C [9]. At 1000°C some minerals such as C₂S, CS and gehlenite (C₂AS) also are observed in the sample. The formation of C₂AS occurs at temperatures above 900°C in the study of Tezic A [17]. The appearance of these minerals explains the smaller decrease in compressive strength when compared to OPC sample at 800-1000°C.

3.4. SEM analysis

![SEM analysis of OPC and S5F15 before and after exposure to high temperature](image)

**Figure 6.** SEM analysis of OPC and S5F15 before and after exposure to high temperature

a) OPC at 25°C; b) S5F15 at 25°C; c) OPC at 800°C; d) S5F15 at 800°C; e),f) S5F15 at 1000°C

SEM analysis results of OPC and S5F15 samples before and after heating are shown in Figure 6. Before heating, CH and CSH were clearly seen in the OPC sample (Fig 6a) with many pores in the
sample. In the S5F15, CH was reduced, less pores than the OPC control are observed due to the high reactivity of SF at room temperature, linking the hydration products with fly ash (Fig. 6c). When heating to 800 °C, a crack is observed on the OPC sample (Fig. 6b) while the S5F15 sample has a higher density (Fig. 6d). This explains the reason why the strength of binder containing additives was increased when compared to the control sample. At 1000°C, crystalline in form of rods are observed (Fig. 6e, 6f). This is a product produced by solid reaction at high temperatures. These results are in a good agreement with the XRD.

4. Conclusions

Based on the empirical results, some conclusions are drawn as follows:

- Using FA and SF improves the properties of binders at high temperatures.
- The heat – resistant binder containing 5% SF and 15% FA give the lowest reduction of compressive strength and volume in the temperature range of 400-1000°C, but better service at temperatures ≤ 800°C. At 800°C, the sample has a volume density of 1838 kg/m³ and a compressive strength of 51.7 MPa.
- Control sample OPC have the highest compressive strength at 200°C but lowest compressive strength from 400-800°C. It was completely destroyed at temperatures superior to 800°C.
- The microstructure investigation indicated the occurrence of wollastonite and gehlenite minerals at about 800-1000°C. Micro voids and cracks was limited in binder containing 5% SF and 15% FA at 800°C and the appearance of new crystals at 1000°C to enhance the heat resistance for binders.

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