The influence of an Austrian fly ash on the reaction processes in the clinker phases of Portland cements

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The aim of the paper is to establish the influence of fly ash on the hydration process of the cement and fly ash mixtures. Particular attention was paid to the influence on the main clinker phases, $C_3S$, $C_2S$ and $C_3A$ being investigated by X-ray methods at various points during the reaction period. The reaction partners used were two normal Austrian Portland cements plus an Austrian brown-coal ash. In addition to the pure cements, a mixture with 30% fly ash and 70% of the respective cements was also investigated. For purposes of comparison, it was also necessary to analyse in each case a cement mixture with an inert substance in the same ratio.

1. INTRODUCTION

Various kinds of fly ash, a waste product formed as a residue in the combustion of brown coal or pit-coal, have latent hydraulic characteristics. In such a case they can be used with cement as a fine aggregate. In Austria 15% of the cement is normally replaced by suitable puzzolanic materials. When fly ash is used the product is marketed under the name PZ 275 F.

For large-scale technical construction projects 30% ash is added to the cement.

Basically, the fly ash reacts with the $Ca(OH)_2$ resulting in the hydration of the cement clinker phases. During the reaction most of the ash is decomposed, thus leading to new phases, mainly $Ca-Si$ hydrates and also a small proportion of $Ca-Al$-hydrates. In various investigations it was shown that the strength developed by the fly ash and $Ca(OH)_2$ can largely be explained by the formation of the above mentioned phases. It was shown thermo-analytically that the hydration of cement fly ash mixtures leads to similar reaction products as in the case of pure cements. But even with modern investigation techniques it is very difficult to identify and classify the reaction products exactly. For this reason it is only practicable to study the reaction process through the decomposition of the initial phases.

The aim of this study was to investigate the reaction mechanisms of two pure cements and of mixtures of fly ash and portland cements in the system with water. For this purpose two portland cements were selected that showed the greatest difference in compressive strength. An attempt was made to draw conclusions from the reaction processes on these differing technological behaviour patterns.

Test conditions, technical and chemical data for the cements used and the fly ash

The two cements used in the reaction tests are designated as cement 1 ($Z_1(100)$) and cement 2 ($Z_2(100)$). In addition, test samples were produced of 70% cement and 30% fly ash ($Z_1(70)$) and ($Z_2(70)$). The ash employed was fly ash from Saint-André.

For the purpose of comparison, mixtures with 30% quartz were also made from the two cements $Z_1$ and $Z_2$.

With all test mixtures a w/c ratio of 0.4 was used for the pastes in the reaction. For each test period a separate reaction sample was used for the examination to avoid disturbing the reaction process by opening the sample prematurely.

2. QUALITATIVE OBSERVATIONS

In addition to the quantitative studies which form the main body of this investigation into the influence of fly ash on the reaction process of the main clinker phases, $C_3S$, $C_2S$ and $C_3A$, a series of qualitative investigations were also made in the system. The aim of these qualitative investigations was to cover the newly formed phases with and without fly ash completely.
Starting with the Ca-Si-hydrates, the cements, including others in addition to the named types, gave no indications of the formation of Ca-Si-hydrates corresponding to Taylor's "semi-crystalline" type of Ca-Si-hydrates. These findings contradict investigations quoted in the literature and no explanation is offered at this stage. In the above mentioned phases one would expect diffraction effects at around 10-12 Å and a marked peak at around 3.03 Å. In general the first two diffraction effects are altogether absent from all the pure hydrated cements investigated or are only vaguely detectable. In the case of cement and fly ash mixtures these "semi-crystalline" phases are of only minor significance. After a reaction period of approx. 18 months, only minimal amounts of the original Ca-Si phases C₃S and C₂S remain, which would suggest that the products formed can only be Ca-Si-hydrates of the "near amorphous" group.

At present only the use of thermobalances can establish these "near amorphous" phases as an independent product. In the X-ray diagram they merely lead to slight bulges in certain areas, which cannot be satisfactorily evaluated quantitatively in any way.

In this connection it is interesting to note that the original phases C₃S and C₂S react differently with 30% fly ash and with pure cement pastes. After a reaction period of 18 months C₃S is still clearly identifiable in pure cement pastes whereas the phase is fully decomposed with cement and fly ash mixtures. Interestingly enough, this effect is reversed for C₂S. With 30% fly ash mixtures X-ray diffraction values can be obtained for this phase, whereas they are completely absent with pure cement pastes. The phenomenon is also found when other cements and fly ash react. This effect is analysed in greater detail for the quantitative investigations.

Ettringite represents the main share of the reacted calcium aluminate (predominantly C₃A) and at the same time it is the most important hydration product of this phase. It was found in all the hydrated cement samples investigated as well as in their fly ash mixtures. For those samples that originally have a higher initial CaSO₄ content more ettringite can be established than for the samples which originally have a lower SO₃ content. The dependence of the quantitative ettringite content on the SO₃ content of the initial material is explained by the sufficient presence of C₃A. With some cements and fly ash cements Ca-Al-monosulphate can occur. This was not the case, however, with Z₁ (100) and Z₂ (100) and their mixtures. With most of the fly ash samples subjected to quantitative investigation, the C₃A content was still sufficient to form other Ca-Al-hydrates, in these hydration phases predominantly C₄AH₁₃ or C₃AC₃H₁₃, which are present in all hydrated cements and fly ash. The latter phase is presumably explained by carbonisation of C₄AH₁₃. C₄AH₆ was absent from all tested samples, because of the excess of Ca(OH)₂ even in fly ash mixtures. The situation with Ca-Al-hydrates for the fly ash and cement mixtures is similar to that of the pure cements.

| TABLE I | CHEMICAL COMPOSITION IN PER-CENT |
|-------------------------|---------------------|---------------------|---------------------|
|                        | Cement 1       | Cement 2       | Fly ash       |
| SiO₂ (tot)*             | 19.80          | 20.65          | 51.67          |
|                        | 19.63          | 20.49          | 50.00          |
| Al₂O₃                   | 7.85           | 7.78           | 6.41           |
|                        | 7.85           | 6.36           | 24.41          |
| Fe₂O₃                   | 2.64           | 2.62           | 2.54           |
|                        | 2.56           | 7.54           | 7.34           |
| CaO                     | 62.65          | 62.10          | 62.12          |
|                        | 62.12          | 61.63          | 61.63          |
| MgO                     | 2.48           | 2.46           | 2.81           |
|                        | 2.81           | 2.79           | 3.45           |
| Na₂O                    | 0.29           | 0.29           | 0.25           |
|                        | 0.25           | 0.25           | 1.06           |
| K₂O                     | 0.67           | 0.65           | 1.10           |
|                        | 1.10           | 1.09           | 3.25           |
| SO₃                     | 3.32           | 3.29           | 3.77           |
|                        | 3.74           | 0.87           | 0.84           |
| Inclus. Insol. Loss     | 0.88           | 0.78           | 3.24           |
| TOTAL (0/0)             | 99.70          | 99.67          | 98.90          |

| PHASE COMPOSITION IN PER-CENT |
|-------------------------|---------------------|---------------------|
|                        | Cement 1 by X-ray  | Cement 2       |
| C₃S                    | 56.9               | 49.5               |
| C₂S                    | 19.5               | 22.0               |
| C₃A                    | 6.3                | 4.1                |
| C₃AF                   | app. 5.0           | app. 4.0           |
| Glass (X-Ray amorph.)  | app. 6.0           | app. 10.0          |
| CaSO₄ and              | 5.5                | 6.4                |
| CaSO₄·2 H₂O             |                    |                    |
| TOTAL (0/0)             | 99.20              | 96.0               |