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INFLUENCE OF CURING TEMPERATURE ON CEMENT HYDRATION AND MECHANICAL STRENGTH DEVELOPMENT OF FLY ASH MORTARS

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ABSTRACT

The influence of fly ash and curing temperature on cement hydration and compressive strength development of mortars was investigated. Test parameters included type of fly ash (two different Class F fly ashes were tested), the level of cement replacement (10, 20 and 30% by mass), and curing temperature (20°C and 40°C). The mortar physical and microstructural properties were determined by means of thermal analyses, compressive strength measurements and SEM observations. Test results confirm that fly ash tends to increase significantly the rate of cement hydration at early age. Data also demonstrate that an elevation of the curing temperature reduces the long-term compressive strength of the reference mortar mixture. In contrast, an increase of the curing temperature seems to have no detrimental effect on the long-term compressive strength of the fly ash mixtures. © 1997 Elsevier Science Ltd

Introduction

Nowadays, civil engineers and concrete specialists increasingly rely on models to predict the evolution of the overall behavior of reinforced concrete structures. The reliability of these models rests on a very good understanding of the influence of various parameters, such as temperature and the use of supplementary cementing materials, on the cement hydration kinetics and the concrete mechanical strength development.

Recently, numerous models have been specifically developed to predict the mechanical strength development of concrete mixtures made of supplementary cementing materials (1-6). Although they differ both in nature and in complexity, most of these models share one common feature. In most cases, the contribution of the supplementary cementing material to the concrete mechanical strength development is attributed solely to the pozzolanic reaction. The influence of the supplementary material on the cement hydration kinetics is rarely taken into account.

However, it is actually widely recognized that the presence of supplementary cementing materials can have a significant influence on the hydration kinetics of cement. For instance, numerous reports have indicated that the presence of fly ash and silica fume particles can

contribute to accelerate the early hydration of cement (6-11). The addition of less reactive minerals, such as fine calcium carbonate fillers, has also been found to accelerate the hydration kinetics of cement at early days (12).

If the effect of supplementary cementing materials on the cement hydration mechanisms has been the subject of a number of investigations, it should be emphasized that there exists, however, very few data on the influence of temperature on the kinetics of the pozzolanic reaction (13). In most cases, the pozzolanic reaction mechanisms have been investigated under isothermal conditions at 20°C. The little information available on the subject tends to indicate that the phenomenon is, like most chemical reactions, temperature-dependent (6, 14).

In this context, the main objective of this investigation was to bring more information on the influence of fly ash and temperature on the cement hydration and the compressive strength development of mortar mixtures. This investigation was carried out as part of a comprehensive study of the influence of fly ash on the physical properties of mortar and concrete (13).

Test Program

In order to determine the influence of fly ash on the cement hydration and the compressive strength development, various mortar specimens were prepared with an ordinary portland cement and two different North-American Class F fly ashes (according to ASTM C 618). The mortar mixtures were produced at a constant water/binder ratio of 0.50 and at a binder/sand ratio of 2.5. In order to evaluate the effect of fly ash on cement hydration, fly ash was used at a cement replacement level of 10%, 20% and 30% (by total mass of binder). The mortar specimens were subjected to an isothermal curing temperature of 20°C and 40°C. The compressive strength and the non-evaporable water content of the mortar mixtures were regularly measured upon a period ranging from 7 hours to 42 days.

Materials, Sample Preparation and Experimental Procedures

Materials. Mortar mixtures were produced with an ordinary Canadian CSA type 10 portland cement and two different North-American ASTM Class F fly ashes. The chemical, mineralogical compositions and the physical characteristics of the cement and the two fly ashes are given in Table 1. Despite its high calcium content, fly ash 1 complies with all the ASTM requirements for a Class F ash. Pertinent information on the morphological and chemical characteristics obtained by scanning electron microscope observations are summarized in Table 2. The mixture characteristics of all mortars are given in Table 3.

<u>Sample Preparation</u>. All mixtures were prepared in accordance with ASTM C 305 requirements. Prior to mixing, all constituents (cement, fly ashes, sand and water) were stored in a temperature-controlled chamber in order to obtain a mixing temperature as close as possible to the specified curing temperature (20°C or 40°C).

At the end of the mixing period, the consistency of the mortar mixture was assessed according to the requirements of ASTM C 230. Test results are presented in Table 5. Each mortar mixture was cast in oiled brass molds ($50 \times 50 \times 50$ mm). The molds were filled with two layers of mortars in accordance with the Canadian standard CSA-A5-M83 requirements.

| OXIDES | CEMENT (%) | FLY ASH (%) | | COMPOUND | CEMENT (%) | FLY ASH (%) | |
|--------------------------------|-------------|-------------|--------|-----------------------------|-------------|-------------|------|
| | CSA TYPE 10 | FA1 | FA2 | | CSA TYPE 10 | FAI | FA2 |
| SiO ₂ | 20.61 | 46.25 | 66.28 | C ₃ S | 52 | - | - |
| Al ₂ O ₃ | 4.23 | 20,64 | 18.52 | $C_2^{\circ}S$ | 19 | - | - |
| TiO ₂ | 0.20 | 1.02 | 1.41 | C ₃ A | 6 | - | - |
| P_2O_5 | 0.23 | 0.31 | 0.00 | C ₄ AF | 9 | - | - |
| Fe ₂ O ₃ | 3.05 | 5.60 | 2.90 | | | | |
| CaO | 61.85 | 18.10 | 7.32 | Blaine (m ² /kg) | 370 | 272 | 225 |
| SrO | 0.25 | 0.56 | 0.12 | (| | | |
| MgO | 2.61 | 4.50 | 1.52 | BET (m ² /g) | - | 0.62 | 0.50 |
| Na ₂ O | 0.20 | 0.51 | 0.38 | (, , , | | | |
| K ₂ O | 0.91 | 0.30 | 1.03 | % passing the | - | 84.7 | 80.7 |
| $\tilde{SO_3}$ | 3.47 | 1.75 | 0.16 | 40-μm sieve | | | |
| Mn ₂ O ₃ | 0.06 | 0.00 | 0.00 | | | | |
| MnO | 0.00 | 0.22 | 0.17 | | | | |
| Cr ₂ O ₃ | 0.00 | 0.01 | 0.02 |] | | | |
| LOI | 2.28 | 0.25 | 0.19 | | | | |
| Total | 99.95 | 100.02 | 100.02 | | | | |

TABLE 1
Chemical, Mineralogical and Physical Analysis of Cement and Fly Ash

<u>Isothermal Curing</u>. Immediately after casting, the mortar samples were immersed in water tanks which were maintained at the required curing temperature (i.e., at 20°C or 40°C). The temperature of each water tank was measured by thermocouples linked to an automatic recorder. The isothermal conditions were maintained during the entire duration of the curing period.

Approximately 24 hours after the initial contact between the water and the cement grains, the mortar specimens were removed from their moulds. With the exception of the samples immediately required for testing, all cubes were replaced in their isothermal water tank.

TABLE 2
Fly Ash Physical Characteristics

FLY ASH I

- The diameter of the various particles ranges between 0.5 and 20 μm. The biggest particles are usually rich in silicon and the smaller are rather rich in calcium;
- The free lime (CaO) is relatively abundant. The mean diameter of the free lime is approximately 2 μm;
- Anhydrite (CaSO₄), quartz and some spherical iron oxide particles were also observed.

FLY ASH 2

- The particle diameter ranges from 1 to 30 μm. The diameter of most particles range from 2 to 10 μm;
- The particles are rich in silicium and aluminum;
- Quartz is also abundant.

| TABLE 3 |
|-------------------------|
| Mixture Characteristics |

| | MIXTURE | CEMENT kg/m ³ | FLY ASH kg/m ³ | WATER kg/m ³ | SAND kg/m ³ | FLOW % | AIR % |
|----|-----------------|-----------------------------|------------------------------|----------------------------|---------------------------|-----------|----------|
| 1 | T10-20°C | 530 | n/a | 265 | 1325 | 128 | 3.6 |
| 2 | T10-40°C | 530 | n/a | 265 | 1325 | 129 | 4.7 |
| 3 | T10-10%FA1-20°C | 477 | 53 | 265 | 1325 | 130 | 3.9 |
| 4 | T10-10%FA140°C | 477 | 53 | 265 | 1325 | 139 | 4.2 |
| 5 | T10-20%FA1-20°C | 424 | 106 | 265 | 1325 | 144 | 3.6 |
| 6 | T10-20%FA1-40°C | 424 | 106 | 265 | 1325 | 148 | 3.4 |
| 7 | T10-30%FA1-20°C | 371 | 159 | 265 | 1325 | 129 | 3.6 |
| 8 | T10-30%FA1-40°C | 371 | 159 | 265 | 1325 | 144 | 2.9 |
| 9 | T10-20%FA2-20°C | 424 | 106 | 265 | 1325 | 139 | 3.7 |
| 10 | T10-20%FA2-40°C | 424 | 106 | 265 | 1325 | 140 | 3.7 |

Small amounts of sodium hydroxide (12.4 g/L) and potassium hydroxide (24.7 g/L) were dissolved in the water to minimize leaching of the pore solution alkalis.

<u>Compressive Strength Measurements</u>. The compressive strength measurements were performed in accordance with the requirements of the Canadian CSA-A5-M83 standard. For each test condition, three cubes were tested. The mortar samples were removed from their curing tank about five minutes prior to testing.

TABLE 4
Non-evaporable Water Contents

| | | | ******** | | | | | | |
|----|-----------------|------------|----------|--------|--------|-------|-------|-------|-------------|
| n° | MIXTURE | | | | | TIME | | | |
| | | | 7h | 10h | 26h | 3d | 14d | 28d | 42d |
| 1 | T10-20°C | Wn(t)/C | - | 0.0355 | 0.0885 | 0.123 | 0.168 | 0.192 | 0.182 |
| 2 | T10-40°C | Wn(t)/C | 0.0587 | 0.0900 | 0.1290 | 0.157 | 0.178 | 0.207 | 0.218 |
| 3 | T10-10%FA1-20°C | Wn(t)/C+FA | - | 0.0409 | 0.0869 | 0.124 | 0.159 | 0.145 | 0.181 |
| | | Wn(t)/C | - | 0.0454 | 0.0966 | 0.138 | 0.177 | 0.161 | 0.201 |
| 4 | T10-10%FA1-40°C | Wn(t)/C+FA | 0.0710 | 0.0889 | - | 0.157 | - | 0.192 | - |
| | | Wn(t)/C | 0.0789 | 0.0990 | - | 0.174 | - | 0.213 | - |
| 5 | T10-20%FA1-20°C | Wn(t)/C+FA | - | 0.0344 | 0.0802 | 0.118 | 0.149 | 0.158 | 0.159 |
| | | Wn(t)/C | - | 0.0430 | 0.1002 | 0.148 | 0.186 | 0.198 | 0.199 |
| 6 | T10-20%FA1-40°C | Wn(t)/C+FA | 0.0577 | 0.0833 | 0.1225 | 0.150 | 0.179 | 0.154 | 0.189 |
| | | Wn(t)/C | 0.0721 | 0.1041 | 0.1531 | 0.188 | 0.223 | 0.193 | 0.236 |
| 7 | T10-30%FA1-20°C | Wn(t)/C+FA | - | 0.0354 | 0.0739 | 0.105 | 0.145 | 0.142 | 0.158 |
| | | Wn(t)/C | - | 0.0506 | 0.1055 | 0.150 | 0.207 | 0.203 | 0.226 |
| 8 | T10-30%FA1-40°C | Wn(t)/C+FA | 0.0571 | 0.0838 | 0.1170 | 0.141 | 0.170 | 0.168 | 0.166 |
| | | Wn(t)/C | 0.0816 | 0.1197 | 0.1670 | 0.201 | 0.244 | 0.240 | 0.237 |
| 9 | T10-20%FA2-20°C | Wn(t)/C+FA | - | 0.0352 | 0.0746 | 0.100 | 0.132 | 0.141 | 0.136 |
| | | Wn(t)/C | - | 0.0440 | 0.0933 | 0.125 | 0.165 | 0.176 | 0.170 |
| 10 | T10-20%FA2-40°C | Wn(t)/C+FA | 0.0555 | 0.0781 | 0.1242 | 0.132 | 0.163 | 0.177 | 0.171 |
| | | Wn(t)/C | 0.0694 | 0.0976 | 0.1552 | 0.165 | 0.203 | 0.221 | 0.213 |

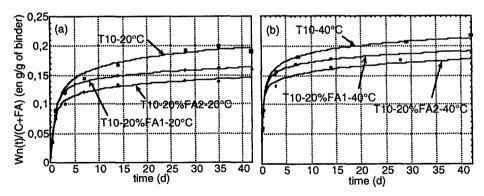


FIG. 1.

Non-evaporable water content for fly ash 1 and 2 for an isothermal curing at 20°C (a) and 40°C (b).

Non-evaporable Water Content Measurements. The non-evaporable water content of the mortar specimens was measured according to the method described by Kjellsen (15). The mortar samples which had been tested for compressive strength were crushed in small fragments. The fragments were immersed in isopropylic alcohol in order to stop the hydration process. The mortar fragments were finely crushed and oven-dried at 105°C for 24 hours. After the drying period, the porcelain crucibles were removed from the oven, cooled in a dessiccator, and weighed. The crucibles were then placed in a furnace where the temperature was progressively increased from 20°C to 1000°C over a 20 minute period. The 1000°C temperature was maintained for approximately 30 minutes. After ignition, the furnace temperature was cooled to 200°C. The crucibles were removed, cooled in the desiccator to the ambient temperature, and then weighed.

TABLE 5
Increase in Non-evaporable Water Content* at Early Days

| MIXTURE | TIME | INCREASE IN NON-EVAPORABLE WATER CONTENT (%) (with respect to reference mixture) | | | | |
|------------|----------|--|-------|--|--|--|
| | | 20° C | 40° C | | | |
| T10-10%FA1 | 10 hours | 27 | 34 | | | |
| | 26 hours | 9 | 10 | | | |
| | 3 days | 12 | - | | | |
| T10-20%FA1 | 10 hours | 21 | 23 | | | |
| | 26 hours | 13 | 15 | | | |
| | 3 days | 20 | 18 | | | |
| T10-30%FA1 | 10 hours | 42 | 39 | | | |
| | 26 hours | 19 | 33 | | | |
| | 3 days | 22 | 29 | | | |
| T10-20%FA2 | 10 hours | 24 | 18 | | | |
| | 26 hours | 6 | 8 | | | |
| | 3 days | 2 | 11 | | | |

^{*}expressed on a unit mass of cement basis

TABLE 6
Compressive Strength Results

| n° | MIXTURE | | | - | | TIME | | | | |
|----|-----------------|------|------|------|------|------|------|------|------|------|
| | | 7h | 10h_ | 26h | 3d_ | 7d | 14d | 28d | 35d | 42d |
| 1 | T10-20°C | • | 2.3 | 17.2 | 26.6 | 37.8 | 43.9 | 45.0 | 49.0 | 51.0 |
| 2 | T10-40°C | 7.1 | 13.4 | 26.2 | 35.3 | 38.9 | 40.7 | 42.8 | - | 44.7 |
| 3 | T10-10%FA1-20°C | - | 1.7 | 15.5 | 27.5 | 31.5 | 39.3 | 48.7 | 51.7 | 53.6 |
| 4 | T10-10%FA1-40°C | 10.5 | 15.9 | 27.0 | 28.1 | - | 41.0 | 45.0 | - | 46.9 |
| 5 | T10-20%FA1-20°C | - | 1.0 | 14.0 | 18.7 | 28.2 | 41.1 | 45.9 | 52.3 | 53.2 |
| 6 | T10-20%FA1-40°C | 4.5 | 9.6 | 22.5 | 28.6 | 39.2 | 42.2 | 50.5 | - | 55.0 |
| 7 | T10-30%FA1-20°C | - | 0.8 | 9.0 | 20.5 | 28.8 | 34.1 | 39.9 | 43.0 | 46.5 |
| 8 | T10-30%FA1-40°C | 3.9 | 9.0 | 22.7 | 29.9 | - | 47.9 | 52.1 | - | 55.2 |
| 9 | T10-20%FA2-20°C | - | 1.5 | 13.6 | 20.1 | 30.8 | 33.8 | 39.9 | 44.1 | 45.9 |
| 10 | T10-20%FA2-40°C | 5.6 | 11.7 | 22.5 | 26.2 | 37.3 | 41.5 | 49.0 | - | 50.6 |

The non-evaporable water content was calculated by the equation proposed by Xu (6):

$$\frac{W_n(t)}{C + FA} = \frac{W_{105^{\circ}C}}{W_{1000^{\circ}C}} = \left\{1 - y + s - c \times (z - y)\right\} - (1 + s) \tag{1}$$

where

Wn(t)/C + FA = non-evaporable water expressed in a unit mass of binder basis;

 $W_{105^{\circ}C}$ = mass of the sample after heating at 105°C;

 $W_{1000^{\circ}C}$ = mass of the sample after heating at 1000°C;

x = loss on ignition of the sand;

y = loss on ignition of the cement;

s = sand/binder ratio;

c= fly ash/binder ratio.

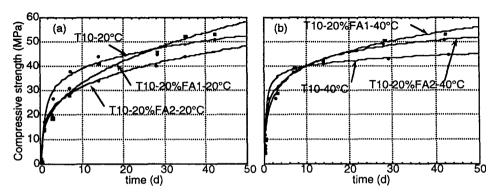


FIG. 2.

Influence of fly ash 1 and 2 on the compressive strength development of mortars cured at 20°C (a) and 40°C (b).

SEM Observations. The microstructural characteristics of selected mortar samples were determined by scanning electron microscope (SEM) observations carried out on both fractured and polished sections. The chemical composition of the hydration products was determined by energy-dispersive X-ray micro-analyses. All measurements were made at a voltage of 15 kV.

Test Results

Non-evaporable Water Content. Results of the non-evaporable water content measurements are given in Table 4. In the table, the non-evaporable water content of each mixture is first expressed on a unit mass of binder basis (Wn(t)/(C + FA)). Test results indicate that the partial replacement of cement by fly ash contributes to reduce the non-evaporable water content expressed on a unit mass of binder basis (Wn(t)/(C + FA)). This effect can be observed for both fly ashes and for both curing temperatures. The reduction in the non-evaporable water content is more pronounced for fly ash 2 (see Figure 1).

The non-evaporable water content can be also expressed on a unit mass of cement basis (Wn(t)/C). The latter values were calculated using equation (2):

$$V(t)/C = V(t)/(C + FA)/(1 - FA/(C + FA))$$
 (2)

Non-evaporable water contents calculated according to Equation 2 are also included in Table 4 where it can be seen that the addition of fly ash appears to significantly increase the amount of non-evaporable water of the mixture. This effect seems particularly pronounced for the first hours of curing, and tends to decrease subsequently.

In order to better visualize the influence of fly ash on the early cement hydration process, the relative increase in the non-evaporable water content (with respect to the reference mixture) was calculated for each fly ash mixture. Results of these calculations are given in Table 5. As can be seen, results clearly indicate that the presence of fly ash markedly increases the amount of non-evaporable water at early days. After only 10 hours of isothermal curing, the increase in non-evaporable water content ranges from 18 to 42%. Curiously, the increase appears to be relatively independent of the curing temperature and the type of fly ash.

Test results also show that the effect of fly ash tends to be substantially reduced with time. This reduction appears to be more pronounced for the mortar prepared with fly ash 2. I should be emphasized that the validity of the results appearing in Table 5 rests on the assumption that fly ash particles act as inert grains during the initial stage of hydration.

Compressive Strength Development of Mortars. The mortar compressive strength results are given in Table 6. Test results indicate that the use of fly ash significantly contributes to reduce the early compressive strength of the mixtures cured at 20°C. For instance, when fly ash 1 is used (mixtures no. 3 to 8), the compressive strength development is approximately reduced from 15 to 25% after 7 days of isothermal curing at 20°C. The compressive strength reduction clearly depends upon the cement replacement level (10, 20 or 30%). A similar tendency can be observed for mixture prepared with fly ash 2 and cured at 20°C.

As can be seen in Figure 2, the detrimental influence of fly ash is markedly attenuated when the curing temperature is raised from 20°C to 40°C. At a curing temperature of 20°C, depending on the cement replacement level and the type of fly ash, the compressive strength of fly ash mortars takes from 25 to 50 days to reach that of the reference mixture

(T10-20°C). On the other hand, at a curing temperature of 40°C, the compressive strength of the fly ash mortars takes only 5 to 10 days to achieve that of the reference mixture (T10-40°C).

Globally, compressive strength results indicated that fly ash mixtures are more sensitive to temperature effects, particularly during the first hours of curing. As can be seen in Table 6, an elevation of the curing temperature from 20°C to 40°C has contributed to multiply the strength of the reference mixture by a factor 6 after only 10 hours of curing. By comparison, the compressive strength of fly ash mortar mixtures cured at 40°C is approximately 8 to 10 time higher that of the mixture cured at 20°C. An increase of this magnitude is very significant.

<u>SEM Observations</u>. SEM observations were carried out after 28 and 42 days of hydration. After 28 days, most of the spherical particles still had a very smooth surface with little evidence of significant reaction of the fly ash itself (see Figure 3).

It should be emphasized that very little distinction could be made between the two fly ashes. Neither was it possible to distinguish clearly the mixtures which had been cured at 20°C from those cured at 40°C. In all cases, etching of glassy materials was rarely visible. In some instances, large Ca(OH)₂ crystals surrounding a spherical fly ash particle could even be observed. In some other cases, fly ash particles appeared to have acted as nucleation sites for C-S-H and sulphoaluminate hydration products. For the mixture prepared with fly ash 2, several quartz particles well embedded in the paste could also be observed.

Besides the presence of the fly ash particles, the microstructure of all mixtures was globally similar. There was no apparent distinction between the C-S-H morphology of the OPC and the fly ash paste. Both appeared to be quite dense. However, bonding between the fly ash particles and the C-S-H appeared to be relatively weak. In many instances, pits, from which the fly ash particles had been pulled out during the sample preparation, could be easily observed.

After 42 days of hydration, SEM observations revealed the evidence of reaction for the mixtures prepared with fly ash 1. This was particularly the case for the mixture cured at 40°C for which numerous ash particles were found to be extensively etched and surrounded by hydration products. Qualitative analyses by EDXA indicated that these hydrated phases were rich in calcium, silicon and aluminum. The reacting particles had, in most cases, retained their spherical shapes. The reaction had clearly improved the bonding between the fly ash particles and the paste.

SEM observations also confirmed the lesser reactivity of fly ash 2. Even after a curing period of 42 days at 40°C, numerous smooth fly ash particles could be observed. During the observations, some ash particles were found to be extensively etched and surrounded by hydration products. In the case of fly ash 2, the extent of the reaction appeared to extremely variable from one particle to another. Such a phenomenon is illustrated in Figure 4.

Discussion

Influence of Fly Ashes on the Cement Hydration Process. The SEM observations carried out as part of this study tend to confirm the assumption that, whatever the curing temperature, the two Class F fly ashes do not react before at least 28 days of curing. This observation is good agreement with the previous conclusions of many authors who also found that most Class F fly ash only begin to hydrate after a substantial curing period (6-9). It also confirms

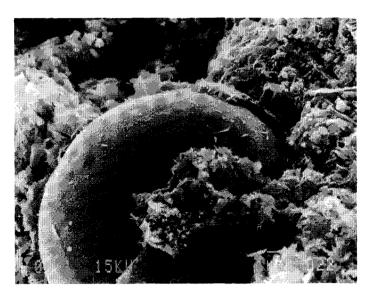


FIG.3 Fly ash 1 after 28 days at 20°C (6000X).

the results of a previous study where the influence of fly ash 1 on the consumption of Ca(OH)₂ was found to be insignificant during the first weeks of curing (16).

If fly ash does not react during the first days of curing, test results clearly indicate that it cannot be considered as a totally "inert" material. Despite very little pozzolanic activity, the presence of fly ash appears to increase the mortar non-evaporable water content at early days. This is particularly true for fly ash 1 which contributed to markedly increase the non-evaporable water content of the mixture. Such a phenomenon has also been observed in previous studies (6-9). Many authors have attributed this increase to an acceleration of the early cement hydration in presence of fly ash.

It should be emphasized that conflicting reports have been published on the influence of fly ash on the kinetics of cement hydration. In some cases, the presence of fly ash particles has been found to retard the early hydration of cement (17, 18). However, there exist numerous experimental evidences which demonstrate that fly can contribute to accelerate the reaction of cement at early days (6-11). As underlined by many authors, the study of the fly ash/cement reaction processes is complicated by the fact that the chemical and physical properties of fly ash tend to differ markedly from one source to another. Even within one source, individual grains are highly variable in nature.

According to many authors, the accelerating effect of fly ash on the cement hydration mechanisms is mainly physical in nature (6-11). In many cases, the addition of fly ash tends to increase the number of fine particles in the system. The presence of these fine particles contributes to increase the density of the matrix. The replacement of cement particles by fly ash is also believed to increase the available space in the floc structure created by the cement grains. Finally, the fine particles provide additional nucleation sites for cement hydration products such as C-S-H, portlandite and ettringite.

In the present study, the use of fly ash should not have had any significant influence on the packing density of the matrix. The physical properties of the two fly ash are very similar. Furthermore, the two materials have grading curves close or coarser than that of the canadian

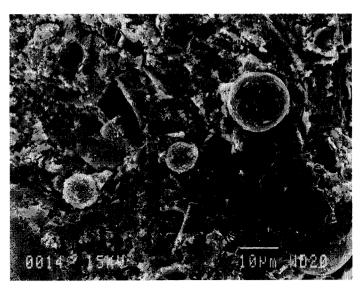


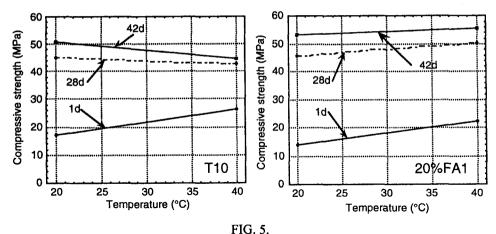
FIG. 4. Fly ash 2 after 42 days at 20°C(1500X).

CSA type 10 cement. Apparently, the effect of fly ash on the hydration cannot be solely explained by the "fine particle effect".

According to Takemoto and Uchikawa (11), the acceleration of cement hydration in presence of fly ashes is mainly related to the preferential adsorption of calcium ions on the fly ash particles. This phenomenon contributes to decrease the calcium ion concentration in the liquid phase which subsequently favors the dissolution of calcium phases from the cement grain. Although the assumption of Takemoto and Uchikawa cannot be confirmed on the basis of our results, it is probable that the acceleration of the early cement hydration is mostly related to an alteration of the pore solution chemistry. As emphasized by Luke and Glasser (19), the aqueous phase composition of fly ash mixtures is governed by the balance of a number of competitive processes which may occur at different rates. For instance, it has been shown that the influence of fly ash on the early hydration of cement is influenced by the relative solubility of the sulfate and alkali sources of the cement and by the soluble alkali content of the ash itself. It is probable that the fly ashes used in the present study (particularly fly ash 1) have created favorable conditions for the hydration of cement.

Test results clearly indicate that the influence of fly ash on the early cement hydration has to be considered in the elaboration of any model aiming at reliably predicting the physical properties of concrete. In that respect, the model developed by De Larrard (4) is probably the one which is the more adapted to account for the influence of fly ash on the concrete compressive strength development. In De Larrard's model, the contribution of fly ash is taken into account through a cement equivalent factor and a time-dependent pozzolanic activity coefficient. The model readily accounts for the influence of the type and the amount of fly ash on compressive strength.

Influence of Fly Ash on the Long-term Compressive Strength. Test results clearly confirmed that an elevation of the curing temperature contributes to reduce the long-term compressive strength of OPC mixture. On the other hand, data also indicate that an increase of



Influence of temperature on the compressive strength development of mortars.

the curing temperature is much less detrimental for fly ash mixtures and that it can, in certain cases, even have a beneficial influence on the long-term compressive strength of the material (see Figure 5). As can be seen in Table 6, an elevation of the curing temperature from 20°C to 40°C has contributed to increase the long-term compressive strength of all fly ash mixtures with a replacement level of 20% and 30%.

The effects of high curing temperatures on long-term compressive strength of OPC concrete have been the subject of much attention in the past decades. According to many studies, the negative effects of high curing temperature are directly related to modifications of the microstructure of the OPC cement paste (13, 20, 21). Other authors have also attributed the detrimental influence of high curing temperatures to the significant difference between the thermal expansion coefficients of the various phases present in the material (22). According to these authors, the increase in the volume of water and air due to a rise in temperature is prevented by the rigid skeleton of the hardening cement paste. This induces significant stresses which contribute to the formation of microcracks.

The beneficial influence of an elevation of the curing temperature on the long-term compressive strength of most fly ash mortars can probably be explained by the fact that the pozzolanic reaction is, like most chemical reactions, significantly influenced by the temperature (6, 14, 23). According to Fraay et al. (23), the relative temperature-sensitivity of the fly ash hydration process can be explained by the fact that the dissolution of fly ash particles is directly affected by the pH level of the pore water solution. These authors showed that the OH⁻ ion concentration increases significantly with temperature. The hydration of fly ash is thus accelerated by an elevation of the curing the temperature. Furthermore, according to Berry and Malhotra (24), once the pozzolanic reaction has been initiated by heat, it will carry on even if the temperature is reduced. It appears that once the surface of fly ash particles has been dissolved, hydration is much easier.

The beneficial influence of an elevation of the curing temperature on the long-term compressive strength of fly ash concrete is particularly interesting for precast concrete producers which regularly rely on steam curing to accelerate the mechanical strength development of their products. Although fly ash tends to slightly reduce the 24-hour compressive strength of the mixtures cured at 40°C, it globally contributes to increase the long-term values.

Conclusion

- Test results indicate that if fly ash does not react during the first days of curing, it cannot
 be considered as a totally "inert" material. Despite very little pozzolanic activity, the
 presence of fly ash appears to increase the mortar non-evaporable water content at early
 days.
- Test results clearly confirmed that an elevation of the curing temperature contributes to reduce the long-term compressive strength of OPC mixture.
- Data also indicate that an increase of the curing temperature is much less detrimental for fly ash mixtures and that it can, in certain cases, even have a beneficial influence on the long-term compressive strength of the material.

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