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DEVELOPMENT OF HYDRATION TEMPERATURES ON CEMENT PASTES

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Abstract. This article deals with the possible combination of high temperature fly ash with fluidised bed fly ash. The main objective of the experiment is to verify the effect of the combination of these two energy by-products on simpler systems – cement pastes. In the experimental part, the evolution of hydration temperatures and the time course of volume changes were monitored. The results obtained indicate that the addition of fluid fly ash to the mixture intensifies the hydration reaction, despite the increase in the value of the water to cement ratio of the mixture. At the same time, there is a slight increase in volume changes, which can be considered as a very valuable contribution to technical practice, taking into account possible ecological or economic aspects.

Keywords: High temperature fly ash, fluidised fly ash, volume changes, cement paste shrinkage.

1. Introduction

Not only concrete mix producers, but also cement producers, are under increasing pressure to reduce harmful emissions into the air. One possible solution is the production and use of Portland blended cements, which have a lower content of the basic component – Portland clinker – and an increased content of another main component – e.g. silica ash, blast furnace granulated slag or limestone [1].

Another way to reduce the amount of cement in the concrete mix is to use so-called active admixtures. These are substances that are involved in the hydration processes in some way and contribute to better physical-mechanical parameters.

Such substances include, for example, high-temperature fly ash. This is a by-product of the so-called high-temperature combustion of coal. The use of this type of admixture in concrete mixtures can positively influence the rheology [2] or the course of the hydration reaction [3], which is widely used especially in massive structures.

However, the gradual transition to a more environmentally friendly – so-called fluidised bed – method of coal combustion is associated with the creation of a completely new and different energy by-product – so-called fluidised bed ash. The grains of this commodity are characterised by an unsuitable chemical composition, which is caused by the more environmentally friendly variant of flue gas desulphurisation. [4] The increased content of reactive CaO and sulphates in the cement composite could have a negative effect on the microstructure of the already hardened concrete due to chemical reactions and the possible formation of secondary ettringite or monosulphate. If these reactions took place at a stage when the concrete was still in a plastic state, the formation of ettringite would not be a defect.

One possible alternative solution could be at least a partial replacement of high temperature fly ash by fluidised bed fly ash. According to previously published studies, it is assumed that reactive free CaO could provide a suitable basis for the initiation and progress of hydration reactions in the cement composite [5], which could positively affect, for example, mechanical parameters [6] and, as a result of the chemical composition of the fluidised fly ash, primary ettringite and monosulphate could be formed, which could at least partially reduce the magnitude of volume changes.

2. Experimental part

At the beginning of the experiment, the starting materials had to be carefully analysed. Specifically, the raw material was CEM II/A-S 42.5 R Portland blended cement from the Mokrá cement plant (Heidelberg – CZ). The high-temperature fly ash came from the production of the Mělník (CZ) lignite thermal power plant (MEL) and the fluid fly ash (ZL) was produced by Heating Plant Zlín (CZ). Their specific surface area was determined using an automated Blain apparatus and the granulometry of the binder and impurities was determined using a laser granulometer. The results are summarised in Table 1.

Raw material	Specific gravity [$g\,cm^{-3}$]	Specific surface [$cm^{-2}\,g^{-1}$]
CEM II/A-S 42,5 R, Mokrá	3.11	4 010
High temperature fly ash Mělník (MEL)	2.21	3 280
Fluid ash Zlin (ZL)	2.82	9 930

Table 1. Selected physical parameters of input raw materials.

In the next phase of the experiment, a total of 7 simpler systems – cement pastes – were mixed. One

(a). (b). (c).

Figure 1. Determination of the consistency of cement paste according to EN 1015-3 [7] (A); Calmetrix F-cal 8000 test rig for determining the development of hydration temperatures (B) and Shrinkage Cone test rig for measuring volume changes (C).

Recipe	**CEM II/A-S 42,5 R, Mokrá [g]**	**High temperature fly ash, Mělník [g]**	**Fluid ash, Zlín [g]**	**Water [g]**	**w* [-]**	**Cone flow diameter [mm]**
REF	900	–	–	322	0.36	190
25_MEL	675	225	–	300	0.33	185
25_MEL_ZL_80:20	675	180	45	315	0.35	190
25_MEL_ZL_70:30	675	157.5	67.5	325	0.36	190
25_MEL_ZL_60:40	675	135	90	335	0.37	185
25_MEL_ZL_50:50	675	112.5	112.5	345	0.38	190
25_ZL	675	–	225	395	0.44	185

* The water to cement ratio value was calculated as the ratio of the weight of water to the total weight of cement and admixtures, regardless of the k-value according to EN 206+A2 [8]

Table 2. Composition of individual cement pastes.

cement paste reference, without any kind of fly ash. In the other cement paste, 25 % of the binder was replaced by high temperature fly ash (25_MEL) or fluid fly ash (25_ZL). In the case of the cement pastes with a combination of both types of fly ash, 25 % of the cement was replaced by high temperature fly ash, while in these mixes there was also a 20 %, 30 %, 40 % and 50 % replacement by weight of high temperature fly ash by fluidised fly ash.

The marking of individual recipes is based on the relative mixing ratio of the binder components, e.g. 25_MEL_ZL_60:40 means that in the cement paste the cement has been replaced by high-temperature fly ash of 25 % and the relative mixing ratio of MEL and ZL fly ash is 60:40 % by weight.

The consistency of all the cement pastes was determined according to EN 1015-3 [7] with a cone flow diameter value of 190 ± 5 mm as shown in Figure 1. This procedure was chosen to directly compare the combination of high temperature fly ash and fluidised fly ash in practical applicability. As can be observed in Table 2, along with the increase in the amount of fluidised fly ash in the cement paste, the water to cement ratio value increased simultaneously. In engineering practice, the consistency of the produced concrete or other cement composite could be further modified using superplasticizing additives. However, its use was ruled out in this experiment due to the elimination of another parameter affecting the course of hydration reactions.

Determination of the hydration temperature history was carried out by the semi-diabatic method according to EN 196-9 [9] using the Calmetrix F-cal 8 000 test rig shown in Figure 2 for 24 hours after mixing. This time interval was in all cases sufficient to reach the maximum hydration temperature. The value of which and the time required to reach it are summarized by Table 3.

Recipe	**$T_m$ax [°C]**	**Time $T_m$ax [h:m]**
REF	73.3	11:10
25_MEL	58.2	13:55
25_MEL_ZL_80:20	61.4	12:05
25_MEL_ZL_70:30	63.3	12:15
25_MEL_ZL_60:40	65.4	12:10
25_MEL_ZL_50:50	65.1	12:15
25_ZL	73.2	12:20

Table 3. Maximum temperature reached and time required.

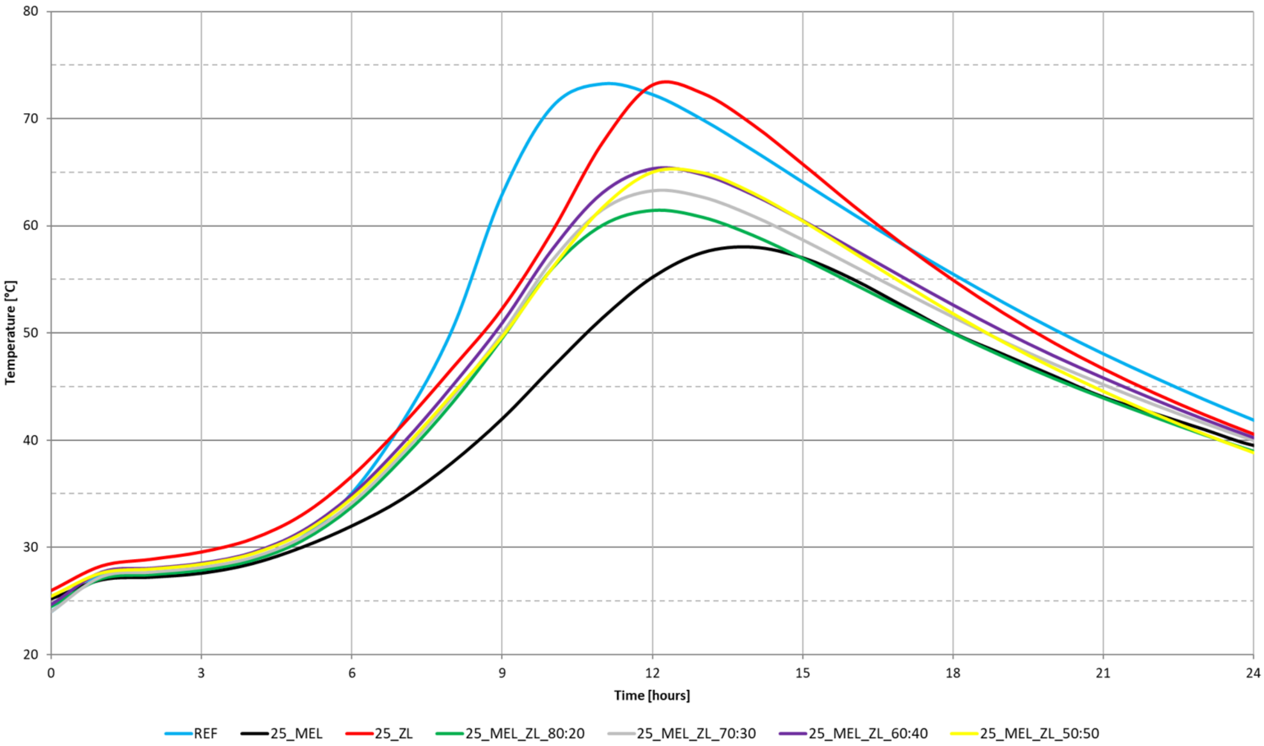

Figure 2. Evolution of hydration temperatures on cement pastes.

Recipe/Time	**1 hours [μm]**	**2 hours [μm]**	**3 hours [μm]**	**9 hours [μm]**	**18 hours [μm]**	**24 hours [μm]**	**72 hours [μm]**
REF	-704.1	-675.2	-738.5	-957.5	-948.8	-949.8	-951.1
25_MEL	-510.5	-592.1	-710.8	-906.7	-903.8	-902.1	-903.9
25_MEL_ZL_80:20	-569.1	-679.1	-801.1	-1 057.4	-1 051.8	-1 048.3	-1 050.3
25_MEL_ZL_70:30	-496.3	-615.6	-733.3	-1 039.9	-1 038.6	-1 034.6	-1 037.2
25_MEL_ZL_60:40	-502.8	-604.9	-710.8	-1 021.1	-1 010.0	-1 001.6	-1 005.5
25_MEL_ZL_50:50	-509.6	-640.4	-711.4	-1 004.6	-999.3	-991.4	-995.2
25_ZL	-544.9	-680.5	-800.3	-1 252.1	-1 241.8	-1 226.4	-1 220.8

Table 4. Overview of volume changes of cement pastes over time.

The determination of volume changes was carried out on a Shrinkage Cone measuring device from Schleibinger Geräte with a conical measuring vessel, see Figure 3. A laser beam was positioned at the centre of the filled measuring vessel and recorded the volume changes of the cement paste with a resolution of 1/10 micron every 5 minutes throughout the measurement period. In this part of the experiment, the volume changes were determined for 72 hours on each cement paste. A significant proportion of the volume changes occur due to chemical and plastic shrinkage in the first 9 hours of curing. Thereafter, the values of volume changes remain almost constant. For better clarity, Figure 3 presents the volume changes only in the first 18 hours after mixing and Table 4 summarizes the values at subsequent time intervals.

3. Results and discussion

As shown in Figure 2, the reference cement paste containing none of the fly ash types shows the fastest evolution of hydration temperature among the cement pastes, as expected. This cement paste reached its highest temperature of 73.3 °C at 11 hours and 10 minutes after mixing. At the same time, it can also be seen from Figure 2 that the cement paste with 25 % cement replacement by high temperature fly ash (25_MEL) confirmed the characteristic effect of this admixture on the cement composite. During the maturation process, the hydration reaction loosens, the hydration temperature increases more gradually and the maximum temperature reached decreases, which is widely used especially in massive structures. The maximum temperature of 58.2 °C reached for this paste was reached after 13 hours and 55 minutes and the water to cement ratio value of this paste was the lowest of all the formulations. It can also be seen from

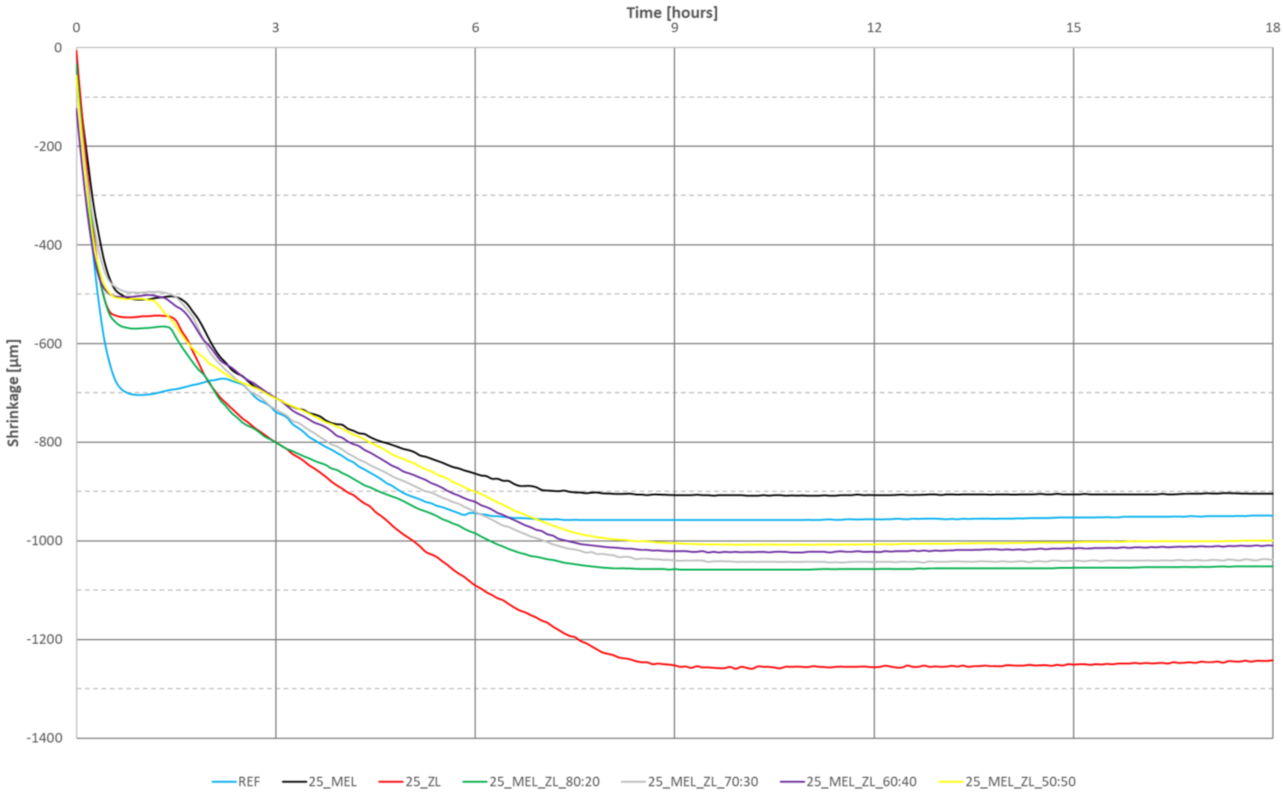

Figure 3. The course of volume changes on cement pastes.

Figure 2 that as the amount of fly ash in the cement paste increased, the maximum hydration temperature increased gradually, almost at the same time, despite the increasing value of water to cement ratio, which has a significant effect on the intensity of the hydration reaction. The hydration temperature of the cement paste 25_ZL also showed a very interesting evolution, reaching almost the same temperature as the reference mixture, despite the fact that 25 % cement was saved in the formulation and it contained 73 g more water than the reference cement paste.

It can be assumed that the reason for the increase in maximum temperatures in cement pastes is the increasing amount of free reactive CaO, which leads to the initiation and acceleration of hydration processes and more intense reaction in the cement composite.

When determining the volume changes on the cement pastes, it was assumed that the reference cement paste, without any kind of fly ash content, would show the greatest shrinkage. It was assumed that the cement paste containing only high-temperature fly ash would exhibit a lower value of volume changes than the reference mixture due to the loosening of the hydration reaction, and it was also assumed that with increasing amounts of fluid fly ash in the mixture, the formation of new formations in the form of primary ettringite and monosulphate would occur, which could have a positive effect on the volume changes. However, this idea could not be confirmed.

As can be seen from Figure 3, the cement paste 25_MEL showed the lowest value of volume changes. This can most likely be due to the partial replacement of cement with high temperature fly ash, which is associated with the loosening of the hydration reaction, which should have a positive effect on the volume changes of the cement composite in particular. On the other hand, the cement paste 25_ZL showed the largest volumetric changes. At the same time, it is also well evident from Figure 3 that the magnitude of volumetric changes gradually increased with increasing amount of fluid fly ash. However, it should be remembered that along with the increasing amount of fluid fly ash in the mixture, the value of water to cement ratio also increased, which also has a negative effect on the magnitude of volume changes of cement composites.

4. Conclusion

The use of suitable energy by-products for concrete production has become commonplace in engineering practice. However, due to the ever increasing costs of concrete and its basic ingredients (cement) and the increasing pressure to reduce the environmental burden, concrete mix manufacturers are looking for other possible alternative solutions to reduce production costs or emissions associated with the production and transportation of raw materials. One possible solution would be to use fluidised fly ash in combination with high temperature fly ash.

Based on the conducted experiment, it was confirmed that with increasing amount of fly ash in the cement paste, the hydration reaction becomes more intense and the maximum hydration temperature increases despite the increasing value of water to cement ratio, which seems to be closely related to the free CaO content.

At the same time, it was found that there is a slight increase in the volume changes of the cementitious composite as the amount of fly ash increases, which is most likely due to the increasing amount in the mixture to achieve the same degree of workability. In engineering practice, however, this problem can be addressed by the use of suitable plasticizing admixtures, which should again reduce the amount of water in the concrete formulation.

Currently, fly ash is mainly used for reclamation or stabilization of soil bodies and its potential as an active admixture is not used at all. The use of this commodity for the production of concrete, at least in partial replacement with high temperature fly ash, could be advantageous not only from an economic point of view, but also from an ecological point of view.

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