Influence of PCP Based Superplasticizer on Heat Emission During Portland Cement Hydration

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Abstract. The paper presents the results of a research on the influence of plasticizing admixture based on modified polycarboxylates on the heat emission parameters of a hardening concrete mix prepared with the use of Portland cement. The admixture was applied in the amount from 0.5 to 4.0%. No influence of admixture dosing on the maximum temperature increase was noted. However, a clear correlation was obtained between the amount of admixture and the time of reaching the maximum temperature and the maximum rate of temperature increase.

1. Introduction
The dependence of the amount and rate of heat release during concrete setting and hardening, depending on its composition, is a complex and still studied phenomenon [1]–[3]. Knowledge of the course of heat generation is particularly important in the design and construction of massive structures such as foundations, structural elements of large dimensions or road surfaces [4], [5]. This results from the necessity to reduce the risk of crack formation due to too large temperature gradients, which is particularly important in this type of structures [5], [6].

The rate of heat release can be regulated by changing the phase composition of the clinker, replacing part of the clinker with other binding materials (e.g. blast furnace slag or fly ash), or by influencing the hydration of cement with admixtures. There is a wide range of admixtures available to accelerate or delay concrete setting, whose influence on the course of heat generation can be studied [7], [8].

Plasticizers, apart from complex admixtures according to PN-EN 934-2+A1:2012 or type G admixtures according to ASTM C 494-10, are often considered to have no or very little influence on the course of heat generation in the concrete hardening process. The research carried out by the authors of this paper and some data from the literature show that the influence of some admixtures reducing the amount of water may be significant [3]. Manufacturers of some plasticizing admixtures inform that in case of their application, the concrete setting time may be delayed at higher doses. However, they do not specify either the dose above which such an effect should be taken into account, or whether, apart from the delay in setting time, it should also be taken into account with its elongation. Meanwhile, the latter effect may affect the course of the heat emission process in the hardening concrete mix.

Design of structures, especially massive ones, can be supported by research on the course of hydration heat generation. They can be conducted on a small scale in calorimeters of high precision, but this solution usually allows to test the cement paste itself. In order to test mortars and concrete, calorimeters of higher volume are used, both semi adiabatic and isothermal, in which it is possible to
test a sample from the size of about 250 cm$^3$ [9] to over 1 dm$^3$. However, even in the case of samples of such volume, certain issues related to the heat generation process are difficult to detect, e.g. autocatalysis of the cement hydration reaction under the influence of heat emission. Therefore, larger-scale research is also carried out, for which isolated forms of the volume from several to several dozen dm$^3$ [10], [11] are used. The results obtained in the course of such studies may be the basis for numerical simulations of heat generation in the designed structure [3], [10].

The paper presents the results of a study on the effect of superplasticizer based on modified polycarboxylates (PCPs) on selected parameters of heat emission by hardening concrete during the first 72 hours. The temperature of concrete mix measured in one point was chosen as the tested feature describing the heat emission. The influence of the admixture on the temperature reached, its increase, changes in time and on the rate of its raise was investigated. The admixture chosen for the study was applied in the amount from 0.5 to 4.0% of cement mass. Additionally, a 28-day compression strength test was carried out to determine whether the admixture had a significant effect on this parameter. The research and its results may contribute to more advanced research on a larger scale and with the use of more sophisticated methods and equipment.

2. Materials and methods

2.1. Mixture composition

A concrete mix of almost the same composition in seven different variants differing mainly in the amount of superplasticizer was used for the study. Due to the use of the admixture, which was assumed to contain 70% of water, the amount of water was adjusted so that the effective w/c ratio remained approximately the same and was equal to about 0.45. The amount of aggregate used was also slightly reduced so that, due to the specificity of the research, the amount of cement per 1 m$^3$ of mix in each variant remained unchanged. The recipes of particular variants of the mixture are presented in Table 1.

| Component          | Designation of a variant of the mixture |
|--------------------|----------------------------------------|
|                    | SP 0   | SP 05  | SP 10  | SP 15  | SP 20  | SP 30  | SP 40  |
| Cement             | 350    | 350    | 350    | 350    | 350    | 350    | 350    |
| Sand (0 – 2 mm)    | 517    | 517    | 516    | 516    | 515    | 514    | 513    |
| Gravel (2 – 16 mm) | 1363   | 1362   | 1361   | 1360   | 1358   | 1356   | 1354   |
| Water              | 158    | 156    | 155    | 154    | 153    | 150    | 148    |
| Superplasticizer   | 0      | 1.75   | 3.50   | 5.25   | 7.00   | 10.50  | 14.00  |
| Effective$^a$ w/c ratio | 0.451  | 0.449  | 0.450  | 0.451  | 0.450  | 0.450  | 0.451  |

$^a$ with water included in the superplasticizer (70% of the admixture weight).

Portland cement CEM I 32.5R from Ożarów cement plant was used as a binder, meeting the requirements of PN-EN 197-1 standard. River sand was used as a fine aggregate and quarry gravel as a coarse aggregate. The plasticizing admixture, whose influence was studied, was based on modified polycarboxylates (PCP), and its recommended by the manufacturer dosage ranged from 0.2 to 3.0% of cement mass. Tap water was used as a mixing water. After preparation of the mixtures, their consistency was tested using the flow table method according to PN-EN 12350-5 standard.

2.2. Performed tests

For concrete strength testing, three cubic specimens of 150 mm edge were prepared from each series. The specimens were demoulded two days after moulding and placed in water where they matured until the test. The test was conducted 28 days after moulding on a ToniTechnik ToniPACT II testing machine with a maximum range of compressing force equal 3000 kN. The rate of stress increase during the test was in accordance with the requirements of the PN-EN 12390-3 standard and amounted to 0.5 MPa/s.
The temperature of the hardening concrete mixture was measured in a cuboid form made of foamed polystyrene with internal dimensions of 140 x 140 x 255 mm and a wall thickness of 30 mm. The form was equipped with a closing lid with a thickness of 40 mm. The volume of the mold allowed for the placement of about 5 dm$^3$ of concrete mix. The form, before the concrete mixture was placed in it, was lined with two layers of polyethylene film inside to allow the removal of the hardened concrete after the end of the test.

Three K-type thermocouples were used for temperature measurement, two of which were placed in plastic pipes and immersed in a concrete mix up to half the height of the form in equal distance from its opposite walls. A third thermocouple was placed outside the form and measured the ambient temperature. The thermocouples were connected to the 4-channel industrial thermometer VOLTCRAFT PL-125 T4USB VS. Subsequent temperature measurements were taken every 90 seconds for at least 96 hours and stored in the memory of the device. The measurements were started after the time of 6-8 minutes from the contact of cement with water, which was the time needed to prepare the mixture and place it in a form.

### 3. Results and discussion

The results of the concrete mix flow measurement with the consistency class assigned to them and the results of the control concrete compression strength test after 28 days are presented in Table 2. Due to the fact that the measurements of the mix temperature changes were carried out at different ambient temperatures, Table 2 also gives the average value of the ambient temperature during 72 hours of measurement and its standard deviation.

**Table 2. The results of tests on secondary parameters.**

| Tested parameter                  | Designation of a variant of the mixture |
|----------------------------------|----------------------------------------|
|                                 | SP 0 | SP 05 | SP 10 | SP 15 | SP 20 | SP 30 | SP 40 |
| Flow diameter [cm]               | 36.3 | 38.5  | 57.8  | 62.0  | 58.0  | 63.5  | 62.3  |
| Class of consistency             | F2   | F2    | F5    | F5    | F5    | F6    | F5    |
| Compressive strength            | 46.6 | 49.6  | 55.8  | 48.5  | 44.5  | 42.1  | 42.7  |
| (after 28 days) [MPa]            | ±1.1$^a$ | ±0.9$^a$ | ±0.7$^a$ | ±2.5$^a$ | ±1.3$^a$ | ±1.5$^a$ | ±2.1$^a$ |
| Average ambient temperature      | 20.7 | 20.7  | 19.3  | 20.4  | 19.2  | 19.5  | 18.9  |
| (during first 72 hours) [°C]     | ±0.6$^b$ | ±0.6$^b$ | ±0.7$^b$ | ±0.4$^b$ | ±0.3$^b$ | ±0.4$^b$ | ±0.4$^b$ |

$^a$ standard deviation for n = 3 measurements; $^b$ standard deviation for n = 2881 measurements.

The analysis of the flow values indicates low effectiveness of the admixture applied in the amount of 0.5% of cement mass and no relation between the amount of admixture applied and the flow diameter at higher doses.

The compression strength results initially show a tendency to increase with the increase in the amount of the mixture used. At a dose of 1.0% of cement mass, maximum strength was achieved and then the values start to decrease. Due to the small number of strength tests carried out, the standard deviation values for each series were quite high, but even so, the differences between the individual series are significant except for the last two series, where similar strength values were obtained. No correlation was found between the average ambient temperature during the first 72 hours of hardening and the concrete compression strength values obtained after 28 days.

The results of tests of heat emission parameters during the process of hardening of mixtures are presented in Table 3. The maximum values of temperatures, maximum temperature increase measured in relation to the average temperature from the first 30 minutes of measurement and maximum temperature increase rate are presented. For each of the above parameters, the time of its achievement was also given. As the last parameter, the time after which the temperature increase rate started to take negative values was given. Selected parameters are also illustrated in Figures 1 to 3.
Table 3. The results of the tests on parameters of heat emission.

| Tested parameter | Designation of a variant of the mixture |
|------------------|----------------------------------------|
| $T_{\text{max}}$ [°C] | SP 0        | SP 05       | SP 10       | SP 15       | SP 20       | SP 30       | SP 40       |
| $t(T_{\text{max}})$ [h] | 24.00   | 26.15   | 29.88   | 32.88   | 34.48   | 37.33   | 36.25   |
| $\Delta T_{\text{max}}$ [°C] | 13.9  | 16.3  | 15.5  | 13.7  | 14.7  | 15.2  | 14.0  |
| $t(\Delta T_{\text{max}})$ [h] | 24.25   | 26.13   | 29.88   | 32.85   | 34.45   | 37.33   | 36.25   |
| $(dT/dt)_{\text{max}}$ [°C/h] | 1.03  | 1.04  | 0.89  | 0.71  | 0.92  | 0.87  | 0.85  |
| $t[(dT/dt)_{\text{max}}]$ [h] | 10.50   | 14.70   | 19.85   | 21.03   | 22.80   | 25.45   | 26.63   |
| $t(dT/dt > 0)$ [h] | 25.23   | 27.25   | 31.23   | 34.00   | 35.05   | 38.05   | 37.55   |

The analysis of the values given in Table 3 indicates that the amount of admixture used does not correlate either with the maximum temperature value obtained or with the maximum temperature increase. Both these parameters change in a rather chaotic way, and due to different initial temperature of concrete mix in particular variants, the value of maximum achieved temperature is additionally burdened with an error resulting from these differences.

Figure 1. Time of achieving $\Delta T_{\text{max}}$ as a function of the admixture dose (two possible forms).

The influence of admixture can be seen very clearly in the length of time periods in which the maximum values were reached. As the amount of admixture increases, the time period for reaching the maximum temperature and its maximum increase becomes significantly longer. At the same time, in case of the maximum admixture dose applied (4.0%), the time of reaching the maximum temperature decreases slightly in relation to the mixture in which the admixture amount of 3.0% was applied. The obtained results are presented in Figure 1 in the form of a relation linking the time of reaching the maximum temperature increase with the applied admixture dose. Possible forms of functions describing this relation are also presented. High values of the $R^2$ coefficient indicate that the matched functions describe the relation very well. The question is whether, if the admixture of more than 4.0% is used, the time of obtaining the maximum temperature value would be further shortened, as it results from the course of the presented functions. This may possibly be the subject of further research.
The obtained results also indicate that the admixture applied has an influence on the rate of temperature increase. There are at least three effects. First of all, as can be seen in Figure 2, increasing the admixture dose leads to prolonging the time when the temperature increase rate reaches its maximum. This effect is not surprising in the light of the previously discussed results concerning the time of reaching the maximum temperature increase. Besides, since the moment when the maximum rate of temperature increase is reached is often identified with the beginning of cement setting, it is not surprising that a larger amount of admixture postpones this moment more in time. However, as it can be deduced from the graph in Figure 2, the effectiveness of the admixture is not proportional to the applied dose. The most evident effect of application of the admixture in relation to the applied dose was observed in case of SP 05 and SP 10 mixes, i.e. at a dose equal to 0.5 and 1.0% of cement mass respectively. Further increase of dosing resulted in proportionally smaller increase of delay, but the increase occurred in the whole dosing range. In this case, no change of the upward to downward tendency was observed in the case of the maximum dose applied.

A much more interesting effect was noticed during the analysis of the dependence of the temperature increase rate on time. Diagrams of changes of this rate are presented in Figure 3. It can be seen that in the case of a mixture prepared without any admixture, the course of temperature increase rate dependence on time is one-modal. Application of 0.5% admixture causes that the graph gains a second, very clear local maximum, after which the temperature increase rate very quickly decreases. This effect is still clearly visible when using 1.0 and 1.5% admixture, then it begins to fade and in the case of 4.0% admixture it is no longer visible. The observed phenomenon probably results from the interaction between the plasticizer and cement components, but in order to confirm it and get to know its mechanism, additional research is needed, which is beyond the scope of the research conducted for the purposes of this study.
Figure 3. Rate of temperature increase in time for all mixtures (positive values only).

The analysis of graphs in Figure 3 also allows to notice a gradual elongation of the time in which the temperature increase rate takes positive values, while starting from the dose of 2.0% the increase is clearly slower in relation to the amount of admixture applied. Along with the dose increase, the minimum value of the temperature increase rate in the period between the beginning of cement hydration and reaching the maximum value decreases as well. The time taken to achieve this minimum is also increased. While the minimum temperature increase rate is reached in less than 4 hours in the case of an admixture-free mixture and the minimum rate is about 0.18°C/h, the minimum rate is reached in the case of a mixture with a 4.0% admixture after 11 hours and drops to 0.01°C/h. The time between reaching the minimum value of the temperature increase rate and the end of the period in which the temperature increase rate is positive is also prolonged. This means that the heat of hydration is emitted over a longer period of time and thus with a slightly lower intensity. This can be important for massive concrete structures, as it can lower the temperature gradients during the hardening of concrete in such structures.

4. Conclusions
The research carried out allowed to formulate the following conclusions:

1. The applied plasticizing admixture does not have an explicit influence on the maximum temperature of the mixture achieved and the maximum increase in this temperature.
2. With the increase in the amount of the admixture applied, the times of reaching the maximum temperature value, maximum temperature increase, minimum and maximum temperature increase rate and the time when the temperature increase rate is positive are prolonged. At the same time, at the maximum admixture dose applied (4.0% of cement mass) the trend is significantly weakened or even reversed.
3. When using smaller admixture doses (from 0.5 to 1.5% of cement mass), the graph of temperature increase rate becomes bimodal with two clearly distinguished temperature maximums.
4. Application of admixture in the amount above 0.5% lowers the maximum value of temperature increase rate, however, this decrease is poorly correlated with the amount of admixture applied.
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