

Improved fire resistance by using Portland-pozzolana or Portland-fly ash cements

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Abstract Our study was directed to the analysis of the influence of various types of cements on the behaviour of concrete at high temperatures. In our experiments binary blended and ordinary Portland cements were involved: two Portland cements with different clinker compositions and Portland cements containing pozzolanic additives as replacement of clinkers. In the first part of the study we focused on the influence of cement types where cement paste specimens were investigated. Then, based on the results of cement paste specimens, concretes specimens were prepared with some selected types of cements. Most important observation of our experimental study was that the pozzolanic additives and their increased amount have a favourable effect on the heat resistance (fire resistance) properties of concrete.

Keywords Fire · Thermal analysis · Strength · Pozzolanic additives · Fly ash · Pozzolans · Trass

Introduction

Effects of high temperatures on the mechanical properties of concrete were studied as early as the 1940s [1]. In the 1960s and 1970s fire research was mainly directed to study the behaviour of concrete structural elements [2]. There was relatively little information on the concrete properties during and after fire [3].

Characteristics of concrete during and after the heating process depend on the type of cement, the type of aggregate and the interaction between them [4–6]. Behaviour at high temperatures depends on parameters like water/cement ratio, amount of C–S–H (calcium–silicate–hydrates), amount of Ca(OH)₂ and degree of hydration. Different cement pastes can perform differently in fire [7]. The dehydration of Portland cement paste plays an important role in the concrete structure explosive spalling at fire. Calcium–silicate–hydrate (C–S–H) and calcium–hydroxide (C–H) are the main hydration phases which dominate the properties of Portland cement paste. The temperature range corresponds to the dehydration of C–S–H is about from 105 to 1000 °C [8].

Pozzolanic supplementary materials are used extensively throughout the world. Pozzolanic materials react with calcium–hydroxide produced during the hydration of cement. Amorphous silica present in the pozzolanic materials combines with calcium–hydroxide and forms cementitious materials. Supplementary materials having pozzolanic behaviour typically improve the durability of concrete and can also reduce the rate of heat liberated due to hydration, which is beneficial for mass concrete

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application. The incorporation of pulverised fly ash (PFA) and slag in Portland cements or blended cements can generally keep the mechanical properties of concrete at a higher level after heating to high temperature. Compared to PC, the residual compressive strength, splitting tensile strength, flexural strength and modulus of elasticity of PC blended with PFA increase by 1.2–270, 1.1–80, 4.5–200 and 3–38%, respectively, while the values for PC blended with slag are 1.5–510, 1.2–43, 1–180 and 1.3–117% higher, respectively. The values vary mainly with different temperatures, replacements and types of aggregates. In the research carried out by Wang [9] the bare PC paste had lost its compressive strength and modulus of elasticity completely at the temperature of 1050 °C. However, 18% of the compressive strength and 81% of the modulus of elasticity still remained for PC blended slag paste with the replacement rate of 80% at the same temperature. Furthermore, PCs blended with PFA and slag also exhibit a high resistance to spalling at high temperatures [10–13].

Karakurt and Topcu [14] found by using SEM analysis that thermal cracking did not occur in PFA, and slag blending samples and that the degradation of C–S–H decreased compared to the reference samples made of Portland cement. Moreover, the incorporation of slag significantly reduces the amount of portlandite in PC. This way the extent of portlandite dehydration due to high temperature is decreasing. As a result of the above three aspects, the total porosity and the average pore diameter of PCs blended with PFA and slag are smaller than those of bare PC at high temperatures [10]. This could explain the higher resistance of PCs blended PFA and slag to high temperature.

Khoury et al. [15] tested ordinary Portland cement (OPC)–PFA cement pastes containing 30% PFA by mass under a series of temperatures till 650 °C. The relative residual compressive strength was 88% at 450 °C and 73% at 600 °C, which was almost double than the residual strength shown by pure OPC pastes. In a recent research, Wong et al. [16] studied the effects of PFA replacement level, water/binder ratio (W/B), and curing conditions on the residual properties of concrete at elevated temperatures. An increase in strength was observed at 250 °C. All PFA concrete specimens showed better performance till 650 °C than pure OPC concrete specimens; however, after that there was no significant difference in the residual strength of all specimens. It was found that a high dosage of PFA enhanced the residual properties of concrete at elevated temperatures. The results were also verified by porosity analysis done by mercury intrusion porosimetry (MIP) technique.

Nasser and Marzouk [17] found that the PFA improved the performance of concrete at elevated temperatures as compared to silica fume or pure OPC concretes. However,

this improvement was more significant at temperatures below 600 °C. Moreover, it was discovered that PFA also reduced the surface cracking of concrete both at elevated temperatures and after post cooling in air or water.

Our study was directed to analyse the influence of various types of cements on the behaviour of concrete at high temperatures. In our experiments binary blended and ordinary Portland cements were involved: two Portland cements with different clinker compositions and three binary blended Portland cements containing trass or fly ash additives as replacement of clinkers.

Experimental

Materials

Cement paste samples

For cement paste specimens two types of Portland cements and three types of binary blended Portland cements (Portland-composite cements) were selected. Cements involved in our comparative study are the following: Portland cement (CEM I 42,5 R); sulphate-resisting Portland cement (CEM I 42,5 N-S); Portland-pozzolana cement (CEM II/A-P 42,5 N) and Portland-fly ash cements (CEM II/A-V 42,5 R; CEM II/B-V 32,5 R). Cement clinkers and other main constituents different from clinkers were ground together during the production of cement. According to the standard EN 197-1:2000 [18] main constituents are specially selected inorganic materials in a proportion exceeding 5% by mass related to the sum of all main and minor additional constituents. According to the standard EN 197-1:2000 [18] amount of the main constituents different from clinkers in case of cements involved in our study, are summarized in Table 1. The composition of clinker minerals was the same in case of the Portland-composite cements as in CEM I 42,5 R ordinary Portland cement. The tested CEM I 42,5 R; CEM II/A-V 42,5 R; CEM II/A-P 42,5 N and CEM II/B-V 32,5 R cements were produced by the same cement plant except the sulphate resistant CEM I 42,5 N-S cement. Composition of clinker minerals of ordinary Portland cements and composition of clinker minerals of the blended cements are usually the same in the same plant however the production of the sulphate-resisting Portland cements requires to satisfy a law ratio of tricalcium-aluminate (C₃A) clinkers. As the production of the different clinker composition needs different composition of feed, and the persistent production do not allow considerable change in clinker composition, the sulphate-resisting PC (CEM I 42,5 N-S) was made by a different cement plant of the same company. In the Portland-fly ash cements (CEM II/A-V 42,5 R and CEM II/B-V 32,5 R) fly

Table 1 Percentages of clinker substituting constituents in case of tested cements involved in our study, according to the standard EN 197-1:2000

Type of cement	Percentages of clinker substituting constituents	
	Fly ash/ <i>V</i> (%)	Trass/ <i>P</i> (%)
CEM I 42,5 R	0	0
CEM I 42,5 N-S	0	0
CEM II/A-V 42,5 R	6–20	0
CEM II/B-V 32,5 R	21–35	0
CEM II/A-P 42,5 N	0	6–20

ash with the same origin and chemical composition was used (siliceous fly ash). In Portland-pozzolana cement (CEM II/A-P 42,5 N) trass (natural volcanic stone) was used as additive. All of the tested cements were standardised products of CRH Hungary Ltd (former Holcim Hungária Ltd). The oxidative compositions of tested cements are given in the Table 2.

During the experiments the influence and role of the clinker substituting constituents were studied, which are also known as supplementary cementing materials [19–25] with pozzolanic behaviour. The test variables were type of cements (CEM I 42,5 R; CEM I 42,5 N-S; CEM II/A-V 42,5 R; CEM II/A-P 42,5 N and CEM II/B-V 32,5 R, Table 1) and maximum temperature loads (20, 50, 150, 300, 500 or 800 °C); the test parameters were water to cement ratio ($w/c = 0.43$) and cement content, while the studied characteristics were surface damages (macroscopic observation) and compressive strength as well as thermoanalytic characteristics of the cement paste samples.

Concrete samples

Three types of cement were selected for the experiments with concrete specimens: CEM I 42,5 R; CEM II/A-V 42,5 R and CEM II/A-P 42,5 N. The selection was based on the results of the tests made on cement paste specimens. In the

concrete mix design we have followed the Palotás–Bolo-mey method [26–28]. The calculated mix proportions are given in Table 3.

The consistency of the fresh concrete was kept at the same flow values between 410 and 450 mm with the use of superplasticizer.

Curing of the specimens

After demoulding all types of specimens (cement paste and concrete specimens) were kept in water for 7 days, then in laboratory condition for 21 days.

Thermal loading

The test cubes of 28 days were heated (heating rate was about 40 °C min^{-1} , the cooling rate was 10 °C min^{-1}) to the given temperatures (50, 150, 300, 500 or 800 °C) in an electric furnace (air atmosphere, static, without flame effect), then they were kept there for 2 h. In our experiments, the applied heating curve was similar to the standard fire curve used for building structures and halls [28–31]. After the 2 h long thermal load, the specimens were removed from the furnace and cooled down in laboratory conditions to room temperature. Figure 1 shows the experimentally applied method of thermal loading. The

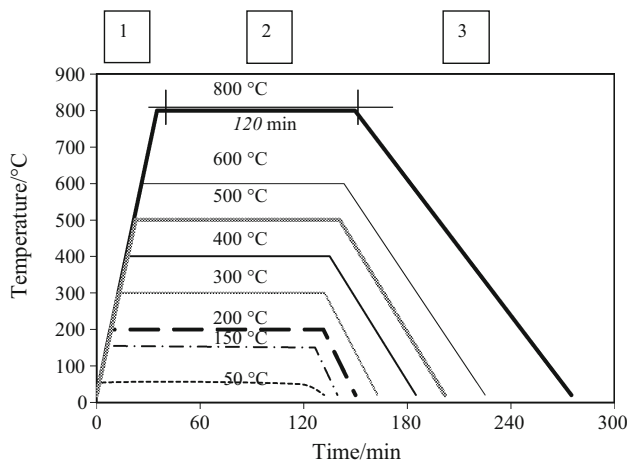
Table 2 The oxidative compositions of cements (m%)

	CEM I 42,5 R	CEM I 42,5 N-S	CEM II/A-V 42,5 R	CEM II/B-V 32,5 R	CEM II/A-P 42,5 N
SiO ₂	19.71	20.16	23.75	26.15	28.23
Al ₂ O ₃	4.46	3.83	6.68	7.79	6.10
Fe ₂ O ₃	2.97	6.03	4.73	5.33	3.42
CaO	64.59	62.9	55.31	50.48	54.54
MgO	1.0	1.88	2.66	2.64	1.0
K ₂ O	0.69	0.43	0.85	0.95	1.15
Na ₂ O	0.31	0.41	0.47	0.51	0.67
SO ₃	2.63	2.6	2.79	2.81	2.84
Cl	0.02	0.009	0.027	0.026	0.01

Data provided by the former Holcim Hungary Ltd

Table 3 Experimentally studied concrete mixes

Mix proportions	M1	M2	M3
Type of cement	CEM I 42,5 R	CEM II/A-V 42,5 N	CEM II/A-P 42,5 N
Cement/kg m ⁻³	350	350	350
Water/kg m ⁻³	151	151	151
Aggregates			
Sand, 0–4 mm/kg m ⁻³	912	912	912
Gravel, 4–8 mm/kg m ⁻³	485	485	485
Gravel, 8–16 mm/kg m ⁻³	544	544	544
Superplasticizer/kg m ⁻³	1.4	1.4	1.4

**Fig. 1** Schematic representation of heating curves, **1** heating, **2** temperature loading, **3** cooling down

heated and then cooled specimens were inspected prior to the compressive strength test to visually observe the size and number of cracks. Laboratory measurements (compressive strength tests) were conducted afterwards.

Test methods

Compressive strength

Compressive strength tests were conducted on cubes prepared both from cement paste (sides of 30 mm) and concrete (sides of 150 mm). Cement paste cubes were tested with a WPM ZDM 10/91 test machine and concrete cubes were tested with an ALPHA 3-3000S test machine (according to MSZ EN 206-1 [32]). The specimens were tested at the age of 28 days.

Flexural strength

Flexural strength of concrete was tested on horizontal concrete prisms with edge lengths of 70 × 70 × 250 mm.

Flexural strength test was carried out on a WPM ZDM 10/91 test machine. The specimens were tested at the age of 28 days.

Thermal analysis

Changes in phases were followed by TG/DTG/DTA curves using MOM Derivatograph-Q 1500 D TG/DTA instrument. During the measurements, the reference material was alumina (Al₂O₃), the mass of samples were ca. 300 mg, and the samples were heated at 10 °C min⁻¹ heating rate up to 1000 °C, in air atmosphere (in static condition). Before the investigations, the specimens were ground in an agate mortar, and directly after that they were measured in the TG/DTA device avoiding samples from further carbonation due to the airborne CO₂. The thermoanalytical test results were evaluated by Winder (Version 4.4) software.

Thermoanalytic (TG/DTA) studies were carried out on samples made of cement paste specimens at the age of 28 days.

Results and discussion

Hardened cement paste specimens

Visual observations

Observation carried out on post-thermal load specimens of hardened cement paste leads to the following statements: in case of specimens prepared of ordinary Portland cement (CEM I 42,5 R) cracks formed at thermal loads of up to 500 °C. The number and size of cracks strongly grew at thermal loads of up to 800 °C, the specimens fell apart after post-cooling prior to the test of compressive strength. *Possible explanation:* cracks may be caused by chemical processes occurring in the cement stone. It is well known that portlandite is decomposed due to the thermal load of 500 °C, as well as part of the C–S–H (calcium–silicate–

hydrate) phases could decompose at different steps up to 800 °C [33].

In case of specimens prepared of sulfate-resisting Portland cement (CEM I 42,5 N-S) cracks did not form at thermal loads of up to 500 °C. The number and size of cracks strongly grew at thermal loads of up to 800 °C, but fewer and smaller cracks formed than on specimens prepared of CEM I 42,5 N-S. *Possible explanation:* part of the total chemically bound water belongs to the CAH (Aft and AFm) phases. The hydration process of the aluminate phase [mainly Brownmillerite, tetra-calcium aluminoferrite (C₄AF)] in sulphate-resisting Portland cement is much slower than that of tricalcium aluminate (C₃A) in ordinary Portland cement [34]. The unhydrated part of ferrite type aluminates could positively influence the resistance of cement paste against high temperatures.

Specimens prepared of Portland-pozzolana cement (CEM II/A-P 42,5 N): cracks did not form at thermal loads of up to 500 °C. The number and size of cracks grew at thermal loads of up to 800 °C.

In case of cement paste specimens prepared of Portland-fly ash cements (CEM II/A-V 42,5 R, CEM II/B-V 32,5 R) cracks formed at thermal loads of up to 500 °C. The number and size of cracks grew at thermal loads of up to 800 °C. After a thermal load, more cracks can be observed on cubes prepared from CEM II/A-V 42,5 N cement than on specimens prepared from CEM II/B-V 32,5 N cement. However, the number and size of cracks are smaller than those of specimens prepared from ordinary Portland cement. *Possible explanation:* the number of cracks can be explained with the different amounts of fly ash in the cements. Increased fly ash or pozzolana content results in

decreased portlandite content of the cements (dehydration of portlandite is at about 450 °C). The decreasing amount of portlandite is the consequence on the one hand of the diluting effect of the clinker substituting constituents and, on the other hand more portlandite is consumed by the higher amount of fly ash in the pozzolanic reaction.

In summary, Fig. 2 indicates the surface area covered with cracks in relation to the entire surface area of the given specimen. When calculating the ratio of cracks, the number and size of cracks were also taken into consideration. It can be assumed that the number and size of cracks as well as the ratio of surface damages is the highest with cement CEM I 42,5 R, while the lowest with cement CEM II/B 32,5 R out of the cements examined (Fig. 3).

Compressive strength

Relative residual compressive strength, $f_{c,T}/f_{c,20}$ is calculated by $f_{c,T}$, which is the compressive strength measured at laboratory condition on heat-loaded then cooled samples, where T is the temperature of heat load; as well as by the use of $f_{c,20}$, which is the compressive strength measured on the reference samples at laboratory condition, without heat load. Compressive strengths ($f_{c,T}$ and $f_{c,20}$) of cement paste specimens was measured on cubes of 30 mm sizes. Compressive strength tests were carried out after a thermal load (in 1 day), once the thermal loaded specimens cooled down to air temperature. The results of the compressive strength tests—calculated as the average of five measurements—are given in relation to the value measured at a temperature of 20 °C (relative residual compressive strength, $f_{c,T}/f_{c,20}$) (Fig. 4). Numerical values are shown in Table 4.

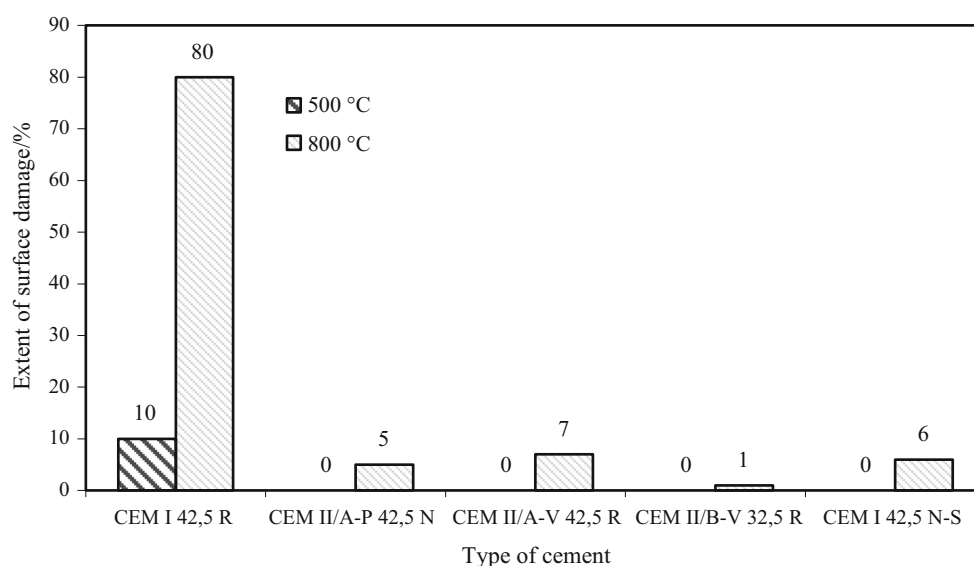


Fig. 2 Ratio of surface damages (cracking, spalling) in relation to the surface area of the specimens given in percentage

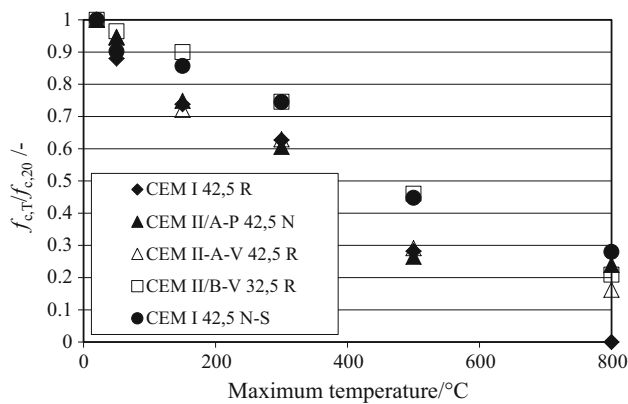


Fig. 3 Relative residual compressive strength ($f_{c,T}/f_{c,20}$) of hardened cement paste specimens, measured in cooled down state (every point is the average of five measurements)

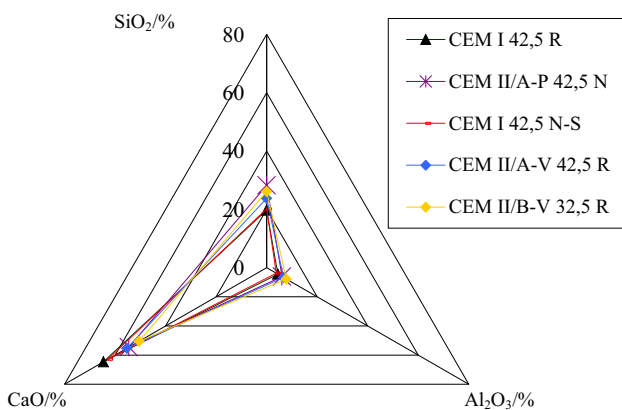


Fig. 4 Ratios of the three main oxides in cement compositions

Based on the results, the following results can be shown:

- relative residual compressive strength of specimens prepared from rapid hardening Portland cement (CEM I 42,5 R) after a thermal load of 500 °C is 28% of the value measured at a temperature of 20 °C. After a thermal load of 800 °C, the specimens fell apart and compressive strength tests could not be carried out;
- relative residual compressive strength of specimens prepared from sulfate-resisting Portland cement (CEM I 42,5 N-S) after a thermal load of 500 °C is 45%. After a thermal load of 800 °C, it is only 28% of the value measured at a temperature of 20 °C;
- relative residual compressive strength of specimens prepared from Portland-fly ash cements (CEM II/A-V 42,5 R, CEM II/B-V 32,5 R) after a thermal load of 500 °C is 19 and 46%; after a thermal load of 800 °C it drops to only 16 and 21%;
- relative residual compressive strength of specimens prepared from Portland-pozzolana cement (CEM II/A-P

42,5 N) after a thermal load of 500 °C is 26%; after a thermal load of 800 °C it is only 24%.

Major differences can be observed between the relative residual compressive strengths of specimens prepared from Portland cement (CEM I 42,5 R) and sulfate resistant Portland cement (CEM I 42,5 N-S) after thermal loads of 500 and 800 °C.

Relative residual compressive strengths of specimens prepared from Portland-fly ash cements (CEM II/A-V 42,5 R, CEM II/B-V 32,5 R) were higher than that of specimens prepared from Portland cement. Relative residual compressive strength of specimens prepared from Portland-pozzolana cement (CEM II/A-P 42,5 N) was higher than that of specimens prepared from Portland cement.

The results of compressive strength tests are in accordance with the crack patterns developed. The highest number of and most marked cracks can be seen on the specimens prepared from Portland cement (CEM I 42,5 R) and also the extent of strength decrease is the smallest with the specimens prepared from Portland cement (CEM I 42,5 N-S).

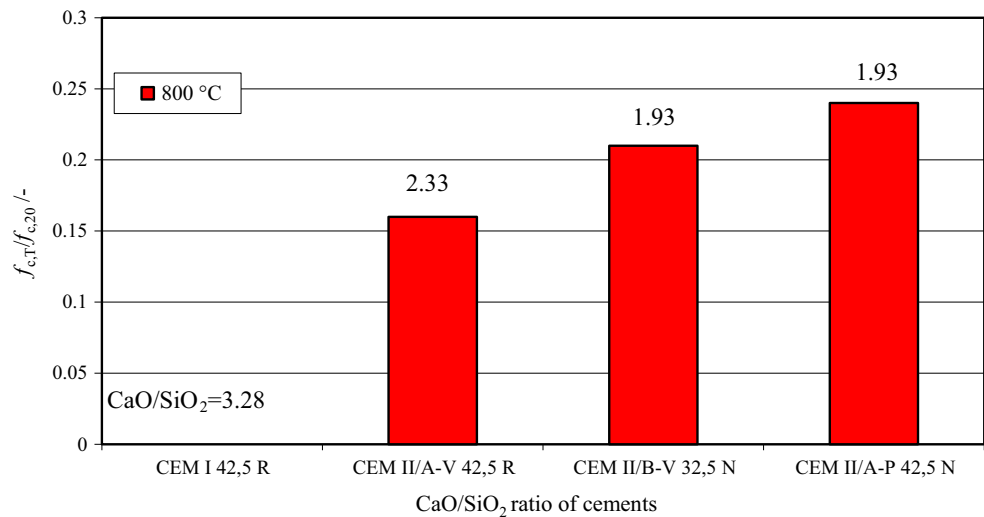
Analysis of the relationship between oxide composition of cements and the relative residual compressive strengths of cement paste specimens

Oxide composition of cements is essential because they define the properties of cements, e.g. the mineral composition of the cement including their behaviour at high temperature. As a result of high temperature, strength is greatly influenced by the chemical composition of the cement stone and its changes. The ratios of the three main oxides (SiO_2 , CaO , Al_2O_3) of the cements examined are shown in Fig. 4.

Figure 5 depicts relative residual compressive strength after the thermal load of 800 °C. CaO/SiO_2 ratios of the cements examined are illustrated above the bars. The graph depicts that a decreased CaO/SiO_2 ratio of the cement means higher relative residual compressive strength of cement paste specimens after the thermal load of 800 °C. The different relative residual compressive strength values in case of the same substituting ratio in CEM II/A type cements indicate that the hydration rate of the different clinker substituting constituents (natural pozzolana—trass or fly ash) is different. On the other hand in case of the same CaO/SiO_2 ratio of the cements, the relative residual compressive strengths depend on the type of substituting constituents as well. The relative residual compressive strength values are also influenced by other parameters as rapid hardening properties or specific surface of cements. We can conclude that in our case probably trass (natural

Table 4 Compressive strengths ($f_{c,T}$) of hardened cement paste specimens according to the heat load and the cement types

Maximum temperature/°C	Type of cement and residual compressive strength/N mm ⁻²		
	CEM I 42,5 R	CEM II/A-P 42,5 N	CEM II/A-V 42,5 R
20	67.31	49.99	59.33
50	61.43	49.92	58.32
150	52.42	44.03	57.739
300	58.21	49.81	61.90
400	56.51	45.56	50.47
500	41.31	34.24	39.30
600	40.02	30.74	36.47
800	12.24	10.51	13.04

Fig. 5 Relationship between CaO/SiO₂ ratio of cements and relative residual compressive strengths of hardened cement paste specimens after heat load of 800 °C

pozzolana—here perlite) has greater pozzolanic activity comparing with the pozzolanic activity of fly ash.

Thermoanalytical results

Thermoanalytical tests were carried out on samples made of hardened cement paste specimens at the age of 28 days. The cement paste cubes used for heat load were stored in the same condition as cement paste cubes used for thermoanalysis. Before the thermal test they were ground and afterward directly tested by TG/DTA. This case the influences of the increasing temperature steps are possible to follow by the heat reactions during thermoanalysis. Portlandite and the part of portlandite already carbonated decompose at different temperature range. Amount of portlandite as well as amount of calcium-carbonate is responsible at different temperature interval for the visually observed changes as well as for the residual compressive strength. This is the explanation, why we do not correct the amount of portlandite with the amount calculated from the

calcium-carbonate. The goal of thermoanalytical tests was to follow the results of compressive strength due to the temperature loads, where the decrease in compressive strength was mainly the consequence of the chemical change related to the certain temperature step.

A typical result of the thermoanalytical test is shown in the Fig. 6. On the thermoanalytical test results peaks both on the DTG and DTA curves indicated the change in phases, e.g. dehydration of AFt and AFm phases, dehydration of portlandite [Ca(OH)₂], and decomposition of calcium-carbonate (CaCO₃) as well as calcium-silicate-hydrate (C-S-H) phases.

During the thermoanalytical test between the temperature range of 20–1000 °C several heat reactions occur. Mean heat reactions of a hydrated cement paste are endothermic reactions: (1) dehydration of ettringite (C₃A·3CaSO₄·H₃₂); (2) dehydration of monosulphate (C₃A·CaSO₄·H₁₂); (3) decomposition of portlandite [Ca(OH)₂]; (4) decomposition of C-S-H and CaCO₃ phases (Fig. 6). The decomposition of C-S-H started at 560 °C but

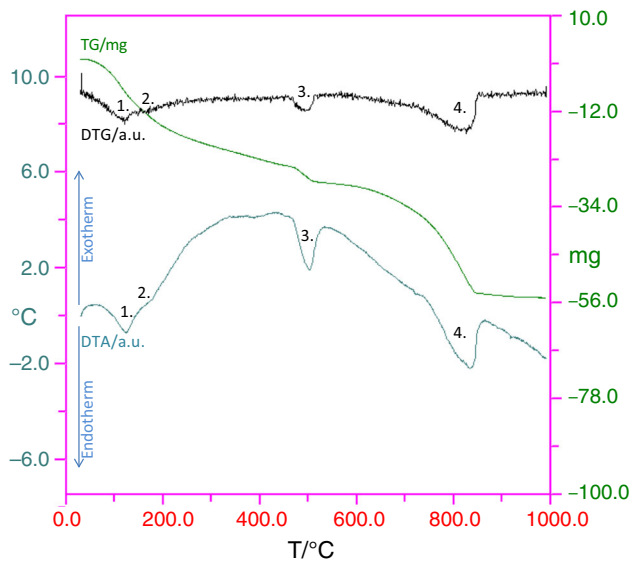


Fig. 6 Thermoanalytical test results of hardened cement paste of CEM II/A-V 42,5 R at the age of 28 days

became significant only above 600 °C. The thermogravimetric (TG) mass losses resulted by the decomposition of portlandite are different in case of the different types of cements. The thermogravimetric mass losses of the cement paste specimens due to the significant heat reactions—dehydration of $\text{Ca}(\text{OH})_2$ at about 500 °C and mostly by the decomposition of C–S–H and CaCO_3 at about 800 °C—are given in Table 5. Table 5 represents the amount of $\text{Ca}(\text{OH})_2$ calculated from the TG mass loss, related to the mass of the sample (hardened cement paste) and related to the mass of the sample reduced by the LOI, expressed in m%. Mass of sample reduced by the LOI equals to the amount of cement in the sample. This means that amount of $\text{Ca}(\text{OH})_2$

related to the mass of the sample reduced by the LOI equals to the amount of $\text{Ca}(\text{OH})_2$ related to the mass of cement.

As we can see, the higher the replacement ratio of cement clinkers by substituting materials, the smaller the portlandite formed due to hydration (Table 5). On the other hand, at the age of testing the specimens (28 days), a part of the portlandite already consumed in the pozzolanic reaction, or reacted with CO_2 and calcium–carbonate was formed. We decided not to compensate the portlandite content by the calcium–carbonate content, because the presence and ratio of the different phases influencing the thermal behaviour of cement paste in the different temperature ranges. In addition, standardised cement products incorporate about 3–5 m% calcium–carbonate, limestone (ground together with the clinkers). The thermogravimetric (TG) mass losses related to portlandite and calcium–carbonate as well as the total TG change in mass of sample (LOI) in the temperature interval between 20 and 1000 °C are shown in the Table 5.

Based on the thermoanalytical tests the following conclusions can be drawn.

Thermal tests indicated lower amount of water released due to the dehydration of portlandite in samples prepared from the Portland-composite cements as for the specimens of Portland cements. This is, on one hand, the consequence of the replacement of the cement clinkers by the additive (diluting effect) and, on the other hand, the result of the pozzolanic reaction between $\text{Ca}(\text{OH})_2$ and the pozzolanic additive.

Amount of $\text{Ca}(\text{OH})_2$ formed due to the hydration process in the cement paste specimens of CEM I 42,5 R is higher as in case of CEM 42,5 N-S (sulphate-resisting Portland cement), tested in the same age. The hydration of

Table 5 Thermogravimetric (TG) mass losses of hardened cement paste specimens and amount of $\text{Ca}(\text{OH})_2$ calculated from the TG mass loss, related to the mass of hydrated cement paste and related to the mass of the sample reduced by the LOI/m%

Type of cement	Dehydration of $\text{Ca}(\text{OH})_2$, TG/m%	Amount of $\text{Ca}(\text{OH})_2$ in the hydrated cement paste/m%	Decomposition of CaCO_3 , TG/m%	LOI between 20 and 1000 °C, TG/m% ^a	Mass% of sample reduced by the LOI (100%—LOI%)/m%	Amount of $\text{Ca}(\text{OH})_2$ related to the mass of the sample reduced by the LOI/m%
CEM I 42,5 R	3.29	14.94	4.80	19.99	80.01	18.67
CEM I 42,5 N-S	2.79	12.66	6.41	21.30	78.70	16.09
CEM II/A-V 42,5 R	1.58	7.17	8.56	24.77	75.23	9.53
CEM II/B-V 32,5 R	2.32	10.53	4.89	22.02	77.98	13.50
CEM II/A-P 42,5 N	2.23	10.12	5.51	23.46	76.54	13.22

^a Meaning of LOI (loss of ignition) here: is the total thermogravimetric mass loss during the thermal test referring to the initial mass of sample, in the temperature interval of 20–1000 °C

rapid type cement could be faster is in case of normal hardening cement.

Although the replacement ratio is higher in cement CEM II/B-V 32,5 R, the amount of $\text{Ca}(\text{OH})_2$ measured is less in cement paste specimen of CEM II/B-V 32,5 R as in case of cement paste specimen of CEM II/A-V 42,5 R. This is due to the Blaine fineness of the mentioned cements, which is in relationship with the specific surface of cements.

Hydration of CEM II/A-V 42,5 R consumes higher amount of $\text{Ca}(\text{OH})_2$ as measured in samples of CEM II/A-P 42,5 N in the same age (28 days), with the same Blaine fineness (Blaine fineness or Blaine specific surface area: the fineness of cement is measured as specific surface. The higher the specific surface is, the finer cement will be. The air permeability method is used and commonly called Blaine method) [29, 31]. This is the consequence of the different pozzolanic activity of the different additives (fly ash and trass).

The deterioration of the cement paste specimens is mostly due to the applied heat load of 500 °C produced by the released water during dehydration of portlandite. Based on the results of the cement paste specimens, cement types were chosen for the tests on concrete with respect to the following characteristics: cements involved in the concrete experiments (1) originated from the same clinker composition (CEM I 42,5 N-S sulphate-resisting Portland cement has different clinker composition); (2) same Blaine fineness and the same standard class of strength.

During testing the concrete specimens the influence of the type of supplementary constituent (pozzolans or flyash) was also studied. For this purpose binary blended cements (Portland-composite cements) with about the same replacement ratio of clinkers were investigated.

Hardened concrete specimens

Changes in the residual compressive strength of quartz-gravel containing concrete by thermal loads were examined with three types of cement: Portland cement (CEM I 42,5 R) in mixture M1; Portland-fly ash cement (CEM II/A-V 42,5 R) in mixture M2; and Portland-pozzolana cement (CEM II/A-P 42,5 N) in mixture M3.

Visual observations

Surface damages and cracks on the specimens were analysed after the thermal load, since the extent of the surface cracks on the specimens is a preliminary indicator of changes in residual compressive strength. During heating, a substantial amount of water was observed to escape from the specimens. The following conclusions are drawn after observing the specimens.

Specimens prepared by ordinary Portland cement (CEM I 42,5 R): Even at a thermal load of 500 °C, the corners of specimens (mixture M1) spalled off. *Possible explanation:* the corners of the specimens may have broken off due to internal tension developing during heating. Specimens were also damaged in the furnace. During the thermal load of 500 °C also the aggregate particles damaged, i.e. the quartz gravels splitted.

Specimens prepared by Portland-pozzolana cement (CEM II/A-P 42,5 N) and by Portland-fly ash cement (CEM II/A-V 42,5 R): After a thermal load of 800 °C, surface cracks formed on concrete specimens, however the corners of the specimens did not spall. It suggests that lower internal tensions developed as a result of thermal load.

To summarize, it can be stated that *concretes made of cements containing fly ash or pozzolans (here trass) as supplementary materials*—similarly to specimens of hardened cement paste—suffered less damages under thermal load than concretes prepared with ordinary Portland cement.

Compressive strength

Residual compressive strength of concrete prepared with quartz gravel is shown in Fig. 7 relating to the cement type and the maximum temperature of thermal load, from which the following statements can be deduced.

As a result of thermal load, relative residual compressive strength of concrete decreases up to a thermal load of 150 °C, then at 300 °C a temporary increase in strength can be observed. At a thermal load of over 300 °C, residual compressive strength decreases again.

As a result of thermal load, the relative residual compressive strength of concrete prepared from pozzolans and

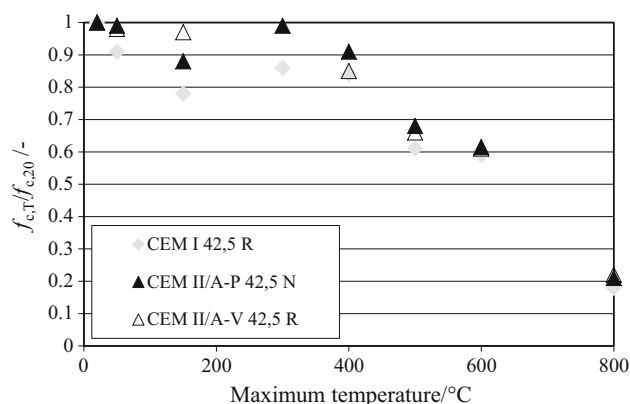


Fig. 7 Relative residual compressive strength of concrete in related to the cement type and the maximum temperature of thermal load (specimens at the age of 28 days, average of 3 measurements)

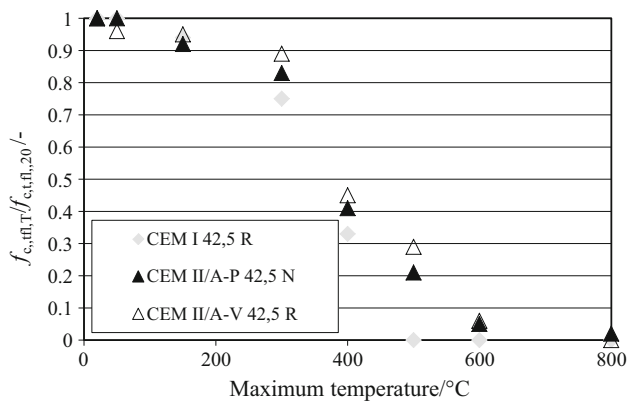


Fig. 8 Relative residual flexural strength of concrete in relation to the cement type and the maximum temperature of thermal load (specimens of 28 days, average of 3 measurements)

fly ash containing Portland-composite cements (CEM II/A-P 42,5 N; CEM II/A-V 42,5 R) is higher or at least equal to those of concrete specimens prepared from cement CEM I 42,5 R (Portland cement).

Flexural strength

Relative residual flexural strength of concrete specimens is given in Fig. 8 in relation to the cement type and the maximum temperature of thermal load, from which the following statements can be deduced.

At thermal loads of 400, 500, 600 and 800 °C, residual flexural strength of concrete decreases more significantly than its residual compressive strength (see Figs. 7, 8).

As a result of thermal load, relative residual flexural strength of concrete prepared from cement CEM II/A-P 42,5 N and CEM II/A 42,5 R proved to be slightly more favorable than concrete prepared from cement CEM I 42,5 R.

Conclusions

Our study was based on the examination of cements with various aggregates under high temperatures (20, 50, 150, 200, 300, 400, 500, 600, 800 °C). In our experiments Portland cements (CEM I 42,5 R; CEM I 42,5 N-S), and Portland-composite (binary blended) cements (CEM II/A-V 42,5 R; CEM II/A-P 42,5 N, CEM II/B-V 32,5 R) were involved.

Experimental constants were the following: water–cement ratio: 0.43, curing of specimens: after demoulding up to 7 days in water and the rest (up to 28 days) in laboratory air, method of heating (normative heating curve), duration of heat exposure (2 h), method of cooling (out of furnace, in laboratory air), age of specimens at the heat load (28 days) and at testing. Concrete specimens were prepared

with three selected cements (CEM I 42,5 R; CEM II/A-V 42,5 R; CEM II/A-P 42,5 N) and quartz-gravel aggregate. The number and size of surface cracks were observed by crack analysis from the photos with photogrammetric methods. The compressive strength was measured on cubic cement paste specimens with dimension of 30 mm as well as on cubic concrete specimens with dimension of 150 mm. Flexural strength was measured on concrete specimens with dimension of 70 × 70 × 250 mm. To understand and explain the findings of the visual observations and development of strength, thermoanalytical tests were made.

Based on the experiments, the following conclusions can be drawn.

Cement experiments

1. The number and size of surface cracks due to heat load on cement paste specimens decreased as a result of supplementing constituents in Portland-composite cements (fly ash, trass). The number and size of surface cracks on specimens prepared by sulphate-resisting Portland cement (CEM I 42,5 N-S) considerably increased due to thermal loads of up to 800 °C, but fewer and smaller surface cracks appeared than on specimens made from ordinary Portland cement (CEM I 42,5 R). It can be explained with the different clinker mineral contents of the cements.
2. In the case of thermal load, the value of the residual compressive strength of the cement stone grew in parallel with the present of supplementing constituents in cements (fly ash, pozzolans). Based on the results of residual compressive strengths, Portland-pozzolana and Portland-fly ash cements proved to be slightly more favourable than Portland cements. From the viewpoint of residual compressive strength following thermal load, sulphate-resisting cement (CEM I 42,5 N-S) proved to be more favourable than the high early strength (rapid) ordinary Portland cement (CEM I 42,5 R).
3. The results of the compressive strength test were in accordance with the crack pattern development. The highest number and most marked cracks were observed on specimens made from ordinary Portland cement (CEM I 42,5 R) along with the most significant decrease in strength due to thermal load.
4. Thermal tests indicated lower amount of water released due to the dehydration of portlandite in samples prepared from the Portland-composite cements as for the specimens of Portland cements. This is, on one hand, the consequence of the replacement of the cement clinkers by the additive (diluting effect) and, on the other hand, the result of the

pozzolanic reaction between Ca(OH)_2 and the pozzolanic additive. Amount of Ca(OH)_2 formed due to the hydration process in the cement paste specimens of CEM I 42,5 R is higher as in case of CEM 42,5 N-S (sulphate-resisting Portland cement), tested in the same age. Although the replacement ratio is higher in cement CEM II/B-V 32,5 R, the amount of Ca(OH)_2 measured is less in cement paste specimen of CEM II/B-V 32,5 R as in case of cement paste specimen of CEM II/A-V 42,5 R. This is due to the Blaine fineness of the mentioned cements, which is determining the rate of hydration. Hydration of CEM II/A-V 42,5 R consumes higher amount of Ca(OH)_2 as measured in samples of CEM II/A P 42,5 N in the same age (28 days), with the same Blaine fineness. This is the consequence of the different pozzolanic activity of the different additives (fly ash or trass). The most significant physical changes due to heat loading of the cement paste specimens was found after the applied heat load of 500 °C. Thermal tests proved that the extent is the consequence of the amount of the water released during decomposition of portlandite.

Based on the results of the cement paste specimens, cement types were chosen for the tests on concrete with respect to the following characteristics: cements involved in the concrete experiments (1) originated from the same clinker composition (CEM I 42,5 N-S sulphate-resisting Portland cement has different clinker composition); (2) same Blaine fineness and the same standard class of strength.

Concrete experiments

1. The corners of concrete specimens prepared from Portland cement broke off already at a thermal load of 400 °C. Concrete prepared from cements containing fly ash or trass as supplementing constituents and quartz-gravel aggregate surface cracks developed at the thermal load of 800 °C, but the corners of the specimens did not break off. It indicates that in the latter case, the thermal load in case of Portland-composite cements caused lower internal tension.
2. As a result of thermal load, the relative residual compressive strength and flexural strength of concretes prepared from binary blended cements containing supplementing constituents proved to be slightly more favourable.

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