

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

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Abstract

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 Portland cements containing trass or fly ash additives as replacement of clinkers.

In the first part of the study we focused on the influence of cement types where various cement paste specimens were investigated. Then, based on the results, concretes prepared with some selected type of cements were also studied.

Our studies have proved 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, Trass

1. 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 few 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 CSH (calcium-silicate-hydrates), amount of Ca(OH)_2 and degree of hydration. Different cement pastes can perform differently in fire [7].

Pozzolanic supplementary materials are used extensively throughout the world. The 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 applications.

The incorporation of pulverised fly ash (PFA) and slag in Portland cements (PC) 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 [8] 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 [9, 10, 11, 12].

Karakurt and Topcu [13] found by using SEM analysis that thermal cracking did not occur in PFA and slag blended 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 [9]. This could explain the higher resistance of PCs blended with PFA and slag to high temperature.

Khoury et al [15] tested ordinary Portland cement (OPC) – PFA cement pastes containing 30% PFA by weight 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 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 [17].

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 Portland cements containing trass, or fly ash additives as replacement of clinkers.

The test variables were the type of cements and the maximum temperature loads (20 °C, 50 °C, 150 °C, 300 °C, 500 °C, 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), compressive strength and thermoanalytic (TG/DTA) characteristics.

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 (i) originated from the same clinker composition (CEM I 42,5 N-S sulphate resistant Portland cement had different clinker composition); (ii) same Blaine fineness and the same standard class of strength.

During testing the concrete specimens, the influence of the type of additive (trass or fly ash) was also studied. For this purpose binary blended cements with about the same replacement ratio of clinkers were investigated.

2. Experimental program

2.1. Materials

2.1.1. Cement paste samples

Two types of Portland cements and three types of binary blended Portland cements were involved in our comparative study: 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. Cement clinkers and additives were ground together during the production of cement. The composition of clinker mineral was the same in the case of the blended 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. Clinkers of ordinary Portland cements and clinkers of the blended cements are usually the same; however, the production of sulphate resistant Portland cements require low ratio of tricalcium-aluminate (C_3A) clinkers. As the production of the different clinker composition needs different composition of feed, and the persistent production does not allow considerable change in clinker composition, the sulphate resistant PC was made by a different cement plant of the same company. All of the tested cements were standardised products of CRH Hungary Ltd (former Holcim Hungária Ltd). In the cements CEM II/A-

V 42,5 R and CEM II/B-V 32,5 R, the same pozzolanic additives (fly ash and trass) were used. The oxidative compositions of cements are given in Table 1 and 2.

Table 1: The amount of additives in the case of different cements

Type of cement	Additives to the cement	
	fly ash	trass
CEM I 42,5 R	0 %	0 %
CEM I 42,5 N-S	0 %	0 %
CEM II/A-V 42,5 R	0 %	6-20 %
CEM II/B-V 32,5 R	0 %	21-35 %
CEM II/A-P 42,5 N	6-20 %	0 %

During the experiments the influence and role of the clinker substituting additives were studied, which are also known as pozzolanic supplementary materials [21-24]. The test variables were the type of cements (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, Table 1) and the maximum temperature loads (20 °C, 50 °C, 150 °C, 300 °C, 500 °C, 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), compressive strength and thermoanalytic characteristics.

Table 2: The oxidative composition of cements (m%) (data provided by the former Holcim Hungária Ltd.)

	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

2.1.2. Concrete samples

Three types of cements 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-Bolomey method [25-26]. The calculated mix proportions are given in Table 3.

Table 3: Experimentally studied concrete mixtures

Mix proportions	M1	M2	M3
type of cement	CEM I 42,5 R	CEM II/A-V 42,5N	CEM II/A-P 42,5N
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

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

2.2. Preparation 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 (atmosphere and temperature) for 21 days. The as-obtained cubes of 28 days were heated (heating rate was about 40 °C min⁻¹) to the given temperatures (50 °C, 150 °C, 300 °C, 500 °C, 800 °C) in the furnace, then they were kept there for 2 hours. In our experiments, the applied heating curve was similar to the standard fire curve used for building structures and halls [27-32]. After the 2 hour 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 heated and then cooled specimens were inspected prior to the compressive strength test to visually observe the size and number of cracks. Laboratory measurements were conducted afterwards.

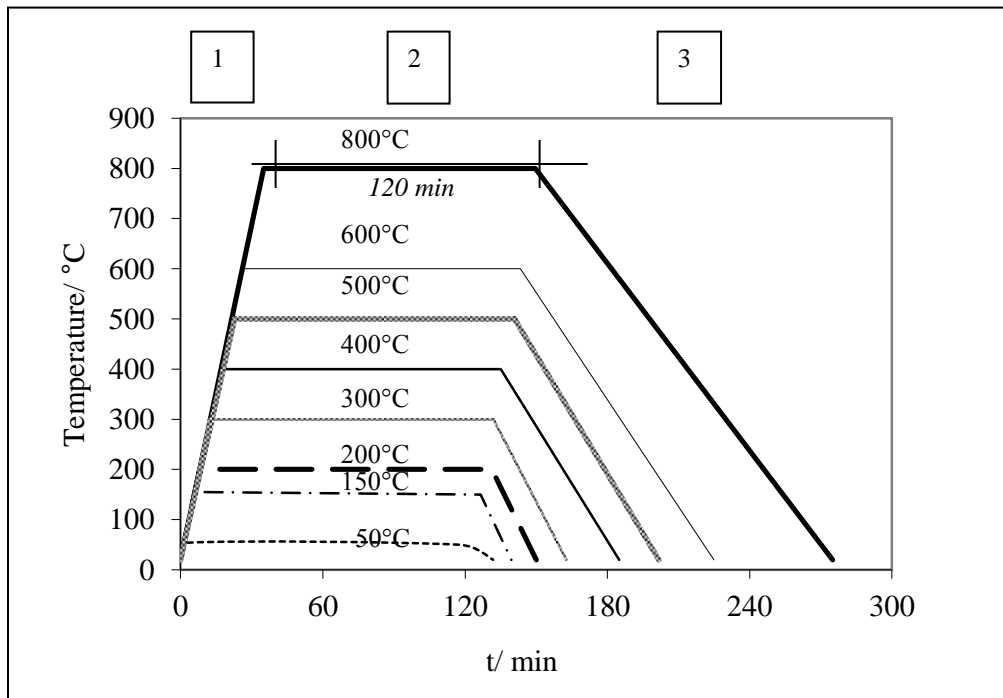


Fig. 1: Schematic representation of heating curves
(1 heating, 2 temperature loading, 3 cooling down)

2.3. Test methods

2.3.1. Compressive strength

Compressive strength tests were conducted on cubes prepared both from cement paste and concrete (Figure 2). Edge lengths of cement and concrete paste cubes were 40 and 150 mm, respectively. Cement paste cubes were tested with a WPM ZDM 10/91 test machine, while concrete cubes were studied with an ALPHA 3-3000S test machine. The specimens were tested when they had an age of 28 days.

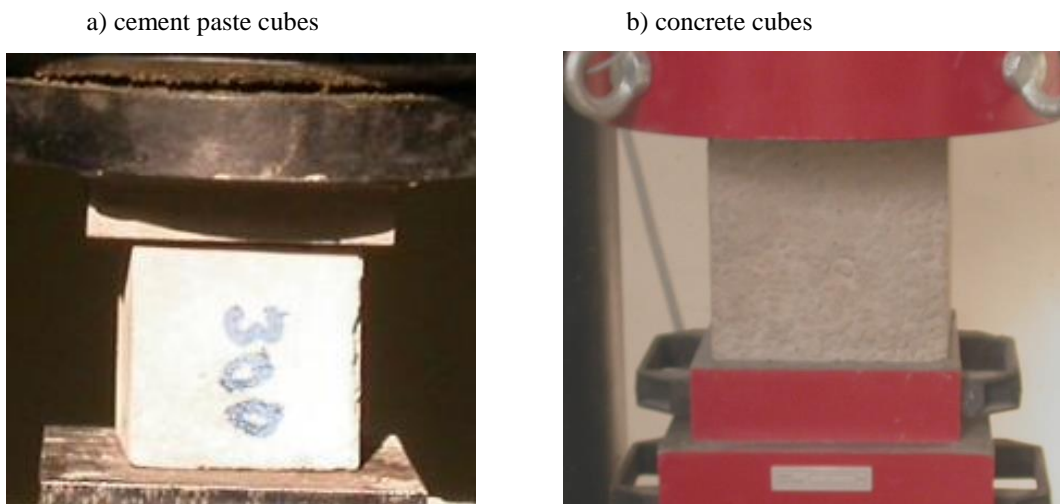


Fig. 2: Compressive strength test of a) cement paste (40 mm edge length) and b) concrete cubes (150 mm edge length)

2.3.2. Flexural strength

Flexural strength of concrete was tested on horizontal concrete prisms with edge lengths of 70x70x250 mm. Flexural strength test was carried out on a WPM ZDM 10/91 test machine (Figure 3). The specimens were tested when they had an age of 28 days.



Fig. 3: Flexural strength tests (beam span=200 mm, beam length=250 mm)

2.3.3. Thermal analysis

Changes in phases were followed by TG/DTA analysis using a MOM Derivatograph-Q 1500 D TG/DTA instrument. During the measurements, the reference material was alumina (Al_2O_3), the sample mass was ca. 300 mg, and the samples were heated at $10\text{ }^\circ\text{C min}^{-1}$ heating rate up to $\sim 1000\text{ }^\circ\text{C}$ in air static atmosphere. Before the investigations, the specimens were ground in an agate mortar, and directly after that they were measured in the TG/DTA device avoiding sample carbonation due to airborne CO_2 . The thermoanalytical test results were evaluated by Winder (Version 4.4.) software. The TG/DTA studies were carried out on samples made of cement paste specimens, when they had an age of 28 days.

3. Results and discussions

3.1. hardened cement paste specimens

3.1.1. Visual observations

Observations carried out on post-thermal load specimens of hardened cement paste leads to the following statements: Specimens prepared from ordinary Portland cement (CEM I 42,5 R): Cracks formed at thermal loads of up to $500\text{ }^\circ\text{C}$. The number and size of cracks strongly grew at thermal loads of up to $800\text{ }^\circ\text{C}$, 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. Portlandite is dehydrated due to the thermal load of $500\text{ }^\circ\text{C}$, part of the CSH (calcium silicate hydrate) phases could decompose at approx. $750\text{ }^\circ\text{C}$.

Specimens prepared from sulfate resistant Portland cement (CEM I 42,5 N-S): Cracks did not form at thermal loads of up to $500\text{ }^\circ\text{C}$. The number and size of cracks strongly grew at thermal loads of up to $800\text{ }^\circ\text{C}$, but fewer and smaller cracks formed than on specimens prepared from CEM I 42,5 N-S. Possible explanation: The hydration of aluminite phase (Brownmillerite) in sulphate resistant Portland cement is much slower than that of tricalcium-aluminate (C_3A) in ordinary Portland cement [29]. The unhydrated part of ferrite type aluminates could positively influence the resistance against high temperatures.

Specimens prepared from trass-Portland 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.

Cement specimens prepared from fly ash-Portland 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 could 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 fly ash content of the cements. Increased fly ash or trass content result 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 additives by substituting the clinkers), and, on the other hand, it is consumed by the pozzolanic reaction.

In summary, Figure 4 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 is conspicuous 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 among the cements examined.

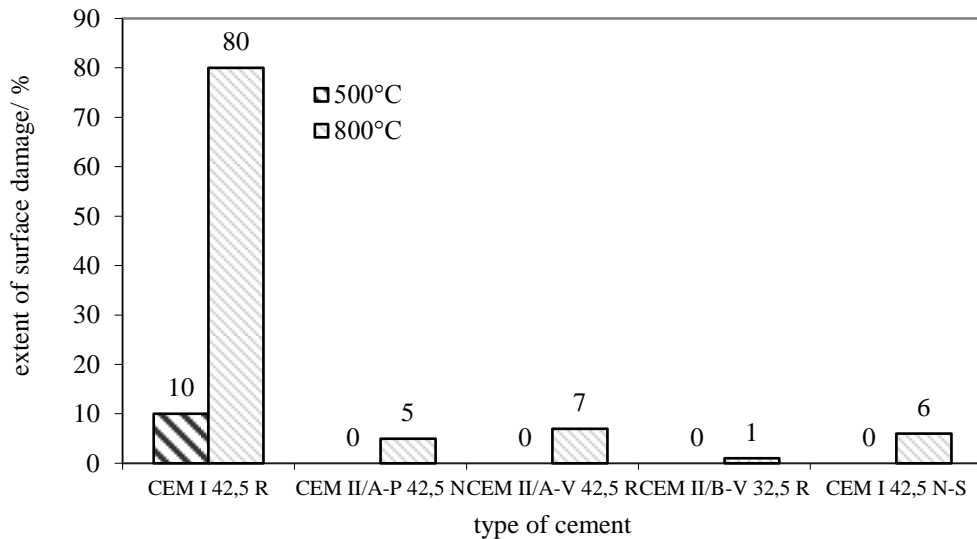


Fig. 4: Ratio of surface damages (cracks, spalling) in relation to the surface area of the specimens given in percentage

3.1.2. Compressive strength

Residual compressive strength is calculated by $f_{c,T}/f_{c,20}$, where $f_{c,T}$ 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 were measured on cubes of 40 mm edge length. Compressive strength tests were carried out in one day after a thermal load, once the specimen cooled down to air

temperature. The results of the residual compressive strength test – calculated as the average of 5 measurements – are given in Figure 5, and the numerical values are shown in Tables 4 and 5. Based on them, the following statements can be drawn:

Relative residual compressive strength of specimens prepared from rapid 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. Following 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 resistant Portland cement (CEM I 42,5 N-S) after a thermal load of 500 °C is 45 %. Following 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 fly ash-Portland cements (CEM II/A-V 42,5 R and CEM II/B-V 32,5 R) after a thermal load of 500 °C is 19 % and 46 %, respectively; following a thermal load of 800 °C it drops to only 16% and 21%, respectively.

Relative residual compressive strength of specimens prepared from trass-Portland cement (CEM II/A-P 42,5 N) after a thermal load of 500 °C is 26 %; following 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 both 500 °C and 800 °C.

Relative residual compressive strength of specimens prepared from fly ash-Portland cement (CEM II/A-V 42,5 R, CEM II/B-V 32,5 R) was higher than that of specimens prepared from Portland cement;

Relative residual compressive strength of specimens prepared from trass-Portland 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. Both the highest number of cracks and the 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 highest with these specimens.

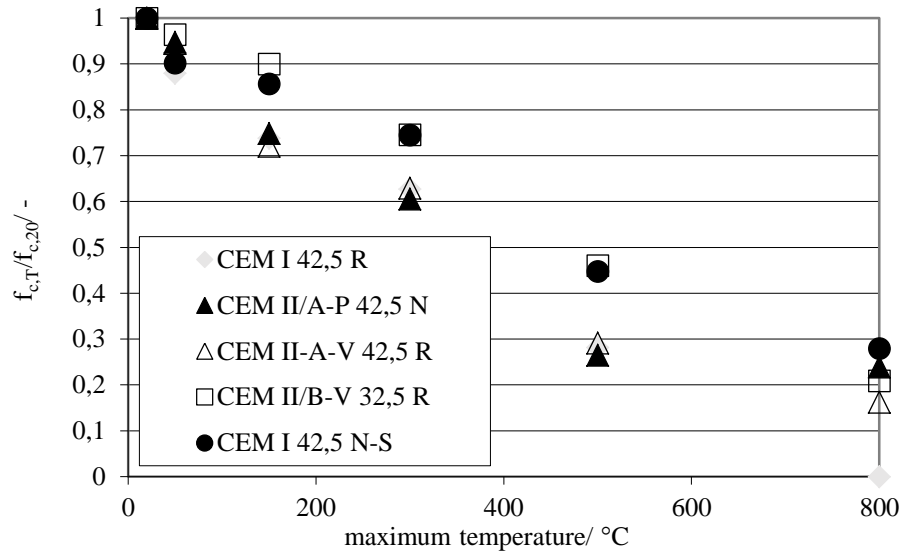


Fig. 5: Relative residual compressive strength ($f_{c,T}/f_{c,20}$) of hardened cement paste in relation to the values measured at a temperature of 20 °C, in a cooled state (every point is the average of 5 measurement values)

Table 4. Relative compressive strength of hardened cement paste in relation to the temperature and the cement types

maximum temperature/°C	type of cement/ 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	CEM II/B-V 32,5 R	CEM I 42,5 N-S
20	76.36	57.62	47.34	48.52	57.17
50	67.19	54.57	44.73	46.78	51.56
150	56.35	43.14	34.1	43.65	48.98
300	47.88	34.89	29.77	36.17	42.59
500	21.51	15.26	8.789	22.32	25.59
800	0	13.78	7.67	10.14	15.99

Table 5. Relative residual compressive strength of hardened cement paste in relation to the temperature and the cement types

maximum temperature/°C	type of cement and relative residual compressive strength/ -				
	CEM I 42,5 R	CEM II/A-P 42,5 N	CEM II/A-V 42,5 R	CEM II/B-V 32,5 R	CEM I 42,5 N-S
20	1	1	1	1	1
50	0.88	0.95	0.94	0.96	0.90
150	0.74	0.75	0.72	0.90	0.86
300	0.63	0.60	0.63	0.74	0.74
500	0.28	0.26	0.19	0.46	0.45

800	0	0.24	0.16	0.21	0.28
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3.1.3. Analysis of the relationship between oxide composition of cements and the residual compressive strengths of cement paste specimens

Oxide composition of cements is essential because it defines the properties of cements, e.g. the mineral composition of the cement and 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 Figure 6.

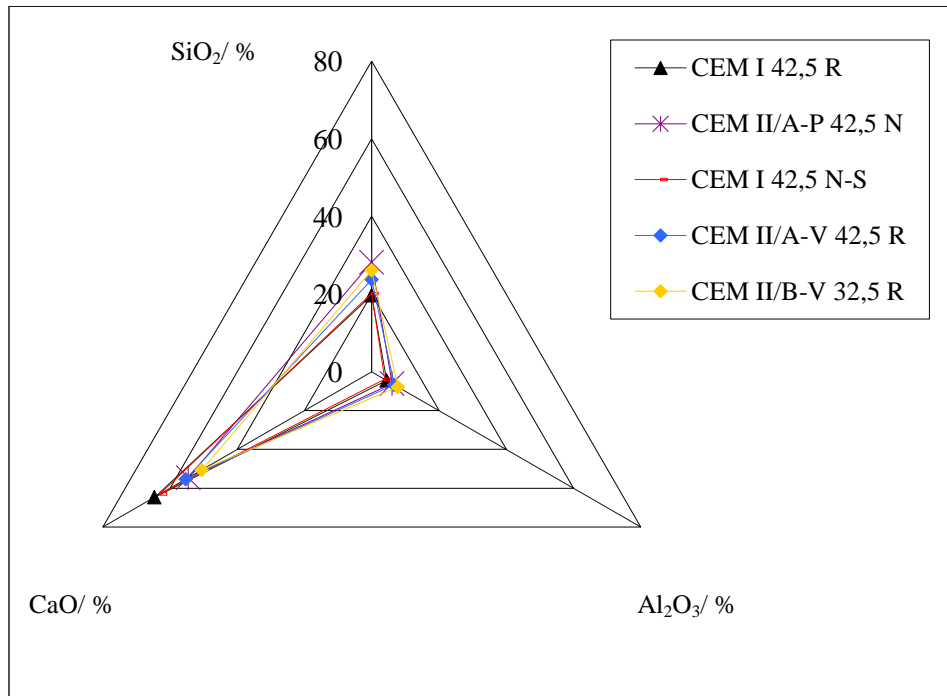


Fig. 6: Ratios of the three main oxides in cement compositions

Figure 7 depicts relative residual compressive strength after the thermal load of 800 °C. CaO/SiO_2 ratios of the cements examined are shown above the bars. The graph reveals that a decreased CaO/SiO_2 ratio of the hardened cement paste means higher relative residual compressive strength after thermal loads of 800 °C.

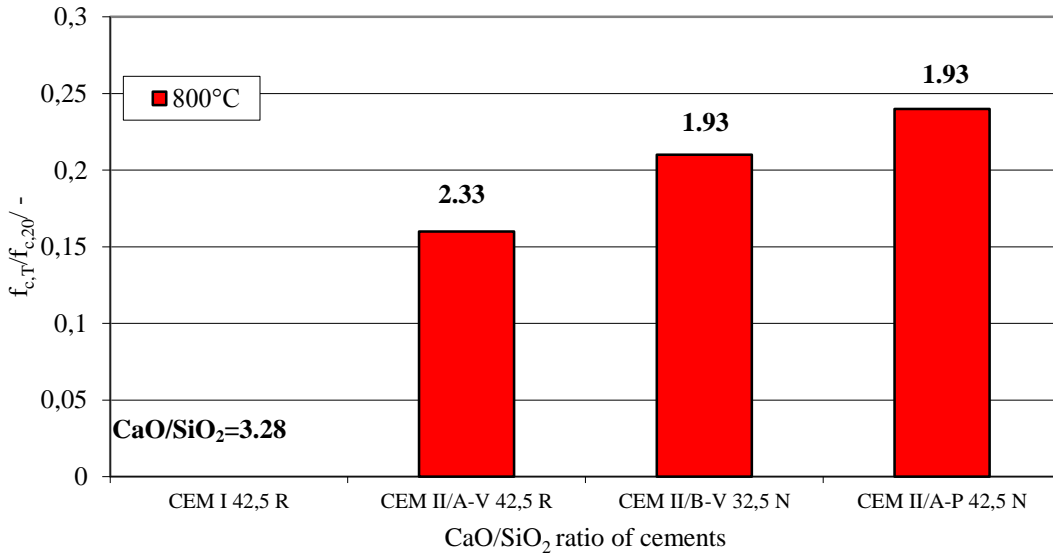


Fig. 7: Relationship between CaO/SiO₂ ratio of cements and relative residual compressive strengths of hardened cement paste specimens after heat load of 800 °C

3.1.4. Thermoanalytical results

Thermoanalytical tests were carried out on samples made of hardened cement paste specimens at the age of 28 days. A typical result of the thermoanalytical test is shown in Figure 8. The DTG and DTA peaks indicate the change in phases, e.g. dehydration of calcium-aluminate hydrate (CAH) phases or portlandite (Ca(OH)₂), then decomposition of calcium-carbonate (CaCO₃) as well as calcium-silicate hydrate (CSH) phases.

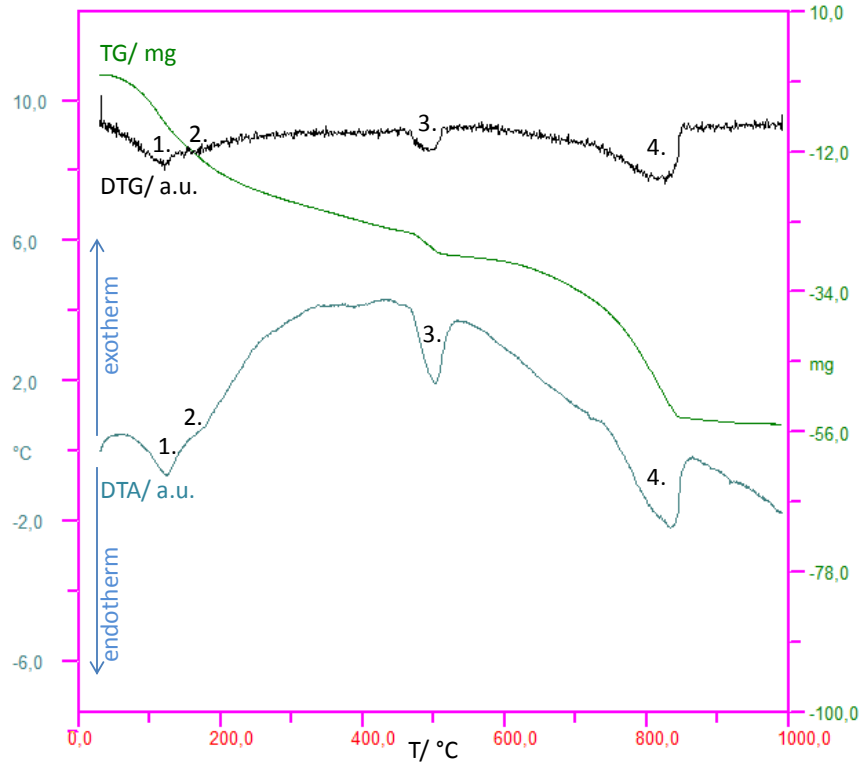


Fig. 8: Thermoanalytical test results of hardened cement paste of CEM II/A-V 42,5 R at the age of 28 days

During the thermoanalytical test due to dynamic heating several reactions occur. Mean heat reactions of a hydrated cement paste are endothermic: 1. dehydration of ettringite ($C_3A \cdot 3CaSO_4 \cdot H_{32}$); 2. dehydration of monosulphate ($C_3A \cdot CaSO_4 \cdot H_{12}$); 3. decomposition of portlandite ($Ca(OH)_2$); 4. decomposition of $CaCO_3$ and CSH phases (Fig. 8). The TG mass losses resulted by the decomposition of portlandite are different in the case of the different types of cements. The TG mass losses of the cement paste specimens due to the significant heat reactions – dehydration of $Ca(OH)_2$ and decomposition of $CaCO_3$ – are given in Table 6.

Table 6: Thermogravimetric (TG) mass losses of hardened cement paste specimens

Type of cement	Dehydration of $Ca(OH)_2$, TG/ m%	Decomposition of $CaCO_3$, TG/ m%	LOI* between 20 °C-1000 °C, TG/ m%
CEM I 42,5 R	3.29	4.80	19.99
CEM I 42,5 N-S	2.79	6.41	21.30
CEM II/A-V 42,5 R	1.58	8.56	24.77
CEM II/B-V 32,5 R	2.32	4.89	22.02
CEM II/A-P 42,5 N	2.23	5.51	23.46

*Meaning of LOI (loss of ignition) here is the total thermogravimetric mass loss during the thermal test in the temperature interval of 20-1000 °C, referred to the initial mass of sample

As we can see, the higher the replacement ratio of cement clinkers by additives, the smaller the amount of portlandite formed due to hydration (Table 5). On the other hand, at the age of testing the specimens, a part of the portlandite already reacted with CO₂ and formed calcium-carbonate. These effects may influence the results of tests (e.g. visual observation) by the behaviour of specimens due to high temperature. We decided not to compensate the portlandite content by the calcium-carbonate content, because the presence of the different phases influences the thermal behaviour in different temperature ranges. In addition, standardised cement products incorporate about 3-5 m% calcium-carbonate (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 °C-1000 °C are shown in the Table 6.

Table 7 represents the amount of Ca(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 Ca(OH)₂ related to the mass of the sample reduced by the LOI equals to the amount of Ca(OH)₂ related to the mass of cement.

Table 7: Amount of Ca(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

Type of cement	Amount of Ca(OH) ₂ in the hydrated cement paste/ m%	Mass % of sample reduced by the LOI (100% - LOI%)/ m%	Amount of Ca(OH) ₂ related to the mass of the sample reduced by the LOI/ m%
CEM I 42,5 R	14.94	80.01	18.67
CEM I 42,5 N-S	12.66	78.70	16.09
CEM II/A-V 42,5 R	7.17	75.23	9.53
CEM II/B-V 32,5 R	10.53	77.98	13.50
CEM II/A-P 42,5 N	10.12	76.54	13.22

Based on the thermoanalytical tests the following conclusions can be made:

Thermal tests indicated lower amount of water released due to the dehydration of portlandite in samples prepared from the blended cements than 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 the case of CEM 42,5 N-S (sulphate resistant Portland cement), tested at the same age.

However, the replacement ratio is higher in cement CEM II/B-V 32,5 R and the amount of Ca(OH)₂ measured is less in cement paste specimen of CEM II/B-V 32,5 R, compared to the 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 Ca(OH)₂ than measured in sample CEM II/A-P 42,5 N at the same age (28 days), with the same Blaine fineness (or Blaine Specific Surface Area: the fineness of cement is measured as specific surface. The higher the specific surface, the finer the cement. The air permeability method is

used and commonly called Blaine method.) [30]. This is the consequence of the different pozzolanic activity of the different additives (fly ash and trass).

The deterioration of the cement paste specimens due to the applied heat load of 500 °C is produced by the released water during dehydration of portlandite.

3.2. Hardened concrete specimens

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 (i) originated from the same clinker composition (CEM I 42,5 N-S sulphate resistant Portland cement had different clinker composition); (ii) same Blaine fineness and the same standard class of strength.

During testing the concrete specimens, the influence of the type of additive (trass or fly ash) was also studied. For this purpose binary blended cements with about the same replacement ratio of clinkers were investigated.

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

3.2.1. 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 prepared from Portland cement (mixture M1) containing quartz-gravel aggregate spalled off (*Figure 9*). Possible explanation: The corners of the specimens may have broken off due to internal tension developing during heating. Specimens were also damaged in the furnaces (*Figure 10*). During the thermal load of 500 °C also the aggregate particles damaged, i.e. the quartz gravels split.

Specimens prepared by trass-Portland cement (CEM II/A-P 42,5 N) and from fly ash-Portland cement (CEM II/A-V 42,5 R): Following a thermal load of 800 °C, surface cracks formed on concrete with quartz-gravel aggregate prepared from cement containing fly ash and trass (*Figure 11*), but 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 trass as supplementary materials – similarly to specimens of hardened cement paste – suffered less damages under thermal load than concretes made from ordinary Portland cement (*Figures 9 and 11*).



Figure 9: Damages of concrete prepared from cement CEM I 42,5 R after a thermal load of 400 °C

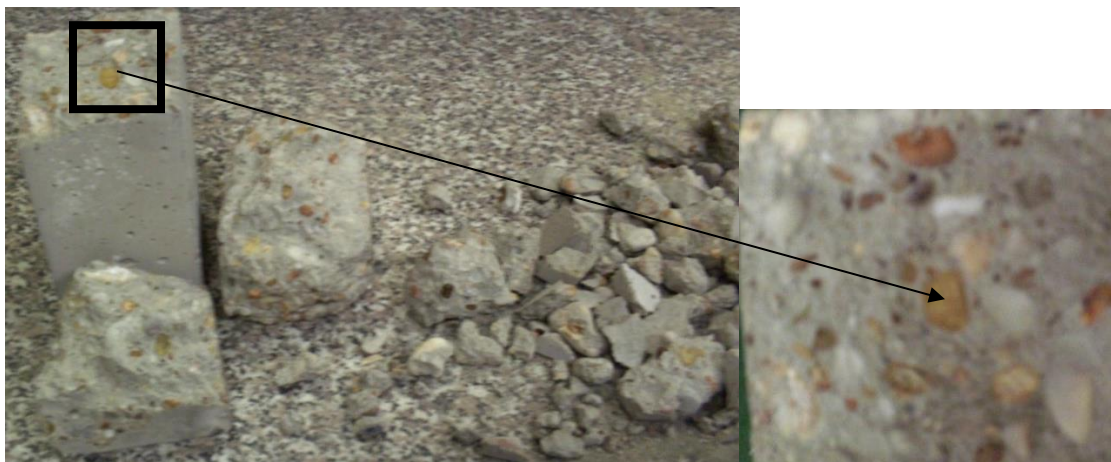


Figure 10: Damages of concrete block prepared from cement CEM I 42,5 R after a thermal load of 600 °C

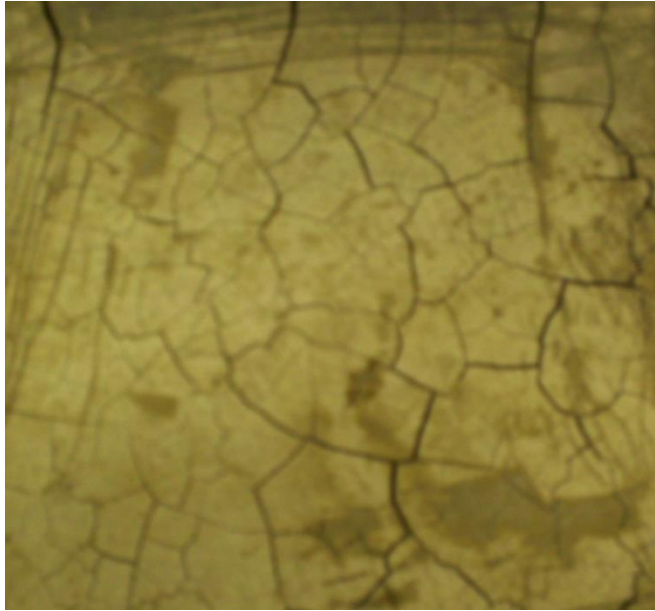


Figure 11: Damages of concrete prepared from cement CEM II/A-V 42,5 R after a thermal load of 600 °C

3.2.2. Compressive strength

Residual compressive strength of concrete prepared with flint-gravel is shown in Figure 12 relative to the cement type and the maximum temperature of thermal load (Table 8 shows values of the Figure 12), 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, relative residual compressive strengths of concrete prepared from trass and fly ash cement CEM II/A-P 42,5 N, CEM II/A-V 42,5 R are higher than or at least equal to concrete prepared from cement CEM I 42,5 R (Portland cement).

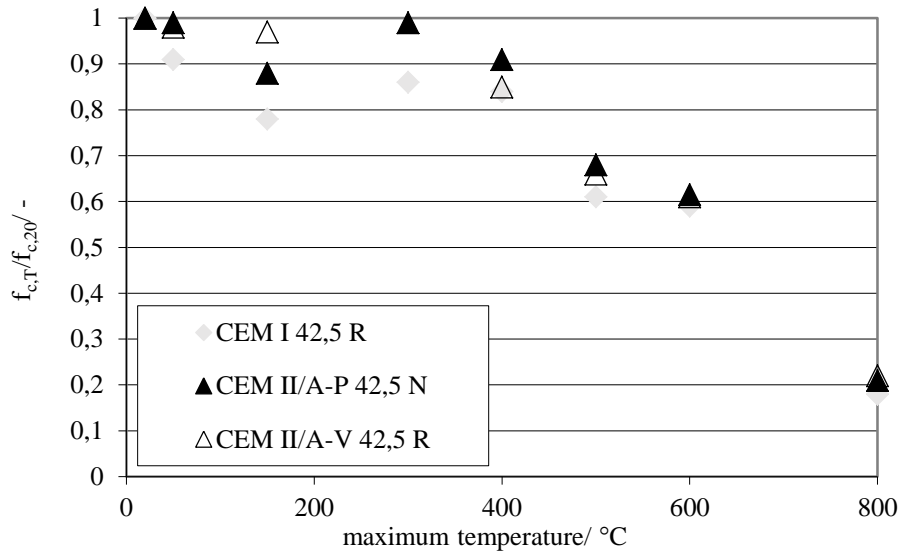


Figure 12. Residual compressive strength of concrete in relation to the cement type and the maximum temperature of thermal load (specimens at the age of 28 days, average of 3 measurements)

Table 8. Residual compressive strength of concrete in relation to the cement type and the temperature

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

3.2.3. Flexural strength

Residual flexural strength of concrete containing quartz-gravel are given in Figure 13 and Table 9 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 °C, 500 °C, 600 °C and 800 °C, residual flexural strength of concrete decreases more significantly than its residual compressive strength (see Figures 12 and 13).

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.

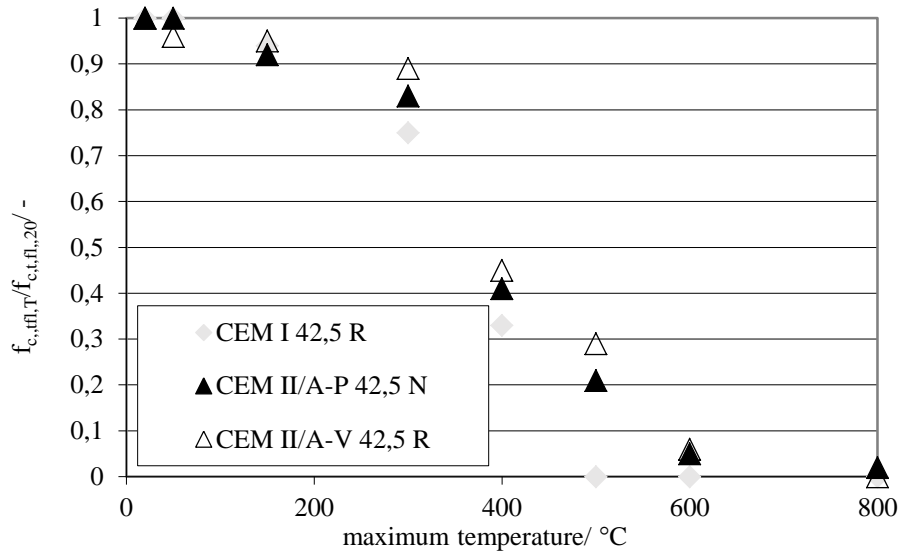


Figure 13. Residual flexural strength of concrete in relation to the cement type and the maximum temperature of thermal load (specimens of 28 days, average of 3 measurements)

Table 9. Residual flexural strength of concrete in relation to the cement type and the temperature

maximal temperature/ °C	type of cement/ residual flexural strength/ N mm ⁻²		
	CEM I 42,5 R	CEM II/A-P 42,5 N	CEM II/A-V 42,5 R
20	6.03	5.67	6.39
50	6.02	5.65	6.14
150	5.65	5.24	6.07
300	4.50	4.73	5.71
400	2.00	2.30	2.89
500	0.00	1.19	1.83
600	0.00	0.30	0.36
800	0.00	0.13	0.00

5. Summary

Our study was based on the examination of cements with various aggregates under several temperature loads (20 °C, 50 °C, 150 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, 800 °C). In our experiments binary blended (composite) cements were involved (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, CEM II/B-V 32,5 R).

The following experimental parameters were controlled: water-cement ratio (0.43), aggregate (quartz-gravel), curing of specimens (after demolding up to 7 days in water and the rest (up to 28 days) in laboratory air), method of heating

(normative heating curve), method of cooling (withdrawing it from the furnace, in laboratory air), duration of temperature exposure (2 hours).

The number and size of surface cracks were observed. On cement and concrete cube specimens the compressive strength was measured. To explain the development of compressive strength thermoanalytical (TG/DTA) tests were made.

Based on the experiments, the following conclusions can be made:

Cement experiments

- (1) The number and size of surface cracks on cement stone decreased as a result of adding heterogeneous cement additive materials (fly ash, trass). The number and size of surface cracks on specimens made from 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 CEM I 42,5 R. It can be explained with 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 adding additional materials. Based on the results of residual compressive strengths, trass and fly ash Portland cements proved to be slightly more favourable than Portland cement. From the viewpoint of residual compressive strength following the thermal load, sulphate resistant cement proved to be more favourable than traditional Portland cement.
- (3) The results of the compressive strength test were in accordance with the developed crack patterns. The highest number and most marked cracks were observed on specimens made from Portland cement (CEM I 42,5 R) along with the most significant decrease in strength due to thermal load.

Concrete experiments

- (1) The corners of specimens of concrete prepared from Portland cement containing flint-gravel aggregate broke off already at a thermal load of 400 °C. Concrete prepared from cement containing fly ash and trass as additives and quartz-gravel aggregate formed surface cracks at a 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 caused lower internal tension.
- (2) As a result of thermal load, the relative residual compressive strength and flexural strength of concretes prepared from cements containing additive materials proved to be more favourable.

6. Acknowledgements

An OTKA-PD-109129 grant is acknowledged. I. M. S. thanks for a János Bolyai Research Fellowship of the Hungarian Academy of Sciences.

7. References

- [1] Schneider U. Concrete at high temperatures - a general review, Fire Safety Journal, 1988:13:55-68.

- [2] Kordina K. Fire resistance of reinforced concrete beams, (Über das Brandverhalten punktgeschützter Stahlbetonbalken), Deutscher Ausschuss für Stahlbeton, Heft 479, ISSN 0171-7197, Beuth Verlag GmbH, Berlin, 1997.
- [3] Waubke NV. Physicalise analysis of strength reduction of concrete up to 1000 °C, (Über einen physikalischen Gesichtspunkt der Festigkeitsverluste von Portlandzement-betonen bei Temperaturen bis 1000 °C-Brandverhalten von Bauteilen), Dissertation, TU Braunschweig, 1973.
- [4] Khoury GA. Effect of heat on concrete material. Imperial College report. 1995, pp. 73.
- [5] Khoury GA, Grainger BN, Sullivan PJE. Transient thermal strain of concrete: literature review, conditions within specimen and behaviour of individual constituents, Magazine of Concrete Research. 1995;37:48-56.
- [6] Budelman H. Strength of concrete with different moisture content after elevated temperature, (Zum Einfluss erhöhter Temperatur auf Festigkeit und Verformung von Beton mit unterschiedlichen Feuchtegehalten), Heft 76, ISBN 3-89288-016-6, Braunschweig, 1987.
- [7] Grainger BN. Concrete at High Temperatures, Central Electricity Resarch Laboratories, UK, 1980.
- [8] Wang HY. The effects of elevated temperature on cement paste containing GGBFS, Cem Concr Compos 2008;30:992–9
- [9] Poon C-S, Azhar S, Anson M, Wong Y-L. Comparison of the strength and durability performance of normal- and high-strength pozzolanic concretes at elevated temperatures, Cem Concr Res 2001;31:1291–300.
- [10] Heikal M, El-Didamony H, Sökkary TM, Ahmed IA. Behavior of composite cement pastes containing microsilica and fly ash at elevated temperature, Constr Build Mater 2013;38:1180–90.
- [11] Mendes A, Sanjayan J, Collins F. Phase transformations and mechanical strength of OPC/slag pastes submitted to high temperatures, Mater Struct. 2008;41:345–50.
- [12] Xu Y, Wong YL, Poon CS, Anson M. Influence of PFA on cracking of concrete and cement paste after exposure to high temperatures, Cem Concr Res. 2003;33:2009–16.
- [13] Karakurt C, Topcu IB. Effect of blended cements with natural zeolite and industrial by-products on rebar corrosion and high temperature resistance of concrete, Constr Build Mater 2012;35:906–11.
- [14] Delhomme F, Ambroise J, Limam A. Effects of high temperatures on mortar specimens containing Portland cement and GGBFS, Mater Struct. 2012;41:345–50.

- [15] Khoury GA, et al. Fire Design of Concrete Materials Structures and Modelling. 1st fib Congress, Osaka, Japan, Oct. 2001.
- [16] X. Yu, Y.L. Wong, C.S. Poon, M. Anson, Damage to PFA concrete subject to high temperatures, Proceedings of International Symposium on High Performance Concrete-Workability, Strength and Durability, Hong Kong, 2000 pp.1093–1100.
- [17] K.W. Nasser, H.M. Marzouk, Properties of mass concrete containing fly ash at high temperatures, ACI J. 76 (4) (1979) 537–551.
- [18] U. Diederichs, U.M. Jumppanen, V. Penttala, Behavior of high strength concrete at high temperatures, Report No. 92, Department of Structural Engineering, Helsinki University of Technology, 1989.
- [19] S. Ghosh, K.W. Nasser, Effects of high temperature and pressure on strength and elasticity of lignite fly ash and silica fume concrete, ACI Mater. J. 93 (1) (1996) 51–60.
- [20] W.P.S. Dias, G.A. Khoury, P.J.E. Sullivan, Mechanical properties of hardened cement paste exposed to temperatures up to 700 °C (1292F), ACI Mater. J. 87 (2) (1990) 160–165.
- [21] Barbara P, Iwona W. Comparative investigations of influence of chemical admixtures on pozzolanic and hydraulic activities of fly ash with the use of thermal analysis and infrared spectroscopy, Journal of Thermal Analysis and Calorimetry, 2015; 120 119-127.
- [22] Yun L, Hung-Liang C. Thermal analysis and adiabatic calorimetry for early-age concrete members, Journal of Thermal Analysis and Calorimetry, 2015;122:937-945
- [23] E. T. Stepkowska, J. M. J. M. Bijen, J. L. Perez-Rodriguez Thermal mass changes of portland cement and SLAG cements after water sorption, Journal of thermal analysis July 1994, Volume 42, Issue 1, pp 41–65
- [24] Pacewska B, Wilińska I, G. Blonkowski G, Investigations of cement early hydration in the presence of chemically activated fly ash, Journal of Thermal Analysis and Calorimetry 2008, Volume 93, Issue 3, pp 769–776.
- [25] Balázs Gy. Építőanyagok és kémia [Buildings material and chemistry], Műegyetemi Kiadó ISBN944493, 1994
- [26] Pekár Gy. Simple basic model for concrete and its application, <http://dx.doi.org/10.14382/epitoanyag-jsbcm.2013.22>, 2013.
- [27] Eurocode 1. Basis of design and actions on concrete structures. Part 2-2: Actions on structures exposed to fire, EN 1991-1-2:2002, November 2002.

- [28] American Concrete Institute. ACI/TMS 216 Standard Method for Determining Fire Resistance of Concrete and Masonry Construction Assemblies. Framington Hills, MI, 1997.
- [29] Ministry of Construction. Ed.. Taika Seinou Kenshouhou no Kaisetu Oyobi Keisanrei tosonso Kaisetu. Guidline on Vertification Method for Fire Resistance and Exemplares. Inoue Shoin, 2001.
- [30] *fib* bulletin 38, Fire design of concrete structures- materials,, structures and modelling. ISBN: 978-2-88394-078-9, 2007.
- [31] Kopecskó K. (2006): Chloride ion binding capacity of clinker minerals and cements influenced by steam curing, <http://www.doktori.hu/index.php?menuid=193&vid=2743>,
- [32] EN 197-1:2000 Cement. Composition, specifications and conformity criteria for common cements