Improved Fire Resistance by Using Different Types of Cements

Éva Lublóy[1], Katalin Kopecskó[2], and György L. Balázs[1](✉)

[1] Department of Construction Materials and Technologies, Budapest University of Technology and Economics, Budapest 1521, Hungary
balasz@vbt.bme.hu

[2] Department of Engineering Geology and Geotechnics, Budapest University of Technology and Economics, Budapest 1521, Hungary

Abstract. Composition and microstructure of hardened cement paste have important influences on the properties of concrete exposed to high temperatures. An extensive experimental study was carried out to analyse the post-heating characteristics of concretes subjected to temperatures up to 800 °C. Major parameters of our study were the content of supplementary materials (slag, fly ash, trass) of cement (0, 16 or 25 m%) and the value of maximum temperature. Our results indicated that (i) the number and size of surface cracks as well as compressive strength decreased by the increasing content of supplementary materials of cements due to elevated temperature; (ii) the most intensive surface cracking was observed by using Portland cement without addition of supplementary materials. The increasing content of the supplementary material of cement increased the relative post-heating compressive strength. Tendencies of surface cracking and reduction of compressive strength were in agreement, i.e. the more surface cracks, the more strength reduction.

Keywords: Fire resistance · Concrete · Cement · Supplementary materials

1 Introduction

Effects of high temperatures on the mechanical properties of concrete were studied as early as the 1940s (Schneider 1988). In the 1960s and 1970s fire research was mainly directed to study the behaviour of concrete structural elements (Kordina 1997). There was relatively little information available about the concrete properties during and after fire (Waubke 1973).

Recent fire cases called again the attention to fire research. Different concrete types may also mean different possibilities for fire design *(EN 1991-1-2; ACI/TMS 216; Guideline on Verification Method for Fire Resistance and Exemplars)* Environmental protection requires the use of cements with low clinker content. Concrete is a composite material that consists mainly of mineral aggregates bound by a matrix of hardened cement paste. Composition and internal structure of hardened cement paste has an important influence on the properties of concrete exposed to high temperatures (Khoury 2001). Characteristics of concrete during and after the heating process depend on the

M. di Prisco and M. Menegotto (Eds.): ICD 2016, LNCE 10, pp. 219–228, 2018.
https://doi.org/10.1007/978-3-319-78936-1_16

type of cement, the type of aggregate and the interaction between them (Khoury 1995; Khoury et al. 1995; Budelman 1987).

Effect of cement type has been hardly studied. Early studies on concretes made of the two commonly used cement types, Portland cement or Portland cement with low amount of slag indicated almost the same residual compressive strength over 400 °C (Schneider and Lebeda 2000; Schneider 1986). The properties of cement paste itself are also influenced by the mixing proportions of the constituents (fib 2007; Barbara and Iwona 2015; Yun and Hung-Liang 2015). 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 (Grainger 1980).

Grainger (1980) studied cements with or without pulverised fly ash (PFA) subjected to a series of temperatures ranging from 100 °C to 600 °C with an interval of 100 °C. In his research the dosage of PFA was 20%, 25%, 37.5% and 50% of the total mass of binders. It was found that the addition of PFA could improve the residual compressive strength of cement paste. The beneficial effect of PFA as part of the binder was in good agreement with the results of Dias et al. (1990) and Xu et al. (2001). Khoury et al. observed that 400 °C was a critical temperature for Portland cement concretes, above which concretes would disintegrate on subsequent post cooling exposure to ambient conditions (Khoury et al. 1990).

In fire, the heated surface region of concrete loses its moisture content by evaporation from the surface and by migration into the inner concrete mass driven by the temperature gradient (Schneider and Weiß 1997). Due to high temperature, the structure and mineral composition of concrete changes. The analysis was made by thermogravimetry (TG). Around 100 °C the mass-loss is caused by water evaporating from the micropores. The decomposition of ettringite ($3CaOAl_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) takes place between 50 °C and 110 °C. At 200 °C there is a further dehydration, which causes small mass loss. The mass loss of the test specimens with various moisture contents was different till all the pore water and chemically bound water were gone. Further mass loss was not perceptible around 250–300 °C (Hinrichsmeyer 1987; EN 1992, 2002). During heating the endothermic dehydration of $Ca(OH)_2$ takes place between temperatures of 450 °C and 550 °C (1). This endothermic reaction is accompanied by loss of mass (Thielen 1994).

$$Ca(OH)_2 \rightarrow CaO + H_2O \uparrow \tag{1}$$

In the case of concretes made of quartz gravel aggregate, other influencing factor is the change in crystal structure of quartz α formation into →β formation at 573 °C. This transformation followed by volumetric increase that influences the strength detrimentally (Hoj 2005). Dehydration of calcium-silicate-hydrates was found at the temperature of 700 °C (Gambarova 2004).

Based on this information, we carried out an extensive experimental study to analyse the post-heating characteristics of concretes subjected to temperatures up to 800 °C. Major parameters of our study were types of supplementary materials (ground granulated blastfurnace slag, fly ash, trass) and the substitutions of cement clinker (0, 16 or 25 m%) in addition to the value of maximum annealing temperature.

2 Experimental Program

2.1 Cements

Main purpose of our experimental study was to determine the influences of supplementary materials (slag, fly ash, trass) content of cements on post-heating characteristics of hardened cement paste as well as that of concrete. The following cements were involved in the comparative study: *ordinary Portland cements* (CEM I 52,5 N; CEM I 42,5 R); *sulphate resistant Portland cement* (CEM I 42,5 N-S; *Portland slag cement* (CEM II/A-S 42,5 N); *Portland trass cements* (CEM II/A-V 42,5 R; CEM II/B-V 32,5 R) and *Portland fly ash cement* (CEMII/A-P 42,5 N).

Cement clinkers and additives were ground together during the production of cement. The oxidative compositions of cements are given in Tables 1a and 1b.

Table 1a. Chemical composition of tested 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
$Si0_2$	19.71	20.16	23.75	26.15	28.23
Al_20_3	4.46	3.83	6.68	7.79	6.10
Fe_20_3	2.97	6.03	4.73	5.33	3.42
Ca0	64.59	62.9	55.31	50.48	54.54
Mg0	1.0	1.88	2.66	2.64	1.0
K_20	0.69	0.43	0.85	0.95	1.15
Na_20	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

Table 1b. Chemical composition of tested cements (m%) (data by Duna-Dráva Cement Heidelberg Cement Group)

	CEM I 52,5 N	CEM II/A S 42,5 N
$Si0_2$	20.59	22.77
Al_20_3	5.55	5.83
Fe_20_3	3.21	2.97
Ca0	65.02	60.30
Mg0	1.44	2.51
$S0_3$	2.88	3.00
K_2O	0.78	0.80
Na_20	0.11	0.13
Cl	0.0055	0.0056

2.2 Test Specimens and Variables

The test variables were:

– types of cements: Portland cements (ordinary and sulphate resistant), Portland slag cement, Portland trass cements and Portland fly ash cement;
– maximum temperatures of heat loading: 50 °C, 150 °C, 300 °C, 500 °C and 800 °C.

The test constants were:

– water to cement ratio (w/c = 0.43);
– cement content. In this paper the studied specimens were cement paste cubes);
– testing of specimens started at 28 days and finished at 30 days.

The studied characteristics were:

– development of surface cracking (studied by macroscopic observation);
– change in compressive strengths (relative residual compressive strengths) due to heat loadings.

2.3 Test Methods

The studied specimens were cube cement paste specimens with dimensions of 30 mm. Cast specimens were removed after 24 h from the formwork, then specimens were stored in water for 7 days and kept at laboratory conditions (temperature 20 ± 2 °C, 65 ± 5% relative humidity) until testing in accordance with the standard (28 days). The experiments on specimens finished at the age of 30 days.

Our experimentally applied heating curve was similar to the standard fire curve (in accordance with EN 1991.1.2) up to 800 °C. Specimens were kept for two hours at the actual maximum temperature levels. Specimens were then slowly cooled down in laboratory conditions for further observations. During the heat load a program controlled electric furnace was used. The compressive strength was measured on the heat loaded and, than cooled down specimens and the average values of the measurements were analysed.

3 Results and Discussions

Results on surface cracking and residual compressive strength after exposing to high temperatures are presented and discussed herein.

3.1 Development of Surface Cracks

Development of surface cracks as a result of the elevated temperatures is presented in Fig. 1.

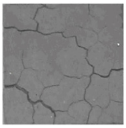
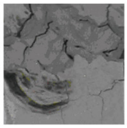
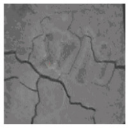
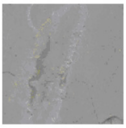
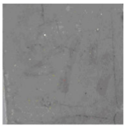
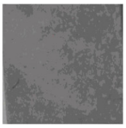
Type of cement	Temperature of heat load	
	500 °C	800 °C
CEM I 52,5 N		
CEM I 42,5 R		
CEM I 42,5 N-S		
CEM II/A-S 42,5 N		
CEM II/A-P 42,5 N		
CEM II/A-V 42,5 R		
CEM II/B-V 32,5 R		

Fig. 1. Effect of cement type on the development of surface cracks as a result of the elevated temperature (hardened cement paste specimens, at the age of 30 days, w/c = 0.43)

Temperature loading on hardened cement paste specimens caused chemical and physical changes leading to surface cracks. There were no macroscopic observable changes on the surface of cubes due to heat loads up to maximum temperature 500 °C.

In the case of *Portland cement specimens* (CEM I 42,5 R, CEM I 52,5 N) cracks already formed by heating up to 500 °C, and the size and number of cracks considerably increased by heating up to 800 °C (see 1st and 2nd rows of Fig. 1). Crack development is explained by the chemical reactions in the hardened cement paste, i.e. dehydration of portlandite, $Ca(OH)_2$ at about 450 °C and decomposition of CSH at about 750 °C (see 1st and 2nd rows in Fig. 1).

In addition to these after cooling rehydration of CaO could considerably increase the extent of the crack development with further changes in volume. Rehydration of CaO takes place by the humidity of air and followed by expansion.

In the case of *sulphate resistant Portland cement* (CEM I 42,5 N-S) only small cracks appeared by heating up to 500 °C, and the amount and size of cracks increased in the case of specimens heating up to 800 °C (see 3rd row in Fig. 1). The hydration of aluminate phase (Brownmillerite) in *sulphate resistant Portland cement* is much slower than for tricalcium-aluminate (C_3A) in *ordinary Portland cement* (Kopecskó 2006). The unhydrated part of ferrite type aluminates could positively influence the resistance against high temperatures.

In the case of *Portland slag cements* (CEM II/A-S 42,5 N, CEM II/B-S 32,5 R), *Portland trass cements* (CEM II/A-V 42,5 R, CEM II/B-V 32,5 R) *and Portland fly ash cement* (CEM II/A-P 42,5 N) *specimens* only small cracks appeared by heating up to 500 °C, and the amount and size of cracks increased in the case of specimens heating up to 800 °C (see 4th row in Fig. 1).

With the increasing substitution of cement clinker by the supplementary material the production of portlandite during hydration in the hardened cement paste decreases; thus, less portlandite dehydrates at about 450 °C, which may give the explanation of decreased amount of cracks.

The supplementary materials are usually latent hydraulic (GGBS) or pozzolanic (trass, fly ash) materials. During the hydration process they consume part of the portlandite forming calcium-silicate-hydrates. The other cause of the decrease of portlandite is the diluting effect: the higher the substitution rate of the clinker, the smaller the amount of portlandite formed. The rate (speed) of pozzolanic reaction is influenced by many factors such as the specific surface/average grain size of the clinkers/supplementary materials, the type of SCMs, etc.

3.2 Compressive Strength

In Fig. 2 the compressive strengths of the hardened cement paste specimens are presented related to the compressive strength measured at 20 °C ($f_{c,T}/f_{c,20}$ called residual relative compressive strength) as functions of the maximum temperature and the cement type.

The relative residual compressive strength decreases up to 150 °C heat loading, then for some cement types slight increase is observable up to 300 °C. In the case of higher temperatures than 300 °C the residual relative compressive strength decreases again (Fig. 2). Specimens loaded up to 300 °C show higher residual strength comparing with the average strengths measured on specimens loaded up to 150 °C because the intensive dehydration in the temperature interval between 60 and 180 °C probably causes the hydration of the unhydrated cement grains in the microstructure.

In the case of *Portland cement specimens* (CEM I 42,5 R, CEM I 52,5 R, CEM I 42,5 N-S) the average of residual relative compressive strength of the test specimens was 28%, 35% and 45% heating up 500 °C and further 1%, 10% and 28% by heating up to 800 °C (Fig. 3).

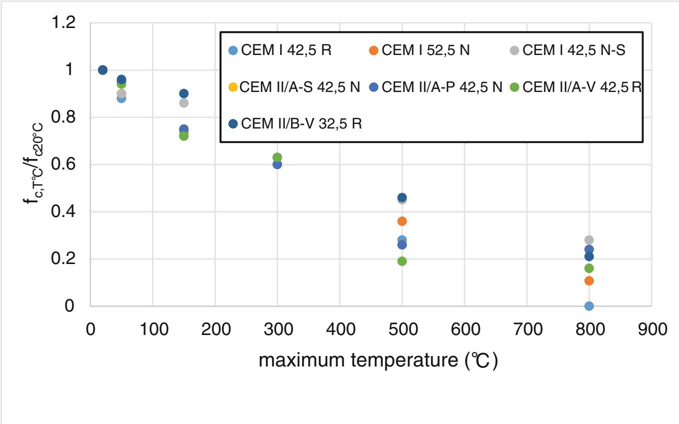


Fig. 2. Residual compressive strength of hardened cement paste with different cement types (strength values are related to strength values of 20 °C); Reference values (N mm^{-2}): CEM I 42,5 R, 76.36; CEM 52,5 N, 78.5; CEM I 42,5 N-S 57.17; CEM II/A-S 42,5 N, 98.5; CEM II/A-P 42,5 N 57.62, CEM II/A-V 42,5 R, 47.34; CEM II/B-V, 48.52.

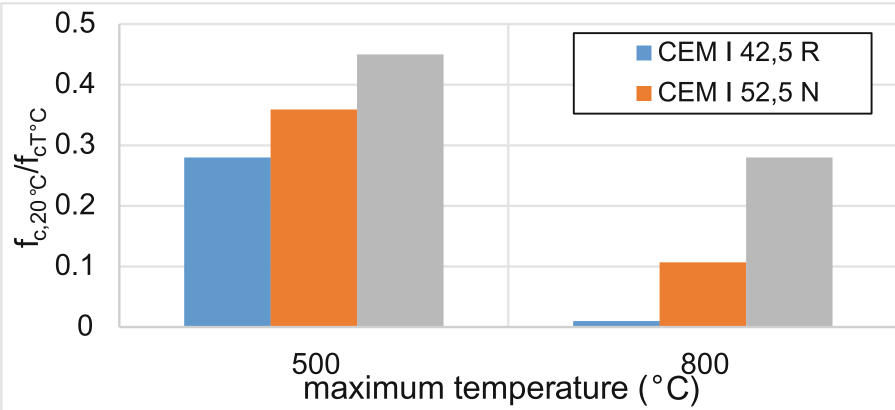


Fig. 3. Residual compressive strength of hardened cement paste with different cement types (strength values are related to strength values of 20 °C); Reference values (N mm^{-2}): CEM I 42,5 R, 76.36; CEM I 52,5 N, 78.5; CEM I 42,5 N-S 57.17.

For *Portland slag cement specimens* (CEM II/A-S 42,5 N) the average of the residual relative strength was 41% by heating up to 500 °C and further 17% heating up to 800 °C, respectively (Figs. 4 and 5).

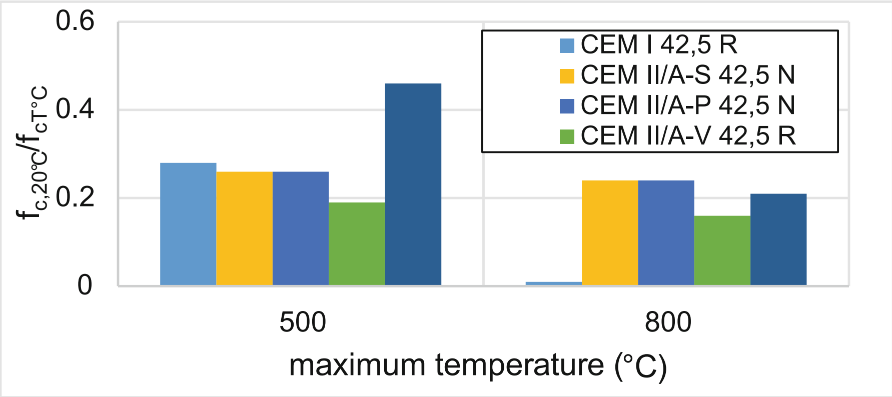


Fig. 4. Residual compressive strength of hardened cement paste with different cement types (strength values are related to strength values of 20 °C); Reference values (N mm^{-2}): CEM I 42,5 R, 76.36; CEM II/A-S 42,5 N, 98.5; CEM II/A-P 42,5 N 57,62, CEM II/A-V 42,5 R, 47.34; CEM II/B-V, 48.52.

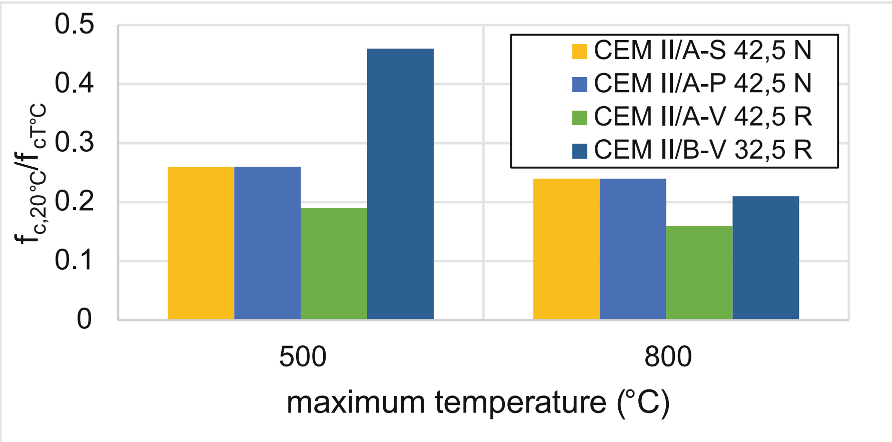


Fig. 5. Residual compressive strength of hardened cement paste with different cement types (strength values are related to strength values of 20 °C); Reference values (N mm^{-2}): CEM I 42,5 R, 76.36; CEM II/A-S 42,5 N, 98.5; CEM II/A-P 42,5 N 57,62, CEM II/A-V 42,5 R, 47.34; CEM II/B-V, 48.52.

For *Portland trass cement specimens* (CEM II/A-V 42,5 R) the average of the residual relative strength was 19% by heating up to 500 °C and further 16% heating up to 800 °C, respectively (Figs. 4 and 5).

For *Portland fly ash cement specimens* (CEM II/A-P 42,5 N; CEM II/B P 32,5 R) the average of the residual relative strength was 26% and 46%by heating up to 500 °C and further 24% and 21% heating up to 800 °C, respectively (Figs. 4 and 5).

The results of the compressive strength tests are in accordance with findings on crack development. The most significant cracks appeared on test specimens made of Portland cement, and the compressive strength loss was also the highest.

4 Conclusions

The purpose of the present study was to analyse the post-heating characteristics of hardened cement paste. Main experimental parameters were the cement types (7 different types: ordinary Portland cements, sulphate resistant Portland cement, Portland slag cement, Portland trass cements, Portland fly ash cement) and the maximal temperature of heat treatment up to 800 °C (20 °C, 50 °C, 150 °C, 300 °C, 400 °C, 500 °C, 600 °C, 800 °C), respectively.

Water to cement ratio was kept constant (w/c = 0.43). Present studies included analysis of surface cracking, compressive strength.

The following conclusions can be drawn from our test results:

1. The composition of cement has an important influence on the post-heating characteristics of cement paste.
2. Relative post-heating compressive strength increases with addition of the supplementary material to the cement.
3. The post-heating behaviour of hardened cement paste specimens were negatively influenced by rapid type cements both for surface cracking as well as for compressive strength.
4. The application of sulphate resistant Portland cement was found to be more favourable at high temperatures.
5. Amount of surface cracking (sum of lengths and widths) is reduced with addition of supplementary materials (here GGBS, fly ash and trass) to the cement.

References

American Concrete Institute (1997) ACI/TMS 216 standard method for determining fire resistance of concrete and masonry construction assemblies. Framington Hills, Oakland

Barbara P, Iwona W (2015) Comparative investigations of influence of chemical admixtures on pozzolanic and hydraulic activities of fly ash with the use of thermal analysis and infrared spectroscopy. J Therm Anal Calorim 120:119–127

Budelman H (1987) 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, Braunschweig. ISBN 3-89288-016-6

Dias WPS, Khoury GA, Sulivan PJE (1990) Mechanical properties of hardened cement paste exposed to temperatures up to 700 °C. ACI Mater J 87:160–166

Eurocode 1 (1991) Basis of design and actions on concrete structures. Part 2-2: actions on structures exposed to fire, EN 1991-1-2:2002, November 2002

Eurocode 2 (1992) Design of concrete structures. Part 1 general rules - structural fire design EN 1992-1-2:2002, 25 February

fib bulletin 38 (2007) Fire design of concrete structures- materials, structures and modelling. ISBN 978-2-88394-078-9

Gambarova PG (2004) Opening addresses on some key issues concerning R/C fire design. In: Gambarova PG, Felicetti R, Meda A, Riva, P (eds) Proceedings for fire design of concrete structures: what now? What next? 2–3 December 2004

Grainger BN (1980) Concrete at high tempereatures. Central Electricity Research Laboratories, Leatherhead

Hinrichsmeyer K (1987) Analysis and modeling of concrete subjected to high temperature (Strukturorientierte Analyse und Modellbeschreibung der thermischen Schädigung von Beton) Heft 74 IBMB, Braunschweig

Hoj NH (2005) Fire design of concrete structures. In: Balázs L, Borosnyói A (eds) Proceedings of fib symposium on keep concrete attractive, Budapest, 23–25 May 2005, p 1097–1105

Khoury GA et al (2001) Fire design of concrete materials structures and modelling. In: 1st fib Congress, Osaka, Japan, October 2001

Khoury GA (1995) Effect of heat on concrete material. Imperial College report, p 73

Khoury GA, Grainger BN, Sullivan PJE (1995) Transient thermal strain of concrete: literature review, conditions within specimen and behaviour of individual constituents. Mag Concr Res 37:48–56

Khoury GA, Sarshar R, Sulivan PJE (1990) Factors affecting the compressive strength of unsealed cement paste and concrete at elevated temperatures up to 600 °C. In: Proceedings of 2nd international workshop on mechanical behaviour of concrete under extreme thermal and hygral conditions, Weimar, p 89–92, ISSN 0863-0720

Kopecskó K (2006) A gőzölés hatása a cement klinkerek és cementek kloridion megkötő képességére. In English: Chloride ion binding capacity of clinker minerals and cements influenced by steam curing. PhD thesis, p 100

Kordina K (1997) Fire resistance of reinforced concrete beams. (Über das Brandverhalten punktgeschützter Stahbetonbalken), Deutscher Ausschuss für Stahlbeton, Heft 479, Beuth Verlag GmbH, Berlin, ISSN 0171-7197

Ministry of Construction (2001) Taika Seinou Kenshouhou no Kaisetu Oyobi Keisanrei tosonso Kaisetu. Guideline on Verification Method for Fire Resistance and Exemplars. Inoue Shoin

Schneider U (1988) Concrete at high temperatures - a general review. Fire Saf J 13:55–68

Schneider U, Lebeda C (2000) Fire protection of builldings. (Baulicher Brandschutz). W. Kohlhammer GmbH, Stuttgart, ISBN 3-17-015266-1

Schneider U (1986) Properties of materials at high temperatures, concrete, 2nd edn. RILEM Publ., Gesamthochschule Kassel, Universität Kassel

Schneider U, Weiß R (1997) Kinethical treatment of thermical deterioration of concretes and its mechanical influences. Cem Concr Res 11:22–29

Thielen KC (1994) Strength and deformation of concrete subjected to high temperature and biaxial stress-test and modeling, (Festigkeit und Verformung von Beton bei hoher Temperatur und biaxialer Beanspruchung Versuche und Modellbildung), Deutscher Ausschuss für Stahlbeton, Heft 437, Beuth Verlag GmbH, Berlin, ISSN 0171-7197

Xu Y, Wong YL, Poon CS, Anson M (2001) Impact of high temperature on PFA concrete. Cem Concr Res 31:1065–1073

Yun L, Hung-Liang C (2015) Thermal analysis and adiabatic calorimetry for early-age concrete members. J Therm Anal Calorim 122:937–945

Waubke NV (1973) Physical 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