



Heat resistance of portland cements

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Abstract

Recent fire cases indicated again the importance of fire research. Fast development of construction technology requires new materials. Initiation and development of fire are strongly influenced by the choice of construction materials. In addition to their mechanical properties, their behaviour in elevated temperature is also of high importance. Residual compressive strength of concrete exposed to high temperatures is influenced by the following factors: water-to-cement ratio, cement-to-aggregate ratio, type of aggregate and water content of concrete before exposing it to high temperatures and the fire process. Therefore, mix design and composition of concrete are of high importance for high temperatures. Based on the literature, the fire resistance of concrete is influenced by the used cement type. As regards the cement type, considerable importance has been attached to the various auxiliary materials, such as slag, fly ash, trass, metakaolines and silica fume. There has been no special research devoted to the fire behaviour of pure portland cements. Pure portland cements can be made with various oxide compositions or with different grinding fineness, which increases the resistance of cements to fire. The question arises what effects grinding fineness and oxide composition have on fire resistance of cements. In my experiments, the resistance of portland cements of different composition and grinding fineness to fire (high temperature) were examined. For the test of the solidified cement paste, cement paste cubes of 30-mm edge length were prepared. The specimens were stored in water for 7 days and then in laboratory conditions for 21 days. The cubes of more than 28 days were heated to the given temperature in the furnace and then kept at the given temperature for 2 h (50, 150, 300, 500, 800 °C). Following the 2 h of thermal load, the specimens were examined once their temperature cooled down to room temperature. I have experimentally demonstrated that in case of portland cements, the grinding fineness and aluminate modulus of the cement (i.e. the oxide composition of the cement) have a significant effect on its fire resistance.

Keywords Portland cement · Fire resistance · Grinding fineness · Oxide composition

Introduction

The quality of cements is fundamentally influenced by the chemical–mineral composition of the clinker, since different clinker minerals—tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF), etc.—undergo different hydration processes (they hydrate at different rates and form hydrate compounds of various strengths, etc.) [1–6]. Tricalcium silicate (C_3S) basically determines the initial

strength of the cement (between days 1 and 28) and dicalcium silicate (C_2S) contributes to the strength at a later stage (after 28 days). The most reactive is tricalcium aluminate (C_3A), so it has a decisive impact on the strength at a very early stage (days 1–2) [7].

Cement auxiliary materials are substances that are added to the clinker (co-grinding technology) or to the cement (separate grinding and mixing technology) in a quantity of over 5 m/m% during the preparation of cement in order to influence specific properties of the cement to be produced, as in addition to the required strength, cement producers try to equip cements with other favourable properties as well—from the viewpoint of application. As in the cements containing auxiliary materials, clinker content is less, tricalcium silicate (C_3S) content has to be at least 55 m/m%, tricalcium aluminate (C_3A) at least 8–9 m/m%—based on

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Bogue calculations—to ensure proper strength of the cement [8, 9].

As regards the physical and mechanical properties of the cement—besides the chemical and mineral composition of the clinker—the grinding fineness of the cement (specific surface area, particle size distribution) plays a determining role [5, 8–17].

Effect of cement type has been hardly studied. Most important 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 [17, 18]. The properties of cement paste itself are also influenced by the mixing proportions of the constituents [13, 19]. 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 [20].

Grainger [21] studied cements with or without pulverised fly ash (PFA) subjected to a temperatures ranging from 100 to 600 °C with an interval of 100 °C. In his research the dosage of PFA was 20, 25, 37.5 and 50%. 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. [22] and Xu et al. [23]. Khoury et al. [24] 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.

In fire, the concrete loses its moisture content by evaporation from the surface and by migration into the inner concrete mass driven by the temperature gradient [25, 26]. Due to high temperatures, structure and mineral content of concrete change. The analysis could be made by thermogravimetry (TG). Around 100 °C the mass loss is caused by water evaporating from the micropores. The decomposition of ettringite (3CaOAl₂O₃·3CaSO₄·32H₂O) takes place between 50 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 [27, 28]. During heating, the endothermic dehydration of Ca(OH)₂ takes place between temperatures of 450 and 550 °C.

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 applications.

The incorporation of fly ash (PFA) and slag in portland cements or blended cements can generally increase the mechanical properties of concrete at 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 [30], the pure 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 [29–31].

Environmental protection requires the use of cements with low clinker content. Present study is directed to the influence of high temperatures on specimens made of different portland cements.

Applied materials

For the experiment, cements of special composition and different grinding fineness were used. Cements were ground in the laboratory with ball mills. The grinding fineness of the cements was controlled with a Balin apparatus.

Experimental parameters:

- oxide composition of cements (CEM1, CEM2, CEM3, CEM4).
- grinding fineness of cements (3500, 4000, 4500 cm² g⁻¹, C3500, C4000, C4500).
- maximum temperature of thermal load (20, 150, 300, 500, 800 °C)

Oxide composition of the cements applied is shown in Table 1.

Experiment matrix is displayed in Table 2.

Applied test methods

Modelling of fire

In our experiments, we used the standard heating curve, which is close to the fire curve applicable to high-rise

Table 1 Chemical composition of tested clinkers (m%)

Comp.	CEM1	CEM2	CEM3	CEM4
SiO ₂	21.82	21.36	21.26	20.85
Al ₂ O ₃	5.03	5.17	4.65	4.07
Fe ₂ O ₃	2.75	3.38	3.90	6.52
CaO	66.57	66.95	65.58	64.34
MgO	0.83	0.80	2.06	1.51
SO ₃	1.02	0.70	0.43	0.23
K ₂ O	0.8	0.36	0.36	0.31
Na ₂ O	0.3	0.03	0.06	0.24

Table 2 Experiment matrix

Cement	Temperature of thermal load				
	20	150	300	500	800
CEM1	9	9	9	9	9
CEM2	9	9	9	9	9
CEM3	9	9	9	9	9
CEM4	9	9	9	9	9
Total	180 pcs				

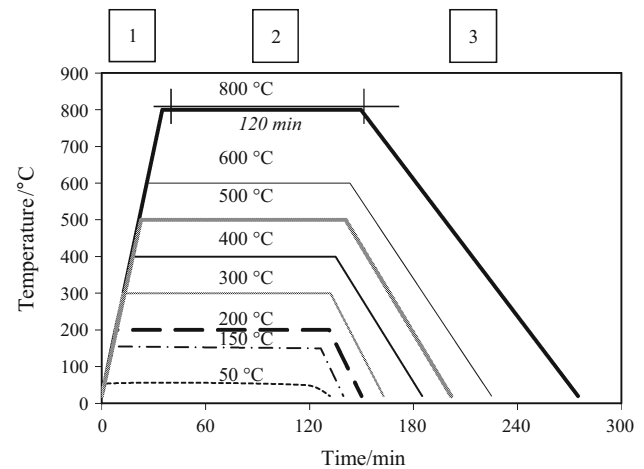
structures and halls. The fire curve of the furnace follows the standard fire curve (applicable to high-rise structures) up to 800 °C. My experiments were conducted up to this temperature.

After demoulding, the specimens were kept in water for 7 days and then in laboratory conditions until thermal loading (for 28 days).

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), and 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. 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 heated and then cooled specimens were tested.

Compressive strength test of the solidified cement paste

Compressive strength test was conducted on cubes prepared from cement paste. Edge length of cement paste cubes was 30 mm. Cement paste cubes were tested with crusher machine WPM ZDM 10/91 with an additional load frame.

**Fig. 1** Schematic representation of thermal load curves used in the experiments (1 heating, 2 holding, 3 cooling)

Results and discussion

For the assessment, we calculated the aluminate modulus of the given cements (referring to the ratio of aluminium oxide to iron oxide: $AM = Al_2O_3\%/Fe_2O_3\%$) and silica modulus (determining the ratio of silicic acid to trioxides: $SM = SiO_2\%/Al_2O_3\% + Fe_2O_3\%$) (Table 3).

The standard Bogue calculation refers to cement clinker, rather than cement, but it can be adjusted for use with cement. Although the result is only approximate, the calculation is an extremely useful and widely used calculation in the cement industry.

The calculation assumes that the four main clinker minerals are pure minerals with compositions:

Alite:	C ₃ S, or tricalcium silicate
Belite:	C ₂ S, or dicalcium silicate
Aluminate phase:	C ₃ A, or tricalcium aluminate
Ferrite phase:	C ₄ AF, or tetracalcium aluminoferrite

Clinker is made by combining lime and silica and also lime with alumina and iron. If some of the lime remains uncombined (which it almost certainly will), we need to subtract this from the total lime content before we do the calculation in order to get the best estimate of the proportions of the four main clinker minerals present. For this

Table 3 Aluminate and silica modulus of the cements applied

	Modulus	
	AM	SM
CEM1	1.83	2.81
CEM2	1.53	2.49
CEM3	1.19	2.47
CEM4	0.62	1.96

reason, a clinker analysis normally gives a figure for uncombined free lime.

Firstly, according to the assumed mineral compositions, ferrite phase is the only mineral to contain iron. The iron content of the clinker therefore fixes the ferrite content. Secondly, the aluminate content is fixed by the total alumina content of the clinker, minus the alumina in the ferrite phase. This can now be calculated, since the amount of ferrite phase has been calculated. Thirdly, it is assumed that all the silica is present as belite and the next calculation determines how much lime is needed to form belite from the total silica content of the clinker. There will be a surplus of lime. Fourthly, the lime surplus is allocated to the belite, converting some of it to alite.

In practice, the above process of allocating the oxides can be reduced to the following equations, in which the oxides represent the mass percentages of the oxides in the clinker:

$$C_3S = 4.0710CaO - 7.6024SiO_2 - 1.4297Fe_2O_3 - 6.7187Al_2O_3$$

$$C_2S = 8.6024SiO_2 + 1.0785Fe_2O_3 + 5.0683Al_2O_3 - 3.0710CaO$$

$$C_3A = 2.6504Al_2O_3 - 1.6920Fe_2O_3$$

$$C_4AF = 3.0432Fe_2O_3$$

Table 4 shows the mineral composition of the used cements based on Bogue calculations.

Changes in compressive strength depending on the temperature of thermal load

Reference measured at 20 °C is shown in Fig. 2. Based on the figure, the following conclusions can be drawn:

1. Increased grinding fineness of the cement at 20 °C led to an increased compressive strength.
2. Change in the aluminate modulus (AM) of the cement did not affect the initial strength values of the cement measured at 20 °C.

Table 4 Mineral composition based on Bogue calculations

	Mineral composition (m/m%)				
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	C ₂ F
CEM1	59.19	17.28	7.48	8.36	–
CEM2	63.12	13.13	8.13	10.28	–
CEM3	65.74	11.12	5.69	11.86	–
CEM4	61.63	13.01	–	19.41	0.22

Based on Fig. 3, it can be concluded that the strength change of pure portland cements can be divided into the following stages, depending on the thermal load's temperature:

1. After a thermal load of 150 °C, a slight decrease in strength could be observed (0–20%). In the case of cement CEM1 of grinding fineness 3500 cm² g^{−1}, it was observed a slight increase in strength (20%). The cause of the phenomenon: the degradation of the unstable CSH.
2. After a thermal load of 300 °C, the value of compressive strength increases to 120–130% of the value measured after a thermal load of 50 °C. The cause of the phenomenon: The released hydrate water reacts with unhydrated clinkers. The high temperature causes an increase in the reaction rate.
3. Behaviour above 300 °C is a crucial factor for fire (high temperature) resistance. Above 300 °C a loss of strength occurs. The cause of the phenomenon: first Ca(OH)₂ and then CSH degradation, which causes a decrease in strength.
4. After a thermal load of 800 °C, residual compressive strength of 10–20% can be measured in every case regardless of the cement type.

Considering that the residual compressive strength following a thermal load of over 300 °C is crucial for the fire resistance, it is examine in the next section.

The impact of grinding fineness on the fire resistance of the cements

I have found that strength decrease of cements with different specific surface areas is the same. I have determined that from the viewpoint of thermal load, cements with a specific surface area of 4000 cm² g^{−1} proved to be the most favourable even after thermal loads of 500 and 800 °C (Figs. 4, 5). The explanation for this may be that larger specific surface area results in smaller cement particles, a lower number of unhydrated clinker particles, increased initial hydration rate and smaller size of CSH fibres formed. In addition, with the increase in the specific surface area, the structure of the cement stone becomes more dense, its capillarity decreases and the destructive effect of the developing gas and vapour pressure is stronger. Therefore, from the viewpoint of the fire, neither too big nor too little cement particles are favourable.

The impact of the chemical composition of cements on their fire resistance

Figures 6–8 leads to the following conclusions:

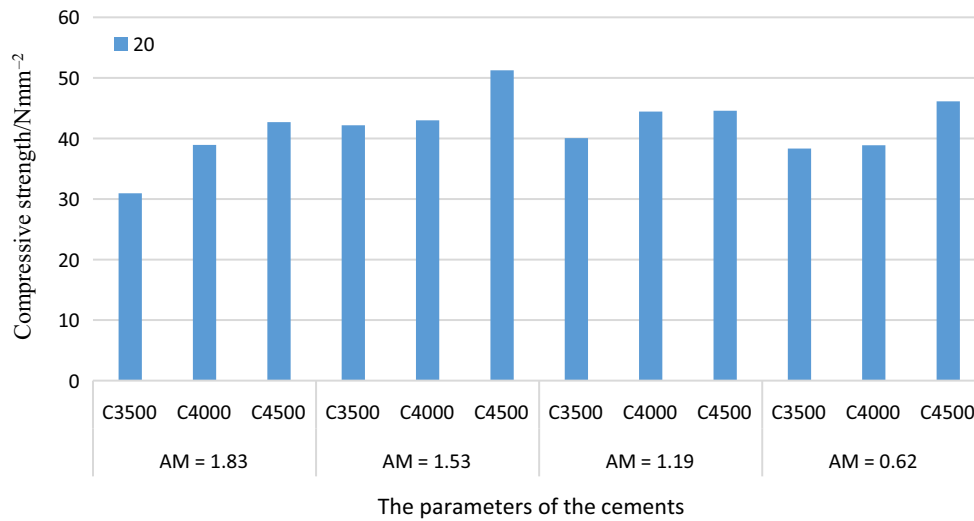


Fig. 2 Strength values of pure portland cements measured at 20 °C (each point is the average of three measurements)

Fig. 3 Strength changes of pure portland cements depending on the temperature of thermal load (each point is the average of three measurements)

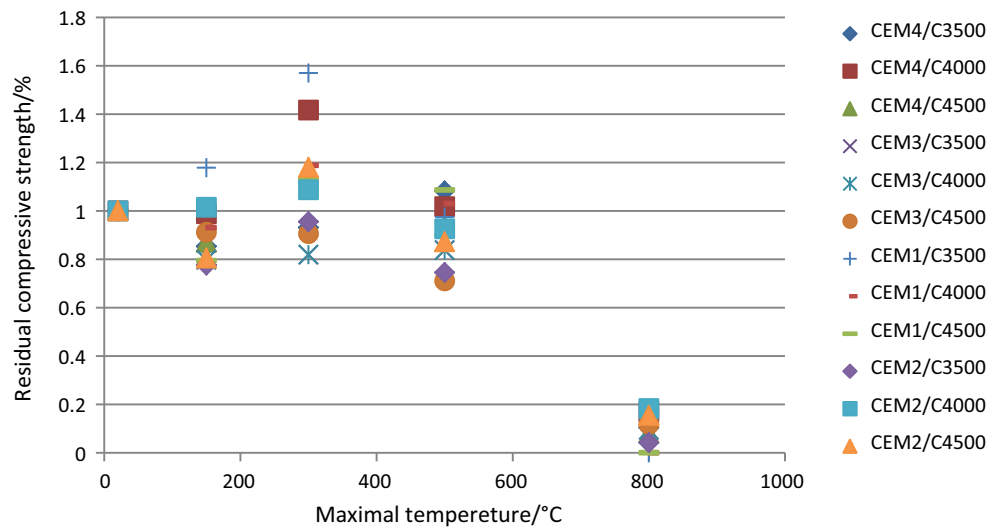


Fig. 4 Relative strength values of pure portland cements measured after a thermal load of 500 °C (each point is the average of three measurements)

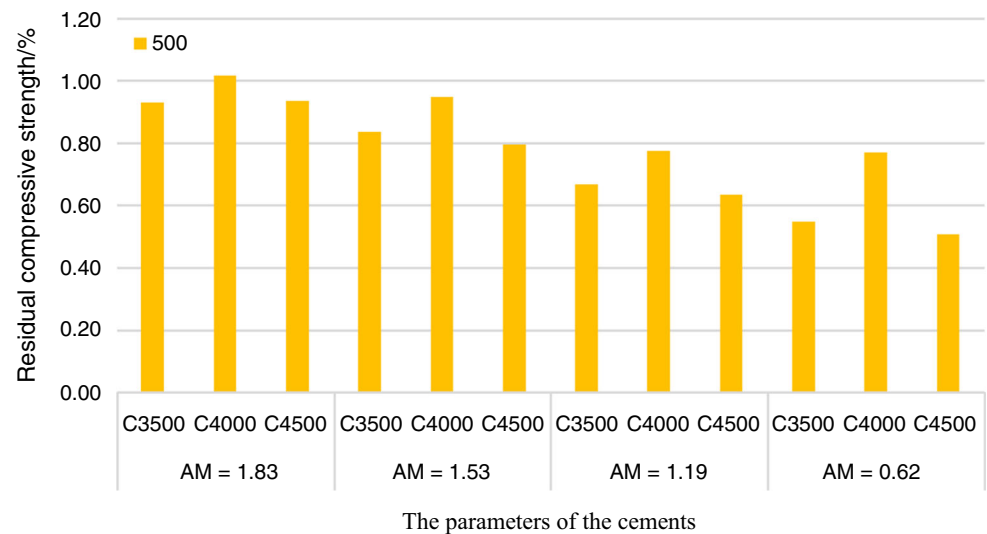


Fig. 5 Relative strength values of pure portland cements measured after a thermal load of 800 °C (each point is the average of three measurements)

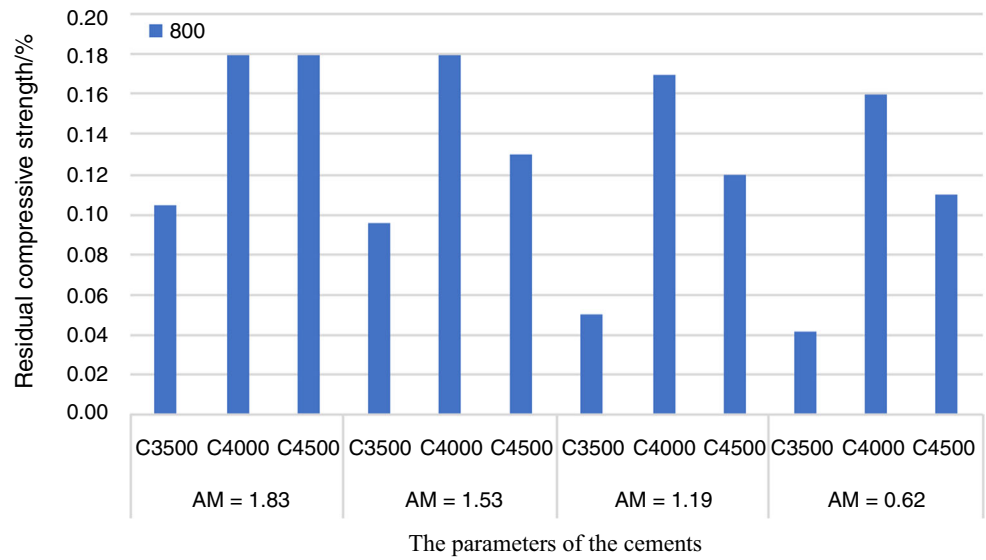


Fig. 6 Strength values of cements of grinding fineness 3500 cm² g⁻¹ measured after thermal loads of 500 and 800 °C (each point is the average of three measurements)

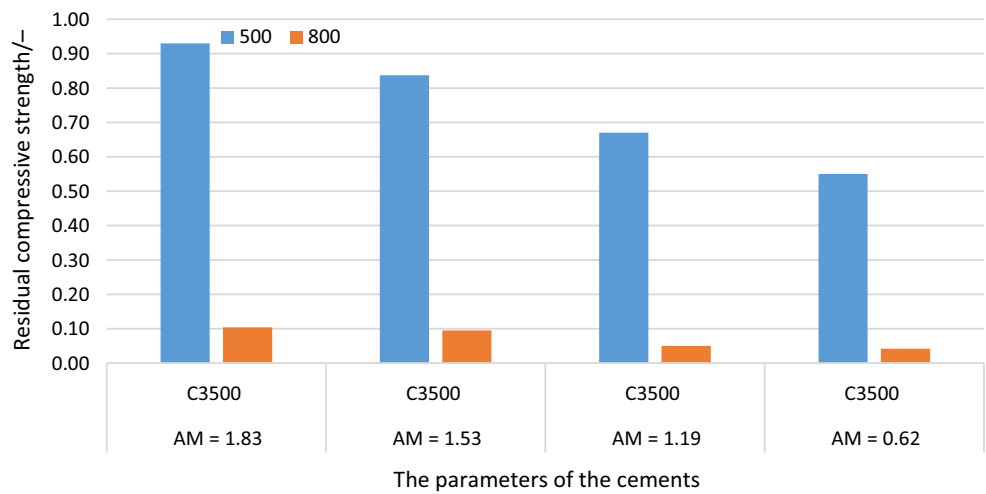
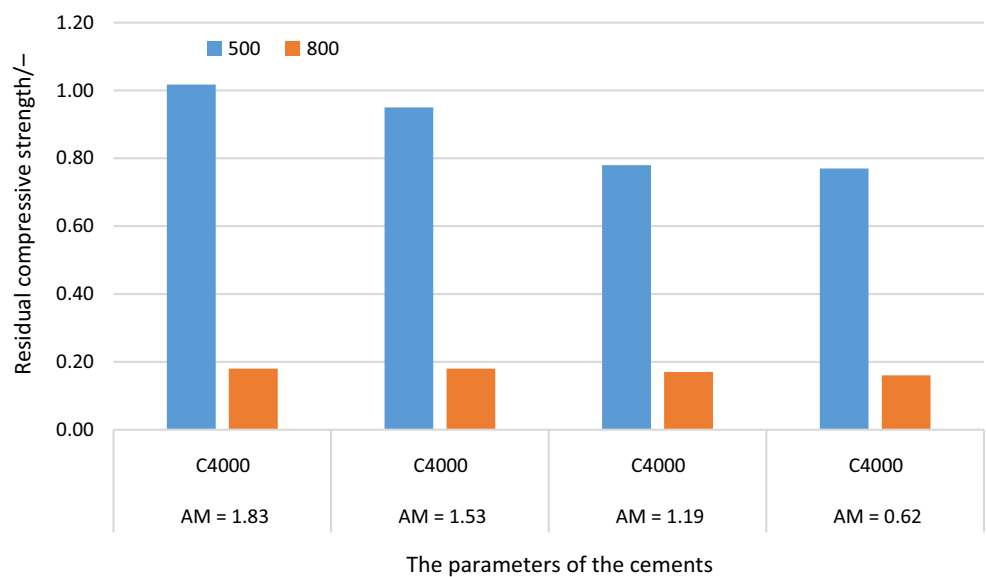


Fig. 7 Strength values of cements of grinding fineness 4000 cm² g⁻¹ measured after thermal loads of 500 and 800 °C (each point is the average of three measurements)



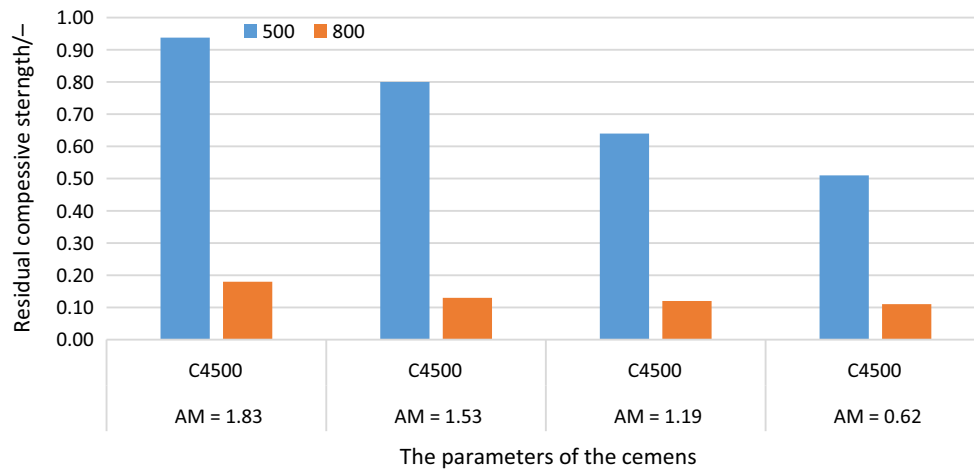
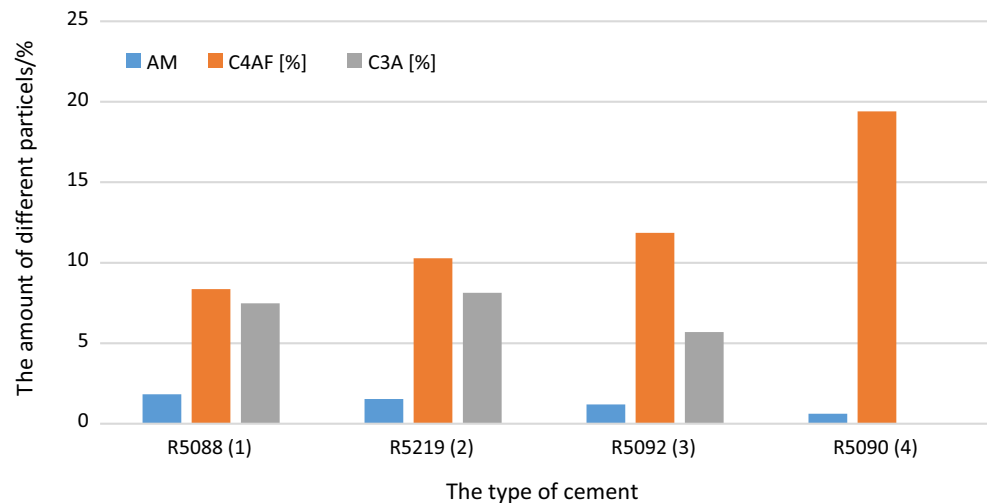


Fig. 8 Strength values of cements of grinding fineness $4500 \text{ cm}^2 \text{ g}^{-1}$ measured after thermal loads of 500 and 800 °C (each point is the average of three measurements)

Fig. 9 Correlation between the aluminate modulus and the amount of minerals with aluminate oxide content (C_4AF , C_3A)



1. Following thermal loadings of 500 and 800 °C, compressive strength loss showed a similar tendency regardless of grinding fineness.
2. The aluminate modulus of cements clearly has an effect on the fire resistance of the cement, i.e. the aluminate modulus increases fire resistance of the cements.

Figure 9 clearly demonstrates that there is a correlation between the aluminate modulus and the amount of clinker minerals C_4AF and C_3A . As the aluminate modulus decreases, the amount of C_4AF increases and C_3A decreases simultaneously. As regards fire resistance, therefore, cements with low C_4AF and high C_3A content are favourable.

Conclusions

In my experiments, I examined the resistance of the Portland cements of different composition and grinding fineness to fire (high temperature).

For the test of the solidified cement paste, cement paste cubes of 30 mm edge length were prepared. The specimens were stored in water for 7 days and then in laboratory conditions for 21 days. The cubes of more than 28 days were heated to the given temperature in the furnace and then kept at the given temperature for 2 h (50, 150, 300, 500, 800 °C). Following the 2 h of thermal load, the specimens were examined once their temperature cooled down to room temperature.

The experiments lead to the following conclusions:

1. After a thermal load of 150 °C, a slight decrease in strength could be observed (0–20%). In the case of cement CEM1 of grinding fineness 3500 cm² g⁻¹, it was observed a slight increase in strength (20%). The cause of the phenomenon: the degradation of the unstable CSH. After a thermal load of 300 °C, the value of compressive strength increases to 120–130% of the value measured after a thermal load of 50 °C. The cause of the phenomenon: The released hydrate water reacts with unhydrated clinkers. Behaviour above 300 °C is a crucial factor for fire (high temperature) resistance. Above 300 °C a loss of strength occurs. The cause of the phenomenon: first Ca(OH)₂, then CSH degradation, which causes a decrease in strength. After a thermal load of 800 °C, residual compressive strength of 10–20% can be measured in every case regardless of the cement type.
2. From the viewpoint of thermal load, the cements with specific surface area of 4000 cm² g⁻¹ proved to be the most favourable even after thermal loads of 500 and 800 °C. The explanation for this may be that larger specific surface area results in smaller cement particles, a lower number of unhydrated clinker particles, increased initial hydration rate and smaller size of CSH fibres formed. In addition, with the increase in the specific surface area, the structure of the cement stone becomes more dense, its capillarity decreases and the destructive effect of the developing gas and vapour pressure becomes stronger. Therefore, from the viewpoint of the fire, neither too big nor too little cement particles are favourable. Too dense cement structure causes cracks after the temperature loading. Too high porosity causes strength reduction in case of hardened cement paste.
3. Aluminate modulus, i.e. the oxide composition of the cements has a clear effect on the fire resistance of the cement. As the aluminate modulus increases, so does the fire resistance of cements. There is a correlation between aluminate modulus and the amount of C₄AF and C₃A clinker minerals. As regards fire resistance, therefore, cements with low C₄AF and high C₃A content are favourable.

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References

1. Dolezsai K, Pauka I. *Cementgyártás*. Budapest: Műszaki Könyvkiadó; 1964.
2. Bereczky E. A cement kötése és szilárdulása. *Cementipari kézikönyv* (szerkesztő: Talabér József). Budapest: Műszaki Könyvkiadó; 1966. p. 237–88.
3. Tamás F. A cementhidratáció. *Szilikátipari kézikönyv* (főszerkesztő: Tamás Ferenc). Budapest: Műszaki Könyvkiadó; 1982. p. 318–23.
4. Riesz L. *Cement- és mészgártási kézikönyv*. Budapest: Építészeti Tájékoztatói Központ; 1989.
5. Taylor HFW. *Cement chemistry*. 2nd ed. London: Thomas Telford Publishing; 1997.
6. Bensted J. Hydration of portland cement. In: Gosh SN, editor. *Advances in cement technology: chemistry, manufacture and testing*. 2nd ed. New Delhi: Tech Books International; 2002. p. 31–86.
7. Zhang YM, Napier-Munn TJ. Effects of particle size distribution, surface area and chemical composition on portland cement strength. *Powder Technol*. 1995;83:245–52.
8. Opczky L. Tudományos kiadvány: a CEMKUT Kft. fontosabb kutatási-vizsgálati eredményeinek összefoglalása 1991–2005. Budapest: CEMKUT Kft; 2006.
9. Opczky L. A HOLCIM Hungária Zrt. Hejőcsabai Cementgyárban klinkertakarékos, környezetbarát cement előállítását elősegítő őrlestechnikai kutatások c. Tanulmány, 2007–2008. (készült a Miskolci Egyetem, Műszaki Földtudományi Kar, Eljárastechnikai Tanszék megbízásából).
10. Opczky L. A pernyék szilikátkémiai tulajdonságai. “Tiszta környezetünkért” Szénerőműi pernyék hasznosításával tudományos konferencián elhangzott előadás, A Miskolci Egyetem Közleménye A sorozat, Bányászat, Egyetemi Kiadó, Miskolc. 2001 55:97–106.
11. Gável V. A csökkentett klinkerhányadú, környezetbarát cementek előállítását megalapozó őrlestechnológiai kutatások. Miskolc, PhD; 2013.
12. 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. *J Therm Anal Calorim*. 2015;120:119–27.
13. Yun L, Hung-Liang C. Thermal analysis and adiabatic calorimetry for early-age concrete members. *J Therm Anal Calorim*. 2015;122:937–45.
14. Stepkowska ET, Bijen JM, Perez-Rodriguez JL. Thermal mass changes of portland cement and slag cements after water sorption. *J Therm Anal Calorim*. 1994;42:41–65.
15. Pacewska B, Wilińska IG, Blonkowski G. Investigations of cement early hydration in the presence of chemically activated fly ash. *J Therm Anal Calorim*. 2008;93:769–76.
16. Kerekes Zs, Beda L. Effect of the macro-structure on the flammability of the oxidized PAN fibre based woven textiles. *J Text Cloth Technol*. 2013 62:222; ISSN 0492-5882.
17. Schneider U, Lebeda C. *Fire protection of buildings* (Baulicher Brandschutz). ISBN 3-17-015266-1. Stuttgart: W. Kohlhammer GmbH; 2000.
18. Schneider U. *Properties of materials at high temperatures, concrete*. RILEM Publ., 2nd edn, Gesamthochschule Kassel, Universität Kassel; 1986.
19. fib bulletin 38 *Fire design of concrete structures- materials, structures and modelling*. ISBN: 978-2-88394-078-9, 2007.
20. Grainger BN. *Concrete at high temperatures*. UK: Central Electricity Research Laboratories; 1980.
21. Dias WPS, Khoury GA, Sullivan PJE. Mechanical properties of hardened cement paste exposed to temperatures up to 700 °C. *ACI Mater J*. 1990;87:160–6.
22. Xu Y, Wong YL, Poon CS, Anson M. Impact of high temperature on PFA concrete. *Cem Concr Res*. 2001;31:1065–73.
23. Khoury GA, Sarshar R, Sullivan PJE. Factors affecting the compressive strength of unsealed cement paste and concrete at

- elevated temperatures up to 600 °C. In: Proceedings of the 2nd international workshop on mechanical behaviour of concrete under extreme thermal and hygral conditions. ISSN 0863-0720, Weimar; 1990. p. 89–92.
24. Khoury GA, Grainger BN, Sullivan PJE. Transient thermal strain of concrete: literature review. Conditions within specimen and behaviour of individual constituents. *Mag Concr Res.* 1985;37:37–48.
 25. Schneider U, Weiß R. Kinethical treatment of thermal deterioration of concretes and its mechanical influences. *Cem Concr Res.* 1997;11:22–9.
 26. Bazant PZ, Kaplan FM. *Concrete at high temperetures.* London: Longman Group Limited. 1996; ISBN: 0-582-08626-4.
 27. Eurocode 2. Design of concrete structures. Part 1 general rules–structural fire design EN 1992-1-2:2002.
 28. 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.
 29. 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.
 30. 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.
 31. 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.