



Fundamental properties of industrial hybrid cement: utilization in ready-mixed concretes and shrinkage-reducing applications

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ABSTRACT: Utility properties of novel hybrid cement (H-Cement) are influenced by pozzolanic reaction of fly ash, latent hydraulic reaction of metallurgical slag together with the alkali activation of inorganic geopolymer based on precipitated waste water coming from bauxite residues. Content of Portland cement clinker is at maximum of 20 mass %, the remaining portion consists of inorganic geopolymer. Up to 80% of CO₂ emissions are saved by H-Cement manufacture compared to ordinary Portland cement (OPC). No heat treatment or autoclaving is needed at H-Cement production. The field application of H-Cement is performed by the same way than that of common cements listed in EN 197-1, and is also connected with highly efficient recovery and safe disposal of red mud waste. H-Cement is suitable for ready-mixed concretes up to C30/37 strength class and is specified by beneficial shrinkage-reducing property of the concrete kept in long dry-air cure opposite to common cements.

KEYWORDS: Hybrid cement; Alkaline waste waters; Ready-mixed concretes; Shrinkage-reducing cement

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RESUMEN: *Características básicas de un cemento híbrido industrial: utilización en hormigón premezclado y aplicaciones como reductor de la retracción.* Las propiedades de un nuevo cemento híbrido (cemento-H) vienen determinadas por la reacción puzolánica de cenizas volantes, la hidráulica latente de las escorias metalúrgicas y la activación alcalina mediante las aguas residuales generadas por el tratamiento de la bauxita para dar un geopolímero inorgánico. La proporción máxima de clínker de cemento en este nuevo material es del 20%, y por ello, en su fabricación se emite hasta un 80% menos de CO₂ que en la producción del cemento portland (OPC). El cemento-H se prepara sin necesidad de tratamiento térmico ni de estancia en autoclave y su aplicación es la misma que los cementos convencionales definidos en la norma EN 197-1. Por otra parte, su fabricación supone la recuperación y la valorización segura de los lodos rojos de bauxita. El cemento-H es apto para la preparación de hormigones premezclados hasta la categoría C30/37, presentando el nuevo material, además, una menor retracción que los cementos convencionales, por lo que su empleo resulta especialmente ventajoso en los hormigones que se curan al aire.

PALABRAS CLAVE: Cemento híbrido; Aguas residuales alcalinas; Hormigón premezclado; Cemento reductor de la retracción

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1. INTRODUCTION

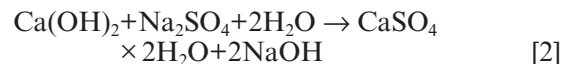
World cement production represented approximately 4 billion tonnes in 2013 (1). About 4.2 GJ energy is required to produce 1 tonne of OPC resulting in approximately 0.8–1.0 tonne of CO₂ released into the atmosphere (2). Global annual production of cement thus accounts for about 5% of the total anthropogenic CO₂ emission (3). A second problem aside from CO₂ emissions, which is worthy of a serious consideration is connected with the negative ecological and health impact of red and brown mud ponds containing high alkaline wastewater rich in NaOH. The large environmental accidents like the one in Hungary in 2010 may occur during the storage of such waste (4). The land filled by this hazardous waste also raises other problems occurred due to the high concentrations of the heavy metals present and the variety of chemical compositions, depending on a large extent on season and weather conditions. High alkalinity can be neutralized by addition of H₂SO₄ and CO₂ with subsequent formation of either Na₂SO₄ or Na₂CO₃ (5).

The main task of the research in recent times is the development of less energy intensive and more environmentally acceptable cements with highly efficient recovery and safe disposal of wastes and industrial by-products such as fly ashes from power and heating plants, metallurgical slags - mainly granulated blast furnace slag (GBFS), highly alkaline wastewaters from red mud ponds as well as sulphuric acid from car battery recovery (6).

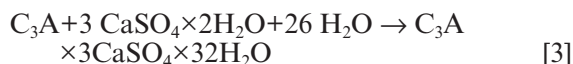
One of potential solutions is the production of new cement binders, like alkali-activated cements (geopolymers) and hybrid alkali cements with Portland clinker addition (7, 8). Hybrid alkali cements have various compositions of alkali-activated aluminosilicates with low Portland cement clinker content (9). Despite of low clinker content, the hybrid binders can also attain useful early mechanical strengths (10).

Typical mixtures of hybrid binders are composed of Portland cement clinker, usually less than 30 of mass % with fly ash activated by Na₂SO₄ and Na₂CO₃ (11); metakaolin and clinker activated by Na₂SO₄ (12); blast furnace slag, metakaolin and clinker activated by Na₂CO₃ and K₂CO₃ (13); the mixture of fly ash, OPC and Ca(OH)₂ activated by a calcined mixture of kaolin with NaOH or KOH (14). The activators Na₂CO₃, K₂CO₃, Na₂SO₄ and K₂SO₄ are not characterized by highly alkalinity.

High-alkaline NaOH is generated at the presence of Ca(OH)₂, which is the reaction product of on-going Portland cement clinker hydration. The alkalinity of the bulky cement matrix increases and creates favourable conditions for the consequent geopolymerisation process by means of high alkaline NaOH as shown in equations [1] and [2]:



Calcite CaCO₃ (Eq. 1) and gypsum CaSO₄×2H₂O (Eq. 2) are generated as by-products. The interaction of gypsum with C₃A present in Portland cement clinker results in the formation of ettringite C₃A×3CaSO₄×32H₂O as demonstrated by equation [3]:



Reaction mechanism (Eq. 1) is quicker but yields calcite only, while the presence of sulphate ions promotes ettringite formation and consequently a denser matrix with the increased early strength (11).

GBFS and siliceous fly ash are predominantly vitreous materials with amorphous structures dissolved in the presence of alkaline NaOH, Na₂SiO₃, Na₂SO₄ and Na₂CO₃ or KOH, K₂SiO₃, K₂SO₄ and K₂CO₃. After dissolution, alkali-activated aluminosilicates, geopolymers are formed. Geopolymers possess a three-dimensional structure expressed by the formula Me_n[-(SiO₂)_z-AlO₂]_n×wH₂O, where Me is Na⁺ (N) or K⁺ (K), which in the framework balances the negative charge of Al(OH)₄; *n* is the degree of polycondensation and *z* means 1, 2, 3 or >>3 (15). As a result, N-A-S-H or K-A-S-H gels are formed, which in the presence of Portland clinker may contain some amount of Ca to get a (C)-N-A-S-H gel. The curing conditions of fresh geopolymers are very important. After a short period, commonly between 6 and 12 hours of steam autoclaving or curing in dry air of about 60 °C to 80 °C, the three-dimensional structure of the geopolymers gets stronger. In contrast, hydration of the Portland cement clinker results predominantly in the formation of C-S-H gels, whose microstructure contain some amount of Al to get C-(A)-S-H gels and portlandite Ca(OH)₂ formed to a smaller extent. Portlandite promotes the pozzolanic properties of fly ashes to get secondary C-S-H and C-A-H gels and the latent hydraulic properties of granulated blast furnace slag to produce secondary C-(A)-S-H gels. Solid solutions of hydrotalcite minerals of Mg₆Al₂CO₃(OH)₁₆×4H₂O kind and C₄AH₁₃, the hydrogarnets C₃AS_{3-n}H_n and C₆AFS₂H₈, strätlingite C₂ASH₈, ettringite and sometimes carboaluminates C₃A.CaCO₃H₁₁ are also created.

Novel hybrid cement binders therefore contain both kinds of gels, C-(A)-S-H as well as (C)-N-A-S-H, whose collective chemical interaction results in the formation of a final (N,C)-A-S-H gel (11). Recently it has been found that hybrid cements based on a high content of fly ash from coal combustion (>70 mass %) and low content of Portland

cement clinker in the presence of an alkaline activator give rise to the development of three different gel-bonding environments, tentatively attributed to C-(A)-S-H, C-A-S-H and (N,C)-A-S-H type gels (16). The related findings showed that the C-S-H/N-A-S-H mixture of the formed gels did not precipitate in a pure state but rather that their composition was affected by the presence of dissolved species (17). In the presence of aluminium C-S-H gel development is specified by next developmental sequence: C-S-H \rightarrow C-(A)-S-H \rightarrow C-A-S-H. In the presence of calcium, the N-A-S-H gel evolved as: N-A-S-H \rightarrow (N, C)-A-S-H \rightarrow C-A-S-H. This last conversion is not complete in these systems because the amount of calcium present is thought to be insufficient (17). Due to the intensive formation of gel-like hydration products hybrid cements are more chemically resistant to aggressive media in comparison with traditional OPC (18–20). The main disadvantage of ordinary geopolymers based on N-A-S-H or K-A-S-H gels lies in the relatively short initial setting time, which is being reduced by increasing alkalinity and steam autoclaving or dry curing. Contrary, their significant benefit is very high heat and fire resistance up to temperature elevation of 1100 °C (21). According to the gained knowledge (19), original strength of hybrid cement is almost doubled after the exposure to 800 °C and even to 1000 °C in contrast with OPC showing steady and continual strength losses as the temperatures rise up.

The second disadvantage of ordinary geopolymers based on the N-A-S-H or K-A-S-H gels that one has to take into the consideration lies in the increased susceptibility to shrinkage (22). Water glass-activated slag mortars and concretes are usually characterized by substantial autogenous and drying shrinkage, which represent a restriction of the widespread use of alkali-activated slag systems as alternative binders to traditional OPC in the structural

elements (22). The shrinkage-reducing admixture based on polypropylenglycol reduces autogenous shrinkage by 85% and drying shrinkage by 50% in water glass-activated slag mortars (22).

Shrinkage is characteristic feature for geopolymer and OPC-based concrete. Shrinkage-reducing admixture such as ye'elimit 3CA.CaSO₄; or calcium sulphoaluminate cements based on 3CA.CaSO₄, C₂S, CaSO₄ and CaO or a mixture of C₃A and CaSO₄ or a mixture of calcium aluminate cement CA and CaSO₄, which provide the formation of expansive ettringite or a mixture of hard-burnt CaO and H₂O providing expansive Ca(OH)₂ can be applied in the concrete as the expansive addition. Hybrid cement takes advantage of material properties of traditional cement and inorganic geopolymer resulting in such benefits of utility properties that the hybrid cement can partly replace energy- and environmentally-intensive OPC (23).

This paper is focus on the basic properties of ready-mixed concretes containing hybrid cement. Expansion-reducing and mainly shrinkage-reducing properties of H-Cement in concrete cured either in water at temperature of 20±1 °C or dry air conditions of 20 °C/60% R. H. and 40 °C/15% R.H are next important observations of this article.

2. MATERIALS

The novel hybrid cement (H-Cement) is composed of fly ash, granulated blast furnace slag (GBFS) and the highly alkaline waste water concentrate from red mud deposit as well as 20 mass % of Portland cement clinker. Chemical compositions of H-Cement and its raw material components are reported in Table 1 and Table 2, respectively.

The composition of H-Cement was adjusted on the minimum content of SiO₂, CaO, SO₃ and Na₂O of 40.0 mass %, 20.0 mass %, 3.0 mass % and 2.0 mass %, respectively. Highly alkaline waste water

TABLE 1. Chemical composition of H-Cement (abbreviated as HC) and its main solid components

(mass. %)	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	L.O.I.
HC	22.55	43.55	17.52	5.86	2.68	3.85	2.74	2.49	1.51
Clinker	66.13	21.69	5.31	2.83	1.44	0.53	1.00	0.04	0.85
GBFS	39.24	40.13	7.19	0.27	10.04	1.50	0.52	0.31	1.10
Fly Ash	3.36	51.42	26.93	7.27	2.10	0.87	3.28	0.17	1.84

Notice: L.O.I. means loss on ignition

TABLE 2. Chemical composition of highly alkaline wastewater from red mud pond as standard water from the pond (Standard) and concentrate water from the evaporator (Concentrate)

(mg/l)	Ca	Si	Al	Fe	Mg	Na	K	(SO ₄) ²⁻	pH
Standard	6.9	59.8	538	0.64	1.9	11820	156	4072	13.0
Concentrate	12.5	189	2143	26.0	4.4	53990	710	24098	13.2

concentrate was obtained by the evaporation and electro dialysis of standard waste water occurring in the deposit. The concentrate was neutralised by sulphuric acid H_2SO_4 with precipitation of solid Na_2SO_4 . The measured pH values before and after neutralisation were 13 and 5 to 7, respectively. The XFR analysis confirmed 99 mass % chemical purity of Na_2SO_4 when using apparatus SPECTRO X-LAB 2000. Main minerals containing fly ash are quartz SiO_2 , mullite $3Al_2O_3 \times 2SiO_2$, hematite Fe_2O_3 and magnetite Fe_3O_4 . GBFS consists mainly of 90% vitreous phase. The content of GBFS in the hybrid cement was estimated by microscope counting method. The sample, taken from a particular GBFS size fraction is examined in transmitted light (magnification degree 100) and counts at least one thousand slag grains in all. The GBFS grains of glassy fracture are clear, homogeneous and transparent for light. The GBFS grains of crystalline phase are darker not fully transparent. The calculation is as follows: % of glassy phase in GBFS = (Number of glassy, transparent grains of GBFS / Total number of all grains of GBFS) \times 100. The portion of glassy phase was also checked by the procedures specified in CEN/TR (24) and EN Standard (25). H-Cement contains 19.3 mass % and OPC 87.59% of clinker minerals. Mineralogical composition, determined by XRD technique at BRUKER AXS D8 Advance device supplemented by Rietveld analysis (26, 27) of both cements is reported in Table 3.

Portlandite $Ca(OH)_2$ (CH) is slowly formed from free lime C_{free} due to partial hydration by air

humidity. Next abbreviations mean quartz SiO_2 (Q), free lime CaO (C_{free}), cubic C_3A (C_3Ac), orthorhombic C_3A (C_3Ao), periclase MgO (M). The expression $^x CaSO_4$ gives the total sum of 4.44 mass % gypsum ($CaSO_4 \times 2 H_2O$) + 2.42 mass % bassanite ($CaSO_4 \times 0.5 H_2O$) + 1.52 mass % anhydrite ($CaSO_4$) + 0.28 mass % calcite ($CaCO_3$), which are the main constituents of calcium sulphate used as the setting time regulator. The total amount of crystalline phases coming from clinker minerals in H-Cement is 20.0 mass %. Majority portion is constituted by the amorphous inorganic geopolymer, which is not detectable by XRD technique. The total content of crystalline phases of OPC clinker minerals is 91.34 mass % opposite to that of H-Cement showing only 20 mass % occurrence of crystalline phases of clinker origin.

3. RESULTS AND DISCUSSION

3.1. Typical characteristic values of H-Cement

Typical values of H-Cement and CEM I 42.5 R (OPC) are given in Table 4. H-Cement is characterized by early reduced and 28-days strengths and lower hydration heat compared to OPC. The low hydration heat predestines H-Cement for use in a similar way than the cements with low hydration heat according to EN 14216 (28). Final setting of H-Cement is slightly prolonged relative to that of OPC. This feature makes it also suitable for use in ready-mixed concretes by the same way as OPC.

TABLE 3. Mineral composition of H-Cement (HC) and OPC

(mass %)	C_3S	C_2S	C_3Ac	C_3Ao	C_4AF	C_{free}	M	Q	K_2SO_4	CH	$^x CaSO_4$
HC	13.28	2.49	0.64	1.30	1.59	0.30	0.07	0.02	0.20	0.11	–
OPC	61.50	10.3	0.65	4.43	10.71	0.26	0.35	0.28	1.63	1.23	8.66

TABLE 4. Characteristic values of H-Cement and reference OPC

Technical parameters	Unit	H-Cement	OPC
Initial setting time	(minute)	200 \pm 20	190 \pm 20
Final setting time	(minute)	300 \pm 40	250 \pm 30
Standard consistency	(%)	32 \pm 2.0	29.1 \pm 1.8
2 days compressive strength	(MPa)	17.5 \pm 3.0 (w/c=0.4)	33.7 \pm 2.0 (w/c=0.5)
28 days compressive strength	(MPa)	36.5 \pm 4.0 (w/c=0.4)	59.2 \pm 1.6 (w/c=0.5)
90 days compressive strength	(MPa)	41.5 \pm 3.0 (w/c=0.4)	63.1 \pm 1.9 (w/c=0.5)
2 days flexural strength	(MPa)	3.5 \pm 0.5 (w/c=0.4)	6.4 \pm 0.4 (w/c=0.5)
28 days flexural strength	(MPa)	4.4 \pm 0.4 (w/c=0.4)	8.9 \pm 0.4 (w/c=0.5)
90 days flexural strength	(MPa)	9.0 \pm 0.3 (w/c=0.4)	9.3 \pm 0.3 (w/c=0.5)
Soundness	(mm)	0.5	0.01
Content of Cr^{VI}	(ppm)	1.0	1.23
Content of C_3A	(mass %)	2.0 \pm 0.5	7.5 \pm 0.8
Hydration heat	(J/g)	185	359

H-Cement acts as a solid plasticizer due to high amounts of present fly ash and GBFS. The OPC mortars are prepared with $w/c=0.5$ according to EN 196-1 (29). H-Cement needs for the same slump $w/c=0.4$ only. According to EN 196-1 (29) water to cement ratio >0.4 leads to bleeding during vibration of fresh H-Cement mortar. This is the reason for which w/c of 0.4 has to be applied for manufacturing of H-Cement mortar instead of 0.5 for OPC mortars as prescribed in EN 196-1. Compressive strength uptakes indicate that H-Cement at $w/c=0.4$ may be classified as the cement of 32.5 R strength class according to EN 197-1 criteria (30). H-Cement is not classified by EN 197-1 criteria due to its composition but is presently specified by the issued Certificate of conformity and Technical approval (31, 32).

3.2. H-Cement utilization in ready-mixed concretes

Table 5 demonstrates the composition of ready-mixed concretes of different compressive strength classes according to EN 206-1 (33), which were measured according to EN 12390-3 (34) for reaching the constant consistence slump of class S3 (100–150 mm) as described in EN 12350-2 (35) without using a plasticizer. The plasticizing effect of H-Cement in the fresh mixture was recognized in C20/25 strength class concrete with cement content of 400 kg/m^3 and w/c ratio of 0.475 (Table 5) and

also in C30/37 strength class concrete with cement content of 350 kg/m^3 and w/c ratio of 0.42 the class S3 consistency.

H-Cement is suitable for ready-mixed concretes of strength classes up to C30/37 without use of any commercial plasticizer as admixture. The effect of different plasticizers on workability of fresh mixtures is shown on ready-mixed concrete of C20/25 strength class having the composition as stated in the 4th row of Table 5. Compositions of fresh C20/25 concretes with different kind of plasticizers with the same consistence slump class S5 are reported in Table 6.

Consistency of fresh concrete mixtures specified by the cone slump test according to EN 12350-2 (35) was adjusted to the value of S5 ($\geq 220 \text{ mm}$). Losses in consistency 60 minutes after mixing and cube compressive strengths are given in Table 7. Fresh concretes with use of a plasticizer showed slightly higher air contents than H-Cement concrete without plasticizer.

Following plasticizers were verified in the fresh concrete mixtures: M1 – no plasticizer as a chemical admixture, M2 – lignosulfonate, M3 – modified polycarboxylate (specific feature designed by a producer: less than 22% polycarboxylate content), M4 – polycarboxylate (30% water-reducing effect), M5 – modified polycarboxylate (more than 22% polycarboxylate content), M6 – polycarboxylate (35% water-reducing effect), M7 – melamine,

TABLE 5. Concrete compositions with H-Cement (HC) at the same consistence slump class S3

Concrete strength class	HC (kg/m ³)	Water (kg/m ³)	Aggregates (mm)			Strengths $f_{ck,cube}$ (MPa)		
			0–4	4–8	8–16	2 $f_{ck,cube}$	7 $f_{ck,cube}$	28 $f_{ck,cube}$
C8/10	270	185	762	362	781	4.8	10.4	16.0
C12/15	300	190	707	372	781	5.7	11.4	18.7
C16/20	360	190	627	376	788	6.9	14.6	22.2
C20/25	400	190	592	361	773	8.0	16.8	25.0
C30/37	350	147	602	565	657	–	–	42.6

TABLE 6. Composition of fresh C20/25 concretes with different kinds of plasticizers with the same consistence slump class S5

C 20/25 (kg/m ³)	H-Cement	Water	Plasticizer	Aggregates		
				0–4 mm	4–8 mm	8–16 mm
M1	400	220	–	753	263	735
M2	400	212	3.0	753	263	735
M3	400	217	2.0	753	263	735
M4	400	217	2.0	753	263	735
M5	400	215	2.0	753	263	735
M6	400	201	2.0	753	263	735
M7	400	216	3.0	753	263	735
M8	400	228	3.0	753	263	735

Notice: Plasticizers used for concrete manufacture are described in text relevant to Tables 6 and 7.

TABLE 7. Properties of fresh concrete mixtures with different kinds of plasticizers and the cube compressive strengths $f_{ck,cube}$ after 2, 28, 56 and 90 days

Concrete C 20/25	Entrapped air after mixing (%)	Consistency – cone slump		Cube compressive strengths $f_{ck,cube}$			
		after mixing (mm)	after 60 min. (mm)	2 $f_{ck,cube}$ (MPa)	28 $f_{ck,cube}$ (MPa)	56 $f_{ck,cube}$ (MPa)	90 $f_{ck,cube}$ (MPa)
M1	1.2	220	120	11.0	23.6	24.8	26.3
M2	2.1	220	130	11.0	25.0	27.1	28.4
M3	1.7	220	60	10.6	21.8	22.5	22.6
M4	1.6	220	70	9.3	21.2	22.5	22.7
M5	1.7	220	110	10.1	23.6	26.6	25.4
M6	1.4	220	170	8.6	22.6	24.1	23.7
M7	2.3	220	40	7.1	24.0	24.6	29.9
M8	1.3	220	190	9.4	22.2	21.1	24.6

M8 – lignosulfonate modified by polycarboxylate. Differences in batch water contents indicated in Table 6 for achieving the constant consistency of the class S5 are caused by use of different kinds and dosages of plasticizers. Table 7 reports higher air contents of fresh concretes with a plasticizer opposite to that with H-Cement only. Increased air contents and reduced w/c ratios in fresh mixtures with a plasticizer caused insignificant strength uptakes towards the compressive strength gain of H-Cement concrete prepared without a plasticizer.

These valuable findings appeared from the test materials and employed test methods:

- 1.) H-Cement is suitable for ready-mixed concretes of strength class up to C30/37 without use of any plasticizer as chemical admixture.
- 2.) Lignosulfonates (M2) and polycarboxylates (M6) and mainly combined plasticizer on the lignosulfonate and polycarboxylate base (M8) are the most appropriate plasticizers for use in H-Cement concrete due to the most prolonged workability 60-minutes after mixing a fresh mixture.
- 3.) H-Cement, currently located outside the compositions of common cements specified by EN 197-1 Standard (30), is applicable in ready-mixed concretes with the above two prescriptions by the same way as traditionally manufactured OPC.

3.3. H-Cement utilization for shrinkage-reducing applications

To verify the reduction of expansion in water and shrinkage in dry environments, the concretes were prepared from a cement mixture made of 2 kinds of cements (H-Cement and OPC) in the selected ratios (expressed as mass %) according to Table 8. Main difference between both cements is based on the content of clinker minerals: H-Cement and OPC contain 19.3 mass % and 87.59 mass %, respectively.

An inorganic geopolymer occupies in H-Cement 79.89 mass % portion (Table 3).

The measurements were performed within the 90-days exposure period in water at temperature of 20 ± 1 °C according to STN 73 1311 (36) and in air at condition of 20 °C/60% R.H. or 40 °C/15% R.H. - dry cure. The exposure in temperature of 20 ± 1 °C/60% of R.H. - air meets the requirement put on curing regime of the above-mentioned standard. This curing is specified as normal laboratory environment. The air with 15% of R.H. at temperature of 40 ± 2 °C was chosen for unambiguously specified dry environment evoking a high susceptibility of cement-based concrete to shrinkage.

In water the expansion of OPC was affected by small additions of H-Cement (5 to 15 mass %) to the cement mixture (in Table 8 marked as PCH 0.95, PCH 0.90 and PCH 0.85). Conversely, in dry exposures the reduction of OPC shrinkage was influenced by higher additions of H-Cement (85 to 95 mass %) (in Table 8 shown as HPC 0.85, HPC 0.90 and HPC 0.95). Mutual ratio of 50 mass % of H-Cement to 50 mass % of OPC (HPC 0.50) represents the mean value between two marginal systems for a comparison to recognize the effects of both cements in equal portion [100% H-Cement (HPC 1.00) and 100% OPC (PCH 1.00)]. This cement mixture was kept in each of the chosen exposures (water at temperature of 20 °C, curing at temperature of 20 °C/60% of R. H. and temperature of 40 °C/15% of R. H. - dry air).

The abbreviations PCH or HPC used in Table 8 and Tables 10 to 12 and Figures 1 to 6 indicate a cement mixture prepared by mixing cements (C) in a certain proportion of H-Cement (H) to OPC (P). PCH is a mixed system with a higher content of P (OPC), while HPC has a higher content of H (H-Cement). The concretes were prepared with a constant water to cement ratio of $w/c=0.475$ according to the mixture proportion: 400 kg/m³ of cement or cement mixture, 190 litres of water, dried river aggregates: 0/4 mm –630 kg per 1 m³, 4/8 mm –390 kg per

TABLE 8. Content of cements in the mixtures according to curing regime of the concrete

Cement mixture	Content of cements (mass %)		Curing regime
	H-Cement	OPC	
PCH 1.00	0	100	in water at 20 °C and in air at 20 °C and 40 °C
PCH 0.95	5	95	in water at 20 °C
PCH 0.90	10	90	
PCH 0.85	15	85	
HPC 0.50	50	50	in water at 20 °C and in air at 20 °C and 40 °C
HPC 0.85	85	15	in air at 20 °C and 40 °C
HPC 0.90	90	10	
HPC 0.95	95	5	
HPC 1.00	100	0	in water at 20 °C and in air at 20 °C and 40 °C

Notice: Content of cements in the cement mixtures in mass % (expressed as HC/PC ratios) according to curing regimes of the concrete are as follows:

- PCH 1.00 (0/100) in water at 20 °C and in air at 20 °C and 40 °C
- PCH 0.95 (5/95) in water at 20 °C
- PCH 0.90 (10/90) in water at 20 °C
- PCH 0.85 (15/85) in water at 20 °C
- HPC 0.50 (50/50) in water at 20 °C and in air at 20 °C and 40 °C
- HPC 0.85 (85/15) in air at 20 °C and 40 °C
- HPC 0.90 (90/10) in air at 20 °C and 40 °C
- HPC 0.95 (95/5) in air at 20 °C and 40 °C
- HPC 1.00 (100/0) in water at 20 °C and in air at 20 °C and 40 °C

TABLE 9. Rheological properties, volume density and 2-days strength of two outer concrete mixtures

Fresh concrete	Consistency (mm)	Volume density (kg/m ³)	Air content (% vol.)	2-days compressive strength (MPa)
HPC 1.00	10.5	2380	1.3	10.1
PCH 1.00	6.0	2420	1.1	19.3

1 m³ and 8/16 mm – 775 kg per 1 m³ of fresh concrete mixture. The concretes were made without any additions and admixtures to exclude their effects on the measured volume changes.

The specimens were manufactured in a concrete mixer according to EN 12390-2 (37). Consistency of the fresh concrete was determined by slump cone according to EN 12350-2 (35), bulk density and air content in the fresh mixture were determined according to EN 12350-6 (38) and EN 12350-7 (39) as basic rheological parameters (as seen in Table 9) of fresh concretes with 100% mass content of H-Cement (HPC 1.00) and 100% mass content of ordinary Portland cement (PCH 1.00).

Concretes from every batch were made in the form of prismatic specimens of (100×100×400) mm dimensions for the testing of volume changes, dynamic modulus of elasticity and strength parameters within the period of 90 days at the given curing regimes and compressive strength testing on the cubes with a 150 mm edges after 28 days of basic curing in water at temperature of 20±1 °C. The specimens were stored in water at temperature of 20±1 °C (indicated as W20), in air at temperature of

20±1 °C with 60% of R. H. (A20) or air at temperature of 40±2 °C (A40) with R. H. of 15% as stated in Table 8.

Tests of volume changes in the hardened concretes were performed according to STN 73 1320 (40), those of the cube compressive and flexural strength according to EN 12390-3 (34) and EN 12390-5 (41), those of the bulk density and dynamic modulus of elasticity values were determined according to EN 12390-7 (42) and STN 73 1371 (43), respectively. Volume changes were measured on the basis of proportional, comparative length changes using prismatic specimens of size of (100×100×400) mm by the length comparator instrument according to STN 73 1320 (40).

3.3.1. Measurements of volume changes

Volume changes (expressed as length changes) of concretes made from OPC (PCH 1.00 marked as OPC-concrete), H-Cement (HPC-H 1.00 marked as H-concrete) and mixtures of these two cements in the ratios shown in Table 8 (PCH 0.85 to 0.95), stored for 90 days in water at temperature of 20±1 °C after basic curing are illustrated in Figure 1.

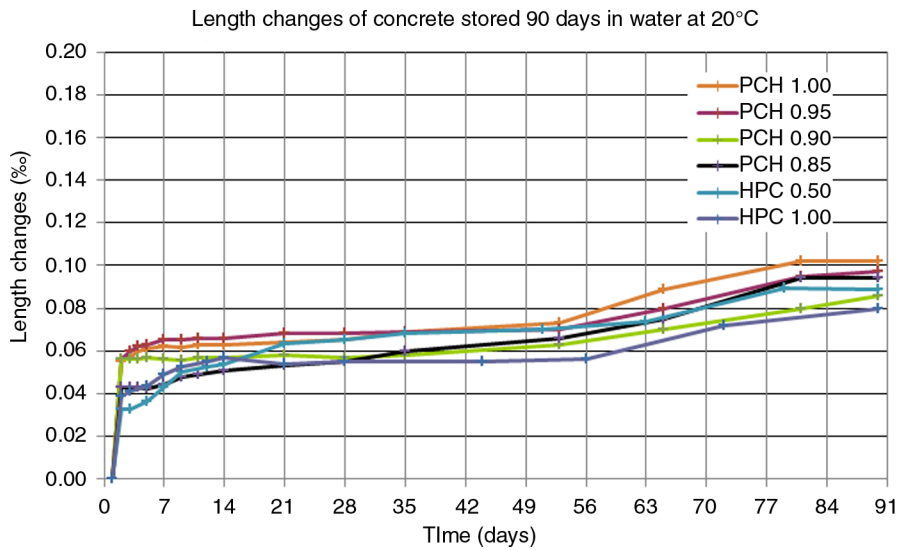


FIGURE 1. Length changes of concretes stored for 90 days in water at (20±1).

After the first day of immersion, rapid expansion was observed in all specimens: the concretes with 0 to 10 mass % of H-Cement content expanded to the level of 0.056‰ while those containing 15, 50 and 100 mass % of H-Cement only up to 0.04‰. The initial (zero) measurement is performed immediately after remoulding the green concrete 24 hours after its manufacturing in the laboratory. The rapid expansion within next 24-hours exposure in water is caused by the change of curing regime and attributed to a hydration of fresh concrete in favourable water environment. Consequently all concretes showed slight expansion with negligible deviations from the trend of moderate expansion. Initial 24-hours expansion represents approximately a half of the total value of the measured final 90-day's

expansion. The largest difference in final expansion values is observed between H-concrete (HPC 1.00) and OPC-concrete (PCH 1.00): OPC-concrete expands of 0.102‰ while H-concrete only 0.080‰. H-Cement demonstrates slight expansion-reducing effect in the concrete compared to the effect of OPC.

Length changes of the concretes made of OPC (PCH 1.00), H-Cement (HPC 1.00) and concretes made of the above cement mixtures (HPC 0.85 to 0.95) stored for 90 days at temperature of 20±1 °C/60% of R. H. and temperature of 40±2 °C/15% of R. H. - dry air are illustrated in Figures 2 and 3. Although all concretes shrink, significant difference among the measured values primarily depends on the used cement and cement mixture, respectively.

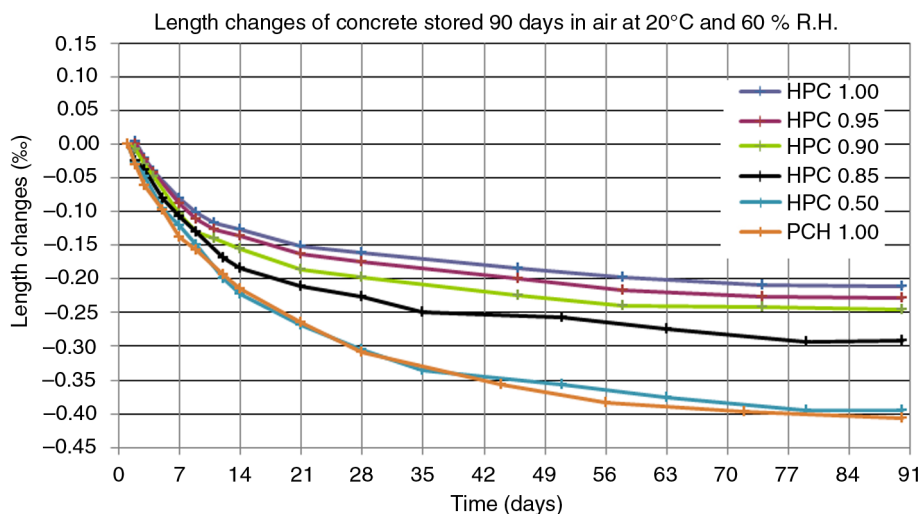
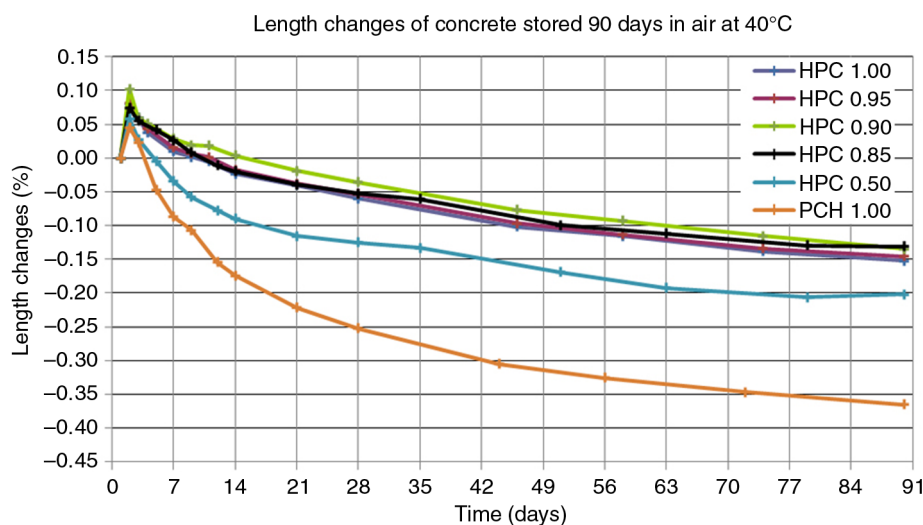


FIGURE 2. Length changes of concrete stored for 90 days in (20±1) °C 60% R.H. - air.


 FIGURE 3. Length changes of concrete stored for 90 days in $(40\pm 2\text{ }^{\circ}\text{C})/15\%$ R. H. - air.

Particular concretes shrink differently in air at temperature of $20\pm 1\text{ }^{\circ}\text{C}$ and 60% of R.H. (Figure 2). H-concrete (HPC 1.00) shrinks the least of all and OPC-concrete (PCH 1.00) the most of all. After 90-days exposure in air at temperature of $20\pm 1\text{ }^{\circ}\text{C}$, OPC-concrete shrinks up to -0.406% while H-concrete to the half level of -0.211% only. This fact proves evident shrinkage-reducing property of H-Cement. The more H-Cement in the concrete is, the less shrinks at $20\pm 1\text{ }^{\circ}\text{C}/60\%$ of R. H. - dry air cure. Higher content of H-Cement in concrete causes larger reduction in shrinkage. This effect is the most apparent at 100 mass % of H-Cement content due to containing only of 19.30 mass % clinker minerals. The concrete containing 50% OPC (53.45 mass % of clinker minerals) shrinks equally as the concrete with 100% OPC content (87.59 mass % of clinker minerals).

Development of length changes of concretes stored for 90 days at temperature of $40\pm 2\text{ }^{\circ}\text{C}/15\%$ of R. H. -dry air (Figure 3) are similar to those observed at temperature of $20\pm 1\text{ }^{\circ}\text{C}$ at 60% of

R.H.-air cure. OPC-concrete shrinks most intensively from all examined specimens. The more H-Cement in the concrete is, the less shrinks at $40\pm 1\text{ }^{\circ}\text{C}/15\%$ of R. H. - dry air cure. In contrast with results at temperature of $20\pm 1\text{ }^{\circ}\text{C}/60\%$ of R. H. - air cure, shrinkage is reduced at temperature of $40\pm 2\text{ }^{\circ}\text{C}/15\%$ of R. H. - dry air also at 50% of OPC substitution by H-Cement in the cement mixture. All concretes containing more than 90% H-Cement (≥ 81 mass % of clinker minerals) in a cement mixture with OPC shrink in warm and extremely dry air approximately equally.

3.3.2. Determination of mechanical properties

Mechanical properties of the studied concretes stored for 28 and 90 days in water at temperature of $20\pm 1\text{ }^{\circ}\text{C}$ (W20) and air at temperature of $20\pm 1\text{ }^{\circ}\text{C}/60\%$ of R. H. (A20) or temperature of $40\pm 2\text{ }^{\circ}\text{C}/15\%$ of R. H. (A40) after initial 28-days basic curing (BC) are reported in Tables 10, 11 and 12.

 TABLE 10. Mechanical properties of the concretes made from a mixture of H-Cement and OPC stored for 90 days in water at $(20\pm 1)\text{ }^{\circ}\text{C}$ (W20) after 28-days basic curing

Concrete kind	After 90 days in water at $20\text{ }^{\circ}\text{C}$					After 28-days BC	
	Content of H-Cement in concrete (mass %)	Dynamic modulus of elasticity (GPa)	Flexural strength (MPa)	Strength at the ends of prism (MPa)	Bulk density (kg/m^3)	Cube strength (MPa)	Bulk density (kg/m^3)
HPC 1.00 W20	100	46.6	5.4	34.2	2330	27.2	2340
HPC 0.50 W20	50	50.3	5.5	49.1	2350	35.7	2370
PCH 0.85 W20	15	55.1	5.5	50.6	2380	40.5	2390
PCH 0.90 W20	10	55.9	5.5	50.7	2380	40.5	2390
PCH 0.95 W20	5	56.6	5.5	51.4	2390	41.0	2400
PCH 1.00 W20	0	56.5	5.5	54.5	2390	41.6	2400

Notice: Basic curing (abbreviated as BC) is specified by 1- day cure in the chamber at $(20\pm 1)\text{ }^{\circ}\text{C}$ at 100% R.H.-air and 27- days curing in water at $(20\pm 1)\text{ }^{\circ}\text{C}$.

TABLE 11. Mechanical properties of the concretes made from a mixture of H-Cement and OPC stored for 90 days in air at 20 °C/60% R. H. (A20) after 28-days basic curing

Concrete kind		After 90 days in air at 20 °C				After 28-days BC	
Concrete mixture	Content of H-Cement in concrete (mass %)	Dynamic modulus of elasticity (GPa)	Flexural strength (MPa)	Strength at the ends of prism (MPa)	Bulk density (kg/m ³)	Cube strength (MPa)	Bulk density (kg/m ³)
HPC 1.00 A20	100	41.7	2.4	32.3	2270	27.6	2280
HPC 0.95 A20	95	41.4	2.8	32.9	2270	29.3	2290
HPC 0.90 A20	90	41.3	2.9	34.8	2270	31.3	2300
HPC 0.85 A20	85	41.4	3.0	37.2	2270	32.4	2310
HPC 0.50 A20	50	41.2	3.3	41.0	2290	38.1	2320
PCH 1.00 A20	0	39.3	3.7	42.0	2310	40.2	2330

TABLE 12. Mechanical properties of the concretes made from a mixture of H-Cement and OPC stored for 90 days in air at 40 °C/15% R. H. (A40) after 28-days basic curing

Concrete kind		After 90 days in air at 40 °C				After 28-days BC	
Concrete mixture	Content of H-Cement in concrete (mass %)	Dynamic modulus of elasticity (GPa)	Flexural strength (MPa)	Strength at the ends of prism (MPa)	Bulk density (kg/m ³)	Cube strength (MPa)	Bulk density (kg/m ³)
HPC 1.00 A40	100	36.7	2.3	30.6	2220	28.7	2270
HPC 0.95 A40	95	36.7	2.4	31.8	2220	30.0	2270
HPC 0.90 A40	90	36.7	2.5	33.0	2220	32.0	2280
HPC 0.85 A40	85	36.6	2.6	34.7	2220	33.2	2290
HPC 0.50 A40	50	36.5	3.2	38.5	2240	38.5	2300
PCH 1.00 A40	0	33.4	3.8	39.0	2260	39.1	2300

The bulk density of concrete is slightly reduced from the 85% mass portion of H-Cement in the cement mixture in both dry exposures; however this decrease is insignificant. In water the bulk density decreases continuously but also very negligibly. The compressive strength clearly decreases with a 50 mass % and higher H-Cement portion in the cement mixture in dry air cure while continual increase is observed underwater.

The 90-days bulk density and flexural strength of the concrete slightly decreases with increasing of H-Cement portions in the cement mixture at all three curing regimes, with the exception of the unchanged flexural strength of concrete kept permanently in water. Compressive strength at the ends of the (100×100×400) mm prisms apparently decreases with 50 mass % and higher H-Cement portion in the cement mixture.

Mutual dependences between length changes and compressive strength developments of the concretes and H-Cement contents permanently kept in water and dry environments (as seen in Figure 4) demonstrate the following important findings:

1.) the cement composition has significant influence on the compressive strength uptakes, while negligible on the achieved expansions at

temperature of 20±1 °C - water cure; the expansion of H-Cement is slightly reduced contrary to that of OPC.

- 2.) the cement composition has significant influence on both studied parameters: linear dependence between shrinkage reduction levels and compressive strength losses is confirmed. Higher H-cement content in the cement mixture gives the concrete of lower shrinkage and compressive strength values. The results indicate possible adjusting of shrinkage rate and strength development to an expected level by the targeted mixing of H-CEMENT with OPC at temperature of 20±1 °C/60% of R.H. - air cure.
- 3.) the cement composition has significant influence on compressive strength uptakes at 50% substitution of OPC by H-Cement (38.5 MPa) that is very similar to that of OPC-concrete (39,0 MPa) but clearly increased relative to H-concrete (30.6 MPa), while length changes are approximately half of the level achieved by OPC at temperature of 40±2 °C/15% of R.H - air cure.
- 4.) the concrete containing of 85 mass % of H-Cement is characterized by the same shrinkage than that observed in H-concrete but its compressive strength is about 12% higher at temperature of 40±2 °C/15% of R.H – dry air cure.

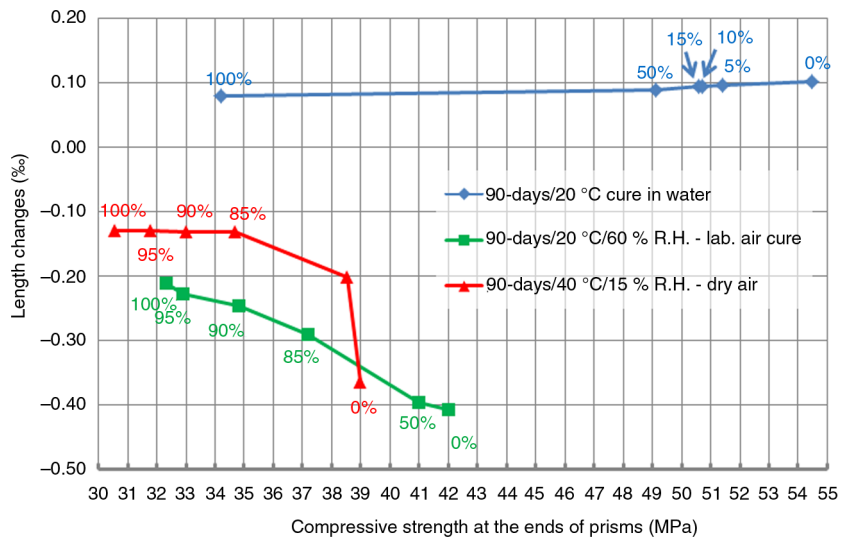


FIGURE 4. The dependence between length changes of the concrete with different H-Cement content in cement mixtures and the compressive strength at the ends of specimens after 90 days of different curing regimes.

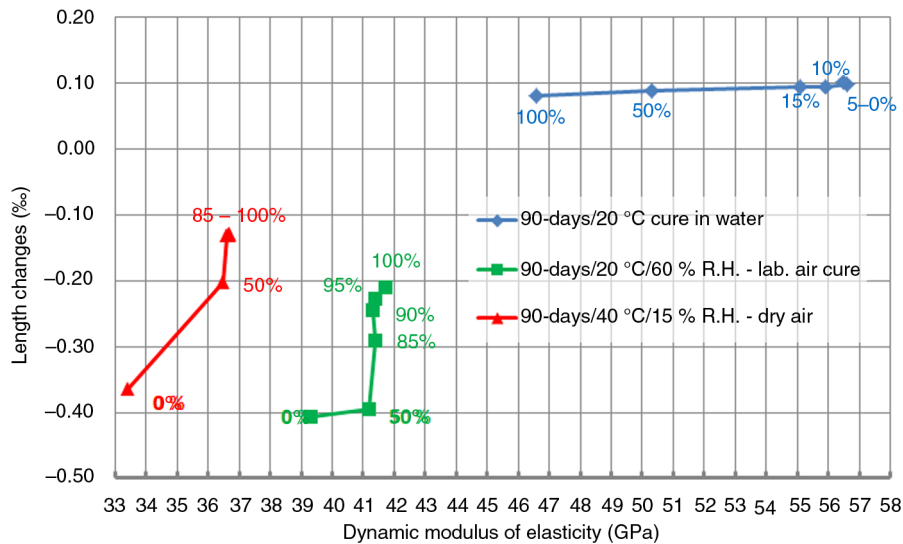


FIGURE 5. The coherence between the length changes of concrete with different H-Cement content in cement mixtures and the dynamic modulus of elasticity after 90 days of different curing regimes.

Mutual dependences between length changes and dynamic modulus of elasticity developments of the concretes and H-Cement contents in the cement mixtures permanently kept in water and dry environments (Figure 5) result in:

- 1.) the same dependence as observed for strength behaviours at temperature of 20 ± 1 °C - water cure.
- 2.) the effect of cement composition is quite different on dynamic modulus elasticity values relative to that on compressive strengths at

- 3.) the effect of cement composition is also quite different on dynamic modulus elasticity values relative to that on compressive strengths at temperature of 20 ± 1 °C/60% of R. H. - air cure. The concrete with 50 mass % substitution of OPC by H-Cement shows elasticity modulus increase approximately 2 GPa opposite to OPC concrete at approximately the same shrinkage level. Next increase in H-Cement content in the mixture leads to pronounced shrinkage reductions without any noticeable change in dynamic modulus of elasticity.

temperature of 40 ± 2 °C/15% of R. H. -dry air cure. The concrete with 50% of OPC substitution by H-Cement shows elasticity modulus increase approximately 3 GPa opposite to OPC concrete but length changes are approximately half of the level achieved with only OPC at temperature of 40 ± 2 °C/15% of R.H. -dry air cure. Next increase in H-Cement content in the mixture leads to continual shrinkage reductions without any noticeable changes in dynamic modulus of elasticity.

3.3.3. Influence of cement mineralogical compositions on concrete behaviour

The aim of this part of study is to demonstrate positive effect of 80 mass % of Portland cement clinker substitutions in hybrid cement by inorganic geopolymer on shrinkage reduction of concrete kept in dry air at the ambient temperature of 20 °C and elevated temperature of 40 °C. Detailed study of the binder phase of the H-Cement is the actual subject of the on-going fundamental research. The dependence between length changes of concrete after 90-days of different exposures and the content of clinker minerals in the cement mixtures is illustrated in Figure 6.

These main observations are derived from the above findings:

- H-concrete expands at temperature of 20 ± 1 °C water by 0.022‰ less than OPC-concrete showing total expansion of +0.102‰
- H-concrete shrinks in air at temperature of 20 °C/60% of R. H. by 0.192‰ less than OPC-concrete showing total shrinkage of -0.406‰

- H-concrete shrinks in air at temperature of 40 °C/15% R. H. by 0.213‰ less than OPC-concrete showing total shrinkage of -0.365‰
- slight expansion-reducing and pronounced shrinkage-reducing property of H-Cement is confirmed
- expansion in water and shrinkage in air is caused by 19.30 mass % content of clinker minerals present in H-CEMENT opposite to 87.59 mass % in OPC
- if clinker minerals content exceeds 50 mass % in the cement mixtures, the shrinkage of concrete is dominantly influenced by OPC at temperature of 20 °C/60% of R. H. - air cure
- if clinker minerals content falls below 30 mass % in the cement mixtures, the shrinkage of concrete is dominantly influenced by H-CEMENT at temperature of 40 °C/15% of R. H. - dry air cure.

4. CONCLUSIONS

The following conclusions are applicable to the particular test cements and test methods employed:

- 1.) H-Cement is suitable for the production of ready-mixed concrete compressive strength classes up to C30/37. The plasticizer to achieve extended workability is based on lignosulfonate or polycarboxylate base; the most plasticity efficiency gives the combination of both admixtures.
- 2.) The expansion of concrete containing H-Cement is reduced by 21.6% compared to OPC concrete of the same composition after 90-days cure at water of temperature of 20 ± 1 °C

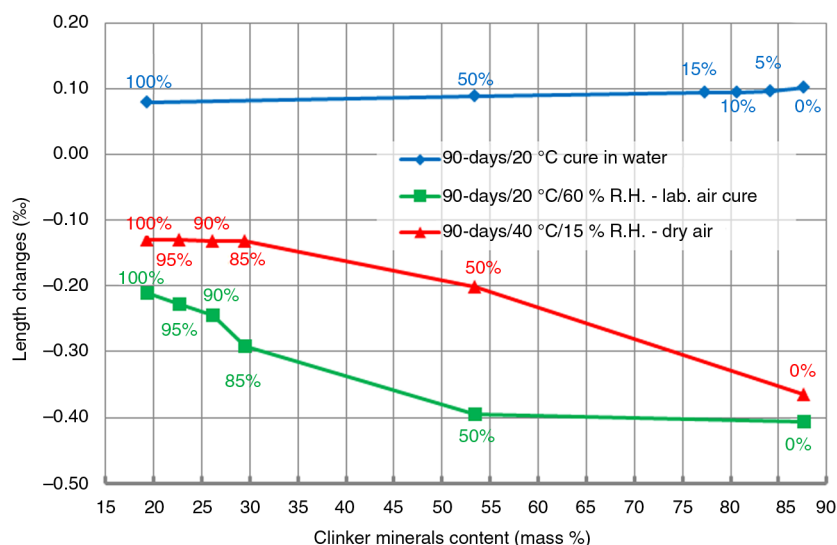


FIGURE 6. The dependence of length changes of concrete on the content of clinker minerals in tested cement mixtures.

- 3.) The shrinkage of concrete containing H-Cement kept for 90 days temperature of 20 °C/60% of R.H. and 40 °C/15% of R.H. - air is reduced by 48.0% and 58.4% compare to OPC concrete.
- 4.) Shrinkage-reducing character of H-Cement is primarily caused by 68.29% drop in clinker minerals content relative to that in OPC.
- 5.) The influence of admixtures on the shrinkage - reducing property of H-Cement is excluded because the concretes contain no any plasticizing admixture.
- 6.) Substitution of OPC by lower-strength H-Cement resulted in no significant decline in the technically important properties, such as compressive strength and dynamic modulus of elasticity.
- 7.) To explain all the factors affecting main utility properties of innovative hybrid cement, a deeper research insight into the mechanism of microstructure and pore structure formation is presently conducted with industrial pilot applications.

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