Chapter

Fundamental Properties of Industrial Hybrid Cement Important for Application in Concrete

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Abstract

Hybrid cement (H-Cement/HC) takes advantages of the material properties of cement and alkali-activated cement with the resulting benefit on utility properties so that hybrid cement can replace in large quantities ordinary Portland cement (PC) as follows: H-Cement is used by the same way as traditional cements; H-Cement is suitable for use in ready-mixed concrete up to C30/37 strength class; H-Cement has shrinkage-reducing and alkali-aggregate-mitigating property; H-Cement shows the same sulphate resistance with sulphate-resistant Portland cement with C3A = 0; H-Cement is a suitable binder for use in concrete containing the swelling steel slag aggregate as a full replacement of natural aggregate. This low-energy, low-cost and environmentally friendly hybrid cement belongs to the group of advanced cements, in which parameters predetermine it to overcome PC serviceability in certain applications. The objective of this chapter is to characterize fundamental properties and some durability aspects of H-Cement in concrete.

Keywords: hybrid cement, concrete, utility properties, durability

1. Introduction

Global annual production of cement accounts for about 5% of the total anthropogenic CO2 emission [1]. About 4.2 GJ energy is required to produce 1 metric ton PC, resulting approximately in 0.8–1.0 metric ton of CO2 release into the atmosphere [2]. A second problem besides CO2 emissions is connected with the negative ecological and health impact of red and brown mud ponds in the manufacture of aluminium-containing high-alkaline waste water rich in NaOH. Landfilling of this hazardous waste raises other problems due to the high concentrations of heavy metals and the variety in chemical composition depending to a large extent on the season and weather conditions. The main task of the current research is the development of less energy-intensive but more ecological cements. One solution is the production of innovative cement binders like alkali-activated cements, geopolymers and hybrid alkaline cements with Portland clinker addition [3, 4]. The hybrid alkaline cements have various compositions of alkali-activated aluminosilicates with...
low Portland clinker content [5]. In spite of the low clinker content, the hybrid binders can obtain useful early-age mechanical strengths [6]. Hybrid cements take advantage of the material properties of a cement and ordinary geopolymer with the resulting benefit on the acquired properties, so that hybrid cement can replace in large quantities energy-intensive PC [7]. The novel hybrid cement H-Cement is produced on the base of industrial by-products and wastes according to the patent application [8]. The content of clinker is always under 30 wt%. A typical feature for H-Cement binding phase formation is the combined effect of hydraulic properties of Portland clinker, pozzolanic properties of fly ashes, latent hydraulic properties of granulated blast furnace slag (GBFS) and geopolymeric properties coming from the alkaline inorganic polycondensing reactions of aluminosilicate materials. Such inorganic material is activated by addition of alkaline waste water separated from the caustic red mud ponds and Na₂SO₄ obtained from alkaline waste water neutralization by H₂SO₄. In the presence of these alkaline agents, the pH value of cement mixture is increased. This results in fly ash (FA) and GBFS dissolution leading to final geopolymerization effect. At the same time, Ca(OH)₂ addition coming from Portland clinker hydration promotes the binding reactions of fly ash and GBFS. H-Cement is characterized by lower early strength and hydration heat but higher long-term strengths. H-Cement possesses high chemical resistance against aggressive action of sulphate, magnesium, chloride and acidic waters [9]. When autoclaving at an elevated temperature and pressure, H-Cement provided volume stability and strength increase in concrete with steel slag replacing a natural aggregate as opposed to PC concrete with steel slag which was disintegrated after the test [10].

The production of H-Cement does not require additional heat treatment. It is cured in the same way as traditional cements and owns the certificate of conformity [11] issued on the base of SK Technical Assessment [12]. H-Cement is a sustainable cement which, due to its material composition, does not meet the categorization of cements according to STN EN 197-1 [13].

This article shows that one possible solution for innovative binders with improved durability and decreased energy requirements is the production of hybrid cement. It is demonstrated that:

- H-Cement is suitable for production of ready-mixed concrete strength classes up to C30/37.
- Shrinkage-reducing and alkali-silica reaction (ASR)-mitigating character of H-Cement is especially relevant because it prevents propagation of shrinkage or expansive cracking during the service life of the concrete.
- H-Cement is specified after 5-year impact of 5% wt. sodium sulphate solution by the same sulphate resistance with the sulphate-resistant CEM I 42.5 R-SR O with C₃A = 0.
- H-Cement is suitable for making concrete with mostly landfilled steel slag when replacing a natural aggregate.

2. Experimental procedure

2.1 Materials and methods

The novel H-Cement and CEM I/42.5 R as a reference were tested. Both are produced by the cement plant Považská cementáreň, a. s., Ladce in Slovakia;
H-Cement is according to internal standard. The cement was used in combination with river aggregates of 0/4, 4/8 and 8/16 mm fraction from Jelka (Slovakia). For the tests with steel slag, the river aggregate was completely replaced by the slag of the same fraction. All river aggregate properties met the requirements of STN EN 12620+A1 [14]. The compatibility of H-Cement was verified with seven types of plasticizers [15]. The concrete without admixture was examined as a reference. The shrinkage-reducing ability was confirmed on the concrete made from H-Cement, PC and selected blended systems [15]. The H-Cement suitability for mitigating alkali-silica reaction was verified on the cement mortars by the procedure reported in STN 721179 [16] (the related ASTM Standards: C289-03 for Chemical method; ASTM C1293-08b for length change of concrete). Resistance to sulphate and higher temperature/pressure attack was verified by own methodologies [10, 17].

2.2 Casting

Specimens of ready-mixed concrete were made according to STN EN 12390-2 [18]. Fresh concrete was compacted on a vibration table (40 Hz) for 60 s and casted into 150 mm cubes or 100 × 100 × 400 mm prisms. Casting of the specimens for verification of specific properties of H-Cement is reported separately for each experiment, either shrinkage-reducing or ASR-mitigating property, sulphate resistance and volume stability of steel slag concrete.

2.3 Curing

The moulds were stored at more than 95% relative humidity of air (abbreviated as RH) at (20 ± 1)°C for the first 24 h, and then the concrete specimens were cured according to the test. A method of treating the specimens for special properties verification is given separately for each test.

2.4 Testing procedures for cement

Both cements were tested for chemical composition by STN EN 196-2 [19]; the Bogue mineral composition was also determined. Standard consistency, initial and final setting, and soundness were verified by STN EN 196-3+A1 [20] and hydration heat by STN EN 196-8 [21]. After 2-, 28- or 90-day cure, flexural and compressive strengths of the mortars with cement-to-sand ratio 1:3 by weight were obtained according to STN EN 196-1 [22]. H-Cement is sensitive to excess of water; the PC and H-Cement mortars therefore differ in water-to-cement ratios.

2.5 Testing procedure for fresh and hardened concrete

The consistency of fresh concrete was estimated by slump by STN EN 12350-2, volume density by STN EN 12350-6 and air content in the fresh mixture by STN EN 12350-7 [23–25]. Concrete specimens were tested for cube compressive strengths [26], compressive strengths of the edges of prisms of standard size [27] and dynamic elasticity modulus [28].

2.6 Partially accelerated test of sulphate resistance

2.6.1 Materials

Cement CEM I 42.5 R (PC) produced by Považská cementáreň, a. s., Ladce cement plant (PCLA) and C₃A-free sulphate-resistant CEM I 42.5 R-SR O (SRC)
produced by Lafarge Zementwerke GmbH, Mannersdorf (Austria) according to STN EN 197-1, both as reference, were chosen for the investigation. H-Cement was tested as the verified sample.

2.6.2 Specimens, casting and curing

Mortars with cement-to-sand ratio of 1:3 by weight adjusted on the constant consistency of 140 ± 1 mm were prepared as prismatic specimens of size 40 x 40 x 160 mm. All specimens were kept for 5-year exposure in 5% wt. sodium sulphate (Na₂SO₄) solution and water as reference medium after 28-day water curing (BC) at (20 ± 1)°C. The tests of chemical resistance were conducted by own methodology of “partially accelerated test” based on keeping the mortars in strongly over-concentrated aggressive solution for a sufficient long time. The aggressive storage was specified by the following way: each 1 cm² of the exposed area of prism must be in permanent contact with at least of 10 cm³ of 5% wt. Na₂SO₄ [33802.8 mg aggressive SO₄²⁻ per 1 litre solution]. The sulphate solution and reference water were refreshed every 30 days within 90 days of testing, every 45 days between 90 and 365 days and every 60 days up to 5 years of exposure, respectively.

2.6.3 Items of investigation

Consistency, density and fresh air content of the mortars were determined according to relevant STN EN Standards. The mortars were continuously tested for length changes, dynamic modules of elasticity (DME) and periodically flexural and compressive strength. After destructive tests the microstructure and pore structure were identified by X-ray diffraction (XRD), thermogravimetry-differential thermal analysis (TG-DTA), mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM) techniques. The ground material was sieved through a 0.063 mm mesh to receive the powder suitable for testing. For the X-ray diffraction, the Philips diffractometer was used in a 2Θ range of 5–65°. CuKα radiation and Ni filter were applied. Thermal analysis was performed on the Netzsch apparatus STA 449 F3 Jupiter in air at heating rate 10°C/min. Basic parameters of the pore structure were identified by MIP using the high-pressure porosimeter Quantachrome PoreMaster 60 GT using small mortar fragments for testing. The JEOL 7500F was used to study microstructure by scanning electron microscopy. Chemical composition, with special emphasis on the bound SO₃ content, was estimated by STN EN 196-2 [19].

2.7 Concrete based on H-Cement and steel slag

Two types of binders (PC and H-Cement as HC) were chosen to prepare concrete based on steel slag. The Sika® ViscoCrete®-225 powder superplasticizer was used to improve the consistency of the fresh concrete mixture. It provides water reduction, excellent fluidity and cohesion, together with a self-compacting effect. Tap water from the water supply system was used as the mixing water.

Two mixes designated as HC concrete and PC concrete were used within the scope of the experimental research.

- HC concrete contained 0/8 mm steel slag fraction as filler, 380 kg of H-Cement, 241 kg of water, Sika superplasticizer in the amount of 0.5% of the cement weight and a retardant additive (Retardal 540) in the amount of 0.4% of the cement weight.
PC concrete contained 0/8 mm steel slag fraction as filler, 380 kg of CEM I 42.5 N, 241 kg of water and Sika superplasticizer in the amount of 0.5% of the cement weight. No retardant admixture was used.

The production of the specimens used to test the properties of fresh and hardened concrete based on steel slag was carried out in two stages. The first stage involved the production of the specimens for testing cube strength after 3, 7, 14, 21, 28 and 90 days of age. The second stage involved the production of the specimens for the comparison of cube and prism strengths after 28 days of curing.

The following properties of hardened concrete were tested: cube and prism concrete strengths. The durability of the concrete based on steel slag was tested in the conditions of a higher temperature and pressure. Determination of the volume changes of the concrete was carried out in a 540-l laboratory autoclave at the maximum saturated steam pressure of 1.2 MPa and a maximum temperature of 189°C. Cubes of 150 mm were used as the test specimens. The temperatures and pressures in the testing laboratory autoclave were set by this way to determine the volume changes of the concrete based on the steel slag as aggregate [10].

3. Experimental results and discussion

3.1 Basic characterization of H-Cement

Chemical composition of main constituents of H-Cement (HC) and Portland cement (PC) clinker are listed in Tables 1 and 2. Table 3 confirms that H-Cement shows different chemical and mineral compositions compared to PC. Both hydrated cements differ in typical characteristic values as stated in Table 4. The results suggest that hybrid cement can be used prospectively in concrete for the same purposes as the blended cements of lower-strength classes, e.g., CEM III–V, probably CEM II/B–S according to STN EN 197-1, preferably in massive constructions due to low hydration heat and aggressively exposed media because of low Portland clinker (and therefore C3A) content.

H-Cement consists essentially in a blend of materials containing 20–30% wt. Portland clinker and 70–80% alkaline cement, in turn a combination of fly ash, granulated blast furnace slag and alkaline sulphates.

| % wt. | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | SO₃ | K₂O | Na₂O | L.O.I |
|-------|-----|------|-------|-------|-----|-----|-----|------|------|
| FA    | 3.36| 51.42| 26.93 | 7.27  | 2.10| 0.87| 3.28| 0.17 | 1.84 |
| GBFS  | 39.24| 40.13| 7.19  | 0.27  | 10.04| 1.50| 0.52| 0.31 | 1.10 |

Abbreviations: FA, fly ash; GBFS, granulated blast furnace slag; LOI, loss on ignition.

Table 1. Chemical composition of fly ash (FA) and blast furnace slag (GBFS).

| % wt. | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | SO₃ | K₂O | Na₂O | P₂O₅ |
|-------|-----|------|-------|-------|-----|-----|-----|------|------|
| Clinker | 64.4| 20.80| 4.80  | 3.08  | 1.45| 0.47| 1.05| 0.28 | 0.49 |
| C₄S | C₃S | C₃A | C₄AF | Free CaO | Arcanite | Periclase |
| 65.1| 10.60| 8.40| 9.72  | 1.40  | 0.82| 0.58|
3.2 Ready-mixed concrete

The cube compressive strengths of ready-mixed concretes of C8/10 to C30/37 strength class for reaching a slump of 100–150 mm (slump class S3 according to [23]) without the use of plasticizers are listed in Table 5. The consistency and cube compressive strength of ready-mixed concretes prepared with different plasticizers with slump values ≥220 mm [slump class S5] are reported in Table 6. Laboratory-made ready-mixed concrete specimens were prepared with the following types of plasticizers coming from various producers: M1, no admixture; M2, lignosulfonate; M3, modified polycarboxylate (<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; and M8, lignosulfonate modified by polycarboxylate.

The results show that H-Cement is suitable for the production of ready-mixed concrete between C8/10 and C30/37 strength classes [29]. Workability of the concretes made from H-Cement is dependent on the specific plasticizer type being used. Admixtures based on a lignosulfonate and a combined lignosulfonate/polycarboxylate mixture are found best to ensure the workability of fresh concrete mixtures and also after the elapsed 60 min.

### 3.3 Shrinkage-reducing property

The concretes were prepared from the cement mixture made of two cements, HC and PC, in the selected ratios (expressed as % wt.) as reported in Table 7. The specimens were stored in water at (20 ± 1)°C and in air at (20 ± 1)°C with 60% RH and at (40 ± 1)°C with an average RH of 15% in order to minimize the length changes within the 90-day period of curing. The concretes were prepared with a constant water-to-cement ratio of 0.475 according to the proportion: 400 kg/m³ of cement (PCHC 1.00 or HCPC 1.00) or cement blend, 190 l of water and dried river aggregates—0/4 mm, 630 kg; 4/8 mm, 390 kg; and 8/16 mm, 775 kg from Jelka (Slovakia). No admixture was used at the concrete production to preclude its influence on the measured length changes. The measurements were performed on the prisms 100 × 100 × 400 mm having a length comparator according to STN
### Table 7.
*Content of cements in the concrete mixtures with w/c = 0.475.*

| Cement mixture in concrete | Content of cements (% wt.) | Curing regime                                           |
|----------------------------|----------------------------|--------------------------------------------------------|
| PCHC 1.00                  | 0                          | In water at 20°C and in air at 20 and 40°C             |
| PCHC 0.95                  | 5                          | In water at 20°C                                       |
| PCHC 0.90                  | 10                         | In water at 20°C                                       |
| PCHC 0.85                  | 15                         | In water at 20°C                                       |
| HCPC 0.50                  | 50                         | In water at 20°C and in air at 20 and 40°C             |
| HCPC 0.85                  | 85                         | In air at 20°C and 40°C                               |
| HCPC 0.90                  | 90                         | In air at 20°C and 40°C                               |
| HCPC 0.95                  | 95                         | In air at 20°C and 40°C                               |
| HCPC 1.00                  | 100                        | In water at 20°C and in air at 20 and 40°C             |

Figure 1.
*Length changes of concrete stored 90 days at 20°C and 60% RH.*

Figure 2.
*Length changes of concrete stored 90 days at 40°C and 15% RH.*
731320 [30] (the related ASTM Standard: C157/C157M-08) and are illustrated in Figures 1 and 2. Mechanical properties of the specimens are listed in Table 8.

The results show that H-Cement has reduced shrinkage. All concretes slightly expand when permanently cured in water. H-Cement concrete (HC concrete) expands by 21.6% less than PC concrete after 90-day immersion in water. The shrinkage of HC concrete exposed for 90 days in 20°C/60% RH air cure and 40°C/15% RH air cure is about 48 and 58% smaller than that of PC concrete. The shrinkage-reducing effect is also recorded by the blended systems.

Depending on its cement blend composition and curing regime, however, blending HC with PC contributes to raising the compressive strength values compared to plain HC concrete. The 90-day compressive strength of HCPC 1.00 (100% wt. HC), HCPC 0.50 (50% wt. of both cements) and PCHC 1.00 (100% wt. PC) in 20 and 40°C air cure is 32.3 and 30.6 MPa, 41.0 and 38.5 MPa and 42.0 and 39.0 MPa, respectively.

### 3.4 ASR-mitigating property

The andesite aggregate with a proven susceptibility to ASR according to the criteria for evaluation of the chemical test according to STN 721179 [16] was used

| Concrete mixture | HC (% wt.) | Curing | 28-day basic curing | 90-day curing |
|------------------|------------|--------|---------------------|---------------|
|                  |            |        | Compressive strength (MPa) | DME (GPa) | Flexural Compressive strength (MPa) | |
| HCPC 1.00        | 100        | W20    | 27.2                 | 46.6         | 5.4 | 34.2 |
|                  |            | A20    | 27.6                 | 41.7         | 2.4 | 32.3 |
|                  |            | A40    | 28.7                 | 36.7         | 2.3 | 30.6 |
| HCPC 0.95        | 95         | A20    | 29.3                 | 41.4         | 2.8 | 32.9 |
|                  |            | A40    | 30.0                 | 36.7         | 2.4 | 31.8 |
| HCPC 0.90        | 90         | A20    | 31.3                 | 41.3         | 2.9 | 34.8 |
|                  |            | A40    | 32.0                 | 36.6         | 2.5 | 33.0 |
| HCPC 0.85        | 85         | A20    | 32.4                 | 41.4         | 3.0 | 37.2 |
|                  |            | A40    | 33.2                 | 36.6         | 2.6 | 34.7 |
| HCPC 0.50        | 50         | W20    | 35.7                 | 50.3         | 5.5 | 49.1 |
|                  |            | A20    | 38.1                 | 41.2         | 3.3 | 41.0 |
|                  |            | A40    | 38.5                 | 36.5         | 3.2 | 38.5 |
| PCHC 0.85        | 15         | W20    | 40.5                 | 55.1         | 5.5 | 50.6 |
| PCHC 0.90        | 10         | W20    | 40.5                 | 55.9         | 5.5 | 50.7 |
| PCHC 0.95        | 5          | W20    | 41.0                 | 56.6         | 5.5 | 51.4 |
| PCHC 1.00        | 0          | W20    | 41.6                 | 56.6         | 5.6 | 54.5 |
|                  |            | A20    | 40.2                 | 39.3         | 3.7 | 42.0 |
|                  |            | A40    | 39.1                 | 33.4         | 3.8 | 39.0 |

Abbreviations: W20, water at 20°C; A20, air at 20°C; A40, air at 40°C; DME, dynamic modulus of elasticity; BC, basic curing specified by 1-day cure in the chamber at (20 ± 1)°C at 100% RH air and 27-day curing in water at (20 ± 1)°C.

Table 8. Mechanical properties of the concretes made from a mixture of HC and PC stored for 90 days in water at 20°C (W20), in air at 20°C/60% RH (A20) and at 40°C/15% RH (A40) after 28-day basic curing.
for the tests. The alkali content expressed as Na₂O equivalent in both cements was estimated. From this content, the amount of NaOH required to achieve the desired Na₂O eq. (1.30 ± 0.05)% wt. by the standard was calculated. The tap water was enriched with a calculated amount of NaOH during laboratory production of the mortars. Prediction criteria of andesite aggregate susceptibility to ASR are given in Table 9. The composition of mortars for 6-month length change test cured at 20 and 40°C/100% RH moist air took into account the requirements of the above standard. Length changes are illustrated in Figure 3.

The results show that H-Cement is characterized by ASR-mitigating property. H-Cement mortar (abbreviated as HC 20 and HC 40), in contrast with PC (abbreviated as PC 20 and PC 40), clearly reduces the expansion markedly below the maximum allowable standard limit [16] of 0.1% (<1%) regardless of the long-term treatment. ASR-mitigating effect under maximum allowable limit of 0.1% (<1%) is confirmed also for the blended cement consisting of 70% wt. PC and 30% wt. HC (abbreviated as HM 20 and HM 40 in Figure 3).

The contemplated cause of ASR mitigation is the presence of alkali-activated pozzolans in the substitution of up to 80% by weight of the PC clinker, which could prevent the expansion [31]. The cause of ASR is a complicated problem and is still not fully understood. In this research focused on the need for industry, the achieved effect was investigated, and its cause is not studied in detail.

### 3.5 Sulphate resistance

Basic physical properties and standard strengths are summarized in Table 10. HC compared to PC is characterized by low C₃A content. Such composition predisposes such cement to be chemically more resistant than PC. Properties of fresh mortars are listed in Table 11. HC mortar compared to both reference is characterized by the higher specific surface area and standardized density. In spite of that

| Aggregate | Loss of alkalinity R (mmol/l) | Molar concentration of SiO₂ S (mmol/l) | Criterion for R value in [16] | Criterion for S value in [16] | Assumption that aggregate contains reactive forms of SiO₂ |
|-----------|-------------------------------|---------------------------------------|-----------------------------|------------------------------|-----------------------------------------------------------|
| Andesite  | 132.42                        | 400.04                                | R > 70                      | S > R                        | Yes                                                        |

Table 9. Prediction of andesite susceptibility to ASR by the chemical test.

![Figure 3](image)

Length changes of the mortars with the ASR aggregate andesite.
fact, water-to-cement ratio of HC mortar is 0.42 compared to 0.5 of PC mortar when both are adjusted on the same consistency of 140 ± 1 mm. H-Cement shows plasticity effect in the mortar; however, it is unable to reach the strength level of both reference mortars, as reported in Table 10. The second reference mortar was prepared from C3A-free industrially made Portland cement (abbreviated as SR). HC and PC mortars were adjusted on the same consistency; that of SR differs. SR and PC were produced with the same w/c ratio of 0.5.

Chemical composition of PC and HC mortar after 28-day basic curing in water at (20 ± 1) °C is listed in Table 12. The cements confirm a substantial difference, especially in CaO content, also evident in Al₂O₃ and detectable in Na₂O eq. amounts. Low CaO in hybrid cement is a prerequisite for the increased chemical resistance. Higher levels of Al₂O₃ and Na₂O eq., as opposed to PC mortar, induce the occurrence of the alkali-activated binder based on pozzolanic components as an inorganic polymer characterized by a binder potential alongside the minor portion of hydrated PC clinker.

Dynamic modulus of elasticity (DME) of mortars after 5 years of exposure in the sulphate and water environment is shown in Figure 4. No evident changes were

| Cement kind | C₃A content (% wt.) | Specific surface area (m²/kg) | Standard density (% wt.) | Initial and final set (min) | Compressive strength (MPa) | Initial and final set (min) | Compressive strength (MPa) | Flexural strength (MPa) | Flexural strength (MPa) |
|-------------|---------------------|-------------------------------|--------------------------|-----------------------------|--------------------------|-----------------------------|--------------------------|--------------------------|--------------------------|
| HC          | 1.95                | 696.8                         | 33.0                     | 230/285                     | 14.9                     | 39.0                        | 4.1                      | 7.8                      |                          |
| SR          | 0.03                | 354.9                         | 27.2                     | 185/225                     | 26.2                     | 52.8                        | 4.7                      | 8.4                      |                          |
| PC          | 14.31               | 344.7                         | 25.8                     | 220/285                     | 26.5                     | 56.5                        | 5.4                      | 8.5                      |                          |

Table 10. Basic properties of the cements.

| Mortar    | Consistency (mm) | Bulk density (kg/m³) | Air content (% vol.) | w/c |
|-----------|------------------|----------------------|----------------------|-----|
| HC mortar | 141              | 2200                 | 5.2                  | 0.42|
| SR mortar | 186              | 2210                 | 6.3                  | 0.50|
| PC mortar | 142              | 2240                 | 4.7                  | 0.50|

Table 11. Properties of fresh mortars.

| Constituent | PC mortar (% wt.) | HC mortar (% wt.) |
|-------------|-------------------|-------------------|
| Ignition loss | 9.43              | 6.79              |
| SiO₂        | 64.69             | 71.50             |
| CaO         | 18.07             | 6.38              |
| Al₂O₃       | 1.86              | 7.91              |
| Fe₂O₃       | 1.17              | 2.28              |
| MgO         | 3.54              | 3.37              |
| SO₃         | 0.98              | 1.17              |
| Cl⁻         | 0.03              | 0.02              |
| Na₂O eq.    | 0.09              | 0.41              |

Table 12. Differences in chemical composition of PC and HC mortar after basic curing.
observed in 5% wt. Na$_2$SO$_4$ for HC and SR mortar, while drops in DME values are found for PC mortar, slightly after 2-year exposure and dramatically after 3-year attack. Elasticity modules at the water curing remain approximately the same.

The effect of sulphate action on the expansion of the mortars is depicted in Figure 5. The HC and SR mortar show negligible expansion in sulphate exposure. PC mortar is specified by negligible length changes underwater, while evident expansion is observed in the sodium sulphate.

Flexural and compressive strength of PC mortar is 9.0 and 63.9 MPa after 4-year curing in water; contrary evident destruction is observed in the sodium sulphate. Determination of the strength was therefore impossible. Excellent resistance of H-Cement to sulphate attack is demonstrated by 5-year strength of HC mortar. Data in Table 13 show that only a slight decrease in flexural and compressive strength is observed between reference water and aggressive sulphate exposure.

The structural integrity of SR and HC mortar is not disturbed, despite the found slight differences between the 5-year strength parameters. The observed HC mortar’s sulphate resistance is determined by the material composition of H-Cement.
that is not sensitive to sulphate attack as well as CEM I 42.5 R-SR 0 but not for the same reason. The cause of high sulphate resistance of H-Cement is explained later.

It is approved in Table 14 that PC mortar is characterized by extremely high bound SO₃ and ignition loss values after 4-year exposure in 5% wt. Na₂SO₄ opposite to HC and SR mortar. The CaO content is dramatically reduced in sulphate exposure as compared to that of HC and SR mortar. HC mortar behaves in the sodium sulphate as well as SR mortar; even the difference between the SO₃ bound in HC mortar in sulphate and water exposure is smaller than that in SR mortar.

Qualitative and quantitative differences in mineral and phase composition of PC and HC mortar after 28-day basic curing (BC) in (20 ± 1)°C water are recognized in Figures 6–9. The basic feature of the difference in the mineral composition of both mortars lies in the absence of portlandite Ca(OH)₂ in the mortar with the hybrid cement. Hydrated hybrid cement without the developed Ca(OH)₂ assumes a realistic chemical resistance in terms of sulphate resistance.

The results of thermal analysis confirmed that H-Cement generates a hydrated phase without the formation of crystalline Ca(OH)₂. This fact can decisively improve the increase in resistance to sulphate aggressiveness.

Mineral and phase compositions of the long-term exposed mortars are given in Figures 10–14. PC mortar in water contains quartz SiO₂ (Q) from the standardized sand and calcium hydroxide Ca(OH)₂ (CH) as a reaction product of cement hydration, also calcite CaCO₃ (Cc) as minor mineral. The high content of gypsum CaSO₄.2H₂O (G) and, to a less extent, more voluminous ettringite 3CaO.Al₂O₃.3CaSO₄.32H₂O (E) are detected in 4-year-old PC mortar exposed to 5% wt. Na₂SO₄ solution. Contrary, 5-year-old SR mortar shows a reduced content of CH in the sodium sulphate compared to water exposure and only a slight indication of the presence of CaSO₄.2H₂O arising as a reaction product of sulphate attack. HC mortar records in the same time negligible differences in mineral composition. The presence of CH and any reaction products of sulphate attack (G and E) are not confirmed; a negligible share of the marginal sodium thiosulfate pentahydrate Na₂S₂O₃.5H₂O (SH) and mirabilite Na₂SO₄.10H₂O (MI) is detected. Both of the latter minerals would be considered as reaction products of sulphate attack, however, with no negative impact on degradation of the mortar. TG-DTA plot confirms the presence of reaction products of sulphate attack in PC mortar by endotherm with maximum peak at 160°C (Figure 13), compared to HC mortar (Figure 14). The presence of CH was not recognized in HC mortar in water and Na₂SO₄ exposure. The minimum presence of calcite CaCO₃ (Cc) is also negligible in terms of mortar damage.

Basic parameters of the pore structure of the mortars are considered in Table 15. PC mortar is characterized by evident coarsening of the pore structure after 4 years of exposure to the sodium sulphate. This finding is proven by one order of increased permeability in contrast to water treatment. HC and SR mortars show no significant differences in the pore structure parameters after 5 years of exposure.

The insignificant detrimental effect of 5-year sulphate attack on HC and SR mortar is also proven by the permeability values, which remain for each mortar the
| Constituent | PC mortar | Contents of the constituents (% wt.) | SR mortar | HC mortar |
|-------------|-----------|--------------------------------------|-----------|-----------|
|             | 28-day BC + 4 years in H₂O | 28-day BC + 4 years in Na₂SO₄ | 28-day BC + 5 years in H₂O | 28-day BC + 5 years in Na₂SO₄ | 28-day BC + 5 years in H₂O | 28-day BC + 5 years in Na₂SO₄ |
| Ignition loss | 10.75 | 22.97 | 16.97 | 19.15 | 7.65 | 10.81 |
| SiO₂ | 60.81 | 50.63 | 45.85 | 42.98 | 68.65 | 55.67 |
| CaO | 22.90 | 7.52 | 30.82 | 28.19 | 7.50 | 10.00 |
| Al₂O₃ | 0.75 | 0.67 | 1.83 | 1.83 | 9.17 | 13.38 |
| Fe₂O₃ | 1.40 | 1.22 | 2.53 | 2.51 | 2.72 | 3.87 |
| MgO | 1.82 | 2.26 | 0.77 | 0.82 | 1.05 | 1.36 |
| SO₃ | 1.19 | 14.31 | 1.01 | 4.21 | 1.66 | 1.75 |
| Cl⁻ | 0.03 | 0.02 | 0.03 | 0.03 | 0.01 | 0.01 |
| Na₂O eq. | 0.06 | 0.05 | 0.10 | 0.22 | 1.51 | 2.46 |

Table 14. Chemical composition of PC mortar after 4 years and HC and SR mortar after 5 years of exposure in aggressive 5% Na₂SO₄ and reference water.
Figure 6.
Mineral composition of PC mortar after 28-day basic curing in water.

Figure 7.
Mineral composition of HC mortar after 28-day basic curing in water.

Figure 8.
TG-DTA plots of PC mortar after 28-day basic curing in water.
same in both exposure conditions (reference water vs. aggressive sulphate), while that of PC mortar is increased by one order even after 4-year exposure to sulphate attack.

Visual and microscopy observations support the previous finding that sulphate resistance of H-Cement is the same with that of the sulphate-resistant Portland cement. Visual observations prove that 5-year-old HC mortar is characterized by well-preserved structural integrity, while PC mortar is considerably destroyed in the sodium sulphate after 4 years of exposure (**Figure 15**).

The gypsum and ettringite presence is confirmed in PC mortar after 4-year exposure in the sodium sulphate, while the same reaction products are not detected in HC and SR mortar after 5-year exposure in Na\textsubscript{2}SO\textsubscript{4} (**Figure 16**). The property of high non-permeability, which is a consequence of the formed hydrate phase character, is a basic condition for the high chemical resistance of a mortar and, in the conveyed meaning of the word, also a concrete made of the same binder system as that which occurred in 5-year-old HC mortar.

**Figure 9.**
**TG-DTA plots of HC mortar after 28-day basic curing in water.**

**Figure 10.**
**XRD patterns of PC mortar after 4 years in 5% wt. sodium sulphate and water.**
Figure 11.
XRD patterns of SR mortar after 5 years in 5% wt. sodium sulphate and water.

Figure 12.
XRD patterns of HC mortar after 5 years in 5% wt. sodium sulphate and water.

Figure 13.
TG-DTA plots of PC mortar stored 4 years in 5% wt. sodium sulphate and water.
Degradation of the hydrate phase of cement-based composite by sulphate attack is characterized by the formation of gypsum $\text{CaSO}_4\cdot\text{H}_2\text{O}(\text{CSH}_2)$ together with ettringite $(\text{CaO})_3(\text{Al}_2\text{O}_3)(\text{CaSO}_4)_3\cdot32\text{H}_2\text{O}(\text{C}_8\text{AS}_3\text{H}_32)$. Gypsum is formed by the reaction of sulphate ions with $\text{Ca(OH)}_2$ or calcium silicate hydrate (C-S-H):

$$2 \text{OH}^- + \text{SO}_4^{2-} + \text{Ca}^{2+} \rightarrow \text{CSH}_2 \text{ or} \quad (1)$$
The formed gypsum binds to tricalcium aluminate (C₃A), in particular to ettringite, but also monosulphate (CaO)₃(Al₂O₃)(CaSO₄)12H₂O(C₄ASH₁₂) is secondary generated:

\[ \text{C₃A} + 3 \text{CSH₂} + 26 \text{H} \rightarrow \text{C₆AS₃H₃₂} \]  (4)

Ettringite formation is also accompanied by another minor reaction:

\[ \text{C₄ASH₁₂} + 2 \text{CSH₂} + 16 \text{H} \rightarrow \text{C₆AS₃H₃₂} \]  (5)

Reaction products of sulphate attack (gypsum and ettringite) are high-volume salts that cause destructive expansion of hydrated cement matrix. The tested H-Cement is specified by the major portion of the cement-less inorganic polymer (80% wt.) and the minor portion of the PC clinker (20% wt.). It contains a little C₃A and when hydrated no Ca(OH)₂. Therefore, just the composition of H-Cement is the cause of its high sulphate resistance because degradation processes, as described by Eqs. (1)–(5), cannot be applied with H-Cement use. Sulphate resistance of H-Cement is therefore regarded the same as sulphate-resistant CEM I 42.5 R-SR 0.

3.7 Concrete based on steel slag as aggregate

The temperatures and pressures in the testing laboratory autoclave were set according to the autoclave curves presented in Figure 17 in order to determine the volume changes of the concrete based on steel slag. The properties of the steel slag used for experimental research are shown in Tables 16 and 17. Figure 18 shows a gradual increase in the cube strength of concretes based on H-Cement and steel slag (HC concrete) as the aggregate compared with that consisting of PC with steel slag (PC concrete). HC concrete reports a smaller increase in strength, which equals that of PC concrete after 90 days of exposure in water. The characteristic concrete strength after 90 days in the case of the HC concrete and PC concrete is approximately the same, 38 MPa.

The gradual increase in the cube strength of concretes based on H-Cement is caused by the fact that the hybrid cement generates lower hydration heat during the
initial hydration and thus makes it possible to reduce the volume changes during setting and hardening of the concrete mixture based on steel slag.

Table 18 compares the average values of cube strengths after 28 and 90 days and prism strengths after 28 days from the first and second stages of the experiment.

When comparing the results of the cube strength from the first and second stage of the experiment, the next partial observations may be drawn:

Table 16.

*Values of bulk density and absorption power of steel slag with the fraction of 0/8 mm.*

| Constituent | Unit | Result | Uncertainty | Element | Unit | Result |
|-------------|------|--------|-------------|---------|------|--------|
| Na<sub>2</sub>O | % wt. | 0.46 | ±0.10 | V | mg/kg | 570 |
| MgO | % wt. | 10.2 | ±1.2 | Cr | mg/kg | 3900 |
| Al<sub>2</sub>O<sub>3</sub> | % wt. | 2.43 | ±0.27 | Ni | mg/kg | 25 |
| SiO<sub>2</sub> | % wt. | 13.7 | ±1.3 | Cu | mg/kg | 38 |
| P<sub>2</sub>O<sub>5</sub> | % wt. | 0.91 | ±0.09 | Zn | mg/kg | 63 |
| SO<sub>3</sub> | % wt. | 0.50 | ±0.06 | Sr | mg/kg | 130 |
| K<sub>2</sub>O | % wt. | <0.003 | | Zr | mg/kg | 140 |
| CaO | % wt. | 38 | ±2 | Nb | mg/kg | 67 |
| TiO<sub>2</sub> | % wt. | 0.29 | ±0.02 | Mo | mg/kg | 36 |
| MnO | % wt. | 3.02 | ±0.13 | Ba | mg/kg | 200 |
| Fe total | % wt. | 22 | | Ta | mg/kg | 110 |
| CaO free | % wt. | 2.34 | ±0.24 | W | mg/kg | 86 |
| — | — | — | — | Loss by annealing | % wt. | −0.74 |

Table 17.

*Results of chemical analysis of steel slag.*

Figure 17.

*Temperature-pressure conditions and concrete autoclaving time.*
After 28 days, HC concrete shows a lower strength by 1.2 MPa (4.1%).

After 28 days, PC concrete shows a lower strength by 5.4 MPa (15.6%).

After 90 days, HC concrete shows a lower strength by 5.0 MPa (13.0%).

After 90 days, PC concrete shows a lower strength by 6.5 MPa (17.1%).

It is therefore evident that:

- The difference between the prism strength of HC concrete is 4 MPa (13.8%).
- The difference in prism strength of PC concrete is 0.9 MPa (2.8%).

The results of durability tests of the concrete based on steel slag showed the suitability of H-Cement as a binder for the production of the concrete based on steel slag in an environment with a higher temperature and pressure. The above-stated fact is well-confirmed by Figure 19, where the comparison of test specimens after the autoclaving process is shown. The PC concrete with steel slag as aggregate was disintegrated into rubbles, while that composed of H-Cement remained compact and without any apparent damage. The autoclaving process (see Figure 17) of concrete containing steel slag and CEM I (PC concrete) resulted in a disruption of the cement compound due to shrinkage with increasing temperature. The autoclaving process accelerated the calcium disintegration and the magnesium disintegration of steel slag, which is associated with volume changes. This process has caused the disintegration of the test specimens. The autoclaving process of concrete

![Figure 18. Average values of cube strengths from the first stage of the experiment.](image)

| Age of concrete | HC concrete (MPa) | PC concrete (MPa) |
|-----------------|-------------------|-------------------|
|                 | First stage       | Second stage      | First stage | Second stage |
| Cube 28 days    | 29.1              | 27.9              | 34.6        | 29.2         |
| Cube 90 days    | 38.4              | 33.4              | 38.0        | 31.5         |
| Prism 28 days   | 29.0              | 25.0              | 31.2        | 32.1         |

Table 18. Comparison of cube and prism strengths after 28 and 90 days from the first and second stage of the experiment.
containing steel slag and H-Cement (HC concrete) has eliminated the volume changes of the steel slag (calcium and magnesium expansion). There was no disruption of the cement compound and the contact zones between the grain of steel slag and the cement compound. This is confirmed by an increase in the concrete strength after the autoclaving process from 29.1 to 43.0 MPa (increase by 32%).

4. Conclusions

From the results of our experimental investigation, it is possible to formulate the following conclusions:

a. H-Cement with the composition that is found to be outside of the EN 197-1 can be used similarly to traditional cements of medium-strength classes like 32.5R and 42.5N and for high long-term flexural strength. No kind of additional heat treatment during early and later hydration is needed.

b. H-Cement is suitable for use in ready-mixed concrete up to C30/37 strength class with a variety of plasticizers, which are compatible with it in the same way as traditional cements. Lignosulfonate-based and combined lignosulfonate-polycarboxylate plasticizers have been found to be the best in terms of workability of fresh mixtures standing for 60 min.

c. H-Cement has under the conditions tested shrinkage-reducing properties. Shrinkage-reducing effect is also recorded in cement blends at replacement level of H-Cement by 5–15% wt. PC. No shrinkage-reducing admixture is necessary in concrete when H-Cement is used.

d. H-Cement has under the conditions tested ASR-mitigating property. The expansion of concrete is also suppressed when using cement blend with replacement level of PC by 30% wt. H-Cement.

e. High sulphate resistance of H-Cement is the result of a special composition; sulphate resistance of H-Cement was found by a 5-year test, the same with that of sulphate-resistant CEM I 42.5 R-SR 0.

f. H-Cement is suitable for use in concrete with 100% replacement of natural aggregate by the artificial steel slag aggregate. No detrimental processes leading to disintegration of such concrete exposed to high temperature and pressure were recognized.
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Conflict of interest

The authors do not register any conflict of interest.

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