Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 29 (1999) 1635–1640

Properties and hydration products of lightweight and expansive cements Part I: Physical and mechanical properties

Vili Lilkov[a,*], Nikola Djabarov[b], Georgi Bechev[a], Konstantin Kolev[a]

[a]University of Mining and Geology, Department of Physics, 1100 Darvenitza, 1100 Sofia, Bulgaria

[b]Central Laboratory of Physico-Chemical Mechanics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Received 16 January 1999; accepted 24 June 1999

Abstract

Results from studies on the physical and mechanical properties of lightweight and expansive cements cured at 20 and 75°C are presented. Lightweight additive (cenospheres from thermoelectric power station "Bobov Dol," Bulgaria) and expansive additive ("Bulexa" with hydroxide type of expansion) were used. The compressive and flexural strength, the gas and water impermeability, and the pore structure of the cement stone of lightweight and expansive cements were investigated. The results are compared with corresponding parameters of cement stone without additives. It was found that the cenospheres are appropriate lightweight additives. The use of expansive additive helps overcome the dry shrinkage of cement stone and strengthens the bond with the bounding surfaces.

Keywords: Cement paste; Expansion; Cenospheres; Physical properties; Thermal treatment

1. Introduction

The great variety of geological, physical, and technological conditions that exist in the drills induce, in the course of their cementation, the use of plugging cement slurries appropriate for each specific case. In all cases the requirements are predominantly toward low density and low viscosity (in order to lower the energetic losses during cementation), low gas and water permeability, and strong bond of the cement paste to the walls of the drill-hole and the casing column [1].

The most common way to obtain lightweight plugging cements is to increase the water content or to add lightweight additives such as diatomite, perlite and bentonite, which display a very high water requirement [2]. The increase of the water/cement ratio results in lowered strength values and increased permeability of the cement stone.

Cenospheres are lightweight additives with low water requirement and low volume density. Their incorporation in cement, alone or in combination with expansive additive, allows a decrease of the density of plugging cements without significantly changing the concentration of the hardened cement paste.

* Corresponding author. Tel.: +359-29-88-53-80; fax: +359-29-62-49-40.

E-mail address: lilkov@staff.mgu.bg (V. Lilkov)

2. Materials and methods

The cenospheres (CS) were a waste material from TEPS "Bobov Dol" (Bulgaria). They were hollow silicate bodies with mass density of 350 to 500 kg/m^3 for the various fractions. Their hardness was 5–6 (according to the Mohs scale). The bigger spheres were grey in color with a porous surface (Fig. 1a) and the smaller ones were white in color with a smooth and dense surface (Fig. 1b). Two fractions of the cenospheres with maximal diameter of 2 and 0.2 mm, designated A and B, with specific surface (according to the Brunauer-Emmet-Teller method) of 767 m^2/g and 450 m^2/g, respectively, were used. Data from the granulometric analysis are shown in Table 1. The emission spectral analysis showed that in the composition of the cenospheres different chemical elements were included but only the quantities of Si, Fe, Al, O, Ca, and Mg exceeded 1 wt%. Table 2 contains data from the X-ray fluorescence analysis.

The water requirement of the cenospheres, $K_A = 0.6$ and $K_B = 0.9$, was determined by testing with the cone of AzNII, according to the equation [3]: $m_w = K_c \cdot m_c + K \cdot m_{cs}$, where m_w, m_c, and m_{cs} are the masses of water, cement, and cenospheres in the cement paste with 21-cm spread. $K_c = 0.55$ is the water requirement for both type of cements to obtain plain cement paste with the same spread.

The expansive additive used was "Bulexa" with a hydroxide type of expansion [4]. The reason for using this ex-

0008-8846/99/$ – see front matter
PII: S0008-8846(99)00150-7

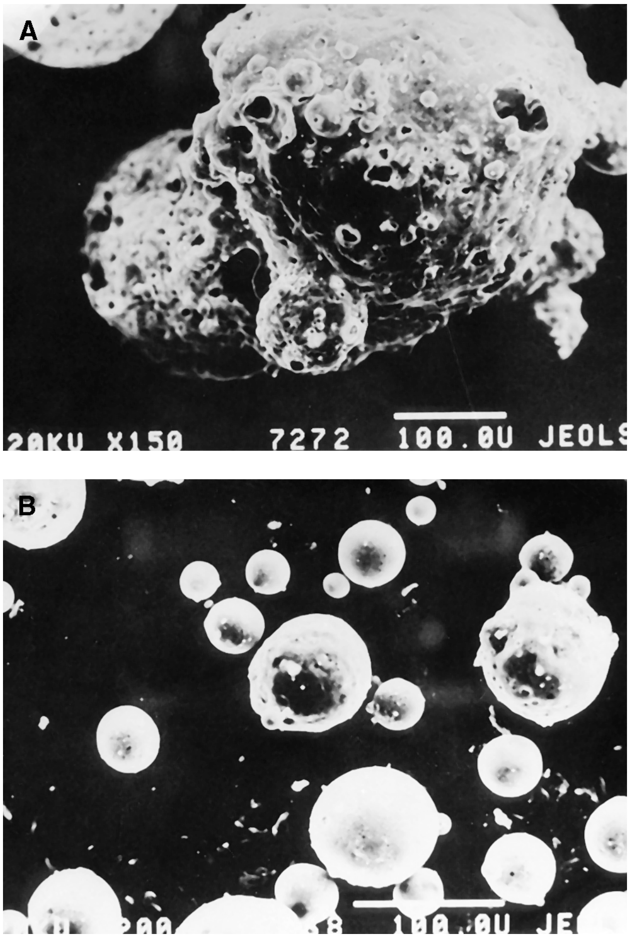

Fig. 1. Scanning electron micrographs of the cenospheres.

pansive additive instead of an ettringite-forming base is because ettringite formation reactions need a greater water quantity to obtain almost the same expansion at equal doses. Moreover, the ettringite crystallization principally takes place in the large pores and capillaries due to its much greater molar volume compared to the calcium hydroxide one. The products of hydroxide expansive additives fill the porous structure, crystallizing in the fine pores of the cement stone.

Two types of cements, PC 45 and PC 35, with specific grain surface of 420 and 314 m^2/g, respectively, were used. The strength properties were determined by testing $40 \times 40 \times 160$-mm prisms (for cement pastes with PC 45) and cylinders with diameter equal to the height (46 or 52 mm) (for cement pastes with PC 35). Two curing regimes were chosen. In the first, the samples were cured for 24 h under air dry conditions and after remoulding were cured in water (20°C). In the second, after 4 h of air hardening, the samples were placed underwater at 75°C. Remoulding of the specimens with expansive additive and specimens hardened at 75°C occurred at the sixteenth hour of hardening.

Table 1
Granulometric analysis of CS

Effective diameter of particles (fraction A) in the interval (mm)	<0.2	0.2–0.50	0.50–2	>2
Mass percents	8.40	80.1	10.8	0.7
Effective diameter of particles (fraction B) in the interval (μm)	<10	10–100	100–150	>200
Mass percents	0.9	57.9	29.4	11.8

Table 2
X-ray fluorescence analysis of CS

Fraction	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Others
A	58.6	21.5	8.5	2.2	2.6	6.6
B	59.2	24.4	7.5	1.6	2.7	4.6

Water impermeability of cements was determined on a series of six samples with the form of a truncated cone with diameter of the bases of 60 and 50 mm and height 20 mm. The water impermeability class (in atmosphere) was determined by the maximum water pressure on the front walls of the samples from a given series when at least four samples remained dry on their back walls. The maximal water pressure by this method is 8 atm.

The gas permeability was measured following the method of CO_2 gas stationary filtration at two different levels of gas pressure (taking under consideration the effect of Klinkenberg, typical for gas filtration in capillary media). The test was conducted by equipment similar to GK-5 (Oil Equipment, Moscow, Russia) on a series of cylindrical samples with diameter equal to the height (30 mm).

Until tested for gas and water permeability, the samples were kept in water. Before the tests samples remained at room temperature for 3 h and then were dried for another 3 h at 50°C. The structure of the pore space was determined by machinery of instrumental porosimitry (Milan, Italy) “Karlo Erba” on pieces from cement prisms after the compressive strength test at day 28 of hydration.

The bond of cement stone B with a metal ring and a rock sample (core) imitating the working conditions of the plug-

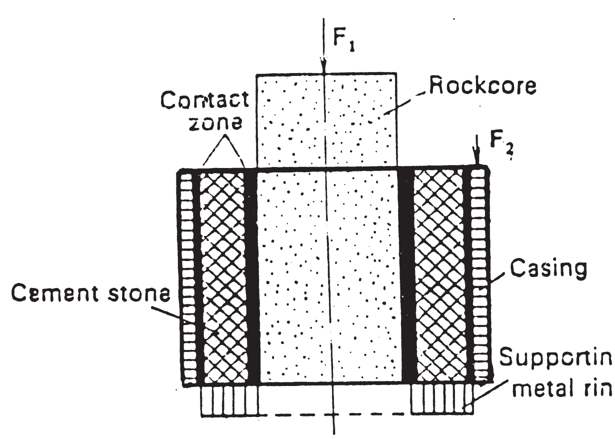

Fig. 2. Test for determination of the cement stone bond.

Table 3
Physical properties of cements hardened at 20°C

No.	PC (%)	CS (% of cement) A	B	W/S ratio	Density (kg/m^3)	Spreading (cm)	Water release (%)	Time of setting (h-min) Start	End
1	100	–	–	0.55	1770	21	3.7	8-00	9-10
2	100	10	–	0.55	1580	20.5	0.9	8-20	9-30
3	100	15	–	0.56	1540	21	0.5	8-30	9-50
4	100	20	–	0.57	1480	21	1.1	–	–
5	100	–	5	0.57	1610	20	1.8	–	–
6	100	–	10	0.58	1540	21	2.8	8-40	10-00
7	100	–	15	0.60	1510	21	2.9	8-45	10-45

Table 4
Strength characteristics of cements hardened at 20°C (PC 45)

No.	Flexural strength (MPa) Day 2	Day 7	Day 28	Day 90	Compressive strength (MPa) Day 2	Day 7	Day 28	Day 90
1	2.9	5.8	7.6	7.7	14.3	32.6	43.2	44.8
2	2.7	5.6	6.8	6.7	17.9	30.6	39.5	39.1
3	2.7	5.1	6.9	7.2	18.6	36.2	38.8	38.7
4	2.6	5.1	6.1	–	16.9	33.3	36.3	–
5	2.7	5.8	7.1	–	14.5	32.1	40.0	40.5
6	2.4	5.8	7.1	–	13.7	33.8	41.8	40.9
7	2.2	4.3	6.0	6.0	11.9	30.4	32.4	31.7

Table 5
Gas permeability and pore structure of cements hardened at 20°C (PC 45)

No.	Gas permeability (md) after hardening Day 2	Day 7	Day 14	Day 28	Pore size distribution in the cement paste (%) according to effective radius (μm) after 28 days <0.01	0.01–0.1	0.1–1	>1	Specific pore volume (cm^3/g)
1	37	6	2.2	0.8	7.0	35.7	43.5	13.8	0.20
2	33	15	4.4	1.0	7.7	26.7	44.2	20.9	0.27
3	36	17	5.2	3.2	7.4	29.6	36.2	26.8	0.31
6	53	31	10	2.1	7.2	26.9	43.0	22.9	0.28
7	69	–	8.5	3.3	7.0	36.7	30.8	25.5	0.34

ging cements in drill holes was determined following the scheme shown in Fig. 2. The numeric values of the bond (*B*) is determined on the base of the force (*F*) at which the relative movement of the metal ring and, respectively, the core in relation to the cement stone starts according the equation: $B = F/S$, where *S* is the area of their contact surface.

3. Results and discussion

Table 3 contains the compositions and some of the physical parameters of lightweight and plain cements. With the increase of the quantity of lightweight additive, the densities of the samples were lowered from 1770 to 1480 kg/m^3 and the water release, determined at the third hour after their preparation, is lower than 5%, the maximum allowed by Bulgarian Standard 8996-71. The times of setting satisfy the same standard; with the increase of the cenospheres quantity the start of the setting as well as its end tended to be delayed.

The lightweight cements had lower strengths compared to plain cement (Table 4). The differences are better outlined on the day 28 of hydration with almost the same values preserved until day 90. Some of the lightweight compositions displayed quick growth of the compressive strength up to day 2 (compared with plain cements), followed by equalization of the strengths up to day 7. The reason is probably the fact that in the early stages of hydration, the main

Table 6
Bond of cement paste with rock sample (B_R) and metal ring (B_C), after hardened at 20°C (PC 45)

No.	B_R (MPa) Day 2	Day 28	B_C (MPa) Day 2	Day 28
1a	0.30	1.88	0.41	0.61
2a	0.31	1.56	0.39	0.53
3a	0.30	1.72	0.37	0.57
4a	0.26	1.04	0.29	0.45

Table 7
Physical properties lightweight and expansive cements

No.	PC 35 (mass %)	CS (A) (mass %)	EA (mass %)	W/S ratio	Spreading (cm)	Water release (%)	Free linear expansion (%)		
							Day 3	Day 7	Day 28
1a	100	–	–	0.55	21	5.0	–	–	–
2a	100	15	–	0.54	22	2.0	–	–	–
3a	100	15	2.5	0.54	22	1.7	0.183	0.224	0.227
4a	100	15	1.8	0.54	22	1.7	0.150	0.168	0.170
5a	100	15	1.2	0.54	22	1.7	0.072	0.088	0.092

Table 8
Strength characteristics of lightweight and expansive cements (PC 35)

	Tensile strength (MPa)		Compressive strength (MPa)			
	Day 2	Day 28	Day 1	Day 2	Day 7	Day 28
Hardening temperature, 20°C						
No. 1a	0.86	3.94	–	3.10	–	13.3
No. 2a	0.74	3.42	–	2.60	–	12.6
No. 3a	0.84	2.10	–	3.20	–	8.0
No. 4a	–	–	–	2.64	–	10.3
No. 5a	1.12	3.83	–	3.70	–	14.9
Hardening temperature, 75°C						
No. 1a	1.90	7.85	7.10	9.80	15.90	17.40
No. 2a	1.96	8.00	7.90	11.10	18.00	18.45
No. 3a	1.53	4.10	5.10	6.10	–	9.40
No. 4a	1.85	6.20	7.60	9.40	–	12.00
No. 5a	–	7.30	8.20	10.50	–	14.80

role in strengthening is played by the cenospheres and they act as energy dissipating inclusions [5]. On the other hand, in the early stage of hydration a mechanical bond between the hydration products of cement with the surface of the cenospheres exists and epitaxial growth of hydration products at the CS surface is realized [6].

At respective ages the gas permeability of all lightweight cements is higher than that of the plain cement (Table 5). For all compositions, the gas permeability values at day 28 of hydration are less than 4 milidarsi (md), which guarantees low gas filtration [1]. At the age of 28 days only the plain cement displays the maximal class of water impermeability. At day 90 all cement compositions have maximal water impermeability class.

The addition of cenospheres increases the relative portion of large pores ($R > 1$ μm) in the cement stone as well as the specific pore volume (Table 5). At the same time, with the increase of the cenospheres quantity, the part of pores with effective radius in the interval ($0.1 - 1$ μm) lowers and that of the pores with radius in the interval ($0.01 - 0.1$ μm) increases, but the gel pores portion remains unchanged.

At day 2 of hydration the bond of lightweight cement No. 2 does not differ from the bond of cement No. 1, while for cement No. 6 it is lower (Table 6). At day 28 of hydration the plain cement No. 1 displayed the strongest bond and composition No. 6 displayed the weakest.

The differences in the strength, permeability, and bond of cements made lightweight with cenospheres of fractions A and B, respectively, can be explained by the features of the contact zone, which forms between the cenospheres and the cement matrix. It is known that in the case of lightweight additives with highly porous surface (as are the majority of cenospheres from fraction A), the contact zone is more dense and homogeneous compared to those between the smooth and nonporous surface of the fine cenospheres and the cement matrix [7]. Moreover, the mechanical adhesion between the cement paste and the highly porous cenospheres significantly strengthens the obtained contact between them.

Table 7 contains the compositions of expansive cements lightened with cenospheres of type A, those of lightweight cement without expanding additive, and plain cement; all show equal spreading. The expanding additive lowers the water release of the cement. The linear expansion of cement compositions is manifested in the first days of hardening and practically ended by day 7. By varying the quantity of the expanding additive a controlled expansion can be achieved.

Table 9
Bond of the cement paste with a metal ring (B_C), hardened at 20°C for 28 days (PC 35)

No.	B_C (MPa)	Percent
1a	0.71	100
2a	0.56	79
3a	1.53	214
4a	1.80	252

Table 10
Pore structure of cement stone of lightweight and expansive cements (PC 35)

Pore size distribution in the cement stone (percentage) according to effective radius in the intervals (μm)					
	<0.01	0.01–0.1	0.1–1	1–50	Specific pore volume (cm^3/g)
Hardening temperature, 20°C, day 2 of hydration					
No. 1a	7	23	43.5	26.5	0.320
No. 2a	4	20	43.5	32.5	0.412
No. 4a	6	21	43	30	0.393
No. 5a	7	26	45	22	0.520
Hardening temperature, 20°C, day 28 of hydration					
No. 1a	17	42	34	7	0.282
No. 2a	9	35.5	40	15.5	0.360
No. 4a	8	26.5	38	27.5	0.446
No. 5a	10	51.5	25	13.5	0.380
Hardening temperature, 75° C, day of hydration					
No. 1a	13	52	34	1	0.191
No. 2a	13	48.5	32.5	6	0.300
No. 4a	12	52	32	4	0.457
No. 5a	13.5	55.5	27	4	0.360

The strengths of the lightweight expansive cements are lower compared to those of the plain cement (Table 8). Only the composition 5a (with the lowest quantity of expanding additive) has higher strength due to the lower value of relative expansion (<0.1%). Hardening at 75°C leads to strength increase that is better expressed in lightweight cements without expansive additive. The reason for the lowering of strengths of the expansive cements with the increase of the expanding additive is the fact that the hardening takes place in unrestricted conditions. There are no limits from outer factors and the expansion is dependent only on the strength of the cement paste, and therefore EA doses that cause expansion lower than 0.1% are optimal. In the case of restrictive conditions (as is the case of casing column in a drill hole) the quantity of EA can be increased because the deformations of the cement paste are not displayed outside and a self-sealing of the cement paste structure is achieved [8].

Doses of expanding additive of 2.5 and 1.8% from the cement mass lead to increase of the casing bond of 2.5 and 2.1 times, respectively, in comparison to the plain cement stone (Table 9).

The specific pore volume of the cement compositions increases with the quantity of the expanding additive due to the nonrestricted conditions of expansion (Table 10). At 20°C hardening temperature, the greatest (29%) increase of the relative part of the micropores ($R < 0.1$ μm) between day 2 and day 28 of hydration was found for the composition with minimum quantity of expanding additive, as well as for the cement without additives. For this reason the expansive lightweight cement (No. 5a) increases its strength between day 2 and day 28; the increase of the micropores portion does not allow the deformation due to expansion to overcome the strength (i.e., the restriction features of the cement paste). On the contrary, in the case of composition with greater quantity of expanding additive the growth of this parameter up to day 28 is lowest (7.5%).

For all cement pastes hardened at 75°C, a lower specific pore volume was observed. At day 28 the ratio of the quantity of pores with $R < 0.1$ μm to those with greater radius is as follows: composition No. 1a, 65:35; No. 2a, 61.5:38.5; No. 4a, 64:36; and No. 5a, 69:31. At the same age and 20°C hardening temperature these ratios are: composition No. 1a, 59:41; No. 2a, 44.5:55.5; No. 4a, 34.5:66.5; and No. 5a, 61.5:38.5.

Obviously, the raised hardening temperature helps the formation of more fine pore structure, especially for the lightweight cements. This is due to the chemical reaction between the cenospheres and the Portlandite, the main constituent of the transition zone, which leads to a more denser contact [5,6,9].

4. Conclusions

1. The use of cenospheres as an additive in cements makes them significantly lighter with lowered water release, especially in the case when expanding additive is used.
2. The expanding additive “Bulexa” causes a dose-controlled expansion to the lightweight cement compositions.
3. The lowered strengths of the cement paste that accompany the making cements lightweight are successfully compensated for at higher temperature of hardening.
4. In hardening at nonrestricted conditions the quantity of EA must be related to a free linear expansion below

0.1%. In real restricted conditions of hardening the dose can be increased because a self-sealing of the cement stone structure is realized.

5. Making cement lightweight leads to an increase of the permeability of the cement stone. The inclusion of expanding additive and the increase of the hardening temperature results favourably on the porous structure of the lightweight cements: the micropores portion increases, the bond of the cement stone with the contact surfaces gets stronger, and the specific pore volume lowers.

References

[1] V. Danjushevski, Design of optimal compositions of the plugging cement slurries, Nedra, Moscow, 1978 (in Russian).

[2] V. Danjushevski, I. Tolstih, V. Milshtein, A summary guide on plugging materials, Nedra, Moscow, 1973 (in Russian).

[3] N. Lucenko, O.I. Obrazcov, Lightweight plugging cement slurries, Nedra, Moscow, 1972 (in Russian).

[4] N. Djabarov, Expansive additive for cements, cement mortars and concretes, Bulgarian patent #72240, 1985.

[5] D. Montgomery, S. Diamond, The influence of fly-ash cenospheres on the details of cracking in fly-ash bearing cement pastes, Cem Concr Res 14 (1984) 767–775.

[6] R. Zimbelmann, A contribution to the problem of cement-aggregate bond, Cem Concr Res 15 (1985) 801–808.

[7] P. Mehta, P.J. Montiero, Material Research Society Symposium Proceedings, Bonding in Cementitious Composites, Boston, Vol. 114, 1987, p. 65.

[8] N. Djabarov, Cement composite material with regulated expansion, D.Sc. Thesis, Bulgarian Academy of Sciences, Sofia, Bulgaria, 1990 (in Bulgarian).

[9] M.-H. Zhang, O.E. Gjorv, Pozzolanic reactivity of lightweight aggregates, Cem Concr Res 20 (1990) 884–890.