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Properties and hydration products of lightweight and expansive cements
Part II: Hydration products

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Abstract

The type and quantity of hydration products in cement stone (plain cement, lightweight cement with cenospheres, and cement mixed with expansive additive) hydrated at 20 and 75°C were studied. The changes in the cement stone structure under the influence of lightweight and expansive additives and raised hardening temperature were studied with complex thermal analysis, infrared spectroscopy, powder X-ray diffraction analysis, and scanning electron microscopy. In the case of raised hardening temperature, the cenospheres and the expansive additive improve the crystallization of hydration products. A chemical reaction between the cenospheres and portlandite formed from the cement hydration was observed, accompanied by a decrease of the portlandite quantity. The expansive additive stimulates the formation of hydration products, which were thermally stable and decompose at temperatures above 600°C.

Keywords: Cement paste; Hydration products; Expansion; Cenospheres

1. Introduction

The main principle in the design of lightweight (LW) cements is the use of additives with low volume density, low water requirement, and low water release, which actively participate in the formation of the strength properties of the cement stone [1]. The cenospheres (CS) from TEPS "Bobov Dol" are a porous filler with low volume density and high hardness and a water requirement comparable to that of cement. Their addition to cement results in a significant weight decrease of the cements but increases the permeability and lowers the strength of the cement paste. At raised hardening temperature and with combination of the cenospheres with expansive additive (EA), the structure is tightened and the strength and the bond of cement paste with the bounding surfaces are increased.

The present paper investigates the hydration products in lightweight (with CS) and expansive lightweight (with CS and EA) cements with hardening temperatures of 20 and 75°C.

2. Materials and methods

The cement (PC) used was type PC 35D with grain specific surface of 314 m^2/g (Brunauer-Emmet-Teller method) and fraction on sieve 49,000 mesh/cm^2 of 12.4%. CS were a waste product from TEPS "Bobov Dol" (Bulgaria) with maximal grain diameter of about 2 mm and specific surface of 767 m^2/kg. EA was Bulexa [2] with a hydroxide type of expansion, which was used in three different doses (in the ratio 1:1.5:2).

The samples studied (Table 1) were placed in plastic containers immediately after preparation. Two curing regimes were chosen, at 20 and 75°C. Before analyses the samples were dried and the hydration process interrupted by soaking the samples in acetone and ether.

The powder X-ray diffraction (XRD) analysis was performed on a DRON 3M diffractometer (Burevestnik, Leningrad, Russia) with Ni-filtered CuK_α radiation (34 kV accelerated voltage and 20 mA electric current) and detector scanning speed of 2°/min (2ϑ). Infrared (IR) spectroscopic analysis was performed on a "Specord 75 IR" equipment (Carl Zeiss, Jena, Germany) on samples weighing 1 mg mixed with 300 mg of KBr to form 0.8-mm thick tablets. The registration time was 4.4 min per sample. Complex

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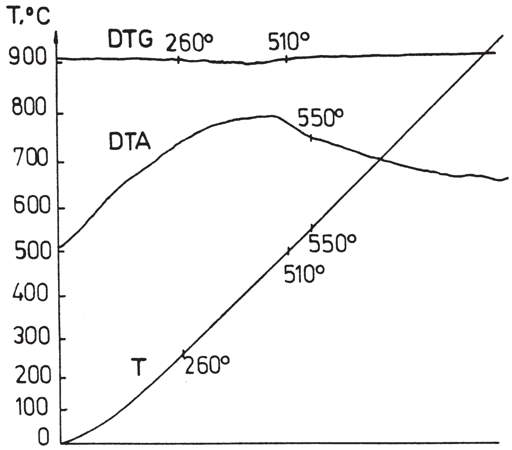

Fig. 1. DTA/DTG curves of the CS used.

Table 1
Composition and physical characteristics of the cements

No.	Composition (mass %) PC	CS	EA	W/S ratio	Density (kg/m^3)	Free linear expansion (% after hardening) Day 3	Day 7	Day 28
1	100	–	–	0.55	1,800	–	–	–
2	100	15	–	0.54	1,560	–	–	–
3	100	15	2.5	0.54	1,580	0.183	0.224	0.227
4	100	15	1.8	0.54	1,580	0.149	0.168	0.170
5	100	15	1.2	0.54	1,580	0.072	0.088	0.092

thermal (DTA/DTG) analysis was done on a MOM 3427 derivatograph (Magyar Optikai Uüvek, Budapest, Hungary) at 10°C/min heating rate in the 20–1000°C temperature range. Scanning electron microscopy (SEM) micrographs were taken on an SEM "Jeol" equipment (Jeol, Tokyo, Japan) in a secondary electron emission regime.

3. Results and discussion

The DTA/DTG analysis of the cenospheres showed about 2 wt% total weight loss during heating (up to

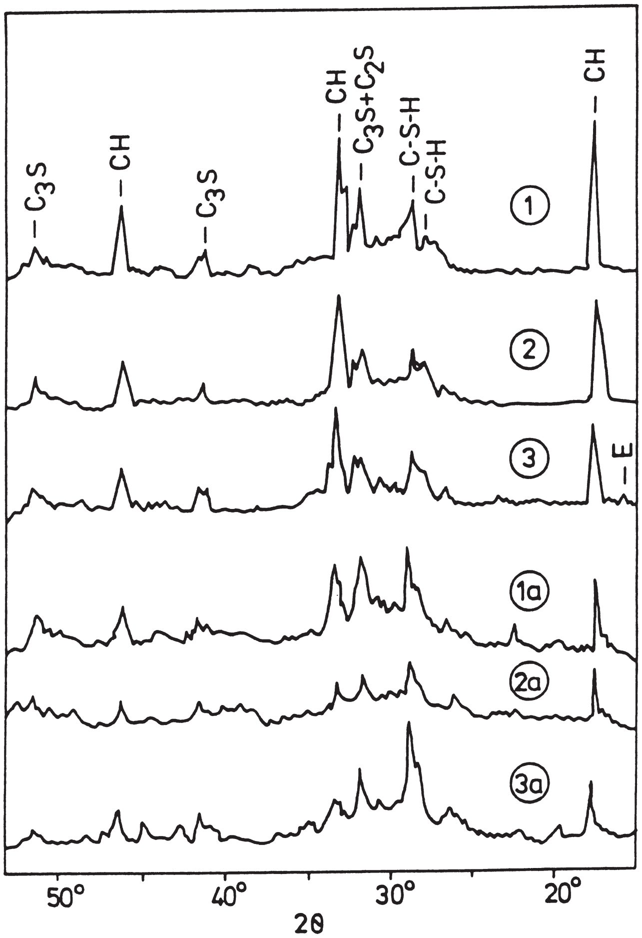

Fig. 2. XRD patterns of plain (1, 1a), LW (2, 2a), and LW with EA (3, 3a) cements hardened for 28 days at 20 and 75°C, respectively.

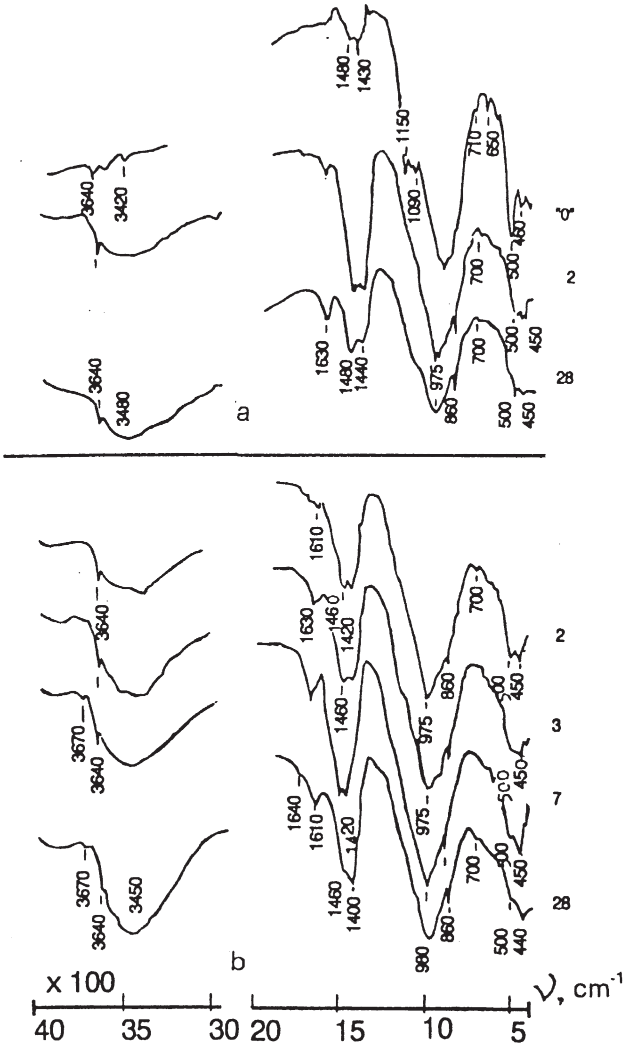

Fig. 3. IR spectra of LW cement without EA hydrated at 20°C (a) and 75°C (b); 0 = nonhydrated cement.

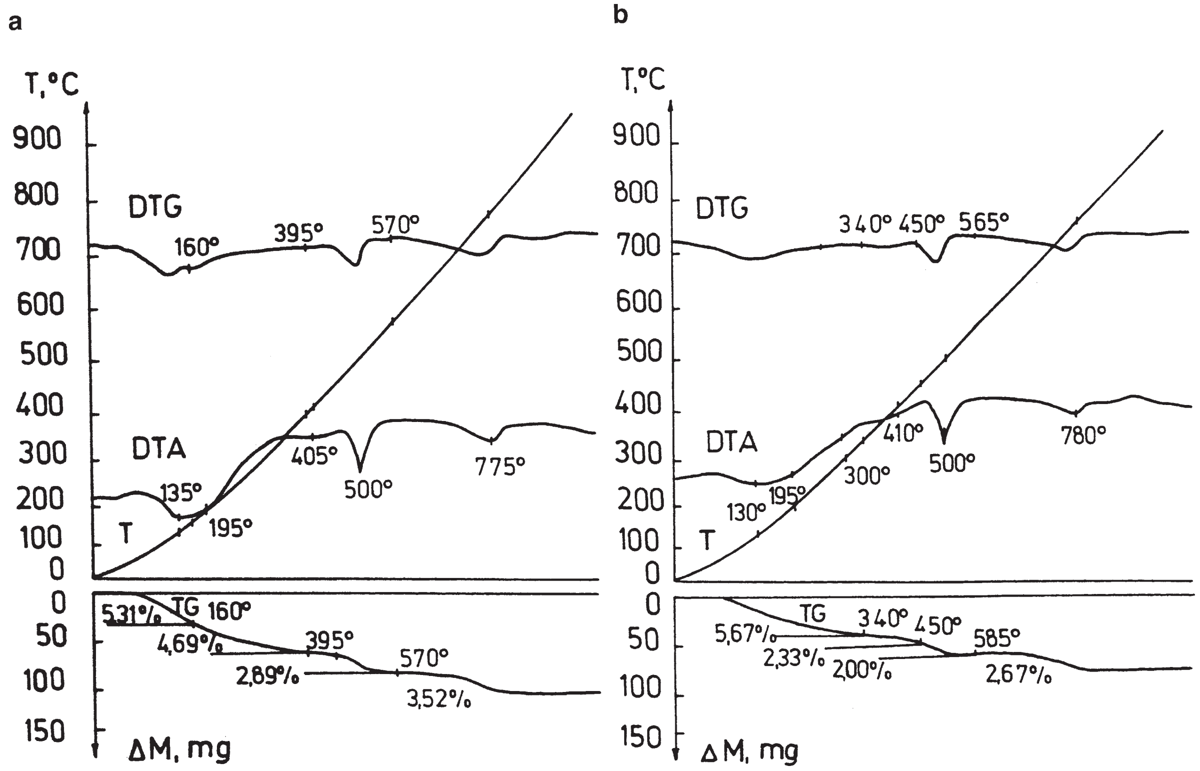

Fig. 4. DTA/DTG curves of plain (a) and LW (b) cements (day 28 of hydration at 20°C).

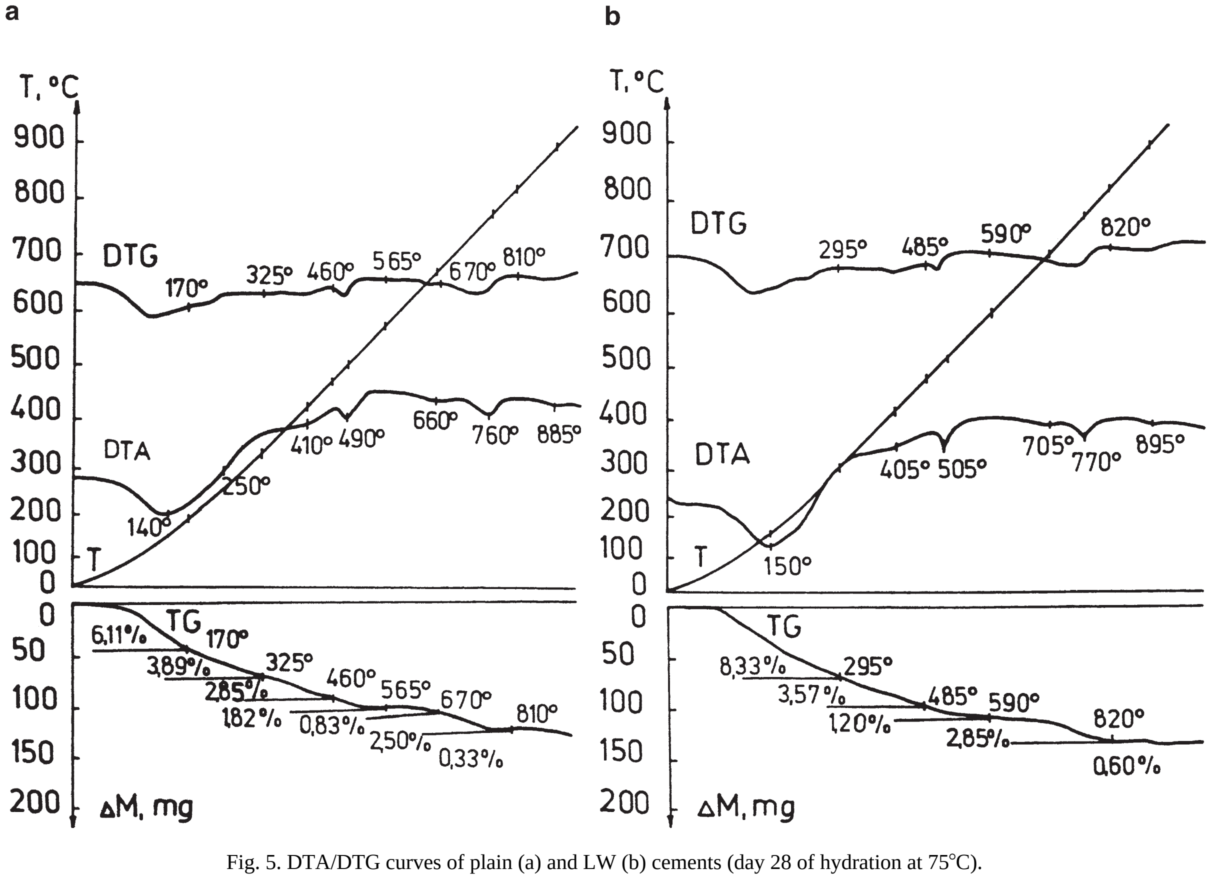

Fig. 5. DTA/DTG curves of plain (a) and LW (b) cements (day 28 of hydration at 75°C).

Table 2
Weight loss of plain and LW cements hardened for 28 days at 20 and 75°C

No.	Hardening temperature (°C)	Weight loss (mg/g cement) in the temperature interval (°C)			Total weight loss during heating (mg/g cement)
		20–450	450–590	590–1000	
1	20	162.6	37.2	54.6	254.4
2	20	135.2	33.8	45.1	214.1
1	75	199.2	28.2	56.7	284.1
2	75	201.1	20.3	58.3	279.7

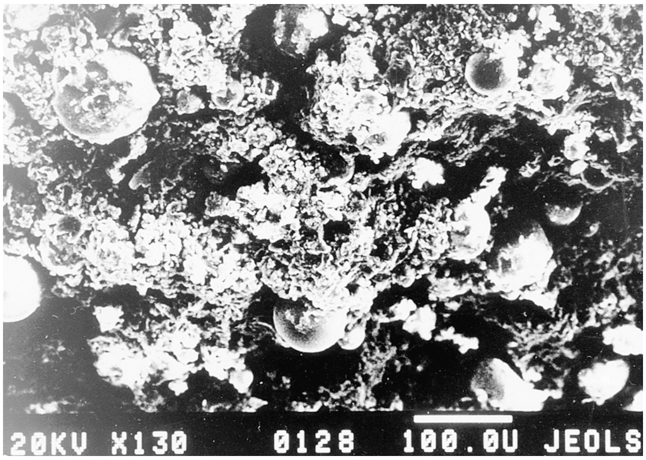

Fig. 7. SEM micrograph of LW cement stone (day 2 of hydration).

1000°C). A broad exothermal effect was registered in the 260–510°C temperature interval (Fig. 1), which probably was due to burning of residual organic particles, a result of poor purification of CS, as well as iron oxidation (at 294°C).

From IR and XRD analyses it was concluded that the main crystalline phases of the cenospheres are quartz, mulite, α-Fe_2O_3, and γ-Al_2O_3.

The XRD powder patterns of plain and lightweight cements and cements with EA, hardened for 28 days at temperatures of 20 and 75°C, are represented in Fig. 2. Well crystallized ettringite (E) was registered only in the patterns of cement with EA hardened at normal temperature. The peaks characterizing calcium silicate hydrates (C-S-H) are better expressed in the patterns of cements hardened at 75°C, especially in the case of cement with EA. The portlandite peaks are most intense in the patterns of plain nonlightweight cement.

IR spectra of lightweight cement without EA, hydrated at 20 and 75°C, are shown in Fig. 3. The bands characteristic for C-S-H (ν = 975–980 cm^{-1}) and sulfoaluminate hydrates (ν = 3450 and 3480 cm^{-1}) [3,4] of the cement hardened at 75°C are more intense. The portlandite band (ν = 3640 cm^{-1}) is more intense in the spectrum of cement hardened at normal temperature. After hydration for 7 days at 75°C, a band characteristic of the cubic calcium aluminate hydrate (ν = 3670 cm^{-1}), which crystallizes above 40°C [5], was registered. The absorption bands with maxima about ν = 1430–1440 and 860 cm^{-1} correspond to the presence of calcite.

The results of the DTA/DTG analyses of plain and lightweight cements after 28 days of hardening at 20 and 75°C are shown in Figs. 4 and 5, respectively. It can be seen that the endothermal effects are displayed at higher temperatures in the case of hardening at 75°C. In the two cements hardened at this temperature a new endothermal effect appeared in the range of 810–910°C, which is related to calcite and C-S-H phases. The hydration products in the cement stone are specified in three groups according to the weight loss for

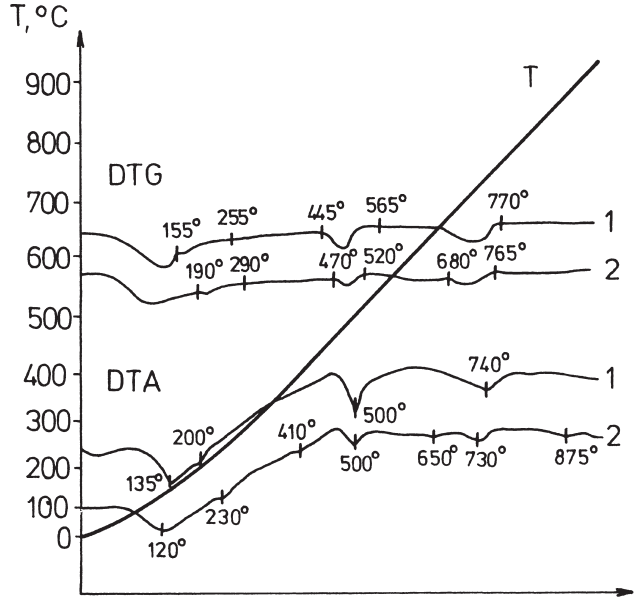

Fig. 6. DTA/DTG curves of LW cement with EA (composition 4) at day 28 of hydration at 20°C (1) and 75°C (2).

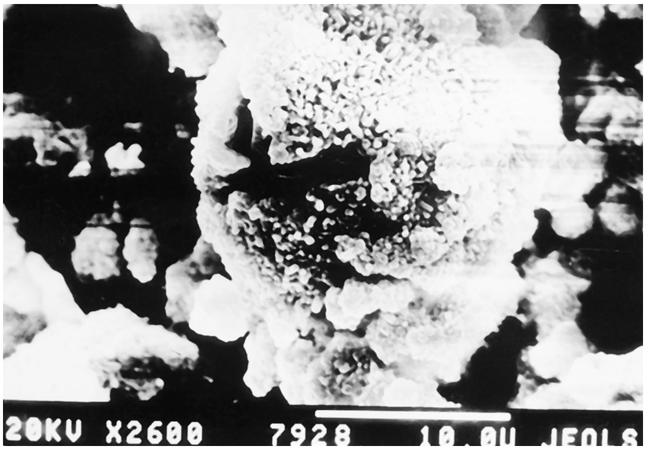

Fig. 8. SEM micrograph of CS-hydration shell (day 2 of hydration, 20°C).

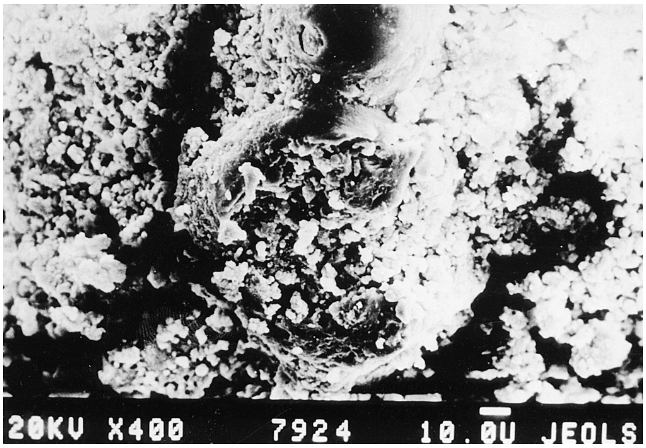

Fig. 9. SEM micrograph of a “cenospheres cement stone” contact (day 2 of hydration, 20°C).

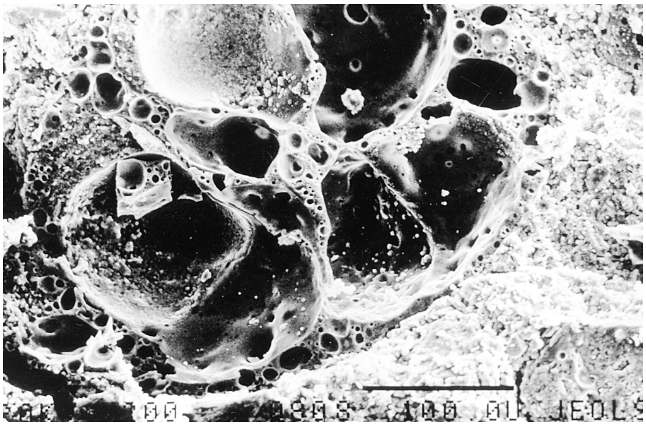

Fig. 11. SEM micrograph of LW cement without EA (day 2 of hydration, 75°C).

a specific temperature interval [6]. The first group includes newly formed phases characterized by dehydration in the temperature interval 20–450°C: ettringite, C-S-H, and C-A-H phases. The endothermal effect at around 500°C corresponds to portlandite. Furthermore, above 600°C the effects are due to decomposition of C-S-H and calcite. When the hardening temperature is raised from 20 to 75°C, the total quantity of hydration products in plain and LW cements (on a unit mass of cement) increases 1.12 and 1.31 times, respectively (Table 2), and the quantity of portlandite decreases 1.32 and 1.67 times.

The increased hardening temperature activates the chemical reactions between the mineral components in the cenospheres and the portlandite formed as a result of cement hydration. The cements without EA hardening at 75°C have an exothermal effect at 340–360°C on the second and seventh day of hydration due to a rearrangement of the gypsum crystal lattice, which disappeared by day 28. This effect was not detected for cement with EA hardened at the same temperature. This can be explained with the greater lime saturation: the sulphate stands firm and this effect was not registered even at the second day of hydration.

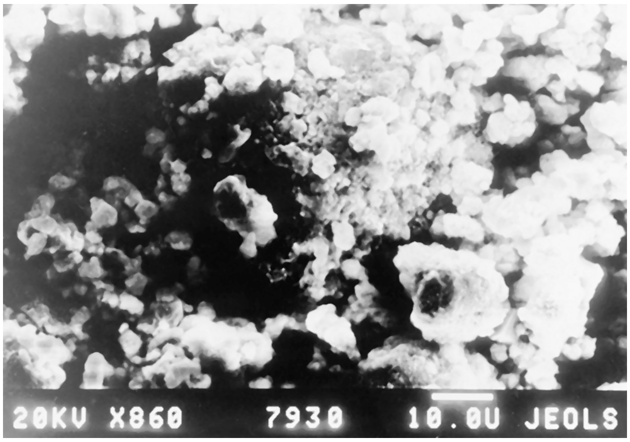

Fig. 10. SEM micrograph of a microsphere with a hydration shell (LW cement with EA, day 2 of hydration, 20°C).

DTA/DTG analyses (Fig. 6) show a portlandite quantity of 31.1 and 23 mg/g, respectively, for the cement samples hardened at 20 and 75°C. For the cements with EA at both regimes of hardening the ratio of the quantities of the hydration products from the first and third group of thermal effects is in the range (1.9–2.9):1, while for the series without EA it is higher, (2.9–3.5):1. This confirms that EA stimulates the formation of hydration products that are more stable and decompose at temperatures higher than 600°C [7].

Figs. 7, 8, and 9 show, respectively, the lightweight effect of the cenospheres in the cement stone, a cenosphere with a hydration shell, and the contact between a cenosphere and the cement matrix at the second day of hydration at 20°C. The addition of EA leads to formation of a greater quantity of hydration products in the pores and the contact voids between the separate particles (Fig. 10). The raised hardening temperature results in a coarser gel and a denser contact between CS and cement stone (Fig. 11).

4. Conclusions

1. At raised hardening temperature (75°C) a chemical reaction between the cenospheres and portlandite takes place, which results in an increase in hydration product formation with low temperatures of dehydration.
2. The relative quantity of hydration products, which are more thermally stable and decompose at temperatures higher than 600°C, increases in lightweight cements with “Bulexa” expansive additive.
3. At normal hardening temperature the “Bulexa” expansive additive causes formation of well-crystallized ettringite. Free gypsum was observed in the case of compositions without expansive additive in the early

stage of hydration at 75°C. Gypsum disappeared by day 28. The sulphate is more firmly bound in the composition with expansive additive, where free gypsum was not detected despite the raised temperature.

4. The raised hardening temperature leads to a certain coarser outlook of the cement paste and to a denser covering of the cenospheres with hydration products.

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