Waldemar Pichór[1]
AGH University of Science and Technology, Faculty of Materials Science and Ceramics
Mickiewicza 30, 30-059 Cracow, Poland, e-mail: pichor@agh.edu.pl

THE INTERFACIAL TRANSITION ZONE BETWEEN FILLER AND MATRIX IN CEMENT BASED COMPOSITES WITH CENOSPHERES

Cenospheres from coal ash are lightweight filler applied in cement based composites. The interfacial transition zone between cement paste and cenospheres was investigated by SEM observations, X-ray analysis into micro regions and XRD method. In case of cement based composites the interfacial transition zone was found only for naturally hardened cement and the zone had discontinuous character. For autoclaved sample of Portland cement the cement paste in the vicinity of cenosphere's surface was compact and there were no difference in relation to distant region of cement paste. In case of cenospheres with lime the pozzolanic properties of filler resulted in formation on its surface the hydration products. A needle-like forms of C-S-H phase and tobermorite were found. The interaction between high aluminum cement paste and cenospheres also leads to formation of bulk products of hydration. No interfacial transition zone was observed for sample with high aluminum cement. The paste close to cenosphere's surface was compact, without microcracks and gaps, that usually indicate good adhesion of hydration products to the surface of filler. Obtained results suggest that the cenospheres are good filler for production of the cement based composites, both naturally hardened and autoclaved.

Keywords: **interfacial zone, cenosphere, cement composites, lightweight fillers**

STREFA KONTAKTOWA MIĘDZY WYPEŁNIACZEM A MATRYCĄ W KOMPOZYTACH CEMENTOWYCH Z MIKROSFERAMI

Mikrosfery stanowiące frakcję popiołów lotnych, pochodzących ze spalania węgla kamiennego w klasycznych paleniskach, są atrakcyjnym lekkim wypełniaczem kompozytów z różnymi rodzajami matryc. Między innymi znajdują zastosowanie jako mikrokruszywo do zapraw i betonów lekkich o podwyższonych właściwościach izolacyjnych. Większość cech takich kompozytów poza właściwościami składników zależy od właściwości strefy kontaktowej między wypełniaczem a matrycą cementową. W przypadku kruszywa w betonie wielu autorów postuluje istnienie porowatej strefy kontaktowej kruszywo--zaczyn cementowy, wzbogaconej w portlandyt, której powodem jest zwiększony współczynnik wodno-cementowy w pobliżu powierzchni kruszywa. Dla lekkich kruszyw porowatych efekt zwiększania lokalnego współczynnika wodno-cementowego w większości przypadków nie występuje. W pracy przedstawiono wyniki badań strefy kontaktowej kruszywo-zaczyn w kompozytach cementowych z mikrosferami. Zaprezentowano wyniki obserwacji mikroskopowych dla różnych rodzajów cementu oraz próbek poddanych autoklawizacji. Dla próbek z cementem dojrzewających naturalnie zaobserwowano strefę o podwyższonym stosunku Ca/Si, występującą jedynie okazjonalnie wokół mikrosfer o stosunkowo dużej średnicy. W większości przypadków strefa kontaktowa nie różni się w zasadniczy sposób od zaczynu cementowego oddalonego od powierzchni mikrosfer. Zaobserwowano dobrą przyczepność produktów hydratacji cementu do ich powierzchni. W przypadku próbek z cementem portlandzkim poddanych autoklawizacji, poza bardziej rozluźnionym upakowaniem produktów hydratacji w bezpośrednim otoczeniu mikrosfer, nie stwierdzono występowania strefy wzbogaconej w portlandyt. Obserwacje wykonano również dla kompozytu z mikrosferami i spoiwem w postaci wapna palonego, poddanych autoklawizacji. W tym przypadku obok występowania $Ca(OH)_2$ stwierdzono obecność produktów reakcji pucolanowej, głównie fazy C-S-H oraz tobermorytu. Mikrosfery wykazują stosunkowo dużą odporność na działanie temperatury do 900°C, co wskazuje na potencjalną możliwość ich zastosowania jako lekkiego wypełniacza tworzyw do izolacji termicznej pracującej w podwyższonych temperaturach. Obserwowana strefa kontaktowa z zaczynem z cementu glinowego nie różni się zasadniczo od zaczynu oddalonego od powierzchni mikrosfery. Zaczyn w otoczeniu mikrosfer jest zwarty, a brak szczelin w tym obszarze wskazuje na dobrą przyczepność zaczynu do wypełniacza. Przeprowadzone obserwacje wskazują na dobrą współpracę mikrosfer z różnymi rodzajami matryc cementowych, poddanych różnym warunkom dojrzewania. Zaobserwowana strefa kontaktowa dla zaczynów z cementów portlandzkich dojrzewających w warunkach naturalnych, o wzbogaconym stosunku Ca/Si, związanym prawdopodobnie z podwyższoną zawartością portlandytu, występuje sporadycznie i jedynie dla mikrosfer o stosunkowo dużej średnicy. Dla próbek autoklawizowanych strefy takiej nie stwierdzono. Mikrosfery glinokrzemianowe stanowią więc atrakcyjny wypełniacz dla lekkich kompozytów z różnymi rodzajami spoiw mineralnych.

Słowa kluczowe: **strefa kontaktowa, mikrosfery, kompozyty cementowe, lekkie wypełniacze**

INTRODUCTION

The cenospheres are lightweight hollow spheres comprised largely of silica and alumina and filled with air and/or combustion gases, mainly CO_2. Cenospheres are the naturally occurring by-product of the burning process at coal-fired power plants, and they have most of the same properties as manufactured hollow-sphered products [1-4]. The properties of cenospheres make possible to use them either in dry or in wet slurry form and

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are easy to handle and provide a low surface area to volume ratio. Due to their properties, they are not affected by solvents, water, acids, or alkalies. Cenospheres are much lighter than mineral matrix and are currently used as a filler; they are also lighter than most of polymer resins. Their addition reduces the weight of composites and thermal conductivity. The spherical shape of cenospheres improves flowability in most of applications and provides more even distribution of the filler material. Cenospheres are also lightweight filler that is applied in cement based composites like plasters, mortars and concretes [5-8]. In this case the cenospheres are excellent small-diameter filler because of low bulk density and very low open porosity that causes the reducing of water absorbability and improving the freeze resistance. Most of the properties of cement based composites depend on those of cement paste alone and of the filler, e.g. sand or aggregates in concrete but also on bonding between cement matrix and filler. As far as we know that the lightweight filler--cement paste matrix interaction may influence the composite strength and other properties the studies of the interfacial zone are important.

The interfacial zone (ITZ) between hardened cement paste and aggregates has been studied extensively in recent years, after it was discovered that the structure of the paste in the vicinity of solid surfaces may differ distinctly from that of the bulk matrix [9]. A numbered studies dealing with interfacial zone are available in the literature for concrete with normal bulk aggregates and only a few papers for concretes with lightweight aggregates. For normal concrete with typical compact aggregate several models are proposed but they have very common elements [10]. Two of them are presented as example in Figure 1 [11, 12]. According to that models the interfacial contact zone is composed of three layers: a film composed of sub-layer of CH in direct contact with aggregate surface and CSH sub-layer with ettringite crystals backing it, large portlandite crystals and porous layer which are smoothly dense to normal bulk C-S-H paste. The thickness of this zone is different and usually is about 30÷100 μm.

This special structure of interface is a result of higher local water/cement ratio in the vicinity of aggregate surface because of wall effect. Also water which is absorbed on the aggregate surface plays important role in this phenomenon [13]. In this region also the contribution of unhydrated cement grains at early stage of hydration is higher [14]. The nature of ITZ and particularly presence of large $Ca(OH)_2$ crystals also depend on type of cement, content of mineral additives e.g. silica fume or using of polymer additives, or others. Significant amount of regions where interfacial zone was formed weren't observed for concretes with water/cement ratio smaller than 0.40 [15].

To the contrary, in case of porous lightweight aggregate in concrete the effect of enlargement the local water/cement ratio in the vicinity of aggregate surface was not present because the surface pores of the aggregate shell absorbed the water built-up at the cement-aggregate transition phase. This effect results in lower water content at the transition zone. Thus, the interfacial zone of the enriched portlandite crystals does not exist [16, 17]. Pre-wetting of porous aggregates causes saturating of open pores by water and consequently, formation a porous layer between aggregate and hardened cement paste [18].

The porous cenospheres, as distinct from typical lightweight filler, e.g. expanded perlite, have different features. The spheres are small particles, which have smooth surface and the volume of an open porosity due to surface that is rather insignificant. In this case an interaction between filler and cement paste similar to the polymer fiber-cement matrix in early stage of cement hydration is suspected [19], but after long-term period of natural hardening of cement the pozzolanic properties of cenospheres will be manifested. The pozzolanic reaction between cenospheres and $Ca(OH)_2$ may lead to densification of the interfacial region. Therefore, the mechanism of increasing the porosity according to enlargement of water/cement ratio near the surface of cenosphere is unexpected.

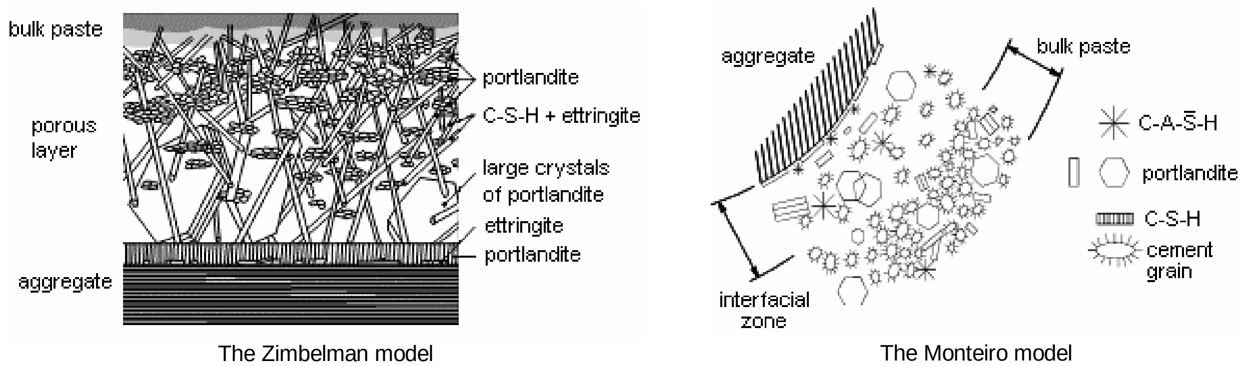

Fig. 1. Examples of models of interfacial zone between cement matrix and aggregate in concrete [11, 12]

Rys. 1. Przykładowe modele strefy kontaktowej kruszywo-zaczyn w betonie [11, 12]

Present work shows the results of SEM observation of the interfacial region between cenospheres and different Portland cement matrix naturally and hydrothermally hardened. The results obtained for samples with High Aluminum Cement and cenospheres bonded by lime are also presented.

EXPERIMENTAL DETAILS AND TEST METHODS

The properties of cenospheres are presented in Table 1. Because this work has focused only on the interfacial zone between cenospheres and cement matrix, only predominant fraction of spheres means 0.125÷0.50 mm was used. Paste mixtures with different composition and water/binder ratio were prepared. Typical Portland cements CEM I and CEM II, High Aluminum Cement (HAC) and burnt lime (CL) were used.

TABLE 1. **Properties of cenospheres**
TABELA 1. **Właściwości mikrosfer**

Bulk density, kg/m^3	400÷420
Particle density, kg/m^3	780÷820
Softenning point, °C	~1000
Thermal conductivity, W/mK	0.09÷0.11
Grain-size distribution: below 0.125 mm - 3.2%; 0.125÷0.25 mm - 46.2%; 0.25÷0.50 mm - 32.7%; above 0.50 mm - 17.9%	
Chemical composition: SiO_2 - 58.0 ±5.0; Al_2O_3 - 26.0 ±5.0; Fe_2O_3 - 5.0 ±0.6; CaO - 2.0 ±0.5; K_2O + Na_2O - 1.2 ±0.4	

Details of sample composition and its treatment are shown in Table 2. The cenospheres content in composites was about 30% V/V. Samples after hardening were broken off or cut and the surfaces of samples were polished.

TABLE 2. **The composition and hardening condition of samples**
TABELA 2. **Skład i warunki dojrzewania próbek do badań**

Sample	Cement type	Treatment
CEM1	CEM I 42.5 NA w/c = 0.40	autoclaved at 180°C for 8 h
CL	burnt lime CL-90Q WR type; w/l = 0.50	autoclaved at 180°C for 8 h
CEM2	CEM II/B-M (S-V) 32.5R w/c = 0.40	natural hardening for 28 and 180 days
HAC	HAC Górkal 70 w/c = 0.40	natural hardening for 24 hours; 100% RH

Microstructures of the composite samples were investigated by the JEOL scanning electron microscope equipped with EDX LINK system. Because the wall effect depends on dimensions of filler and investigated cenospheres have diameter only about 200 μm the XRD method of examined the orientation of portlandite crystals in interfacial zone, proposed by Grandet and Oliver was not applicable [19]. The mapping and the X-ray linescans of selected elements were presented. The phase analysis of each sample was made. Powder XRD patterns were recorded using a Philips X-ray diffractometer X'pert system with monochromatic CuK_{α} radiation.

RESULTS

Samples of cenospheres with Portland cement are natural and hydrothermal conditioned. Figure 2 shows the XRD analysis of those samples. Typical patterns for hardened cement paste have been recorded in this investigation. In both cases except of unhydrated cement minerals the portlandite was observed, but in case of autoclaved cement paste the peaks of tobermorite have been also visible. Mullite and quartz are connected with partially crystallized phases from cenospheres.

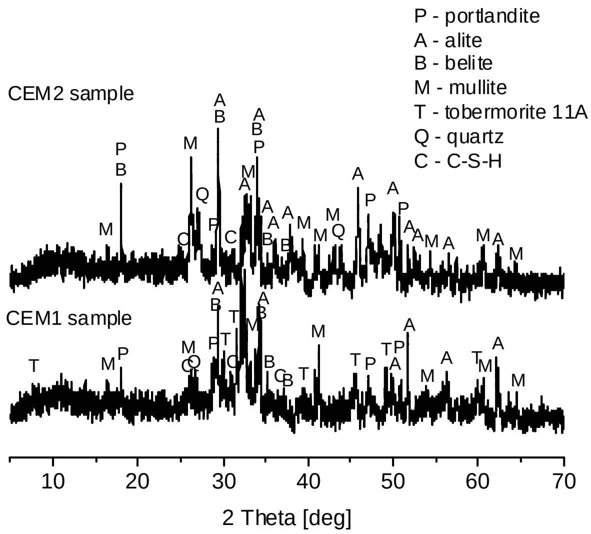

Fig. 2. The XRD analysis of CEM1 and CEM2 samples
Rys. 2. Analiza rentgenograficzna próbek CEM1 i CEM2

For autoclaved cement sample at the interfacial transition zone between hardened cement and cenosphere the different microstructure wasn't observed. The X-ray linescans analysis of Al, Si and Ca across the interfacial transition zone between autoclaved cement paste and cenosphere shows that concentration of Ca is smaller in the vicinity of cenospere's surface. It may be connected more likely with insignificant higher porosity in this region than changes of chemical compositions of hydration products. SEM observation of this region and linescans are presented in Figure 3.

In Figure 4 the SEM observation of the polished sample of naturally hardened cement paste with cenospheres for 180 days is shown. In this case the effect of Ca concentration on the interfacial region is obser-

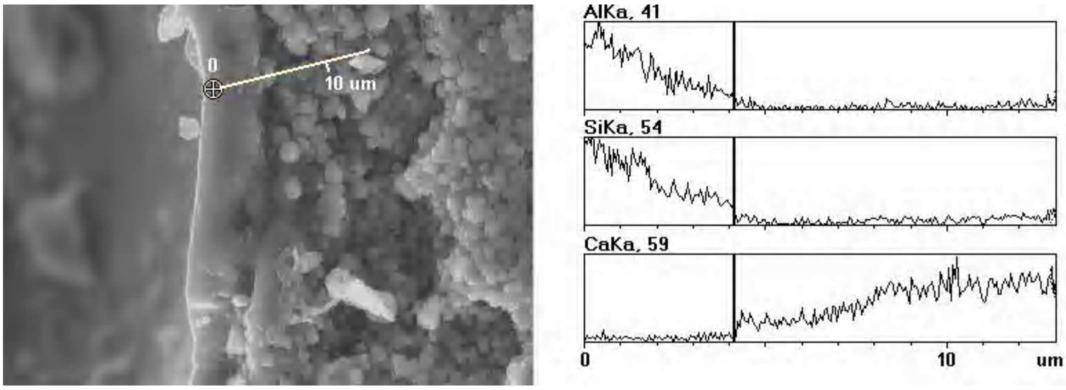

Fig. 3. SEM observation and X-ray linescans trace of Al, Si and Ca across the interfacial transition zone between autoclaved cement paste and cenosphere (CEM1)

Rys. 3. Strefa kontaktowa zaczyn cementowy-mikrosfera oraz analiza liniowego rozmieszczenia wybranych pierwiastków dla autoklawizowanej próbki cementowej (CEM1)

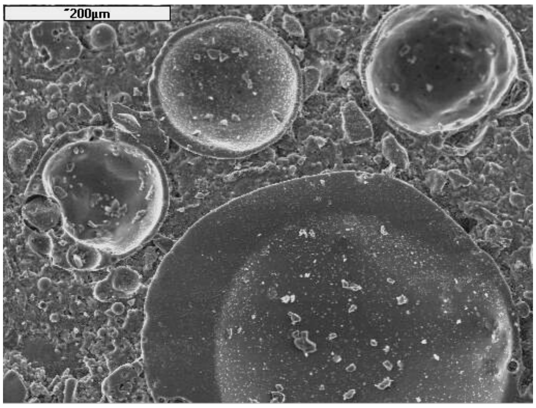

Fig. 4. SEM observation of the polished sample of naturally hardened cement paste with cenospheres for 180 days (CEM2)

Rys. 4. Obraz SEM zgładu próbki zaczynu cementowego z mikrosferami, dojrzewającej w warunkach naturalnych przez 180 dni (CEM2)

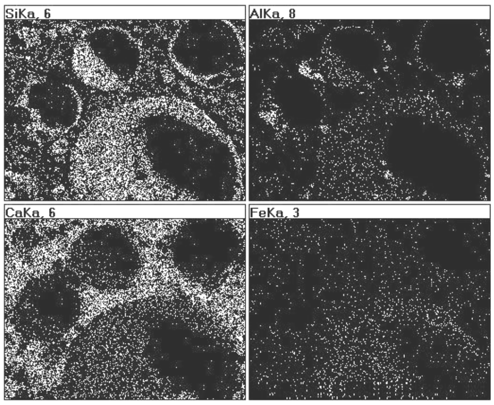

Fig. 5. Dot maps of Si, Al, Ca and Fe distribution in the naturally cured Portland cement sample (CEM2). Arrows indicate the Ca rich area on the cenosphere's surface

Rys. 5. Analiza punktowa rozmieszczenia Si, Al, Ca i Fe w próbce z zaczynem cementowym dojrzewającym w warunkach naturalnych (CEM2). Strzałką wskazano strefę o podwyższonej zawartości Ca

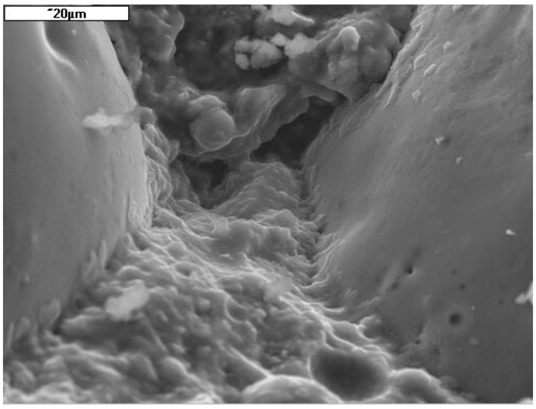

Fig. 6. SEM observation of the interfacial transition zone between naturally hardened cement paste and cenosphere after 28 days of cement hydration (CEM2)

Rys. 6. Strefa kontaktowa zaczyn cementowy-mikrosfera dla próbki dojrzewającej w warunkach naturalnych przez 28 dni (CEM2)

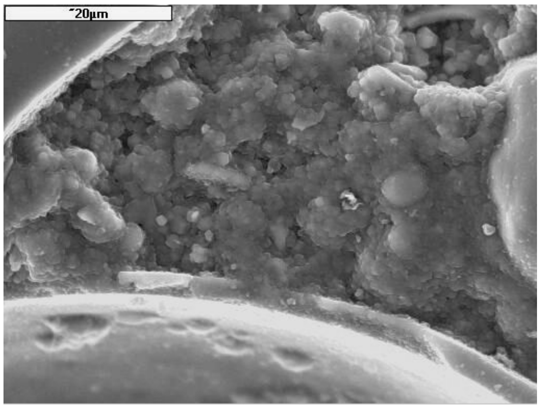

Fig. 7. SEM observation of the interfacial transition zone between naturally hardened cement paste and cenosphere (CEM2 180 days)

Rys. 7. Strefa kontaktowa zaczyn cementowy-mikrosfera dla próbki dojrzewającej w warunkach naturalnych przez 180 dni (CEM2)

ved only for higher cenosphere, which diameter about 400÷500 μm.

The X-ray analysis presented as dot maps of Ca and Si shows that on the surface of cenosphere locally the interfacial transition zone with elevated Ca/Si ratio may exist. The higher concentration of calcium in this case is probably caused by wall effect (Fig. 5). Despite of pozzolanic properties of cenospheres after 180 days of hydration the Ca-enriched zone is still present, however it should be noted that the phenomenon has rather occasionally character. Figure 6 shows the region of interfacial transition zone after 28 days of hydration for sample of CEM II B-M type cement paste. The bulk paste on the cenosphere's surface was formed. After long period of hydration the microstructure of cement paste in the vicinity of cenosphere is similar to distant region from its surface (Fig. 7).

In Figure 8 the X-ray pattern of phase composition analysis for autoclaved sample with cenospheres and lime is presented. Because of volume of lime greater then needed for binding the cenospheres the main product of hydration was portlandite, C-S-H phase and tobermorite.

Similarly to typical fly ash the cenospheres have the pozzolanic properties. After autoclaving process on its surface needle-like products of hydration, mainly C-S-H phase and tobermorite were formed. Figures 9 and 10 show the products of hydration on the cenosphere's surface.

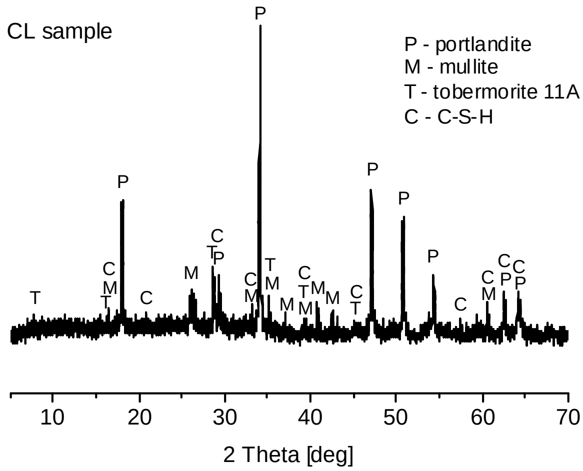

Fig. 8. The XRD analysis of autoclaved CL sample

Rys. 8. Analiza rentgenograficzna próbki z wapnem po autoklawizacji

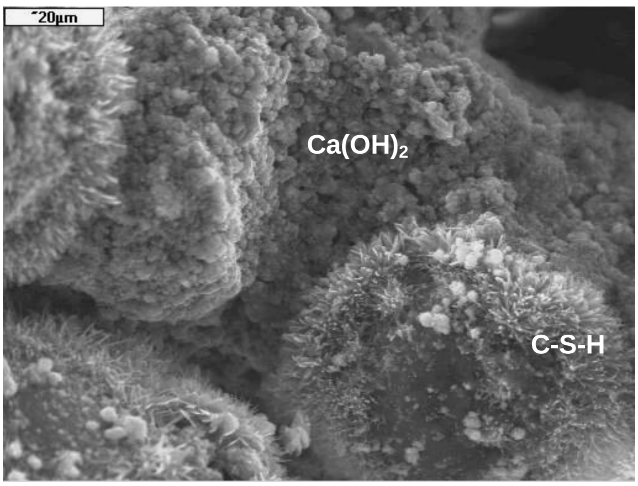

Fig. 9. SEM observation of autoclaved CL sample. Hydration products on the cenosphere surface

Rys. 9. Obraz SEM próbki autoklawizowane ze spoiwem wapiennym. Widoczne produkty hydratacji na powierzchni mikrosfer

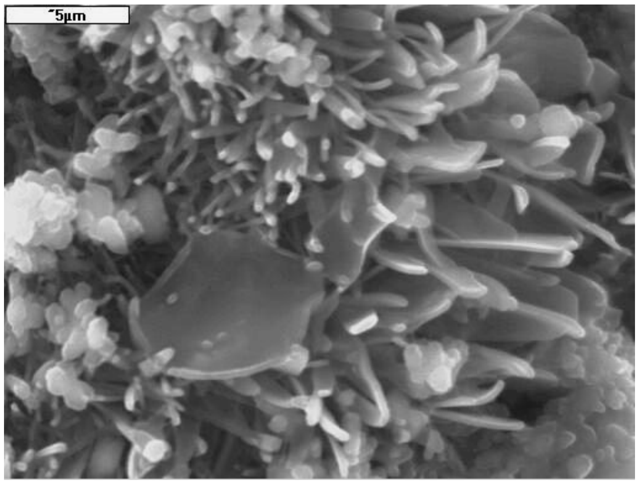

Fig. 10. Hydration products on the cenospheres surface: needle-like forms of C-S-H phase and tobermorite crystals

Rys. 10. Produkty hydratacji na powierzchni mikrosfery: włókniste formy fazy C-S-H i tobermoryt

Different products of hydration were found in the HAC paste. In this case except of unhydrated cement phases (calcium aluminum oxide and corundum) a dominant were cubic calcium aluminium oxide hydrate and weak crystallized $Al(OH)_3$ (Fig. 11).

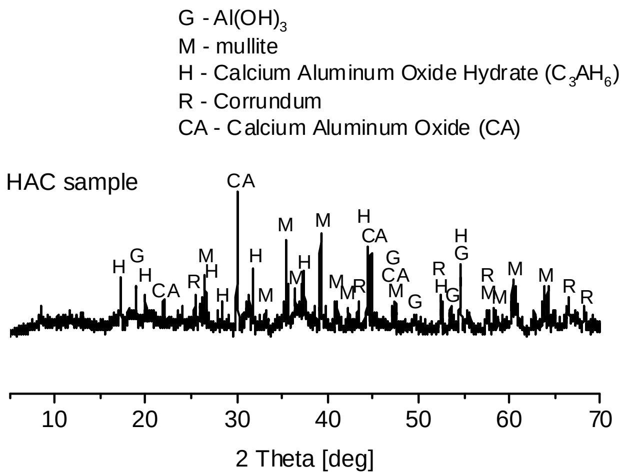

Fig. 11. The XRD analysis of hardened HAC paste sample

Rys. 11. Analiza rentgenograficzna próbki ze stwardniałym cementem glinowym

Likewise in previous samples, the compact paste near the cenosphere's surface was here observed. The cement paste in the vicinity of cenosphere's surface appears more dense, amorphous and massive (Figures 12 and 13). No interfacial transition zone of special microstructure was observed. Absence of microcracks or gaps in transition region indicates on good adhesion of hydration products to the cenosphere's surface.

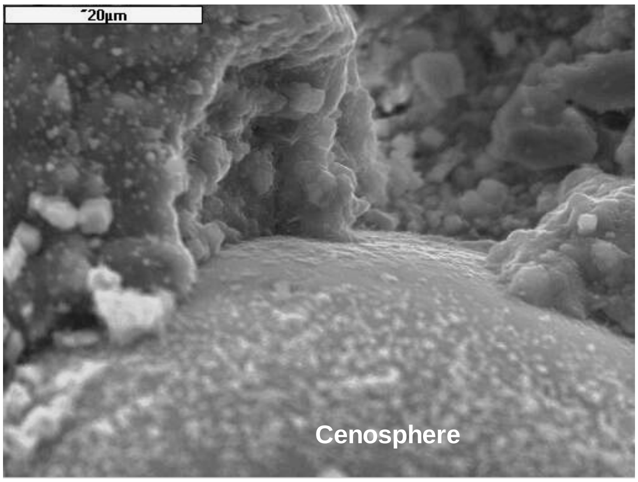

Fig. 12. SEM observation of the interfacial transition zone of hardened HAC paste sample. Overall view

Rys. 12. Obraz SEM powierzchni mikrosfery w stwardniałym zaczynie cementu glinowego

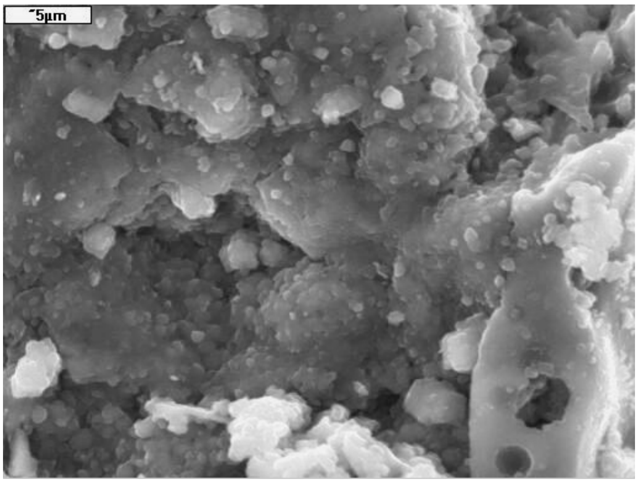

Fig. 13. The interfacial transition zone of hardened HAC paste sample and cenosphere

Rys. 13. Obraz SEM strefy kontaktowej między mikrosferą a stwardniałym zaczynem cementu glinowego

CONCLUSIONS

Taking into consideration obtained results the following conclusions may be formulated:

1. The interfacial transition zone between cenosphere and naturally hardened cement paste only occasionally has different microstructure than cement paste, but usually distinguishing of different microstructure of paste near cenosphere's surface was not clear. The Ca-enriched region has discontinuous form and was found only for large cenospheres.
2. In case of autoclaved cement sample the paste in the vicinity of cenosphere was similar to distant regions. Only higher porosity was observed in this region.
3. Cenospheres are a potential filler for autoclaved composites with lime as binder. After 8 h of autoclaving in 180°C except of large amount of $Ca(OH)_2$ a needle-like forms of C-S-H phase and tobermorite on the cenosphere's surface were observed. Its presence suggests that it may be a way to obtain lightweight composites to thermal insulation.
4. No interfacial transition zone was observed for sample with high aluminum cement. The paste close to cenosphere's surface was compact, without microcracks and gaps, that indicates well adhesion of hydration products to the surface of filler.

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Recenzent
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