Stability of Cenospheres in Lightweight Cement Composites in Terms of Alkali-Silica Reaction

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Abstract:

This paper presents an experimental study on characteristics and stability of cenospheres used in lightweight cement composites. ASTM C227 and C1260 tests were used to evaluate if cenospheres are potentially deleterious due to alkali-silica reaction (ASR). Natural sand was used as control. Examination by scanning electron microscope with energy-dispersive X-ray spectroscopy and analyses by X-ray diffractometer and thermogravimetry were conducted on samples with cenospheres after 9-month C227 and C1260 tests to better understand the behavior of cenospheres exposed to high alkaline environments and higher temperatures in these tests. Results indicate that cenospheres are not potentially deleterious due to ASR. Expansion of the mortar specimens tested to ASTM C227 and C1260 seems to be affected by the pozzolanic reactivity of cenospheres. Fine cenospheres showed limited pozzolanic reactivity at 28-30 ^{o}C and 38°C, but exhibited significant pozzolanic reactivity at 80 ^{o}C with aluminum tobermorite [$Ca_5Si_5Al(OH)O_{17} \cdot 5H_2O$] identified as the main reaction product.

Keywords: cenosphere; cement composites; alkali-silica reaction; pozzolanic reaction; aluminum tobermorite

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1. Introduction

Cenospheres are hollow alumino-silicate spheres obtained from fly ash from coal-burning power plants [1,2]. They are formed from cooling and solidification of inorganic molten coal residues around trapped gas. Cenosphere particles have spherical shapes with sizes typically ranging from 10 – 400 μm [3]. They generally have a hollow interior that is covered by a thin shell with thicknesses about 5-10% of its diameter [4]. Due to its hollow structure, cenospheres have low particle densities typically ranging from 600 to 900 kg/m^3. Because of their low particle densities, cenospheres have been used for making lightweight cement composites in recent years [5-8]. Blanco *et al.* [5] used powder-packing principle to produce lightweight concrete with cenospheres as primary "aggregate". Tiwari *et al.* [6] investigated effect of cenospheres on acoustic properties of cement paste and asphalt concrete matrices to explore the feasibility of using cenospheres in developing lightweight sound absorbing structural materials. McBride *et al.* [7] studied mechanical properties of a lightweight concrete with cenospheres. Chia *et al* [8] developed an ultra lightweight cement composite (ULCC) with a density of 1,430 kg/m^3 and 28-day compressive strength of about 60 MPa. These published information indicate that cenospheres have great potential for production of lightweight structural materials for applications in practice.

Since cenospheres are derived from fly ash of coal-burning power plants, they may contain amorphous silica and have pozzolanic reactivity as fly ash. However, their relatively large sizes up to several hundred microns suggest that the pozzolanic reactivity of the cenospheres might be limited at ambient temperatures. Due to the sizes and amorphous silica in the cenospheres, there is a concern of long-term durability of lightweight cement composites due to possible alkali-silica

reactivity (ASR) of the cenospheres. Although this durability problem generally occurs in concretes/mortars containing aggregates with reactive silica, it was reported that undispersed silica fume agglomerates might act as "reactive aggregates" and cause similar durability problem [9,10].

This research was carried out, therefore, to investigate the characteristics and alkali reactivity of the cenospheres used in lightweight cement composites. ASTM C227 [11] and ASTM C1260 [12] tests were used to evaluate the potential ASR of the cenospheres up to 9 months. Natural sand was used as control. Size of the cenospheres was taken into consideration in the evaluation. Examination by scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDX) and analyses by X-ray diffractometer (XRD) and thermogravimetry (TG) were conducted on samples with cenospheres after C227 and C1260 tests to have a better understanding on behavior of the cenospheres exposed to high alkaline environments in these tests.

2. Experimental details

2.1 Characterization of cenospheres

Density of commercially available hollow-centered cenospheres was determined by AccuPyc 1330 Pycnometer. Specific gravity of the material for the cenospheres was determined by the same equipment using ground material of the cenospheres. Particle size distribution of the cenospheres was determined by dry sieving.

Chemical composition of the cenospheres was determined by ARL 9800 XP Sequential X-ray fluorescence spectroscopy (XRF). X-ray diffraction (XRD) spectra of the cenospheres was obtained by Shimadzu X-ray diffractometer (XRD-6000) with Cu Kα radiation at 40 kV and 30 mA with a scan speed of 0.5°/min between 2θ of 5° to 60°. Mineral composition was determined by using a software 'Siroquant version 3'.

To evaluate whether the cenospheres have pozzolanic reactivity at ambient temperature, two cement pastes were prepared, one with a cement/cenospheres ratio of 6.5/1.0 by mass and the other was a control paste without cenospheres. Size of the cenospheres used was less than 106 μm, and water/ (cement+cenospheres) was 0.36. After mixing, the cement pastes were cast in small plastic containers and cured at about 30°C in a sealed condition. At ages of 7, 28, 91, 182, and 365 days, samples were taken and dried to determine $Ca(OH)_2$ and non-evaporable water contents in the hardened cement pastes. The $Ca(OH)_2$ content was determined by thermo-gravimetric (TG) method using Linseis L81-II thermo-gravimetric analyzer. For each TG test, approximately 100 mg of dry powder sample was heated from about 30 to 950 $^{\circ}$C at a rate of 10 $^{\circ}$C/min in nitrogen environment. Non-evaporable water content was determined by mass loss from ignition of the samples in a furnace at 950°C for 2 hrs.

2.2 Mortar mixtures and test methods for evaluating alkali-silica reactivity of cenospheres

Two test methods ASTM C227 and C1260 were used to evaluate potential expansive behavior of mortars incorporating cenospheres.

2.2.1 Mortar mixtures and test specimens

In order to evaluate effect of particle size on potential ASR, the cenospheres were separated into four size ranges of 0-106μm, 106-150μm, 150-212μm, and ＞212μm and incorporated separately into four of six mixtures. The other two mixtures were Mix "OP-CE-0" which contained as received cenospheres and a control mixture which contained natural sand. The mix proportions of the mortars are given in Table 1. ASTM Type I (also EN CEM I 52.5N) Portland cement was used in this study, and its chemical composition is given in Table 2. Sodium oxide

equivalent (Na_2O_{eq}) of the cement was approximately 0.48%. Natural siliceous sand conforming

to ASTM C33 [13] was used in the control mixtures for comparison. The sand was sieved with

grading shown in Table 3 to satisfy the requirements of ASTM C227 and ASTM C1260. A

polycarboxylate-based superplasticizer (ADVA 181, W.R. Grace Asia Pte Ltd) was used to achieve

similar flow of the mortars (120% according to ASTM C1437 [14]). Volume fraction of cement

paste in the mortars was 0.53 instead of 0.49 as specified by ASTM C1260 since the cenospheres

had higher specific surface areas than natural sand, and more cement paste was required to achieve

the workability requirement.

Six mixtures were evaluated according to ASTM C1260, while 12 mixtures were evaluated

according to ASTM C227. Mix proportions of the mortars for C227 test were similar to those used

for C1260 test except for Na_2O content. For C227 test, NaOH was added into mixing water and

mixed in the mortars to attain Na_2O_{eq} of 0.8% and 1.25% by mass of cement, respectively.

Therefore, C227 test contained 12 mortar mixtures.

For each mixture, four $25 \times 25 \times 285$-mm specimens were made for the test. The specimens

were cast at ambient temperature (28-30 ^{o}C) and cured at similar temperature in sealed plastic

bags for 24 ± 2 hrs. This temperature was selected to simulate temperatures in tropical

environment.

2.2.2 ASTM C227 test

Initial lengths of the mortar specimens were measured at ambient temperature (28-30 ^{o}C)

after demold at about 24 hrs. The specimens were then stored in pails at a relative humidity (RH)

of about 100% and a temperature of 38 ^{o}C according to the standard for 9 months. Before each

measurement, the pails containing the mortar bars were conditioned at the ambient temperature for

at least 16 hrs. Length change of these specimens was measured by a digital length comparator (model: ID-C150XB, Mitutoyo corporation).

2.2.3 ASTM C1260 Test

All the specimens were demoulded after about 24 hrs and stored in distilled water bath at 80 ^{o}C for another 24 hrs before being immersed in 1N NaOH solution at 80 ^{o}C. Length change of these specimens was measured by the same equipment described above. Readings on the specimens after storing in the distilled water at 80 ^{o}C for 24 hrs were taken and used as "zero readings" according to the standard. Subsequently, readings were taken at various ages up to 9 months.

2.2.4 SEM examination and XRD and TG analyses of mortar samples after ASTM C227 and C1260 tests

In order to have a better understanding on behavior of the cenospheres exposed to high alkaline environments in these tests, microstructure of mortar samples with cenospheres < 106 μm tested to C227 and C1260 for 9 months were examined using a scanning electron microscope (JSM5610LV) with energy dispersive X-ray spectrometer (Oxford INCA X-Act EDX System). Fractured samples coated with platinum were examined by SEM in secondary electron image mode with an acceleration voltage of 15kV.

In addition, dried powder samples from the mortar specimens tested to C227 and C1260 were analyzed by XRD and TG method to identify the possible reaction products and to determine $Ca(OH)_2$ content, respectively. The same equipment, parameters, and software as described in Section 2.1 were used.

3. Results and discussion

3.1 Characteristics of the cenospheres

The cenospheres had a specific gravity of 2.48, which was determined by grinding the cenospheres into fine powder. Average particle density of the hollow-centered cenospheres was approximately 870 kg/m^3. Particle size distribution of the cenospheres is given in Fig.1. Approximately 15, 33, and 50% of the cenospheres were in size ranges of 0-106, 106-150, and 150-300 μm, respectively. Less than 2% of the cenospheres had sizes greater than 300 μm.

Chemical compositions of the cenospheres of different sizes were not significantly different (Table 4). The cenospheres had low CaO content of less than 1% but high SiO$_2$ and Al$_2$O$_3$ contents. Sum of the SiO$_2$ and Al$_2$O$_3$ content was approximately 90%. The cenospheres had relatively high K$_2$O contents of more than 3%.

X-ray diffraction spectra of the cenosphere materials from different size ranges are shown in Fig.2. The cenospheres contained quartz and mullite crystals and amorphous phase shown as "humps" in the spectra. Mineral composition was given in Table 4, and did not seem to be affected by particle size of the cenospheres significantly. High amounts of the amorphous phase with SiO$_2$ in the cenosphere particles raise the question of long-term stability of the cenospheres in alkaline environment in cement composites.

The increase in the non-evaporable water contents of the cement pastes with and without fine cenospheres at w/(c+cenospheres) of 0.36 cured in a sealed condition are shown in Fig.3. The non-evaporable water contents in the paste with cenospheres were slightly lower than those without cenospheres at various ages up to one year. The non-evaporable water is a useful measure on the degree of cement hydration for Portland cement paste. When cement reached complete

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hydration, the non-evaporable water content in cement paste will be approximately 23% [15]. At

one year, the non-evaporable water content in the control cement paste was about 0.19 g/g dried

sample, indicates that almost 83% of the cement had hydrated. The non-evaporable water content

in the paste with cenospheres was slightly lower than that without cenospheres at various ages up

to one year. However, it is difficult to use non-evaporable water to measure the degree of cement

hydration for cement paste with pozzolanic materials.

Calcium hydroxide content in the cement pastes with and without fine cenospheres are shown

in Fig.4, expressed as g/g cement. The $Ca(OH)_2$ content in the paste with the cenospheres was

slightly lower than that of the control Portland cement paste after 28 days. As pozzolanic reaction

consumes $Ca(OH)_2$, the reduction in the $Ca(OH)_2$ content in the paste with the cenospheres

indicates pozzolanic reactivity of the cenospheres. However, the data suggest that the pozzolanic

reactivity of the cenospheres may be limited when cured at ambient temperature (28-30 ^{o}C) in

sealed condition at w/(c+cenpsheres) of 0.36. As the data were based on a sample with

cenospheres < 106 μm, pozzolanic reactivity of larger cenospheres would be even lower.

3.2 Potential alkali reactivity of cenospheres

3.2.1 Based on ASTM C227 test

Expansions of the mortar bars with Na_2O_{eq} of 0.80 and 1.25% determined according to

ASTM C227 up to 9 months are shown in Fig.5 (a) and (b), respectively. According to ASTM C33,

while the line of demarcation between innocuous and potentially deleterious aggregate is not

clearly defined, expansion that exceeds 0.05% at 3 months or 0.10% at 6 months is generally

considered excessive. In addition, expansion greater than 0.05% at 3 months should not be

considered excessive when the 6-month expansion is below 0.10%.

From Fig.5 (a) and (b), it was observed that the expansions of the mortars with the cenospheres were well below the limits at 3 and 6 months regardless of the Na_2O_{eq} levels. This indicates that the cenospheres are not potentially deleterious due to ASR. The expansions of the mortars with the cenospheres were not significantly different from those with natural sand based on this test. No visible crack was observed on the mortar bars after C227 test. As expected, the expansions of the mortars with 1.25% Na_2O_{eq} were greater than those with 0.80% Na_2O_{eq}.

3.2.2 Based on ASTM C1260 test

Expansions of the mortar bars determined according to ASTM C1260 up to 28 days and 9 months are shown in Fig. 6 (a) and (b), respectively. There is good agreement in the published literatures [11,16-19] for the expansion limits:

- Expansions of less than 0.10% at 14 days after conditioned in 1N NaOH solution are indicative of innocuous behavior in most cases;

- Expansions of more than 0.20% at 14 days after conditioning in 1N NaOH solution are indicative of potential deleterious expansion;

- Expansion between 0.10 and 0.20% at 14 days after casting include both aggregates that are known to be innocuous and deleterious in field performance.

As shown in Fig. 6 (a), mortars with cenospheres and natural sand had expansions of less than 0.1% at 14 days. This indicates that the cenospheres were stable in the mortar specimens and would not cause potential expansion problems due to ASR. Even after about 9 months, the expansions of the mortar bars with cenospheres were less than 0.25%, which was much lower than that with the natural sand at 1.1% (Fig. 6 (b)). Comparing the mortars with cenospheres of different sizes, the mortar with cenospheres < 106 μm had lower expansion than those with larger

or as-received cenospheres. However, the difference was not significant. These might be attributed to pozzolanic reactivity of the fine cenospheres at high temperature of 80 ^{o}C, which will be discussed further in Section 3.4.

3.3 SEM examination, XRD and TG analyses of mortar samples with cenospheres after C227 and C1260 tests

3.3.1 Samples with cenospheres after ASTM C 227 test

Fig.7 is an SEM micrograph of the mortar sample with cenospheres of <106 μm and 1.25% of Na_2O_{eq} after ASTM C227 test at 38 ^{o}C. The cenospheres can be easily identified in the sample. Some cenospheres were broken, whereas others were still in one piece. Shell of the broken cenospheres seems to have close physical contact with surrounding cement paste. The surface of an unbroken cenosphere shown in Fig.7 appears relatively smooth and only limited reaction products were observed on the surface.

Cross-section of a sample with as-received cenospheres embedded in epoxy was examined by SEM and analyzed by EDX in comparison to that of the mortar sample after the C227 test. Voids in the shell were also observed in the as-received cenospheres, similar to those observed in the mortar sample shown in Fig.7. EDX analyses of the cenosphere shell at 5 randomly selected spots did not show significant different chemical compositions of the as-received cenosphers compared with those after the C227 test.

Calcium hydroxide ($Ca(OH)_2$) was detected in the sample with cenospheres after C227 test by XRD (Fig.8) and TG analysis. Calcite ($CaCO_3$) was also identified in the sample due to carbonation of the sample after 9-month test.

Although the temperature for C227 test was 38 ^{o}C, the above results support the finding in

Section 3.1 that the pozzolanic reactivity of the cenospheres was limited at ambient temperature or temperatures not significantly above that.

3.3.2 Samples with cenospheres after ASTM C1260 test

No $Ca(OH)_2$ was detected by thermo-gravimetric (TG) analysis in the mortar sample with cenospheres < 106 μm after C1260 test at 80 ^{o}C. This indicates that pozzolanic reaction between the cenospheres and $Ca(OH)_2$ at the high temperature may have consumed the $Ca(OH)_2$.

X-ray diffraction analysis of powder sample from the mortar indicates that aluminum tobermorite [$Ca_5Si_5Al(OH)O_{17}\cdot 5H_2O$] [20,21] (JCPDS No 19-0052) was the main reaction product (95%) and katoite [$Ca_3Al_2SiO_{12}H_8$] [22,23] (JCPDS No 32-0151) was a minor reaction product (5%) at the high temperature (Fig.8). The former has monoclinic crystal structure and the latter has cubic crystal structure.

Fig.9 shows SEM micrographs of the mortar sample after ASTM C1260 test. Shell of some cenospheres seems disappeared, and plate shaped crystals were observed in the space originally occupied by the cenospheres (Fig.9(a)). However, residual cenospheres with reduced shell thickness as shown in Fig.9(b) still exist. EDX analyses of the plate crystals (Fig.9(c)) at 10 to 20 randomly selected spots at different cenospheres show Ca, Si, and Al as the main elements. Average mole ratio of Ca / Al was approximately 4.8 with standard deviation of 0.4, while average mole ratio of Si / Al was approximately 4.6 with standard deviation of 0.5 for these crystals. The mole ratio of Ca/ Si/ Al was similar to that of the aluminum tobermorite. Similar plate shaped aluminum tobermorite crystals were observed and reported by Mostafa et al. [21] in a sample containing CaO, SiO_2, and Al_2O_3 treated at a hydrothermal condition at 175 ^{o}C for 24 hours. No cubic crystal of katoite was observed in the sample. It is possible that the small amount of katoite

crystals were embedded in the mortar sample.

3.4 Effect of pozzolanic reactivity of cenospheres on expansion of the mortar specimens tested to ASTM C 227 and C1260

As mentioned in Section 3.1, there is experimental evidence of pozzolanic reactivity of the cenospheres at ambient temperature of about 28-30 ^{o}C, although the reactivity is limited. As the temperature of C227 test was 38 ^{o}C, it was likely that the pozzolanic reactivity of the cenospheres was also limited. However, with the increase in the temperature to 80 ^{o}C in C1260 test, pozzolanic reactivity of the cenospheres was increased significantly with no $Ca(OH)_2$ detected in the sample after 9 months.

Fly ash has been used to reduce the effect of ASR for many years. The beneficial effects of fly ash have been attributed to (1) a dilution of cement due to partial replacement with the fly ash, (2) a reduced pH of pore solution, (3) the resulting increase in solubility of calcium, and (4) the subsequent formation of nonexpanding calcium-alkali-silicate-hydrate in place of swelling alkali-silicate-hydrate [24].

The expansion of the mortar specimens tested to ASTM C227 and C1260 seem to be affected by the pozzolanic reactivity of the cenospheres. In C227 test, the expansion of the mortars with the cenospheres was not significantly different from that with natural sand. In C1260 test, however, the expansions of the mortars with the cenospheres at both 14 days and 9 months were significantly lower than those with natural sand. The lower expansions of the mortars with the cenospheres might be attributed to the pozzolanic reactivity of the cenospheres at the high temperature of 80 ^{o}C which reduced pH of pore solution and permeability of the mortar.

4. Conclusions

Based on the above results and discussion, following conclusions can be drawn:

(1) Cenospheres used in this study had a specific gravity of 2.48 and average particle density of about 870 kg/m^3. The cenospheres had low CaO content but high SiO_2 and Al_2O_3 contents with great amount of amorphous material. Both chemical and mineral compositions were not affected significantly by the size of the cenospheres.

(2) ASTM C227 and C1260 test results indicate that the cenospheres used for lightweight cement composites are not potentially deleterious due to alkali silica reaction.

(3) Fine cenospheres showed limited pozzolanic reactivity at 28-30 ^{o}C and 38 ^{o}C, but exhibited significant pozzolanic reactivity at 80 ^{o}C with aluminum tobermorite [$Ca_5Si_5Al(OH)O_{17}\cdot5H_2O$] identified as the main reaction product.

(4) The expansion of the mortar specimens tested to ASTM C227 and C1260 seem to be affected by the pozzolanic reactivity of the cenospheres. The lower expansion of the mortars with the cenospheres in C1260 test in comparison to that with natural sand might be attributed to the pozzolanic reactivity of the cenospheres at 80 ^{o}C which reduced pH of pore solution and permeability of the mortar.

Acknowledgements

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Table 1 - Mix proportions of mortars for ASTM C1260 and ASTM C227* tests

| Mix No. | Water, kg/m^3 | Cement, kg/m^3 | Aggregate, kg/m^3 | | | Superplasticizer, L/m^3 |
			Cenospheres	Sand	Size	
Control	320	680.8	-	1222	-	0
OP-CE-0	320	680.8	357.2	-	As received	5.0
OP-CE-I	320	680.8	357.2	-	> 212 μm	2.5
OP-CE-II	320	680.8	357.2	-	150-212 μm	2.5
OP-CE-III	320	680.8	357.2	-	106-150 μm	4.6
OP-CE-IV	320	680.8	357.2	-	0-106 μm	7.1

* For ASTM C227 test, NaOH was added in mixing water to achieve total Na_2O_{eq} of 0.80 and 1.25% by mass of cement respectively.

Table 2 - Chemical and mineral composition of cement

	Composition	%
Chemical composition	Calcium oxide, CaO	64.3
	Silicon dioxide, SiO_2	20.0
	Aluminum oxide, Al_2O_3	4.7
	Iron oxide, Fe_2O_3	2.9
	Magnesium oxide, MgO	2.1
	Sodium oxide, Na_2O	0.17
	Potassium oxide, K_2O	0.47
	Total Alkalinity as $Na_2O+0.658K_2O$	0.48
	Sulphur oxide, SO_3	1.9
	Insoluble Residue	0.3
	Loss on Ignition (LOI)	2.2
Mineral composition	Tricalcium Silicate, C_3S	54.1
	Dicalcium Silicate, C_2S	24.8
	Tricalcium Aluminate, C_3A	7.5
	Tetracalcium Alumninoferrite, C_4AF	7.5

Table 3 - Grading of natural sand

Sieve Size	Retained, % by mass
2.36 mm	10
1.18 mm	25
600 μm	25
300 μm	25
150 μm	15

Table 4 - Chemical and mineral composition of the cenospheres

Chemical composition, % by mass	0-106μm	106-150μm	150-300μm
SiO_2	58.1	60.9	60.1
Al_2O_3	32.0	28.2	28.4
Fe_2O_3	3.7	4.5	4.8
CaO	0.9	0.7	0.8
MgO	1.4	1.5	1.5
Na_2O	0.8	0.9	0.9
K_2O	3.1	3.3	3.5
SO_3	0.04	0.01	0.02
Loss on Ignition (LOI)	1.04	1.04	1.04
Mineral composition, % by mass	0-106μm	106-150μm	150-300μm
Quartz	4.5	5.6	6.0
Mullite	12.6	10.6	8.6
Amorphous phase	82.9	83.8	85.4

Fig.1. Particle size distribution of the cenospheres.
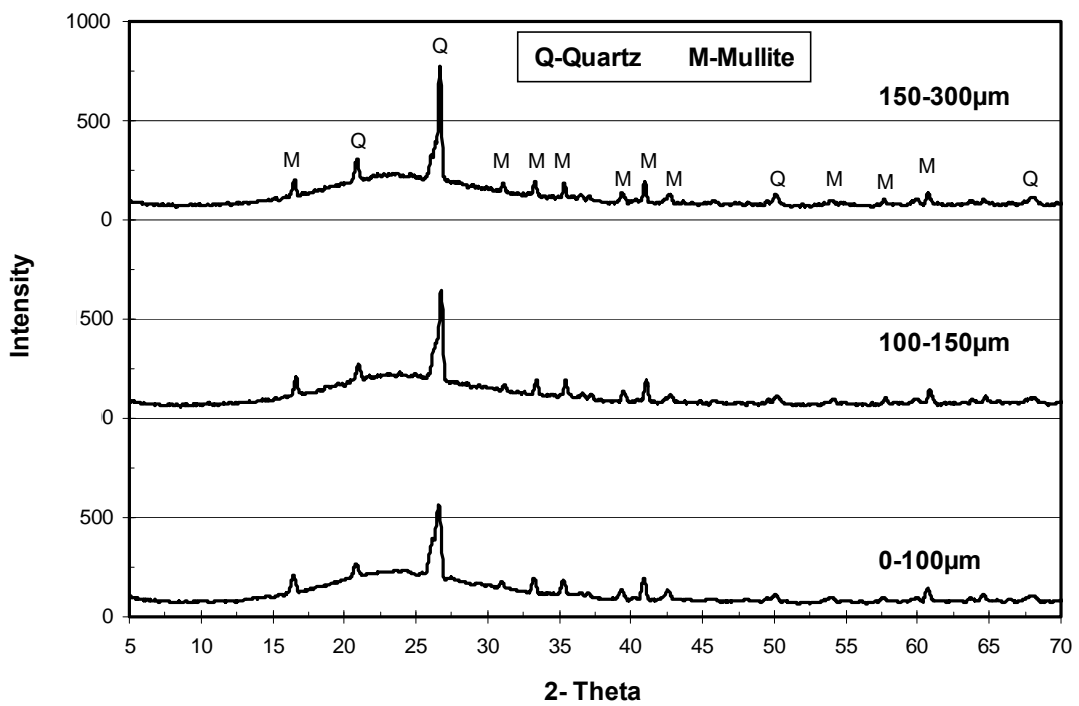
Fig.2. X-ray diffraction spectra of the cenosphere material of different size fractions.
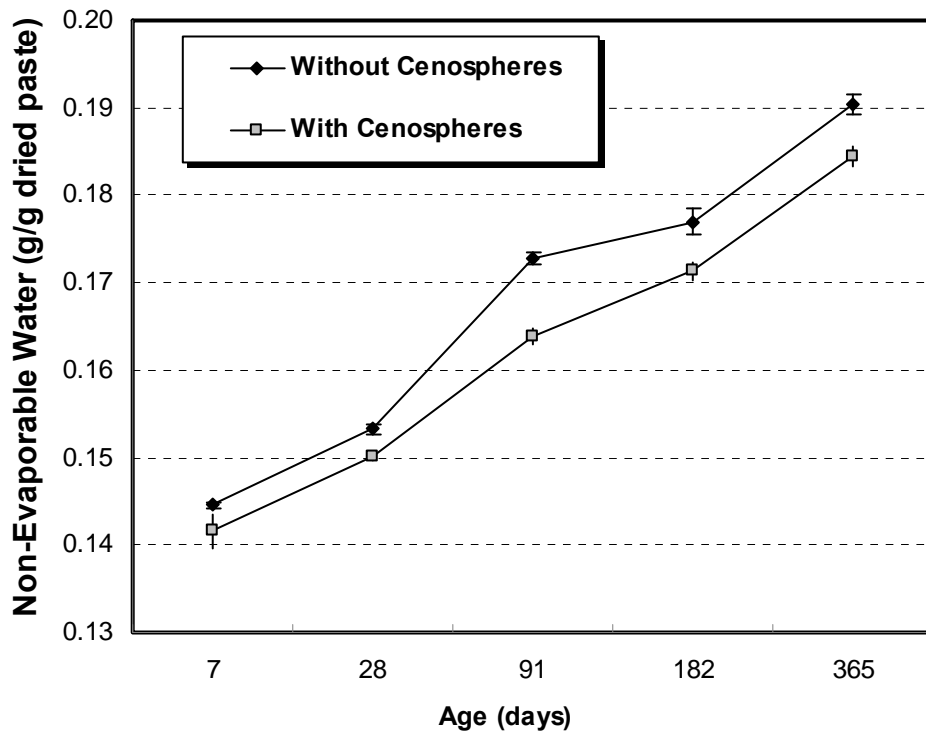
Fig.3. Non-evaporable water in hardened samples with and without cenospheres of <106 μm.
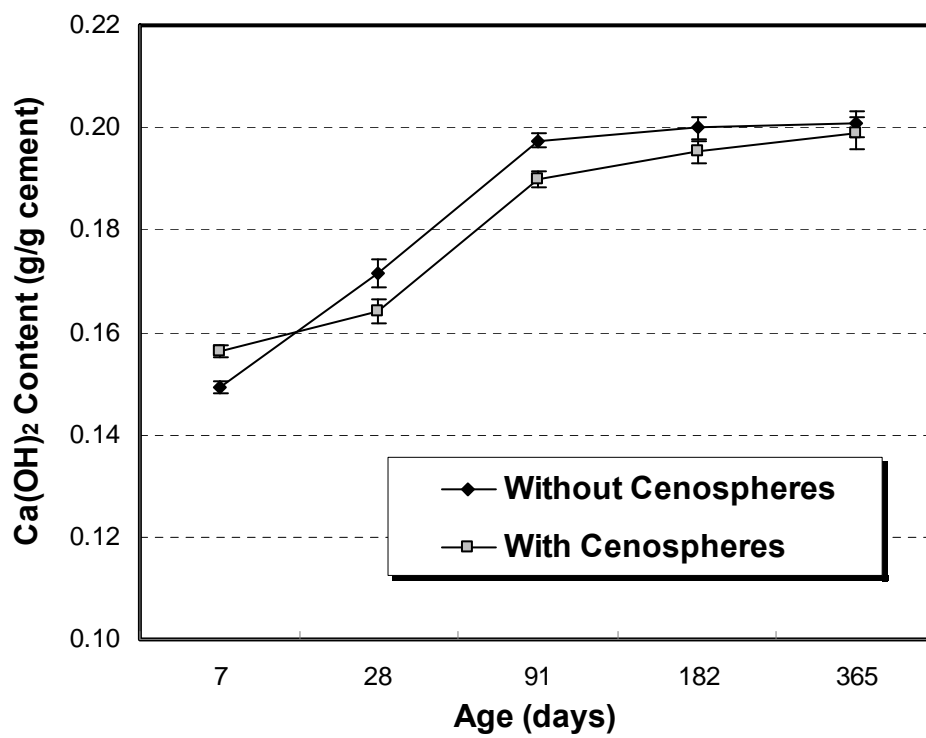
Fig.4. Calcium hydroxide content in samples with and without cenospheres of < 106 μm.
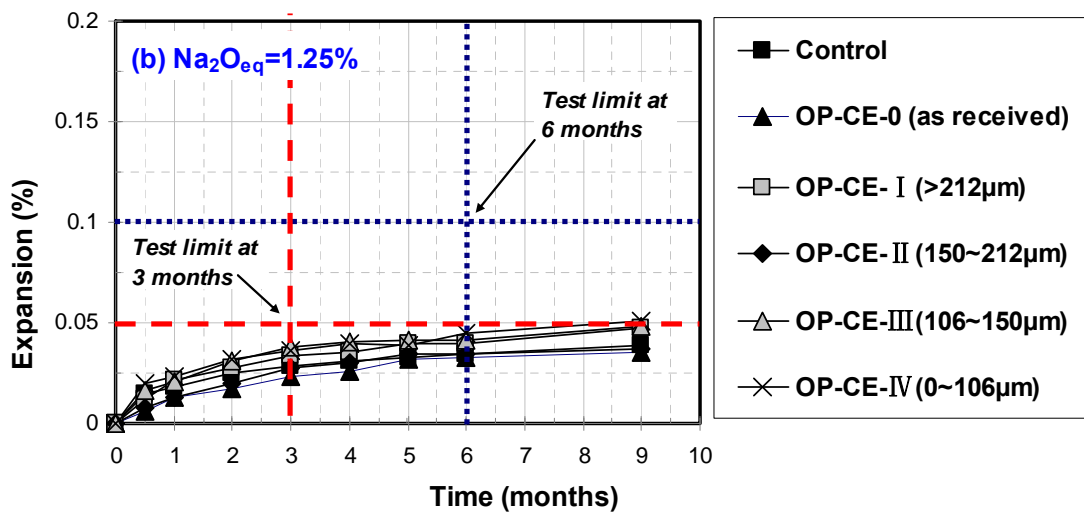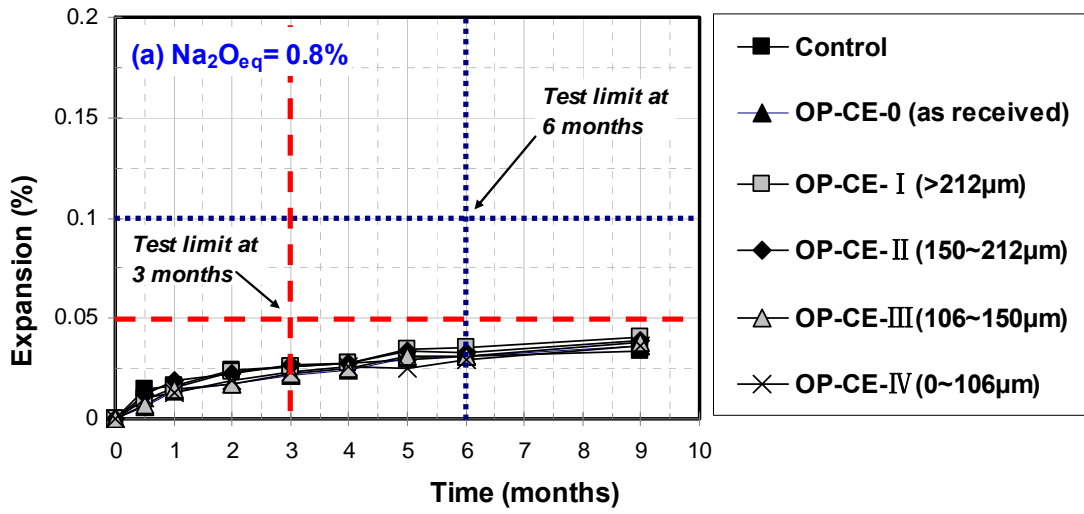
Fig.5. Expansion of the mortar bars determined according to ASTM C227 test: (a) Na_2O_{eq}=0.8%;

(b) Na_2O_{eq}=1.25%.
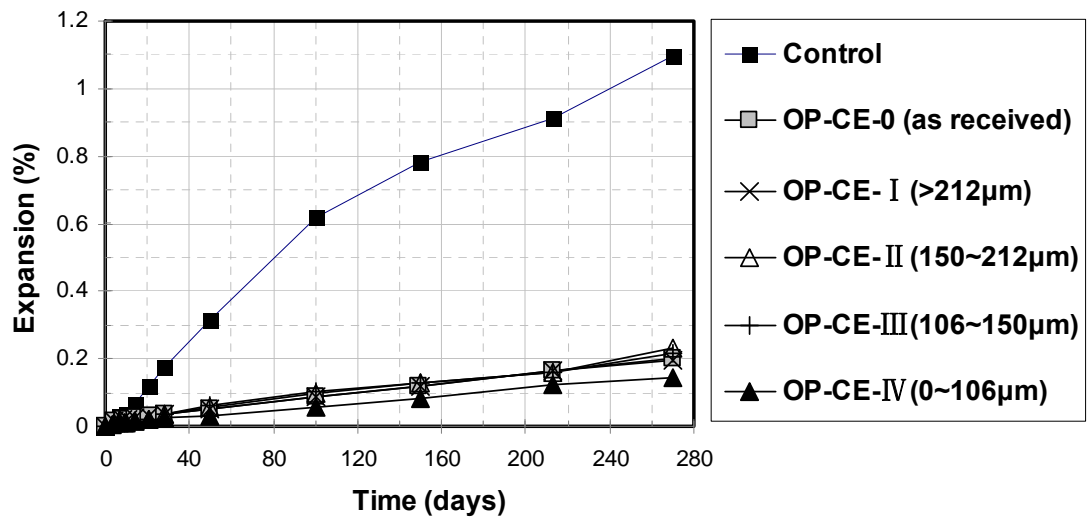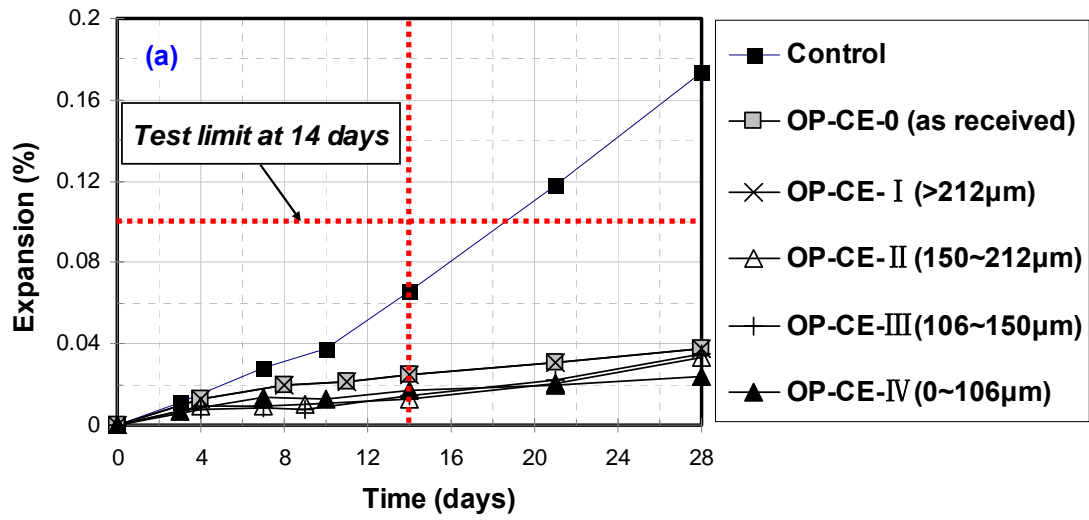
Fig.6. Expansion of the mortar bars determined according to ASTM C1260 test: (a) up to 28days;

(b) up to 9 months
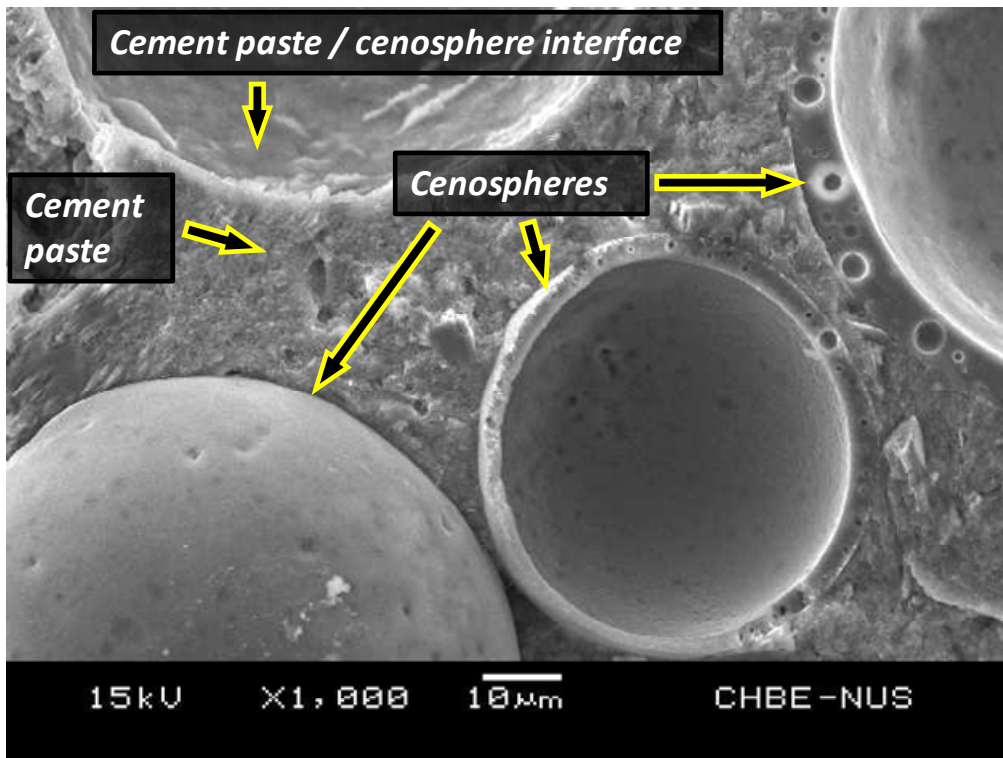
Fig.7. SEM micrograph of ASTM C227 mortar bars with cenospheres at 9 months (with

Na_2O_{eq}=1.25% by mass of cement).
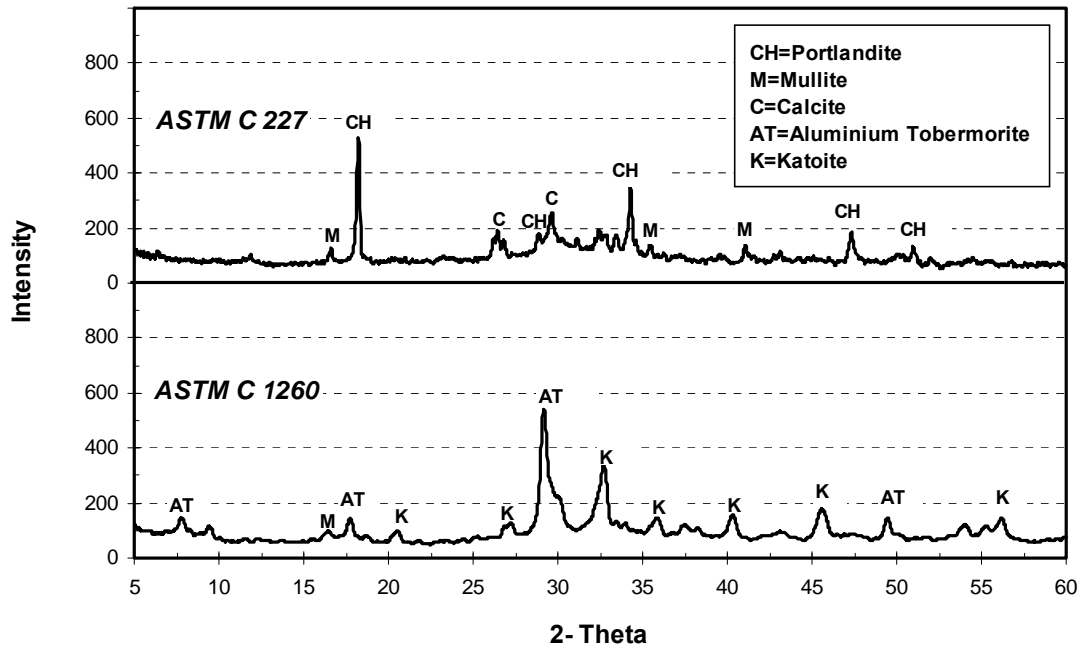
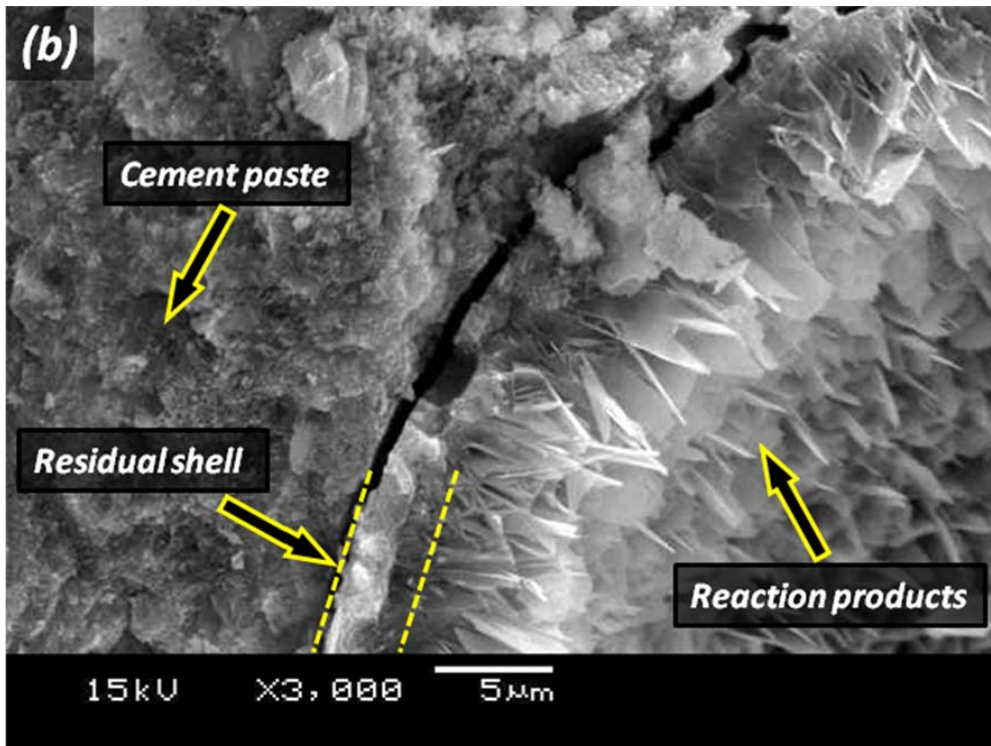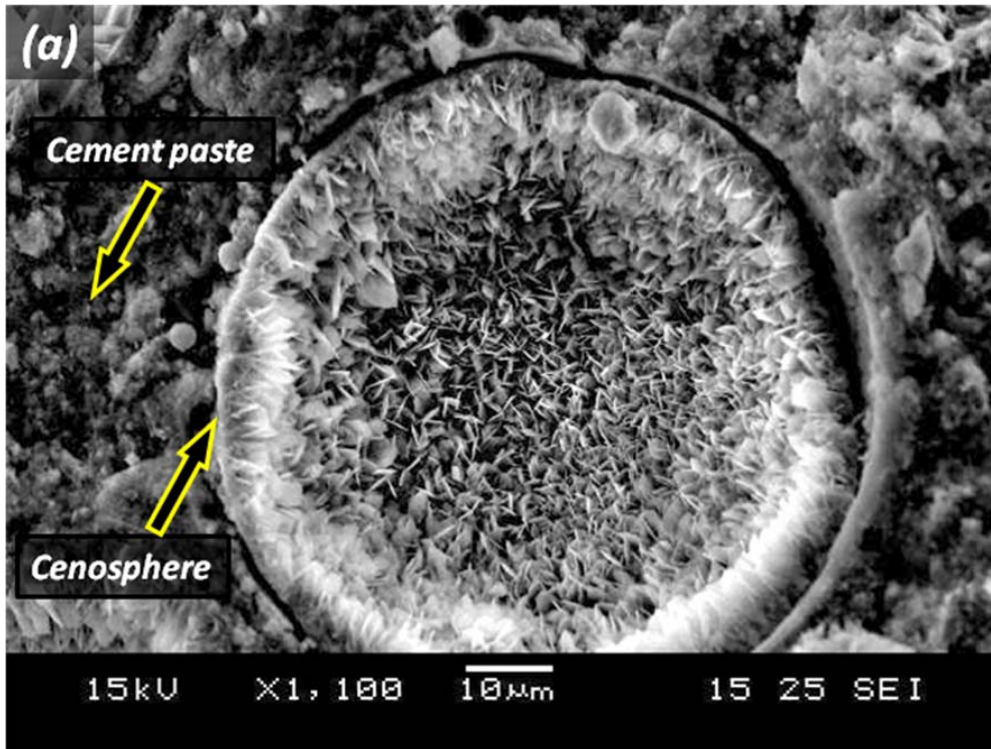Fig.8. X-ray diffraction spectra of samples from the mortar bars after ASTM C227 and C1260
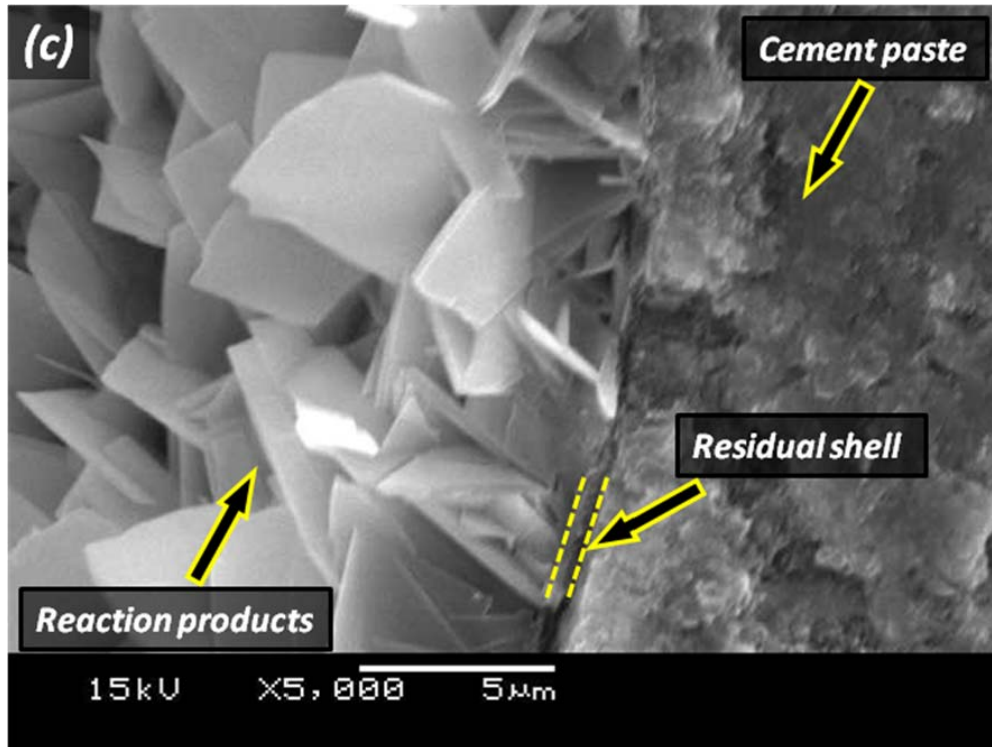
tests.

Fig.9. SEM micrographs of sample from the ASTM C1260 mortar bar with cenospheres at 9 months: (a) mortar with reaction products in a space originally occupied by a cenosphere; (b) residual shell of a cenosphere; (c) plate shaped crystals in space originally occupied by a ceneopsheres.