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Thaumasite form of sulfate attack in limestone cement mortars: A study on long term efficiency of mineral admixtures

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Abstract

Concrete and mortar made from limestone cement may exhibit a lack of durability due to the formation of thaumasite. The addition of minerals that improve the concrete durability is expected to slow down the formation of thaumasite. In this work the effect of natural pozzolana, fly ash, ground granulated blastfurnace slag and metakaolin on the thaumasite formation in limestone cement mortar is examined. A limestone cement, containing 15% w/w limestone, was used. Mortar specimens were prepared by replacing a part of limestone cement with the above minerals. The specimens were immersed in a 1.8% MgSO₄ solution and cured at 5°C and 25°C. The status of the samples after a storage period of 5 years was reported based on visual inspection, compressive strength, mass measurements, ultrasonic pulse velocity measurements and analytical techniques. It is concluded that the use of

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specific minerals, as partial replacement of cement, inhibits thaumasite formation in limestone cement mortar.

Keywords: Portland limestone cement; mineral admixtures; long-term performance; sulfate attack; thaumasite

1. Introduction

As is well known, sulfate attack may cause severe damage to cementitious materials. Besides the conventional sulfate reaction in mortars and concretes involving the formation and the expansive properties of ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot31\text{H}_2\text{O}$), another kind of sulfate attack attributed to the formation of thaumasite ($\text{CaSiO}_3\cdot\text{CaCO}_3\cdot\text{CaSO}_4\cdot15\text{H}_2\text{O}$) has been widely discussed during the recent years. There are several reports concerning either the presence of thaumasite in damaged structures [1] or its formation in laboratory scale experiments [2-10].

Portland limestone cement is susceptible to thaumasite sulfate attack (TSA) and it is a serious problem because limestone has increasingly been used as a filler or as a main cement constituent for many years [11-12]. Thaumasite formation requires a source of calcium silicate, sulfate and carbonate ions, excess humidity and preferably low temperature. Recent research shows that carbonate ions can also come from atmospheric carbonation [13]. Thaumasite formation may also be connected with the prior formation of ettringite or the presence of some reactive alumina [14-15]. According to Kohler et al. [16], thaumasite uses ettringite as a template for its initial nucleation, due to the structural similarities of these compounds.

The use of mineral admixtures lowers the permeability and refines the pore structure of cementitious materials. This is expected to contribute to a better performance of mortars and concretes containing limestone against sulfate attack. Some authors suggest that there are also chemical reasons for the higher resistance of blended cements, as the silicon rich C-S-H which is formed in the presence of pozzolanic materials shows higher resistance against the formation of thaumasite [17-18].

This paper reports results related to the effect of a second mineral addition on the sulfate resistance of limestone cement. Limestone cement mortars containing natural pozzolana, blastfurnace slag, fly ash or metakaolin were exposed to sulfate solution at low and room temperature and their performance was studied for 5 years.

2. Experimental

Portland cement clinker of industrial origin and limestone (L) of high calcite content (CaCO_3 : 95.7%) were used (Tables 1 and 2). Portland limestone cement, containing 15% w/w limestone, was produced by intergrinding clinker, limestone and gypsum in a pro-pilot plant ball mill of 5 kg capacity (sample LC1 of Table 3). The specific surface of the cement was $3950 \text{ cm}^2/\text{g}$, according to the Blaine method.

The minerals used and their chemical analysis are given in Table 2. Natural pozzolana (P) and fly ash (F), with high Ca content (ASTM type C), are Greek minerals and they are used by the cement and construction industries for the production of composite cements. Ground granulated blastfurnace slag (ggbs, S) is an imported mineral from Italy and is also used as a main cement constituent. The above minerals were ground and their mean particle size (d_{50}) was 10.5, 12.3 and $10.9 \mu\text{m}$ for the pozzolana, fly ash and ggbs respectively. Metakaolin (M) is a commercial product (Metastar) of high purity with a mean particle size of $5.1 \mu\text{m}$.

The mixes of Table 3 were prepared by replacing a given amount of the Portland limestone cement LC1 with the specific minerals. Depending on the mineral, a replacement of 10-50% by mass of LC1 was used. These percentages were selected on the basis of the reactivity of the minerals. Mortars were prepared, using the mixes of Table 3 (w/b=0.5, binder/sand=1:2.50). Siliceous (s) and calcareous (c) sand were used in order to study the effect of the sand type on thaumasite formation. The mortars containing siliceous sand are referred as XXX-s (for example LC1-s) while the mortars containing calcareous sand are referred as XXX-c (for example LC1-c). Mortar prisms of size 40x40x53 mm were prepared. The specimens were left in the mould for 24h, then they were water cured for 6 days and finally they were air-cured for 21 days at laboratory temperature ($25\pm 2^{\circ}\text{C}$). This curing program is believed to be close to the conditions in field constructions.

After the 28-days initial curing the specimens were stored in 1.8 %w/w MgSO_4 solution. The samples were cured at: i) 5°C (laboratory refrigerator, $\pm 2^{\circ}\text{C}$) and ii) 25°C (laboratory environment, $\pm 5^{\circ}\text{C}$). In both cases, the MgSO_4 solution was replaced every 3 months.

The visual examination of the samples was performed at regular intervals and all significant variations, such as changes to surface colour and texture, formation of coatings, deterioration, expansion and cracking were recorded.

The compressive strength of the specimens was measured after 28 days and after 9 months exposure in MgSO_4 solution, in order to investigate the influence of the sulfate attack on the strength loss of the samples. Changes in specimen's mass were recorded at regular intervals. The ultrasonic pulse velocity test (apparatus: 58-E48, Controls Testing Equipments Ltd) was used as a measure of the internal soundness of the samples. The measurements were carried out at regular intervals up to one

year. Concerning the mass and ultrasonic pulse velocity, three prisms for each measurement were used and the presented results are the average value.

XRD measurements were performed on samples at regular intervals in order to identify any compounds formed during the exposure to MgSO_4 . A Siemens D-5000 X-ray diffractometer, with Cu Ka1 radiation ($\lambda = 1.5405 \text{ \AA}$) was used. Measurements were carried out on samples coming from either the hard core or the deteriorated part of the specimens.

3. Results And Discussion

3.1. Visual inspection

Visual inspection of the specimens was carried out monthly. Photos of the specimens stored in sulfate solution for 11, 16, 35, 41, 53 and 60 months at 5°C are presented in Figures 1 and 2.

Indications of starting deterioration were first observed on specimens with 15% limestone (LC1-s, LC1-c) and natural pozzolana (LPC-s, LPC-c) for both kind of sand after 8 months of exposure at 5°C . A longer time (11 months) was required for the beginning of deterioration in samples with fly ash (LFC-s, LFC-c). The specimens with metakaolin and siliceous sand (LMC-s) showed the first signs of deterioration after 16 months of exposure. Finally, a slight damage of specimens with blastfurnace slag (LSC-s, LSC-c) and with metakaolin and calcareous sand (LMC-c) was observed after 30 months. In all cases, the first sign of attack was the deterioration of the corners followed by cracking along the edges. Progressively, expansion and spalling took place on the surface of the specimens. The surface of the cracks was covered with the white soft substance.

It is obvious that the use of ggbs and metakaolin improved the resistance of the limestone cements against sulfate attack at low temperatures. The use of fly ash seemed to retard the sulfate attack, whereas the pozzolana addition did not practically affect the vulnerability to sulfate attack at 5°C.

No damage was observed in the specimens exposed to sulfate solution for 60 months at 25°C (figs 3 and 4). It can be stated that “conventional” sulfate attack of well made mortars is very slow, much slower than thaumasite sulfate attack (TSA) at low temperatures. Some researchers have reported the formation of small quantities of thaumasite, even at room temperature [19-22]. It is generally accepted that extensive thaumasite formation is related with low temperature. However, other factors (cement type and composition, specimen composition, degree of carbonation, type and concentration of sulfate solutions, pH of the pore solution) may also affect thaumasite formation. In any case, further research is needed in order to have a thorough insight on the effect of temperature on thaumasite formation.

3.3. Compressive strength

The 28day compressive strength of the specimens with siliceous sand, prior to any exposure to sulfates, is shown in Fig. 5. The addition of ggbs (sample LSC) and metakaolin (sample LMC) increased the strength while the addition of fly ash (sample LFC) had no detectable effect on the strength. The pozzolana addition (sample LPC) decreased the strength measured after 28 days. After nine months exposure in the MgSO₄ solution at 5°C, a significant loss of strength has been measured in limestone cement mortar and in the mortar containing pozzolana (Fig. 5). The mortar containing fly ash showed a lower strength loss. More specifically, the loss of strength was 18% of the 28day strength for the Portland limestone cement (LC1), 34% for the limestone

cement mortar containing 20% pozzolana (LPC) and 9% for the limestone cement mortar containing 30% fly ash (LFC). The strength of the mortar containing metakaolin was found to be the same as the 28day strength. On the contrary, the addition of ggbs led to a strength increase. Based on the strength results, it is concluded that ggbs and metakaolin improve the resistance of the limestone cements against sulfate attack at low temperatures. The use of fly ash seems to retard the sulfate attack, whereas the presence of pozzolana impairs the resistance of limestone cement against sulfate attack. Concerning the specimens cured at 25°C, their compressive strength increased with storage time in all samples. This fact was expected as no visual damage of the specimens had been observed.

The 28day compressive strength of the specimens with calcareous sand, prior to any exposure to sulfates, is shown in Fig. 6. The addition of ggbs (sample LSC) and metakaolin (sample LMC) led to an increase of the strength, the addition of fly ash (sample LFC) had no effect on the strength, while the pozzolana addition (sample LPC) decreased the 28day strength. After nine months exposure in the $MgSO_4$ solution at 5°C, a significant loss of strength has been measured in limestone cement mortar and in the mortar containing pozzolana (Fig. 6). More specifically, the loss of strength was 21% of the 28day strength for the Portland limestone cement (LC1) and the same for the limestone cement mortar containing 20% pozzolana (LPC). The 9month strength of the mortar containing metakaolin was found to be the same as the 28day strength. On the contrary, the addition of ggbs and fly ash led to a strength increase. Based on the strength results, it is shown that fly ash, ggbs and metakaolin improve the resistance of the limestone cements against sulfate attack at low temperatures. The pozzolana addition impairs the resistance of the limestone cement against sulfate attack. Concerning the specimens cured at 25°C, their compressive

strength increased with storage time in all samples. This fact was expected as no visual damage of the specimens has been observed.

3.3 Ultrasonic pulse velocity

Ultrasonic pulse velocity test is a non-destructive test method that determines the velocity of longitudinal waves. This determination consists of measurement of the time taken by a pulse to travel a measured distance (specimen's width). The test gives information about the interior of the specimen and provides evidence of internal microcracking and of the soundness of the microstructure of the material. The test is, therefore, useful to detect cracking, voids, deterioration and the uniformity of the material. The presence of void or crack on the pulse path will increase the path length, as pulse goes around the void, leading to the decrease of the pulse velocity [23-24].

The ultrasonic pulse velocity was measured periodically, after the first signs of damage were observed. The experiments were carried out for 13 months. After this time, the condition of specimens' surfaces did not permit to take any reliable measurements. The results for specimens with siliceous and calcareous sand are presented in Figs. 7 and 8 respectively. As can be seen, the limestone cement with natural pozzolana (LPC-s, LPC-c) showed the worst behavior while the addition of fly ash (samples: LFC-s, LFC-c), ggbs (samples: LSC-s, LSC-c) and metakaolin (samples: LMC-s, LMC-c) seemed to improve the behavior of limestone cement mortar.

3.4 Mass measurements

The changes in specimens' mass were also measured periodically, and the results are shown in Figs. 9 and 10, for siliceous and calcareous sand respectively. The mass loss is expressed as the ratio m/m_0 , where m_0 is the initial mass and m is the mass after the exposure in sulfate solution.

In the case of siliceous sand, LC1 showed the worst behaviour, losing after 60 months of exposure 79% of its mass. The specimens containing natural pozzolana (LPC), fly ash (LFC) and metakaolin (LMC) lost 54%, 33% and 31% of their mass respectively. The specimen with ground granulated blastfurnace slag showed the best behaviour, losing only 18% of its mass.

In the case of calcareous sand, LC1 and LPC showed the worst behaviour, losing after 60 months of exposure 59% and 57% of their mass, respectively. The specimens containing fly ash (LFC) lost 44% of its mass. The specimens with ground granulated blastfurnace slag (LSC) and metakaolin (LMC) showed the best behaviour, losing 32% and 34% of their mass respectively.

As can be seen, the use of the added minerals, especially ggbs and metakaolin, improved the sulfate resistance of the mortars.

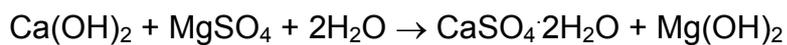
It is not easy to evaluate the effect of the sand type on the low-temperature sulfate resistance of mortar, based on the mass measurements. It seems that, in the case of limestone cements with fly ash, pozzolana, ggbs or metakaolin, the type of the sand (calcareous or siliceous) did not much affect the thaumasite form of sulfate attack. Further investigation is needed in the case of pure limestone cement where the use of siliceous sand seems to accelerate the deterioration of the mortar specimens.

3.5 Analytical Techniques

The identification of products formed as a result of the sulfate attack was based on XRD. In all cases, the composition of the sound core of the specimens corresponded to that of a normal hydrated cement containing mainly calcite and/or quartz (depending on the composition of the mortar) as well as calcium hydroxide.

The XRD patterns of the sound core of the samples LC1-c and LMC-c is presented in Fig 11. Calcite and portlandite are the main constituents. The absence of gypsum indicates that the diffusion of sulfates into the sample is very slow.

XRD measurements were also carried out on the soft, white material covering the surface of the cracks. The XRD patterns of surface materials of the samples LC1-c, LPC-c and LMC-c, after 60 months of exposure, are presented in Fig 12. In all cases, the degradation material was found to consist mainly of thaumasite, gypsum, sand (calcite or quartz) and traces of brucite. It must be noted that no calcium hydroxide was detected in the degradation products. Portlandite most probably has reacted with magnesium sulfate to form gypsum and brucite, both found in the degradation products, according to the reaction:



The low solubility of brucite favors the consumption of calcium hydroxide. This leads to a reduction of pH and as a result C-S-H becomes more susceptible to sulfate attack.

Figure 13 present the SEM photos of LPC-c and LMC-c samples, after 12 and 35 months of exposure, respectively. As it is seen, the deterioration area in sample LPC-c is covered with the needle-like grains of thaumasite (Fig. 13a). Fig. 13b shows the starting formation of thaumasite as well as the cubic grains of gypsum, formed according to the above reaction on the surface of the specimen LMC-c.

As it is concluded, certain minerals, especially those that have a strong effect on pore structure refinement, like ggbs and metakaolin [25-26], substantially improve the resistance of limestone cement mortars against TSA. The use of fly ash delays the sulfate attack of the mortars while natural pozzolana does not have any considerable beneficial effect. It must be noted that this mineral is a very good pozzolanic material, widely used in cement production. However, its pozzolanic reaction is initially slow and is accelerated mainly after the first 28 days. It seems that the storage of the specimens at low temperature, further depressed the pozzolanic reaction and, as a result, the sulfate resistance of these mortars is impaired.

4. Conclusions

The following conclusions can be drawn from the present study:

- Limestone cement mortar is susceptible to thaumasite sulfate attack at low temperature.
- The use of specific mineral replacements retards thaumasite formation in limestone cement mortar.
- Incorporation of metakaolin and ggbs substantially improved the resistance of the limestone cements against sulfate attack. The use of fly ash seemed to retard sulfate attack. Natural pozzolana was not very effective against sulfate attack, probably because the pozzolanic reaction of this material is slow, compared with the other minerals.
- No damage was observed in the specimens exposed to sulfate solution at 25°C for 60 months. It seems that in MgSO₄ solutions the “conventional” sulfate attack, at ambient temperature, is much slower than thaumasite sulfate attack, at low temperature.

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Table 1

Chemical and mineralogical composition of clinker

Chemical composition (% w/w)		Mineralogical composition (%w/w)	
SiO ₂	21.47	C ₃ S *	65.0
Al ₂ O ₃	5.00	C ₂ S	12.6
Fe ₂ O ₃	3.89	C ₃ A	6.7
CaO	65.67	C ₄ AF	11.8
MgO	1.89		
K ₂ O	0.68	Moduli	
Na ₂ O	0.16	Lime Saturation Factor (LSF)	95.79
SO ₃	1.04	Silica Ratio (SR)	2.42
TOTAL	99.70	Alumina Ratio (AR)	1.29
fCaO	1.15	Hydraulic Modulus (HM)	2.18

* Cement chemistry notation: C: CaO, S: SiO₂, A: Al₂O₃, F: Fe₂O₃**Table 2**

Chemical analysis of minerals (% w/w)

Oxide	Limestone (L)	Natural Pozzolana (P)	Fly ash (F)	Ggbs (S)	Metakaolin (M)
SiO ₂	0.54	59.18	49.33	36.74	54.41
Al ₂ O ₃	0.43	16.12	20.72	10.44	43.94
Fe ₂ O ₃	0.20	6.14	7.98	1.20	0.35
CaO	53.61	4.92	10.26	40.32	0.37
MgO	1.29	1.96	2.19	7.60	-
K ₂ O	0.06	2.15	1.94	0.31	0.31
LOI	43.73	4.78	2.02	0.44	-
TOTAL	99.86	95.25	94.44	97.05	99.38

Table 3

Codes and composition of the produced mixes

Code	Composition of samples
LC1	Portland limestone cement (clinker: 85% w/w, limestone: 15% w/w) (gypsum: 5% of clinker by mass)
LPC	LC1: 80% w/w, Natural pozzolana (P): 20% w/w
LFC	LC1: 70% w/w, Fly ash (F): 30% w/w
LSC	LC1: 50% w/w, Ggbs (S): 50% w/w
LMC	LC1: 90% w/w, Metakaolin (M): 10% w/w

Table 4Visual inspection of specimens cured in a 1.8% MgSO₄ solution at 5°C.

Sample	Exposure (months)														
	7	8	9	10	11	16	30	37	42	48	49	50	53	56	60
LC1-s	0	1	2	2	2	3	5	5	5	6	6	7	8	8	9
LPC-s	1	2	3	3	3	4	4	4	4	5	5	6	7	7	8
LFC-s	0	0	0	0	1	1	2	2	2	3	4	4	4	4	5
LSC-s	0	0	0	0	0	0	2	2	2	2	2	3	3	4	4
LMC-s	0	0	0	0	0	1	2	2	2	2	2	3	4	4	5
LC1-c	0	1	2	2	3	3	4	4	5	6	6	6	7	8	9
LPC-c	0	2	3	3	3	4	5	5	6	7	7	7	8	8	8
LFC-c	0	0	0	0	1	1	2	2	3	4	5	5	5	6	6
LSC-c	0	0	0	0	0	0	1	1	2	3	3	3	4	5	5
LMC-c	0	0	0	0	0	0	1	2	3	3	3	3	4	4	5

0: no visible deterioration,

1: some deterioration at corners

2: deterioration at corners

3: deterioration at corners and some cracking along the edges

4: deterioration at corners and cracking along the edges

5: cracking and expansion

6: bulge of surfaces

7: extensive cracking and expansion

8: extensive spalling

9: complete damage

FIGURE CAPTIONS

Fig. 1 Specimens with siliceous sand, cured for 11, 16, 35, 41, 53, 60 months in a 1.8% MgSO₄ solution at 5° C

Fig. 2 Specimens with calcareous sand, cured for 11,16, 35, 41, 53, 60 months in a 1.8% MgSO₄ solution at 5°C

Fig. 3 Specimens with siliceous sand cured for 60 months in a 1.8% MgSO₄ solution at 25°C.

Fig. 4 Specimens with calcareous sand cured for 60 months in a 1.8% MgSO₄ solution at 25°C.

Fig. 5 Effect of the curing temperature conditions on the compressive strength of specimens made with siliceous sand

Fig. 6 Effect of the curing temperature on the compressive strength of specimens made with calcareous sand

Fig. 7 Ultrasonic pulse velocity of specimens with siliceous sand (5°C, 1.8% MgSO₄ solution)

Fig. 8 Ultrasonic pulse velocity of specimens with calcareous sand (5°C, 1.8% MgSO₄ solution)

Fig. 9 Changes in mass of specimens with siliceous sand (5°C, 1.8% MgSO₄ solution)

Fig. 10 Changes in mass of specimens with calcareous sand (5°C, 1.8% MgSO₄ solution)

Fig. 11 XRD patterns of the sound core (LC1-c, LMC-c) (1: Calcite, 2: Portlandite)

Fig. 12 XRD patterns of deterioration products (LC1-c, LPC-c, LMC-c) (1: Thaumasite, 2: Gypsum, 3: Calcite, 4: Brucite) (60 months, 5°C, 1.8% MgSO₄ solution)

Fig 13 SEM photos of LPC-c (a) and LMC-c (b), cured in a 1.8% MgSO₄ solution at 5°C (T: Thaumasite, G: Gypsum).

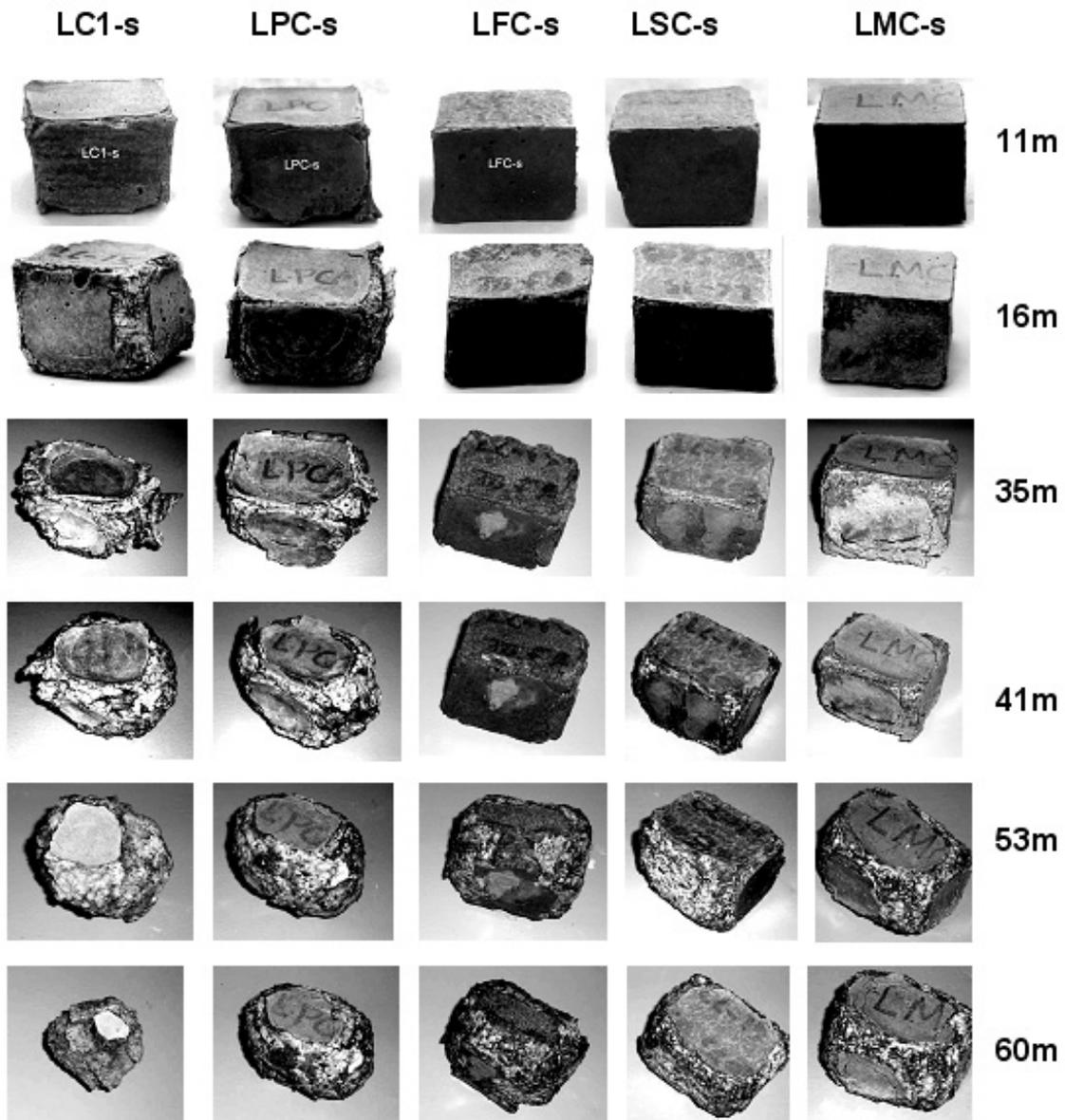


Fig. 1

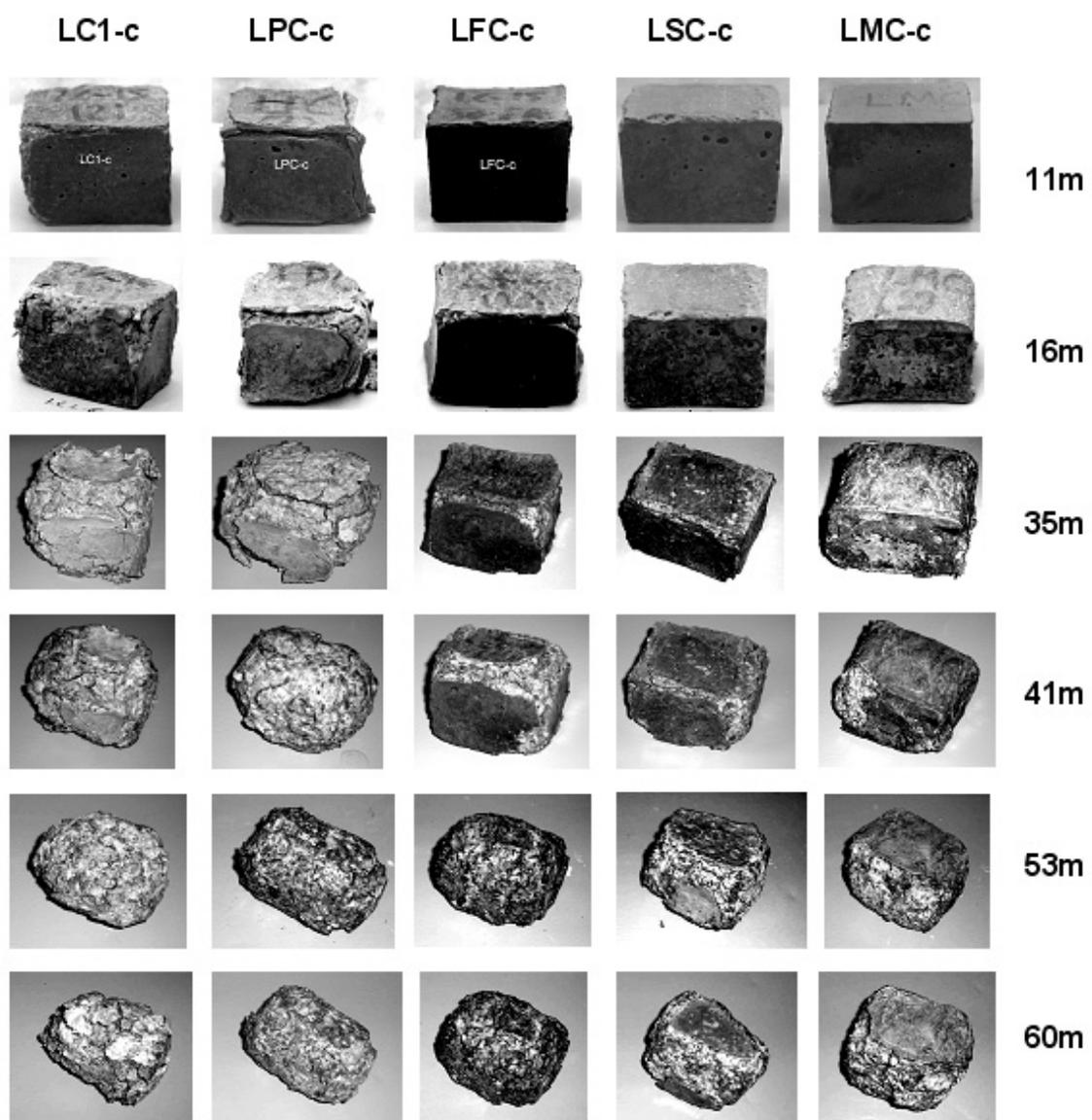


Fig. 2

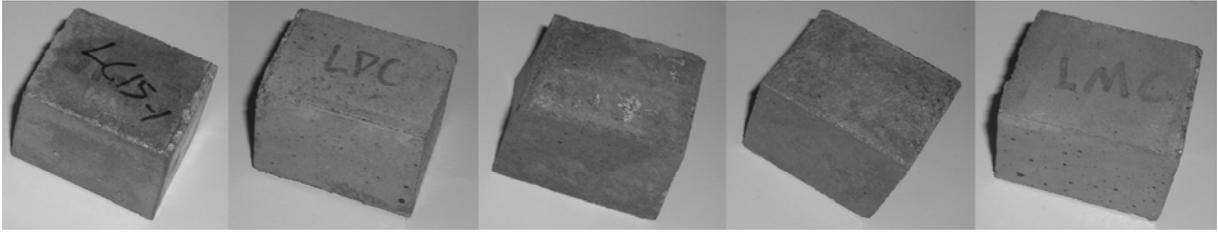


Fig. 3



Fig. 4

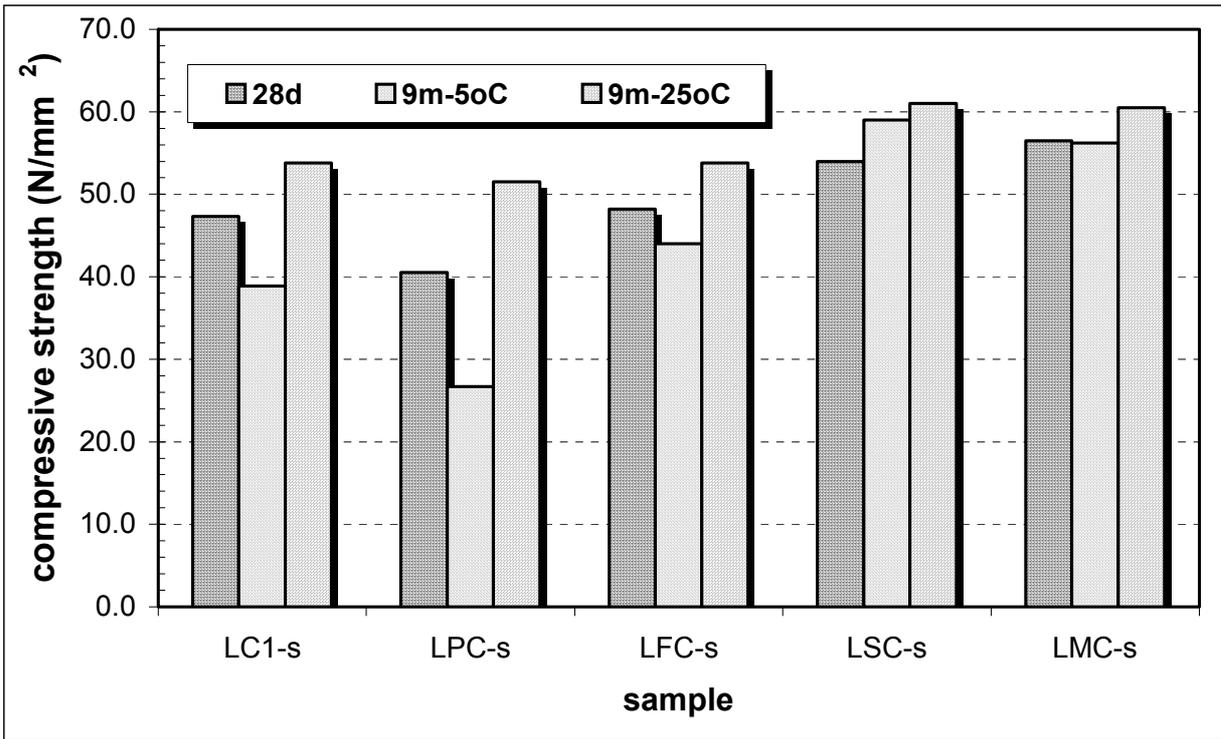


Fig. 5

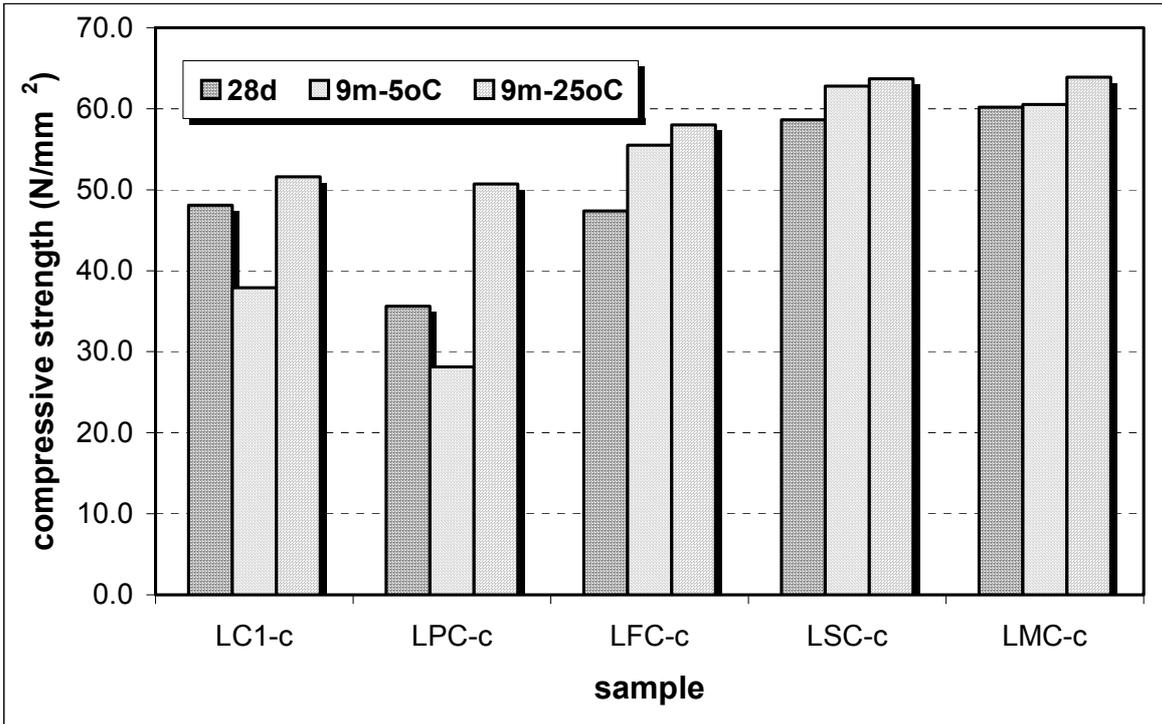


Fig. 6

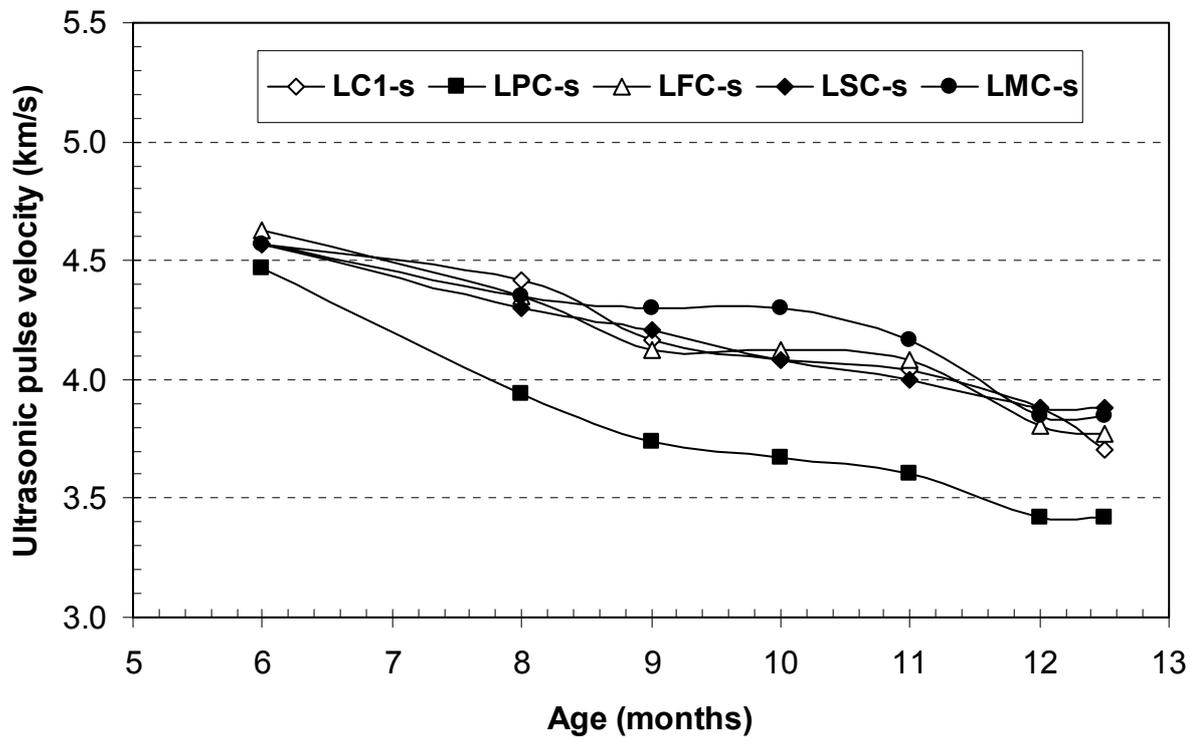


Fig. 7

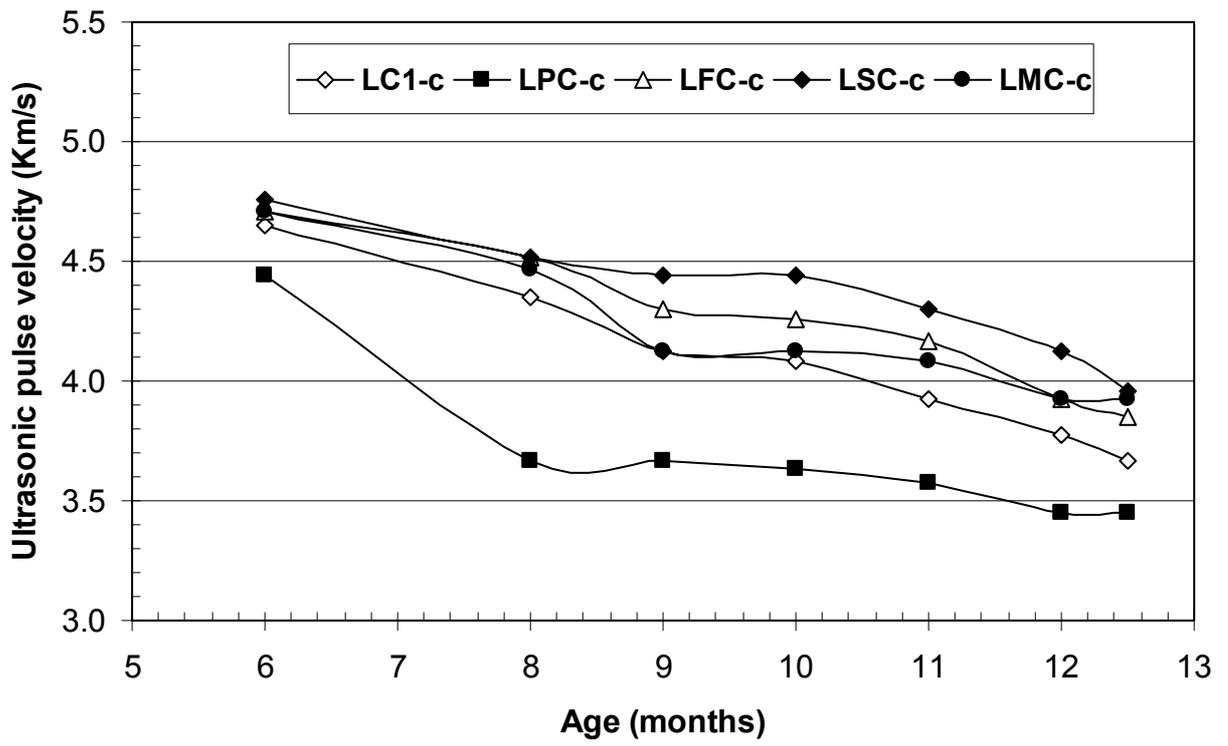


Fig. 8.

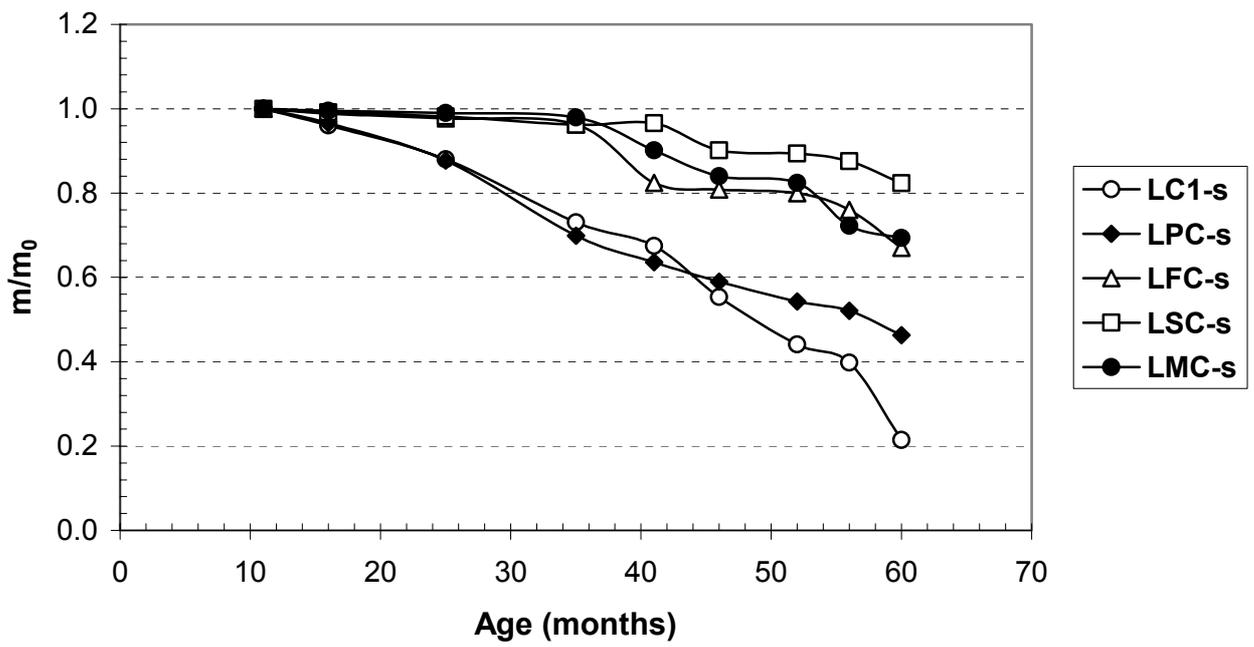


Fig. 9

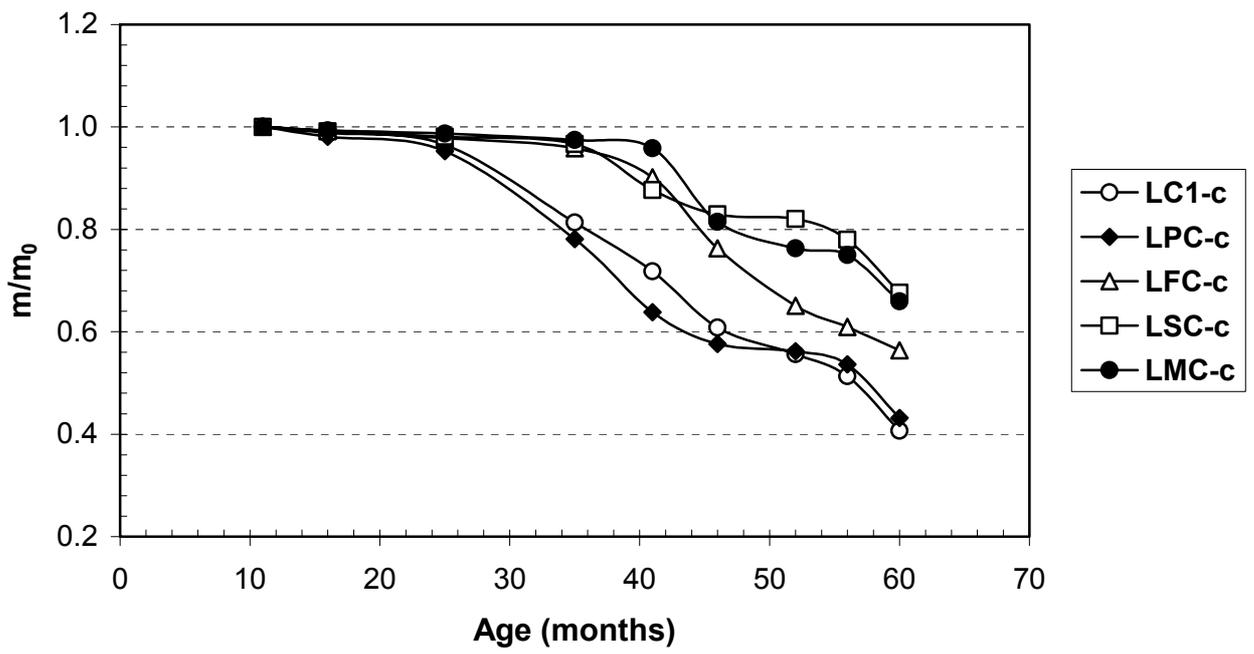


Fig. 10

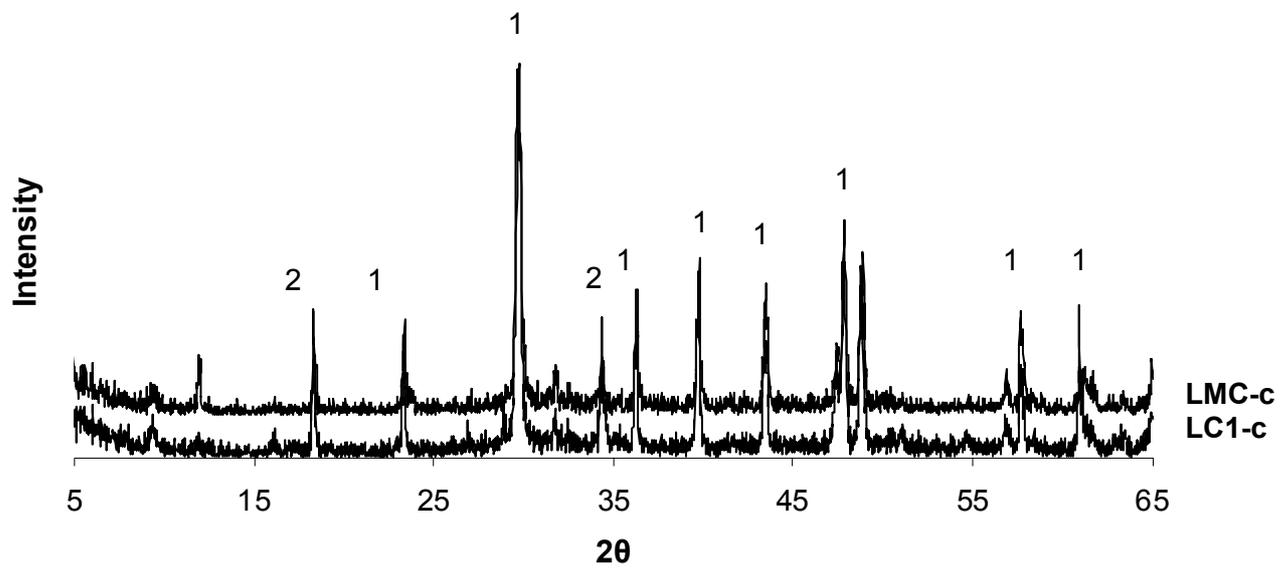


Fig. 11

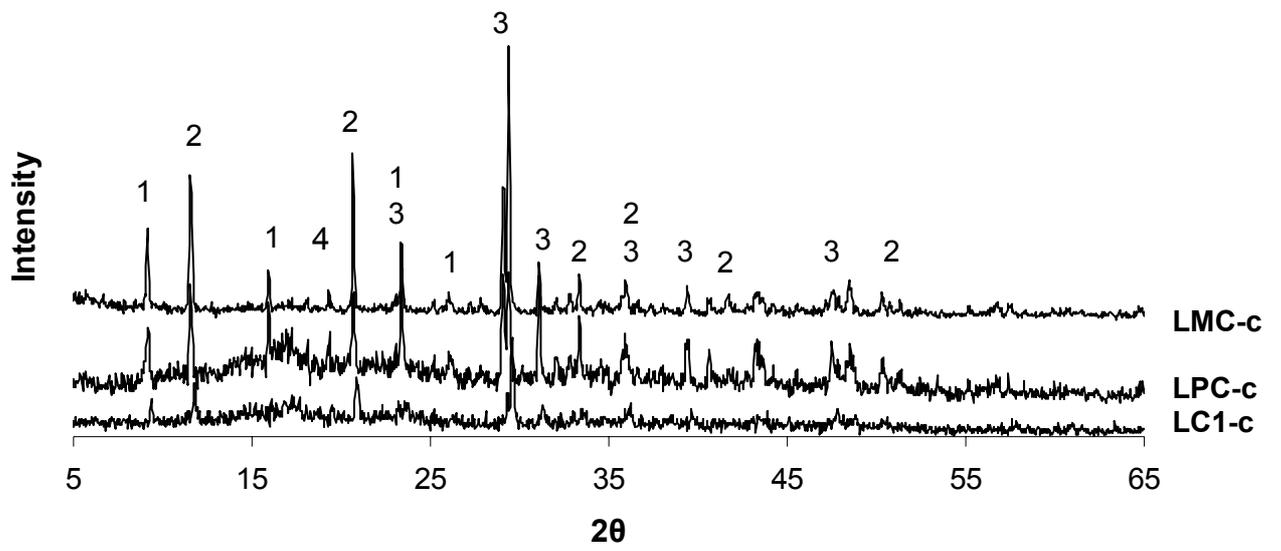
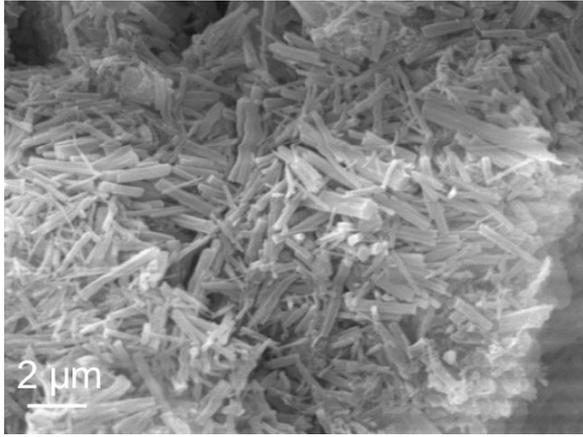
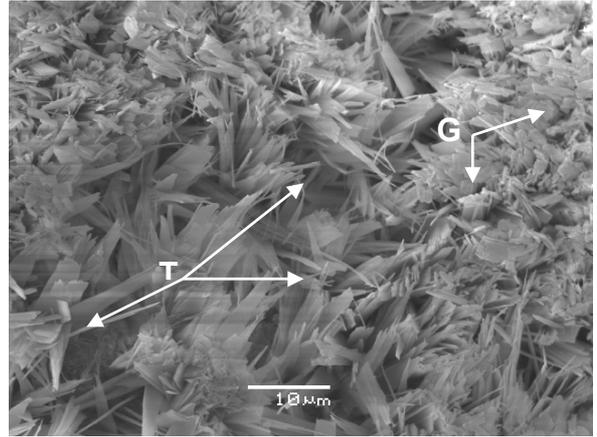


Fig. 12



a



b

Fig. 13