Hydration Behavior of Celitement®: Kinetics, Phase Composition, Microstructure and Mechanical Properties

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Abstract

A new type of cementitious material named Celitement has been developed at Karlsruhe Institute of Technology (KIT). Celitement is characterized by its low energy demand and CO_2 emissions during production. Celitement is made in a two step process including hydrothermal processing and further mechanochemical treatment of the products together with silicates or silica. Basically Celitement is composed of hydraulic calcium hydrosilicates and non-reactive components, i.e. in contrast to OPC it contains structural water.

This study presents the hydration behavior of one particular product of the Celitement family. The starting material was obtained by hydrothermal treatment of $Ca(OH)_2$ and quartz sand at 200°C and co-milling of the autoclaved product with granulated blast furnace slag (BFS). The bulk material (90wt% as seen by XRD) is amorphous and built up mainly of monomeric (SiO_4) and dimeric (Si_2O_7) silicate species, which were identified by spectroscopic methods. The crystalline part (10wt%) consists of non-hydraulic α-dicalcium silicate hydrate (α-C_2SH).

The hydration of Celitement was investigated on pure paste samples by in-situ XRD. Due to the nearly amorphous nature of Celitement it is relatively easy to detect and distinguish between the phases formed in course of the hydration process. In the first 17 hours of hydration we did not observe any newly formed hydrates detectable by XRD. After 17-20 hours well ordered C-S-H phase becomes visible in XRD. The period 20-30h is characterized by an increased growth of C-S-H, AFm ($C_8A_2C(bar).24H$) and subordinated hydrotalcite. Maximum intensity of the main reflection of C-S-H phase (d=3.05Å) is reached after about 48 hours. The C-S-H phase built upon hydration of Celitement shows similar XRD features as that obtained as result of hydration of OPC. Spectroscopic evidence (IR, Raman, Trimethylsilylation) points to a higher connectivity of the silicon tetrahedra. No formation of $Ca(OH)_2$ was observed.
After adding water we observed a similar calorimetric curve as in OPC: initial wetting was followed by a dormant period of 4 hours succeeded by substantial release of heat with a maximum at 16 hours. After 7 days the heat of hydration was about 200J/g, which is comparable to composite cements of type CEM III and much lower than OPC. The results show that the main hydration process takes place in the first 48 hours of the Celitement hydration. The rapid evolution of the microstructure of the hardened Celitement paste as evidenced by SEM, mercury-porosimetry and tomography is the prerequisite for the excellent mechanical properties of this novel material.

Originality

*This contribution presents for the first time the hydration behavior of one example of the Celitement family, a completely new hydraulic binder. It is the second of two papers, which we propose to the ICCC. For more information about the main concept, processing and further development please refer to **CELITEMENT® – A NEW SUSTAINABLE HYDRAULIC BINDER BASED ON CALCIUM HYDROSILICATES** by Stemmermann et al. The innovation involves a sustainable manufacturing process, which is completely different from the standard OPC production.*
The hydration behavior of Celitement shows on one side great similarities with OPC in terms of workability and applicability, making Celitement a real alternative to OPC. On the other side there are important differences regarding phase composition, heat of hydration, development of microstructure and resulting durability.

Chief contributions

Beyond its environmental friendly production in terms of energy and CO_2 emissions the new hydraulic binder Celitement is characterized by its broad applicability and durability. These properties are highly influenced by the development of microstructure of the hardening paste during hydration. The composition and the structural features of the resulting C-S-H phases are key issues for the understanding of the hydration behavior and further development of the new binders. The application of a broad band of complementary investigation methods including conventional and synchrotron based techniques is a necessary prerequisite for understanding the challenging amorphous structure of both: Celitement itself and the resulting hardened Celitement paste.

Keywords: Celitement, Hydration, In situ XRD

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Introduction

Celitement is a general name for a new family of binding materials which have been developed at Karlsruhe Institute of Technology (KIT). The main feature of Celitement is its production in a two step process including hydrothermal preparation and further mechanochemical treatment of the products together with silicates or silica (Stemmermann et al., 2010, Beuchle et al., 2007, Beuchle et al., 2008[1,2,3]). This results in two very important properties of Celitement: 1) highly variable in the C/S, and 2) low energy demand and CO_2 emissions during production. In terms of phase composition there is a large difference between Celitement and Ordinary Portland Cement (OPC). Whereas the OPC consists of clinker minerals and hydrous and anhydrous calcium sulfates, Celitement is built up of hydraulic calcium hydrosilicates.

In this paper we will describe the hydration behavior of Celitement on one example and highlight the similarities and differences to OPC.

Experimental procedure

Synthesis. The sample upon investigation was prepared in a two step procedure. $Ca(OH)_2$ (4.6 m^2/g) and SiO_2 (quartz) (0.4m^2/g) have been treated hydrothermally at 190°C for 6 hours. After drying the product at 60°C for 24 hours, it was treated mechanochemically in a ball mill together with an equal mass of blast furnace slag (BFS, Blaine 3000).

XRD. XRD was performed on an X`Pert MPD (PANalytical) in Θ/Θ geometry equipped with Cu tube and a multi strip PIXel detector. Measurements were done on powders (hydrothermal product and cementitious material) and cement pastes (*in situ* hydration). The first XRD *in situ* pattern was taken 1 hour after mixing with water. Successively the sample was measured every 15 minutes. The sample was covered with Capton foil in order to avoid contact with atmospheric CO_2.

Vibrational spectroscopy. IR-spectroscopy was performed on KBr pellets with a IFS 66v/S spectrometer (Bruker) in MIR. Near infrared (NIR) spectra were acquired with a MATRIX-F spectrometer (Bruker) on powders and cement pastes.

Calorimetry. Calorimetric investigations were performed with a TAM Air calorimeter.

Compressive strength. Standard prisms of Celitement mortars (40x40x160mm) were prepared after DIN EN 196 T1 and tested for compressive strength after 1 day, 2 days and 28 days of hydration (2 prisms for each test were used). The same samples were used for Hg-porosimetry tests.

Results and Discussion

1. Celitement. The phase composition of the hydrothermal product is shown in Fig. 1A. The main constituent is α-dicalcium silicate hydrate (α-C_2SH) along with jaffeite, quartz and portlandite. Additionally, a minor quantity of calcite was observed. After mechanochemical treatment the sample consists of up to 90 wt% amorphous material. The crystalline part is built up mainly of α-C_2SH with accessory quartz (Fig. 1B). In addition the X-ray diffraction pattern of hydrated Celitement (w/s=0.4) after 4 days of hydration is shown (Fig 1C).

One of the main features of the Celitement is its water content, which is due to the presence of calcium hydrosilicates. It is manifested by the high lost of ignition (LOI) shown in Table 1, and by the IR-spectra in the MIR and NIR regions which show H_2O present as OH groups (α-C_2SH), bonded molecular H_2O and silanol groups involved in hydrogen bonding system. Additional striking feature is the low C/S ratio of Celitement (in this case C/S=1.64).

2. Hydration behavior. Figure 2 shows the XRD patterns of hydrated Celitement as a function of time within a period of 95 hours. In the first 15 hours of hydration there are no visible changes in the diffraction pattern which could suggest formation of hydrated phases. After 16 hours an increased scattering is observed in the ranges 10-11°2Θ and 28-30°2Θ. This time interval is marked with a dashed red line in Fig. 3. In the former region a sharp reflection at 10.7°2Θ occurs belonging to the AFm phase tetra calcium aluminate hemicarbonate hydroxyl hydrate (or known as hemicarbonate,

reflection 006). Its presence is due to reaction of carbonate (which in turn is formed via 1) carbonation of Ca(OH)$_2$ used as starting material and 2) partial carbonation of the calcium hydrosilcates during the mechanochemical treatment) with the BFS. At the same time in the second region a broad scattering "hump" grows showing the formation of C-S-H phase of type C-S-H(I). This reflection could be assigned as (110) (Garbev et al., 2008). Direct observance of C-S-H in the X-ray pattern of hydrated OPC is rather unusual, but in the case of hydrated Celitement it is very pronounced.

Table 1: XRF analysis of the Celitement sample after mechanochemical treatement.

Oxides	wt [%]
SiO$_2$	34,3
Al$_2$O$_3$	6,0
Fe$_2$O$_3$	0,6
CaO	52,6
MgO	3,5
SO$_3$	1,5
K$_2$O	0,18
Na$_2$O	0,48
P$_2$O$_5$	0,03
TiO$_2$	0,67
Cl	0,02
Mn$_2$O$_3$	0,18
LOI	4.5

Figure 1: XRD patterns of autoclave product (A), Celitement (B) and hardened paste of Celitement after 5d reaction with water. Formation of portlandite during hydration was not observed.

After 20 to 30 hours of hydration the growth of both $C_8A_2CbarH_{24}$ and C-S-H is accelerated. In a further step of the hydration process (30-40 hours) the C-S-H phase shows a maximal intensity of the (110) reflection. Shortly after 40 hours of hydration a broad reflection right to the (006) reflection of hemicarbonate grows. This is centered at about 11.3°2Θ and most probably belongs to newly formed hydrotalcite (marked as LDH in Fig.2). The intensity of this reflection maximizes in a relatively short period of time (between 40-45 hours). After reaching its maximum after 40 hours of hydration the intensity of the (110) reflection of the C-S-H phase does not vary significantly until the end of the experiment. The intensity of the (006) reflection of the hemicarbonate reaches its maximum between 60-70 hours and slowly decreases after that. Most probably CO_2 present in the sample as amorphous carbonate reacts with the hemicarbonate upon formation of monocarbonate, $C_4ACbarH_{11}$ (Damidot, Glaser, 1995). This is indicated by a small shoulder in the broad reflection of the hydrotalcite occurring at about 11.6°2Θ. No formation of portlandite has been observed at any point of our investigation.

3. Calorimetry. The calorimetric curve of the Celitement sample is shown in Fig. 3. Interestingly all features known from the calorimetry of Portland cements are also present in the Celitement curve. After wetting the sample a 3 hour dormant period follows. Between 4 and 16 hours after hydration a steep increase in the heat flow is observed. A maximum of the heat release follows between 16 to 20 hours. After that a gradual decrease in the heat flow until 40 hours is observed. A small maximum at about 40 hours is immediately succeeded by a further gradual decrease in heat flow. In Fig. 3 the calorimetric curve is compared to the development of the peak area in the regions 8-12°2Θ comprising the (006) reflection of hemicarbonate, (003) reflection of hydrotalcite and (001) reflection of the monocarbonate from one side and 28-30°2Θ region characteristic for (110) of C-S-H on the other side.
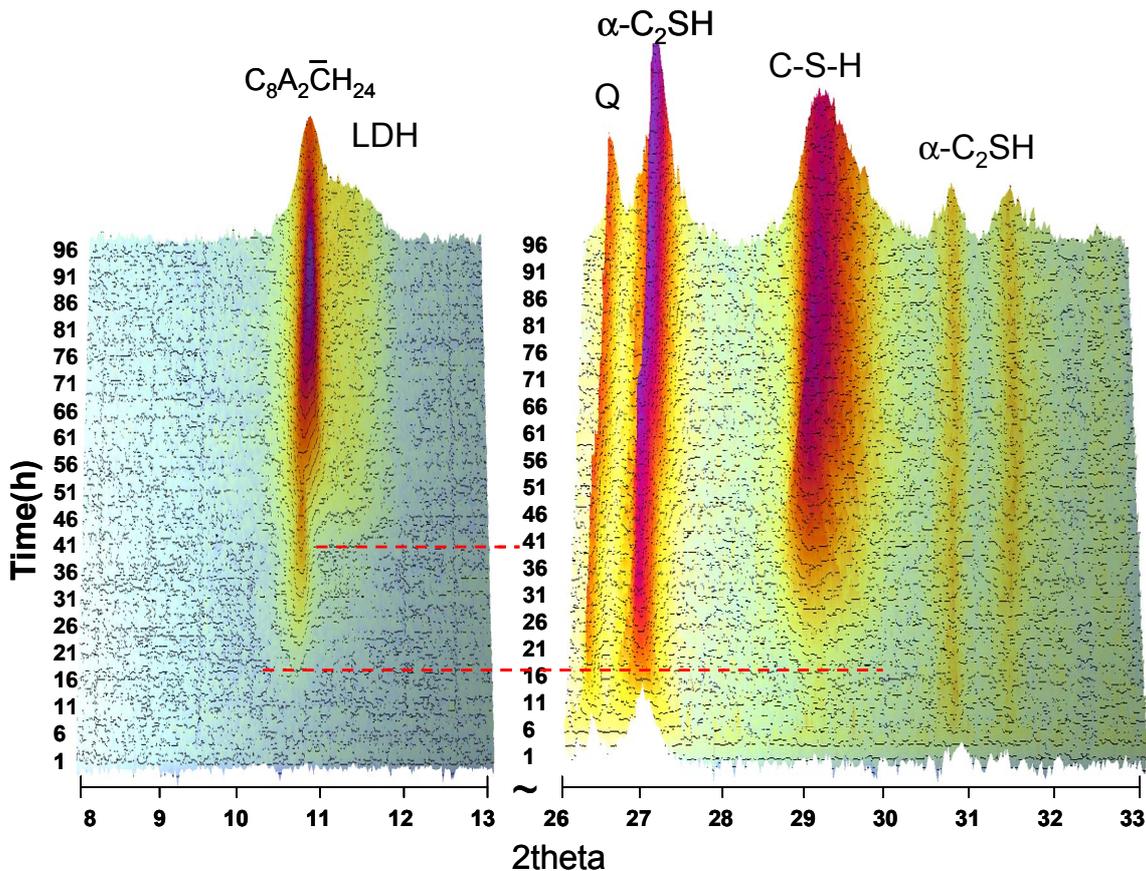

Figure 2: XRD patterns of hydrated Celitement taken as function of time (from 1 to 96 hours). Dashed lines mark the formation of C-S-H and hemicarbonate (lower line) and hydrotalcite (upper line)

A fairly good correlation is observed between the heat flow maxima and the crystallization of C-S-H and especially AFm phases. The sudden increase of the peak area in the range 10-12° 2Θ is related to the small maximum of heat release after 40 hours hydration and correlates with the formation of the hydrotalcite phase. This particular example shows one of the general properties of Celitement- its much lower heat flow (maximum 1,2 mW/g) compared to OPC (> 4 mW/g). This is due to the lack of portlandite and ettringite formation. As a result the investigated Celitement sample shows much lower total heat release after 7 days of hydration (200J/g) than CEM I 42.5R (320J/g) and CEM I 52.5R (370J/g)
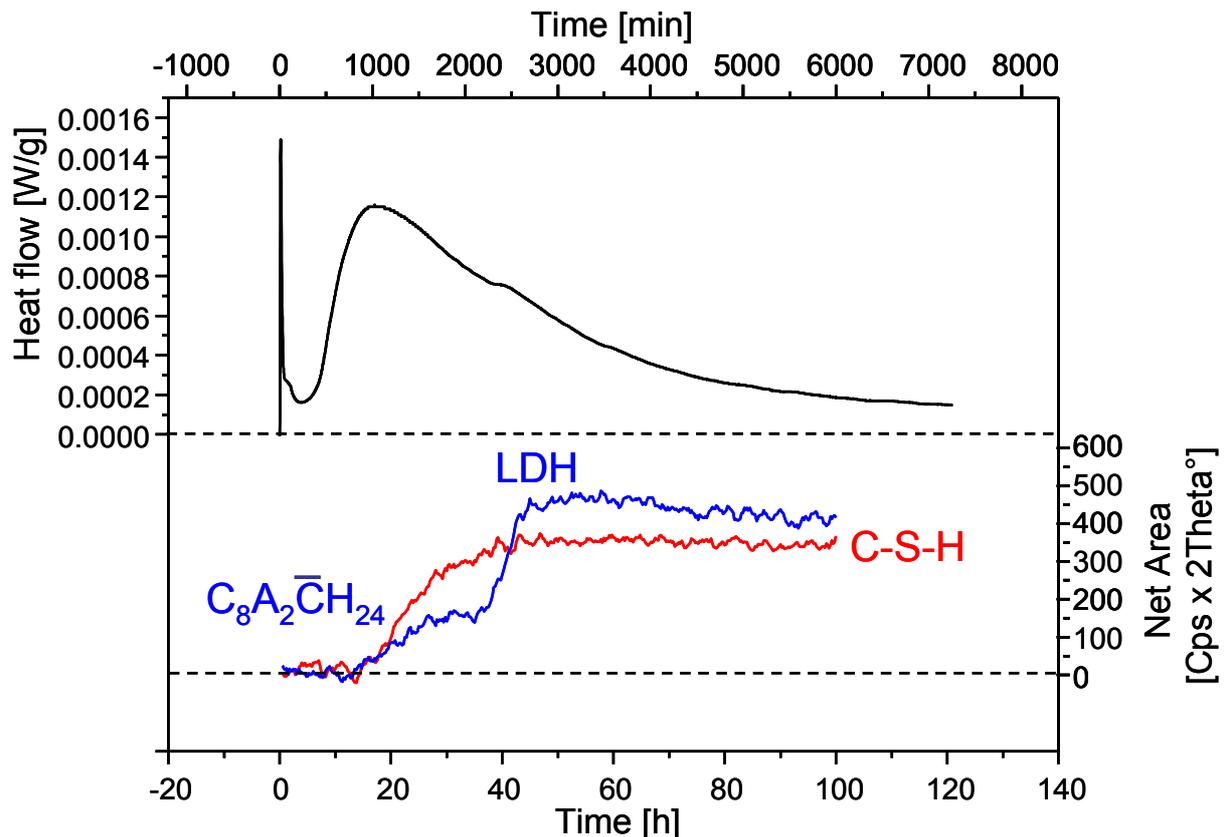
Figure 3: Calorimetric curve of hydration of Celitement compared with the development of the peak area in the 2Θ regions 10-12° 2Θ ($C_8A_2\bar{C}H_{24}$ and Hydrotalcite, LDH, blue) and 28-30° 2Θ (110 of C-S-H, red)

4. Microstructure. Figure 4 represents scanning electron micrographs of rupture surfaces of a frozen hardened Celitement paste in different stages of hydration. In Figure 4A the very early hydration after only 10 min is shown. Characteristic spherical particles with a size between 100nm and 1-2μm are seen. No evidence of hydraulic reaction is visible. The grains of the BFS are "coated" with the Celitement binder. As no mechanical strength should be expected, the sample "breaks" along primary particles. In a further stage of the hydration (after 8 hours, Fig 4B) an amorphous (no evidence in XRD patterns) cellular microstructure around the primary particles is clearly distinguishable. Partial interconnection between single particles is observed, but still large pores (up to 1μm) are present. In Figure 4C taken after 24 hours hydration well formed hexagonal platy crystals up to 0.5μm large are filling the interstitial space. These belong to the AFm phase hemicarbonate. Although the C-S-H phase is not only bridging particles but also filling the space increasing with time, there are still pores up to 200nm large. Figure 4D presents the microstructure of the hardened sample after 7 days hydration. In general, a very tight impermeable structure is seen with some sporadically distributed closed pores of

up to several tens of nm. On the right hand side of the picture a freshly broken grain of BFS enclosed by C-S-H phase is present. Data from Hg-porosimetry support the idea of a rapid development of a tight microstructure pointing to a bimodal pore size distribution with maxima at 100 nm and 10 nm after 24 hours of hydration and an unimodal distribution with a maximum at 10 nm after 48 hours hardening (Fig. 5B). In comparison CEM I 52.5R shows after 48 hours a bimodal pore size distribution with maxima at 60nm and 7nm.
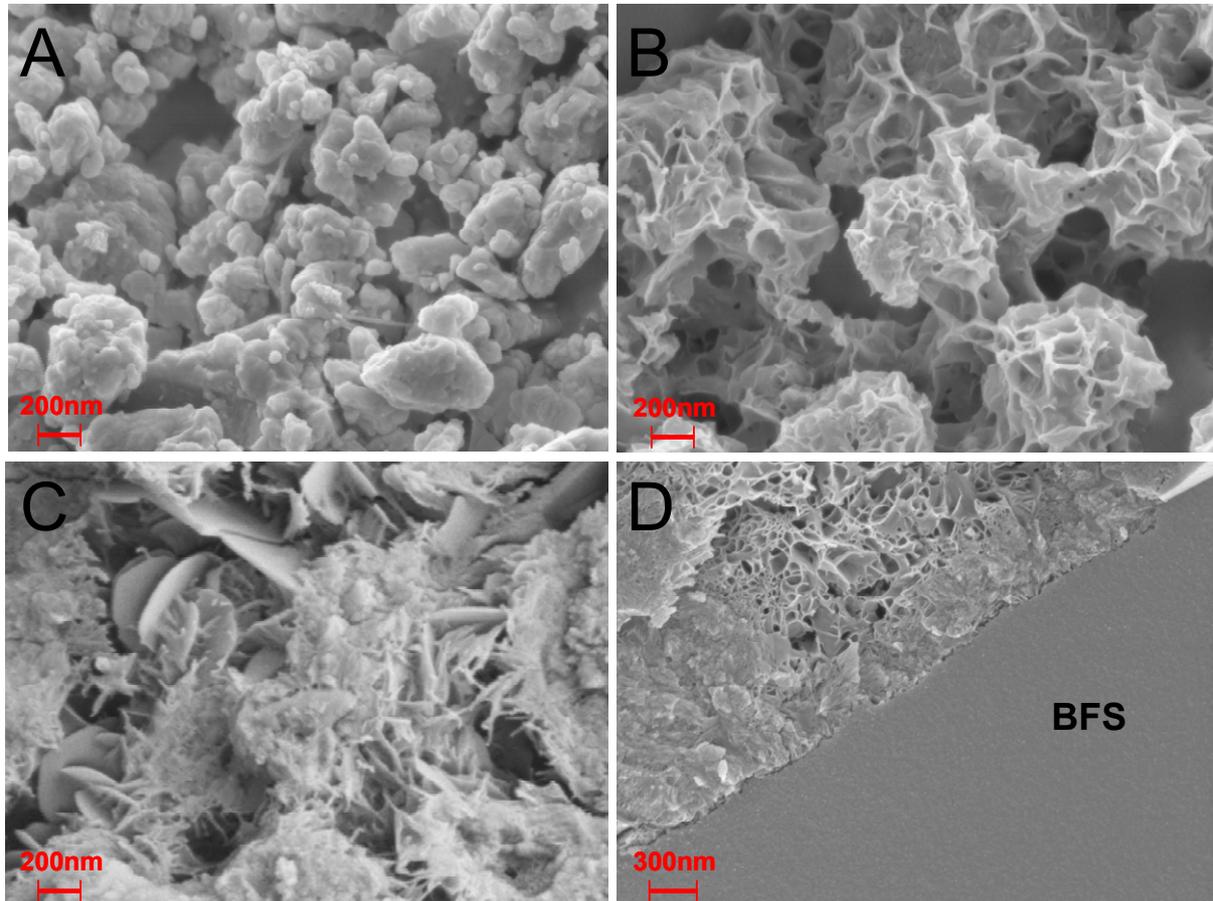
Figure 4: Microscopic images of frozen Celitement pastes after hydration time of 10min (A), 8 hours (B), 24 hours (C) and 7 days (D)

5. Compressive strength. In Figure 5A results from the tests on compressive strength of Celitement samples hardened at 20°C are shown. After one day hydration the compressive strength of Celitement is little worse than those of CEM I 42.5R but much better than CEM III B 42.5 N-LH/HS. After 2 days Celitement mortars show better results than CEM I 42.5R. The tests after 28 days show that Celitement possesses a mechanical strength comparable to that of CEM I 52.5R. In all cases Celitement shows better compressive strength than composite cements of type CEM III with blast furnace slag.

Conclusions

In this manuscript we present in one example some of the properties of a new hydraulic binding material of the Celitement family, which refers to novel cements produced via hydrothermal process and subsequent mechanochemical treatment of the products together with a silicate carrier (BFS in this particular case). Celitement possess a very low C/S ratio (1.64) thus building C-S-H and AFm phases upon hydration. No portlandite has been observed as a hydration product. Therefore Celitement shows much lower heat flow than OPC upon hydration. A very good correlation exists between the in situ

observations with XRD, calorimetry, and electron microscopy. Upon hydration the new material shows rapid development of a tight impermeable microstructure. The backbone of this structure is the C-S-H phase, which shows cellular morphology to some extend different than that formed by hydration of OPC. The fact that the C-S-H phase could be distinguished very clearly in the XRD points to better ordering and simplicity of the phase composition of the hardened Celitement paste.
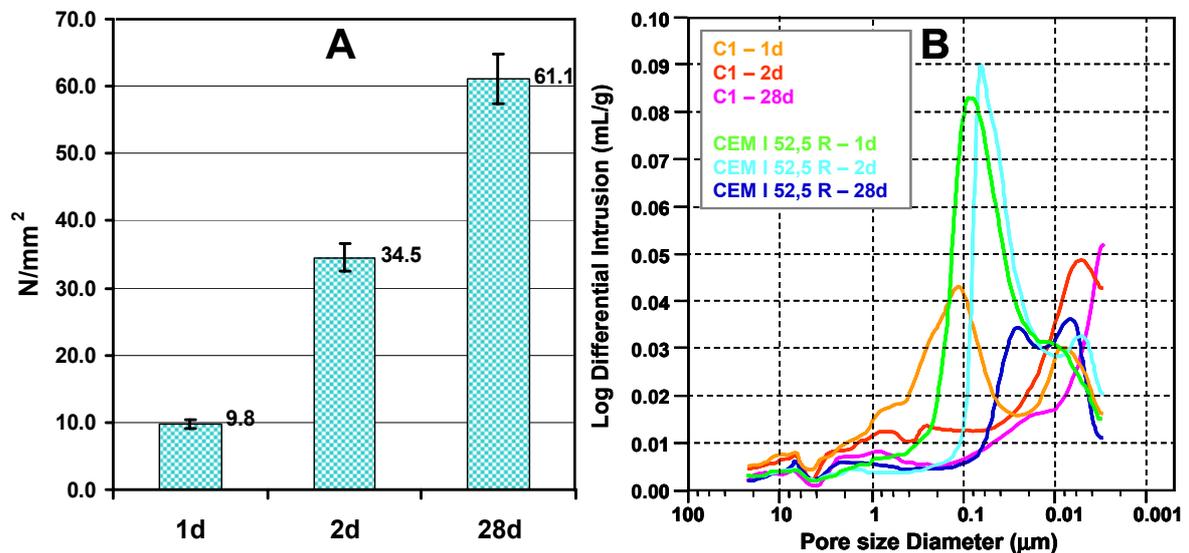

Figure 5: A - Compressive strength of Celitement prisms after 1, 2 and 28 days at 20°C;
B – Results of Hg –porosimetry of the same test prisms compared to CEM I 52.5 R.

The mechanical tests of the norm prisms show comparable compressive strength of Celitement and CEM I 42.5R and CEM I 52.5R. In all cases the mechanical properties of the investigated samples were much better than CEM III B 42.5 N-LH/HS.

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