Celitement® – A new sustainable hydraulic binder based on calcium hydrosilicates

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Abstract

Celitement is a new family of cementitious binders, similar in mixing, setting and hardening to standardized cements based on OPC. However, its production on an industrial scale could save up to an estimated 50% CO_2-emission and primary energy. It is based on a new class of amorphous hydraulic calcium hydrosilicates. Hardening proceeds through formation of Calcium Silicate Hydrate phases (C-S-H) comparable to those from OPC hydration. No other hydration products are necessarily formed. Suitable raw materials for the production of Celitement include carbonates, e.g. marl or limestone and a wide range of natural and secondary silicates e.g. natural sand, slags, glasses and fly ash. Carbonates are calcined before processing. The carbonate fraction in the raw material varies in the range from 30 to 40% (OPC about 75%). In the most simple case quicklime and quartz sand are used; the use of hot meal from clinker production is also possible. About one half of the raw material, which includes all the calcined lime, is hydrothermally treated in an autoclave at temperatures around 200ºC and saturated steam pressure. Calcium silicate hydrates are formed similar to the processing of autoclaved aerated concrete (AAC).

In a second step the synthesised calcium silicate hydrates are mixed and milled together with the remaining siliceous materials. During milling hydrogen bonds, which stabilize the autoclaved products, are destroyed and new amorphous calcium hydrosilicates are formed around cores of non reactive co-milled silicates.

Due to its simple phase content Celitement enables simple formulations. Compressive strength, freeze-thaw resistance and shrinkage resemble standardized cements. Since newly formed C-S-H-phases are the only hydration product of Celitement, the heat of hydration is strongly reduced. Capillary pores are quickly transformed to gel pores, which has been demonstrated by SEM and Hg-porosimetry. Calcination of limestone is the dominant endothermic step in cement production and responsible for the fast majority of CO_2-emissions. Reduction in energy demand and CO_2 emission mainly result from the strongly reduced carbonate content of the raw material. The necessary thermal treatment (calcination, 1000ºC hydrothermal processing, 200ºC) takes place at comparatively low temperatures (OPC up to 1450ºC). In addition, only about half of the raw material is thermally processed at all.

Celitement and the process for its production are proprietary inventions of the Karlsruhe Institute of Technology (KIT). The production capacity is 1 kg/day at the moment. At present a pilot plant is constructed with a production capacity of 100 kg/d, which will be in operation in 2011, in collaboration with the SCHWENK group as industrial partner. In 2014 a first plant is scheduled to enter commercial production.

Originality

The contribution presents for the first time hydraulic calcium hydrosilicates as one member of a new type of sustainable hydraulic binders. In order to produce the materials an innovative new concept of coupling a hydrothermal and a mechanical process has been developed. Composition range, processing intermediates and final product are presented. Energy and carbon footprint of the process are estimated.

Important material properties of hydrated samples, e.g. standardized compressive strength, freeze-thaw resistance, pore size analysis etc. are discussed. The contribution HYDRATION BEHAVIOR OF CELITEMENT□: KINETICS, PHASE COMPOSITION, MICROSTRUCTURE AND MECHANICAL PROPERTIES by Garbev, K. et al. describes the hydration process in detail.

Chief contributions

A new amorphous type of calcium hydrosilicate has been synthesized for the first time. It is hydraulic and hardens under formation of calcium silicate hydrates (C-S-H), similar to the ones from OPC hydration. No other hydrates, especially no portlandite, AFm and AFt are formed. Thus, compared to OPC, only roughly half the mass fraction of the new binder is needed to produce the same amount of C-S-H-"glue". In order to keep the volume of the binder matrix constant, the new calcium hydrosilicates are diluted with non-reactive silicates. The concept results in an estimated reduction of 50% in energy consumption and CO_2 emission in production. The product is similar to OPC in all its major qualities, except the development of porosity. The transformation of capillary porosity to gel porosity is much quicker then for OPC. For production, a new process has been developed, which comprises a hydrothermal and a milling step. Estimated production costs do not exceed conventional OPC manufacturing.

Keywords: *calcium hydrosilicate, C_3S hydration, mechanical activation, novel binding materials*

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Introduction

Calcium silicate hydrates (C-S-H) are the crucial "glue" in a wide variety of cement-based building materials. Ultimately, they are responsible for the strength development as well as for the resistance of dense concretes and mortars to attacking media. A high yield of calcium silicate hydrates is one necessary prerequisite for an excellent performance of calcium silicate based cements.

The composition range for C-S-H from cement hydration has been controversially discussed. About 2 kg of Ordinary Portland Cement (OPC) are needed to obtain one kilogram of C-S-H, if a molar CaO/SiO_2 ratio of 1.8 is assumed for the freshly formed solid solution. According to own investigations (Garbev et al., 2008a) however, the calcium-rich end member of the C-S-H solid solution series possesses a maximum CaO/SiO_2 ratio of 1.25. The CaO/SiO_2 ratios actually measured in concrete are attributed to the intercalation of $Ca(OH)_2$ in the C-S-H. If the intercalated fraction of $Ca(OH)_2$ is taken into account then even 2.5 kg OPC has to be hydrated to obtain 1 kg C-S-H.

Besides the formation of C-S-H the other half of the cement is transformed during hydration into other products, such as calcium aluminate hydrates and calcium hydroxide. These hydrates have a slight, or even very significant, detrimental effect on the mechanical properties of the product. They also have an adverse effect on the chemical resistance of a mortar or concrete to various ambient influences. Based on this observation we tried to prepare a durable and effective hydraulic binder based on calcium silicates that during hydration reacts as fully as possible to C-S-H. It follows from composition that such a binder system has to have a CaO/SiO_2 ratio of smaller than 2.

Early hydration of calcium silicates alite and belite

Many investigations have been performed to clarify the initial reaction of calcium silicates with water (e.g. Taylor, 1990). Some investigators found hints for the initial formation of a C-S-H phase with a very small CaO/SiO_2 ratio. Own experiments (Black et al., 2003) on the reaction of tricalcium silicate and dicalcium silicate with atmospheric carbon dioxide and moisture gave us a clue on the nature of these initial hydration products. With XPS a surfacial layer of $CaCO_3$ and C-S-H was detected. Based on comparative measurements on different natural and synthetic materials the C/S ratio of the C-S-H phase was calculated to be smaller then 0.7. In addition, we proposed (Garbev et al., 2008b) that there exists an miscibility gap in the C-S-H solid solution series somewhere in the region of C/S = 1-0,85. When a C-S-H with a C/S ratio at the upper limit of the miscibility gap decalcifies in contact with CO_2 it decomposes under formation of SiO_2(am.) and $CaCO_3$. Thus the low calcium C-S-H detected with XPS in the presence of CO_2 can not be formed by decalcification. It must be formed from a reactive initial product, low in calcium, similar to the one reported in Taylor (1990). This reactive initial product seemed to be a good candidate for a low calcium binder. We started experiments to synthesise such a material based on the assumption that the initial reactive product consists of small silicate units and silanol groups, which polymerize during further reaction according to the schematic equations (1-4):

(1) Hydrolysis $4\ Ca_3SiO_5 + 8\ H_2O \rightarrow 2\ Ca_3[HSiO_4]_2 + 6\ Ca(OH)_2$ (aq.)

(2) Hydrolysis and condensation $Ca_3[HSiO_4]_2 + H_2O \rightarrow Ca_2[H_2Si_2O_7] + Ca(OH)_2$ (aq.)

(3) Hydraulic reaction $Ca_3[HSiO_4]_2 + Ca_2[H_2Si_2O_7] + 8\ H_2O \rightarrow 5\ CaO.4\ SiO_2.10\ H_2O$

(4) Overall $4\ Ca_3SiO_5 + 17\ H_2O \rightarrow 5\ CaO.4SiO_2.10\ H_2O + 7\ Ca(OH)_2$

The hypothetical, protonated and partially condensed, unstable calcium hydrosilicates from the partial reactions (1) and (2), namely $Ca_3[HSiO_4]_2$ and $Ca_2[H_2Si_2O_7]$, show a way how the calcium content of hydraulic binders can be lowered. Firstly, calcium can formally be exchanged for protons. Calcium is then replaced and simultaneously monohydrosilicates condense to, for example, dihydrosilicates.

Preparation of hydraulic calcium hydrosilicates

Structural element of the proposed calcium hydrosilicates are known to exist in several phases in the system CaO-SiO_2-H_2O under ambient and hydrothermal conditions. Two sample structures where selected for further experiments: α-$Ca_2[HSiO_4]OH$ (α-C_2SH) and a XRD-amorphous C-S-H phase with the idealized formula $Ca_5[HSi_2O_7]_2.8\ H_2O$ ($C_{1,25}$-S-H).

α-C_2SH and $C_{1,25}$-S-H were synthesized from $Ca(OH)_2$ and quartz. The raw materials were finely ground and processed for 6h at 200ºC (α-C_2SH) and 190ºC ($C_{1,25}$-S-H) respectively under hydrothermal conditions in an autoclave. The product consisted of up to 90 mass % α-C_2SH or $C_{1,25}$-S-H respectively. Both phases do not show any hydraulic activity, when exposed to water under ambient conditions.

The apparent stability especially of α-C_2SH against water is attributed to a strong system of hydrogen bonds in the structure (Marsh, 1994). In order to transform α-C_2SH and $C_{1,25}$-S-H in a reactive state, structural disorder is necessary, especially in the system of hydrogen bonds. One route is to introduce crystal defects by thermal treatment. In both cases this approach was not successful. α-C_2SH loses its hydrosilicate units between 300ºC and 500ºC accompanied by dehydration and partial condensation. Although the resulting C_2S polymorphs show hydraulic activity, they do not have any structural similarity to the proposed initial products of C_3S hydration. On heating $C_{1,25}$-S-H loses its structural water continuously until at around 800º to 850ºC wollastonite crystallises. No hydraulic activity was observed.

Another way to introduce structural disorder is mechanical milling. Samples were made by milling together a calcium hydrosilicate with 50% by mass of quartz sand or blast furnace slag (bfs) respectively in a planetary ball mill, until a specific surface of about 2 m^2/g (BET) was reached. The resulting bulk compositions are given in figure 1: α-C_2SH calcium hydrosilicate was milled together with quartz (Composition (2)) and blast furnace slag (Composition 1) respectively. In addition $C_{1,25}$-S-H was co-milled with quartz-sand (Composition 3).

Characterisation of the milled product: Celitement

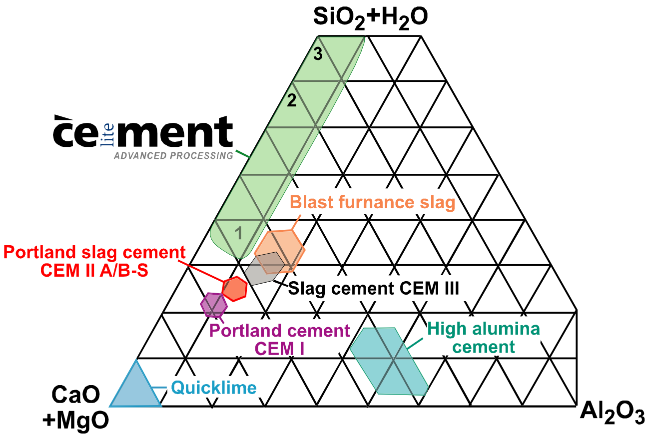
The product made from α-C_2SH and bfs was nearly amorphous. In X-ray powder patterns only a broad hump in the range between 4Å and 2,3Å and some very weak residual reflections of α-C_2SH are visible. Both samples co-milled with quartz sand show broadened quartz reflections, and besides an amorphous hump again very weak residual reflections of α-C_2SH or $C_{1,25}$-S-H respectively. The IR-spectra of the samples with α-C_2SH show a shift in the ν_1 OH(Si) of α-C_2SH from 2450 cm^{-1} and 2840 cm^{-1} to 2470 cm^{-1} and 2930 cm^{-1} respectively, characteristic for longer and weaker hydrogen bonds. Similar bands are present in the sample with $C_{1,25}$-S-H too. Thus hydrogen bonds in the intermediate product are destroyed; reactive fragments are deposited in a heavily disordered state on the silicate surfaces of the interground raw material with partial condensation, as was proven by Trimethylsilylation (Beuchle et al., 2007a). Structures are completely changed. The actual “glue”, i.e. new hydraulic calcium hydrosilicate, forms on the surface of the interground not reactive cores.

Hydration

After mixing with water (water/solid ratio 0.5) all three samples react hydraulically and form a C-S-H phase similar to the one that originates from OPC hydration. No other phases are necessarily present.

Calorimetric curves are given in figure 2. After wetting, a less marked induction period follows. The heat maximum occurs after 5 to 15 h. Compared to OPC the heat of hydration is generally lower. Details about the hydration reaction of calcium hydrogen based Celitement are given in Garbev et al. (2010).

Samples of composition 1 were synthesized in amounts that made the preparation of standardized test possible. They yielded compressive strength of test mortars after 28 days hardening of up to 80 N/mm^2. No differences were found from standard cements in the shrinkage or in initial tests of the resistance to freeze-thaw cycles. The same applied to creep and shrinkage properties. In some properties mortars made with Celitement exhibited significantly higher potential. This was shown by initial tests, e.g. of chemical resistance (Stemmermann P. et al., 2010). The pore solution in Celitement mortar has a lower buffer capacity because of the low calcium content. On the other hand they posses an extremely low capillary pore content, which should make carbonation very difficult. In general calcium hydrosilicate based cements show a lower water need, due to the fact that they already contain some chemically bound water in the unreacted material.



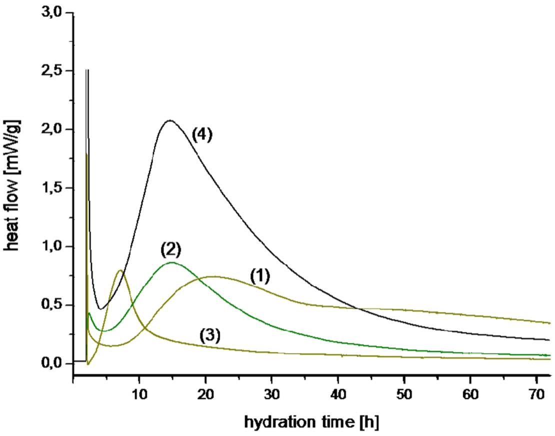


Figure 1 (left): Composition of various hydraulic binders in a projection on the system (CaO+MgO) – Al_2O_3 – (SiO_2+H_2O). The shaded area marked with Celitement represents the range of composition realised to date with the new process. Due to the preferred chemical binding of water to the silicate units in Celitements water and SiO_2 are combined in the upper corner. The distance between grid lines amounts to 10 % by weight. Arabic numbers represent the following formulations mentioned in the article: (1): α-C_2SH co-milled with blast furnace slag; (2) α-C_2SH co-milled with quartz; (3) $C_{1,25}SH$ co-milled with quartz.

Figure 2 (right): Heat evolution rate of (1): α-C_2SH co-milled with blast furnace slag; (2) α-C_2SH co-milled with quartz; (3) $C_{1,25}SH$ co-milled with quartz and (4) CEM I 42,5 R for comparison.

Properties of different Celitement binders can be controlled over wide ranges. This is possible in particular by varying the composition. So far various calcium hydrosilicates have been ground with a wide spectrum of different silicates or, alternatively, with quartz sand (Beuchle et al., 2007 a,b,c). Thus Celitement does not represent a single binder but rather an entire family of mineral binders based on calcium hydrosilicates. The range of compositions achieved so far is shown schematically in Fig. 1 for the main oxides. The properties can also be influenced by the grinding conditions, the particle size distribution and the fineness.

Celitement is compatible with conventional cements, puzzolans and granulated blast furnace cements. Mixing with known binders is possible. Celitement contains only one hydraulically active phase and should therefore be easy to control with additives to establish good workability. This is confirmed by initial tests. A variation in colour extending to white products is possible, depending on the choice of starting materials.

Enthalpy of formation

To date Celitement has been produced in a laboratory plant, which allows for a throughput of approximately 1 kg per day. One fundamental parameter in order to estimate the suitability of a process for industrial production is the energy needed. As the final limit for all technical optimization the standard enthalpy of formation ΔH_f^0 from the raw materials can be used. Based on ΔH_f^0 it is even possible to compare systems with such a different level of technological maturity as OPC and Celitement.

Celitement, as ground Portland cement clinker, can be used as a main constituent of a binder system. It can be blended with various secondary constituents like granulated blast furnace slag, fly ash, lime, gypsum, etc. Besides the actual formulation it is the quantity of newly formed calcium silicate hydrate that is the most important precondition for the performance of the binder. It is almost the same for all three samples (Stemmermann et al., 2010). The energy balance of Celitement and ground Portland cement clinker are therefore directly compared in figure 3.

One kilogram of lime-rich Celitement, which is produced by intergrinding $\alpha\text{–}Ca_2[HSiO_4]OH$ and quartz sand (50 mass % each, composition 2), is considered as an example. ΔH_f^0 of $\alpha\text{-}Ca_2[HSiO_4]OH$ is not exactly known. Instead ΔH_f^0 of hillebrandite is used (Newman, 1956). As hillebrandite is the high temperature polymorph of C_2SH, its ΔH_f^0 is marginally overestimated. ΔH_f^0 from the raw materials limestone and quartz calculates to about +555 kJ/kg or about one third of the ΔH_f^0 of Portland cement clinker from raw materials (see Fig. 3). For Celitement processed via $C_{1,25}SH$ from limestone and quartz ΔH_f^0 calculates to +294 kJ/kg. ΔH_f^0 of $C_{1,25}SH$ was calculated from a mixture of C-S-H with jennite and tobermorite composition respectively using data from Lothenbach et al. (2008). However, the efficiency of the entire plant is also needed for estimating real consumptions. In Stemmermann et al. (2010) efficiencies were estimated using the efficiencies of plant components from comparable processes. For processing a Celitement rich in lime (Compositions 1 or 2) an estimated total of 3150 kJ/kg primary energy results (which includes all thermal and electrical energy from grinding the raw materials to final grinding of the product). This value compares to +4360 kJ/kg primary energy for the production of fine milled OPC clinker. Energy demand is further reduced to an estimated 2170 kJ/kg for Celitement low in lime (Composition 3). However, reliable values can only be obtained by measurements on actual plants.

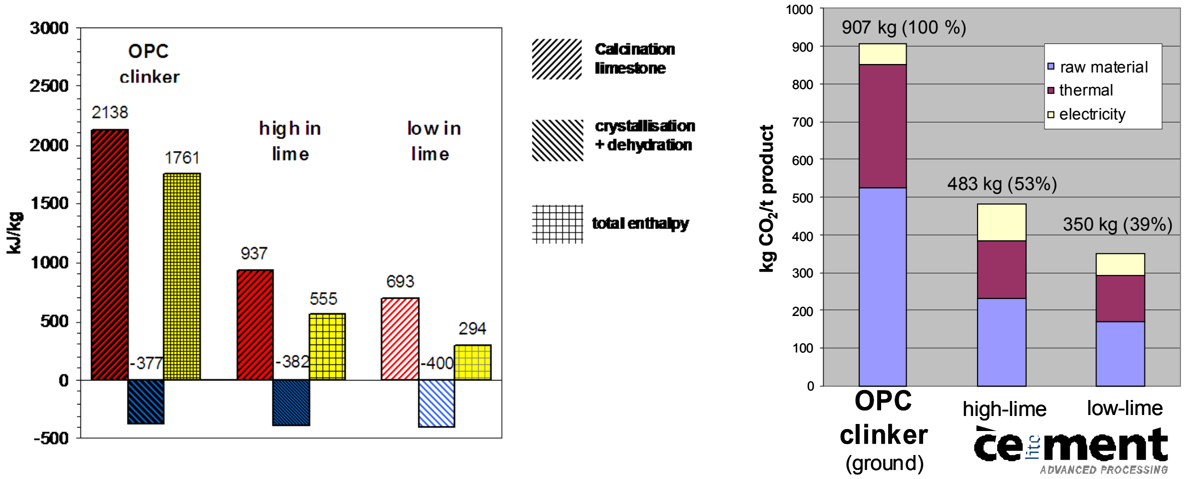


Figure 3: left: Enthalpy of formation from the raw materials of ground OPC clinker, a high-lime (Compositions 1 and 2) and a low lime Celitement (Composition 3). All three processes are dominated by the calcination of lime. The further reaction steps are exothermic. Right: CO_2 emission per ton ground OPC clinker, high-lime and low-lime variant of Celitement.

CO_2 balance

Based on energy calculations and suitable raw materials the physical release of CO_2 in the atmosphere from the process was calculated for different compositions (see Fig. 3 right, Stemmermann et al., 2010). No distinction was made for CO_2 from renewable or non-renewable energy sources as this approach is highly case sensitive.

CO_2 emitted during production of lime-rich Celitement stems from the CO_2 released during calcination of limestone (231 kg/t) and CO_2 resulting from the use of energy (252 kg/t from fuels and electricity based on a german electricity mix). In total this calculates to 483 kg/t, which corresponds to about half (53%) of the emissions from clinker production. For low-lime Celitement the release of CO_2 from limestone and in addition from electricity used for grinding is further reduced and totals up to 350 kg/t.

Process development to the industrial scale

Suitable raw materials for producing Celitement are available worldwide. The raw materials for the process taking place in the autoclave must contain CaO bound as hydrate or silicate and SiO_2. Higher condensed silicates, such as feldspars and clays or glasses, can be used instead of quartz. The use of a wide range of secondary raw materials and recycled building materials, such as granulated blast furnace slag, fly ash and even old concrete as raw material components has been tested successfully on a laboratory scale. Old concrete in particular was used as a raw material for synthesizing calcium hydrosilicates (Stemmermann et al., 2005). In order to transform the intermediate product into a hydraulically active binder it is dried and interground with another, unreactive, raw material that contains SiO_2, such as quartz sand, glass, feldspar, etc.

Discontinuously operating hydrothermal plants are used on an industrial scale and in a slightly different design, e.g. for the production of autoclaved aerated concrete or sand-lime blocks. Thus plants that are suitable for producing Celitement are in principal available.

The technical properties of the binder produced during the reactive grinding can be varied over a wide range by suitable choice of the hydrothermal intermediate product and the interground quartz or silicate. The developments outlined are protected by three basic patents (Beuchle et al., 2007 a,b,c). Another patent has been awarded in the related field of binders that contain belite (Stemmermann et al., 2005). The “Celitement” trademark is also protected.

4 Outlook

Celitement GmbH was founded at the beginning of 2009. The partners are the KIT, four inventors and the Schwenk Group. The basic aim of the company is, alongside the development of the process and the product until it is ready for the market, to promote the marketing of protective rights to “Celitement”. The binder should be available to the widest possible circle of users. Initial trial product samples will only be available after completion of a pilot plant.

Celitement GmbH is currently building a pilot plant on the grounds of the Karlsruhe Institute of Technology to enable practical testing of the production process and of the application of the new building material. This plant will be able to provide up to 100 kg/d of the new binder. It will also help to develop and test all the key technologies, including the energy requirement and its environmental relevance, up to the stage where it is ready for practical applications. This includes the optimization and further development of the grinding and the underlying tribochemical process stages.

The special potential of Celitement as a material and a technical product initially directs to demanding fields of application that at present are still dominated by high grade Portland cements. This includes special building materials, plaster, mortar and adhesive applications and other building products, such as for interior finishing and renovation work. The next step will be to investigate the market opportunities for application as a homogeneous mass material. The industrial partner Schwenk is planning to build a first reference plant at one of its production sites in 2014 when the basic material and technical principles for industrial production have been confirmed.

References

- Beuchle G., Garbev K., Schweike U., Stemmermann P. (2007a) Einphasiges hydraulisches Bindemittel, Verfahren zu seiner Herstellung und mit diesem Bindemittel hergestellter Baustoff. DE 10 2007 035 259.
- Beuchle G., Garbev K., Schweike U., Stemmermann P. (2007b) Einphasiges hydraulisches Bindemittel, Verfahren zu seiner Herstellung und mit diesem Bindemittel hergestellter Baustoff. DE 10 2007 035 258.
- Beuchle G., Garbev K., Schweike U., Stemmermann P. (2007c) Einphasiges hydraulisches Bindemittel, Verfahren zu seiner Herstellung und mit diesem Bindemittel hergestellter Baustoff. DE 10 2007 035 257.
- Black L., Stumm A., Garbev K., Stemmermann P., Hallam K. R., Allen G. C. 2003. X-ray photoelectron spectroscopy of the cement clinker phases tricalcium silicate and [beta]-dicalcium silicate. Cement and Concrete Research, 33(10), 1561–1565.
- Garbev K., Beuchle G., Schweike U., Stemmermann P. Hydration behavior of Celitement: Kinetics, phase composition, microstructure and mechanical properties. ICCC 2010, Madrid.
- Garbev K., Beuchle G., Bornefeld M., Black L., Stemmermann P. 2008a. Cell Dimensions and Composition of Nanocrystalline Calcium Silicate Hydrate Solid Solutions. Part 1: Synchrotron-Based X-Ray Diffraction. Journal of the American Ceramic Society, 91 (9), S. 3005–3014.
- Garbev K., Bornefeld M., Beuchle G., Stemmermann P. 2008b: Cell Dimensions and Composition of Nanocrystalline Calcium Silicate Hydrate Solid Solutions. Part 2: X-Ray and Thermogravimetry Study. Journal of the American Ceramic Society, 91(9), 3015–3023.
- Lothenbach B., Matschei T., Möschner G., Glasser F. 2008 Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement. Cement and Concrete Research, 38(1), 1-18.
- Marsh R.E. A Revised Structure for –Alpha-Dicalcium Silicate Hydrate. Acta Cryst. C, 39 (50), 996-997.
- Newman E. S. 1956 Heats of formation of Xonotlite, Hillebrandite and Foshagite. Journal of Research of the National Bureau of Standards, 57 (1), 27–30.
- Stemmermann P., Schweike U.,Garbev K., Beuchle G. Celitement – a sustainable prospect fort he cement industry Cement International, 8 (5), 52-66.
- Stemmermann P., Garbev K., Schweike U., Beuchle G. 2005 Verfahren zur Herstellung von Belit-Bindemittel. DE 10 2005 037 771.
- Taylor H.F.W. 1990 Cement Chemistry 162ff., Academic Press, London 475 p.