Celitement -
A novel cement based on hydraulic calcium hydrosilicates (hCHS)

H. Möller[a,b]

[a] Celitement GmbH & Co.KG, Hermann-von-Helmholtz-Platz-1, D-76344 Eggenstein-Leopoldshafen
[b] Schwenk Zement KG, Hindenburgring 15, D-89077 Ulm

Introduction

Celitement is a new class of hydraulic binders (cements) based on patents of the Karlsruhe Institute of Technology (KIT). The development of this new class of hydraulic binders is a good example how results from pure fundamental research can lead to innovative industrial products.

While analysing the hydration mechanisms of pure alite (C_3S), the main calcium silicate cement phase in classical Portland cement, KIT researchers found out that the final phase responsible for strength development in cement hydration, namely **C-S-H** (**C**alcium-**S**ilicate-**H**ydrate), is formed via an "intermediate" or "precursor" of comparable structure but slightly different chemical composition.

It was designated **h**ydraulic **C**alcium **H**ydro **S**ilicate **(hCHS**) to distinguish it from its final hydration product, a **C-S-H** phase. The needle like structure of C-S-H in concretes, grouts and mortars binds together sand and aggregates. It can be considered as the "glue" in cementitious applications.

The "simple" and later patented idea was to synthesize and stabilize this short time intermediate of C-S-H-formation and to produce it as a hydraulic binder in its own right.

The crystal structure of hCHS contains both, structural water molecules and hydroxyl groups bound to Ca- and Si-atoms. So it was clear from the beginning that the production of this highly reactive material by a high temperature route in rotary kilns would not be feasible. At very high temperatures these substances would completely dehydrate. So instead of a rotary kiln, an autoclave process working at 200°C and saturated steam pressure (12 bar) was optimised to prepare large amounts of pure CSH phases of appropriate composition.
This intermediate product from the autoclave is not hydraulic active, as it is stabilized by strong hydrogen bonds. In order to distinguish this material from both, the hCHS and the C-S-H, it will be written as CSH in the following.

In a second step the material coming from the autoclave is transformed into the final product hCHS by a special grinding operation.

As the term **h**ydraulic **C**alcium **H**ydro **S**ilicate **(hCHS**) sounds clumsy and too scientific, the final product was called **Celitement**®. "**Ce"** and "**ment"** stand for "Cement", the middle term "**lite**" is an acronym for "light" (here in CO_2) in order to express the favourable ecological aspects of that new family of hydraulic binders (cf. Coke "light"). The name is used for both, the company (Celitement GmbH&Co.KG) and the whole material group itself (**Celitement**®).

Celitement GmbH was founded in 2009 and the binder concept was developed from laboratory to an industrial scale together by KIT and Schwenk Zement KG as the industrial partner.

In order to test and fine tune the complete production process, Schwenk Zement KG financed the installation and operation of a small pilot plant with a production capacity of around 100 kg per day on Campus North of the KIT in Karlsruhe. In autumn 2021 it was upgraded to a capacity of up to 5t per week by installing a larger mill. The pilot plant is used for both, process and product development, but also provides material samples of different Celitement® types for customer application tests. Since mid 2016 first samples of Celitement have been handed out to about 40 selected innovators covering 21 different fields of application/use.

These innovators test Celitement® in various practical applications and provide the market feedback needed for the envisaged investment in a first industrial reference plant.

Celitement® is considered to be market ready and a business case for the erection of a first, 50.000t/year industrial reference plant is actually being evaluated by the owner of Celitement GmbH&Co.KG, the Schwenk Building Materials Group from Ulm, Germany.
In this first industrial reference plant Celitement® would be produced using only two basic raw materials to start with: Hydrated lime - $Ca(OH)_2$ - and a quarz sand slurry known e.g. from the production of autoclaved aerated concrete (AAC).

For one tonne of Celitement® approximately 600 kg of high quality $Ca(OH)_2$ and 400 kg of pure sand are needed.
At full capacity of the first industrial reference plant a total of around 30.000 t/year of $Ca(OH)_2$ would be needed.

The Celitement® production process is made up of two main process steps.
The first uses an autoclave to produce the not reactive CSH intermediate product. The second consists of a special grinding step necessary to transform the autoclave product into the final product. In other applications the term tribochemical or mechanochemical reactor is used for that kind of process. So Celitement® in principal only consists of CaO, SiO_2 and water. However, the chemical composition is changed from CaO-rich (Portland cement clinker) to SiO_2 rich. The chemical analysis for a typical Celitement® would give a content (by mass) of e.g. 43% CaO and 41% of SiO_2 respectively. This can be compared to a typical Portland cement clinker having around 65% CaO and 20% SiO_2.

The new idea behind the production process of Celitement®

The general principles of how to obtain C-S-H phases in autoclaves are well known from the production of e.g. aerated concrete bricks or lime-sand-bricks for a very long time. In both processes lime and sand are used to form C-S-H-phases such as tobermorite which provides the mechanical strength to the stones produced in the autoclaves. In both processes this final C-S-H is however already formed in the autoclave and then “glues” together all components of the stones at the same time.

The new and patented idea of Celitemen®t production is based on a new and unusual approach for the manufacture of this new type of cement:

In the autoclave step pure **CSH** phases are formed which are then partially “destroyed” or “transformed” by the special grinding step to obtain the reactive C-S-H precursor designated **hCHS** (Celitement®). Only by adding water, this hCHS will transform back to C-S-H known from traditional cement hydration.

At first sight it sounds strange to produce something only to partially "destroy" it in order to get something back during application that is again close to the starting material. But there are big advantages following this approach. Working with pure C-S-H phases which are formed from hCHS, avoids many difficulties known from traditional multiphase cements.

The "activation grinding" step is crucial, as it transforms the CSH phases from the autoclave step, which are as already indicated not hydraulic active, into the desired reactive material. "Tribochemistry" is not only changing the internal structure of the phases, but also changes the particle size distribution considerably. There is this paradox that this process not only changes the mineralogy, but also leads to a desired "coarsening" of the starting material. Tribochemistry or mechanochemistry is the general technical term for chemical reactions which are normally induced by very high energy grinding. Using specially designed grinding equipment, chemical reactions in crystalline or amorphous matter can be initiated which sometimes lead to new phases with interesting properties. Activation grinding is therefore more than simple comminution, as the mill is also used as a kind of "chemical reactor". As the mill is also used as a "chemical reactor" it might be considered as a possibility to further electrify the production of hydraulic binders.

To come from two opposite directions compared to the classical approach of Portland cement production, is new. While Portland clinker production relies on the formation of "dry" calcium silicates (as main phases), and the aim of traditional cement milling is mainly particle size reduction, the Celitement process aims at the formation of "wet" (water containing) phases which are produced in a grinding process aiming to reduce specific surface and - on average - produces "coarser" particles. This sounds like a paradox but works fine.

By following this new process, pure hCHS (Celitement®) is present in the final product if a complete transformation of the CSH coming from the autoclave is accomplished during the reaction grinding.

Celitement® offers variability in both, the initial composition (CaO/SiO_2-ratio) of the material coming from the autoclave and the degree of long and short range structural rearrangement achieved during activation grinding. Other important physical properties such as the particle size distributions (PSD) and specific surface area (BET) are also of crucial importance. By carefully controlling the raw mix chemistry (mainly the ratio and reactivity of $Ca(OH)_2$ and SiO_2) and by later carefully controlling the activation grinding step, almost single phase hydraulic binders of tailor made properties can be obtained.

Advantages of Celitement®

Applications using binders with only one or very few reactive constituents are advantageous from a time to market perspective. "Simple" systems as Celitement® are in general easier to understand in formulations. Controlling their properties should in general be more straightforward than with multiphase cements. Fewer reacting phases in any receipt using modern hydraulic binders, generally stands for a higher "robustness".

Robustness is an important feature of the novel "calcium hydrosilicate" based binders (Celitement®) described here. They can be produced with a rather simple, in principal even single (mono) phase composition. In the pilot plant we aim at a conversion rate from CSH to hCHS of 85-90%. Besides the desired reactive hCHS-phase, only some not reactive phases from impurities coming with the raw materials (e.g. feldspars, unreacted limestone, spurrites from lime production) and smaller levels of reactive “impurities” (residual portlandite, belite, etc. <5%) are present in the final product.

For the first time a new hydraulic binder system is available which, by reaction with water, only forms large amounts of pure C-S-H phase, the traditional “glue” in mortars and concretes.

Properties of Celitement – hCHS

So the product coming out of the activation grinding, mainly consist of amorphous, highly disordered phases of high specific surface. The fact that Celitement® is mainly amorphous makes it difficult to characterise, at least using the traditional analytical tools known from modern quality control systems used in Portland cement production. A completely new quality assurance system and appropriate analytical tools had to be developed to control the entire production process. It is not trivial to analytically distinguish CSH, hCHS and C-S-H.

Using high quality raw materials, Celitement® can replace e.g. white cement in many applications. Large scale tests performed during the production of concrete paving stones, AAC and fibre cement material such as cladding and building boards showed, that Celitement® can be used and applied just like traditional cement in many production processes traditionally relying on Portland cement.

Strength development is comparable to Portland cement of classes 42,5R and 52,5R. Many long term durability tests have already been performed. When it comes to sulphate resistance (no calcium-aluminates present in hCHS), alkali silica reaction (only few soluble alkalis), chloride migration or freeze-thaw resistance (very dense microstructure), Celitement stands for very good durability properties. Some other properties related to the large amounts of pure C-S-H-phases formed are still under investigation. Different types of Celitement® also show different properties. To end up with suitable products, a constant exchange with future users and innovators of Celitement® has proven the best way to optimise the new material.

The most interesting material properties worth mentioning are:

1. Compatible with traditional cements
   This new class of binder is 100% compatible with traditional cements. So not only pure, but also “composite” systems with Portland cement clinker, even in combination with other main constituents from EN197 cements (limestone, fly ash, slag, etc.) are possible.

2. White colour (if desired)
   If pure (e.g. low in Fe_2O_3) starting materials are used, strictly white binder (L>90%) can be produced. The production process itself must not be changed, so it is a bit easier than in classical white cement lines to end up with pure white Celitement. Just like in white cement production however, a correlation between production costs (selected, pure starting raw materials) and the final degree of whiteness exists.

3. Minimised efflorescence
   As nearly no surplus $Ca(OH)_2$ from the hydration of the traditional calciumsilicates know from clinker, like C_3S or C_2S is produced, and nearly no sulfates and soluble alkalies are present, efflorescence is very much reduced. This could be an advantage in many applications.

4. Good connection to fibres and steel reinforcement bars
   Having low Ca-concentrations in the pore solution, the formation of portlandite double layers at fibre boundaries of e.g. fibre reinforced mortars is reduced. In traditional cement based systems the formation of such $Ca(OH)_2$ double layers is considered problematic with respect to the optimised coupling of the fibre surface to the C-S-H matrix.

5. A unique combination of very low heat of hydration and early strength
   The low CaO content of Celitement® and the fact that no highly reactive calcium aluminates such as C_3A are present, leads to very low heats of hydration. With on average only 120-150 [J/g] values determined by isothermal calorimetry are well below the threshold of 220 [J/g] for VLH (Very Low Heat) cements such as CEM/III-B. Despite its low heat of hydration however, early strength development of Celitement® is nevertheless comparable to Portland cements of strength classes 42,5R to 52,5R. So this new kind of binder allows for the first time the decoupling of the heat of hydration from early strength development. This might prove interesting especially for applications dealing with early constraint of young concrete or massive steel reinforced concrete structures.

6. Very dense microstructure, resembling UHPC
   As only pure C-S-H-phases are formed during hydration and taking into account the materials high specific surface, very dense microstructures are possible at the required low w/c-ratios (preferably <0.4). The microstructure resembles those found in UHPC systems often produced adding considerable amounts of e.g. expensive microsilica.

7. Allows new, “nanoporous” C-S-H microstructures
   When increasing the w/c-ratios on the other hand, nanoporous C-S-H structures can be realized. This was shown in a project with public funding together with a partner coming from aerated concrete production (Project NAPOS).

8. Simple phase composition simplifies interactions with construction chemicals
   As only C-S-H type phases have to be considered when it comes to interactions with construction chemicals such as superplasticisers (PCE´s), slump retainers, etc., control of properties in many practical applications should be easier. Although traditional PCE´s available on the market work with Celitement®, there is still room for improvement as tests have shown. By cooperation with a leading producer of construction chemicals, new formulations with even better performance are under development.

9. Main raw material composition shift from calcium rich (PC) to silica rich (hCHS)
   Compared to the production of Portland clinker, less $CaCO_3$ per unit of C-S-H is needed due to the difference of basic raw material chemistry. Further reduction by designing composite materials is possible.

10. Abundant raw material sources available at traditional cement or lime production sites
    As the main oxides necessary, namely CaO and SiO_2, are part of the raw material mix traditionally used in Portland cement production, large production sites with abundant raw material resources are available.

11. High sulphate resistance
    Working with pure C-S-H is an advantage when it comes to sulphate resistance. In some practical applications with very high external sulphate attack, Celitement® turned out to be the only binder system stable even under the most pessimistic conditions with respect to sulphate attack.

12. Curing at high temperatures possible
    Due to the lack of aluminates and sulphates, no detrimental effects of secondary ettringite formation by high temperature curing of prefabricated concrete elements occur. By using higher curing temperatures very high early strength can be obtained in special concretes.

More details with respect to the process can be obtained from our homepage. We would especially recommend the FAQ page (https://celitement.de/en/faq/) and the page dealing with product advantages (https://celitement.de/en/the-product/advantages-overview/).