

Concrete produced with calcium sulfoaluminate cement – a potential system for energy and heat storage

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ABSTRACT: In general the selection of materials proposed for storing solar energy is based on one of two principal processes: sensible heat storage or latent heat storage. Sensible heat storage utilizes the specific heat capacity of a material, while latent heat storage utilizes the change in enthalpy, or heat content, associated with a phase change of the material.

Concrete has been proposed for sensible heat storage, but relatively low energy densities and high storage temperatures are some of the drawbacks of this material. However, ettringite, one of the cement hydration products, exhibits a high dehydration enthalpy. Hence, a more efficient latent heat storage system displaying a high storage energy density at relatively low temperatures based on this cement hydrate phase is proposed.

In conventional Portland cement concrete, ettringite is found in relatively low quantities (around 10 mass-%), resulting in a very low energy storage potential. In order to obtain higher ettringite contents, calcium sulfoaluminate cements (CSA) can be used as binder. In CSA concretes, ettringite is the main hydration product (often > 50 mass-%).

In this paper a latent energy storage system based on CSA concrete or mortar is presented, which potentially can be used to store solar energy or heat in small home storage systems or large facilities. It is shown that with this system, based on dehydration of ettringite at temperatures around 100° C and subsequent wetting, permanent (e. g. seasonal) storage at high energy densities is possible.

1 INTRODUCTION

Heat or energy (e. g. solar energy) storage is generally based on one of two principal processes: (i) sensible heat storage utilizes the specific heat capacity of a material, which is the heat required to increase its temperature, while (ii) latent heat storage utilizes the change in enthalpy, associated with a phase change of the material. Typical phase changes are hydrationdehydration or melting-freezing. Generally, sensible heat storage has the disadvantage that energy storage requires excellent thermal insulation and hence is less suitable for seasonal storage than latent heat storage.

Concrete or mortar has been proposed for sensible heat storage (e. g. van Berkel (2000)) due to its quite high specific heat capacity of 0.75 $J/(g\cdot K)$, originating mainly from the chemical bound water. However, this sensible heat storage makes no use of phase changes, i.e. no systems for



dehydration and rewetting are foreseen. The addition of phase change materials (PCMs) like paraffin (or microcapsules containing such PCM) to concrete and the use of such materials for passive latent heat storage would be possible. In this case, the latent heat storage potential is attributed to the PCM material only. The addition of PCM materials to concrete has the deficiency of a limited amount of PCM that can be added to concrete without losing its strength and compactness. Additionally PCM materials are expensive when compared with concrete.

Ettringite (calcium aluminate trisulfate hydrate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$) is one of the hydrate phases of Portland cement, the usually applied binder in concrete. It starts to dehydrate at quite low temperatures ($\approx 30^{\circ}\text{C}$, about 50-150°C for practical application, see Struble & Brown (1986)) as hydroxy groups and water molecules are removed from the structure. The result is the so-called "metaettringite", which contains only 10-13 water molecules per formula unit instead of 32 (Pourchez et al. (2006)). A subsequent addition of water to metaettringite leads to a rehydration to ettringite. The process of dehydration of ettringite and the rehydration of metaettringite is fully reversible. The enthalpy needed for dehydration is high, about 600 kJ/kg ettringite (Struble & Brown (1986)), and is regained, when metaettringite is hydrated again. Figure 1 (modified from van Berkel (2000)) shows ettringite in comparison with other materials used for latent and sensible heat storage, illustrating the favourable properties - low operation temperature at high energy density - of ettringite as energy and heat storage material. For practical reasons the operation temperature should be higher than the ambient temperature.



Figure 1. Energy density of storage materials versus temperature modified after van Berkel (2000). Remark: data for concrete is for sensible storage. The values for ettringite represent the data from Struble and Brown (1986) (circle) and the range of operation temperature proposed in this study (grey line).



Thus, ettringite is of potential interest regarding energy and heat storage. Ettringite itself occurs in the form of crystals, and thus its use as latent heat storage material has different deficiencies. Such crystals can only be loosely packed in a vessel, so that a low apparent density with many voids between the particles results. This leads to a low storage energy density, poor heat exchange, and considerable amount of water needed for rehydration. Furthermore, this water (having a high specific heat capacity) must be heated by the regained energy first, so that a low rehydration temperature difference results.

In hydrated Portland cement concrete ettringite is found in relatively low quantities (< 15 mass-% of the hardened cement paste) and hence a very low energy storage potential results, as there is only a very minor contribution of other cement hydrates. This may be the reason why neither concrete as a latent heat storage material, nor a system based on the de- and rehydration of concrete has been published in a patent or proposed elsewhere so far. However, there are other cementitious binders besides Portland cements available, which can be used to produce a cementitious, stable building material with a much higher content of ettringite in the hydrated binder matrix. Among the candidates are the calcium sulfoaluminate cements (CSA), which generate ettringite as main hydration product. In this contribution, it is shown that a cementitious building material on CSA cement can be used in a latent heat storage system based on ettringite dehydration/rehydration.

2 CALCIUM SULFOALUMINATE CEMENTS

2.1 Manufacturing

Calcium sulfoaluminate (CSA) cements contain ye'elimite $(4CaO \cdot 3Al_2O_3 \cdot SO_3)$ as major constituent (30-70%). While CSA cements are not widely used in Europe and the U.S., they have been produced, used and standardized in China for about 30 years, where they are known as the "third cement series" (Juenger et al. (2011)). The clinkers are interground with different levels of calcium sulfate in order to obtain rapid-hardening, high-strength, expansive, self-stressing or low alkali cements.

CSA cements are receiving increasing attention because they promise to provide a low- CO_2 alternative to Portland cement (Gartner (2004), Juenger et al. 2011)). Compared to alite (tricalcium silicate), the main phase of an ordinary Portland cement, which releases 1.80 g CO_2 per ml of the cementing phase, when made from limestone and silica, calcium sulfoaluminate releases only 0.56 g CO_2 per ml of cementing phase, when made from limestone, alumina and anhydrite. The firing temperature used to produce CSA clinker is typically 1250°C, about 200°C lower than that used for Portland cement clinker. One reason for this is that the heat of formation of ye'elimite (800 kJ/kg) is substantially lower than that of alite (1848 kJ/kg).

2.2 Hydration

About 15-25 wt.-% of gypsum is usually interground with the CSA clinker for optimum setting time, strength development and volume stability. The hydration of the CSA cements mainly depends on the amount and reactivity of the added calcium sulfate as well as on the kind and amount of minor phases present (Zhang & Glasser (2002), Winnefeld & Barlag (2009), Winnefeld & Barlag (2010), Winnefeld & Lothenbach (2010)). The required water/cement ratio for complete hydration is around 0.60 for technical cements, and thus higher compared to an OPC (≈ 0.40).

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With water, ye'elimite reacts according to equation (1) to monosulfate and aluminium hydroxide. With gypsum or anhydrite, it forms ettringite and aluminium hydroxide, see equation (2), until the calcium sulfate is consumed. Afterwards, monosulfate is generated according to equation (1). Kinetics is generally very rapid (see figure 2). Gypsum content can be adjusted in a way that ettringite (see figure 3) is the main hydration product.

$$4\text{CaO·3Al}_2\text{O}_3 \cdot \text{SO}_3 + 18 \text{ H}_2\text{O} \rightarrow 3\text{CaO·Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O} + 2 \text{ Al}(\text{OH})_3$$
(1)

(monosulfate formation)

$$4\text{CaO}\cdot3\text{Al}_2\text{O}_3\cdot\text{SO}_3 + 2\text{ CaSO}_4 + 34\text{ H}_2\text{O} \rightarrow 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O} + 2\text{ Al}(\text{OH})_3 (2)$$



(ettringite formation)

Figure 2. Thermodynamic modelling of the phase development of a CSA paste (water/cement = 0.80) as a function of hydration time, modified after (Winnefeld & Lothenbach (2010)). The volumes refer to the initial volume of cement plus water, which is set to 100 cm^3 .

2.3 *Properties and applications*

The properties of CSA cements partly differ from those of ordinary Portland cements (Juenger et al. (2011)). Setting times are typical between 30 min and 4 h. Strength development exhibits generally a higher early and late strength compared to Portland cement. Heat of hydration is quite high (e. g. close to 400 J/g cement after 72 h) and mostly develops during the first 24 hours. In the absence of calcium oxide or calcium hydroxide, CSA cements are often dimensionally stable. However, expansion may occur if ettringite forms in reasonable amounts after setting, which can be triggered by the amount of added calcium sulfate. They exhibit a chemical shrinkage about twice as high as Portland cements (Lura et al. (2010)).

The durability of building materials made from CSA cements, as derived from laboratory tests and from field studies, seems to be in general at least comparable to conventional Portland cement-based materials (Juenger et al. (2011)), however more data concerning long-term

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behavior is needed. CSA-based concretes exhibit a high resistance to freeze-thaw and against chemical attack by seawater, sulfates, chlorides, magnesium and ammonium salts. Much of this resistance could be due to the dense pore structures developed by CSA cements. Carbonation depends on the water/cement ratio and appears to be more rapid than in Portland cement concretes, leading to the decomposition of ettringite, which may cause a moderate strength loss. Despite that the alkalinity of CSA cements is about 1 pH unit lower than for Portland cements, the steel reinforcement seems to be protected from corrosion. The low alkalinity also seems to be favorable concerning alkali aggregate reaction.

Since the Seventies, CSA cements have been used mainly in China as binder for concrete in a wide range of concrete applications (Zhang & Glasser (2002)). Blends with ordinary Portland cement and calcium sulfate can on one hand be used for shrinkage compensated or expansive cements. On the other hand they are applied in special rapid setting and hardening mortars like tile adhesives, self-levelling screeds or high performance composites (Pelletier et al. (2010)). Furthermore, due to their low pH, their low porosity and the ability of ettringite and monosulfate phases to bind heavy metals, calcium sulfoaluminate cements are of interest in the field of hazardous waste encapsulation.



Figure 3. Scanning electron micrograph of prismatic ettringite crystals in a hardened CSA cement mortar.

3 ETTRINGITE-BASED CEMENTS AS HEAT STORAGE MATERIAL

3.1 General considerations

An effective heat or energy storage system based on concrete or mortar rich in ettringite phases making use of the large dehydration enthalpy of ettringite is proposed. The concrete or mortar thereby is heated to dehydrate and then later supplied again with water to generate heat upon rehydration.

Novel binder systems containing calcium, aluminum and sulfate sources, yielding ettringite when hydrating will be used. Among the most promising binder systems are CSA cements, which might be combined also with other binders like ordinary Portland cements. Those ternary mixes are able to yield around 80 mass-% of ettringite in the hardened binder matrix (see figure 4). The binder system is mixed with water (admixtures might be added) to produce a paste. Mortar or concrete might be produced by adding sand, or sand and gravel, respectively. Standard concrete mixing and placing technologies can be applied to manufacture compact, rigid and durable materials with up to 80 mass-% of ettringite.







Figure 4. Mass-% of ettringite in a 100% hydrated ternary blend of CSA cement, ordinary Portland cement and gypsum, as calculated by thermodynamic modelling (Winnefeld & Lothenbach (2010), Pelletier et al. (2010)).

3.2 First experiments

First experiments of dehydration and rehydration of CSA cement pastes were done using calorimetric measurements. A CSA paste was prepared from a commercial CSA clinker mixed with reagent grade gypsum in a ratio 78/22 by mass applying a water/binder ratio of 0.72. For comparison a paste was produced using an ordinary Portland cement CEM I 42.5 N (OPC) according to European Standard EN 197-1 with a water/binder ratio of 0.50. Two kinds of samples were prepared: (i) small cylinders of 9.1 mm diameter and 5.5 mm height and (ii) larger cylinders of 55 mm diameter and 50 mm height. The cylinders were cured at 20°C in sealed conditions for at least 28 days, allowing a high hydration degree.

The dehydration was carried out in a laboratory oven at 110°C for 2 days (small cylinders) and 6 days (larger cylinders), respectively. The rehydration of the small samples was done in the 20 ml Admix ampoule (Wadsö 2005)) of a TAM Air isothermal conduction calorimeter by injection of 2 ml demineralized water and measuring the resulting hydration heat flow. The larger samples were rehydrated with 500 ml of demineralized water in a semiadiabatic calorimeter according to European Standard EN 196-9.

Figure 5 shows the rehydration enthalpy of the CSA cement paste in comparison with the OPC paste. In both systems the rehydration enthalpy is mainly due to the conversion of metaettringite to ettringite, as the other phases present (mainly monosulfate and Al(OH)₃) lose their crystal water at higher temperature. As the CSA paste contains significantly higher ettringite contents than the OPC paste, its dehydration enthalpy is remarkably higher as well (factor 3.5-4.0). The enthalpy release is quite rapid in the small samples; most of the enthalpy is regained after 15 min. In subsequent cycles the rehydrated samples were several times dried and rewetted again, showing even 10-20% higher rehydration enthalpies. The larger samples showed similar results, however the enthalpy release was somewhat slower.

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The rehydration enthalpy after 60 min of the investigated CSA paste is about 25% of the value reported by Struble & Brown (1986) for pure ettringite. This can be explained by the facts that (i) the ettringite content of the CSA paste was roughly 50%, (ii) the paste was probably not fully hydrated, which is also indicated by the higher heat release in the second cycle, (iii) the applied dehydration conditions need to be optimized.



Figure 5. Heat development as measured by isothermal conduction calorimetry during rehydration of hardened binders previously heated at 110°C for 24 h (Kaufmann & Winnefeld (2010)).

3.3 Possible realisation

Energy is stored in a CSA-based concrete block by the dehydration of ettringite at moderate temperatures, e. g. between 50 and 160°C. The concrete is composed in a way that it does not lose its structure. It may be reinforced with steel or textile reinforcement or fibers for this purpose.

The energy is recovered by rewetting the concrete, allowing the metaettringite to recover a crystal structure containing more water molecules. The heat released is captured by a heat exchange system. The amount and moment of the heat release can be triggered by the moment/amount of water added. For long/medium term storage the concrete block has to be prevented from water access during storage. While for medium storage time dry climate storage may be sufficient, special measures like impermeable membranes or vapour dense concrete confining the system may have to be applied for long term storage.

The concrete block is equipped with one or two piping systems. Generally the first piping system containing water or another heat carrying liquid substance is used (i) to heat the massive concrete block or a pile of concrete plates or smaller blocks to a certain temperature to allow dehydration and (ii) for heat exchange upon rehydration. The second loop is used to (i) allow the vapor resulting from dehydration to be removed and (ii) for the supply of water or vapor for rehydration. It may be possible to use just one loop for both heat supply/water remove upon dehydration and water supply/heat exchange upon rehydration by circulation dry (dehydration) or wet (hydration).

The water obtained from dehydration may be collected in storage tanks to be used for the later rehydration. The concrete may be produced with sea water. Like that the system may be installed in desert regions. Combined sensible and latent heat storage systems are possible due



to the relatively high specific heat capacity of ettringite (about 1.3 J/($g\cdot K$) (Struble & Brown (1986)).

4 CONCLUSION

Concrete based on calcium sulfoaluminate cement is proposed to be used as latent heat or energy storage system e. g. for solar energy. The storage principle is based on the dehydration and subsequent rehydration of ettringite, the main hydration product of CSA cements. The dehydration takes place at temperatures above 30°C (50-150°C for practical application) and is connected with a high dehydration enthalpy. Thus, ettringite based storage systems exhibit superior properties compared to many other materials used for heat and energy storage.

The potential use of ettringite-based cementitious materials for heat and energy storage was filed into a Swiss patent application (Kaufmann & Winnefeld (2010)). Currently a prototype involving a piping system for wetting and heat exchange is constructed. A further development to realize economical technological solutions and commercial products will be necessary. This is planned together with potential industrial partners.

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