



Effect of Carboxylic Acids on the Hydration of Calcium Sulfate Hemihydrate Pastes

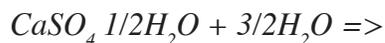
Carsten Vellmer

University of Kassel Department of Structural Materials
Kassel, Germany

TA Instruments, 109 Lukens Drive, New Castle, DE 19720, USA

INTRODUCTION

In the past few decades calcium sulfate based building products have become materials of choice for various interior construction purposes, The basis of gypsum technology is the ability of gypsum to transform into various calcium sulfates (hemihydrate, anhydrite) when being heated. When hemihydrate or anhydrite is mixed with water calcium sulfate dihydrate is formed again due to re-hydration. During re-hydration of hemihydrate, the following exothermic reaction occurs:



Depending on the industrial production process, hemihydrate occurs in two different forms (α - and β -hemihydrate). Autoclave processes result in well formed transparent crystals with sharp crystal outlines (α -hemihydrate). Directly fired rotary kilns or indirectly heated kettles produce flaky particles made up of small crystals (β -hemihydrate). The two different forms vary in their application characteristics (Wirsching 1985).

For technical application the setting of calcium sulfate based building products is accelerated (anhydrite) or retarded (hemihydrate) by a variety of chemical additives (Reul 1991). Widely used retarders are carboxylic acids and their salts. Retarders may affect the rate of dissolution of hemihydrate, change saturation or super saturation, poison growing gypsum nuclei of critical size, slow down the growth of dihydrate crystals, etc. However, Fourier Transform Infrared (FTIR) spectroscopy studies (Vellmer et al. 2004)

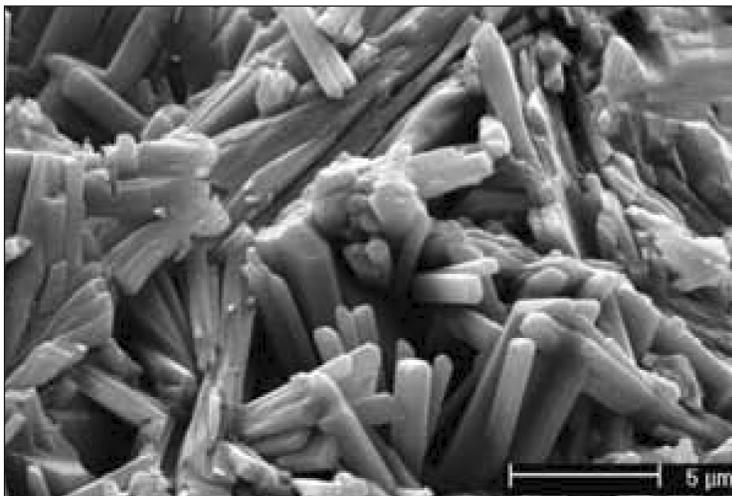


Figure 1. Scanning electron microscope (SEM) image of hardened α -hemihydrate paste.

confirm changes in the vibrational modes of SO_4^{2-} group of sulfate dihydrate suggesting that carboxylic acids are chemisorbed at calcium sulfate dihydrate crystal faces having high amount of SO_4^{2-} groups and act as nuclei poisons.

MATERIALS AND METHODS

The setting of hemihydrate pastes in the presence of carboxylic acids was examined by monitoring the heat evolution rate and total hydration heat using a TAM Air isothermal conduction calorimeter. Hemihydrate paste's heat evolution goes through a number of stages and the setting generally corresponds to the location of the large peak in the heat evolution curves that is related to the formation of prismatic needle shaped calcium sulfate dihydrate crystals with a high degree of interlocking (Figure 1).

For the hydration studies α -hemihydrate (BPB formula, Walkenried, Germany) with a specific surface area of $4390 \text{ cm}^2/\text{g}$ (laser granulometer) was used. For comparison hydration studies were also performed on β -hemihydrate ($5850 \text{ cm}^2/\text{g}$; Orth, Hundelshausen, Germany) and an additional α -hemihydrate ($2540 \text{ cm}^2/\text{g}$; BSH Grenzebach, Bad Hersfeld, Germany).

The amount of hemihydrate was 10 g while the water/solid ratio was 0.30 (α -hemihydrate) and 0.50 (β -hemihydrate), respectively. The required amount of carboxylic acids and water were weighed into 20 ml polyethylene scintillation vials. After complete dissolution of the carboxylic acids the hemihydrate was added and subsequently mixed using a VortexTM laboratory mixer and loaded into the TAM air calorimeter.

RESULTS

Figure 2 compares the heat evolution rate and total hydration heat of different hemihydrate pastes at 25°C . Different hemihydrates show different heat evolution rates and total hydration heats. Since the used industrial products have different particle-size distributions and are derived from different raw materials the observed differences cannot unequivocally related to differences in the thermodynamic properties (cf. Kuzel 1987, Wirsching 1985; Eipeltauer 1956).

Figures 3 and 4 show the heat evolution rate and total hydration heat of α -hemihydrate pastes in the presence of carboxylic acids at 20°C .

Compared to a control sample without carboxylic acid the duration of induction periods of the setting process varied with the type of carboxylic acid. The results suggest that the carboxylic acids affect the formation of gypsum nuclei of critical size during the induction period. In case of citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and succinic acid ($\text{C}_4\text{H}_6\text{O}_4$) the width of the large peak in the heat evolution curves is increased compared to the control sample as well as samples containing tartaric ($\text{C}_4\text{H}_6\text{O}_5$) and malic acid ($\text{C}_4\text{H}_6\text{O}_5$).

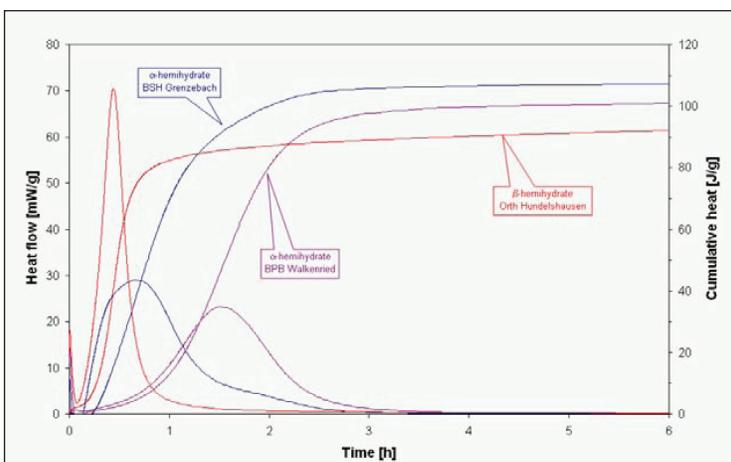


Figure 2. Heat evolution rate and total hydration heat of different hemihydrate pastes at 25°C . Notes added in proof: Different heats of hydration may be related to different amounts of impurities; differences in heat evolution rate might be a function of particle-size distribution.

Figures 5 and 6 show the heat evolution rate and total hydration heat of α -hemihydrate pastes containing different amounts of succinic acid at 20°C. With an increasing amount of succinic acid the width of the large peak in the heat evolution curves increases while the induction period is almost constant.

DISCUSSION

The current study describes the effect of carboxylic acids on the hydration of α -hemihydrate pastes. Pastes containing different carboxylic acids of equimolar concentration exhibit distinct heat evolution characteristics. For equimolar concentrations the induction period and hence the retarding effect of the carboxylic acids increases in the following sequence:

Tartaric acid < Succinic acid <

Citric acid < Malic acid

This type of study provides valuable information to optimize both the type and the concentration of retarder for calcium sulfate based building materials. This is important because chemical additives not only alter the hydration behavior but also modify the calcium sulfate dihydrate crystal morphology and the overall microstructure and consequently the physico-mechanical properties of calcium sulfate based building materials (Middendorf et al. 2004).

The TAM air isothermal conduction calorimeter proved to be the method of choice to evaluate the effect of carboxylic acids on the hydration of hemihydrate pastes. Among others the simultaneous measurement of 8 samples and the high reproducibility of the quantitative data are a real benefit.

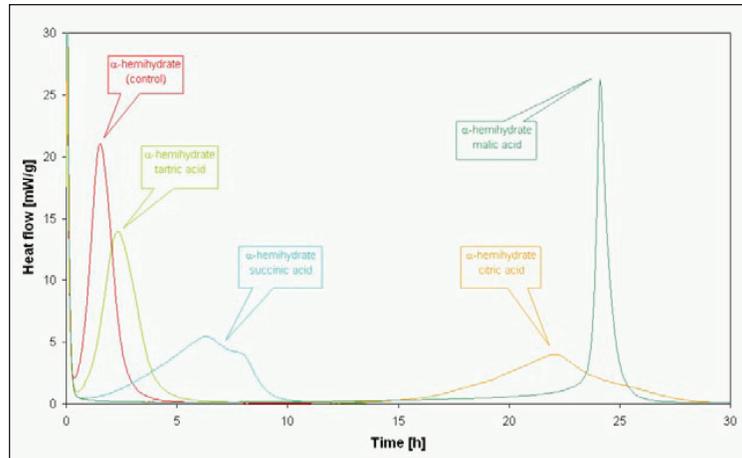


Figure 3. Heat evolution rate of α -hemihydrate pastes at 20°C (water/solid ratio 0.30) containing equivalent molar concentrations of carboxylic acid ($2 \cdot 10^{-3}$ Mol in respect to α -hemihydrate).

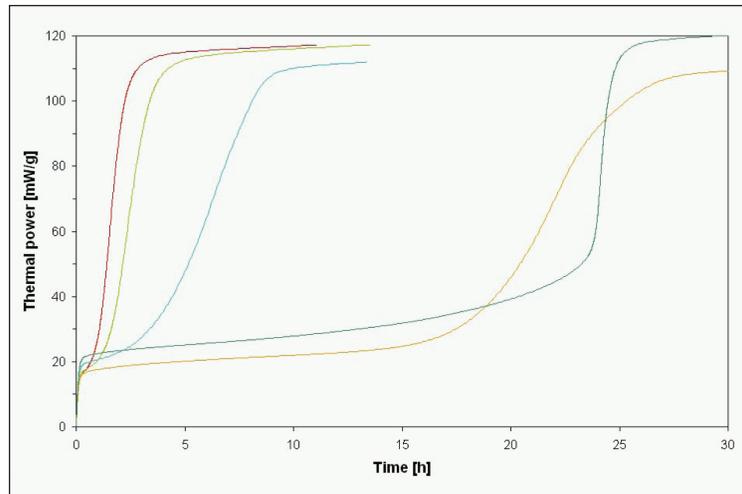


Figure 4. Total hydration heat of α -hemihydrate pastes at 20°C (water/solid ratio 0.30) containing equivalent molar concentrations of carboxylic acid ($2 \cdot 10^{-3}$ Mol in respect to α -hemihydrate).

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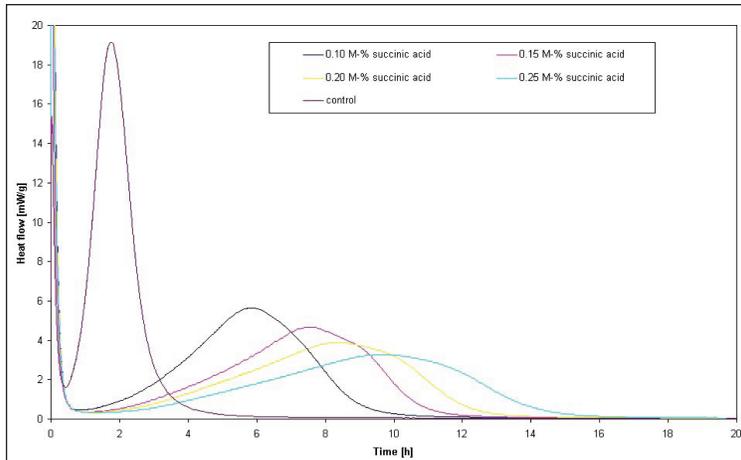


Figure 5. Heat evolution rate of α -hemihydrate pastes at 20°C (water/solid ratio 0.30) containing different concentrations of succinic acid.

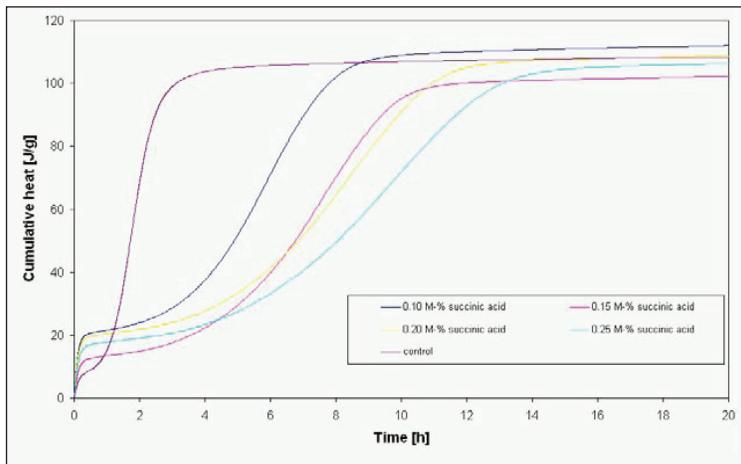


Figure 6. Total hydration heat of α -hemihydrate pastes at 20°C (water/solid ratio 0.30) containing different concentrations of succinic acid.