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HYDRATION OF α-HEMIHYDRATE IN THE PRESENCE OF CARBOXYLIC ACIDS

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α-Hemihydrate was allowed to hydrate in the presence of tartaric, succinic, malic or citric acids at room temperature at a water/binder ratio of 0.35. Hydration of hemihydrate leading to the crystallisation of calcium sulphate dihydrate is an exothermic process. The temperature rise during hydration was measured as a function of time using a semi-adiabatic method. The temperature rise–time curves are similar for all investigated systems but with different induction period. The results showed that calcium sulphate dihydrate crystallisation is a nucleation controlled process and different acids are chemisorbed at the surface of forming nuclei to different extent. Processes taking place during nucleation may control the morphology of resultant crystals. Infrared spectral and differential scanning calorimetric studies confirmed the adsorption of carboxylic acids at the surface of dihydrate crystals.

Keywords: *calcium sulphate, chemisorption, crystallization, microstructure, nucleation*

Introduction

In the past few decades calcium sulphate based building materials have become the materials of choice for various construction purposes. The use of calcium sulphate dihydrate in construction industries depends on its ability to transfer itself into various modifications when being heated. The dehydration or calcination as well as rehydration or setting are the basis of calcium sulphate dihydrate technologies. For example, plaster of Paris (hemihydrate) is prepared by calcining calcium sulphate dihydrate. Furthermore special purpose hemihydrates are prepared by autoclaving calcium sulphate dihydrate to use this material as mould gypsum. When hemihydrate is again mixed with water calcium sulphate dihydrate is formed due to rehydration.

During hydration of hemihydrate, the following exothermic reaction occurs:

$$CaSO_4{\cdot}0.5H_2O+1.5H_2O \Rightarrow CaSO_4{\cdot}2H_2O+Q$$

where Q is the amount of heat evolved. When the hydration is taking place in a paste, prismatic needle shaped calcium sulphate dihydrate crystals with a high degree of interlocking are formed. The morphology of calcium sulphate dihydrate crystals depends on the formation conditions and the presence and type of chemical additives [1–3]. Zhang and Nancollas [4] have reported that crystallographic surfaces can be increased or decreased in the presence of additives. Middendorf [5] found that the morphology of the calcium sulphate dihydrate crystal is changed in the presence of citric acid with the formation of short prisms and enhanced growth of the (010) surface.

Badens *et al.* [2] studied the role of different carboxylic acids on the morphology of calcium sulphate dihydrate crystals, crystallized from hemihydrate. They tried to explain the retarding effect of carboxylic acids in terms of structural matching (i.e., position of Ca^{2+} ions) between the crystal faces involved and the functional groups of additive molecules. Bosbach and Hochella [3] have found that chemical additives affect the growth of different crystallographic faces in different ways. Baruah *et al.* [6] studied the sulphate behaviour during the dissolution of calcium sulphate dihydrate in the presence of organic acids and proposed that calcium forms complexes with different acids. This could also be one of the reasons for modifying the crystal morphology of calcium sulphate dihydrate crystals in the presence of carboxylic acids.

Due to industrial and geochemical significance, there has been a considerable amount of research on the mechanism of calcium sulphate dihydrate growth in the presence of carboxylic acids. Despite the intensive research work during the past decades, there is still considerable debate and uncertainty over the mechanism.

In order to develop and optimise calcium sulphate based building materials, it is important to understand the role of additives modifying the calcium sulphate dihydrate crystal morphology and the overall microstructure. In the present investigation the effect of succinic, tartaric, citric and malic acids on the hydration of α-hemihydrate has been studied with a view to understand the process of nucleation and crystal growth and morphological changes in calcium sulphate dihydrate.

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Experimental

Materials

For the hydration studies α-hemihydrate provided by BPB formula, Walkenried, Germany was used. The hemihydrate is produced in dry autoclave process using natural gypsum of Permian age. The specific surface area of the hemihydrate was 4390 $cm^2 g^{-1}$ (laser granulometer) and the chemical composition is given in Table 1. Pure calcium sulphate dihydrate (Merck) was also used.

DL-malic acid, succinic acid, *L*(+)-tartaric acid and citric acid were used as the retarding admixtures. The given concentrations of the carboxylic acids were always with reference to the amount of α-hemihydrate.

Preparation of hydrated samples

About 10 g of the mixtures prepared as below for temperature rise measurements were taken separately in polyethylene bags and the hydrations were stopped at 1 day with isopropyl alcohol. Subsequently the samples were dried in an oven at 40°C until constant masses were obtained. A small piece of the hardened paste of each sample was stored in isopropyl alcohol for SEM studies.

Preparation of calcium sulphate dihydrate-carboxylic acid samples

10 g calcium sulphate dihydrate was mixed with 10 mL of acid solutions (0.5714 g acid dissolved in 100 mL water), mixed thoroughly in polyethylene bags and stored for 5 days at room temperature. After 5 days the samples were dried at 40°C and stored in a desiccator.

Methods

Measurements of temperature rise during hydration

300 g of α-hemihydrate of calcium sulphate was mixed with 105 g of water (water/binder=0.35) in the presence and absence of carboxylic acids. This amount of water was required to make a paste of standard consistency. The concentration of citric acid was 0.05 mass% whereas that of other acids was 0.2 mass%. The mixtures were stirred for 2 min. 250 g of each mixture was weighed in a plastic cup and put in four different hollow cylindrical container (6 cm diameter and 8 cm deep) made of Polystyrol/thermocoal in order to avoid thermal losses. Mixing water or carboxylic acid solution with hemihydrate and placing the paste in the plastic cups took about 3 min. During this period practically there was no temperature rise. Each cup was covered with a thermocoal lid in which a small hole was made at the top through which NTC thermistor was inserted. The thermistors in each cup were allowed to dip into the paste up to 4 cm. The other end of each thermistor was then connected with a temperature data logger. The hydrations were allowed to take place till the rise in temperature ceased and room temperature (≈23°C) was visible at the logger. The experiments were also performed using equimolar concentrations ($2\cdot10^{-3}$ M) of the carboxylic acids.

Powder X-ray diffraction studies

The powder X-ray diffraction patterns of the hydrated samples were recorded with the help of Philips PW1710 including JCDPS data base using CuK_α radiation which indicated that the hydration reactions were complete within one day.

SEM studies

SEM studies on the hydrated samples were made with the help of Philips XL 30i scanning electron microscope by making carbon coating on each sample.

IR spectral studies of calcium sulphate dihydrate-carboxylic acid samples

The IR spectra of the samples were recorded with PerkinElmer-FTIR spectrophotometer RX-1 in KBr phase.

DSC studies of calcium sulphate dihydrate-carboxylic acid samples

DSC studies of the samples were made with Netzsch STA 409PG/PC in N_2 atmosphere at a heating rate of 10°C min^{-1} using Al_2O_3 as reference.

Results and discussion

Calorimetric studies on the hydration of β-hemihydrate have shown that the kinetic results are quite comparable with the results obtained from X-ray diffraction studies [7]. When water was added to α-hemihydrate, hydration started with rise in temperature which was recorded with a semi-adiabatic set-up. Results are given in Table 2 and Figs 1 and 2. In case of reference sample the temperature rise started immediately after adding the water and reached to its maximum value (62°C) at 49 min of

Table 1 Chemical composition of α-hemihydrate (BPB)

Components	CaO	SO_3	SiO_2	Al_2O_3	Fe_2O_3	MgO	Water of crystallisation	LOI
Composition/mass%	38.6	54.4	0.54	0.07	0.05	0.13	5–6	5–6

Table 2 Effect of carboxylic acids on the induction period, time for maximum rise in temperature and maximum temperature during the hydration of α-hemihydrate (w/b=0.35)

Carboxylic acids	Concentration	Induction period/min	Time for T_{max}/min	T_{max}/°C
Reference	–	<1	50	60
Citric acid	0.05 mass%	230	285	61
	$2\cdot10^{-3}$ M	880	1150	52
Malic acid	0.2 mass%	575	640	55
	$2\cdot10^{-3}$ M	260	750	55
Succinic acid	0.2 mass%	75	300	55
	$2\cdot10^{-3}$ M	50	260	57
Tartaric acid	0.2 mass%	5	79	62
	$2\cdot10^{-3}$ M	12	110	62

T_{max} – maximum temperature

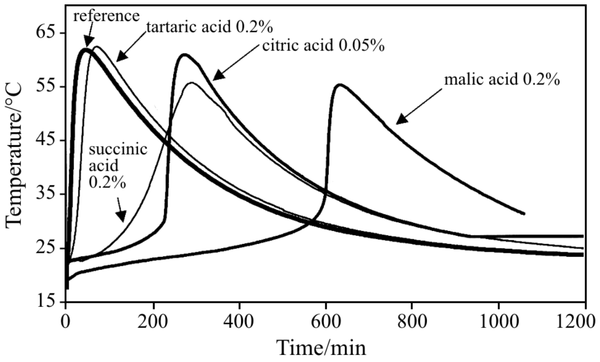

Fig. 1 Variation of temperature with time during the hydration of α-hemihydrate in the presence of carboxylic acids (w/b=0.35)

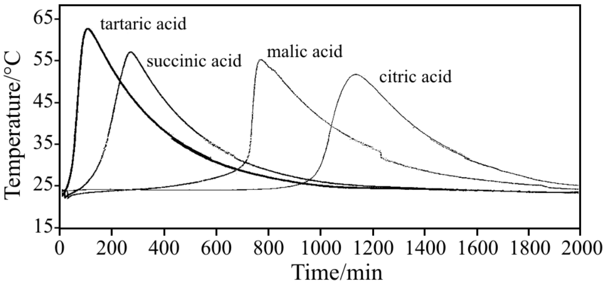

Fig. 2 Variation of temperature with time during the hydration of α-hemihydrate in the presence of carboxylic acids having equimolar concentrations ($2\cdot10^{-3}$ M)

hydration. Subsequently the temperature decreases because of heat loss. This temperature rise is due to heat release during the crystallization of calcium sulphate dihydrate. Since there is a rapid temperature rise, the crystallization of calcium sulphate dihydrate starts immediately. In the presence of 0.2 mass% tartaric acid the temperature rise is similar to that of the reference sample with slightly longer induction period. It appears that tartaric acid has little effect on the hydration behaviour of hemihydrate. 0.05 mass% citric acid retards the hydration with an induction period of 230 min. After the induction period a rapid temperature rise takes place with its maximum value at 285 min of hydration. In the presence of 0.2 mass% succinic acid, after the induction period, there is comparatively a slow rise in temperature with its maximum value at 300 min of hydration. The retarding behaviour of 0.2 mass% malic acid is quite high with an induction period of 575 min. After the induction period the temperature increases rapidly with a maximum at 640 min of hydration.

The effect of equimolar concentration ($2\cdot10^{-3}$ M) of acids on the temperature rise during the hydration of hemihydrate is shown in Fig. 2. The induction period, time for maximum temperature and the maximum temperature are also given in Table 2. For equimolar concentrations the induction period or the retarding effect of the acids is in the following sequence:

citric acid>malic acid>succinic acid
>tartaric acid>reference

The maximum temperature given in Table 2 show that they are almost in the same range. The two concentrations of the same acid have different induction periods.

It is almost established that the hydration of hemihydrate leading to the formation of calcium sulphate dihydrate occurs through solution mechanism. The solubility of hemihydrate in water at room temperature is higher than that of calcium sulphate dihydrate. Thus when hemihydrate is mixed with water, a part of it immediately dissolves making the solution saturated with respect to Ca^{2+} and SO_4^{2-} ions. This saturated solution becomes supersaturated with respect to calcium sulphate dihydrate leading to the nucleation and crystal growth. A number of kinetic models including the nucleation–growth model have been proposed to describe the reaction kinetics [8]. In order that a crystallization can take place, the nucleating embryo must have a critical size. The critical radius (r_c) is expressed with the following equation [9].

$$r_c = \frac{2\sigma\nu}{kT\log S} \qquad (1)$$

where σ is the surface energy per unit area, ν is the molecular volume, k is Boltzmann constant, T is the temperature and S is supersaturation of the solution. From Eq. (1) it is obvious that the decreasing supersaturation decreases the nucleation probability by increasing r_c.

In the absence of any chemical additives during the induction period, clustering of hydrated Ca^{2+} and SO_4^{2-} ions occur, leading to the formation of calcium sulphate dihydrate nuclei. These nuclei when acquire certain critical size, crystallization of calcium sulphate dihydrate starts. However this depends on various factors such as solution saturation/supersaturation, impurities, type of hemihydrate and its surface area, temperature, water/binder ratio, etc. In the case of reference it is possible that a large number of calcium sulphate dihydrate nuclei of critical size are formed quickly with a rapid crystallization. In the presence of carboxylic acids the nucleation and growth processes are delayed. In order to understand this delay process an approximate calculation of surface area of the acid molecules has been made by calculating the molar volumes. The surface area of molecules present in 0.002 g succinic acid (0.2 mass% acid) added to 1 g hemihydrate comes out to be $1.5\cdot10^{-3}$ cm^2. This value is very low to cover the total surface of 1 g hemihydrate (sp.surface area of hemihydrate –4390 cm^2 g^{-1}). Thus the delay in nucleation and crystal growth process may not be due to adsorption of carboxylic acids on the surface of hemihydrate.

The carboxylic acids are ionised in water and the carboxylate ions as well as undissociated acid molecules get adsorbed at the surface of forming calcium sulphate dihydrate nuclei. This hinders the crystal growth. Different carboxylic acids adsorb in a different way at different crystallographic surfaces [3]. As a result of this the rates of nucleation and crystal growth in the presence of different carboxylic acids are different.

If one examines the Figs 1 and 2, it is obvious that in the presence of acids, the induction periods are different but once the hydration starts, the maximum rise in temperature is almost the same in all the cases. This suggests that during early hour of hydration, acids are adsorbed (chemisorbed) at the growing calcium sulphate dihydrate nuclei and this may act as a coating. The extent of coating and its durability depend on the nature and value of forces involved in chemisorption. The coating of poorly chemisorbed acids is broken statistically faster and in that case the nucleation and crystal growth start first. Once the growth starts the mechanism is the same irrespective of the carboxylic acids as indicated by the same temperature rise. It appears that carboxylic acids modify the nucleation process and also control the morphology of the final crystals.

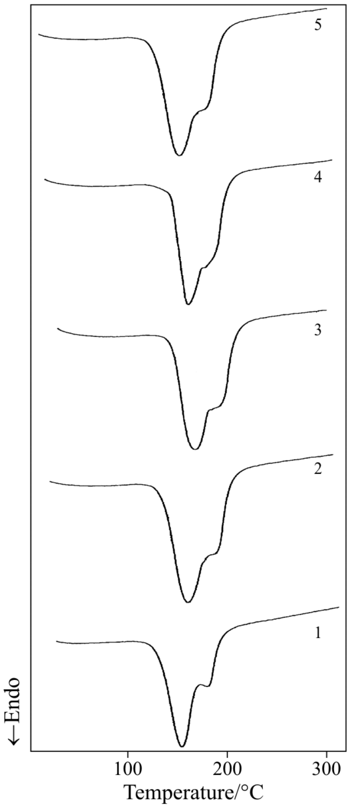

Fig. 3 DSC curves: 1 – calcium sulphate dihydrate;
2 – calcium sulphate dihydrate+tartaric acid;
3 – calcium sulphate dihydrate+succinic acid;
4 – calcium sulphate dihydrate+malic acid;
5 – calcium sulphate dihydrate+citric acid;

Table 3 Endothermic peak temperatures of calcium sulphate dihydrate-carboxylic acid systems

System	Peak temperature/°C	
	reaction I	reaction II
Calcium sulphate dihydrate	154.3(s)	181.1(s)
Calcium sulphate dihydrate+tartaric acid	170.2(s)	198.8(sh)
Calcium sulphate dihydrate+malic acid	173.5(s)	200.1(sh)
Calcium sulphate dihydrate+succinic acid	174.3(s)	192.8(sh)
Calcium sulphate dihydrate+citric acid	169.7(s)	196.1(sh)

s – strong, sh – shoulder

In order to prove about the adsorption of carboxylic acids on the surface of calcium sulphate dihydrate, DSC studies were made and the curves were recorded (Fig. 3). The endothermic peak temperatures are given in Table 3. When calcium sulphate dihydrate is heated, following decomposition reactions occur:

$$CaSO_4\cdot2H_2O \Rightarrow CaSO_4\cdot0.5H_2O+1.5H_2O \qquad \text{I}$$

$$\mathrm{CaSO_4\cdot 0.5H_2O \Rightarrow CaSO_4+0.5H_2O} \qquad \text{II}$$

The decomposition reactions are indicated by two sharp endothermic peaks. The bigger peak at lower temperature corresponds to reaction I whereas the smaller peak at higher temperature corresponds to the reaction II. In the presence of carboxylic acids, the two peaks are shifted to higher temperatures. The sharpness of the first peak corresponding to decomposition reaction I remains unchanged whereas the second peak, corresponding to the decomposition reaction II is broadened and it appears like a shoulder. Shifting of peaks to higher temperatures and broadening of the second peak clearly indicate that the carboxylic acids are chemisorbed at a particular surface of calcium sulphate dihydrate and hinders the decomposition process.

In order to confirm further the adsorption of carboxylic acids at the surface of calcium sulphate dihydrate crystals, infrared spectra were recorded and the vibrational modes of $\mathrm{SO_4^{2-}}$ group examined. The free sulphate ion belongs to the high symmetry point group T_d. A major and broad band appearing at 1134.3 $\mathrm{cm^{-1}}$ is due to S–O stretching vibrations of $\mathrm{SO_4^{2-}}$ group. Weak bands appearing at 609.7 and 673.7 $\mathrm{cm^{-1}}$ are due to bending vibrations of $\mathrm{SO_4^{2-}}$ group. In the presence of carboxylic acids the weak bands due to bending vibrations are shifted to lower frequency with a decrease in intensity and the intensity of the major band (stretching vibration) at 1134.3 $\mathrm{cm^{-1}}$ is decreased and broadened. These changes are due to some weak interaction between $\mathrm{SO_4^{2-}}$ group and carboxylic acids. This might be due to the process of adsorption of carboxylic acid at calcium sulphate dihydrate crystal face with high amount of $\mathrm{SO_4^{2-}}$ groups. Compared to the reference sample the broadening of the peak in the presence of acids increases in the following sequence:

no acid<tartaric acid<malic acid
<succinic acid <citric acid

The results indicate that the adsorption (chemisorption) of citric acid on the surface of calcium sulphate dihydrate is maximum. These results support the hypothesis that the acids adsorb at the surface of forming nuclei of calcium sulphate dihydrate during the hydration of α-hemihydrate.

The delay in nucleation and crystal growth in the presence of carboxylic acids may modify the morphology of dihydrate crystals. In order to have an idea about morphological changes SEM images of the

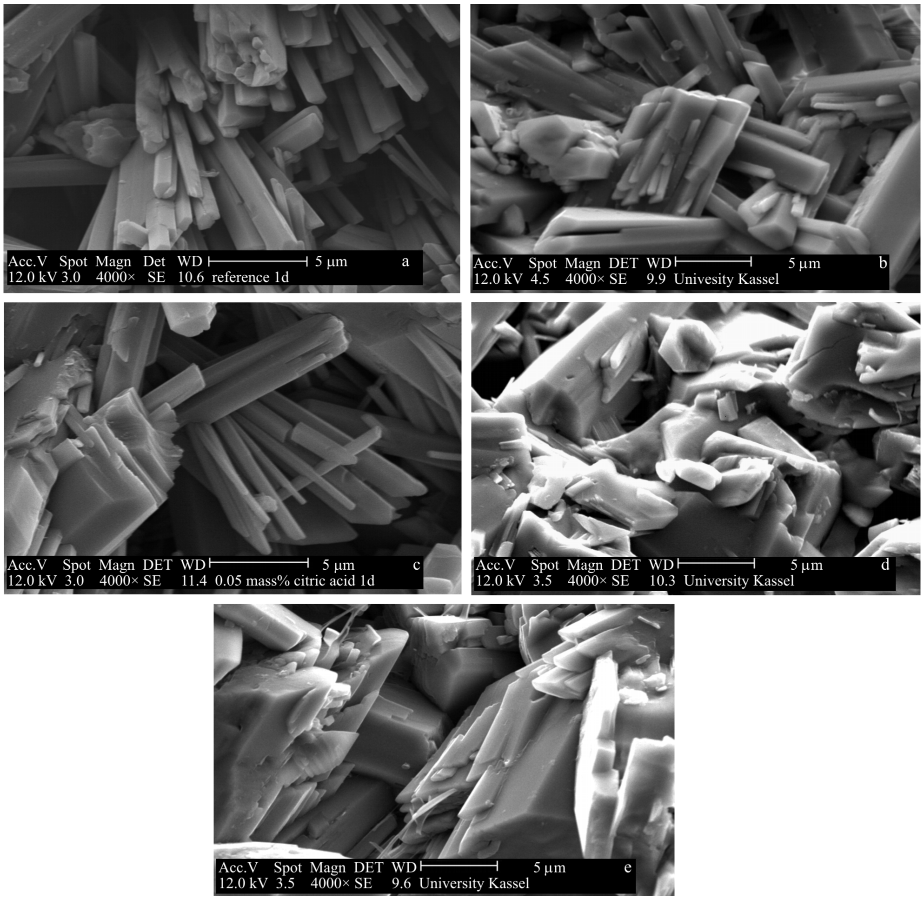

Fig. 4 SEM images of α-hemihydrate hydrated for one day: a – reference, b – 0.2 mass% tartaric acid, c – 0.05 mass% citric acid, d – 0.2 mass% malic acid and e – 0.2 mass% succinic acid

pastes hydrated for one day in the absence and presence of carboxylic acids were recorded (Fig. 4). In the case of the paste without chemical additive (reference sample) prismatic, needle shaped crystals with high degree of interlocking were obtained. Crystal morphology remained unchanged in the presence of 0.2 mass% tartaric acid. It is already known [10] that tartaric acid is an effective retarder only in the presence of $Ca(OH)_2$. In the presence of 0.05 mass% citric acid prismatic shaped crystals grew with a lower degree of interlocking as compared to the reference sample. 0.2 mass% malic acid changed the crystal morphology and microstructure. Xenomorph short prismatic crystals dominate the microstructure. However, in the presence of 0.2 mass% succinic acid, the crystal morphology is changed and short prismatic shaped crystals are obtained. There is very little interlocking of the crystals in the microstructure.

Conclusions

Results have shown that the hydration of α-hemihydrate is a nucleation controlled process leading to the formation of calcium sulphate dihydrate crystals. Carboxylic acids retard the hydration by adsorption (chemisorption) at the surface of growing nuclei. Different acids modify the nucleation process by changing the solution saturation and/or surface energy per unit area in different ways. As a result, the extent of adsorption of the acids (carboxylate ions and undissociated acids) on the surface of growing nuclei is different. This leads to different induction period for the crystallization process. But once the crystallisation started the process became almost similar in all the studied cases. This indicated that acids mainly play a role during induction period where the nuclei of critical size are formed. In the presence of different carboxylic acids calcium sulphate dihydrate crystals with different morphology are formed. In fact the forming nuclei control the morphology of the calcium sulphate dihydrate crystals.

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