Effect of carboxylic acids on the morphology, physical characteristics and hydration of $\alpha$-hemihydrate plaster

N B Singh", C Vellmer" & B Middendorf"*

"Department of Chemistry, DDU Gorakhpur University, Gorakhpur 273 009, India
"Department of Structural Material, University Kassel, Mönchebergstraße-7, D-34109 Kassel, Germany

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Hydration of $\alpha$-hemihydrate in the presence of different concentrations of tartaric, succinic, malic and citric acids was studied. All the acids, except tartaric acid, retard the hydrations. $p$H measurements have shown that during hydration acids are adsorbed at solid surfaces, leading to the retardation of hydration. E-modulus of elasticity, tensile strengths, total porosity, compressive strength, morphological and temperature changes during hydration were studied. It is found that morphological changes control the strength properties.

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Calcium sulphate hemihydrate commonly known as gypsum plaster sets and hardens on addition of water (paste) as a result of gypsum crystallization. The setting involves physical as well as physicochemical processes. The hardened mass is not a compact solid, but a highly porous material with a relatively large internal surface, consisting of interlocking crystals in the form of plates and needles. The microstructure of hardened gypsum pastes affect most of the physical and engineering properties particularly its rigidity. In the presence of admixtures both physical and physicochemical processes change. As a result of this, process of gypsum crystallization, crystal habits and strength developments are changed. In an earlier paper¹, we studied the effect of carboxylic acids on the hydration of $\alpha$-hemihydrate and proposed that gypsum crystallization is a nucleation controlled process. The acids mainly play a role during induction period where nuclei of critical size are formed and these nuclei control the morphology of gypsum crystals.

In this paper, attempts have been made to understand the morphological, strength, porosity and temperature changes in the presence of L(+) tartaric acid, succinic acid, DL malic acid and citric acid.

Experimental Procedure

Materials

For the hydration studies $\alpha$-hemihydrate provided by BPB formula, Walkenried, Germany was used. The $\alpha$-hemihydrate is produced in dry autoclave process using natural gypsum of Permian age. The specific surface area of the hemihydrate is 4390 cm$^2$/g (laser granulometer). The chemical composition and the particle size distribution of the hemihydrate are given in Table 1 and Fig. 1 respectively. This particular batch of hemihydrated is contaminated with small amounts of impurities such as anhydrite, dolomite and calcite as identified by X-ray diffraction.

DL Malic acid (MA), succinic acid (SA), L(+) tartaric acid (TA) and citric acid (CA) were used as the retarding admixtures. The given concentrations of the carboxylic acids were always with reference to the amount of $\alpha$-hemihydrate.

Temperature rise measurements

The details of the method is described elsewhere¹. 300 g $\alpha$-hemihydrate was mixed with 90 g water (w/b=0.3) in the absence and presence of carboxylic acids (0.05, 0.10, 0.15, 0.20 and 0.25 wt% with reference to hemihydrate) and 300 g of this paste was taken in a plastic cup and placed in a hollow cylindrical container (6 cm diameter and 8 cm deep) made of Polystyrol/thermo coal in order to avoid radiation losses. The temperature rise was recorded with a thermistor using data logger at room temperature (23°C).

$p$H measurements

$p$H of carboxylic acids in water (0.025 and 0.01 wt%) and suspension of $\alpha$-hemihydrate (10 g
hemihydrate in 100 cc solution) in the same solution of carboxylic acids were measured with Knick microprocessor pH meter.

**Strength measurements**

900 g of α-hemihydrate was mixed with 270 g of water (water/binder = 0.3) in the presence and absence of carboxylic acids. The concentrations of acids were 0.25, 0.2, 0.15 wt% with reference to hemihydrate. The mixtures were stirred for one minute, placed in two steel moulds (4×4×16 cm³) and vibrated on a vibration table for 2 min. The prisms were taken out after one day and kept under RH of 65% till 28 days, i.e., the time of measurements. The E-modulus was determined and each value is an average of twelve measurements. The tensile and compressive strength measurements were measured with an INSTRON model 6025 testing machine. Each value of tensile strength is an average of two measurements whereas each compressive strength value is an average of four measurements.

**SEM studies**

The broken pieces obtained after compressive strength measurements (at 28 days) were stored and SEM images were taken with the help of Philips XL 30i scanning electron microscope by making carbon and gold coating on each sample.

**Porosity measurements**

Porosity measurements of the samples hydrated for 28 days were investigated with mercury intrusion porosimeter (MIP) AUTOPORE II 9220 obtained from MICROMERITICS. The MIP technique is based on the intrusion of mercury into a porous structure under controlled pressures. Since mercury does not wet the plaster and will not spontaneously penetrate pores by capillary action, it must be forced into the pores by the application of external pressure. From the pressure versus intrusion data of mercury, using the Washburn equation² pore volume and size distributions can be generated. A characteristic piece of the hydrated sample was converted into small pieces (grain size 2-4 mm) by using a pincer. For measuring the porosity 2-4 g of the grains were dried at 40°C and filled into a MIP penetrometer. The porosity was measured by applying pressure (1 atm to 400 Mpa).

**Results and Discussion**

The variation of change in temperature with hydration time during the hydration of α-hemihydrate in the absence and presence of different carboxylic acids are shown in Figs 2-6. The nature of the curves in all the figures is similar with following differences:

(i) length of the induction period varies with the acid and its concentration, (ii) the time for maximum rise in temperature also varies with the acid and its concentration. When α-hemihydrate was added to water, calcium and sulphate ions go into the solution making the solution saturated or supersaturated with respect to dihydrate. After this the gypsum nuclei of critical size are formed (induction period) and the crystallization starts with hardening of the hemihydrate. However in the presence of carboxylic acids, gypsum crystallization and hardening processes are delayed. In the earlier paper¹, we showed that the carboxylic acids are chemisorbed at the surface of growing gypsum nuclei during the induction period delaying the crystallization and hardening processes. This suggests that in the presence of carboxylic acids the normal growth kinetics is changed. The degree of change will depend on the extent of chemisorption and its rate. These two will however depend on the method of preparation of the hemihydrate, its surface area and surface topography, affinity of carboxylic acid molecules towards the surface of gypsum crystals and molecular configuration and concentration of acids. Considering other factors constant, it is expected that the retardation of hemihydrate hydration

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**Table 1—Chemical composition of α-hemihydrate**

<table>
<thead>
<tr>
<th>Components</th>
<th>CaO</th>
<th>SO₃</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>Water of crystallisation</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition wt%</td>
<td>38.6</td>
<td>54.4</td>
<td>0.54</td>
<td>0.07</td>
<td>0.05</td>
<td>0.13</td>
<td>5-6</td>
<td>5-6</td>
</tr>
</tbody>
</table>

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Fig. 1—Particle size distribution of α-hemihydrate

```plaintext
0.01 1 10 100 1000 10000

0 2 4 6

particle size, μm volume, % cumulative volume
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will depend on acid concentrations (upto certain limit). Higher the concentration of the acid, higher the retardation, resulting into prolonged induction period. However, this is not found to be true in the case of citric and tartaric acids, i.e., there is no sequence. α-

Hemihydrate is contaminated with some impurity of anhydrite, dolomite and calcite. Depending on the acidic character and above certain concentration the acids may react with the impurities. All the acids are weak carboxylic acids and their acid character depends on 1st pKa values. Lower the pKa value, higher the acidic character. The acidic character is in the following sequence.

Tartaric acid (pKa=3.02) > citric acid (pKa=3.14) > malic acid (pKa=3.40) > succinic acid (pKa=4.21).

Thus, there is a possibility that part of the acids above 0.15 wt% might have reacted with the impurities. Temperature measurement experiment was also made in the presence of 1.0 wt% tartaric acid and it was observed that after 24 h of hydration the length of the hardened paste increased by 1 cm and there were lot of air bubbles (probably CO₂) inside the hardened paste. This indicates that tartaric acid of this concentration reacts with carbonate impurities evolving CO₂ gas. When the acid concentration is below certain optimum limit, its reaction with the carbonate impurities is negligible. Since malic and succinic acids are weak acids as compared to citric and tartaric acids, their reactivities with the impurities might be lower and probably negligible with concentrations of the order of 0.25 wt%.

In order to have an idea about the adsorption of the acids, pH measurements were made (0.025 and 0.010 wt% acids with reference to α-hemihydrate, w/b=10)). As soon as hemihydrate came in contact to the acid solutions, pH increased considerably indicating that there is a rapid adsorption of the acids at the surface of hemihydrate. This might decrease the supersaturation of the solution causing delay in the nucleation process. In due course the acids might be desorbed and the nucleation starts. The desorbed and the remaining acids in the solution then adsorb on the
surface of growing calcium sulphate dihydrate nuclei resulting into delay of gypsum crystallization. The effect of 0.05 wt% carboxylic acids on the temperature rise during hydration of hemihydrate is shown separately for comparison (Fig. 6). The induction period in the presence of equal concentrations of the carboxylic acids (0.05 wt%) is in the following sequence:

Citric acid > malic acid > succinic acid > tartaric acid > reference

Higher the induction period, higher the retardation of hydration. However, the concentrations above 0.15 wt% do not follow the above sequence. Results show that all the acids get adsorbed at the surface of growing nuclei but even then tartaric acid has very little effect on the retardation. This indicates that it is not only the adsorption but also the permeability of the adsorbed layer which contributes towards retardation. Bosbach and Hochella have reported that high concentrations of tartaric acid lead to the formation of an amorphous coating on the (010) surface of calcium sulphate dihydrate crystals. This coating might be quite permeable.

E-modulus of elasticity, tensile strength, compressive strength and total porosity values of α-hemihydrate hydrated for 28 days in the presence of carboxylic acids are given in Figs 7-10. There is no regular change in the values with the acids and their

![Fig. 7—Effect of different concentrations of carboxylic acids on E-modulus](image)

![Fig. 8—Effect of different concentrations of carboxylic acids on tensile strength](image)
concentrations. One of the reasons could be that acids react with the impurities present in α-hemihydrate to different extent. However the variations in the above mentioned properties at 0.15 wt% carboxylic acids are in the following sequence.

\[
\text{E-Mod.Elast}_{\text{MA}} > \text{E-Mod.Elast}_{\text{CA}} > \text{E-Mod.Elast}_{\text{Ref}} > \text{E-Mod.Elast}_{\text{TA}} > \text{E-Mod.Elast}_{\text{SA}}
\]

\[
\text{Tens.Str}_{\text{Ref}} > \text{Tens.Str}_{\text{CA}} > \text{Tens.Str}_{\text{MA}} > \text{Tens.Str}_{\text{TA}} > \text{Tens.Str}_{\text{SA}}
\]

\[
\text{Comp.Str}_{\text{TA}} > \text{Comp.Str}_{\text{Ref}} > \text{Comp.Str}_{\text{MA}} > \text{Comp.Str}_{\text{CA}} > \text{Comp.Str}_{\text{SA}}
\]

\[
\text{Total Poros.}_{\text{TA}} > \text{Total Poros.}_{\text{Ref}} > \text{Total Poros.}_{\text{MA}} > \text{Total Poros.}_{\text{SA}} > \text{Total Poros.}_{\text{CA}}
\]

The compressive strength variation may be related with the morphological changes. The scanning electron microscopic images of α-hemihydrate hydrated for 28 days in the absence and presence of different concentration of carboxylic acids are shown in Fig. 11. In the case of reference needle shaped crystals with high degree of interlocking are observed. The presence of carboxylic acids except tartaric acid modify the morphology of calcium sulphate dihydrate crystals. In the presence of 0.15 wt% malic acid, bigger crystals without any definite shape having macro defects at the surfaces are obtained whereas in the presence of 0.20 wt% malic acid, sheets of broken crystals are seen. In the presence of 0.25 wt% malic acid the crystal size (prismatic) is decreased and the
(a) reference

(b) 0.15 wt% TA

(c) 0.20 wt% TA

(d) 0.25 wt% TA

(e) 1.05 wt% MA

(f) 0.20 wt% MA

(g) 0.25 wt% MA

(h) 0.10 wt% CA
number of small crystals are increased apparently with no interlocking. In the presence of 0.1 wt% citric acid needle shape crystals with low interlocking are obtained whereas in the presence of 0.15 wt% citric acid the number of needle shape crystals decreased and some prismatic crystals with bigger size are obtained. However in the presence of 0.20 and 0.25 wt% citric acid prismatic crystals with micro and macro defects at the surfaces are obtained giving an impression that with these type of crystals the strength developments will be lower. In the presence of succinic acid bigger prismatic crystals with macro defects lying over each other are seen. The morphologies indicate that lower strengths will be developed in the presence of succinic acid.

Morphological studies have shown that the strength developments in the hydrating hemihydrate paste is related to interlocking structure, size, shape and macro defects of gypsum crystals. Finot et al.\textsuperscript{4} with the help of atomic force microscopic studies proposed...
that the mechanical properties, besides interlocking structures, are also due to forces of adhesion between gypsum crystals during the setting and these forces are higher in magnitude than vander Waals forces. Mathieu and Boistelle\textsuperscript{5} also proposed that the mechanical strength of the set plaster is due to interlocking structure and inter crystalline interactions. As the crystal morphology changes, the faces of the crystals involved in the interaction also change. In the present investigation, different carboxylic acids modify the morphology of gypsum crystals to different extent. Different carboxylic acids have different molecular structure, functional groups, acidic character and affinity for adsorption on growing gypsum crystals and hence they will affect the force of adhesion between different faces of gypsum crystals to different extent. Thus, it is the combined effect of the interlocking structure and the force of adhesion between gypsum crystal faces, which control the mechanical properties.

Conclusions

During hydration of $\alpha$-hemihydrate, different acids are adsorbed at solid surface to different extent leading to the retardation of hydration. Extent of adsorption however depends on the molecular configuration of the acids. The acids modify the crystal morphology of dihydrate crystals, crystallizing out during hydration resulting into change of force of adhesion between gypsum crystal faces. E-modulus of elasticity, tensile strength, total porosity and compressive strength values are different in the presence of different acids. In order to have correlation between the acids and the properties studied, study of surface topography of gypsum and $\alpha$-hemihydrate crystals and the molecular configuration of the acids used are essential.

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References