

The setting of gypsum plaster

Part III *The effect of additives and impurities*

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The effect of calcium sulphate presented as soluble anhydrite (γ -CaSO₄) on the setting of gypsum plasters was investigated by measurement of the set strength and a microstructural examination of the set plasters. The anhydrite reduced the set strength by disrupting the interlocking crystal matrix of dihydrate needles. Additives, such as the nucleating agent calcium sulphate dihydrate and the accelerator potassium sulphate, increased the rate of the hydration reaction by increasing seeding and the rate of dissolution of calcium sulphate hemihydrate. The additives also alter the crystal habit of the dihydrate needles in the set plaster, resulting in reduced intercrystalline bonding and as a consequence reduced strength. The use of a novel *in situ* nucleation/acceleration system using KHSO₄ and Ca(OH)₂, to generate microcrystalline dihydrate nuclei in the presence of K₂SO₄, resulted in a rapidly setting plaster with high strength.

1. Introduction

The main constituent of commercial gypsum plasters is calcium sulphate hemihydrate, CaSO₄ · 1/2H₂O, produced by the dehydration of calcium sulphate dihydrate, CaSO₄ · 2H₂O, in the form of the mineral gypsum. Soluble anhydrite, γ -CaSO₄, is present as an impurity, in amounts ranging from 2 to 13 wt % (see Part I [1]) due to over-dehydration during the production process.

Manufacturers often use additives such as nucleating agents, accelerators and retarders to control the setting of gypsum plasters, according to the required use. Splinting applications require a rapid build-up of strength and a high final set strength from the plaster. Thus plasters used for medical applications contain a mixture of the α and β forms of hemihydrate, to which a few weight per cent of dihydrate (as a nucleating agent) and potassium sulphate (as an accelerator) are added.

Accelerators are believed to promote the hydration of hemihydrate to dihydrate by two mechanisms [2]:

- (i) increased nucleation by a seeding action, and
- (ii) modifying the rate at which calcium and sulphate ions are transported to, and built into, the lattice of the growing phase by increasing the dissolution rate of hemihydrate.

Ridge and Hill [3] have shown that dihydrate accelerates the hydration by mechanism (i), but when it is very finely ground it also has an effect similar to mechanism (ii). Neutral salts have been shown by Ridge [4] to accelerate the hydration by mechanism (ii) on the basis of observed kinetic effects. Mikhail and Malek [5] measured the compressive strengths of set

plasters and found that a few per cent of the neutral salt sodium chloride reduced the strength to approximately a quarter of that of the unmodified plaster.

This study has examined the effect of soluble anhydrite on the microstructure and mechanical properties of the set plasters, and attempts to relate this to the reactivity of the anhydrite with water. The effect of the additives dihydrate and potassium sulphate on the hydration reaction and the microstructure and set strength of α -hemihydrate have been investigated; the use of a novel *in situ* nucleation/acceleration system has been studied with the aim of improving commercial formulations.

2. Experimental Procedure

2.1. Materials

2.1.1. Hemihydrate (CaSO₄ · 1/2H₂O)

The α and β -hemihydrates were commercial products from British Gypsum and a full characterization was carried out as outlined in Part I [1].

2.1.2. Soluble anhydrite (γ -CaSO₄)

" β " soluble anhydrite was prepared by dehydrating a flat bed of British Gypsum β -hemihydrate in an oven at 140 °C for 4 days. When " α " soluble anhydrite was prepared by the same method it was found by powder X-ray diffraction (XRD) that a substantial amount of insoluble anhydrite (β -CaSO₄) was present. Reduction of the dehydration temperature to 120 °C resulted in the production of a negligible amount of insoluble anhydrite.

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Both reagents were characterized by XRD, differential thermal analysis (DTA)–thermal gravimetric analysis (TGA), particle size analysis and scanning electron microscopy (SEM) [1]. This indicated that the soluble anhydrite reagents were approximately 90 wt % pure, with hemihydrate and insoluble anhydrite present as the impurities. The dehydration process gave soluble anhydrite with a particle size and morphology the same as the hemihydrate starting materials.

2.1.3. Dihydrate

Calcium sulphate dihydrate was obtained from two sources: (i) BDH Analar grade reagent (99%) and (ii) British Gypsum Ltd, a natural product which had been washed, ground and then passed through a 200 mesh (75 μm) sieve [6]. Both materials were then ground in either a Tema mill (dry or ethanol slurry) or a ball mill (ethanol slurry).

XRD of both reagents indicated that dihydrate was the only detectable phase present. Thermal analysis (DTA–TGA) confirmed the XRD findings and calculations [1] showed that both reagents contain over 98% dihydrate. Energy-dispersive X-ray analysis of the reagents, for elements above Na, showed that only Ca and S could be detected.

Particle size distributions were obtained using Malvern analysis [1] and the results are quoted as the statistical mean (\bar{x}). These results, along with the specific surface area determinations measured on a standard nitrogen adsorption rig and analysed using BET theory, are given in Table I.

The SEM studies showed that lightly ground BDH material consisted of well-formed crystals. The result of dry grinding in the Tema mill was to alter the particle shape to near spherical and introduced surface roughness. Ball-milling, which acts by shearing,

resulted in smaller but still well-formed crystals. The as-received British Gypsum materials consisted of well-formed crystals with a relatively rough surface.

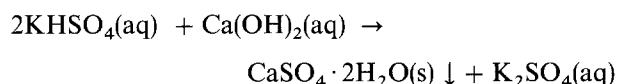
2.1.4. Potassium sulphate

The potassium sulphate used was a BDH Analar (99.5%) grade reagent and XRD showed this was the only phase which could be detected.

2.2. Measurements

2.2.1. An *in situ* nucleation/acceleration system

It was proposed that the following reaction:



could be used to generate *in situ* microcrystalline nuclei of the dihydrate in the presence of K_2SO_4 , which acts as an accelerating agent.

Potassium hydrogen sulphate (1.58 g, AG) and calcium hydroxide (0.43 g, AG) were mixed together and then added to water (30 g) with stirring. If the stoichiometry of the above reaction was correct this would result in the formation of 1 g of dihydrate and 1.0 g of potassium sulphate. After 1.5 min the above suspension was filtered and any dissolved solids were precipitated with ethanol. Examination by XRD of the solids showed the phases present to be $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (approximately 70%) and $\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (approximately 30%). The solids which precipitated from solution were found to be K_2SO_4 .

2.2.2. Strength and microstructure

The bending strengths of the modified and unmodified plasters were measured using a standard three-point

TABLE I Effect of surface area of dihydrate additions on nucleation of the hydration reaction and the full set strength of α -hemihydrate (w/s = 0.6)

Dihydrate addition	wt %	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Relative surface area (m^2) ^a	Max. dT/dt ($^\circ\text{C min}^{-1}$)	Time to T_{max} (min)	Modulus of rupture (MN m^{-2})
BDH						
10.7 μm	10	1.6	1.6	1.13	34.3	–
	5	1.6	8.0	0.97	44.4	–
	2	1.6	3.2	0.97	48.5	11.5 \pm 0.6
7.2 μm	2	3.5	7	1.42	35.5	11.2 \pm 0.5
	1	3.5	3.5	1.09	39.0	–
	1/2	3.5	1.75	0.83	44.6	–
6.7 μm	2	7.4	14.8	1.43	34.9	10.9 \pm 0.3
	1	7.4	7.4	1.24	38.7	–
6.3 μm	5	5.9	29.5	1.67	31.7	–
	2	5.9	11.8	1.53	32.8	10.7 \pm 0.5
	1	5.9	5.9	1.39	35.5	–
	0.5	5.9	2.95	1.11	40.8	–
British Gypsum						
54 μm	2	0.9	1.8	1.28	40.4	12.2 \pm 0.2
4.7 μm	2	15.1	9.4	2.36	25.1	11.0 \pm 0.4
No addition		0	0	0.75	52.5	12.5 \pm 0.4

^a Relative surface area = specific surface area \times weight of dihydrate added (units: m^2).

bend test (see part II [7]). The microstructure of the plaster was investigated by examining the fracture surface of specimens from the three-point bend test with an SEM [7].

2.2.3. Hydration reaction

The hydration reaction was followed by obtaining a continuous temperature–time curve from a plaster slurry placed in a simple adiabatic calorimeter [1].

2.2.4. The reactivity of soluble anhydrite

To simulate the reactivity of soluble anhydrite in a plaster slurry, the reactivity in a saturated dihydrate solution was investigated. Soluble anhydrite (3 g) was mixed with a saturated solution of dihydrate (3 cm³) and then placed in a paper Soxhlet thimble. This was then placed in a sealed container to prevent evaporation and left to react for 1, 10 and 100 h at 30 °C and 63% RH. The reaction was then stopped by washing with excess ethanol which was pulled through with a water pump. After drying, the reaction products were finely ground for XRD and thermal analysis.

2.2.5. Reaction conditions

The effect of potassium sulphate additions on the hydration reaction and products was investigated with the water/plaster (w/p) ratio constant at 0.6 to ensure constant reaction conditions. When considering the effect of soluble anhydrite and dihydrate additions, the “water requirement” of the solids is important [8]. The water requirement is dependent on the nature of the grains, and soluble anhydrite and dihydrate have a similar particle morphology and size to the hemihydrate. Therefore to ensure constant hydration conditions, the water/solid (w/s) ratio was kept constant at 0.6.

2.2.6. Nucleation/acceleration systems

It was decided to compare four systems: two using the *in situ* generated reagents and two using the commercial reagents K₂SO₄ (AG) and British Gypsum (54 μm) dihydrate. The systems were as follows.

(i) *In situ* systems:

(a) System 1: Ca(OH)₂ (0.86 g) and KHSO₄ (3.16 g) were added to α-hemihydrate (100 g) and mixed in a ball-mill for 24 h. In all further hydration/setting experiments the w/p ratio was kept constant at 0.6. If the nucleation/acceleration reaction was stoichiometric, 2 g of CaSO₄ · 2H₂O and 2.02 g of K₂SO₄ would be produced.

(b) System 2: as system 1, except that Ca(OH)₂ (0.43 g) and KHSO₄ (1.58 g) were used to produce 1 g of CaSO₄ · 2H₂O and 1.01 g of K₂SO₄ *in situ*.

(ii) Reference systems:

(a) System 3: as system 1, except that the Ca(OH)₂ and KHSO₄ were replaced by K₂SO₄ (2 g) and 2 g of British Gypsum (54 μm) dihydrate.

(b) System 4: as system 3, except that the weight added of the reagents was changed to 1 g of each.

3. Results and discussion

3.1. The effects of soluble anhydrite

The investigation of the reactivity of soluble anhydrite in a saturated solution of dihydrate has shown that soluble anhydrite hydrates to the dihydrate by a two-stage reaction. Firstly, soluble anhydrite reacts with water to form hemihydrate which is probably by the absorption of water by the anhydrite particles. This reaction takes longer (> 1 h) than the normal hydration reaction of plaster. Secondly, the hemihydrate formed reacts further to form dihydrate by a “through solution” mechanism to precipitate needle-like crystals.

The effect of soluble anhydrite on the properties of set α and β plasters was to decrease the strength (Fig. 1). A 10% anhydrite content results in a strength reduction of between 15 and 20% in the set plasters. Examination of the microstructure by SEM showed no visible changes with anhydrite addition.

The mechanism of strength reduction by anhydrite addition can be postulated from an observation of the anhydrite’s reactivity. When the plaster mix is reacting with water, the hemihydrate will hydrate to form dihydrate, whilst the anhydrite is hydrating to hemihydrate. Thus an interlocking crystal matrix of dihydrate will be formed containing hemihydrate particles. The next stage would be for these hemihydrate particles to hydrate further to dihydrate. This would result in disruption of the original crystal matrix reducing the overall set strength. Since both reactants will eventually form dihydrate, little change will be observed in the microstructure.

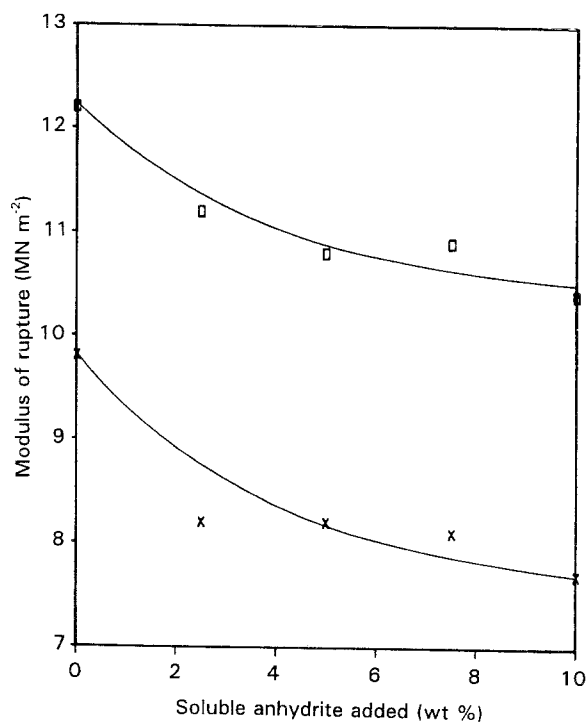


Figure 1 Effect of soluble anhydrite on the full set strength (□) α- and (×) β-hemihydrate.

3.2. The effect of dihydrate

The effect of dihydrate additions, of various weight percentages and particle size, on the hydration reaction of α -hemihydrate is shown in Table I. Dihydrate additions were found to accelerate the hydration reaction; decreasing the particle size or increasing the amount of dihydrate resulted in a greater degree of acceleration. This indicated that the reaction is accelerated by dihydrate, which provides sites for crystal growth. The relationship between the maximum rate of reaction (or precipitation from solution [1]) and the relative surface area is shown in Fig. 2. Increasing the relative surface area led to increased hydration rates, as would be expected if the dihydrate acted as a nucleating agent. With one exception all the data points lie between upper and lower limits. This implies that surface area is not the only factor, with surface roughness also playing a part. Surface roughness may be induced by grinding and would provide a larger number of nucleation sites. This appears to be confirmed by the fact that the most highly ground BDH reagent (6.3 μm) is on the upper limit while the least ground reagent (BDH, 10.7 μm) is on the lower limit.

The effect of dihydrate additions on the microstructure (Figs 3 and 4) was to change from a pattern of interlocking needles (15 $\mu\text{m} \times 1 \mu\text{m} \times 1 \mu\text{m}$) for the set α plaster to thinner, shorter needles (10 μm

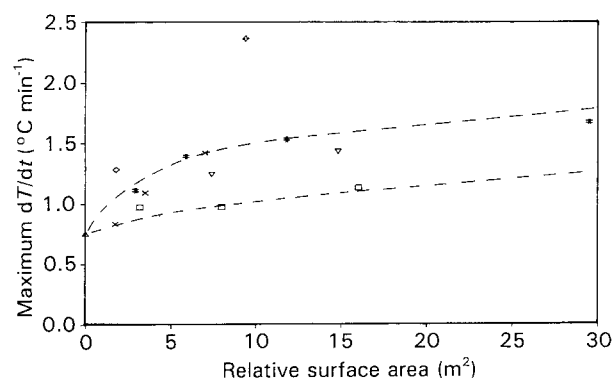


Figure 2 Effect of the relative surface area of dihydrate additions on the maximum rate of hydration: (Δ) no addition, ($\#$) BDH 6.3 μm , (∇) BDH 6.7 μm , (\times) BDH 7.2 μm , (\square) BDH 10.7 μm , (\diamond) British Gypsum 54 μm , (\oplus) British Gypsum 4.7 μm .



Figure 3 Scanning electron micrograph of the set plaster from α -hemihydrate ($w/s = 0.6$).



Figure 4 Scanning electron micrograph of the set plaster from α -hemihydrate plus 2 wt % BDH (6.7 μm) dihydrate ($w/s = 0.6$).

$\times 0.5 \mu\text{m} \times 0.5 \mu\text{m}$) with a 2 wt % addition. The reduction of needle size is to be expected if the number of nuclei was increased. The aspect ratio of the needles was also increased and this was probably due to the increased precipitation rate, and was discussed in an earlier paper [7]; this change in morphology gave a reduction in intercrystalline bonding. The overall effect would be that the greater the degree of acceleration due to nucleation, the larger the reduction in set strength (see Table I).

3.3. The effect of K_2SO_4

Neutral salts such as K_2SO_4 are believed to increase the rate of reaction by increasing the rate of hemihydrate dissolution [9]. A mechanism to account for this has been proposed by Chatterji and Kapse [10] on the basis of rheological studies. These indicated that hemihydrate grains were covered with an adsorbed layer of water molecules. Neutral salts stabilize this layer and orientate neighbouring water molecules, resulting in a multilayer water structure. As this probably constitutes the first steps in hemihydrate dissolution, an increase in the area and depth of coverage of the adsorbed water layer would result in an increased dissolution rate. Ridge *et al.* [11] made a systematic study of the accelerating effect of various anions and cations which indicated that K^+ and SO_4^{2-} constituted the best accelerating anion-cation pair.

In this study potassium sulphate additions have been shown to accelerate the rate of hydration (Table II) with the reaction rate increasing with the amount of added K_2SO_4 up to 2 wt %. Additions greater than this showed very little change in the degree of acceleration. The limit of the accelerating effect can be explained in terms of Chatterji and Kapse's mechanism. A 2 wt % K_2SO_4 addition results in a stabilized multilayer water structure and greater additions would result in more water layers. These extra layers will be a relatively large distance from the hemihydrate grain surface, and therefore would not contribute as much to the dissolution rate as those more closely bound. The result of this could explain the limiting effect on the degree of acceleration.

TABLE II Effect of potassium sulphate additions on the hydration reaction and full set strength of α -hemihydrate ($w/p = 0.6$)

K ₂ SO ₄ added (wt %)	Time to T _{max} (min)	Max dT/dt (°C min ⁻¹)	Induction period (min)	Modulus of rupture (MN m ⁻²)
0	52.5	0.75	5.4	12.6 ± 0.5
0.5	27.1	2.48	3.4	11.5 ± 0.1
1	19.4	3.40	2.2	11.2 ± 0.3
2	13.9	5.23	< 1	10.5 ± 0.3
5	13.8	5.33	< 1	9.6 ± 0.3

Increasing amounts of K₂SO₄ progressively increased the dihydrate precipitation rate and decreased the set plaster's strength (Table I). Microstructural observations (Figs 3 and 5) showed that the size of dihydrate needles was increased and the aspect ratio lowered, from 15 $\mu\text{m} \times 1 \mu\text{m} \times 1 \mu\text{m}$ with no addition to 25 $\mu\text{m} \times 4 \mu\text{m} \times 3 \mu\text{m}$ with 2 wt % K₂SO₄. From previous work [7] it was seen that a higher precipitation rate results in lower strength, mainly due to reduced intercrystalline bonding from a microstructure consisting of needles of a higher aspect ratio.

K₂SO₄ additions increased the precipitation rate and this would be expected to increase the rate of crystal growth in the [001] direction, producing longer needles. This was observed, but K₂SO₄ also enhanced growth in directions perpendicular to the [001] direction and in this respect acted as a crystal modifier.

The anomaly is that additions of K₂SO₄ above 2 wt % did not increase the precipitation rate but reduced the strength. The K₂SO₄ therefore appears to weaken the structure by an additional mechanism, which could possibly involve it either being built into the dihydrate needles and/or weakening the cementing action of residual dihydrate by being co-precipitated with it.

3.4. The use of an *in situ* acceleration/nucleation system

KHSO₄ and Ca(OH)₂ were used to generate microcrystalline dihydrate nuclei in the presence of K₂SO₄.



Figure 5 Scanning electron micrograph of the set plaster from α -hemihydrate plus 2 wt% K₂SO₄ ($w/s = 0.6$).

Two *in situ* systems were compared to two reference systems using BDH K₂SO₄ and British Gypsum (54 μm) dihydrate (see Section 2.2.6).

The KHSO₄-Ca(OH)₂ systems reduced the reaction time to less than 70% of the reference formulations (Table III), but the strength reduction from the unmodified plaster was limited to 6%, as compared to 17% for the reference formulation. The KHSO₄-Ca(OH)₂ system therefore has the advantage of an increased hydration rate with a smaller reduction in strength.

Microstructural observations of the plaster with the nucleation systems differ very little from the unmodified plaster. This was probably because dihydrate reduced the needle size while K₂SO₄ increased it, each effect cancelling out the other.

4. Conclusions

1. Soluble anhydrite, which is present in all commercial plasters, has been shown to rehydrate in two stages, going first to hemihydrate and then to dihydrate. The presence of soluble anhydrite reduces the strength of set plasters by disrupting the interlocking crystal matrix.

2. Additions of dihydrate nucleate the hydration products of hemihydrate, the effectiveness increasing with surface area and roughness.

3. Increased nucleation rates gave rise to finer and smaller dihydrate needles with reduced intercrystalline bonding and consequently lower mechanical strengths.

4. K₂SO₄ accelerates the hydration reaction by increasing the rate of hemihydrate dissolution. The accelerating effect increased with up to 2 wt % addition; additions over 2 wt % had no further accelerating effect.

5. K₂SO₄ increased the rate of dihydrate crystal growth in both the [001] directions and directions normal to the needle axis. The resulting dihydrate needles were larger, and had a lower aspect ratio and reduced intercrystalline bonding. Consequently the set plaster had a reduced mechanical strength. Additions of K₂SO₄ in excess of 2 wt % produced further reductions in set strength despite having no further effect on the dihydrate's crystal habit.

6. The use of KHSO₄ and Ca(OH)₂ additions provided *in situ* microcrystalline dihydrate nuclei in the presence of K₂SO₄. This gave rise to a rapidly setting

TABLE III Effect of nucleation/acceleration systems on the hydration and full set strength of α -hemihydrate ($w/p = 0.6$)

System ^a	Time to T _{max} (min)	Max dT/dt (°C min ⁻¹)	Induction period (min)	Modulus of rupture (MN m ⁻²)
No addition	52.5	0.75	5.4	12.6 ± 0.5
1	6.42	9.38	< 1	- ^b
2	9.84	6.37	< 1	11.8 ± 0.5
3	11.5	5.71	< 1	10.5 ± 0.3
4	14.4	4.87	< 1	11.1 ± 0.3

^a See Section 2.2.6.

^b Plaster set too rapidly to allow production of strength test specimens.

plaster with a smaller reduction in set strength than present commercial formulations.

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