

HARDENED GYPSUM PASTES  
SURFACE PROPERTIES AND MICROSTRUCTURE

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By

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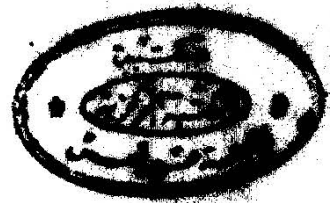
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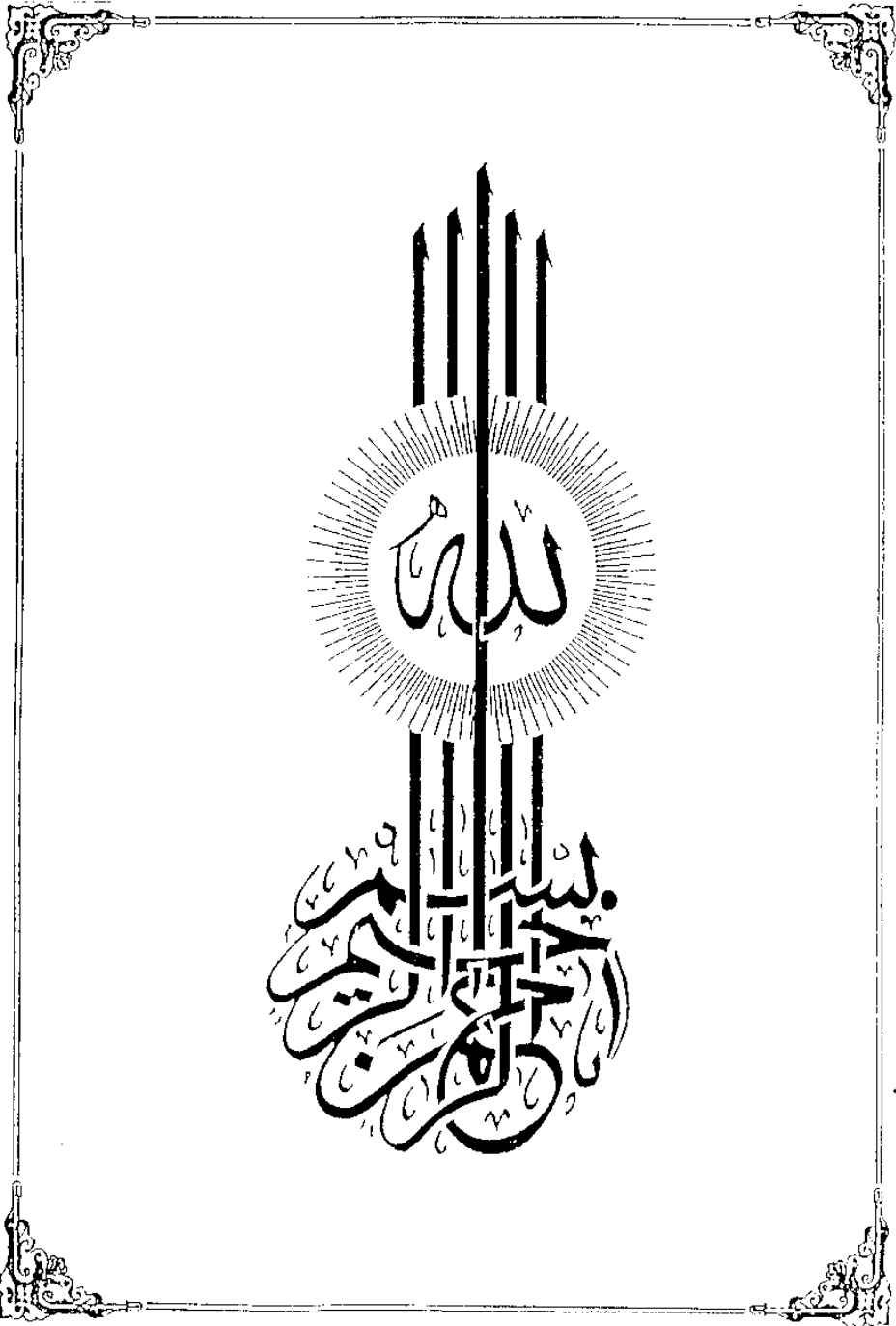
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## INTRODUCTION

The reaction that produces calcium sulphate dihydrate in concentrated aqueous suspensions of calcium sulphate hemihydrate is of fundamental interest to the plaster industry, and has features of interest concerning the reactivity of solids. It has a further interest in connection with the use of gypsum plasters as a binding material, and in future prospects as a building material.

The microstructure of gypsum plaster is one of the most, if not the most important property which affects the main physical characteristics of the hardened paste.

Gypsum plaster has attracted the attention of numerous investigators in the field. A historical review might help in giving a short account of the work done on this substance with a particular emphasis on its microstructure. This review is not meant to give a full account of all work done in the field but will furnish few examples of the various angles attacked by the various investigators.

### A. Historical Review

The hydration of commercial calcium sulphate hemihydrate (Plaster of Paris) has attracted the attention of numerous investigators in the field.

Ridge<sup>(1)</sup> (1960) in an excellent review summarized all the previous work done, including the theories proposed for the setting of gypsum plaster, the kinetics of setting, dimensional changes during setting and drying, mechanical strength of cast plaster, ...etc. In a concluding remark in his review Ridge considered that there are two aspects for following the setting of gypsum: (a) the induction period, or the duration of the initial set, and (b) the exponential increase in the rate of the reaction. He defined the induction period as the time required for the rate of increase of a mixture of 100 g of plaster and a selected volume of water held in a dewar flask to exceed 0.1°C/min.

In his review, Ridge summarized all work done to date to establish an acceptable mechanism for the hydration of calcium sulphate hemihydrate. The "Gel theory" suggested by Rohland<sup>(2)</sup> and Baykoff<sup>(3)</sup> was the first attempt to explain the process of setting. This theory states that water is taken into the hemihydrate "in a colloidal form" and that the initial thickening was due to gelation which may be best regarded as a felt of gypsum crystals rather than a "gel". This gel or adsorption complex formed protects the particles of hemihydrate from the action of water, thus producing the induction period which is presumably ended by crystallization of the gel allowing the

water to form the hemihydrate. But there is no reason why, during the induction period, the remaining hemihydrate should not also form a gel.

Ridge proposed that during setting, the calcium sulphate hemihydrate is dissolved and calcium and sulphate ions diffuse to sites in the system where they are built into the lattice of the dihydrate. These sites exist in the unmixed (dry) plaster as nuclei and potential nuclei; where the term nucleus is used to refer to a particle that is larger than the critical nucleus; and the term potential nucleus is used to denote a particle that is smaller than the critical nucleus, a foreign particle, or a region of damage or strain in a crystal which may act as a favourable site for the formation of a new lattice.

Ridge assumed that growth and dissolution are reciprocal processes, and the following equation is applicable

$$dx = (DS/\delta) (C_2 - C_0) dt$$

where D is the diffusion coefficient, S is the surface area of the crystal,  $\delta$  is the thickness of the layer through which diffusion is taking place,  $C_0$  and  $C_2$  are respectively the concentration of the saturated solutions and that actually prevailing in the case studied. This equation can be only applied to the system  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  - water when the following points are considered - (a)  $\delta$  is the average distance between

is constant, since the hemihydrate retreats as the dihydrate advances; and (b)  $C_2$  and  $C_3$  are functions of the solubilities of the dihydrate and hemihydrate and usually remain constant throughout the reaction, where a concentration gradient is established between the particles of the hemihydrate and dihydrate as the excess calcium sulphate in solution is.

It would be expected from the above theory that the rate of hydration of  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  in pastes of gypsum plaster is determined by the number (per unit volume) of nuclei for the growth of the dihydrate, the area of the effective surface associated with them, and the capacity of the system to supply calcium sulphate to the growing phase, which will be determined by the surface area of the hemihydrate and the distance over which diffusion must occur. The latter factor depends on the density of nuclei present, as the greater the number of nuclei the shorter the average diffusion path is. It might also be expected that substances adsorbed at the interfaces would alter the rate of the reaction by modifying  $C_1$  and  $C_2$ .

Ridge attributed the acceleration of gypsum plaster to be brought about by increasing the effective surface area of the dihydrate, or by increasing the capacity of the system to supply calcium and sulphate ions to the growing lattice. However, increasing the number of nuclei has the effect of increasing that capacity as the length of the path over which diffusion



of the reaction, and the rate of processes at the interface. However, the situation of variables seems to be more complex than that of accelerators. Some retarders appear to reduce the rate of growth of the dihydrate, others are removed from the system during the reaction by being built into the growing phase as impurities.

Ridge and Hill<sup>(4)</sup> studied the variation in the rate of setting of six plasters from different sources and they attributed this variation to different densities of seeding nuclei and the effective surface area associated with them.

Finally, Ridge<sup>(1)</sup> proposed that strength of plaster to be dependent upon:

- (a) the shape and size of the component crystals.
- (b) the strength of the bond between the various crystals.
- (c) the strength of individual crystals
- (d) the amount of empty space in the set mass, which is determined by the water content of the mixture. Russell and Blokey<sup>(5)</sup> have demonstrated the increase in strength as the water/plaster ratio is reduced.

In practice the water content of the mixture used is largely determined by the nature of the plaster, some plasters requiring much more water than others to be workable. If the amount of water required could be reduced, the strength of the cast would be increased appreciably.