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IMPROVEMENT OF THE MECHANICAL PROPERTIES OF SET PLASTERS BY MEANS OF FOUR ORGANIC ADDITIVES INDUCING {101} FACES

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The aim of the present study is to establish whether there is a relationship between the crystals habits, textures and mechanical properties of plasters set in the presence of some phosphonic or carboxylic acids. From the results it turns out that hardness can be improved with or without additives. The observations of the textures clearly show that the improvements are not correlated with a drastic change of the crystal habits but rather to a better and more homogeneous arrangement of the crystals. When used at high concentrations some of the organic molecules give rise to thin platelets of gypsum exhibiting a hexagonal outline and being limited by a large unusual ($\overline{101}$) face. The inhibitor adsorption on this face is particularly strong due to the good match between the molecular conformation and the surface lattice structure. With such crystals, the plasters have very low mechanical strengths.

1. Introduction

When inhibitors are introduced into a solution, they affect the whole crystallization process. They may adsorb either immediately on the embryos and nuclei, impeding their development above the critical size, or, later on some faces of the already formed crystals. The amounts of adsorbed molecules may be very different according to the nature of the crystal faces, the surface morphology of which depends on the crystal structure. If the adsorption energy is large enough, it often involves a habit modification. Moreover, when adsorption occurs, the charge of the surface, the composition of the double electrical layer and consequently the tendency of the crystals to disperse or to agglomerate is modified [1,2]. Some foreign molecules may also achieve bridges between the solid particles [2]. All these points are particularly important in the case of dense crystal suspensions and we have tried to make use of them in order to improve the mechanical strengths of set plasters.

Many inhibitors of gypsum were used under different crystallization conditions [3-12]. Most of them are carboxylic and phosphonic acids. How-

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ever, very few studies deal with the influence of crystal shapes and crystalline textures on the mechanical properties of dispersed structures [13-18]. The empirical exponential law [13,19-21] which links the hardness D and the total porosity p of a set plaster:

$$D = D_0 \exp(-kp), \tag{1}$$

 D_0 and k being constants, describes fairly well the experimental results but does not provide any information on the origin of the mechanical strengths. Soroka [20], for instance, has pointed out the importance of the particle size and shape, the contact area between crystals, the degree of tangling up of the crystals and the bond strengths.

Thus, our aim is to find some organic molecules able to modify the gypsum habit, and/or the conditions which ensure the cohesion of the set plasters. In this study we use four of those molecules. They are good habit modifiers of gypsum and allow a significant hardness improvement when used at low concentrations.

2. Experimental

The primary plaster is calcium sulfate hemidyrate β obtained by dehydratation of pure gypsum at 175°C for 50 min, under atmospheric

pressure. Hemihydrate α , which is obtained by dehydratation under high pressure, is not used as a building material. Therefore it is not considered in the present study. The mean diameter of gypsum crystallites, estimated with a Sedigraph 5000 granulometer is about 15 μ m. This corresponds to a calculated specific area of 0.15 m^2/g . The stoichiometric amount of water required to hydrate one gram of hemihydrate is 0.186 g. Nevertheless, in order to get a fluid and homogeneous paste, all our plasters were prepared at a weight ratio (water/plaster) of 1. This corresponds to 27.5 vol% of solid particles in the paste. After hydration, such a preparation involves a theoretical porosity of 62.8% for a set plaster. Actually this value is rarely achieved due to a slight sedimentation of the crystallites during the setting. The porosity of the samples was measured with a Purcell mercury porosimeter which also provides the distribution of the pore diameters in between 0.01 and 100 μ m. The diameter of the most frequent pores is one of the plaster characteristics.

The plaster samples of $15 \times 15 \times 50 \text{ mm}^3$ were placed in an oven (40°C) from 24 h after their preparation, for one week so as to be completely dry. Later on, they were sawn along their largest dimensions and the hardness was measured on the flat surfaces by means of a Zwick device, graduated from 0 to 100 Shore C units. Here the hardness of plaster is its resistance to the penetration of a needle of 0.75 mm diameter which is applied with a force of 50 N. The relationship between Shore C units and kg/cm^2 is given by fig. 1. Since there is an important dispersion of the experimental value due to the investigated material, we made about one hundred measurements on each sample. The resulting histograms (fig. 2) give mean hardnesses which are subsequently normalized, so that all values correspond to the theoretical porosity of 62.8%.

The flexion and compression strengths were measured by means of a Roëll-Korthaus press RKM 100 on six samples strictly calibrated to $10 \times 10 \times 40$ mm³. The accuracy of this press is about 0.5% but, for a given plaster, the uncertainty on its mechanical characteristics is actually 6%.

The texture of the set plaster was observed on



Fig. 1. Relationship between hardness expressed in terms of Shore C units and kg/cm².

fractures, ina scanning electron microscope JEOL 35 C.

The additives (table 1) were introduced into the solution prior to the hemihydrate. Their influence on the crystallization kinetics of gypsum was first determined by recording, versus time, the conductivity of diluted suspensions of hemihydrate (50 g/l water). Fig. 3 gives some typical curves of hydration in pure aqueous solution and in presence of NTMP. The inflexion point, t_1 , representative of the hydration time, is given in table 2 for some of the systems we have used. The discussion of the kinetic study is beyond the scope of the



Fig. 2. Hardnesses measured on a standard plaster set from pure aqueous solution.

Table 1

Additives used to improve the mechanical properties of plasters and giving rise to $\{\overline{1}01\}$ faces

Name	Formula
Nitrilotri methylene phosphonic acid, NTMP	$N(CH_2PO_3H_2)_3$
1,6 Diamino hexane N,N,N',N' acetic acid, DHTA	$(HOOCCH_2)_2 (HCH_2CH_2 N(CH_2COOH)CH_2CH_2 N(CH_2COOH)_2)$ $(HOOCCH_2)_2 N(CH_2)_6 N(CH_2COOH)_2$
1,3 Diamino 2 hydroxypropane N,N,N',N' tetra- cetic acid, D2HPTA	$HOCH(CH_2N(CH_2COOH)_2)_2$

Table 2

Characteristics of hemihydrate (HH) plasters set under different initial conditions: hardness D, flexion and compression strengths σ_t and σ_c , and most frequent pore diameter; typical reaction times t_1 obtained from the conductivity curves are also given

Plaster composition	<i>t</i> ₁ (min)	D (Shore C units)	$\sigma_{\rm f}$ (kg/cm ²)	σ_c (kg/cm ²)	Diameter (µm)
Pure HH	$10\frac{1}{2}$	53	24	47.5	4.2
Ground HH	8 1 .	70	32.5	61.5	2.1
HH + 5% ground gypsum	$7\frac{1}{2}$	78	38.3	71.1	1
HH+DTPAA 0.05 g/1	31	62	28	51	3.4
HH + D2HPTA 0.5 g/1	54	61	30	52	4.2
HH+DHTA 0.5 g/1	45	60	29	51	4.2
HH + NTMP 1 g/l	23	60	26	51	10.7



Fig. 3. Typical conductivity curves of the hydration of a hemihydrate suspension at 50 g/l. (a) Pure aqueous solution; (b) + NTMP 1 g/l; (c) + NTMP 5 g/l.

present paper and will be described elsewhere [18,22].

3. Results

As a standard for set plaster we consider that obtained from a pure solution. Its texture is built up of aggregates of crystals exhibiting needle and rod-like habits (fig. 4). It is apparently disordered and heterogeneous. The mean tickness e, length Land width l of the individual crystallites are 1, 11 and 2.5 μ m respectively. For the aggregates e is about 5 μ m. The hardness D of this standard plaster is 53 Shore C units.

Two other textures, significantly different from the previous one can be achieved even without any additive. First, when the hemihydrate is ground to



Fig. 4. Crystalline texture of a standard plaster set from pure aqueous solution.

171

 $S_0 = 0.6 \text{ m}^2/\text{g}$ before hydration, the resulting texture is more homogeneous (fig. 5): no aggregates occur and the crystals essentially exhibit rod-like shapes (e = 0.7, L = 11 and $l = 1.5 \mu$ m). Moreover, there are many more crystals than in the standard. The set of rods form a very regular and close network with a wealth of contacts between the crystallites, which certainly provides the better hardness to the plaster (D = 70). Accordingly, the crystalline cohesion is still better (D = 78) when the network (fig. 6) consists of still finer needles (e = 0.3, L = 3.3 and $l = 0.6 \mu$ m). This texture results from the hydration of hemihydrate initially seeded with 5% of finely ground gypsum grains ($S_0 = 0.6 \text{ m}^2/\text{g}$).

In the presence of the four inhibitors we have selected, the crystal sizes increase. Yet, hardnesses better than 60 were obtained (table 2), provided that the additives are used in low concentration. For NTMP 1 g/l (fig. 7) the gypsum crystals are significantly bigger than those of the standard but they still form large aggregates. The textures due to the presence of D2HPTA and DHTA 0.5 g/l (fig. 8) are more homogeneous than the standard and are made up by tabular crystals. On the other hand DTPAA 0.1 g/l mainly originates plates, together with some rods and fine needles (fig. 9).

The gypsum habit modification is much more pronounced when the amount of additive is greater. A beautiful example is that of NTMP. When used at 20 g/l this molecule gives rise to a



Fig. 5. Texture after grinding of the hemihydrate.



Fig. 6. Texture resulting from the addition of 5% gypsum seeds to the hemihydrate.



Fig. 7. Texture due to the presence of NTMP 1 g/l.



Fig. 8. Texture due to DHTA 0.5 g/l.

L. Amathieu, R. Boistelle / Improvement of mechanical properties of set plasters



Fig. 9. Texture due to DTPAA 0.1 g/l.

plaster, the setting kinetics of which are considerably reduced $(t_1 \ge 72 \text{ h})$. Moreover the sample remains extremely friable (D = 10). Its texture (fig. 10) is distinguishable from all others owing to very flat crystals displaying a hexagonal outline. There are large pores (diameter 15 μ m), a poor tangling up of the crystals and consequently very few bonds between them. Similar textures, with somewhat thicker crystals, are originated by high concentrations of DHTA, D2HPTA and DTPAA. These crystals are particularly interesting, for their habit notably differs from the usual acicular one which is made up by $\{010\}$, $\{120\}$, $\{011\}$ and $\{\overline{1}11\}$ faces [23-25]. In order to find the indices of



Fig. 10. Texture due to NTMP 20 g/l.



Fig. 11. Gypsum crystals grown from a solution of high ionic strength: NaCl, 1.54M; Na₂SO₄, 1×10^{-1} M; CaCl₂·2H₂O, 1×10^{-1} M; DTPAA, 0.4 g/l.

the faces limiting these peculiar crystals, it was necessary to grow some large crystals from a solution of high ionic strength (NaCl: 1.54 M; Na₂SO₄: 1×10^{-1} M; CaCl₂ · 2H₂O: 1×10^{-1} M). In such a solution the solubility of gypsum is higher than in pure water, about 5.4×10^{-2} M, the supersaturation, defined as the ratio between the formation product and the solubility product, being about 2.9. It was also checked that NaCl had no effect on the habits of the crystals grown in presence of NTMP 1 g/l or the other acids 0.4 g/l (fig 11).

A precession camera was used to first identify the most developped face. A single crystal was placed in the device in such a way that its largest



Fig. 12. Orientation of the crystallographic axes on the hexagonal crystals of gypsum grown in presence of DTPAA 0.4 g/l.

diagonal was parallel to the X-ray beam (fig. 12), the precession axis being the *b*-axis. Two further photographs were also taken after the crystal has been rotated around the *b*-axis as shown in fig. 12. From this it was concluded that the large basal planes were $\{\overline{101}\}$ faces. Additional measurements carried out by optical goniometry showed that these faces are limited by $\{120\}$ and $\{010\}$ facets.

4. Discussion

The first important point to emphasize is that it is possible to improve the mechanical properties of a standard set plaster without any additive. only by increasing its setting kinetics. Hardness in particular can be enhanced by about 30% by grinding the hemihydrate or even by about 50% by adding gypsum seeds to the powder prior to its hydration. In both these cases, there is a sharp increase of the heterogeneous nucleation of gypsum, either onto the hemihydrate particles (additional sites have been originated by the grinding) or onto the gypsum seeds which generate secondary nuclei. In the former case hemihydrate also dissolves more rapidly. In these pure systems the examination of the textures show that, at constant total porosity, the smaller the crystal sizes and the mean pore diameters, the better is the plaster hardness. For various plasters prepared under similar conditions [18] hardness varies linearly versus the diameter of the most frequent pores (fig. 13).

In such plasters the cohesion mostly arises from the large number of contacts between the crystallites. Many small and thin crystallites, well interlaced, with a lot of contact points originate a harder continuous matrix than large and thick crystals randomly distributed. This is a rather surprising result since one would have expected a dominant role for the individual strength of each crystal. It may also be asked whether the crystal aggregates may be considered as flaws originating areas of weaker resistance. The answer to this question is not very simple because the texture of the standard plaster is a set of aggregates. Therefore, an aggregate is not a real heterogeneity of the texture and, from this point of view, it cannot be



Fig. 13. Correlation between the hardness D and the diameter of the most frequent pores for different set plasters.

considered as a defect of the material. It is true that a spherical aggregate, built up of many long needles achieves much less contact with its neighbours. We may also point out that hardness is improved when the size and number of crystals forming the aggregate is reduced or when spherical aggregates are replaced by more planar or elongated ones. Finally, the best strengths are really obtained when no aggregates occurs and when the number of contacts between crystallites is the largest. In addition to this, it is likely that some residual water molecules also achieve hydrogen bonds in the vicinity of the angles formed by the crystals in contact [26]: their contribution is more important when the texture is made of thinner crystallites. All this is just as valid when setting occurs in the presence of inhibitors. As a matter of fact, for the plasters grown with the four additives we have described above, the better hardness corresponds to crystals which are larger than in the standard. Because of the uncertainty in the measurements it is impossible to discriminate between the four additives in terms of efficiency. The hardness improvement is rather low, compared with that obtained in the pure system. Nevertheless it is significant. This is in variance with some ideas commonly stated, according to which any additive destroys the mechanical properties of plasters. Moreover, it is no longer possible to find a linear

dependence between hardness and porosity (fig. 13), neither for the four molecules quoted above, nor for many other ones [18]. Therefore we have also tried to correlate the flexion and compression strengths with the mean pore diameter according to Griffith's law [27]:

$$\sigma = \left(2\gamma_{\rm S} E/\pi C\right)^{1/2},\tag{2}$$

where γ_s and E are the surface energy and elasticity modulus of the sample; C is the half length of a crack taken here as the mean pore diameter. With this model the scattering of the experimental points is as important as in the previous one. Here it is also confirmed that the pore size is not the only factor affecting the mechanical properties of plasters. The impurities we have used originate crystal shapes which are different from those occurring in pure solution. They also induce attractive and/or repulsive forces between the crystals, after or during the setting. In the latter case they may favour the formation of crystallization knots and a better tangling up of the crystals.

Actually the improvement of the mechanical strengths by means of inhibitors results from a compromise. When the additives are used at low concentration, nucleation and growth rates are only slightly affected. Consequently the number of crystals does not vary too much and new bonds and contacts may also form. At higher concentration, the number of nuclei is significantly decreased. The crystals develop separately, without coalescing; they become larger and exhibit habits which do not allow the achievement of sufficiently good contacts. The mechanical properties of the resulting plasters are always bad.

Finally, from the crystal structure of gypsum [28,29] it was possible to deduce the surface lattice structure of the faces usually occurring on the crystals and also of the unusual ($\overline{1}01$) face. Contrary to the (010) and (120), where the uppermost molecules are essentially water molecules, there are mainly calcium and sulfate ions which alternatively emerge on ($\overline{1}01$) (fig. 14). Hence, the formation of covalent bonds between calcium ions and additive is easier. By superimposing the molecular models of the four inhibitors over the crystal surface representation, it was found that a NTMP



Fig. 14. Surface lattice structure of a $(\overline{1}01)$ face and adsorption sites of NTMP and DTPAA molecules. The level of the uppermost ions involved in the adsorption process is given in Å with respect to the calcium ion indicated 0.0.

molecule (fig. 15) can simultaneously anchor at five sites onto the (101) face. A covalent bond forms between a calcium ion and the charged oxygen atom of a PO_3H^- or PO_3^{2-} group. It is completed by a hydrogen bond between another oxygen atom belonging to the same group and the water molecule close to the calcium ion. These two bonds are strengthened by three hydrogen bonds between hydroxyl groups and sulfate ions. The DTPAA molecule is flat (fig. 15) and easily adsorbs on (101): it achieves three covalent bonds and one hydrogen bond. The DHTA and D2HPTA are sufficiently flexible so that different conformations are possible on the crystal surface. These different points qualitatively explain the selectivity of adsorption on (101). On the (010) and (120)faces, where calcium and sulfate ions are more or less hidden by water molecules the whole adsorption energy is undoubtedly weaker. This mechanism is in agreement with the conclusions of Van Rosmalen [3] used to explain the inhibitor effect of some phosphonic acids on the crystallization of gypsum.



Fig. 15. Molecular conformation of NTMP and DTPAA molecules. The numbers refer to the adsorption sites displayed in fig. 14.

5. Conclusion

The hardness of a standard set plaster can be improved either by grinding the hemihydrate or by adding 5% of finely ground gypsum seeds. In both these cases the nucleation rate is much higher involving the formation of smaller crystals displaying more regular sizes and shapes.

The striking fact is that the strength of plasters can be also improved by means of additives despite what is commonly stated. When used at low concentration, the additives give rise to a better arrangement of the crystals and to additional contacts or attractive forces between the crystals. At higher concentrations, the molecules we have used are powerful habit modifiers: the good bonds achieved between their active groups and the uppermost calcium and sulfate ions on the ($\overline{101}$) face lead to thin gypsum platelets exhibiting a hexagonal outline. Such habits induce plasters with bad mechanical properties.

The extrapolation of the present results to all

industrial plasters is not very simple for these plasters contain many solid and soluble impurities which might modify the influence of the organic molecules.

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