Cement and Concrete Research 39 (2009) 289–295

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Cohesion and expansion in polycrystalline solids formed by hydration reactions — The case of gypsum plasters

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ARTICLE INFO

Article history:
Received 8 November 2008
Accepted 21 January 2009

Keywords:
A: Hydration
B: Microstructure
C: Expansion
Mechanical properties

ABSTRACT

When powdered plaster ($CaSO_4 \cdot 1/2H_2O$) is mixed with sufficient water to give a plastic paste, hydration occurs rapidly, forming a hardened mass of gypsum ($CaSO_4 \cdot 2H_2O$), usually with slight bulk expansion. The addition of certain compounds can greatly increase the expansion, which may lead to destructive pressures. Here I show that this effect increases with the size of the alkyl group in an homologous series of simple water-soluble calcium carboxylate salts: $Ca(HCOO)_2$; $Ca(CH_3COO)_2$; $Ca(CH_3CH_2COO)_2$. The latter two, when used at aqueous concentrations of 10% or more, cause large expansions. The results can be explained by a delicate balance between crystal growth pressures and cohesive interactions at the interfaces between crystallites, on the assumption that only two principal classes of interface exist in the hardened structure: "bridging" and "non-bridging." This hypothesis allows us to make some useful conjectures about the performance of mineral-based hydraulic binders in general, with potential implications for their durability.

1. Introduction

Gypsum plasters were almost certainly the first examples of "hydraulic cement" known to mankind, with evidence for their use in construction going back well over 9000 years; and they are still widely used today for construction and modelling purposes. They are easily produced by heating gypsum ($CaSO_4 \cdot 2H_2O$) in air to temperatures of 125–200 °C, when it dehydrates to produce a friable microcrystalline solid known formally as β-hemihydrate ($CaSO_4 \cdot 1/2H_2O$) but which is often referred to simply as "plaster" or "stucco". When powdered plaster is mixed with sufficient water to give a plastic paste the reverse reaction occurs rapidly, forming a hardened mass of gypsum. Slight bulk expansion usually occurs during hardening, but the addition of certain additives, such as calcium acetate, [1] can greatly increase this expansion, leading to significant volume increases with destructive effects.

Due to the natural abundance of gypsum, its very low toxicity, and the relatively low amount of energy and temperatures required to dehydrate it, gypsum plaster might be considered to be a very "sustainable" cement. However, hardened gypsum plasters are intrinsically soft, have appreciable water solubility and show high wet creep, so their use is mainly restricted to indoor applications. Despite this, gypsum plasters can serve as useful model systems to help us better understand the behaviour of many of the more complex hydraulic cements available for use in modern construction, where destructive expansive processes do sometimes occur but are difficult to predict due to limited mechanistic understanding [2,3].

Hydraulic cements are, by definition, powders that can harden into a solid mass under water. The simplest applications are "pastes", in which the powder and water are mixed to give a concentrated suspension that can be moulded or cast into a form and then sets and hardens to give an object of the desired shape. "Plaster of Paris" (another name for β-hemihydrate) is widely used in paste form for modelling, and the moderate expansion (0.15–0.3%) that occurs during hardening is in this case advantageous in filling the fine details of complex moulds.

Hydraulic cement pastes can also be extended by the addition of unreactive fillers, referred to as "aggregates," to give "mortars" if the filler is a sand, or "concrete" if the filler also contains larger stones. By far the most widely used hydraulic cement is "Portland Cement," made from basic calcium silicates, which is the principal binder in the approximately 10 km^3 of concrete manufactured worldwide every year.

Although Portland cements and gypsum plasters are the main mineral-based hydraulic binders used globally by the construction industry, due to their relatively low resource costs per unit volume of finished product, there are still many unanswered questions about the nature of bonding in such mineral-based binders. In addition, the durability of the hardened products is evidently of great public interest. Failure can occur for many reasons but the one of interest here is the expansive growth of certain crystalline phases, which can produce cracks and ultimately completely destroy the hardened product. We know by experience how to avoid such problems in practice, but we have only a poor physical understanding of the basic

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doi:10.1016/j.cemconres.2009.01.008

phenomena, which makes theoretical prediction impossible. In this paper we demonstrate what we believe to be the simplest case of this phenomenon, involving only a single solid phase, gypsum. It is hoped that the results of this study will put us on the path to the high level of mechanistic understanding needed to accurately predict the risk of destructive expansions in far more complex systems such as Portland cement concretes.

2. Hydration reactions

In the current context, the term "hydration reaction" refers to any reaction in which a solid inorganic compound reacts with water to form one or more new solid phases with a higher degree of hydration than the original compound. This is typical of cement and gypsum plaster hydration, etc., but also of a wide range of geochemical processes such as the weathering of rocks, hydrothermal mineral transformations, etc. One might even consider it to include the corrosion of metals in water, although of course that type of reaction also has a strong redox component which greatly complicates both the thermodynamic analysis and the kinetics.

Clearly, our main interest in hydration reactions relates to hydraulic cements, and in particular to cements based on calcium silicates and aluminates, such as Portland cements and blast-furnace slag cements. Gypsum plasters also represent a class of "hydraulic cement," although there are some who argue that they cannot be considered to be hydraulic since they do not maintain strength after long periods under water. However, in my opinion, that is just a question of the time scale and relative solubilities. Gypsum plasters do initially set and harden under water, so they can be considered hydraulic, even though, after initial hardening, they lose strength when stored under water for days or weeks. But, of course, hydrated Portland cement pastes will also soften and eventually even dissolve completely in pure water if it is present in large enough excess!

The most intriguing aspect of hydration reactions is their ability, at least in some cases, to provide a binding action, i.e. to be able to form a cohesive solid assemblage and even to glue other solids together. This does not always happen, so we have to ask ourselves why it does happen in some cases and not in others; or, perhaps more quantitatively, why the structures formed in some cases are very weak, and in other cases very strong. But there is another even more intriguing phenomenon associated with this type of reaction, and that is expansion. Many hydraulic binders can sometimes undergo a form of "chemical" expansion either during setting or sometimes at a later time due to some external change (temperature, the presence of additional phases, etc.) If the expansion causes problems in use, such binders are said to lack "volume stability". In some cases, this can be a serious durability problem, so we need to understand it well. But it can also have some useful applications if it can be well controlled.

2.1. Plaster hydration

The system is chemically very simple: calcium sulfate hemihydrate reacts with liquid water at typical ambient temperatures and pressures to form calcium sulfate di-hydrate:

$$\mathrm{CaSO_4{\bullet}1/2H_2O + 3/2H_2O \Rightarrow CaSO_4{\bullet}2H_2O}$$

$$145.15 + 27.03 \Rightarrow 172.18 \ (\text{molar masses in g})$$

$$53.1 + 27.0 \Rightarrow 74.6 \ (\text{molar volumes in ml})$$

$$(-14385.9) + (-355.7) \Rightarrow (-1797.4) \ (\Delta G_f^o \text{in kJ/mol})[4] \qquad (1)$$

This reaction is well understood from both the chemical and the bulk thermodynamic viewpoints. As is typical of hydration reactions, there is a decrease in total condensed-phase volume but the volume of solids increases. Thus, if the bulk volume of an initially gas-free paste remains constant after set, some of this volume must be accounted for by intrusion of either water or air, giving a porosity of about 5.5 ml per mol of gypsum. If the bulk paste expands after set, the final porosity will be even greater.

The Gibbs free energy decrease in this reaction is 5.8 kJ/mol with a probable error of about 1.2 kJ/mol [4]. If this were reversibly converted to PV work, (e.g. by growth of gypsum from a plaster-saturated solution against a hypothetical water-permeable piston), the maximum pressure that could theoretically be sustained would be $[(5.8 \pm 1.2) / 0.0746] = 78 \pm 16$ MPa. This derivation is essentially equivalent to Correns' equation [5].

The kinetics of the reaction are also reasonably well understood [6]. Plaster (which is usually supplied in the β-form, having a very high specific surface area) dissolves rapidly in water to give a saturated solution which, (at 20–25 °C), has more than three times the concentration of a saturated solution of gypsum and is thus significantly supersaturated. Heterogeneous nucleation of gypsum occurs essentially immediately, either on the surface of hemihydrate particles or on other solid particles, usually including small gypsum particles present as impurities. Some homogeneous nucleation may also occur. The remainder of the reaction is essentially a dissolution and growth process, and at the water/plaster ratios required to give initially mouldable pastes (typically well over the stoichiometric mass ratio of 0.186) the process can continue until all of the hemihydrate has been consumed. The initial reaction rate is controlled essentially by the growth of gypsum and the final rate is usually controlled by the dissolution of hemihydrate, with (ionic) diffusion through the aqueous solution playing some role in the overall rate but without any evidence for the formation of identifiable "diffusion barriers" around either gypsum or plaster particles.

The result of hydrating a simple (un-admixtured) gypsum plaster at about 20–25 °C is the production of a porous interlocking mass of what appear to be reasonably "perfect" gypsum crystallites, typically elongated tablets of lengths of 10–20 μm and thicknesses of only a few μm, with the dominant face being {010} and other common faces being {011}, {111}, {120} and $\{\bar{1}01\}$. Twinning is sometimes observed in a form referred to as "swallowtail" twins [7]. The current consensus on the microstructure and texture of hardened gypsum plasters and their influence on mechanical properties seems to be based on the following assumptions [8,9]:

1. The gypsum crystallites are randomly oriented with respect to each other
2. Mechanical strength increases as the mean crystallite size decreases
3. Strength is related to the total surface area of "crystal interlocking" contacts/unit volume
4. Fractures propagate principally between crystals rather than through them
5. Most organic additives retard gypsum crystal growth, change crystallite morphology, and decrease the number of crystallites/unit volume, leading to reductions in contact area and strength (except in a few cases, at low dosages).

However, a truly random relative orientation of the gypsum crystallites seems unlikely to me. If we assume that nucleation is essentially heterogeneous, then the number of crystallites per unit volume in the fully hydrated paste must relate in some simple way to the number of initial nuclei — in fact, it should, in the most simplistic model, be just equal to the number of "active" initial nuclei. The orientation of any given crystallite must therefore depend on the orientation of its initial nucleus coupled with changes in orientation produced by gravity, fluid motion, and, almost unavoidably, by interactions with neighbouring crystallites and possibly also with other phases that may be present in the setting plaster during hydration.

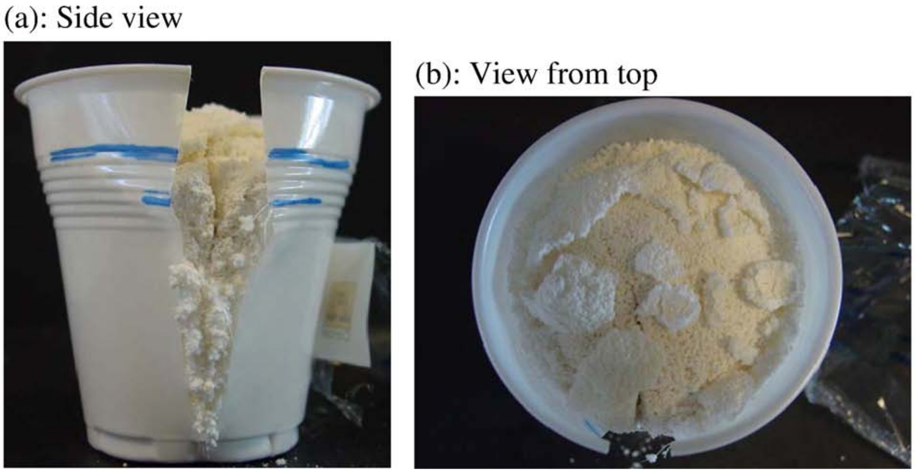

Fig. 1. Expansive gypsum plaster paste made with 20% calcium acetate solution. The lower horizontal line marked on the side of the cup represents the initial height of the fluid paste, and the upper line represents its final height (at the circumference). The cup is shown as found; the split in the side was solely due to the expansive reaction, and the apparent gash in the hardened paste appears to have been due to a combination of shear forces produced during partly-restrained expansion and drying shrinkage occurring afterwards, once the hoop constraint had been released due to the splitting of the cup.

Let us imagine a series of randomly-oriented gypsum nuclei present initially in a suspension, together with dissolving plaster particles. Initially, we might imagine that these nuclei do not interact with each other at all, but we must remember that it is widely accepted that, in the absence of deliberately-added gypsum nuclei, most nucleation occurs on the surfaces of the initial hemihydrate particles, so it is quite possible that they remain attached for some time while the hemihydrate is continuing to dissolve and the gypsum to grow. In a more typical industrial case we do usually have a large number of deliberately added gypsum particles that serve as growth sites (the term nuclei would seem a bit misleading here, since they are no doubt far larger than one would assume to be the minimum necessary for nucleation). In any case, we can assume that the gypsum crystallites grow from the initial nuclei but also tend to move relative to one another due to the influence of gravity, Brownian motion, and inter-particle forces. Most such forces are very weak or very short range (Van-der-Waals), but it is also known that certain faces of the gypsum crystal (primarily the {120} faces, according to Finot [10]) have a significant tendency to develop surface charge as a function of the ionic composition of the liquid phase, and so we must assume that some longer-range electrostatic interactions could occur as well. Thus, it seems very likely that at least the first gypsum/gypsum crystal contacts that form will not be entirely random, but will instead be determined largely by inter-particle forces, especially in fluid suspensions at a time where the structure is still not well formed and there is plenty of room for the small particles to rotate. If this is true, then we would expect the initial flocculated structure that forms to have a significant level of non-randomness in its relative orientation distributions, i.e. interfaces that tend to attract each other more strongly should be preferred. Once the basic structural framework, built mainly of such “flocs,” has formed, the relative orientations of the flocs themselves must at some point become fixed – in fact, this is likely to correspond roughly with what we call set – presumably equivalent to a percolation of flocs. After flocculation, further crystal growth might either reinforce or weaken the existing microstructure, depending on the growth directions and interfaces that are preferred. In practice it usually seems to strengthen it, which is what we would expect if the more attractive interfaces continued to increase their area of contact. Presumably, this is one of the factors that differentiates between an effective and an ineffective binder. However, according to Shchukin et al., [11] significant internal stresses can also build up in the crystallites during the hardening process, as can be demonstrated by analyzing their X-ray diffraction peaks [12].

3. Strength and volume stability

One important aspect of gypsum plasters, when compared to Portland cements, is that they usually show significant bulk expansions on setting, and these expansions can be strongly influenced by chemical admixtures. They also show relatively small drying shrinkages. In addition, the ratio of wet strength/dry strength is much lower than it is for Portland cements, and the wet creep is also very high. Now, all of these effects must be due primarily to solid–solid interfaces; but just what can we conclude from these observations in a quantitative way?

Shchukin's group at Moscow State University studied the formation of bonds between crystals in a solvent in a systematic way [13]. They found that the probability of forming strong bridges between any two crystals increased as a function of the time of contact, the contact force (pressure), the degree of supersaturation of the surrounding aqueous solution, and the relative orientations (e.g. in their case, the

Fig. 2. Scanning electron micrograph of a fracture surface of a hardened plaster without admixtures.

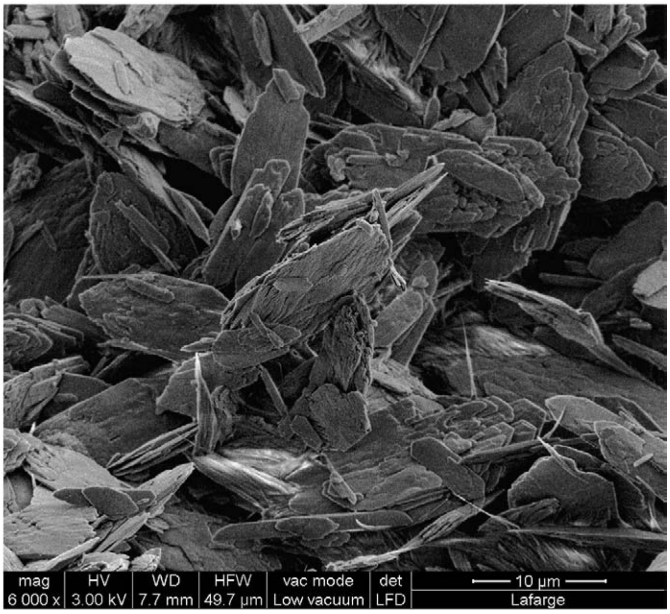

Fig. 3. Scanning electron micrograph of a fracture surface of a hardened plaster made with a 20% calcium acetate solution.

edges of contact) of the crystals. In a general sense, they distinguished two types of attractive (or "cohesive") interactions between simple inorganic crystals (e.g. gypsum) in a solvent (e.g. water):

1. very low-energy attractions, primarily due to Van der Waals forces, which form what they refer to as "coagulation contacts" between particles — essentially, "point contacts" that can cause flocculation of suspensions but can easily be broken again by agitation.
2. much stronger interactions (strong "bridges," essentially irreversible) between the particles, which they call "phase contacts", which involve intimate contact between the atoms or molecules of the solid phase over an interfacial area consisting of many atoms — equivalent to, for example, a "grain boundary" inside a solid.

Essentially, what they observed in most hydrating suspensions (such as gypsum plasters) was the initial formation of coagulation contacts, some of which over time transformed into "bridges" (phase contacts) due to a high local supersaturation and/or normal pressures [11].

The weakly attractive Van-der-Waals forces involved in coagulation contacts must also compete with repulsive forces due to the solvation of the outer layer of the solid surfaces involved (if they are lyophilic), together with electrostatic forces (if they have some net electrostatic charge in the given solution). Thus, there may well be a small gap between the solid phases even at the point of closest contact, due to these solvation forces — sometimes called "disjoining pressure". If so, new solid material can presumably migrate into the gap at an appreciable rate — for example, if the solid phase is itself growing from a supersaturated solution. It is thus conceivable that such coagulation contacts are the sites at which crystal growth pressures can be generated, provided that the gap is big enough for the expansive growth process to continue at an appreciable rate. The factors that would be expected to retard or inhibit such growth at any given degree of supersaturation seem likely to be:

(a) The formation of a "bridge," (which irreversibly changes the nature of the interface).
(b) An increased pressure (normal force) at the point of nearest contact. (Note: when this pressure becomes equal to the maximum value thermodynamically possible, e.g. as given by Corren's equation, [5] no further growth can possibly occur at this site).

It seems likely that, in plain gypsum plasters, much of the potential expansion that might occur if all of the excess free energy contained in the initial supersaturation were converted into expansive growth, is, in fact, consumed by the formation of bridges between the impinging crystallites, which is what results in a strong hardened material. However, the probability of formation of such bridges depends on the relative orientations of the impinging crystallites [11]. Faces that are not oriented appropriately to form bridges rapidly can continue to grow for a long time, producing internal stresses in the existing solid framework, and potentially also giving rise to significant bulk expansions. From this analysis, one can imagine that the strength and volume stability of the hardening system will depend strongly on the total surface areas (per unit volume) of the two principal types of interface, which I will, for convenience, label as (a) "bridging" and (b) "non-bridging", although the latter interfaces are actually in most cases weakly attractive at long distances even in water, and are much more attractive in air, vacuum, or in most types of non-aqueous media, where the Hamaker constants between the two mineral phases are higher [14].

In order to investigate the reasons why some simple salts increase the expansion of gypsum plasters, I conducted a few simple experiments, as outlined below:

4. Experimental

4.1. Methods and materials

Batches of paste were prepared by mixing 100.0 g of β-hemihydrate (Meriel) with 80.0 ml of de-ionized water at 20 ± 3 °C. Aqueous solutions of three calcium salts of simple carboxylic acids (calcium formate (CaFo); calcium acetate (CaAc); and calcium propionate (CaPr)) were prepared at concentrations of 1%, 2%, 5%, 10% and 20% by mass and were used to replace the mix water in some of the pastes. In some cases the pH of the system was modified, either by adding 1% solid $Ca(OH)_2$ to the hemihydrate (giving a pH of about 12) or by adding a little acetic or propionic acid as appropriate (giving a pH of 4–5).

The pastes were hand-mixed for 1 min in thin-walled translucent polystyrene cups (72 mm in height and 200 ml in capacity) which were then covered with PVDC film to minimise water evaporation.

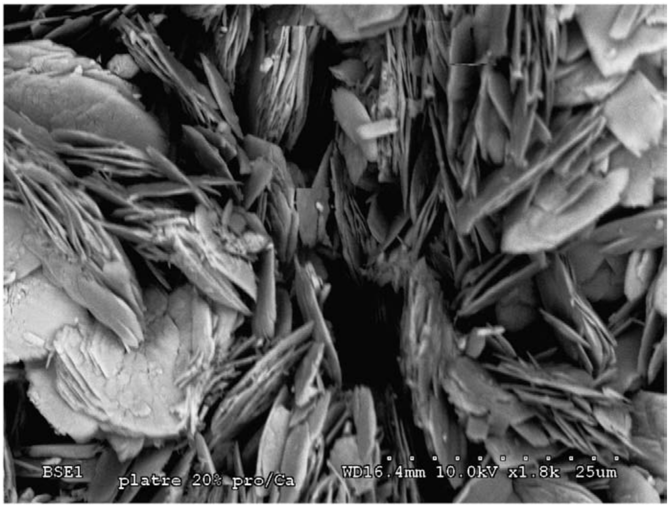

Fig. 4. Scanning electron micrograph of a fracture surface of a hardened plaster made with a 20% calcium propionate solution.

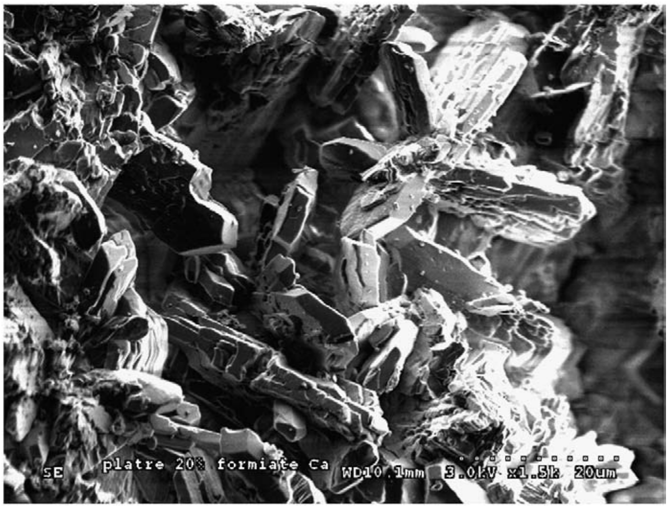

Fig. 5. Scanning electron micrograph of a fracture surface of a hardened plaster made with a 20% calcium formate solution.

The initial height of paste was marked on the outside of the cup in order to help see whether there was any vertical movement of the surface during setting. In some cases, more water was added to the surface later (after initial set). The cups were stored in the laboratory at 20 ± 3 °C.

4.2. Observations

The control paste set about 1 h after mixing. No expansion was seen even after 4 months.

The mix made with 10% CaAc set after about 10 h, and after over a day for the 20% solution. In both cases, large expansions were observed within a few days, first manifesting itself by an upward movement of the top surface of the paste, forming a dome. Adding water to the top surface generally increased the amount of expansion. Despite the top surface being unrestrained, the expansions often cracked the wall of the cup, as shown in Fig. 1. Half of the cups (2/4) broke with 10% CaAc, and all of them (4/4) broke with 20% CaAc. Increasing the pH reduced the setting time slightly but didn't have much effect on expansion.

CaPr retarded hydration even more than CaAc — the 10% solution delayed initial set beyond one day. For concentrations of 10% or more, large expansions were observed several days after set. The effects of pH were similar to those with CaAc.

CaFo was only tested at 10% and 20% and no expansions were observed in any case.

X-ray diffraction scans of air-dried expanded pastes showed gypsum peaks plus weak peaks for CaAc or CaPr. However, only gypsum peaks were observed in the wet pastes (before first drying), implying that the calcium carboxylate salts had probably remained in solution during the expansion. No peaks for residual hemihydrate or unknown crystalline phases were observed.

The morphology of the gypsum crystals changed significantly as a result of calcium carboxylate salt additions. Fig. 2 shows a fracture surface of the "control" paste, showing typical bundles of acicular crystals. Fig. 3 shows the effects of the 20% CaAc solution, which produced many stacks of thin "pseudo-hexagonal" platelets. The most highly developed faces here are apparently $\{\bar{1}01\}$ faces, as commonly observed in the presence of gypsum growth retarders [9]. CaPr (Fig. 4) gave morphologies similar to those observed with CaAc, but CaFo (Fig. 5) gave crystals that were much more "blocky" and appeared to be bonded together at various angles.

5. Discussion

Looking at the above results, it seems conceivable that one could explain expansive hydration of gypsum plasters simply as a function of the relative amounts of non-bridging vs. bridging interfaces. The results on plasters with solutions of calcium salts of three different simple carboxylic acids indicate that the tendency to both to retard gypsum crystal growth and also to promote expansive hydration increases along the homologous series formic: acetic: propionic (HCOOH, CH_3COOH, CH_3CH_2COOH). In fact, the main difference occurs between calcium formate, (which is only a weak gypsum growth retarder and produces very little expansion), and calcium acetate, (which is a much stronger retarder and also produces strong expansions). Calcium propionate seems to be an even stronger retarder but it is not yet clear whether or not it actually produces any greater expansive pressures than the acetate. I believe that this phenomenon can be explained by the preferential adsorption of the carboxylate salts onto one (or more) specific growth faces of gypsum. Combe and Smith [7] noted that acetates retarded the setting of plaster and alter the crystal morphology; and calcium acetate is known industrially as a promoter of gypsum expansion [1]. Evidently, this type of adsorption would be expected to stabilize the faces concerned, and reduce their growth rates, hence the observed overall growth retardation. This will lead to a change in typical crystal morphology, displaying a preponderance of the retarded faces. Meanwhile, the non-retarded faces can continue to grow and presumably to form bridging contacts once they meet. However, when a retarded face meets a non-retarded face, it is far less likely to be able to form a bridging contact, because of the size and inherently hydrophobic nature of the retarding groups (in this case, carboxy-alkyl groups) adsorbed on the retarded face. Thus, the non-retarded face may continue to grow and so exert a crystal growth pressure between it and the retarded face with which it is in close contact (separated only by the solvation layer).

This hypothesis can explain the tendency for certain specific retarders, such as acetates, to increase crystal growth pressures. Note, however, that this is not a universal property of retarders, since it is known that some retarders can actually decrease expansion and increase strengths, [9] perhaps because in some cases they may favour the formation of bridging contacts by other mechanisms. Note also that the type of "cohesive" expansion that we observed here in the case of calcium acetate- or propionate-modified gypsum plasters implies that a significant fraction of bridging interfaces must still be present along with the non-bridging interfaces. If all the interfaces were non-bridging, the structure should undergo a complete mechanical collapse, i.e. the disappearance of any significant shear yield stress; but this is clearly not what happens in the cases that we demonstrate here — at least, not at the early stages of the expansion. Instead, the pastes are observed to expand quite a lot while maintaining significant mechanical integrity, such that they are capable of exerting fairly large hoop stresses on the walls of cylinders into which they have been placed, even while the ends of the cylinder are open to free expansion. It is notable that the pastes do ultimately become very weak and friable after undergoing large free expansions, but this is hardly surprising considering the large increase in porosity that occurs during the process.

In addition to the potential for expansion, the existence of different types of interface in the hardened structure might also explain variations in compressive strength, and especially the influence of moisture content on the strength. While bridging interfaces should be relatively insensitive to the presence of water, at least in the short term (noting, however, that, over a longer time frame, dissolution could occur to weaken the interface, especially if it is in tension — i.e. a kind of stress corrosion process), non-bridging interfaces can be more or less "repulsive" depending on the details of the interfacial forces and the solvent. Thus, in water, solvation forces and electrostatic forces (which presumably involve some combination of double-layer forces and ion correlation forces) [15] may in some cases lead to quite large equilibrium distances between certain pairs of faces at the point of minimal interaction energy, which might in some cases even give rise to a "secondary minimum" in the particle–particle interaction energy vs. distance curve (the primary energy minimum in such cases presumably being the one that occurs during bridging, i.e. grain-boundary-type contacts). The larger the equilibrium distance, the less one would expect such interfaces to be able to transmit shear forces — in fact, they should tend to exhibit lubricated slip. This is bound to weaken the overall structure, and should also increase the rate of creep. On the other hand, during drying, such interfaces should become significantly stronger in tension, and thus probably also much better able to transmit shear forces: firstly, due to capillary tension in the residual liquid water, and, after further drying, due to the higher Van-der-Waals attractions that should occur once the liquid water has all evaporated [14]. The effect of drying should evidently tend to cause these interfaces to close up, giving rise to drying shrinkage. One can see, therefore, that the relative difference in strength between a wet and a dry paste can be related to the ratio of the area of "bridging" interfaces to the total area of all interfaces; and the tendency to shrink on drying should relate to the ratio of "non-bridging" interfaces to the total area of all interfaces.

Another observation that can be explained well by the above hypotheses is the fact that ordinary (un-admixtured) gypsum plasters are known to give significantly higher compressive strengths if they are mechanically constrained during setting and hardening [16]. This makes sense if we assume that the growth pressures exerted at certain interfaces are transmitted throughout the whole flocculated structural framework as it grows, and, if restrained, can result in higher interfacial pressure which increase the probability of forming strong bridges.

The explanation of the very high wet creep exhibited by gypsum is likely to be more complex than simple strength effects because it occurs over fairly long time periods and so could well be due to dissolution–precipitation processes at points of contact, [17] but it seems likely that at least some part of wet creep (and a much larger part of dry creep) is due to slip at non-bridging interfaces. If this is indeed the case, one might imagine that the interfaces where creep is most strongly manifested would be those that formed last during the build-up of the final hardened structure — i.e. the interfaces between the different "flocs" or "domains" that may make up the hardened structure. It is not yet known whether or not such domains exist, but this is a question of considerable interest and deserves further experimental study. If domains do exist, their relative orientations may well be completely random, whereas the crystals within each domain should have well-defined relative orientations with respect to one another. The size of the domains should relate to the early formation history of the structure, and it is conceivable that the formation of each domain might be dominated by growth from a single initial nucleus. On the other hand, if the relative orientations of the crystallites are confirmed to be truly random, then the "domains" will simply be the individual crystallites themselves, each of which must have formed from a separate initial nucleus.

It is important for us to try and develop quantitative relationships that express the concepts that I have outlined above and allow them to be tested experimentally. Assuming that we have a solid phase with known mechanical properties, in the form of small particles or crystallites, and we construct a microstructure from it (plus porosity), we can define the solid–solid interfaces as being the areas where the solid particles are in contact at the near-atomic level, i.e. at distances of the order of just a few nm or less (in air). If we divide these interfaces into only two principle classes, bridging (b) and non-bridging (n), as explained above, then we can specify the specific surface areas (per unit volume) of each of them as B and N, respectively. For a porous material element in air (porosity fraction $= p$), we can define the mechanical properties such as strength (S) and modulus (E) as a function of the properties of the pure 100% dense solid (with no internal solid–solid interfaces) multiplied by a coefficient $f(p)$ which is always less than unity and which decreases with increasing p. If we assume that the strength and moduli of bridging interfaces are essentially the same as those of the continuous solid, and the strength and moduli of non-bridging interfaces are both zero, then the strength of the polycrystalline material should simply be given by Eq. (2):

$$S = S_0 \cdot f(p) \cdot [B/(B+N)] \tag{2}$$

[Note: the $f(p)$ term in this equation is defined for the particular property of interest — in this case, for example, compressive strength. In reality, it is clear that $f(p)$ will depend not only on the total porosity but also on the pore size distribution, and even more so on the "defect" size distribution. But, for the purpose of simplicity, it will be assumed here that all of these distributions vary simply as a function of p. In any case, this equation is intended mainly for making comparisons during which both p and the defect size distribution are held constant.]

If we assume that the effective strength of the non-bridging interfaces is some fraction, δ, of that of the bridging interfaces, then we should modify this formula accordingly, as in Eq. (3):

$$S = S_0 \cdot f(p) \cdot [(B+\delta N)/(B+N)]. \tag{3}$$

In practice, the value of δ will depend on the nature of the solvent (fluid phase) filling the pores, and especially the very small pores (essentially, the nanometric pores representing the non-bridging interfaces). If the solvent is air or a vacuum, then δ will presumably have its highest value $\delta_{\max}$ (although capillary tension could conceivably give even higher values at relative humidities where the non-bridging gaps are just filled with liquid solvent). If the solvent is one in which the non-bridging interface has some repulsive character, then δ will be zero or very small. So we can see that δ will vary in an understandable way with the nature of the solvent and its partial pressure (relative humidity) in the system. For a simple comparison of wet strength to dry strength at constant microstructure, we should then have Eq. (4):

$$S_{wet}/S_{dry} = [B/(B+\delta_{\max} N)]. \tag{4}$$

We might also assume that a similar relationship would apply to the ratio between wet and dry creep, if creep were due uniquely to slip at non-bridging interfaces.

Regarding the maximum crystal growth pressure that can be exerted, this will presumably be proportional to the fraction of the interfacial SSA contributed by "non-bridging" interfaces, which is $[N/(N+B)]$, multiplied by the maximum possible pressure as given by Corren's equation (about 78 MPa in this case). It should also presumably be multiplied by the volume fraction of solids $(1-p)$ to allow for the diluting effects of porosity, as shown in Eq. (5):

$$\text{maximum expansive pressure of plaster} \sim 78[N/(N+B)](1-p)(\text{MPa}). \tag{5}$$

As for drying shrinkage, it seems likely that all of the shrinkage occurs at the non-bridging interfaces. If we assume that the average gap at such interfaces is given by (g) in the wet (solvated) state, and this reduces to zero in the dry state, then the overall bulk linear shrinkage should simply be proportional to Ng. Of course, it is restrained by the modulus, E, of the solid skeleton, so the overall relationship is probably something like that shown in Eq. (6):

$$\text{Linear shrinkage} \sim Ng/E. \tag{6}$$

The interest of Eq. (6) is that only the properties (total amount and gap spacing, etc.) of the non-bridging interfaces are involved. The bridging interfaces are factored into the overall elastic modulus of the material. Thus, this formula predicts that the drying shrinkage should increase roughly linearly with the inverse of the mean particle (crystallite) size. Strength, on the other hand, should be far less sensitive to particle size.

6. Summary

The mechanical properties of hardened polycrystalline materials are assumed to be mainly determined by the properties of the bulk solid phases and by the quantities (in terms of area per unit volume) of all the various different possible types of solid–solid interfaces. Especially when it comes to tensile strength and creep, it seems likely that it is the quantity and nature of the interfaces that should dominate over the bulk properties of the crystals.

This concept is exemplified here by the case of gypsum plasters. It is shown here that a simple classification of the solid–solid interfaces into two main types, “bridging”, (in which strong atomic bonds occur over a significant area, as in a “grain boundary”), and “non-bridging”, (in which only long-range forces hold the interface together weakly and thus can allow a solvent to enter the gap) can help us better understand the bonding and mechanical behaviour of hardened plasters. The “non-bridging” interfaces can be very sensitive to the effects of the surrounding medium, and can become effectively “repulsive” (i.e. can exert a significant expansive pressure) if one side of the interface is growing by deposition from a supersaturated solution. Our experimental work has shown that calcium acetate and calcium propionate solutions, which both retard set, can also greatly enhance the expansive forces generated by hardening gypsum plasters while yet maintaining significant cohesion; whereas calcium formate solutions, which are less retarding, produce no significant expansions. As an explanation, it is suggested that specific adsorbates (such as acetate or propionate) that modify the crystal growth process by depositing on and stabilizing certain crystal faces, can also modify the tendency of the resulting faces to form bridging interactions with other impinging faces, thus increasing the fraction of potentially expansive interfaces in the resulting paste.

7. Concluding remarks

There remains an enormous amount to be learned about the nature of the solid–solid interfaces that exist in hardened plasters, cements, and other inorganic materials, and how they influence the mechanical strength and volume stability of those materials. The experimental techniques required to make quantitative analyses of all of these interfaces and their properties are not currently available; but it will be well worth the effort to develop them if we wish to obtain a better ability to predict and control the mechanical properties and chemical durability of construction materials in general, and hydraulic cements in particular.

Note also that the subdivision of solid–solid interfaces into only two classes – “bridging” or “non-bridging” – in this paper is clearly a great over-simplification. In reality, there may be many different types of interface present in most binder systems, with a wide range of possible physical and chemical properties. Our long-term goal should be to understand all of the possible surface interactions, and, if possible, be able to control the relative proportions of different types of interface so as to get the desired ultimate material properties.

The fact that harmful expansive processes tend to manifest themselves after the pastes have initially gained significant strength suggests that the freedom of the fundamental particles (or crystallites) to “rotate” to the lowest energy position relative to their closest neighbours is an important aspect of the setting and hardening process. As long as such adjustments are possible, one would not expect bulk expansions to manifest themselves. However, once most of the solid skeleton has formed and begin to rigidify, expansive processes can become potentially very destructive because there are few alternative ways in which the skeleton can grow. This also helps explain the sensitivity of hardened porous brittle materials to destructive crystal growth processes. A better understanding of these processes is therefore critical for durability prediction for plasters, concretes and other brittle construction materials.

Acknowledgements

I would like to thank Jia Wang for help with the experiments, Sylvain Meille and Eugene Shchukin for many stimulating discussions in the past, and Lafarge for supporting the work.

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