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BY

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QUELQUES PARTICULARITES DU VIEILLISSEMENT DE LA CHAUX

SOMMAIRE

La présente étude du vieillissement de la chaux englobe le cas particulier des échantillons de chaux de compactage, qu'on estime représenter le comportement de la chaux dans la pâte hydratée de ciment Portland. Les auteurs ont étudié le vieillissement de la chaux par la mesure des variations de longueur d'échantillons, obtenus par compactage de matériaux pulvérisés, dans diverses conditions cycliques ou stables d'humidité. Ils ont analysé les résultats en vue de trouver l'explication du comportement particulier des échantillons de chaux de compactage. Ils examinent diverses possibilités, et avancent l'hypothèse de l'existence d'un mécanisme fondamental, d'après lequel un nouveau produit se forme, tout au moins aux points de contact des particules, lorsque les échantillons obtenus par compactage sont exposés à un degré d'humidité dépassant un certain niveau. En outre, ils affirment que ce produit est plus modifiable que le matériau original, et qu'il peut donc se consolider sous l'action des forces engendrées par la présence de ménisques et par les variations de l'énergie superficielle libre. Cette action se manifeste par un retrait irréversible pendant l'entreposage à un degré d'humidité moyen, ou par une dessiccation après l'entreposage, ou encore par l'apparition de changements cycliques entre deux niveaux d'humidité.

SOME AGEING CHARACTERISTICS OF LIME

By E. G. SWENSON and P. J. SEREDA

This study involves the special case of lime compacts which are considered to serve as models for the system of lime in hydrated Portland cement paste. The ageing of lime was studied by measuring length changes of powdered samples under various steady-state and alternating conditions of humidity. As an explanation for the unique behaviour of lime compacts, a primary mechanism is proposed based on the theory that recrystallisation occurs at least at areas of particle contact when lime compacts are exposed to humidities above a certain value. Furthermore, this recrystallised product is more accommodating than the parent material, and hence it can be consolidated by forces due to menisci or changes in surface free-energy. This action is manifested by irreversible shrinkage on storage at intermediate humidities, by drying after storage or by alternating between two levels of humidity.

Introduction

In the hydration of Portland cement the lime which is liberated may constitute some 20% by weight of the fully matured paste. Thus, changes that occur in lime may be reflected in changes in the properties of the hardened cement paste. The study of the ageing of lime, therefore, should yield useful information that may be applied to hydrated cement. The fact that lime in this study was compacted is particularly applicable to the cement system, because the lime in this system is deposited in a confined space during the chemical reactions.

The term 'ageing' is usually applied to the process where a solid becomes less 'reactive' with time, and is observed as a decrease in the surface area. The process is slow at normal temperatures and requires the presence of moisture. Ageing not only involves the limiting case where larger crystals or particles grow at the expense of the smaller ones, as in aggregation, but also implies processes where changes to the surface itself may occur by molecular rearrangement.

Hunt *et al.*¹ have observed that the colloidal structure of hardened cement paste cured at ordinary temperatures can undergo changes which lead to a decrease in surface area and which in some respects resemble ageing effects observed in other colloidal gels. They also observed that comparatively little attention has been given to the ageing phenomenon and that it may have an important bearing on such properties of concrete as creep, drying shrinkage and the development or loss of strength.

While determining sorption isotherms for lime, Glasson² noted that the material tended to age appreciably during the 3 to 5 h allowed for equilibrium. He based his conclusion on reduction in surface area measured by N₂, O₂ and H₂O adsorption. Above 20 m²/g, ageing rates were considerable; below this value they were extremely low.

Gregg,³ when referring to the active solid produced by thermal decomposition, introduces the term 'micelle' in place of 'crystallite' to avoid the implication that the lattice is perfect. He suggests that the micelle can have a pseudo-lattice which is unstable and under the correct conditions will recrystallise to the stable form. This process as well as the 'micellar growth' is used by Gregg to describe ageing. He considers that both sintering and ageing involve 'micellar growth'.

This investigation used the powder compaction technique and associated methods developed in this laboratory.⁴ Evidence of ageing of lime was observed and studied, using apparent volume change as a basis.

Methods and apparatus

The calcium hydroxide used was reagent grade powder. A second material was prepared by calcining the above powder at 500° and rehydrating the oxide in the vapour phase at 25% R.H. The two materials had surface areas, by N₂ adsorption, of 10 and 15 m²/g, respectively, as shown in Table I. All experiments were conducted with the reagent grade Ca(OH)₂ except where it is specifically stated that the other preparation was used.

TABLE I

Dimensional changes during storage at conditions of 50% and 95% R.H. of compacts of reagent grade and rehydrated lime (Compacts made at 20,000 lb)

Source of lime	Surface area by N ₂ methanol, m ² /g	Length change, %			
		50% R.H.			95% R.H.
		2 days	14 days	25 days	25 days
Reagent grade	10	-0.008	-0.022	-0.030	+0.020
Rehydrated in vapour	15	-0.021	-0.036	-0.042	+0.064

Compacts (1.25 in. dia.) of these products were made at loads of 20,000 lb and higher.⁴ From these, wafers were cut to fit small optical extensometers which measured length change to 0.000004 in. Conditioning was carried out in special cells as well as desiccators fitted with flat lucite tops to permit reading of the extensometers (Fig. 1a and b).

Extreme precautions were taken to prevent even traces of carbonation during preparation of the samples in dry boxes and during conditioning over the sodium hydroxide solutions, made with boiled distilled water, used for controlled relative humidities.⁵ Periodic, magnetic stirring was employed. The air in the conditioning cells or desiccators was evacuated to the boiling point of the liquid before conditioning was begun.

Experimental observations

Ageing process under steady-state conditions of relative humidity

Length change as a function of equilibrium conditions of storage

Ageing of Ca(OH)₂ was observed by the measurement of length change of compacts while these were exposed at constant conditions of relative humidities of 20, 50, 75, 80, 85,

Fig. 1. Apparatus for the study of carbonation by length change of compacts

90 and 95%. The results plotted in Fig. 2 show that maximum contraction occurred at 50% R.H. and an expansion occurred at conditions above 85%.

Effect of duration of conditioning on ageing

Compacts of $\text{Ca}(\text{OH})_2$, initially vacuum-dried, were exposed to 50% or 95% R.H. for various periods and in some cases were re-dried. Typical results are shown in Fig. 3. Initial expansion on exposure of the dry specimens to elevated humidities was extremely rapid. At 50% R.H. practically the full expansion had occurred within 5 min. In the same period nearly three quarters of the total expansion had occurred for the 95% R.H. exposure.

Fig. 2. Dimensional changes of $\text{Ca}(\text{OH})_2$ compacts (20,000 lb compaction) with conditioning (ageing) over NaOH solutions

In the 50% R.H. condition, the slow contraction begins within the first day of exposure and reaches apparent equilibrium after about one month. In the 95% R.H. condition the initial rapid expansion was completed in about one or two days for these samples and was followed by a slower expansion which reaches apparent equilibrium in about two weeks.

Samples that had undergone prolonged ageing at 50% R.H. and had exhibited the characteristic ageing shrinkage did not again undergo this slow contraction after intermediate drying periods as illustrated in Fig. 4.

The results in Fig. 4 demonstrate quite conclusively that no carbonation had taken place during the prolonged ageing and drying experiments. If shrinkage in the first cycle during storage at 50% condition was due to leakage of CO_2 into the system, then further carbonation shrinkage should occur for each successive exposure to constant conditions of 50% R.H.

Effect of surface area on ageing

The rate and degree of ageing of lime compacts, as exhibited by length change, increased with increase in surface area as shown in Table I. It is to be noted that the surface

Fig. 3. Dimensional changes of $\text{Ca}(\text{OH})_2$ compacts (20,000 lb compaction) subjected to 50 and 95% R.H. Expansion after 5 minutes exposure to each R.H.

Fig. 4. Irreversibility of slow contraction of compacts (60,000 lb compaction) due to ageing and irreversible shrinkage due to cycles of drying

areas determined by adsorption methods are only relative because the drying treatment necessary in the method is itself an ageing condition.⁶ It is thus possible to compare the surface areas of two separate materials, but it would not be meaningful to compare the surface areas of a given product before and after an ageing period.

The rehydrated Ca(OH)_2 may be considered to have retained, in part, the original lattice of the CaO . The gradual change from this pseudo-lattice to the normal Ca(OH)_2 lattice may be responsible for an ageing effect, as Glasson proposes.²

Effects of compaction pressure upon ageing

Lime compacts made at loads of 20,000, 100,000 and 200,000 lb were mounted in optical extensometers and exposed to 50% and 95% R.H. over NaOH solutions. The calculated pore volumes of these specimens were 33%, 20%, and 12%, respectively. Length changes to 29 days are shown in Fig. 5. At 95% R.H. where expansion occurs and at 50% R.H. where contraction occurs, the rate and the magnitude of length change due to ageing increase as the apparent density of the compact increases. This can be explained on the basis of a solution/redeposition reaction at the points of contact of particles. As the apparent density increases, the number of particles per unit length increases and hence the cumulative change of all the particles per unit length will increase. Compaction at higher pressure should cause more fracturing into smaller particles and this should add to the total effect.

Ageing in two directions, normal and parallel to the direction of compaction

The possibility that the process of compaction will produce directional properties that might invalidate the various relationships studied was examined. Several 60,000 lb compacts were glued together to form a multiple 'sandwich' and a sample wafer was cut out so that length measurements could be made in the direction of compaction. This was conditioned together with a normal compact, measured in a direction normal to that of compaction, at 50% R.H. and 95% R.H. for 41 days.

The ageing shrinkages at 50% R.H. were 0.088% for the 'sandwich' and 0.066% for the other compact, and there were comparable rates throughout the conditioning period. The ageing expansions at 95% R.H. were 0.046 and 0.022, respectively. This approximately doubled expansion measured in the direction of compaction agrees with previous experience with compacts and is an inherent property of them which should not affect the relationships developed.

Fig. 5. Dimensional changes of lime compacts compacted at different pressures

○ 20,000 lb ● 100,000 lb □ 200,000 lb Ca(OH)_2 compacts

Ageing process under alternating conditions of humidity

Fig. 3 shows the effect of drying after a 4-day exposure to the two humidity conditions. In both cases, the samples contract to a length shorter than the original dried length, the net ultimate shrinkage being the greater for samples pre-conditioned to 95% R.H.

The irreversible portion of shrinkage associated with each drying cycle as shown in Fig. 4 is a demonstration of ageing or internal change having taken place prior to the step of drying. This resulted in an internal rearrangement produced by the drastic change in conditions at the internal surface, the basic reason for the irreversible shrinkage being the same as that producing shrinkage under steady-state conditions.

Compacts of lime were subjected to various alternating sequences. Fig. 6 shows the dimensional changes for alternating between 50% and 75% R.H., each point being an equilibrium point insofar as sorption is concerned. The incremental irreversible shrinkage of the compacted specimen

Fig. 6. Dimensional changes of Ca(OH)_2 compacts (20,000 lb compaction) alternated between 50% R.H. and 75% R.H. equilibrium at each point

○ Equilibrium at 75% R.H. ● Equilibrium at 50% R.H.

occurring after each completed cycle is of the same order of magnitude as ageing shrinkage on storage at one of these conditions.

Alternating between 50% and 0% R.H. resulted in total shrinkages of about 0.25% and net irreversible shrinkages at the upper and lower limits of about 0.04% for each cycle. The latter represents a type of ageing.

Effect of ageing on mechanical properties

The modulus of elasticity of samples showed an increase with duration of conditioning at both 50% and 95% R.H. One set of 20,000 lb compactions had a modulus of 0.56×10^6 p.s.i. after 3 h exposure at 50% R.H., and a modulus of 0.75×10^6 p.s.i. after 22 days' exposure. A similar set of compacts was exposed to the 95% R.H. condition. At 3 h the modulus was 0.60×10^6 p.s.i. and at 23 days, 0.83×10^6 p.s.i.

The results which show an increase in modulus of elasticity can be expected when compacts are stored at conditions at or above 50% R.H. if one postulates that the effective internal area of contact or bond between crystals should increase under these conditions as the result of recrystallisation or re-gelation at points of contact which have been deformed, strained or even fractured.⁷ This hypothesis will be developed later in the light of other experimental results.

Discussion

This study of the ageing of lime involves the special case of lime compacts which are considered to serve as models for the system of lime in hydrated Portland cement paste. It is known that a compacted solid system can be described as an assemblage of particles (crystals) which have been strained, deformed or fractured and may represent areas of contact between particles with considerable residual strain. Nevertheless, this model is considered justified on the basis of the following findings: that calcium hydroxide crystals are strained in hydrated cement paste;⁸ that the mechanical properties of compacts of hydrated Portland cement compare well with those of paste samples;⁹ and that carbonation of compacts of lime shows the same physical characteristics as the carbonation of cement paste.⁵

Although the study of the ageing of lime in the form of a compacted porous system based on measurements of length change is justified, and the mechanisms postulated are considered applicable to the lime component in the hydrated cement system, it is not readily apparent that it is comparable with the studies on ageing of lime based mainly on surface area measurements of a powder in either an air or a liquid environment.

The ageing occurring in hardened Portland cement paste as a decrease in surface area has been considered to be a collapse of layered structures.¹ Irreversible changes resulting from the adsorption/desorption cycle of such a system are believed by Powers to be caused by particles being drawn more closely together during desorption and new points of contact being produced under forces of contraction.¹⁰

The similarity between ageing and sintering has been recognised. Gregg considers that the process involving decrease of surface area is sintering if it occurs at elevated temperatures, and ageing if it occurs at room temperature.³ He considers that a change of mechanism may take place with increase in temperature. In both ageing and sintering of compacted powders, a shrinkage occurs under certain conditions of temperature and relative humidity.

In ageing, as in sintering, one force that tends to reduce surface area has its origin in interparticle attraction.^{11,12} The resulting tendency of particles to 'merge' has the effect of deforming them at the area of contact.¹³ In sintering, the melting temperature of the strained material at the contact areas may be only half the normal melting temperature of the bulk material. Similarly, when a compacted powder such as lime, is exposed to some degree of humidity, it presents strained contact areas with material having a higher rate and degree of solubility. Both systems can account for shrinkages on the basis of contractive or negative menisci forces at areas of contact, and on the basis of a drawing together of particles after a transfer or movement of molten material in the case of sintering, and dissolved material in the case of ageing.

In sintering there is lack of agreement as to the mechanism by which the material is actually moved or transferred so as to produce a decreased surface area and shrinkage. Explanations proposed involve evaporation/condensation, surface diffusion, volume diffusion, viscous flow, plastic flow, and capillary forces. None of these appears to be applicable to the ageing phenomena observed with the lime compacts.

The ageing of lime in compacts may occur as the result of a major process and one or more contributing secondary processes. It is suggested that the primary process is based on a dissolution at areas of contact of material under stress and a redeposition (precipitation) at sites of reduced stress. Above a certain relative humidity the adsorbed and free water can provide the medium through which the slightly soluble lime can be transferred. The redeposition of solid would create additional contact points, somewhat analogous to a stalactite/stalagmite system. This primary mechanism is essentially the same as has been proposed for another process.⁷

All experimental evidence supports this theory that above a certain level of humidity (exact value as yet unknown), recrystallisation, which may be confined to the areas of contact, begins to occur, but evidence from studies on carbonation indicates that it is more extensive. The resultant product is more accommodating in the sense that it is more compactable than the parent material under menisci or changing surface free-energy consolidating forces.

The results described under the heading of ageing under steady-state conditions of relative humidity can be explained in this way since the new product formed is under a compressive force of menisci in a certain range of humidity. Above 85% R.H. this force will be small so the new product is formed with resulting expansion.

Physical effects, especially in a compacted system, could be expected to be a maximum in the intermediate humidity region because there is enough sorbed water on the one hand for maximum surface interaction, and on the other for reinforcement by the maximum menisci forces contributed from bulk water. In addition, there is adequate bulk or film water to contribute to processes such as solvation, recrystallisation and physical accommodation. The facts that in the intermediate humidity region Hunt *et al.*¹ found greatest change to surface area of Portland cement paste on storage, Meyer¹⁴ found a maximum in the apparent thermal expansion of hardened Portland cement pastes, and carbonation produces maximum shrinkage in cement pastes and compacts as found by the present authors,⁵ lend support to the above explanation.

The irreversible shrinkage that is described in the results on ageing under cyclic conditions of humidity can be considered to be a manifestation of the same process that is

observed under steady-state conditions. In the former case, however, the cycle of drying from a condition of humidity at some intermediate or high value to 0% R.H. involves putting the material through a large surface free-energy change and correspondingly large consolidation and shrinkage forces. The new product experiences large irreversible apparent volume changes as a result of these large forces. A similar result is observed in the case of hydrated Portland cement paste where it may be a reflection of the behaviour of the lime constituent.

It may be noted that with alternating changes in humidity, other compacted systems such as silica and calcium carbonate which were studied previously in the Division of Building Research laboratory show the opposite effect, namely an irreversible expansion.

To compare the ageing shrinkage of lime under steady-state conditions with that of some other materials, compacts of gypsum (solubility in the same order of magnitude as lime) and of illite (insoluble) were exposed to long periods of conditioning at 50% R.H. No evidence was obtained of ageing shrinkage of the type found for lime. Neither was it found for compacts of bottle-hydrated cement. Hunt *et al.*, however, have measured a decrease in surface area in hydrated cement over a period of time.¹ This change showed maximum effects at intermediate evaporable water contents. It would appear therefore that this characteristic of ageing which involves a change in surface area may not always be accompanied by the shrinkage process that occurs for lime compacts.

The type of ageing that involves a change from a pseudo-lattice to a normal lattice has already been mentioned. This may have been a contributing mechanism in the case of the ageing of the Ca(OH)_2 prepared by vapour hydration of CaO which had been prepared in turn by thermal decomposition of reagent grade Ca(OH)_2 . Because of the apparently small contribution of this process, it is probable that the length change observed represents the measurement of the 'tail-end' portion of an initially rapid process.

The concept that new linkages are formed as a result of solution and reprecipitation of lime in areas of contact accounts for the increase in modulus with ageing, even at the higher relative humidities where expansion rather than ageing shrinkage occurs. It explains the increase in rate and magnitude of ageing shrinkage with increase in density of compact, and with increase in surface area of lime.

The experimental results obtained on the volume change characteristics of lime compacts on ageing, both at a constant relative humidity or under alternating conditions, are indicative of changes that can be expected to be transmitted to hardened cement pastes. It is certain that the ageing processes exhibited by lime affect the quantitative measurements of properties of paste, mortar and concrete such as creep, drying shrinkage and strength.

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References

- ¹ Hunt, C. M., Tones, L. A., & Blaine, R. L., *J. Res. natn. Bur. Stand.*, 1960, **64A**, 163
- ² Glasson, D. R., *J. appl. Chem., Lond.*, 1958, **8**, 798
- ³ Gregg, S. J., *J. chem. Soc.*, 1953, p. 3940
- ⁴ Sereda, P. J., & Feldman, R. F., *J. appl. Chem., Lond.*, 1963, **13**, 150
- ⁵ Swenson, E. G., & Sereda, P. J., in the press
- ⁶ Tones, L. A., Hunt, C. M., & Blaine, R. L., *J. Res. natn. Bur. Stand.*, 1957, **59**, 357
- ⁷ Rehbinder, P., & Segalova, E., *Proc. 2nd Int. Congr. on Surface Activity*, 1957, **3**, 492
- ⁸ Gillott, J. E., & Sereda, P. J., *Nature, Lond.*, 1966, **209**, 34
- ⁹ Sereda, P. J., Feldman, R. F., & Swenson, E. G., Symposium on Structure of Portland Cement Paste and Concrete, *Spec. Rep. 90 Highw. Res. Bd.*, 1965
- ¹⁰ Powers, T. C., *Proc. Fourth Int. Symp. on the Chemistry of Cement, Natn. Bur. Stand. Monogr. 43*, 1960, **2**, 577
- ¹¹ Mikhail, R. Sh., *J. phys. Chem., Ithaca*, 1963, **67**, 105
- ¹² Bangham, D. H., *J. Soc. Glass Technol.*, 1947, **31**, 264
- ¹³ Shaler, A. J., *Trans. Am. Inst. Min. metall. Engrs*, 1949, **185**, 796
- ¹⁴ Meyer, S. L., *Proc. 30 Ann. Meet., Highw. Res. Bd.*, 1950, **30**, 193