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Tamtsia, B. T.; Beaudoin, J. J.; Marchand, J.

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Time-dependent load-induced deformation of $\text{Ca}(\text{OH})_2$

B. T. Tamtsia,* J. J. Beaudoin* and J. Marchand†

National Research Council of Canada; Université Laval

Short-term time-dependent strains were monitored on calcium hydroxide compacts having a porosity of 19.7%. The creep experiments were conducted in a controlled environment chamber maintained dry (0% RH) at $22 \pm 2^\circ\text{C}$ with nitrogen purging. Prior to loading, the compact specimens were vacuum dried at 105°C for 3 h (equivalent to D-drying). The applied stress for the creep test corresponds to 5% of the compaction pressure (386 MPa). The $\text{Ca}(\text{OH})_2$ compact specimens were in the form of T-shaped columns with a minimum thickness value (for the web and flanges) less than 1.2 mm. The AC impedance spectra of loaded and unloaded $\text{Ca}(\text{OH})_2$ compact specimens were also monitored in real time. This was achieved by the coupling of the impedance analyser to the creep experiment. An assessment of the relevance of the high frequency arc depression angle obtained from the impedance analysis to an understanding of the load-induced deformation behaviour of the $\text{Ca}(\text{OH})_2$ compacts was made.

Introduction

Calcium hydroxide is a primary reaction product in cement-based materials. It occupies up to about 26% by volume of hydrated Portland cement paste. For this reason its role in determining the engineering properties of these systems is important.

Previous experiments on the mechanical performance of calcium hydroxide compacts have been reported.^{1,2} These include engineering properties of $\text{Ca}(\text{OH})_2$, e.g. strength and modulus of elasticity. Other physical characteristics such as length and mass changes of $\text{Ca}(\text{OH})_2$ under various experimental conditions have been widely investigated.^{3–7} It appears, however, that no information on the time-dependent deformation of

calcium hydroxide under a sustained load has been published.

The microstructure of hydrated Portland cement paste has been characterised by several authors using AC impedance spectroscopy.^{8–14} Cement-based materials generally contain pores having a broad size distribution. These are generally filled or partially filled with electrolyte and are electrically conducting.^{8,9} The pore network continuously changes during the drying process.^{9–11} This change can be detected in AC impedance spectra.^{9–13} In very dry materials the content of the electrolyte is insufficient to cover the internal pore surfaces.¹⁴ Hence the conductivity is significantly changed when drying occurs and is primarily dependent on the electrical properties of the solid.

The main objective of this paper is to identify and evaluate the contribution of calcium hydroxide to the time-dependent deformation of hardened Portland cement paste under sustained load. AC impedance spectroscopy is used in conjunction with creep measurements to assist in understanding the behaviour of $\text{Ca}(\text{OH})_2$ specimens. An interpretation of information from AC impedance spectra in terms of parameters such as the high frequency resistance and the depres-

* Institute for Research in Construction, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

† Department de génie civil, Université Laval, Sainte-Foy, Québec, Canada, G1K 7P4.

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sion angle is attempted in order to understand the deformation process.

Compacts of calcium hydroxide and other hydrated cement minerals as structural models

The use of compacted powders of unhydrated or hydrated cement minerals including calcium hydroxide to form solid bodies for use in studies of engineering behaviour is now well established.^{15,16} For example, both the modulus of elasticity and hardness of cement paste are dependent on porosity and the log mechanical property—porosity relation for cement paste (*in situ* hydrated), ground and compacted cement paste and compacts of bottle hydrated cement are co-linear at porosities in the range of 20–50%. It is apparent that the bonds formed during the hydration reaction are similar to those formed by compaction. It has been argued that the interparticle bonds are solid-to-solid contacts, which are responsible for the limited swelling of cement paste. These bonds appear to be of such a nature that they can be broken and remade without suffering a permanent decrease in mechanical performance. It has been further shown that both the stress intensity factor (derived from fracture mechanics analysis)—porosity and modulus of elasticity—porosity relations for calcium hydroxide compacts yield values (of the corresponding mechanical property) of a magnitude similar to those for Portland cement paste.¹ The absolute values at a given porosity are lower for calcium hydroxide. Sorption phenomena for calcium hydroxide compacts are also similar to those of other inert adsorbents.⁶ Surface area measurements performed on the compacts (using nitrogen as adsorbate) give values of about 12 m²/g, which are consistent with published values.

Impedance spectroscopy

Impedance spectra can be obtained over a wide range of frequencies, allowing for the separation of bulk cement paste and electrode polarisation effects. The high-frequency arc (HFA) is attributed to the bulk paste impedance behaviour and the low-frequency arc to the cement paste—electrode surface capacitance contribution.¹⁷ The impedance spectrum is normally an inclined semi-circle with its centre depressed below the

real axis by a finite angle referred to as the depression angle. This behaviour, often associated with a spread of relaxation times,¹⁸ cannot be described by the classical Debye equation employing a single relaxation time.¹⁹ Interpretation of an impedance spectrum usually involves modelling with an equivalent circuit until the electrical response of the elemental microstructure of the cement paste is well simulated. A dispersive, frequency-dependent element or the constant phase element (CPE)²⁰ can be introduced to account for the shape of the depressed complex plot. The impedance contribution of this element ($Z(\text{CPE})$) can be expressed as follows

$$Z(\text{CPE}) = A_o^{-1}(j\omega)^{-n} \quad (1)$$

where $n = 1 - \theta_d$ and $\theta_d \cdot \pi/2$ is the depression angle. Therefore, n can be used to represent the degree of perfection of the capacitor and is a measure of how far the arc is depressed below the real impedance axis.

Experimental programme

Specimen preparation and characteristics

A special cylindrical mould was made to produce compacts of calcium hydroxide having a thickness of about 6 mm and a diameter of 38 mm. The calcium hydroxide powder was compacted at a pressure of 386 MPa. The chemical analysis of the calcium hydroxide used for this study is presented in Table 1. These compacts were used to cut T-shaped specimens with isopropanol as a lubricant (given the negligible solubility of calcium hydroxide in this solvent). The specimens had a cross-section 7.0 mm deep with a flange width of 12.7 mm and flange and web thickness of 1.2 mm. The specimens were 25.4 mm long. The total porosity of the compacts was determined from the mass and volume of the compacted samples. A solid density for $\text{Ca}(\text{OH})_2$ of 2.24 g/cm³ was used for the calculation. Porosity was found to be 19.7%. The modulus of elasticity of 17.2 GPa was obtained from T-shaped specimens loaded incrementally up to an applied stress of 19.3 MPa (the applied stress for the creep test) which corresponds to 5% of the compaction pressure. The T-shaped specimens were D-dried (vacuum dried at 105°C for 3 h) prior to the creep measurements. D-drying is a term used in cement technology for drying the specimen to the equilibrium vapour pressure of dry ice at –78°C. Vacuum drying cement paste at 105°C

Table 1. Chemical analysis of calcium hydroxide (quantities, %)

Ca(OH) ₂	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	SO ₃	CaSO ₄	CaCO ₃
97.7	0.38	0.05	0.05	0.49	—	0.035	0.15	0.58

for 3 h has given similar sorption isotherms to those produced by conventional D-drying and is considered equivalent.²¹

The creep measurement system

The creep experiment was performed in an environmentally controlled chamber maintained dry (0% RH) at $22 \pm 2^\circ\text{C}$ and flushed with nitrogen. In the chamber, the creep frames were placed in the cells containing a drying agent (magnesium perchlorate). This doubled the protection against carbonation. During the creep experiments, unloaded companion specimens were also placed in the cells in order to determine the environmental effect on the deformation of the T-shaped specimens. No significant variation in length was observed for the unloaded specimen indicating that the creep strains obtained from loaded specimens represented the dry basic creep strains only.

The coupled AC impedance—creep spectral responses were obtained by mounting the T-shaped specimens in a miniature creep frame (two per frame) linking the specimens to a load cell through electrode interfaces connected to a Solartron 1260 frequency response analyser. The details of the creep measurement system are presented elsewhere.²²

Results and discussion

The compliance result is presented in Fig. 1 for which the initial value J_0 was obtained indirectly from the elastic modulus (17.2 GPa) previously determined. It is important to note that the modulus of elasticity obtained by the present approach lies between the values reported previously by Beaudoin¹ and Wittmann² for calcium hydroxide compacts having similar total porosity. From Fig. 1 it can be observed that Ca(OH)_2 compacts do creep and show at the very beginning a trend similar to that observed in cement paste systems. However, during the first half-hour, the

Fig. 1. Compliance (J) of Ca(OH)_2 compacts conditioned at 0% RH and loaded at a stress level corresponding to 5% of the 386 MPa compaction pressure

observed basic creep strain and/or compliance seems to be linear reaching a short steady state at about an hour following the loading. The creep observed at very early times may be due to the rearrangement of the Ca(OH)_2 crystals along preferential planes of minimum energy with an effect of stabilising the specimens. The nature of Ca(OH)_2 in cement paste may not be exactly similar. The possibility that amorphous Ca(OH)_2 (in addition to crystalline Ca(OH)_2) is present in hydrated cement paste in different amounts has been reported.²³ This may alter the nature of its contribution to creep strain of cement paste. The present result is however significant given the large amount of this phase in cement paste (20–26% by volume) and the importance of understanding the role of Ca(OH)_2 in cement-based materials. The random distribution of Ca(OH)_2 in cement pastes has provided evidence that some Ca(OH)_2 may be porous.^{7,24} This is further justification for the use of controlled porosity specimens.

The behaviour of Ca(OH)_2 in cement pastes may follow a similar pattern and may have a greater contribution to creep strain compared to the values observed on loaded Ca(OH)_2 compacts. The previous results on hydrating cement pastes have shown that creep is related to the state of hydration of the paste. However, as the cement paste is hydrating, the formation of C-S-H is accompanied by the precipitation of Ca(OH)_2 . Consideration of C-S-H as the focal point for creep suggests that the basic creep strain observed at the macroscopic level (at the D-dry state) may be a result of sliding of C-S-H sheets with respect to one another and to a lesser extent the deformation of crystalline or amorphous and porous Ca(OH)_2 particles. The contribution of Ca(OH)_2 to creep may be more significant than previously thought. A major problem in quantifying the contribution of Ca(OH)_2 lies with the difficulty in identifying and determining the amount of amorphous and porous Ca(OH)_2 in hydrated cement pastes.

It is important to take into account the fact that the Ca(OH)_2 compacts were loaded at a stress level corresponding to only 5% of the compaction pressure compared to a value of up to 30% of the strength used for tests performed on cement pastes. However, the level of compaction pressure employed corresponds to an applied stress of 19.3 MPa, which is almost twice the stress applied on well hydrated normal strength cement paste. The initial compliance and/or strain of Ca(OH)_2 compacts obtained experimentally was several times greater than the basic creep strain and/or time-dependent compliance (see Fig. 1). It appears that Ca(OH)_2 in cement systems does contribute to their overall deformation. It may however have a greater contribution to the initial deformations than to the long-term deformations. These are, nevertheless, not negligible. The creep recovery of Ca(OH)_2 compacts indicates that part of the deformation taking place after loading (even at 0% relative humidity) is irreversible,

similar to the creep recovery generally observed in cement paste systems. Perhaps the more important observation is that the load-induced strain of D-dried $\text{Ca}(\text{OH})_2$ compacts after 3 days is greater than that observed previously on D-dried Portland cement paste.²² For calculation of stress-strength ratio the compressive strength of $\text{Ca}(\text{OH})_2$ compacts was estimated indirectly from its flexural strength. The applied stress of 19.3 MPa, corresponded to a stress-strength ratio of 0.15. This resulted in a creep strain at 3 days of $320\mu\epsilon$. The well hydrated D-dried Portland cement paste ($w/c = 0.50$) (even at stress-strength ratio of 0.30) was reported to have creep strain of $296\mu\epsilon$ after 3 days.²² These results indicate that despite the lower amount of calcium hydroxide in the cement paste (relative to C-S-H), it may significantly contribute to the observed creep strains.

The impedance spectra of loaded and unloaded $\text{Ca}(\text{OH})_2$ compact specimens were also monitored in the coupled creep experiments. Given the dry state of the $\text{Ca}(\text{OH})_2$ compacts, a conductive metal epoxy was spread at both ends of the specimens in order to improve conductivity at the electrode interface during the impedance measurements. The spectra obtained from unloaded companion specimens were found to be almost similar after 0, 1, 2, 5, 12, 24, 48 and 72 h following conditioning at 0% relative humidity (in a nitrogen atmosphere). In contrast to this, the loaded specimens showed a slight but consistent changing of the spectra during the same period of time. A typical spectrum for the unloaded specimens is presented in Fig. 2. The variation of the change in high frequency resistance R_Ω (defined as the high frequency intercept of the 'bulk paste arc' with the real axis) with the time under load is presented in Fig. 3 illustrating the effect of load alone on R_Ω . The actual impedance data presented correspond to frequencies ranging from 2–70 kHz. The change of the resistance R_Ω with time corresponds to the change in deformation observed during the creep experiments.

It is instructive to consider the impedance spectra obtained in the case where an electrode is in contact

Fig. 2. Complex impedance plot for unloaded $\text{Ca}(\text{OH})_2$ compacts conditioned at 0% RH

Fig. 3. The variation of the change in the high frequency resistance R_Ω for loaded $\text{Ca}(\text{OH})_2$ compacts conditioned at 0% RH at a stress level corresponding to 5% of the 386 MPa compaction pressure

only with an electrolyte solution as reported by Mulder and Sluyters.²⁵ The straight line spectra observed can be represented by equivalent circuit made up of a high frequency resistance in series either with a capacitor or with a constant phase element. The spectra obtained in the present study are all in the form of an arc in the high frequency range and therefore can be represented with an equivalent circuit. The circuit generally consists of a high frequency resistance R_Ω in series with a distributed element (DE) from which the high frequency arc diameter can be obtained as well as the corresponding depression angle parameter n . The arc diameters obtained from the simulation are very large, varying between 3600 kΩ and 35 000 kΩ.

The effect of sustained load on the depression angle parameter n is presented in Fig. 4. The depression angle parameter increases from about 0.947 to 0.966 at 72 h indicating that the degree of perfection of the semi-circle ($n = 1$ is ideal) is increasing and the depression angle itself is decreasing. This indicates that the pore structure is changing under load tending

Fig. 4. The variation of the depression angle parameter n for loaded $\text{Ca}(\text{OH})_2$ compacts conditioned at 0% RH at a stress level corresponding to 5% of the 386 MPa compaction pressure

toward a more uniform distribution. The reason why the spectra obtained here do not show ideal semi-circles in the high frequency range may be due partly to the lack of an electrolyte in the D-dried specimens studied. Non-ideal behaviour is generally observed in Portland cement systems especially with the removal of evaporable water as indicated by Brantervik and Niklasson¹⁴ in their studies of mortar samples from which evaporable water was partially or totally removed.

Conclusions

- (1) $\text{Ca}(\text{OH})_2$ compacts exhibit creep. They show at the very beginning, a creep response similar to that observed in cement systems. This may be due to the structural rearrangement of the $\text{Ca}(\text{OH})_2$ crystals along their preferential planes of minimum energy.
- (2) The contribution to creep strain of $\text{Ca}(\text{OH})_2$ in hardened cement pastes may be different compared to the values observed on loaded $\text{Ca}(\text{OH})_2$ compacts due to the possible presence of both crystalline and amorphous (porous) $\text{Ca}(\text{OH})_2$. However, the creep response of these compacts provide real evidence that creep of calcium hydroxide in cement paste is important.
- (3) AC impedance measurements of loaded calcium hydroxide compacts provide evidence that load is effecting real change in the microstructure of this material.
- (4) The loaded $\text{Ca}(\text{OH})_2$ compact specimens showed a slight but consistent real-time change of the high frequency resistance with time.
- (5) The depression angle parameter n increases rapidly during the first six hours followed by a very slight variation. The increase in n with time suggests that the pore structure is changing under load possibly tending to greater uniformity.

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