Kinetics of Moisture Expansion in Fired Clay Ceramics: A (Time)$^{1/4}$ Law

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We report the results of experiments to estimate the moisture expansion of several modern and ancient clay brick ceramics from the time of manufacture. From these data we propose a new expansion law, in which the expansive strain increases as (age)$^{1/4}$ approximately. Such time dependence is consistent with a mechanism in which expansion arises from a diffusion-controlled rehydration reaction on a linear or low-dimension structure. Our results provide new guidance for the engineering design of masonry and suggest a possible new method for archaeological dating of ceramics.

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Long term moisture expansion is a classic and important property of fired clay ceramic materials. It is an example of a chemically driven deformation, and is one of a class of chemomechanical phenomena found widely in engineering and biology. Despite extensive study no unifying description of this expansion process in ceramics has yet been developed. It has long been recognized that all fired clay ceramics used in the manufacture of brick, tile, and pottery expand on aging and that this is associated with the slow chemisorptive uptake of water. That such moisture expansion is one cause of the crazing of ceramic glazes was first proposed by Schurecht [1] in 1928. The first observation of cracking in brick masonry that could be reliably attributed to moisture expansion did not come until later [2], and was concurrent with the introduction of hard cement-based mortars. Before that time brickwork had been built with softer lime-based mortars which were able to absorb the expansive strains in the bricks without damage to the overall structure. In modern masonry construction, the long term expansion of clay bricks is accommodated by providing movement joints which take up the moisture expansion. For engineering design it is therefore necessary to be able to estimate the magnitude of this expansion over the life of the structure.

Although there have been many studies of moisture expansion in clay bricks, these have concentrated on monitoring expansive strains in freshly fired bricks over necessarily limited time scales [3,4]. In this Letter, we present new data which we believe give a capsule view of the expansion process over much greater times and which suggest a new general relationship defining the kinetics of moisture expansion in fired clay ceramic materials. These data have been obtained from short term measurements of the expansions of freshly fired bricks; from estimates of the total cumulative expansions that have occurred in specimens of Roman, 19th century, and modern bricks; and from measurements of the expansions produced by various hydrothermal treatments of brick ceramic.

A mechanical gauge system was used to measure dimensional changes of brick specimens consisting both of whole bricks and slices of brick. The reference points between which expansion was measured were marked on metal discs located in small cavities drilled into the surfaces of the specimens. To eliminate the effects of variability between different bricks of the same type each result presented here is the mean of measurements made on two sets of reference points on a single specimen. The pairs of measurements agreed to better than 3%. Expansive strains ϵ were first measured on a series of freshly fired bricks of the same type as these were exposed to a range of different environmental conditions. In Fig. 1 we show the expansion vs time curve for one of these bricks as it ages under ambient conditions in the open laboratory (approximately 20 °C, 50% relative

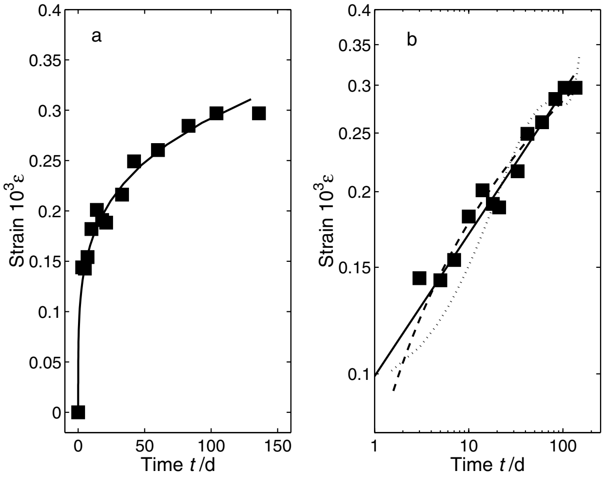

FIG. 1. The expansion of a freshly fired brick aging under ambient conditions (approximately 20 °C, 50% relative humidity) in the laboratory. The solid line is the power-law fit $\epsilon = 9.9 \times 10^{-5}(t/\mathrm{d})^{0.24}$. (a) Linear axes. (b) Log axes; logarithmic (dashed line) and polynomial (dotted line) regression fits are shown for comparison.

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humidity). The same brick ceramic stored under vacuum shows no expansion over the same period of time. We conclude that the brick ceramic takes up water from the atmosphere to sustain the expansive reaction. We note that the mass gain of the sample is proportional to the expansive strain [5]. In Fig. 1 we show expansion vs time data plotted on both linear and logarithmic axes. The power-law character of the data is evident in Fig. 1(b) and we see that the expansion increases as $(\text{time})^{1/4}$ approximately. Simple polynomial functions cannot be fitted satisfactorily to the data. A logarithmic function $\epsilon = a\log(bt)$ can achieve an adequate fit over limited time scales, but the behavior of this function is unsatisfactory as $t \rightarrow 0$; and it does not provide an acceptable fit over long time scales as we show later (Fig. 4).

Some exploratory experiments show that the early time expansions are rather insensitive to the environmental conditions provided only that some water is available. In Fig. 2 we compare the total expansions of specimens of the same type of freshly fired brick subject to a range of treatments varying in temperature and water activity. In respect of accelerating the expansion process, steaming at 100 °C for 6 h (*A*) produces a similar expansion to that which is produced in a similar sample that was aged for 104 d in the laboratory (*B*). Much greater expansion results from steam autoclaving at 186 °C (*H*), and if we extrapolate the best fit curve of Fig. 1 we predict that over 200 yr of laboratory aging would be needed to produce a similar expansion to that resulting from the autoclaving process. The other results *B*–*G* in Fig. 2 show the effects of differences in environment on the total expansion produced after 104 d. Comparing results *C*, *D*, and *E* with *B* we see that aging in saturated conditions results in a significant increase in expansion over that produced in the relatively dry laboratory conditions. Results *C* and *D* are similar, indicating that increasing the temperature to 50 °C has little effect. However, comparing results *F* and *G* with *B* shows that increasing the temperature to 105 °C (with or without cyclic wetting and drying) has a much greater expansive effect

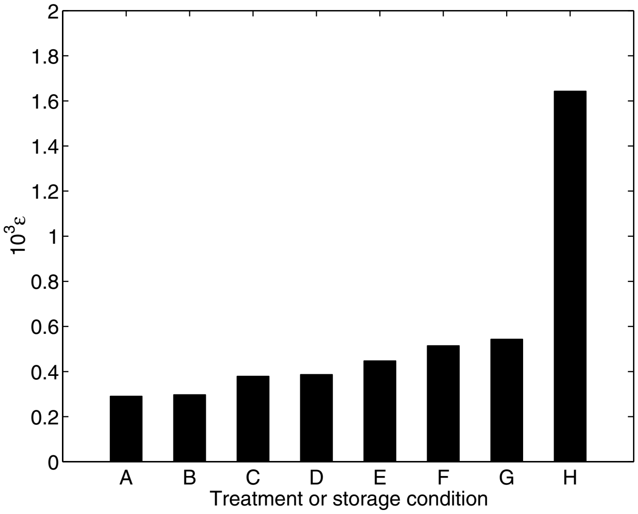

FIG. 2. The expansion of freshly fired bricks subject to different treatments. *A*: steaming at 100 °C for 6 h; *B*: aging in ambient laboratory conditions for 104 d; *C*: aging under water at 20 °C for 104 d; *D*: aging under water at 50 °C for 104 d; *E*: aging in 100% relative humidity at 20 °C for 104 d; *F*: aging at 105 °C in a ventilated oven for 104 d; *G*: alternate vacuum saturation with water and oven drying, total of 14 separate saturations over 104 d; *H*: steam autoclaving at 1.15 MPa, 186 °C for 4 h.

While such measurements give useful information on the kinetics and magnitude of the early time expansion, data are needed over much longer time scales. To estimate long term expansions, we have examined a set of bricks of different ages, to each of which we have applied two test procedures. First, we estimate the expansion which has already occurred in natural aging by heating the material at 450 °C for 2 h to drive off the chemisorbed water and cause the specimens to contract to their original as-fired sizes. Consistent with the results reported by McBurney [2] and by Schurecht [1] we find that heating at these temperatures removes the expansions produced in bricks aged in the laboratory, including those subject to high pressure steaming. Second, we use steam autoclaving at 186 °C to provide an estimate of the long term potential expansion. The choice of autoclaving schedule was based in part on the work of Smith [4] who showed that a similar schedule produced specimens that remained stable throughout 28 yr of exposure. As already noted our data suggest that this treatment produces expansions equivalent to hundreds of years of exposure. These two procedures were applied to specimens of modern bricks that had been stored in the laboratory for 20 yr, to specimens of 19th century bricks that were approximately 120 yr old, and to specimens of Roman bricks from the 2nd century A.D. The clays used in the manufacture of the new and 20 yr old bricks were coal measures shales from the English Midlands, which were fired at about 1100 °C. The 19th century bricks had been made from similar clays from the same region. The Roman bricks were from London and from Lancashire. Both would have been made from surface clays. The structure of both 19th century and Roman bricks indicated that they had been hard burnt, as had the modern bricks.

In Fig. 3 we show the strains obtained in a series of experiments in which each specimen is first steam autoclaved (producing strain ϵ_1), then heated to 450 °C (ϵ_2) and finally steam autoclaved once again (ϵ_3). All strains are calculated by reference to the initial length before treatment. The dimensions of the specimens after the second steam autoclaving treatment are approximately the same as after the first ($\epsilon_1 \approx \epsilon_3$). This gives us confidence that the treatments are appropriate. For a brick material of any age we suggest that the magnitude of the contractile strain on heating to 450 °C ($|\epsilon_2|$) is equal to the cumulative expansion that has occurred since manufacture, while the expansive strain after steam

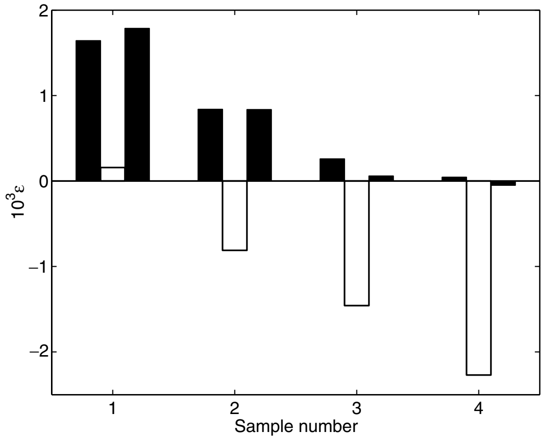

FIG. 3. Strain ϵ produced by steam autoclaving and heating four clay bricks of different ages. Zero strain corresponds to the initial condition of each brick. The solid bars represent strains resulting from steam autoclaving as in Fig. 2. The open bars represent strains resulting from heating at 450 °C for 2 h. The cycle of treatments in each case was autoclaving, heating, autoclaving, reading from the left for each sample. 1: Kiln fresh brick; 2: 20 yr old brick; 3: 19th century brick (120 yr old); 4: Roman brick (1900 yr old).

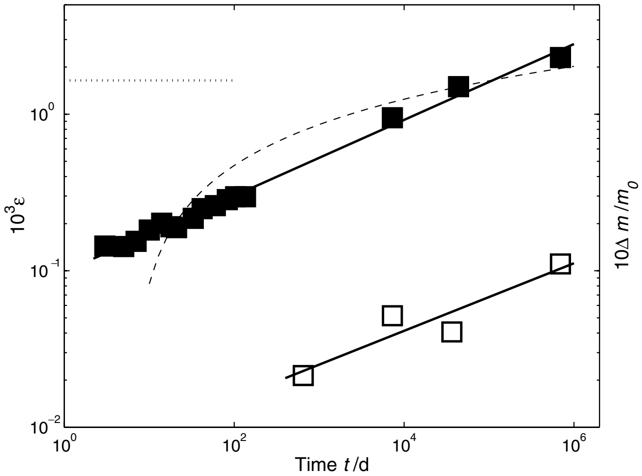

FIG. 4. The total expansive strain ϵ (solid squares) and fractional mass gain $\Delta m/m_0$ (open squares) from the time of original manufacture for bricks tested. The power-law regression equations are $\epsilon = 9.87 \times 10^{-5}(t/d)^{0.24}$ and $\Delta m/m_0 = 5.7 \times 10^{-4}(t/d)^{0.22}$ where t is the time. The dashed curve is the best fit logarithmic function. The dotted horizontal line shows the strain produced by autoclaving a freshly fired brick as in Fig. 2.

autoclaving is an indication of the potential further expansion. The sum of contraction and expansion strains $|\epsilon_2| + \epsilon_1$ gives an estimate of the long term potential expansion strain from the time of manufacture. The results show that this long term potential strain is much the same for the new, 20 yr old, and 120 yr old bricks. (For these bricks the sum of heating and autoclaving strains are seen to be consistent to within less than 7%.) This is to be expected because the autoclaving schedule adopted is equivalent to a much longer period of aging than 120 yr. The Roman brick specimens showed a greater total strain, reflecting their much greater age.

The data obtained from the older bricks are remarkable because they are consistent with the short term expansion data obtained from freshly fired bricks. Thus the Roman brick data show that a relatively large expansive strain (~ 0.0023) has already occurred over the 1900 yr since they were made. A similar total strain is also obtained by extrapolating the empirical equation fitted to the data of Fig. 1 over 4 orders of magnitude in time. The contractions produced by heating the bricks that were 20 yr old and those that were 120 yr old are also entirely consistent with the short-time data. The steam autoclaving treatment shows clearly that there remains some expansive reactivity in the 20 yr old and 120 yr old bricks. It would be necessary to design a longer/higher temperature autoclaving treatment to produce expansions equivalent to thousands of years of aging, but it is significant that the autoclaving treatment used has been adequate to reverse the heating contractions in the Roman bricks.

The strain–time data for all bricks are plotted in Fig. 4. Fitting an empirical equation to these results shows that the expansion increases from the time of original firing as $(\text{time})^{1/4}$ approximately, just as for the short term expansion data shown in Fig. 1. This is a better representation of the data than the logarithmic law used elsewhere [5,6]. The slow power-law kinetics strongly suggests a diffusion-controlled process on a structure of low dimensionality [7–9]. Such would be the case for migration of water molecules via linear defects or grain boundaries to fixed rehydroxylation sites acting as traps (an $A + B \longrightarrow 0$ annihilation reaction). As we show in Fig. 4, the mass gain is proportional to the expansive strain.

It is well established that clays which have been fired only lightly, certainly to 550 °C but in some cases to as high as 930 °C, show some rehydroxylation or rehydration [10,11] when exposed to water or water vapor. The evidence comes from experiments of rather short duration (mostly hours and days). We suggest that bricks which have been fired to considerably higher temperatures must retain some capacity for at least a small amount of rehydroxylation/rehydration on a longer time scale, and that some brick ceramics contain small quantities of material which has not been fully transformed into stable substances. From studies of ancient pottery, Shoval *et al.* [12] associate the potential for rehydroxylation with the presence of amorphous matter in the fired clay. We have synchrotron x-ray diffraction data on these and other brick ceramic specimens that indicate a high content of amorphous materials, as found also by Dondi *et al.* [13].

For a molecule (in this case a water molecule) diffusing in three dimensions, the mean square displacement $\langle r^2 \rangle$ varies as t. However, when the diffusion of molecules is restricted to a one dimensional structure $\langle r^2 \rangle \sim t^{1/2}$ [14]. We suggest that the reaction which causes expansion of fired clay ceramics involves the diffusion of water molecules (A) within a low-dimension system which contains rehydroxylation sites (B), and that A reacts irreversibly as soon as it encounters a B site. Following the notation of Mojaradi and Sahimi [7] the reaction is an annihilation process of the form $A + B \rightarrow 0$. The progress of the reaction depends on the rate at which diffusing water molecules encounter B sites. We envisage the water molecule A diffusing down linear pathways along which there is a uniform distribution of B reaction sites. As one water molecule diffuses along such a path it is chemisorbed as soon as it encounters the first reaction site. A second molecule continues along the same path until it encounters the second reaction site and so on. The distance covered by diffusing water molecules along such a linear pathway is proportional to $t^{1/4}$ and this is proportional to the number of sites encountered. Hence the progress of the reaction $A + B \rightarrow 0$ is also proportional to $t^{1/4}$.

Microstructural studies show that clay bricks typically possess a network of well connected micron-scale tubiform pores [15]. However, the results given in Fig. 2, which compares the early stage expansion of brick in different environments, show that even filling these pores with water by complete saturation under vacuum does not greatly increase the expansion rate. Because these pores are extremely large compared to the size of water molecules we speculate that any reaction sites located on the surfaces of the pore system are eliminated immediately by combination with available water molecules. This is consistent with the fact that the expansion vs time curves did not vary with specimen size. Indeed it is likely that reactions on the surfaces of the pores occur within minutes of clay brick being removed from the kiln after manufacture. The diffusion process which results in $t^{1/4}$ expansion is orders of magnitude slower and must therefore involve water molecules moving to reaction sites through networks that are on a much finer scale than the observed pore structure, probably associated with grain boundary and other defects which can produce pathways of similar dimensions to those of a diffusing water molecule. The atomic arrangements in clay materials produce sheet structures. The junctions between sheets that are not coplanar produce lines of discontinuity. These may form the random linear pathways of the type needed to produce $t^{1/4}$ kinetics. That the data from 19th century and Roman bricks fit a common expansion–time curve reflects the similarities in these ceramics, although it has been shown that the source clay mineralogy does not exert a strong influence on moisture expansion [16]. On the other hand Smith [4] has reported that firing temperature does have a significant effect on expansion, higher firing temperatures being associated with smaller expansions. These results are consistent with our model. Higher firing temperatures result in increased mineralization and sintering and therefore tend to reduce the number of linear pathways available for diffusing water molecules.

In this Letter, we have shown that the moisture expansion of fired clay ceramics can be described approximately by a $t^{1/4}$ law. This new expansion law should be of value both in engineering design and, more speculatively, in archaeological dating. Modern brick masonry structures, which are designed to have a life of a century or more, are built using hard cement mortars that lack the compliance of earlier lime-based mixes. The $t^{1/4}$ law shows that expansion is a continuing process which, in the absence of movement joints, must produce increasing compressive stresses in brickwork. Taken as a whole our data indicate that moisture expansions are not much influenced by the environmental conditions to which bricks are normally exposed in construction engineering.

For archaeological dating, our results suggest that heating a ceramic sample of unknown age to 450 °C returns the sample to its as-fired state. If we have well established calibration data on the $t^{1/4}$ expansion kinetics of ceramics of similar mineralogy, then the age can be estimated by measuring the heating contraction.

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