journal

J. Am. Ceram. Soc., 98 [2] 398–401 (2015)
DOI: 10.1111/jace.13336

Experimental Variability in Kinetics of Moisture Expansion and Mass Gain in Ceramics

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The rehydroxylation dating method of archeological fired-clay artifacts relies on the reliability of the (time)$^{1/4}$ power law model considered for long-term moisture expansion and mass gain in ceramics. Here, we reanalyze different moisture expansion datasets that were previously used to verify this model. We show that these data obey an accurate (time)$^{1/N}$ power law, but they reveal a variability in the values of the exponent $1/N$ between ~1/2 and ~1/4. It is possible that this value is an intrinsic property of ceramics, naturally varying between a behavior governed by a Brownian process ($t^{1/2}$ power law) and a behavior controlled by a one-dimensional diffusion process ($t^{1/4}$ power law).

I. Introduction

Wilson *et al.*[1] and Hall *et al.*,[2] hereafter referred to as W2003 and H2011, found that moisture expansion data from industrial fired-clay bricks, sometimes acquired over several decades, follow a time power law in $t^{1/4}$. This observation is particularly important because it constitutes the fundamental condition of the rehydroxylation (RHX) dating method of fired-clay ceramic artifacts proposed by Wilson *et al.*[3] Let us recall that it has been shown that moisture expansion and mass-gain variations in ceramics follow the same kinetics [e.g., Ref. (4)]. Since the seminal article of Wilson *et al.*,[3] other groups around the world have tried to reproduce this method, but without success [e.g., Ref. 5–9)]. These studies highlighted several complexities with the method and in particular, the foundation of the RHX dating method itself, that is, the universality of the $t^{1/4}$ time power law.[5,6,8,9]

From numerical simulations, Le Goff and Gallet[8] illustrated the difficulty to experimentally confirm the $t^{1/4}$ power law model, which requires extreme precision in mass measurement, and especially problems surrounding the fit of the data using a (time)$^{1/N}$ power law. Moreover, RHX datasets obtained over several weeks by Le Goff and Gallet[8] from fired-clay (pottery and bricks) samples of different ages and geographical origins showed mass variations behaving according to a $t^{1/N}$ power law, in agreement with H2011, except that N varies between ~3 and ~5 [see also Ref. 5,6)]. The divergent values of N could explain both the concave and convex mass-gain behaviors recently described by Wilson *et al.*[10] and Le Goff and Gallet[9] [see also Ref. (11)].

The H2011 paper is particularly interesting because it presents moisture expansion data that are at the origin of the determination of exponent ¼ for the time power law. For this reason, and given our results, we reanalyze the H2011 data. Furthermore, H2011 did not use a statistical method to obtain the optimal exponent 1/N for the $t^{1/N}$ law fit of the data. Here, we show that the H2011 data describe a $t^{1/N}$ power law model, yet the uniqueness of a ¼ exponent is unfounded.

II. Methods

The nine datasets reported in H2011 were acquired over periods of several years to tens of years. These durations are much longer than that of the RHX experiments proposed by Wilson *et al.*,[3] which do not exceed a few weeks. The H2011 data are thus essential to extend the validity of the $t^{1/4}$ power law over archeological periods. In addition to the original moisture expansion data provided in Zsembery *et al.*,[12] we digitalized the H2011 data shown in their figs. 3, 4, 5, and 6 (vectorial plots). The comparison between the data reported in Table I (H2011) and the digitalized data (middle curve of fig. 3) shows a very good agreement, to within half of the last significant digit of the expansion values (in %) and better than the 1/1000th of a year in the time domain.

It is of interest to stress some peculiarities of the (re) hydroxylation phenomenon. Variations obeying a $t^{1/4}$ power law imply that the first 10% of the total expansion are achieved over a time interval 10 000 times shorter that the entire duration of the experiment, that is, 2 d or 12 h according to the longest and shortest datasets analyzed by H2011 (58 and 13 yr, respectively). Another point is that the time ($t_0 = 0$) of the "true" start of the (re)hydroxylation process is difficult to determine after the heating of ceramics. Furthermore, even if t_0 is known (for instance using vacuum or desiccation), ε at $t = 0$ does essentially represent the beginning of a (re)hydration stage (referred to as stage I), which superimposes itself to the "true" (re)hydroxylation, as first shown by Savage *et al.*[4] Therefore, in addition to strictly metrological difficulties, the $\varepsilon(t = 0)$ value cannot be directly measured.

For this reason, when dealing with (re)hydroxylation purposes, most authors use an equation with only two free parameters (α and ε_0), which we write here with an additional parameter $1/N$ (i.e., not fixing this exponent to ¼):

$$\varepsilon(t) = \alpha t^{(1/N)} + \varepsilon_0 \quad (1)$$

where α is the (re)hydroxylation rate constant and ε_0 is a rapid transient expansion which occurs immediately after the firing and which stabilizes within (at most) several days [see in Ref. (2)].

Because the additive term ε_0 is not zero, the use of linear regression in Ln(ε) vs. Ln(t) space for determining the best $1/N$ is not safe. Any offset indeed causes a significant bias in the Ln(ε) vs. Ln(t) analysis, that is, a nonlinearity in the graphic representation, leading to erroneous or uncertain $1/N$ estimates. In this study, we used the method of determining the best fit to Eq. (1), in the mean-squared sense, which relies

J. Ferreira—contributing editor

Manuscript No. 35242. Received July 4, 2014; approved October 17, 2014.
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on finding the $1/N$ value, α and ε_0 that maximize the regression coefficient r^2, the latter becoming closer to one as the sum of the squared deviations between the expansion data $\varepsilon(t)$ and the calculations is closer to zero. This r^2 coefficient is thus very useful to express the quality of the fit to experimental data. In addition to determining $1/N$ with the highest r^2 value, we also calculated how r^2 varies as a function of $1/N$. We further assessed the stability of our results for each dataset through a jackknife approach, that is, by successively removing one datum and by computing each time a new curve $r^2 = f(1/N)$. Each panel of Fig. 1 contains the curve computed using all available data (shown with yellow circles; the value of r^2 obtained with $N = 4$ is represented by a larger circle), together with a number of curves equal to the number of data in the given series.

We also illustrated the predictability of a $(\text{time})^{1/N}$ power law. For this, we applied a method simply based on the comparison between a fit computed using the moisture expansion data available within a certain time interval, chosen from the beginning of the experiment, and the data obtained later, which are not used in the computations (Fig. 2).

III. Results and Discussion

First we consider the data obtained by Zsembery *et al.*[12] These data result from a 35-yr-long experiment over 300 Australian fired-clay bricks that were grouped according to their steam autoclave expansions, 0.005% [Fig. 1(a), upper curve in fig. 3 of H2011], a global average [Fig. 1(b); middle curve in fig. 3 of H2011], and 0.075% [Fig. 1(c); lower curve in fig. 3 of H2011]. Here, we show that if the values for the 0.075% steam autoclave expansion indeed behave according to a $(\text{time})^{1/N}$ power law with an exponent $1/N$ very close to 0.25 [$1/N = 0.240$ with all the data, Fig. 1(a)], the "best" $1/N$ for the two other expansion datasets is in all cases arguably closer to 1/3 [0.325 for the global average and 0.378 for the 0.005% steam autoclave expansion when considering all data; Figs. 1(b) and (c)].

The global average moisture expansion dataset obtained by Zsembery *et al.*[12] were used by Hall *et al.*[2] to attest the undeniable superiority of the $t^{1/4}$ power law fit relative to that derived from a logarithmic model (see their fig. 2). For this dataset, we tested the predictability of a $t^{1/N}$ power law using 3 and 10 yr of data, with different values of $1/N$ (0.25, 0.325, and 0.4; recall that 0.325 is the best $1/N$ value previously determined). Figure 2 shows the excellent prediction

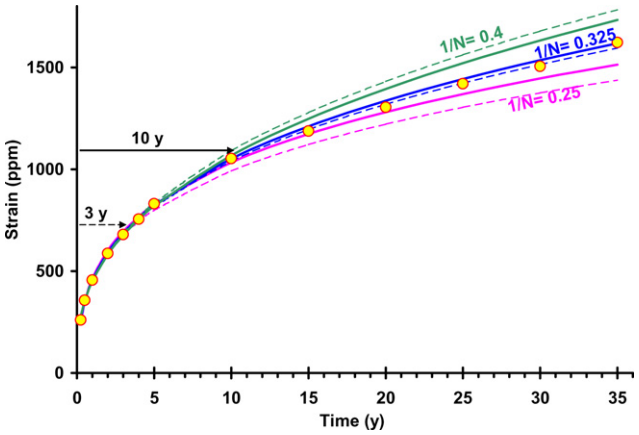

Fig. 2. Example of predictability of a $\text{time}^{1/N}$ power law for the global average moisture expansion dataset obtained over 35 yr by Zsembery *et al.*[12] The approach consists in comparing the fits computed using the first 3 and 10 yr of data (dashed and continuous curves, respectively), with different values of $1/N$ (0.25, 0.325, and 0.4; see color code on the figure) to the data obtained later.

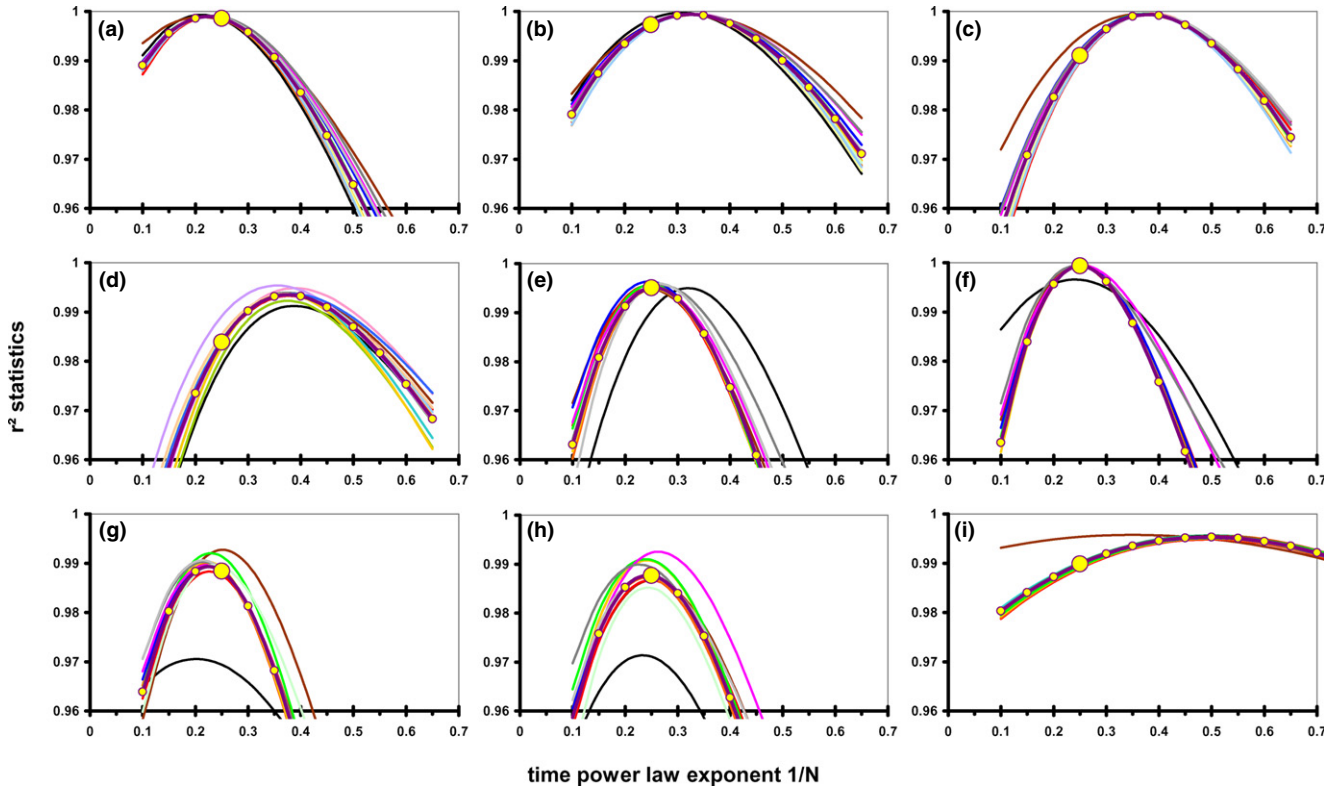

Fig. 1. Search of the exponent $1/N$ of the power law in $\text{time}^{1/N}$ best fitting the nine expansion datasets used by Hall *et al.*[2] In each panel, the variations in r^2 statistics are reported as a function of $1/N$. The curve in violet with yellow dots (the largest dot highlights the "theoretical" value of 0.25) corresponds to the computations performed using all the available data. The other curves are obtained after the successive removal of one datum from the concerned dataset (in brown, after removing the first datum; in black, after removing the last datum). Panels (a)–(c), (d), (e)–(h), and (i), respectively, display the data reported in fig. 3 (top, middle, and bottom curves), fig. 4, fig. 5 (curves a, b, c, and d) and in fig. 6. in Hall *et al.*[2]

provided by a time power law in $t^{1/N\ =\ 0.325}$, even when the fit is computed using only the first 3 yr of data (i.e., about one tenth of the total duration of this experiment). The predictability of this fit is undoubtedly better than that of the $t^{1/4}$ power law. We observe for instance that the predictability of the $t^{1/N\ =\ 0.325}$ time power law computed using the first 3 yr of data is much better than that of the $t^{1/4}$ power law model derived from the first 10 yr of data.

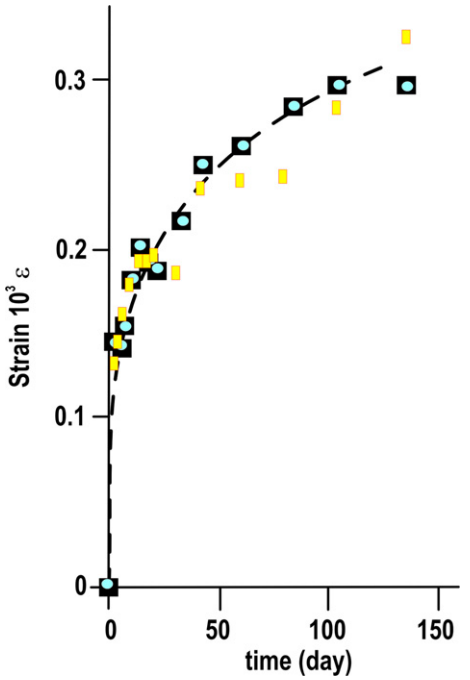

Fig. 3. Comparison between the expansion dataset acquired by Wilson *et al.*[1] over a period of 136 d (black squares and blue dots; see discussion in the text) and the data (yellow rectangles) stated as equivalent by Hall *et al.*[2] and reported in their fig. 4.

We next look at the series of data displayed in fig. 4 of H2011 [our Fig. 1(d)]. This dataset is described as an extension to 13 yr of the data previously obtained by W2003 over a period of 136 d. Figure 3 shows the W2003 data [black squares from a bitmap of their fig. 1(a)]. Our dataset, also reported in Fig. 3, was created by considering the centre point of the squares (blue dots) and the first 13 data points (yellow rectangles) digitalized from fig. 4 of H2011. Contrary to what is asserted by H2011, the latter series is surprisingly different from W2003. The dates do coincide, but the expansion values are significantly different. Therefore, these are two different series of data but we lack information in H2011 and W2003. In both cases, the scatter of the data does not allow one to state that they obey an accurate $t^{1/4}$ power law (recall the numerical simulations in Le Goff and Gallet.[8] Figure 4 compares the computations carried out from the two 136 d long series of data. The effects due to scatter are considerable, which is illustrated both by low values of r^2 and by significant differences between the curves computed after removing a single datum from each series. The use of the expansion value at $t = 0$, as carried out by W2003, which is very remote from the subsequent data points, strongly influences the fit that can be computed. Note that the W2003 study was performed before the discovery of the stage I by Savage *et al.*[4] and consequently, this value is probably biased. Furthermore, one sees that the use of the moisture expansion value at 136 d significantly changes the estimate of $1/N$ in both cases, better approximating 1/4 in one case [panel (f)] but high divergent in the other [~1/2, panel (c)]. On another hand, Fig. 1(c) clearly shows that the extension of the W2003 data to 13 yr reported in H2011 leads to a $1/N$ value of ~0.4.

The reanalysis of the length data obtained by Johnson;[13] see also Cole[14] from a 50-m long wall built in 1908 at the National Physical Laboratory (NPL, UK) is also striking (fig. 6 in H2011). Using these data, H2011 concluded that the fit of the data to a time$^{1/4}$ power law model was "*remarkable*", with L_0 (the initial length) = 49.9806 m, i.e., 2 cm less than the nominal length. No indication for such a difference

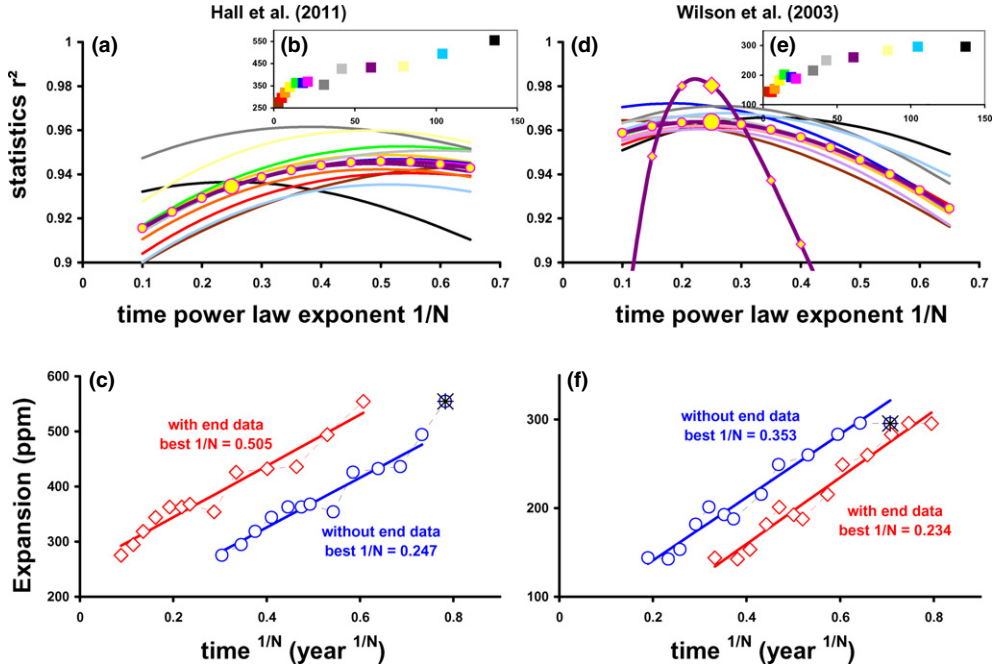

Fig. 4. Analysis and comparison between the two datasets displayed in Fig. 3. The left (a)–(c) and right (d)–(f) panels, respectively, use the 136-d dataset shown in fig. 4 of Hall *et al.*[2] and the data described by Wilson *et al.*;[1] see their fig. 1). Panels (a), (d): curves of r^2 variations computed after removing each time a different datum from the dataset (see text). The curve with yellow diamond in panel (d) was computed using the data point at $t = 0$ ($\varepsilon = 0$). Insets (b) and (e) show the individual moisture expansion data with the same color code as for the curves computed in panels (a) and (d) after exclusion of the concerned data point. Panels (c) and (f) illustrate the influence in both series of the last datum on the computations of the exponent $1/N$.

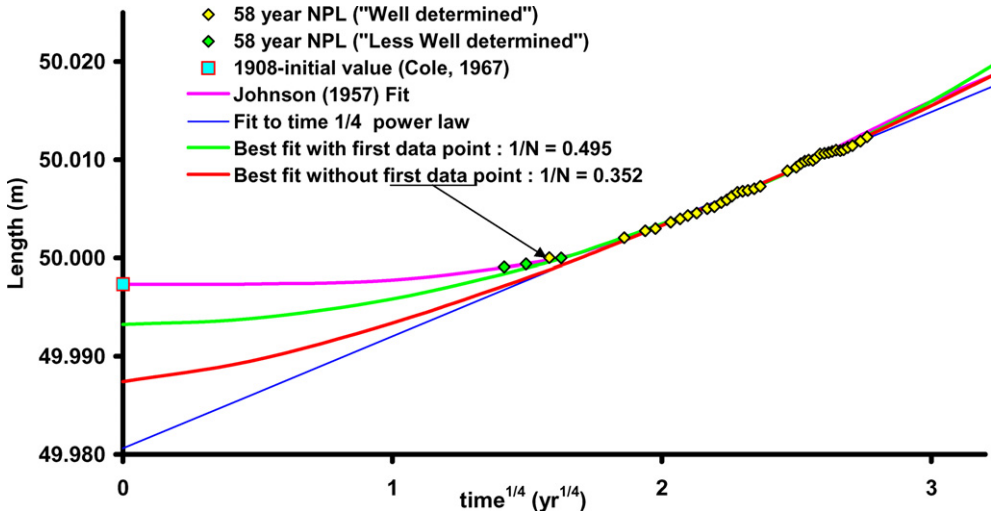

Fig. 5. Comparison between different fits obtained from length data acquired from a 58-yr-long moisture expansion experiment conducted at NPL; [13,14] see also fig. 6 of [2]. Details are provided in the Figure.

is found in Johnson,[13] whereas Cole[14] reported an initial length in 1908 of 49.99734 m. The data are displayed in Fig. 5 (yellow diamonds; note that these data are annual means standardized at 20°C), together with the initial length provided by Cole[14] (square) and three additional data obtained during the first 7 yr of the observation (green diamonds) but which are considered as "less well determined" by Johnson[13] (these data were omitted in the computations by H2011 and in this study). Figure 5 clearly shows that the best fit of the "well determined" data to a $t^{1/N}$ time power law model gives a $1/N$ exponent close to ½ rather than ¼ [see also Fig. 1(i)].

Our investigations suggest that the four 28-yr-long expansion datasets, selected among 37 different series of data obtained from British bricks by Smith,[15,16] obey a $t^{1/4}$ power law model [Figs. 1(e)–(h)]. We note, however, a puzzling effect in r^2 when removing the last datum from each dataset, and the fact that the first series [curve "a" in fig. 5 of H2011; Fig. 1(e)] is far from reaching an expansion value of 0% at $t = 0$ (−0.03%). Finally, concerning the Smith[15] data, Hall *et al.*[2] noted values for $r^2 \geq 0.98$ as an argument in favor of exponent 1/4. Our Fig. 1 clearly shows that such high r^2 statistics are not sufficient to discard other $1/N$ values.

IV. Conclusion

Our analyses show that currently available moisture expansion and/or mass-gain data do not allow one to conclude that the (re)hydroxylation process acting in archeological or industrial fired-clay materials systematically and accurately follows a $t^{¼}$ power law. The data used by H2011 indicate a high variability in the exponent values of $1/N$, similar to that observed in archeological fired-clay ceramic artifacts.[8] It is worth mentioning that this variability does not originate from the energy of activation characterizing each studied sample.[9,17] It is possible that the $1/N$ value is an intrinsic property of the earthenware, depending on the nature of clays and/or on the temperature reached during the original firing of the ceramics. It may also be possible that the experimental conditions (temperature, relative humidity) have some influence on the underlying process. The kinetics of moisture expansion (or of the mass-gain variations) in fired-clay ceramics may naturally vary between a behavior governed by a Brownian process ($t^{1/2}$ power law) and a behavior controlled by a one-dimensional diffusion process [$t^{1/4}$ power law; e.g., Ref. (18)]. It is clear that the observed variability in exponent $1/N$ has crucial implications for the validity and applicability of the RHX dating method as proposed by Wilson *et al.*[3]

Acknowledgments

We are grateful to Stuart Gilder, who made a careful reading of our manuscript, and two anonymous reviewers. We also thank Eva Fareau for her documentary assistance. This work was supported by IPGP and INSU-CNRS via the PNP program. This is IPGP contribution no. 3582.

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