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International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on Historical Masonry
22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

INFLUENCE OF pH DURING CHEMICAL WEATHERING OF BRICKS: LONG TERM EXPOSURE

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Abstract
Within the framework of environmental weathering of bricks in historical structures, this study focuses on new bricks currently employed for restoration projects. The bricks were subjected to an accelerated chemical weathering test by immersion in solutions with pH ranging from 3 to 13 for different lengths of time up to 432 days, data to 288 days are presented since the project is still ongoing. The study analyzed the changes of pH induced in the solutions by the presence of the bricks (this also served to adjust the pH to the intended value), as well as the concentration of various ions extracted from the bricks over time. As the bricks were taken out at the different times, their capillary absorption curves were determined, followed by a vacuum saturation with water for the determination of the open porosity, as well as the density. Finally, a 24 hour total immersion in water was also carried out proving to be practically the same as achieved after the capillary absorption rate stabilized after 6 hours in this test. The results obtained showed that the two main deterioration mechanisms are the ion-exchange at acid pH, and the alkaline corrosion undergone particularly at pH 13.

1. Introduction

The bricks used in this study are those currently employed for restoration projects, such as at the fortress walls surrounding the Royal Castle of Kronborg at Helsingør—made famous by Shakespeare in Hamlet—which was added to the UNESCO World Heritage List in 2000. The restoration started some 20 years ago and is still ongoing. So far there has been no indication of initial weathering of these bricks and none have been replaced according to the supervisory architect.

Historic brick masonry buildings have a long service life during which they can deteriorate, for example from acid precipitation [1,2]; or salt crystallization [3-5]. This will entail repairs and

International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on Historical Masonry
22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

treatments for their conservation, i.e., desalination [6,7]; or repointing [8-10]. While many studies have focused on mechanical failure of brick masonry materials, the slower chemical deterioration has only been explored to a limited extent. Many examples have documented how the wrong choice of materials for repairs results in chemical induced deterioration in the original material [9,11,12]. But because this is a slow process it has not received the attention it deserves.

In a preliminary large scale study [13] a correlation could be established between the weathering of fired clay bricks exposed to water with acid or alkaline pH and the glass phase theory [14-16]. However, several results were puzzling so the study was repeated and extended to include a highly alkaline solution (pH 13) and immersion lengths to 288 and 432 days. Since during the preliminary study it was noted that the pH of the solution changed over time, here the pH of the solutions was monitored regularly and regulated by addition of sulfuric acid and/or sodium hydroxide and data up to 340 days is reported.

2.   Materials and Methods

2.1 Brick
The bricks used in the study are produced by Falkenløwe A/S, in Sønderburg, for restoration of historic brick structures. They are generally called Munkesten because they have the dimensions of old traditional Danish bricks (~ 28x7x14 cm) [17]. The medium red colored bricks were chosen for this study and specimens of approximately 11x5x5 cm, were cut from the center of the brick.

2.2 Weathering
The brick specimens were totally immersed in solutions having different pH values and varying immersion times at about 20ºC. A total of 30 specimens were used, with 5 specimens immersed in six solutions with pH of 3, 5, 7, 9, 11 and 13 in covered vats. After 24 days, 1 specimen was removed for analysis from each of the different pH solutions; the subsequent 3 specimens were removed after 120, then 144, and last 288 days. After removal from total immersion the specimens were dried at 105ºC prior to analysis. As reference samples, data from the previous study were used [13, 17].

2.3 Analysis
The changes in pH undergone by the different immersion solutions were monitored in order to adjust it weekly with a pH meter (MeterLab®CDM220). Samples from the various water baths were taken fairly regularly for analyses by ion chromatography (ICP optical Emission spectrometer Varian 720-ES). They were taken weekly both for the first 8 weeks and for the last 25 weeks, the last one corresponding to 340 days, but for reasons beyond our control, none were taken in between. After the samples were taken out of the various pH solutions, capillary absorption curves were determined following the standard RILEM procedure [18]. The samples, were placed in a closed container with water covering their base (5x5 cm) to about 3mm, and regularly weighed to monitor the capillary rise. The capillary water absorption coefficient ($kg/m^2sec^{1/2}$) was determined while the amount of capillary water absorption (%w/w) was calculated from the capillary water uptake at 6 hours, since this is close to the maximum absorbed under these conditions. The samples were then dried again and subjected

International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on Historical Masonry
22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

to vacuum saturation with water and the open porosity and apparent density were determined according to standard EN 1936. After drying them again, they were totally immersed in water for 24 hours. The mass loss after each of these steps was determined for each specimen.

3. Results

3.1 Ion and pH changes of immersion solutions

For most ions the measured concentration oscillated initially but tended to stabilize after about 150 to 200 days. The average concentrations measured for these ions are summarized in Table 1. Some ions, such as Al^{3+}, Ca^{2+}, and SiO_4^{2-} did not stabilize at all pH conditions, while $Fe^{2+/3+}$ and $Ti^{2+/3+}$ only had minimal dissolution at the extreme pH, i.e., 3 and 13. Table 2 summarizes the data for only those ions whose concentrations stabilized at some pH.

Table 1: Average concentration (in ppm) for ions when stabilized by 150-200 days. Standard deviation in italics between brackets.

	K^+(mg/l)	Mg^{2+}(mg/l)	Mn^{2+}(mg/l)	Cl^-(mg/l)	NO_3^-(mg/l)
pH 3	19.0 *(2.7)*	18.6 *(1.6)*	0.87 *(0.08)*	5.5 *(1.8)*	17.1 *(0.7)*
pH 5	10.0 *(1.4)*	12.8 *(0.7)*	0.066 *(0.009)*	5.95 *(0.22)*	84 *(16)*
pH 7	12.8 *(1.6)*	7.4 *(0.4)*	0.012 *(0.012)*	8.38 *(0.96)*	1 *(3)*
pH 9	7.5 *(1.1)*	4.0 *(0.4)*	0.010 *(0.011)*	6.29 *(0.18)*	29.1 *(0.9)*
pH 11	12.4 *(1.9)*	0.08 *(0.03)*	0.008 *(0.008)*	6.12 *(0.46)*	0.37 *(0.23)*
pH 13	436 *(60)*	0.005 *(0.01)*	0.038 *(0.014)*	21 *(10)*	94 *(37)*

Table 2: Average stabilized concentrations (in ppm) measured with standard deviation in italics between brackets. Notes: (-) indicates that the concentration did not stabilize and either increased or decreased (see Figure 1); (0) indicates below detection level.

	Al^{3+}(mg/l)	Ca^{2+}(mg/l)	$Fe^{2+/3+}$(mg/l)	$Ti^{2+/3+}$(mg/l)	SiO_4^{2-}(mg/l)
pH 3	(-)	(-)	1.51 *(0.28)*	0.004 *(0.004)*	111 *(21)*
pH 5	0.57 *(0.23)*	78.8 *(8.0)*	(0)	(0)	25.3 *(5.8)*
pH 7	0.08 *(0.02)*	55.2 *(5.0)*	(0)	(0)	16.9 *(3.8)*
pH 9	0.06 *(0.02)*	(-)	(0)	(0)	14.9 *(3.5)*
pH 11	1.17 *(0.27)*	7 *(11)*	(0)	(0)	33.6 *(6.3)*
pH 13	(-)	0.8 *(2.4)*	0.17 *(0.06)*	0.058 *(0.008)*	(-)

Figure 1 shows the plots of the concentration changes for the most relevant pH for Al^{3+}, Ca^{2+} and silicate ion. While the concentration of Al^{3+} increases significantly from pH 3 to pH 13, the concentration of Ca^{2+} decreases with increasing pH, and for silicate ion, it is relatively low

International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on Historical Masonry
22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

at acid pH, decreases to a minimum at pH 9 and increases for pH 11, reaching concentrations that oscillate between 1500 and 2500 ppm at pH 13.
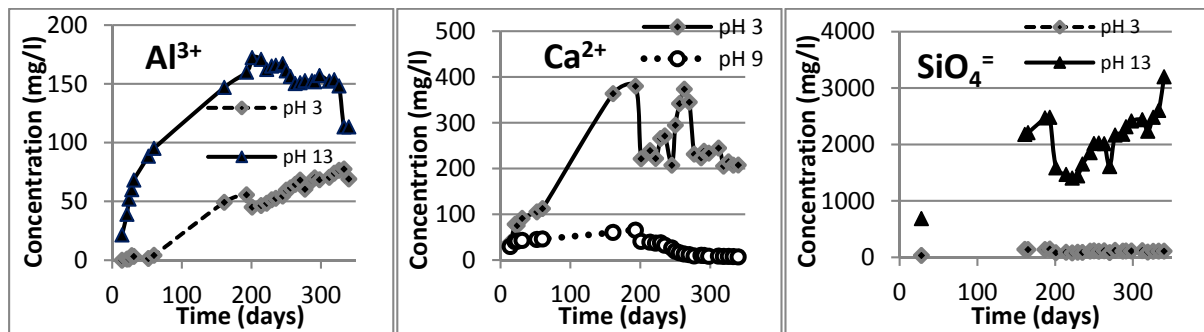

Figure 1. Left: Changes in Al^{3+} concentration at pH 3 and 13. Center: Equivalent curves for the Ca^{2+} at pH 3 and 9; these curves showed some spikes that were attributed to pH changes and therefore not included. Right: Changes in $SiO_4^=$ concentration at pH 3 and 13.

For solutions with pH 3 to 7, the pH increases initially —over the first 50 days—, with pH 3 having the highest increase (occasionally reaching pH 7); followed by pH 5 (occasionally reaching pH 7); and then pH 7 (occasionally reaching pH >8). On the other hand, the alkaline solutions show an initial decrease of the pH, with pH 9 showing a decrease to pH 8; followed by pH 11 that initially reaches pH 9; and for pH 13 which has a minimal decrease. The pH of these solutions subsequently stabilized between 100 and 300 days and the data dispersion is smallest for pH 13 and 11, with the highest values corresponding to pH 5 and 7. Figure 2 shows the pH values measured prior to adjustment and the changes in the concentration of Na^+ not including those for pH 13 because it ranges from an initial 7000 ppm to around 25000 ppm (7 g/l to 25 g/l).
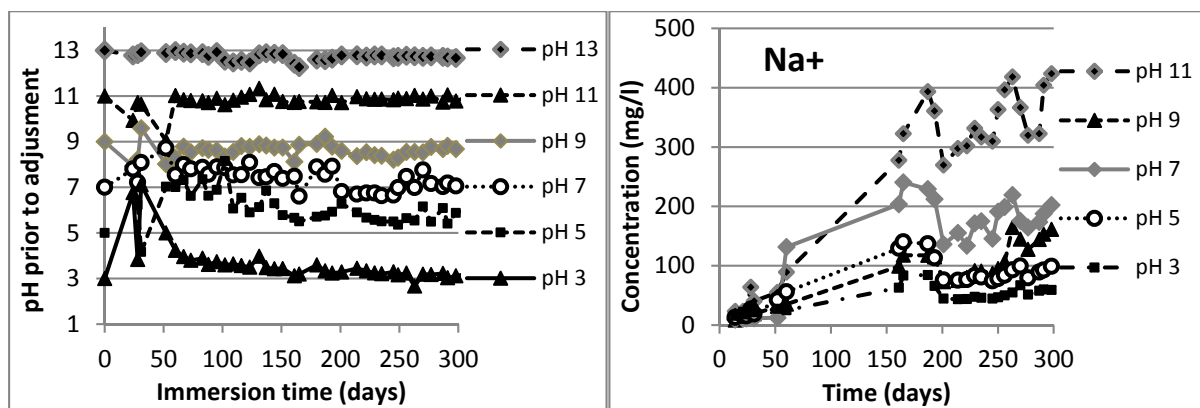

Figure 2. Left: Measured pH values prior to its adjustment. Note that after 100 days the pH remains fairly stable and that pH 9 is below pH 7. Right: Na^+ concentration in the immersion solutions (excepting that for pH 13 which reaches over 50 times the maximum value shown).

Since to keep pH fairly constant, H_2SO_4 and NaOH were added, the data for SO_4^{2-} are not reported. The pH was monitored regularly, and initially (24 to 161 days) for solutions having pH 3 to 7, acid was used to maintain the pH. For the case of pH 7, only after 165 days was NaOH occasionally added to keep it constant; of the 34 times where pH was adjusted, only 9 times required addition of NaOH.

International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on Historical Masonry
22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

3.2 Weight changes of the samples

The samples were weighed initially and subsequently, after drying, when they were taken out of the immersion solutions. They were also weighed after each of the subsequent tests. Figure 3 shows the weight changes after immersion for the specified time; the uncertainty in the measurements is about 0.004%. After 24 days, all samples increased in weight except those at pH 9 and 11 (Figure 3 left). Samples at pH 9 were the ones that lost or gained minimal weight (0.015%) while those at pH 11 only lost weight initially (0.014%) and subsequently started gaining weight (Figure 3 right). Those that changed most corresponded to the extremes: pH 3 increased in weight for the first two immersion times (0.022 and 0.012%) and then lost weight significantly (0.014 and 0.141%). The same pattern was observed for pH 13, initial weight increase (0.161 and 0.061%) and subsequent decrease (0.420 and 0.668%). To be noted is that efflorescence developed mainly on samples immersed at pH 13, and to a lesser extent, for those at pH 11. The initial weight increase suggests the presence of soluble salts that might have been retained in the sample during immersion in pH adjusted water (with H_2SO_4 and/or NaOH).
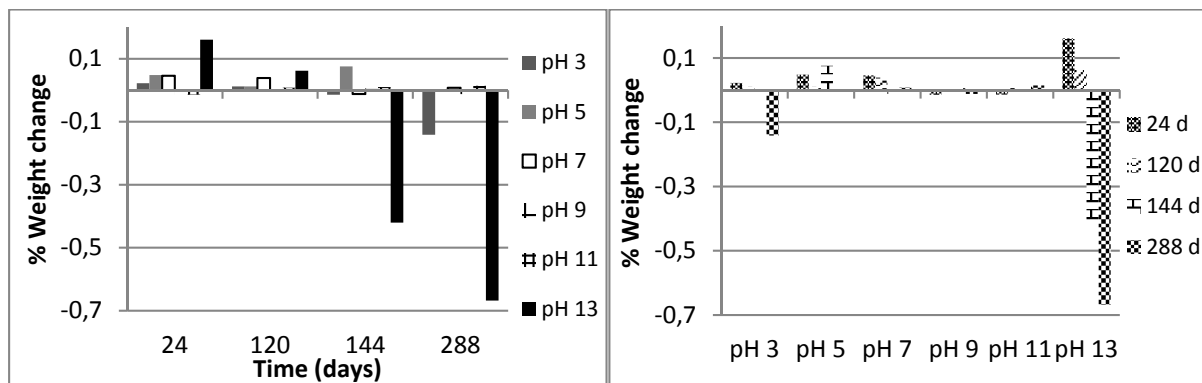

Figure 3. Percent weight change of samples after immersion at different pH for various time lengths, plotted as a function of time or pH. Uncertainty in the measurement is about 0.004%.

3.3 Capillary absorption test

The capillary absorption coefficient, CAC [$kg/m^2.sec^{1/2}$], also referred to as water absorption coefficient (WAC), was calculated from the trend line of the initial straight line. Table 3 gives the average values for the CAC at the different pH and immersion times, as well as that for the reference [13].

Table 3: Average capillary absorption coefficient ($kg/m^2.sec^{1/2}$) for samples exposed to different pH and different immersion times. Standard deviation between brackets.

pH 3	pH 5	pH 7	pH 9	pH 11	pH 13	Ref
0.39*(0.02)*	0.39*(0.01)*	0.48*(0.09)*	0.51*(0.04)*	0.52*(0.05)*	0.52*(0.03)*	0.46*(0.02)*

For the case of pH 7, the data show an increase in the average obtained for 24 and 120 days (0.40 $kg/m^2.sec^{1/2}$) and that after 144 and 288 days of immersion (0.55 $kg/cm^2.sec^{1/2}$) as seen in Figure 4 and in the significant higher standard deviation obtained reflecting the changes required to keep a steady pH (initial 165 days with H_2SO_4 and subsequently a few times with NaOH as mentioned). The CAC obtained in acid solutions is slightly lower than that at pH 7

International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on Historical Masonry
22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

which in turn is lower than the one measured in alkaline solutions suggesting an increase in porosity through alkaline corrosion of the matrix.
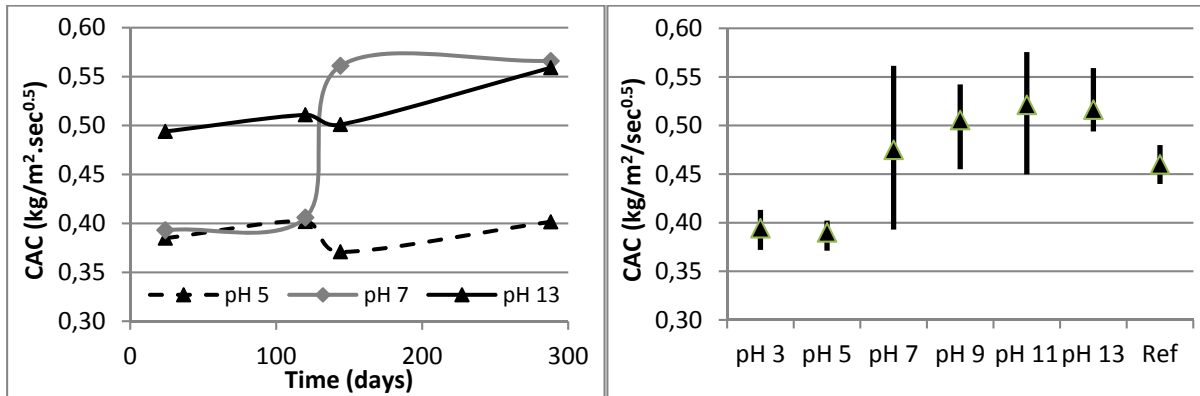

Figure 4. Left: Capillary absorption coefficients for pH 5, 7 and 13 having significantly different standard deviations. Right: Maximum, minimum and average CAC values obtained at the various pH; the spread of data is slightly more than twice the standard deviation.

The amount of water absorbed by capillarity after 6 hours of the CA test is very similar to that absorbed after 24 hour total immersion in water for all samples. This amount varies with exposure time and pH of the solution, and the same trend is observed for the amount of water absorbed by vacuum impregnation as discussed in the subsequent section. Figure 5 shows the percent weight increase for the samples after 6 hours absorption during the capillary absorption test. Samples from immersion in pH 3, 9, and 13, show an increase in absorption with time. Sample from pH 5 shows a minimal decrease, and that of pH 11 the minimum change, while that for pH 7 has an initial decrease followed by an increase. Also shown in this figure is a graph of the average values and data spread. The spread of the data is largest for pH 7 and minimum for pH 11. The data spread (approximately twice the standard deviation) ranges between ±0.4 and ±1 for most samples, except that from pH 7 for which it is ±2.
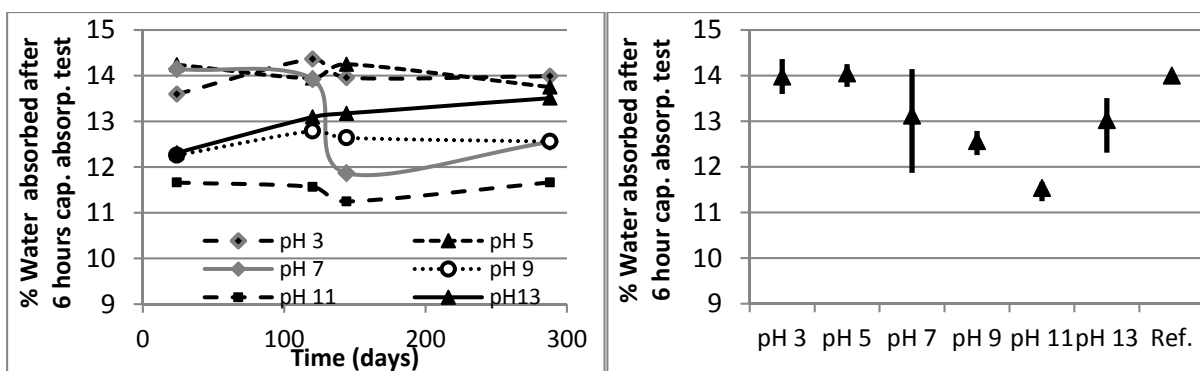

Figure 5. Left: Amount of water absorbed by capillarity after 6 hours of CA test at the various pH. The most regular patterns are obtained at pH 9 and 11. Right: Maximum, minimum and average values obtained at the various pH and for the reference.

International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on Historical Masonry
22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

3.3 Apparent density and open porosity

The average apparent density of the samples immersed in solutions between pH 3 and 7 ranged between 1778 kg/m^3 at pH 3, and 1774 kg/m^3 at pH 7, while reference samples were 1780 kg/m^3 ($\pm$27) [17]. The lowest standard deviation was obtained for pH 5 1776 kg/m^3. Figure 6 shows this data graphically and as well as that for open porosity. Average open porosity was around 33.9% for samples in solutions between pH 3 and 5; 33.7% for pH 7; and 32.2% for the alkaline pH, while, the reference sample was 33.0 % ($\pm$ 1.9) [17].
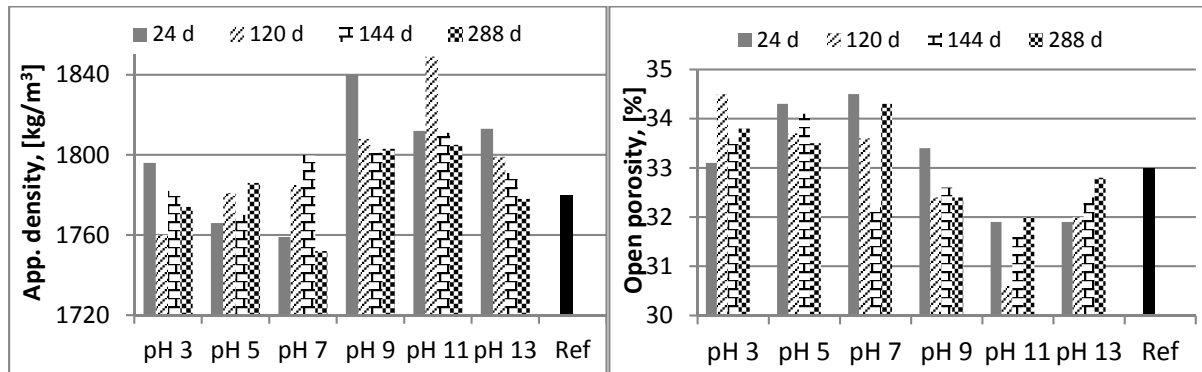

Figure 6. Left: Apparent density (kg/m^3), average standard deviation $\pm$18. Right: % Open porosity, average standard deviation $\pm$1.

For pH 9, both density and porosity show a slight initial decrease that remains fairly constant with longer immersion times. On the other hand, for pH 13 there is a regular decrease in density and increase in open porosity. This reflects the relative mass loss (final weight after all tests and initial weight) of the sample for the brick specimens depending on the pH to which they were subjected (Figure 7). It is clear that specimens immersed at pH 5, 7, 9 and 11 show a minimum mass loss (Figure 3 right), whereas the sample at pH 3 shows a slightly higher loss (0.4% w/w), while samples in pH 13 underwent a significant mass loss (2% w/w).

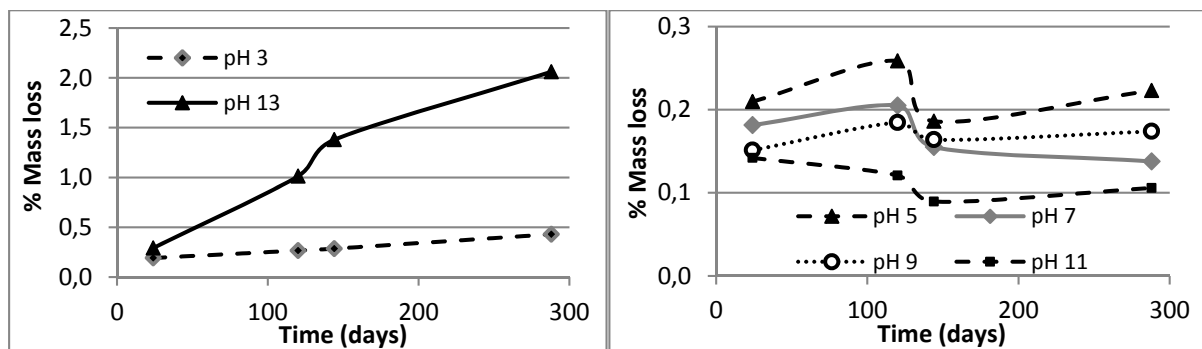Figure 7. Mass loss (%) over time during immersion at different pH solutions.

4. Discussion and Conclusions

The immersion of bricks at different pH and for varying intervals showed that the concentration of some leached ions, i.e., K$^+$, Mg^{2+}, Mn^{2+}, Cl$^-$ and NO$_3^-$, stabilized after a time. Initially, 5 samples were immersed in each solution, and then they were removed one at a time, so that by

International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on Historical Masonry
22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

144 days only 2 samples remained. While for Ca^{2+}, Mg^{2+} and Mn^{2+} the highest concentration was obtained at pH 3, as expected from the ion-exchange mechanism [15,16,19] and reflected in the mass loss over time (Figure 7), the highest concentration of K^+ was obtained at pH 13, being about twenty times higher than for pH 3. This suggests that the K^+ results from alkaline corrosion of the siliceous phase, glassy or ceramic, and the high extraction of Al^{3+} and silicate ion at pH 13 would appear to confirm this hypothesis [14]. The anions, Cl^- and NO_3^- were mostly extracted at pH 13, possibly also due to the same mechanism. The ion exchange of Al^{3+} at pH 3 has been found to proceed beyond 288 days, whereas that for Ca^{2+} had stabilized (Figure 1). In pH 13, minimal Ca^{2+} was detected and Al^{3+} was found to stabilize around 80 mg/l by 340 days. On the other hand corrosion of the siliceous phase was measured between 288 and 340 days (Figure 1) and is expected to increase as this phase constitutes 71-87 %w/w in a historical brick [1].

The weight of most of the samples increased after immersion in the solutions (Figure 3), reflecting the possible formation of soluble salts, especially at alkaline pH where uniform efflorescence formed on brick surfaces from pH 13, lesser at pH 11. These were found to be Na_2CO_3 since the Na^+ remaining from pH adjustment would react with CO_2 from the air.

The main objective of the study was to assess the effect of pH on the brick matrix, so average values were calculated from the four results over time per pH for the tests, as only one specimen per pH per immersion time was available. Therefore, the corresponding calculated standard deviation also includes variation from the effect of exposure length. This rather unorthodox procedure was used as a first approach in the analysis of the data. For the case of the capillary absorption coefficient, the average CAC at pH 7 is similar to that of the reference sample, but its standard deviation is higher, possibly due to pH fluctuations resulting from the pH adjustment over the length of the experiment, initially with acid (up to 165 days), and then occasionally with NaOH. These additions could explain the increase in the average value obtained between those calculated for the two first data points (0.40 kg/m^2.$sec^{1/2}$) and the last two (0.55 kg/m^2.$sec^{1/2}$). The CAC shows that capillary water absorption is slower in acid solutions compared to alkaline ones (Table 3, Figure 4) reflecting the alkaline corrosion by the brick/glassy phase in this environment resulting in an increased pore size.

The amount of capillary water absorbed after 6 hours is practically identical to that absorbed for these samples when totally immersed for 24 hours, indicating that most of the pore sizes in these bricks fall within the capillary range (1μm to 1 mm) [20] and correspond to about 70% of that absorbed under vacuum. The capillary water absorbed after 6 hours expressed as % open porosity (v/v) ranged from about 24.3% for pH 3 and 5, to 23% for pH 7, and 22.4% for pH 9 and 13, while pH 11 showed the lowest value of 20.9%. This agrees with the overall mass loss measured for these samples which for pH 3 and 13 samples follows the expected trend resulting from the two deterioration mechanisms (Figure 7L). For pH 11, a minimal mass loss occurs, while those at pH 5 and 9 show an initial mass loss followed by a slight weight increase between 120 and 144 days. The sample at pH 7 shows the same initial mass loss followed by a slow mass increase slightly above its original weight (Figure 7R). These patterns are similar to those observed for the amount of water absorbed after 6 hours capillary absorption (Figure 5R). These variations could also be attributed to differences in the individual brick specimens and is a point that requires further analysis.

International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on Historical Masonry
22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

Density and porosity of the samples varied over time during their immersion in acid or alkaline solutions. However, these changes fall within the standard deviations obtained for the reference sample. The clearest trend was observed for samples in pH 13, with a decrease in density and a corresponding increase in porosity with longer immersion times that can be attributed to the alkaline corrosion; in the words of Lewin and Charola [19] *"as the porosity increases, the rate of deterioration also increases, both because of increased access of water and solutes to the interior, and the increased chemical reactivity of the decay products."*

Studies of brick and mortar combinations have shown that lime-water, i.e., $Ca(OH)_2$ solution migrating from mortar to brick results in an ion exchange between the Ca^{2+} for Na^+ ions, and to a lesser extent for K^+ [21,22], a point that may be relevant for cement containing mortars as these may retain uncarbonated lime for at least a century [23]. Also, some cements may supply significant amounts of soluble sulfates and alkalis promoting formation of salts, e.g., Na_2SO_4, whose crystallization will contribute to brick deterioration [8].

The study has shown that bricks tested under rather forced conditions—one of the intrinsic problems when trying to accelerate slow damage mechanisms—resulted in some data that require further examination. For example, the unexpected changes found for samples at pH 7 in capillary water absorption after 6 hours (or 24 hour total immersion) between 120 and 144 days and which are also evident in the mass loss for samples in pH 5 to 11 (Figure 7). The project is still ongoing and it is hoped that further analyses will elucidate these questions.

In conclusion, chemical weathering is a slow but significant process for historic brick masonry over centuries of service life. To minimize the damage that could be introduced by required repairs with new bricks, these have to have compatible properties to the original and be as weather-resistant, hence the need for evaluating them.

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International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on Historical Masonry
22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

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