

THE ACTION OF SALT-WATER SOLUTIONS IN THE DETERIORATION
OF THE SILICO-ALUMINATE MATRIX OF BRICKS

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Abstract

The deterioration of brick is due to many factors. These factors can act either by a chemical attack on the matrix of the brick and/or by mechanical damage due to induced stress.

This study tries to assess the relative importance of the chemical corrosion of the silico-aluminate brick matrix by concentrated sodium chloride solutions. From the laboratory data obtained and the examination of actual specimens of deteriorated brick from Venice, where this type of chemical attack can be expected, it is concluded that the effect of chemical corrosion is negligible compared to the mechanical damage produced by salt crystallizing in the pores of the brick.

Introduction

The deterioration of bricks is a world-wide problem, not only from an industrial-economic point of view, but also out of historical considerations when monuments, such as those found in Venice, are constructed with them. The safeguarding of this cultural heritage is of great importance and therefore worthy of special study.

For any effective preservation method to be developed, it is of importance to understand thoroughly the mechanism of deterioration. The causes of deterioration are manifold; the principal agents can be summarized as: (a) water; (b) pollutants, and (c) salts (Torraca, 1979). The action of these agents can be subdivided into: (1) mechanical damage, i.e., water freezing, salts crystal-

lizing; and (2) chemical attack, i.e., dissolution of the mineral and/or glassy phases of the bricks by the water and/or acid pollutants (Lewin and Charola, 1979). It is this latter mechanism towards which this study is directed.

Building bricks are usually fired at about 900°-1000°C, so that just enough vitrified material is produced to bond together the raw materials (clays, quartz, feldspars and chalk) (Searle and Grimshaw, 1959). The glass phase formed is, therefore, the sustaining matrix of the brick. That glass can suffer from corrosion by water, acid and alkaline solutions is a well known fact (Bacon, 1968). Feldspar minerals also are liable to such an attack but to a lesser degree (Lindsay, 1979). Clays and quartz are less reactive, but any chalk remaining after firing is, of course, especially susceptible to acid agents.

This research is concerned with the action of concentrated sodium chloride solutions on the silico-aluminate matrix of bricks. Sodium chloride is the most important salt constituent in sea-water, and in the case of bricks in Venice, which are in frequent, if not constant contact with it, it is of importance to understand the corrosive action this salt may have. The concentration of sodium chloride in sea-water is about 3%. When this water rises in the bricks through capillary action and evaporates, the sodium chloride concentration can reach values of up to 36%. If a steady state develops there will be a region in which the bricks will be essentially in contact with a saturated solution of sodium chloride (Lewin, 1981).

The degree of chemical corrosion undergone by bricks in contact with concentrated sodium chloride solutions is assessed in this paper by means of the experiments described.

Experimental I

A brick sample was powdered to pass a 200 mesh sieve (>149 μm) and 5 g of this powder were suspended in 500 ml of 5 M NaCl. The suspension was stirred continuously throughout the length of time of the experiment. Small samples of the solution, (so that the powder/solution ratio would not be essentially changed), were taken periodically and monitored for the concentrations of Si, Al, K and Ca. The determinations were made by x-ray Energy Dispersive Spectrometry (EDS).

To carry out the analysis, 2 ml of the solution were removed, taking care not to include any of the suspended particles, dried out, and pelleted in an evacuable die under vacuum at a pressure of 15,000 psi for about 2 minutes. The dried NaCl acted as the pelleting agent. Each finished pellet, of 13 mm diam-

eter, was analyzed on 5 or more 1 mm^2 areas at 20 kV and counts were gathered for 200 seconds.

The experiment was duplicated with a different granulometry, to check on surface area effect. The brick sample was ground less, and only the fraction that remained between the 10 and 40 mesh sieves ($>2 \text{ mm}$, $<0.42 \text{ mm}$) was used. Again, 5 g of this coarser powder were suspended in 500 ml of 5 M NaCl. Sampling and analysis were carried out in the same manner.

Results and Discussion

In Figure 1 the experimental data obtained for the Si measured in solution at increasing periods of time are represented. The units for Si are relative as the data are close to the limit of detection for this method. Below 100 ppm Si, the precision of the method drops sharply. This explains the spread of the data at the lower concentration values. The highest concentration of Si in solution that was measured, corresponding to 70 days of the brick powder suspended in the sodium chloride solution, was between 75 and 50 ppm Si.

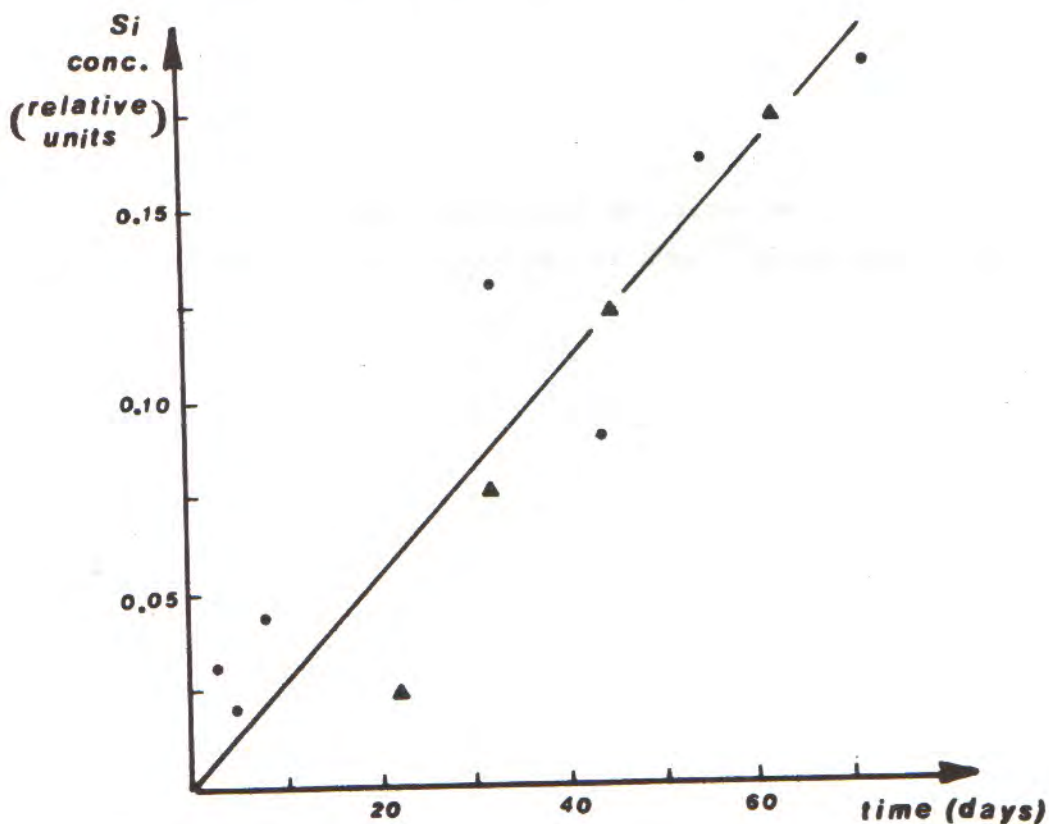


Figure 1. Concentration of solubilized Si in a 5 M NaCl solution as a function of time. Points indicated by (●) correspond to powder $>149 \mu\text{m}$. Points marked by (▲) correspond to coarser powder ($>2 \text{ mm}$, $<0.42 \text{ mm}$).

The reason this method was used, even with its uncertainties at the low concentrations, was that it enabled us to perform the analysis on a very small sample, thus not affecting the experimental design on sample removal. It is an extremely simple procedure and the presence of the high NaCl concentrations was turned into an advantage instead of being a problem for the analysis. Furthermore, it enabled the simultaneous monitoring of the sample for other elements (Al, Ca, K) that might also leach out into the solution.

From the graph we can observe that the dissolution rate follows a linear function. Also, for both particle sizes studied, the rate observed was essentially the same. The earlier points, obtained for the finer particle size powder, fall above the line. This can be explained by the dissolution of the ultrafine and strained particles produced during the grinding (Berner, 1981).

The dissolution of glass in aqueous solutions is an extremely complex phenomenon. The studies done on water attack show a migration of Na^+ from the glass into the solution and replacement by H^+ forming a silica sponge. The rate of attack follows a parabolic function that can be explained in terms of the migration of Na^+ through this surface layer (Holland, 1964). If, however, the experiment is carried out over longer periods of time, and the attacking solution is renewed, so that the reaction products can not accumulate in contact with the glass surface, the rate of attack is linear (Raña and Douglas, 1961). In our case, the presence of high Na^+ concentrations in the solution should retard, if not inhibit, the Na^+ leaching. Other mechanisms though, can take place, such as adsorption of water and subsequent hydrolysis of the hydrated alkali silicate formed, or Ca^{++} ions in the glass can be replaced by Na^+ from the solution (Holland, 1964).

In our experiments, neither Ca, K nor Al ions were found to increase in concentration above the minimum found in control blank runs. Considering that the ratio Si:Al for the particular brick used in the experiment was 4:1, and that the ratios Si:K and Si:Ca were much lower than that, the concentrations of these ions that would be produced, even considering total dissolution of the brick, would fall below the detection limits of the method used.

A linear dissolution function is also observed for the weathering of feldspars (Holdren and Berner, 1979) and pyroxenes and amphiboles (Berner et al., 1980). The rate-controlling step in the mechanism proposed for the weathering is the chemical reaction at the water-mineral interface (Dibble and Tiller, 1981).

The thickness of the glassy layer that would be corroded away by the action of concentrated NaCl solutions can be calculated on the basis of the

observed data. The rate measured can be taken as approximately 1 ppm Si/day. This corresponds to 1 mg SiO₂/day and, assuming a typical soda-lime glass, it would correspond to 1.3 mg glass/day. The thickness can be calculated from the particle size involved. Taking the most extreme case, that all the particles were 2 mm in diameter, the erosion rate would be 800 Å/day. On the other hand, if a more realistic estimate of particle size is taken, i.e., an average diameter of 0.1 mm, the erosion rate reduces to 0.4 Å/day. This estimate is valid for a system in which the reaction products are not left in contact with the reacting surface, and for the length of time this experiment was carried out. It could be said then, that brick, with a constant flow of concentrated NaCl solution through it, for a period of three months, would lose a layer of the glassy matrix of about 40 Å. The three month estimate can be taken as equivalent to a yearly estimate because seasonal changes will vary the area in which the brick would be in constant contact with the solution.

This rate is not very significant. Over a century the loss would be 0.4 μm. Taking into account that bricks do not have a fast flow of solution through them, but, at the most, are permanently wet with saturated NaCl solution, it is valid to assume that the erosion rate in this case would follow a parabolic function, the reaction rate being diffusion controlled. If this is the case, the dissolution rate that could be expected would be even smaller.

This picture is still far from the real situation in that successive wet-dry cycling was not considered with the subsequent crystallization-solubilization-recrystallization of the salt taking place, and the mechanical damage this produces (Pauly, 1976). Furthermore, acid air pollution, which is not negligible in Venice (Fassina, 1976; Fassina et al., 1979) was not taken into account. Nor was the fact that bricks are laid with mortar. Mortar will produce an alkaline environment. Attack of glasses by alkaline solutions is more pronounced. On the other hand, this alkalinity will in part neutralize the acid pollutants. This will produce new salts, i.e., gypsum, and the system complicates even further. It is possible to have then, in one single brick diverse microenvironments and different attack mechanisms operating simultaneously.

To test the proposed theory that the corrosive action of concentrated sodium chloride solutions is not very significant in the deterioration of brick, samples of Venetian brick were collected. Flakes of very deteriorated bricks from different sites across the city were studied by scanning electron microscopy and their elemental composition determined by EDS.

Experimental II

The samples obtained were from the following sites: Campanile, S.Giovanni Evangelista, S.Felice (3 samples), S.Moisè, Abbazia della Misericordia, arches by the side of the Abbazia, campanile of S.Geremia (2 samples) and from an old house by S.Stefano.

For Scanning Electron Microscopy (SEM), the fracture surface of the brick flakes was studied.

For EDS analysis, the samples were powdered to pass a 60 mesh sieve (>0.250 mm), mixed with 10% w/w of H_3BO_3 (Kim and Choi, 1981), and pelleted in the same manner described previously. Each pellet weighed about 600 mg. The analysis was carried out on 6 or more 1 mm^2 areas on each pellet at 20 kV for 200 seconds.

Conclusions

From the data obtained by EDS analysis of the brick samples no significant decrease in the concentration of SiO_2 could be observed with respect to published data of similar, but not as deteriorated, Venetian bricks (Biscontin et al., 1979).

The concentration of Cl obtained in these analyses ranged from $0.3 \pm 0.1\%$ for the Campanile sample, to $18 \pm 2\%$ for the S.Stefano one. All the other samples had an average Cl concentration of about $2.5 \pm 0.2\%$.

The concentration of S obtained ranged from $2.4 \pm 0.1\%$ for the S.Geremia samples, to $0.08 \pm 0.04\%$ for the S.Felice samples. The S concentration in the samples did not appear to have a central tendency.

From these data it can be seen that on the average, the presence of chloride is more than twice as large, on a mole basis, as the presence of sulfate. Therefore, twice as many moles of NaCl than of $CaSO_4 \cdot 2H_2O$ were crystallized in these specimens. As the determining factor for the destructive forces in salt crystallization decay is the number of crystal seeds that form and their growth rate (Charola and Lewin, 1979) it follows that the decay induced by the crystallization of sodium chloride is more important than that produced by gypsum.

This is substantiated by the SEM examination of the samples. The presence of halite crystals was ubiquitous, as can be seen in Figures 2 and 3. Gypsum crystals, on the other hand, had a more localized distribution.

Examination of Figure 2B, which is a higher magnification of the glassy matrix of the brick, does not show any appreciable evidence for the etching or dissolution that could be expected if significant chemical attack had occurred. What this picture does show is the many "seedlings" of halite growing on that matrix. The growth of these "seedlings" into full-grown crystals is

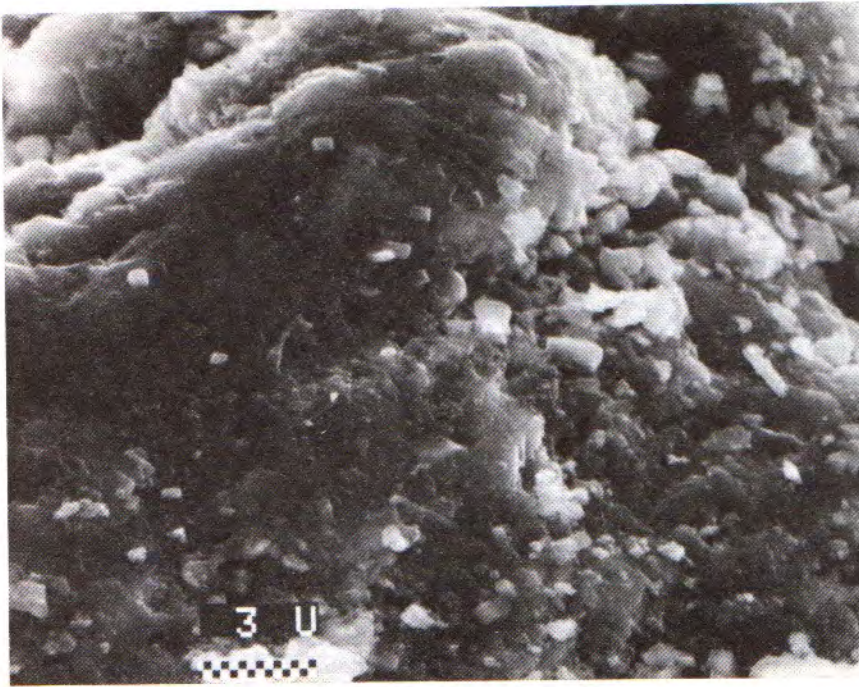


Figure 2 A. Glassy matrix of the brick. Note the number of sodium chloride crystals.

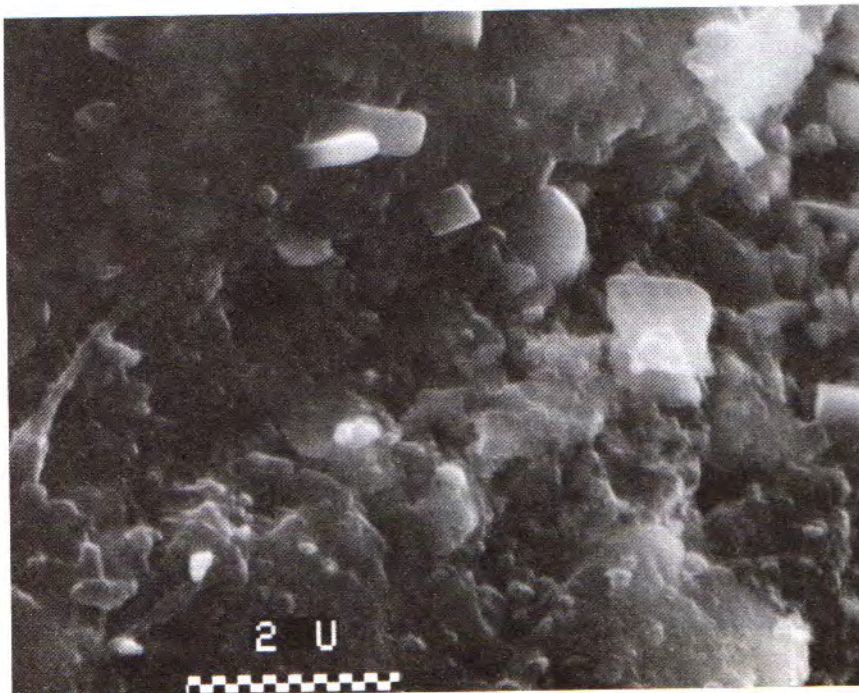


Figure 2 B. Detail of the preceding picture. No evidence of etching of the glassy matrix can be seen.

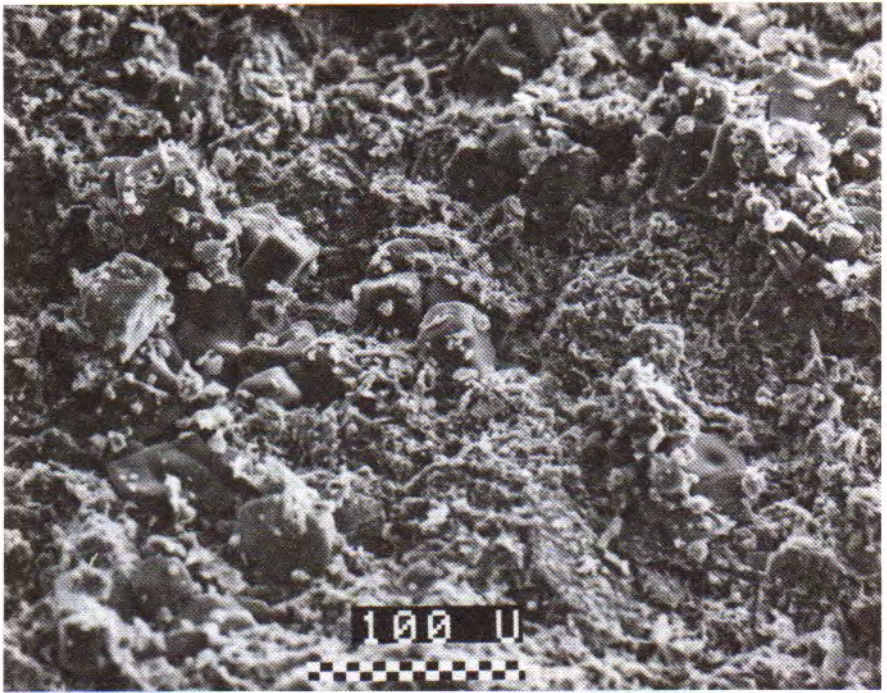


Figure 3 A. Fracture surface of brick flake with masses of sodium chloride crystals



Figure 3 B. Detail of a group of sodium chloride crystals. Note the brick debris that has resulted from the fracturing produced by the growth of the crystals.

shown in Figure 3A. As the crystals grow, the brick matrix is mechanically disrupted; the result can be seen in detail in Figure 3B where brick debris is still attached to the crystals that produced it.

In conclusion, from the laboratory data, the EDS analysis and the observations under the SEM, it can be said that the chemical attack on the silico-aluminate matrix of brick by saturated sodium chloride solutions is negligible in comparison to the mechanical damage suffered by the brick when this salt crystallizes in the pores.

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