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Weathering traces in ancient bricks from historic buildings

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Abstract

The aim of this work was to determine the type of weathering suffered by bricks belonging to a number of historic buildings in Toledo, Spain. These bricks had been exposed to either aerial or burial environments, came from different places in the selected buildings, were of different mineralogical composition, and had been fired at different temperatures. X-ray diffraction, scanning electron microscopy and the analysis of their physical properties showed the best conserved to be those that had been buried. Buried Roman bricks made from non-calcareous materials fired at $>900\,^{\circ}C$ and with a vitrified matrix showed few signs of weathering. Buried Islamic and Mudejar-Romanesque bricks made from calcareous clays and fired at temperatures of $<800\,^{\circ}C$ were similarly well conserved. These showed calcareous cementation of their pore systems, which improved their physical properties. Bricks from the external and internal walls of buildings (e.g., Islamic–Mudejar and Romanesque bricks from inner courtyards and cellars) that had been exposed to aerial conditions were less well conserved. These were made from calcareous materials and had been fired at high temperatures ($>900\,^{\circ}C$). They showed a number of weathering traces but overall were still in relatively good condition. The worst conserved of all were neoclassical bricks from upper storey internal walls. These were made of calcareous material and had been fired at temperatures of between 800 and 900 °C.

The mineralogical composition of the raw materials, the firing temperature, the location of the bricks in the buildings, the environments to which they had been exposed, the action of natural or polluted filtration water, the action of microorganisms and the reigning environmental conditions, all contributed towards the state of conservation of the bricks. Such knowledge may help in the choice of appropriate cleaning or restoration treatments for architectural heritage of brick construction.

Keywords: Heritage; Historical buildings; Bricks; Physical, chemical and biological weathering

1. Introduction

In geological terms, a brick can be defined as a metamorphic rock that is stable only under the final conditions of pressure and temperature of its artificial firing. When exposed to sub-aerial conditions (as part of a building) or to burial environments, bricks become exposed to very different temperatures, pressures and moisture regimes, as well as to the actions of aqueous solutions, atmospheric gases and organisms. Under these conditions they become unstable and suffer micro-structural and mineralogical changes known as weathering or deterioration. This causes the mineralogical breakdown of their crystalline lattices, allowing ionic migration to produce new minerals with a tendency to enter thermodynamic equilibrium with their environment. Rock deterioration can be physical, via the disaggregating mechanisms of frost and salt weathering, or chemical, via reactions between the rock surface and the atmosphere (when exposed to the air), the soil (in burial environments), or dissolved ions (when exposed to water). Mineral decomposition produces new phases following processes such as: (i) changes in self-energies through structural phase-transition, (ii) loss of coherency in micro-twinning and ex-solution interfaces

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in mixed phases (e.g., alkali feldspars), (iii) alkali–proton exchange at mineral surfaces and acid drainage of alkalis, (iv) the chemical sulphating of calcium-bearing surfaces, and (v) crystallization of neo-formed phases via the interaction between fluids and minerals (calcite, sulphates, phyllo-silicates, and iron oxo-hydroxides). Biological weathering occurs concurrently with physical and chemical weathering; in fact it can be described as physical and chemical weathering caused by biological agents [1–2]. The characterization of weathering traces in ancient bricks from historical buildings is a crucial task when conservation activities or cleaning treatments are planned. To avoid any further deterioration, appropriate surface cleaning machines and products must be chosen, appropriate for the specific chemical properties of the material to be treated. Cleaning treatments are chosen according to their method of action, e.g., the following have been used to remove black gypsum dendrite crusts: (i) sepiolite, because of its solvent action, (ii) ammonium bicarbonate, because of its exchange action, (iii) EDTA, because of its chelating action, (iv) hydrogen peroxide, because of its toxic action on organisms and (v) nylon brushes, because of their abrasive action [3].

The high level of air pollution near industrial sites leads to significant increases in the deterioration rates of buildings, engineering structures and historical monuments. Burning fossil fuels increases the concentration of NO_x and SO_2 in the atmosphere—the agents most harmful to masonry [4]. The factors influencing the oxidation of sulphite to sulphate include the type and porosity of the stone under attack, moisture level, nature of the oxidizing agents involved and the presence of extraneous reactants, e.g., metal oxides, chlorine and ammonium salts [5]. The sulphuric acid generated by the catalytic oxidation and hydrolysis of SO_2 attacks carbonates and Ca-rich, high-temperature silicates such as wollastonite, gehlenite and Ca-feldspars, resulting in the formation of gypsum crystals [6]. Sulphating can proceed in two ways: (i) SO_2 can be adsorbed onto the stone where it reacts with calcium carbonate and water to form calcium sulphite, which is then further oxidised to gypsum, or (ii) it can be transformed into H_2SO_4 either directly on the stone or in the air, the subsequent attack on the carbonate leading to the formation of gypsum crust [7].

With respect to other pollutants, baked bricks can be used as geochemical monitors of heavy metal fallout. Analysing samples of different ages collected from old monuments can reveal the recent history of heavy metal pollution [8,9].

Microorganisms influence brick weathering in a number of ways: (i) via the decomposition of organic matter, from which many elements, organic acids and CO_2 are mobilized, (ii) by directly decomposing minerals (by exuding metabolically produced organic acids and releasing enzymes that enhance chemical reactions), (iii) by putting strain on cavities and fissures, (iv) by giving rise to chemical weathering and (v) by taking part directly in the crystallization process (bacteria can precipitate calcite and other minerals). Many bacilli form calcite crystals on solid media that contain sodium acetate [10,11]. Bacterial action may facilitate brick decay through the consumption of chemical compounds in the stone and via their metabolic products [3]. It is reported that spherulite and polycrystalline aggregates of calcite are produced by the activity of *Escherichia coli* in a gel medium; metabolic products such as CO_2 and H_2O form from polysaccharides, and with calcium ions form carbonic acid, leading to a crystalline deposit [12]. The colonization of buildings by lichens has been studied in churches and granite monuments [13,14]. Lichens can, in some instances, protect exposed brick surfaces from atmospheric weathering, reducing the losses of mobile elements. They can also prevent grain disaggregation since their thalli (frequently accompanied by bacteria, cyanobacteria, algae and fungi) retain water, increasing the wetting period and avoiding salt crystallization. However, they can also be destructive [1]. Microorganisms can form biofilms on stone surfaces or at the lichen–rock interface. These play an important role in the biodeterioration of stone monuments [15] by exuding acids that break down rock-forming minerals (leading to etching and disaggregation). Lichens also expand and contract with changes in moisture levels, and thereby effect mechanical damage through the loss of rock fragments.

Manganese micro-nodules (around 2 μm in diameter) have been found growing under the external biofilm surface of buried bricks. SEM studies have shown that biofilms precipitate these micro-nodules on ancient brick surfaces, possibly through the imbibing of aqueous solutions rich in anthropogenic MnO_4K in a reducing environment, or through the oxidation of Mn^{2+} [16].

Weathering processes occur in open systems in non-equilibrium conditions. Although the mechanisms can be studied separately, the physical, chemical and biotic reactions involved proceed concurrently. The aims of this work were to study and classify the different types of weathering in ancient bricks from historical buildings of Toledo, Spain, and to relate these findings to their state of conservation.

2. Materials and methods

The experimental material included 15 brick samples from the historic buildings of Toledo, Spain. These were first classified according to whether they had been exposed to a (I) burial or (II) an aerial environment. Those from aerial environments were sub-classified according to their specific location in the building: (A)