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An Accelerated Chemical Weathering Assay: Sulfation of Acinipo Limestone in a Humid and SO_2 Rich Environment

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Abstract Sulfation is one of the main factors of calcareous stone deterioration. In a bid to better preserve our cultural and historic heritage for future generations, the sulfation of limestone from the archeological site of the ancient Roman city of Acinipo was investigated. To simulate sulfation, limestone samples from Acinipo were subjected to accelerated weathering by chemical attack of SO_2 in a humid environment. Weathering provoked the substitution of the calcite matrix for crystals of both calcium sulfate dihydrate and calcium sulfite hemihydrate. The results offer interesting leads into further investigation, while demonstrating the educational utility of the proposed methodology.

Keywords Limestone, Accelerated Chemical Weathering, Sulfation, Monuments and Architecture Damage

1. Introduction

Throughout history stone has been used in architecture and art on account of its longevity. Unfortunately, the changes in morphology and composition which result from the interaction of stone with its environment are often aesthetically and functionally detrimental to monuments and buildings. In unpolluted environments, reactions are often extremely slow, unfolding over centuries. In the twentieth century however, atmospheric pollution, due to increased industrial activity, has had a dramatic effect on the rate of anthropogenic alteration, resulting in an alarming increase in the deterioration of our artistic and cultural heritage [1]. In order to better inform the actions required to prevent further damage and to safeguard our heritage for future generations, it is very important to elucidate the mechanisms of stone degradation.

Stone degradation results from an interplay of numerous alteration factors, both natural and anthropogenic. It is also dependent upon the inherent lithology of the stone, the function it is serving and the treatments to which it has been subjected. The indicators of alteration are equally diverse and dependent upon the weathering factors. The overall mechanism is thus a potential combination of mechanical, physical, chemical and biological processes, and as such extremely complex to determine [2].

One of the principal causes of damage to monuments and architecture in Europe and North America is sulfation of carbonaceous stone, such as limestone [3, 4]. Sulfation occurs primarily in industrialized and urban areas, where atmospheric sulfur dioxide abounds.

Oxidation of atmospheric sulfur dioxide results in sulfur trioxide which dissolves in liquid water or vapor giving rise to sulfurous or sulfuric acid which in turn attacks the stone and provokes the substitution of the calcite matrix for calcium sulfate dihydrate, commonly known as gypsum [1, 3]. Gypsum is relatively stable but moderately soluble in water and thus liable to dissolution by rain water and consequent wash out. In areas not exposed to mechanical stress, the formation of gypsum can result in the buildup of crusts, which vary in depth from microns to millimeters. Such crusts often appear black when impregnated with highly porous oil-fired carbonaceous particles, which catalyze sulfation and nucleate the genesis of gypsum crystal [5]. Moreover, the adhesion between the healthy stone and the gypsum layer is poor, such that the crusts are prone to separation from the stone's surface, thereby exposing fresh stone [1]. To better understand sulfation, studies of different types of limestone in sulfur dioxide rich atmospheres have been conducted [6-11]. These studies are commonly known as accelerated weathering assays. Accelerated weathering assays facilitate mechanistic elucidation by allowing the control of variables in isolation [6]. However, in doing so they also obliterate the possibility of synergism. Since no single factor ever acts in isolation in a real environment, weathering assays can never fully simulate the mechanism of true weathering. Moreover, the magnitude of the weathering factors is many times greater than in real environments [3]. Accelerated weathering tests are also an important tool for

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the evaluation of the behavior of conservation and restoration treatments [12, 13]. Consequently, although accelerated weathering assays are very important tools, they are also oversimplified approximations, and results must be considered comparatively with caution and skepticism.

Acinipo (Ronda, Andalucía, Spain) is an important archeological site dating back to 202 BC. It boasts impressive ruins of a roman theatre and baths overlooking the Spanish Sierra de Grazalema [14]. The stone under current investigation is found in abundance over excavations on the site and is the same as that found in the Formation of Setenil [14, 15]. A full petrographic description of Acinipo limestone is included in the report of the findings by IAPH [15]. It is a fine grained, sandy textured, biochemical limestone. It is macroscopically homogeneous (with the exception of a few shells and grains of quartz) facilitating the preparation of small stone samples. It is pale beige; most likely on account of the small iron content in the form of limonite.

The main objective of the present work is to propose a methodology to study the effect of a sulfur dioxide rich environment on samples of limestone from the ancient roman city Acinipo. To investigate the overall process of sulfation, previously characterized stone samples from Acinipo were exposed to a humid environment with high sulfur dioxide concentration. Changes in the stone's composition were followed over time using different analytical techniques.

2. Materials and Methods

2.1. Chemicals and Samples

Stock samples of Acinipo limestone were prepared as 60 mm^3 blocks and left to equilibrate in laboratory conditions (20°C, 55-60% RH).

Twice deionized water and analytical grade reagents were used throughout.

Barium acetate precipitating solution was prepared by dissolving 20g of barium acetate in 75 cm^3 10 N acetic acid and 25 cm^3 5% aqueous arabic gum solution, which was subsequently filtered.

Iodine solution was prepared from 2g potassium iodide and ca. 0.15g potassium iodate (accurately weighed to 0.1 mg) in acid media (10 ml of 0.5 mol dm^{-3} H_2SO_4 dissolved in ca. 50 ml water).

Sulfurous acid solution was prepared by diluting 500 cm^3 of sulfurous acid containing 5% SO_2 in mass in 150 cm^3 water.

2.2. Chemical Characterization

The following methods were based on those proposed by A. Martín [16].

Loss by Calcination

With the aid of a muffle oven and an analytical balance, the loss of CO_2 by calcination was determined. Specifically, 0.7 g of finely ground stone, previously dried at 110°C, was accurately weighed into a porcelain crucible of known mass and calcined at 950°C for two hours before cooling in a desiccator. The process was repeated until the obtained mass was constant and the result expressed as the percentage mass lost.

Acid attack: determination of insoluble silica and preparation of solution for inductively coupled plasma atomic emission spectroscopy (ICP)

Soluble stone solutions were prepared in triplicate for ICP analysis by acid attack and the percentage mass of the insoluble quartz (SiO_2) determined by calcination.

One gram of finely ground stone, previously dried at 110°C, was accurately weighed into a 500 cm^3 beaker equipped with a watch glass and stirrer. 35 ml HCl (39%, d = 1.19 g cm^{-3}) and 1 ml HNO_3 (d = 1.39 g cm^{-3}) were then added to the beaker with care. Any solid fragments were broken up with the stirrer and the solution heated gently in the covered beaker to dryness on a sand bath. The process of adding acid media and heating to dryness was repeated three times; HNO_3 was omitted from the third addition.

Water was added to the stone residue and the solution filtered through ash free analytical filter paper (pore size 140 μm) into a 250 ml volumetric flask, ensuring full transference. The paper was subsequently transferred to a crucible of known mass (pre-calcined at 950°C for two hours) and dried in an oven at 110°C. It was then calcined with a Bunsen burner, taking great care to avoid loss of ash, and subjected to 1000°C in the muffle oven for an hour, before being left to cool in a desiccator and weighed.

The elemental composition of the solution was determined by atomic emission spectrometry by Plasma ICP (Horiba Jobin Yvon, model Ultima 2) courtesy of CITIUS, Universidad de Sevilla.

2.3. Accelerated Weathering Assay

The procedure followed was based on the 2002 European standard for natural stone tests: Determination of resistance to ageing by SO_2 action in the presence of humidity [17].

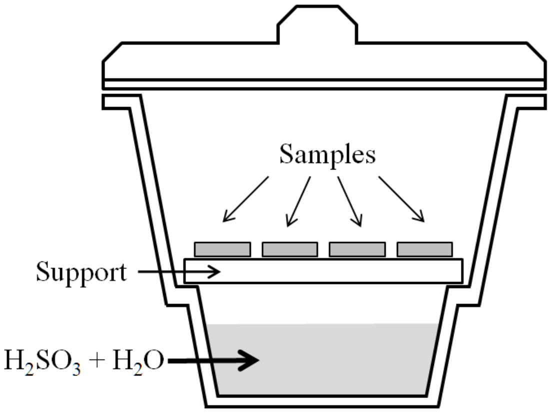

Figure 1. Schematic of the accelerated weathering assay setup

Several 20 mm × 10 mm × 5 mm stone samples, each supported on a watch glass, were placed on a ceramic support above 650 cm^3 sulfurous acid solution in a 6 dm^3 desiccator (Figure 1).

The samples were removed from the weathering assay after predetermined exposure times and analysed by the following instrumental and chemical analytical methods:

- percentage mass increase;
- conductivity: soluble salt formation;
- barium sulfate gravimetric analysis: determination of calcium sulfate formation;
- iodometric back titration: determination of calcium sulfite formation.

Samples of stone in their natural state in laboratory conditions and samples previously saturated in water were analysed for each exposure time. The saturated state was achieved by complete and immediate submergence in twice deionized water. After 24 hours they were removed from the water and wiped with a damp cloth (to prevent the crystallisation of salt on the watch glass) prior to introduction into the desiccator.

2.4. Water Assay

The water content of stone samples in both natural and pre-saturated states was determined as a function of time in a desiccator containing 650 ml water. In order to mimic the experimental conditions of the weathering chamber, water content was determined at atmospheric temperature and pressure. Water content (**W**) was calculated from the percentage mass difference between dry stone (**Ms**) and stone in its state of interest (**M**):

$$\mathbf{W} = 100 \times (\mathbf{M} - \mathbf{Ms}) / \mathbf{Ms}.$$

Dry stone was dried at 60°C, since this was the temperature used in the evaluation of the weathering assay (section 2.5).

2.5. Analytical Methods: Weathering Evaluation

As above, the following methods were based on those proposed by A. Martín [16].

Mass Difference

After predetermined exposure times, weathered samples were dried in an oven at 60°C to ensure the evaporation of moisture without loss of crystallization water. Once dry, the stone samples were left to equilibrate to their natural state in laboratory conditions and their mass measured on an analytical balance ($\mathbf{M_F}$). The percentage mass difference (% **MD**) of each sample was then calculated with respect to its pre-exposure mass ($\mathbf{M_0}$),

$$\% \mathbf{MD} = 100 \times (\mathbf{M_F} - \mathbf{M_0}) / \mathbf{M_0}.$$

The mass difference is dependent upon the conversion of $CaCO_3$ to $CaSO_3.½H_2O$ and $CaSO_4.2H_2O$, both of which have a higher molecular weight than $CaCO_3$.

Conductivity

Having calculated the mass difference, *ca* 5 g of stone was ground in an agate mortar and sieved to a particle size smaller than 200 μm. Approximately 1 g of ground stone was accurately weighed into an airtight plastic container, to which 100 ml of water was accurately pipetted. The solution was then stirred for 24 hours before leaving to the solid fraction to settle overnight.

The corrected conductivity (**K**), which corresponds to 1g of stone in 100 ml of solution, was determined by a GLP 32 Crison Conductimeter as follows:

$$\mathbf{K} = (\mathbf{a} - \mathbf{b}) / \mathbf{m},$$

where **a** (μS cm^{-1}) is the conductivity of the aqueous stone solution, **b** (μS cm^{-1}) is the conductivity of a blank solution prepared as per the test solution but without stone, and **m** (g) is the mass of the stone in the aqueous solution.

Turbidimetric Sulfate Determination

To a 50 cm^3 volumetric flask containing 10 ml aqueous stone solution diluted in 30 ml of water, 1 cm^3 of barium acetate precipitating solution was added and the solution made up to 50 cm^3 with water.

The flask was agitated for 2 minutes and left to rest for a further 10 minutes before measuring the absorbance at 425 nm using a UNICAM UV 500 UV/visible spectrometer. A blank was prepared in exactly the same manner but omitting the aqueous stone solution. The results were calculated by comparison with a calibration curve, constructed from a standard solution of SO_4^{2-}.

Sulfite Determination

The sulfite content of the stone was determined by iodometric back titration.

Iodate reacts with iodide to yield iodine:

$$IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O.$$

A known excess of iodine solution (in I_3^- form) was added to a known weight of the solid stone and was left in the dark for 15 minutes for quantitative sulfite to sulfate oxidation:

$$SO_3^{2-} + I_3^- + H_2O \rightarrow SO_4^{2-} + 3I^- + 2H^+$$

The remaining un-reacted iodine was then back-titrated using previously standardized 0.1 M sodium thiosulfate solution:

$$2S_2O_3^{2-} + I_3^- \rightarrow S_4O_6^{2-} + 3I^-$$

3. Results

3.1. Chemical Characterization of Acinipo Limestone

The results of chemical characterization (Table 1) were in agreement with those from IAPH [15]. That is, the limestone proved to be almost pure calcite with a relatively high quartz content (9.35%).

Table 1. Chemical characterization of Acinipo stone: percentage mass of elements, determined in triplicate by ICP, present in Acinipo limestone

Element	% Mass
CO_2 (loss by calcination)	39.29
Insoluble SiO_2	9.35
Ca	47.71
K	0.27
Mg	0.07
Na	0.04
S	0.23
Al	0.45
Ba	< 0.01
Fe	0.47
Mn	0.02
Si	0.03
Sr	0.01
Ti	< 0.01
P	0.05

3.2. Water Assay

The water content of Acinipo stone samples in their natural state in laboratory conditions was 0.25% to 0.35% by weight. The water content of saturated samples ranged from 7% to 8%. During exposure to the humid environment, saturated samples lost water while the water content of unsaturated samples increased (Table 2). After 120 hours, the water content of all samples ranged from 1.5% to 2%.

Table 2. Acinipo Limestone Water Content

	% water content
Natural state	0.25%-0.35%
Saturated state	7%-8%
Natural state (after 48h)	1%-1.5%
Saturated state (after 48h)	2.5%-3%
Natural and Saturated (after 120h)	1.5%-2%

3.3. Weathering Assay

During the accelerated weathering assay the samples showed progressive de-cohesion, as well as the appearance of macroscopic fissures, which were more evident in the pre-saturated samples. A pre-saturated sample exposed for 626 hours suffered a complete rupture resulting in fragmentation.

Figure 2 shows the increase in mass of the samples over time. There was little qualitative difference between trends across pre-saturated samples and those exposed in their natural state. Regardless of state, there was an initial phase of rapid mass increase during the first 120 hours, reaching an average 10% mass increase. Followed by a slower increase, reaching 14% after 624 hours.

Trends over time in conductivity (Figure 3) and calcium sulfate concentration (Figure 4) were similar to one another, and resembled the trend in mass increase over time. Conductivity depends on the presence of soluble salts, so was expected to follow calcium sulfate formation.

The rate of sulfate formation was initially fast, decaying after 120 hours (Figure 4). The rate is thought to drop with the occlusion of available pore space and the consumption of oxygen in the exposition chamber.

In contrast to calcium sulfate formation, the trend in calcium sulfite concentration over time was approximately linear over time (Figure 5). The formation of sufite likely contributed to mass increase after 120 hours: the concentration of calcium sulfate increased little after 120 hours, while the concentration of calcium sulfite almost quadrupled.

The initial water content of weathered samples had little effect on final reactivity. This is in good accordance with results obtained from the water absorption essay: it was observed that all samples, independently of initial water content, tend to equilibrate with the humid environment and reach the same water percentage with time.

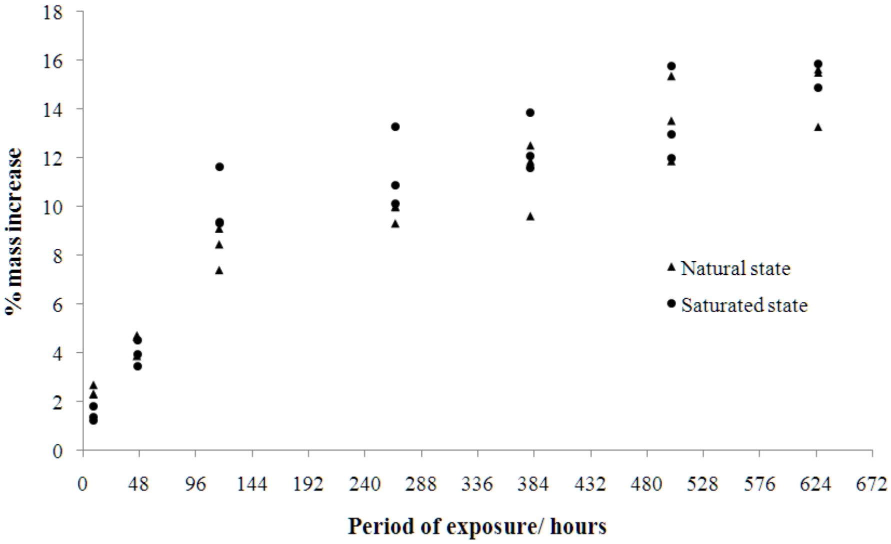

Figure 2. Percentage mass increase of weathered stone samples over time

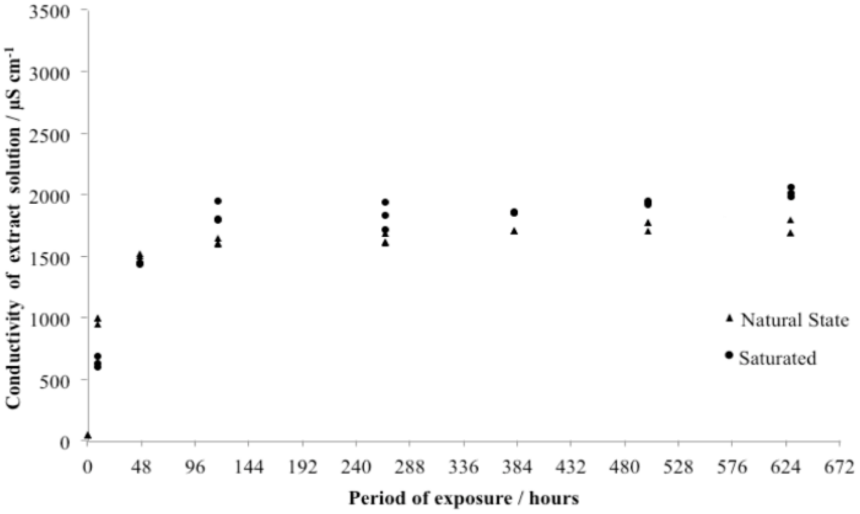

Figure 3. Corrected conductivity of 100 ml aqueous solution containing 1 g of over time

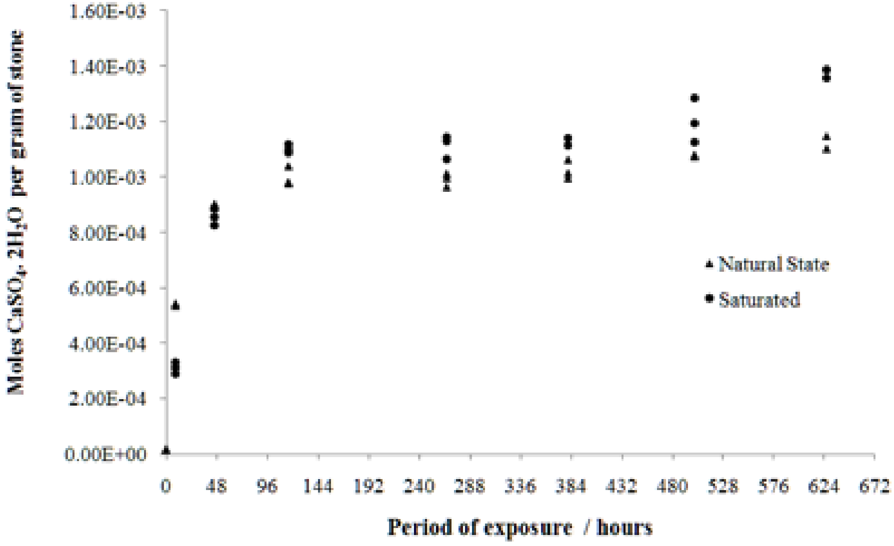

Figure 4. Number of moles of calcium sulfate in 100 ml aqueous solution containing 1 g of stone, as a function of time

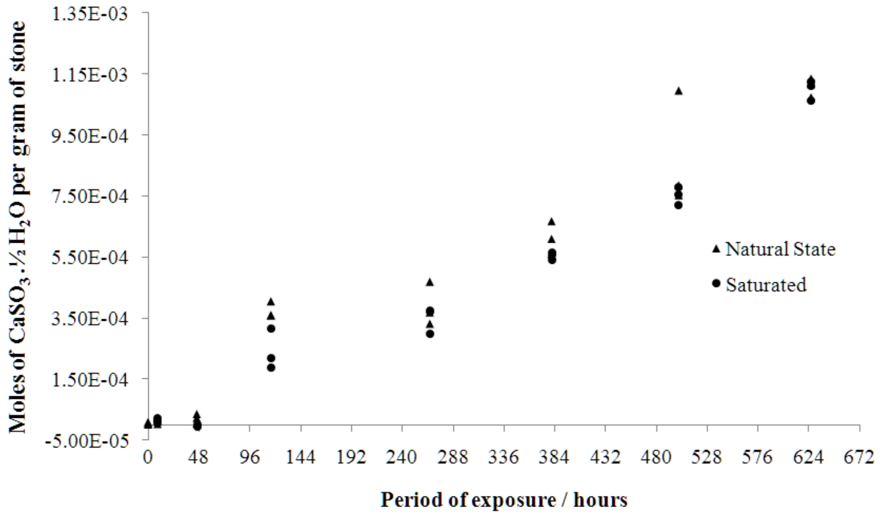

Figure 5. Number of moles of calcium sulfite in a 100 ml aqueous solution containing 1 g of stone, as a function of time

4. Discussion

The sulfation of limestone from Acinipo in a humid and SO_2 rich environment was investigated. The results support the existence of an interaction between the limestone and the weathering environment. Figures 3, 4 and 5 provide evidence that the reaction involved the decomposition of the calcite matrix to gypsum and calcium sulfite, thereby testifying that both species are thermodynamically more stable than $CaCO_3$ in the conditions found within the weathering chamber.

Over the exposure times studied, the formation of calcium sulfite over time was approximately linear, whereas the rate of formation of gypsum declined. This can be explained assuming a rapid conversion of calcium sulfite to calcium sulfate by S(IV) to S(VI) oxidation.

Conductivity of aqueous stone solution increases with the concentration of the electrolytes (ions of soluble salts). The soluble salts commonly found as a result of sulfation are: gypsum ($CaSO_4.2H_2O$), $MgSO_4$, and Na_2SO_4 in varying degrees of hydration and calcium sulfite in the form of $CaSO_3{\cdot}1/2H_2O$ [3]. Since Acinipo limestone is almost pure calcite (Table 1) the observed increase in conductivity (Figure 3), was likely due primarily to the formation of gypsum. The formation of calcium sulfite appeared to have little bearing on the increase in conductivity, concurrent with its low solubility in water. On the contrary, the mass increase (Table 2) is compatible with the conversion of $CaCO_3$ to both calcium sulfate and sulfite. Weathering not only produces an increase in atomic mass, but also affects the hygroscopicity of the stone, which itself is a function of the chemical and morphological alteration induced by the attack.

5. Conclusions

In this paper we present results from the sulfation of limestone in a humid environment. The proposed methodology allowed characterization of the involved processes. The different chemical processes involved (acid-base and redox reactions, gas-solid and gas-liquid reactions, and quantitative aspects) also illustrate the connection between chemical principles and the preservation and study of cultural heritage. With a simple and un-expensive experimental set-up that was easy to implement in an educational laboratory, and with the use of classical (redox titrations) and instrumental (turbidimetry, conductimetry) techniques, this methodology is accessible, informative and interesting for undergraduate students.

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