

Salt mixtures phase equilibria: a tool of preventive conservation against salt weathering

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Abstract

Coastal architectural heritage is contaminated by sea spray which constitutes a multi salt solution. The thermodynamic assessment of salt mixtures has been recently suggested in order to predict optimal conditions for preservation against salt weathering. This development in the form of the computer based model ECOS has been used as a diagnostic tool at the coastal archaeological site of Delos. Despite the dominance of halite as the main contaminant, quantitative analysis of the salt content in two monuments revealed significant variety due to fractionated infiltration and secondary contamination by ground moisture capillary rise. The thermodynamic assessment, comprised by phase transition diagrams have been correlated to the monitored environmental conditions. The results underline the role of minor species in the generation of damage and the importance of the halite-gypsum mixture. The investigation provided arguments for the application of environmental control along with data that can be used in various conservation treatments.

Keywords: salt weathering, ECOS, Delos, marine aerosols, salt mixtures.

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توازن خليط الأملاح: طريقة جديدة للحماية الوقائية
ضد تعرية الأملاح فى المباني الحجرية
فادى بلعاوى - باتروس بروكس
ملخص

التراث المعمارى فى المناطق الساحلية معرض للأملاح من رذاذ البحار والمكونة من خليط من الأملاح. عمليات تقييم سلوك خليط الأملاح التيرمودينامكى هو من أحدث الطرق التى يتم الاستعانة بها لعمل لحماية وقائية فى المناطق الساحلية من أخطار الأملاح. وهذا العمل تم تطبيقه فى من تطبيقه من منطقة ديوس الساحلية فى اليونان عن طريق استخدام برنامج كمبيوتر يدعى (ECOS) فى مواقعى الدراسية فى الموقع الأثرى، على الرغم من وجود الهاليت كملح أساى، تحليل الأملاح دل على وجود تباين كبير فى محتوى الأملاح فى هذين الموقعين.

التقييم التيرمودينامكى وبمقارنته مع الظروف البيئة المحيطة نتج عن وضع تصور للظروف البيئية التى تقلل من خطورة الأملاح الموجودة. الدارستقلت على أهمية الاختلافات البسيطة فى محتوى الأملاح من مكان لآخر ومدى تأثير ذلك على الحماية الوقائية فى الموقع وكذلك أكدت الدراسة على أهمية وخصوصية خليط الهاليت مع الجببوسوم فى هذه المواقع.

الدراسة قدمت اقتراحات لكيفية عمل معالجات وقائية عن طريق التحكم بالظروف البيئية جانباً إلى جنب مع استخدام العلاجات الفعلية فى عمليات المحافظة على الآثار.

1. Introduction

Salt weathering is particularly aggressive in the coastal environment. The deposition of marine aerosols is considered a major hazard for the loss of coastal architectural heritage. Although the composition of marine aerosols is dominated by halite (NaCl), sea salt contains other species that compose a complex mixture. Laboratory simulations have shown that sea salt is more destructive than halite alone (Rivas et al. 2000). Furthermore, due to fractionated infiltration, alternative contamination pathways, continuous deposition and removal of salt efflorescence, monuments are contaminated with salt mixtures that differ considerably from the composition of sea salt.

Attempting to investigate the key factors of damage in this aggressive environment we applied a thermodynamic approach considering the interactions of salts and the resulting equilibrium conditions of the salt mixtures found at the archaeological site of Delos, Greece. The investigation concerned the deterioration of the Hellenistic wall paintings in a number of monuments according to a variables system for the course of one year. Samples have been extracted by microdrills and analysed quantitatively for the ionic composition. The salt data has been assessed by ECOS software and the results, composed by multi-salt phase transitions diagrams, have been correlated to the environmental conditions and other monitored variables.

2. Methodology

2.1 Objectives

Phase transitions occur at a specific relative humidity for each salt, at a given temperature and pressure, called equilibrium relative humidity (RH_{eq}). Hence niter's (KNO_3) RH_{eq} is 94% while halite's (NaCl) RH_{eq} is 75.3% at $20C^{\circ}$. It could then be easy to predict the rate of salt phase transitions just by correlating the mineralogical identity of the present salts to the monitored hydrothermal conditions of a monument and thereby prevent damage by keeping the relative

humidity in ranges below or above this value (Aires-Barros 1996).

Single salts however are rarely found in nature. In practice buildings are contaminated by salt mixtures, which present a totally different behavior. As a matter of fact salt mixtures do not present individual RH_{eq} but rather a range of relative humidity within which progressive and multiple crystals growth occurs. This range does not necessarily correspond to the RH_{eq} of the individual components. Thus a mixture of halite (NaCl) and sylvite (KCl) presents a broader range of relative humidity where phase transitions occur, higher than the RH_{eq} of the less soluble sylvite and lower than the RH_{eq} of the more soluble halite. In the context of salt weathering, the interaction of salts has been studied by Price & Brimblecombe (1994) and Steiger & Zeunert (1996), using the approach of Pitzer (1973). The result of their effort was the computer based model ECOS (Environmental Control Of Salts) that predicts crystal volumes in a given system under given environmental conditions (Price, 2000).

The present investigation aims to evaluate the weathering environment which triggers the action of salts resulting in the deterioration of wall paintings at Delos. Taking advantage of the above-mentioned recent developments concerning the interaction of salts we assessed in situ the parameters that influence the generation of damage. The investigation followed a comparative approach guided by variables which permitted the comparison of the climatic conditions, the origin of salts, the salt content and the pathology of the wall paintings between the sampling locations.

2.2 Case study

The island of Delos belongs to the Cyclades complex (Aegean Sea) and its climate is typically Mediterranean. The atmospheric temperature in the Cyclades follows a simple oscillation with a maximum in July or August and a minimum in January. The sea, which acts as a heat reservoir, offers small fluctuations annually and diurnally. The mean relative humidity (RH) values follow the opposite oscillation of the temperature. However a closer look at diurnal fluctuations shows that relative humidity depends strongly on wind

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direction and speed and frequently presents strong diurnal variations.

The coastline of Delos corresponds to the site's boundaries. The whole island is practically a vast archaeological site (fig.1) with monuments that date from the early Cycladic (2.500BC) to the Roman period (69BC). The excavations started at 1872 and since 1990 Delos is a World Cultural Heritage site. Indications of salt weathering have been early recognized. A number of monuments with significant lime renderings and paintings have been sheltered with concrete slabs but the new microenvironment did not prevent the action of salts.

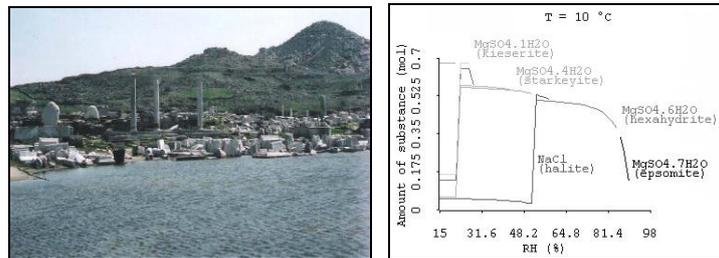


Figure 1. Delos.(The case study site) The central archaeological site during sea flood.

Figure 2. ECOS graph, an example of The Environmental Control of Salt soft wear that had been used in this research.

2.3 Sampling and analysis

The coastal location of the investigated site directed the variable of cardinal orientation, since the wind direction controls the deposition of sea spray. Sheltering, as well, was another control factor, both in terms of deposition and environmental conditions. Two monuments have been selected for the needs of this investigation, the “House of Hermes” and the “House of Masks”, both found at around 300m from the coast and at an elevation of around 30m from the sea level. The sampling areas have been selected according to their orientation and the degree of exposure. The height variable corresponded to three distinct damage zones in the sheltered areas. The samples have been extracted from the wall paintings in the form of micro-drills in depth

sequence. The mortar samples have been weighted and diluted in 20ml of distilled water. The water extract was then analysed by Ion Chromatography(IC) for the anions and Inductive Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) for the cations. The raw data has been calculated in molar/1000 (mM) which was used as input for ECOS software.

The ECOS results have been used to explain previous damage and to investigate whether this damage is ongoing. The results of periodic sampling should therefore follow a reasonable continuity upon which we attempted to construct a weathering model. According to phenomenological data, such as salt efflorescence and debris release, an annual cycle was considered to serve this purpose. Sampling has been repeated during the winter and summer temperature peaks and during the transition periods. The thermodynamic assessment has been supported by aerosols sampling and analysis, environmental monitoring and crystallographic analysis and microscopy of salt crusts (Prokos 2005).

3. Results and discussion

3.1 General stoichiometry

As expected Na^+ and Cl^- were the most abundant ions, followed by Ca^{+2} and SO_4^{-2} . Sheltered areas presented lower concentrations than the exposed areas. The sampling location facing the dominant wind direction (North) and receiving the highest amount of sea spray presented the highest salt content during the dry period. The concentrations in this location decreased during the wet season, probably as a result of rain-wash. The other exposed locations presented significantly lower concentrations throughout the year. The homogenous height distribution of Na^+ and Cl^- in the exposed areas indicates that they originate from direct sea spray deposition. In the sheltered areas Ca^{+2} and SO_4^{-2} decreased with height while Na^+ and Cl^- were dominant in the upper zone. The height distribution in the sheltered areas indicates salt infiltration by ground moisture capillary rise.

3.2 Thermodynamic assessment

Only a few characteristic examples of ECOS applications will be

presented in this section since it is impossible to describe the complicated thermodynamic assessment in its entirety. In the sheltered areas the absence of marine aerosols permits the monitoring of salts infiltrating by ground capillary rise. The height distribution follows in general the solubility based model (Arnold & Zehnder 1991) but the thermodynamic investigation revealed a much more complex behaviour due to salts interactions. Thus a part of Mg^{+2} which usually seemed to relate to Cl^- is consumed in epsomite ($MgSO_4 \cdot 7H_2O$) and other forms of hydrated sulphates in the mid zone (fig 2). As a result the absence of the more soluble salts from the upper zone permits halite to stabilise its RH_{eq} near the normal value (75.3%) (fig. 3). In another sheltered area sulphates mainly crystallised as mirabilite ($Na_2SO_4 \cdot 10H_2O$), which dehydrated to thenardite (Na_2SO_4) during the warm period (witnessed by efflorescence analysis), permitting a part of Ca^{+2} to produce the very soluble antarcticite ($CaCl_2 \cdot 6H_2O$) which reached the upper zones and decreased considerably halite's RH_{eq} (fig. 4).

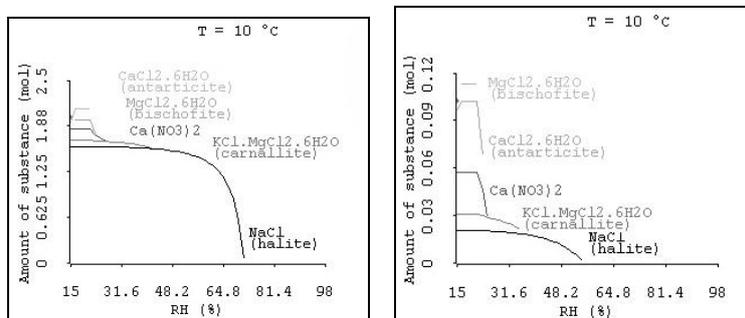


Figure 3. ECOS graph. Halite's equilibrium at 75%RH during the rainy season.

Figure 4. ECOS graph. Decreased halite's equilibrium due to the dominance of more soluble species during the dry season.

The recorded environmental conditions in the sheltered areas are above the crystallisation RH of halite during most of the year. In the mid zone sodium sulphates, supplied by ground moisture, crystallise slowly on the surface growing a dense crust. This prediction agrees with the absence of damage in this area. Preventive measures of environmental control or drainage should be very cautious and coastally

monitored not to disturb this delicate balance. The complete loss of mortar in the lower zones of the sheltered areas is probably related to gypsum, which was found as efflorescence. In this case ECOS presented technical difficulties in executing the calculations and consequently we had to adjust the input data significantly. Damage according to ECOS hypothetical resolutions takes place during the fast transition from the cold to the warm period when there is still moisture supply from ground waters and temperature increases significantly.

Halite efflorescence was found at the same height in both sheltered areas which constitutes probably the evaporation zone. Halite crystals present whisker habits due to the low supply of moisture (fig. 5). Crystallisation takes place right under the surface resulting to detachment of the external layer. In this case damage takes place during a short period of very high temperature and according to ECOS calculations it might be activated diurnally. The crystallisation RH must be a bit lower than the predicted RH_{eq} .

The same weathering pattern is present on the exposed surfaces of the House of Hermes which face the North but the mechanism is quite different. Although halite seems to be responsible for the generation of damage, since it dominates quantitatively, the conditions predicted by ECOS were not met. We had thus to presume the influence of a kinetic factor which according to hypothetical ECOS calculations should supply higher temperatures. A logical explanation is the direct solar radiation which, as recorded by pyranometer during the warm period in Delos, can supply energy of 900w/m^2 . The sharp rise of temperature on the rendering surface generates fast evaporation and high supersaturations. The crystallisation site lies at the interface of the wall painting's layers due to hydraulic discontinuity.

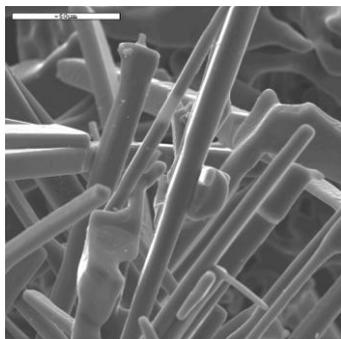


Figure 5

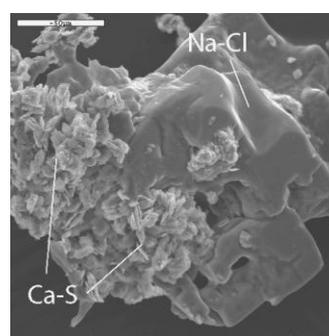


Figure 6

Figure 5. Halite whisker-like crystals, which has a main role in the type of salt damage at the site.

Figure 6. Mixture of halite and gypsum, the two salts were found alongside in damaged areas.

Nonetheless the results of ECOS also raised serious arguments for the interaction of gypsum and halite. The two salts have been frequently found alongside in damaged areas (fig. 6). The depth variable has revealed a constant presence of halite and gypsum at the interface between the external lime wash layer and the mortar in areas receiving direct sea spray. Although the results were confirmed by laboratory simulations that will be published in the future (Prokos 2005), the conditions of damage could not be defined precisely. Another experiment conducted by Environmental Scanning Electron Microscopy has revealed a very unstable behaviour of the mixture at very low relative humidity conditions during the hydration of the anhydrite. It is presumed that these conditions might be met in Delos under direct solar radiation.

Another important factor in the definition of the weathering mechanism was the presence of hydrated species and especially magnesium and sodium sulphates. According to ECOS calculations transitions between the hydrated phases of these salts occurred frequently. One aspect of the importance of these species lies in the strong influence on other salts during phase transitions by depleting or supplying water independently of the ambient relative humidity. The

outcome of this behaviour cannot be predicted without thermodynamic calculations. The other aspect is the intensity of damage due to the generation of high supersaturations during hydration (Rodriguez-Navarro & Doehne 1999). In this case damage occurs during the rise of the ambient relative humidity.

3.3 Implications for conservation

ECOS periodical in situ application provided the opportunity to investigate open systems under real conditions of continuous and varied contamination, which along with automigration and solubility fractionations resulted in multiple thermodynamic potentials. Different sampling locations even on the same wall presented strong deviations. To what extent can we thus apply a unique environmental control approach? The height variable although limited to three components revealed significant variation. Especially in the sheltered areas the relation of sulphate salts to ground moisture produced an interesting fractionation which resulted in varied equilibrium conditions in height. In this case the maximum upper limit can be set as a boundary for optimal conditions.

On the other hand the presence of ground moisture does not only transport salts in the masonry but controls their phase transitions as well. Environmental control seems more plausible for the parts of the masonry that are not influenced by ground moisture. Nevertheless we can argue that relative humidity controls the height of moisture rise and the crystallisation location (Lewin, 1982). Although the resultant is a function of many parameters ECOS predictions can support in situ environmental control projects by setting the upper boundaries. Environmental control is more realistic by means of a long-term slow transition towards the optimal conditions rather than alarm triggered air-conditioning. The stability of the environmental condition at the optimal range can also be achieved by alternative means of insulation, which can buffer the macroclimatic fluctuations.

Still even if we manage to ensure stable hygrothermal conditions at a unique optimal range the continuous sea spray deposition and differential contamination might shift the equilibrium from the initial

predictions. The periodic investigation revealed that the RH_{eq} changes significantly during the year as a result of salt input and removal. There is no doubt that a combined approach implying elimination of one or more sources and blocking of contamination pathways along with desalination techniques would have more effective results. Again the thermodynamic approach is essential in controlling such operations by predicting hypothetical conditions of preservation. Sawdy (2001) had the chance to investigate simultaneously areas that have been previously desalinated with intriguing results. Although this is not always feasible it underlines the multiple function of thermodynamic analysis, which can provide insight in various questions. Additionally phenomenological approaches in combination with non destructive analysis can provide sufficient information based on which we can predict hypothetical equilibrium conditions for future investigations on maintenance and restoration risks.

Nonetheless the environmental control should not only focus on hydrothermal conditions stability. The air movement plays a determining role. Research has produced clear evidence (Bala'awi, 2006) and we should reasonably expect that evaporation is enhanced by air movement. It was clear that relative humidity fluctuations were smaller outdoors while the maximum values were lower in the sheltered room which was better ventilated. The upper zones of the sheltered areas that were contaminated mainly by halite, although less susceptible to atmospheric deposition than the exposed sites presented more intense weathering. As justified by ECOS this was attributed to the microenvironment's increased upper limits of relative humidity.

Direct solar radiation, which was a significant factor in the particular case of Mediterranean climate, can also influence the transition process without traceable indications in the ambient temperature. In many cases the intense solar radiation was the only reasonable explanation for damage. Although from a first point of view this restricted sea spray penetration, it might have induced fast evaporation of entrapped solution pockets inside the mortars. Furthermore rainfall comprises another important environmental parameter. The absence of efflorescence on the exposed surfaces has

been partly attributed to rain-off while ground moisture infiltration was increased during the rainy season.

As far as it concerns the exposed sites there is no doubt that sheltering provides the only means to control the environmental conditions. The methodology proposed by this project can help in the determination of the new artificial environment in order to prevent the conditions that lead to the intense weathering of the already sheltered areas. Keeping the relative humidity higher than the upper limit of phase transitions might induce other problems like biological damage or gases deposition. While ECOS provides the chance to investigate hypothetical conditions for preservation with varied temperature and relative humidity we must state clearly that combined approaches are absolutely necessary in decision-making investigations. This way we could construct a theoretical model of annual and diurnal fluctuations in order to test potential solutions in relation with other weathering mechanisms.

4. Conclusions

Although the presence of marine aerosols is considered by itself a risk for architectural heritage along the coasts the thermodynamic approach applied at Delos has revealed a much more complicated situation. Monuments contaminated by salt mixtures such as sea salt present variable concentrations even in adjacent locations. As a consequence the application of environmental control becomes problematic. The present investigation underlined the role of minor species of sea salt in the generation of damage and the importance of the halite-gypsum mixture which needs further kinetic investigation. The comparative approach and the supplementary investigations proved to be essential in the interpretation of ECOS results. Apart from setting the upper limits for environmental control we retrieved diagnostic data that can be used variously in conservation treatments such as desalination or drainage. The limitations of the theoretical model testified the need for more kinetic investigations on salt weathering. Sheltering is the only means to control the environmental conditions.

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