



Contract no.: NMP2-CT-2005-515762

I-STONE

Re-engineering of natural stone production chain through knowledge based processes, eco-innovation and new organisational paradigms

Instrument: Integrated Project
Thematic Priority: 3

D5.6. Key literature list on Durability

Due date of deliverable: August 2006
Actual submission date: 11 December 2006

Start date of project: 1 March 2005

Duration: 42 months

Organisation name of lead contractor for this deliverable:

SP

Revision [1]

Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	X

CONTRIBUTORS

BGC – database, reporting

BBRI – climate, oxidation test

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EXECUTIVE SUMMARY

This report presents part of the work performed for WP5, Task 5.1 “Quality of stone products and materials in construction and use”, Sub-task 5.1.1, the main aim of which is to develop an expert system for evaluation of durability and specification criteria.

A literature database concerning the use of natural stone in the building industry has been created. The database contains more than 480 records of references selected among approximately 1200 references. These references cover a wide spectrum of the literature – from scientific research papers, guidelines, teaching books to commercial (news) articles. In addition, they cover various areas within the use of building stone, from degradation and weathering mechanisms, durability and physical properties, climatic influence on stone behaviour to actual performance of building stone in different climatic exposures (case studies) and constructions requirements.

The aim of this database is to give the user the most comprehensive reference database available of studies in stone durability, which will lead to a more complete and accurate understanding of degradation mechanisms and material properties related to the performance of the stone in its application. This database also constitutes an important part of the background to create an expert system for evaluation of durability and specification criteria that will help to find correlations between various properties and the performance of natural stone as a building material.

In order to establish the durability of building stone all factors influencing the application of stone for specific uses and its ability to resist different weathering factors have been evaluated. Frost action has been considered to be one of the most critical parameters concerning durability. However, other durability aspects have been reviewed and described, e.g. damages due to salt action, thermal and moisture influence (wetting and drying), thermal shock, harmful components and abrasion. These have all been identified as critical parameters for the overall service life of stone products. All the critical parameters will be addressed, when creating guidelines concerning the choice of suitable stone types for a certain application in a certain climate.

INTRODUCTION

The purpose of the created literature database is to give the reader the most comprehensive reference database of available studies on stone durability. Eventually is believed that it will lead to a better understanding of ageing mechanisms and material properties that are related to the performance of the actual stone product and its application. The database is also part of the work to create an expert system that will help in finding correlations between various properties and the natural stone performance as a building material and in defining relevant requirements. The database will also include guidance for building cases, where experts will be able to extract relevant information for their actual problem.

The durability aspects considered here are primarily related to frost action, which is the main focus of the study Subtask 5.1.1. However, other durability aspects are also considered and have been reviewed, e.g. damages due to salt action, thermal and moisture influence, thermal shock, abrasion and harmful components. They have all been identified as critical parameters for the overall service-life of stone products and are key aspects when providing guidance concerning the choice of suitable stone types for a certain application in a certain climate. In addition, many of these parameters have been identified as having a poor correlation between results obtained by testing according to the new European standards and their actual performance. This state-of-the-art, together with related testing activities in I-STONE, may also be used when reviewing and improving the first generation of European standards.

1. THE NATURAL STONE LITERATURE DATABASE

This report concerns Natural Stone Literature Database. A print-out of instructions and examples is given in Annex 1 and the enclosed CD-ROM. All references on the various subjects may not be included in this report. However, they can be found in the database. The database includes selected relevant publications concerning the use of natural stone in the building industry. At this point, 483 references have been selected to be included in the database among approximately 1200 references. The references cover a wide spectrum of literature like teaching books, scientific research papers, technical papers and news articles. The contents of each reference have been screened, and on that basis are divided into categories with keywords assigned to each reference (Figure 1). All references in the database can thus be searched by categories and/or keywords. The categories and keywords are given in Table 1.

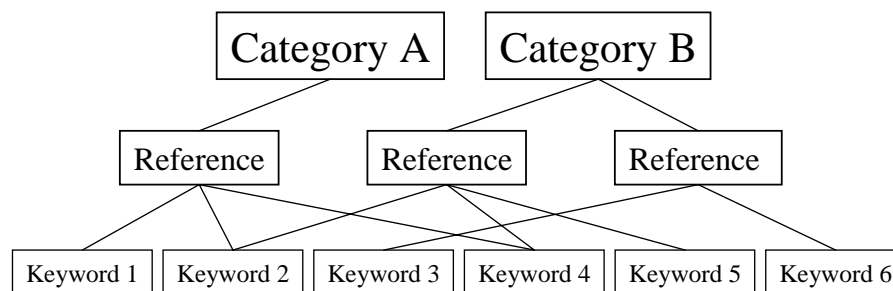


Figure 1. Schematic diagram of the build up of the Natural Stone Literature Database.

Table 1. Categories and keywords of the Natural Stone Literature Database

Categories	Keywords	
Biochemical weathering	Acid rain	Mechanical
Case studies: Historic buildings - sculptures - monuments	Alteration	properties/characterization
Case studies: Modern buildings	Bowing	Mineralogical/petrological
Chemical weathering	Building	characterization
Conservation	Cladding, pavements, flooring etc.	Pollutants
Frost action	Cleaning agents	Porosity, permeability
General description - weathering, durability etc.	Climate	Reaction with
Maintenance - cleaning - repair	Colour stability	components in the stone
Mechanical degradation	Construction procedures	Residual expansion
Other relevant subjects related to our work.	Discoloration	Rock
Physical and chemical properties of stone materials	Encrustation	mechanics/structures
Salt exposure	Formation of rust	Salt crystallization
Stone specification - in general	Freeze/thaw	Stain removal
Thermal and/or moisture cycles	Graffiti/anti-graffiti	Strength
	Historic use of stone materials	Stress relief
	Impregnation/consolidation	Sunburn
	Installation	Super saturated solutions
	Macro- and microstructure	Surface treatments
		Test Method
		Thermal stability
		Traffic
		Weathering
		Wetting/Drying
		Wind, water

The compiled references deal with various areas of building stone:

- Degradation mechanisms, including weathering of stone (e.g. freeze-thaw, salt exposure, thermal hysteresis etc.)
- Durability and physical properties of stone
- Construction requirements
- Case studies of buildings and monuments of natural stone
- Climatic influence on stone durability

The work of updating the database will continue throughout the whole project duration. Durability, climate and testing of natural stones properties are parameters that are analysed in the next chapters.

2. DURABILITY

The durability of a building stone element can be defined as the period of time that the properties of the stone element will remain unchanged, in the best of cases during its designed service-life. The properties of the stone do however change with time because of various factors like for example weathering. In order to establish the durability of the stone all factors influencing the stone element for each specific use must be considered. Therefore, concerning weathering an assessment of the stone element ability to resist the weathering factors must be made along with an evaluation of the rate by which the stone will degrade as a consequence of weathering. The durability properties are reported in Figure 2.

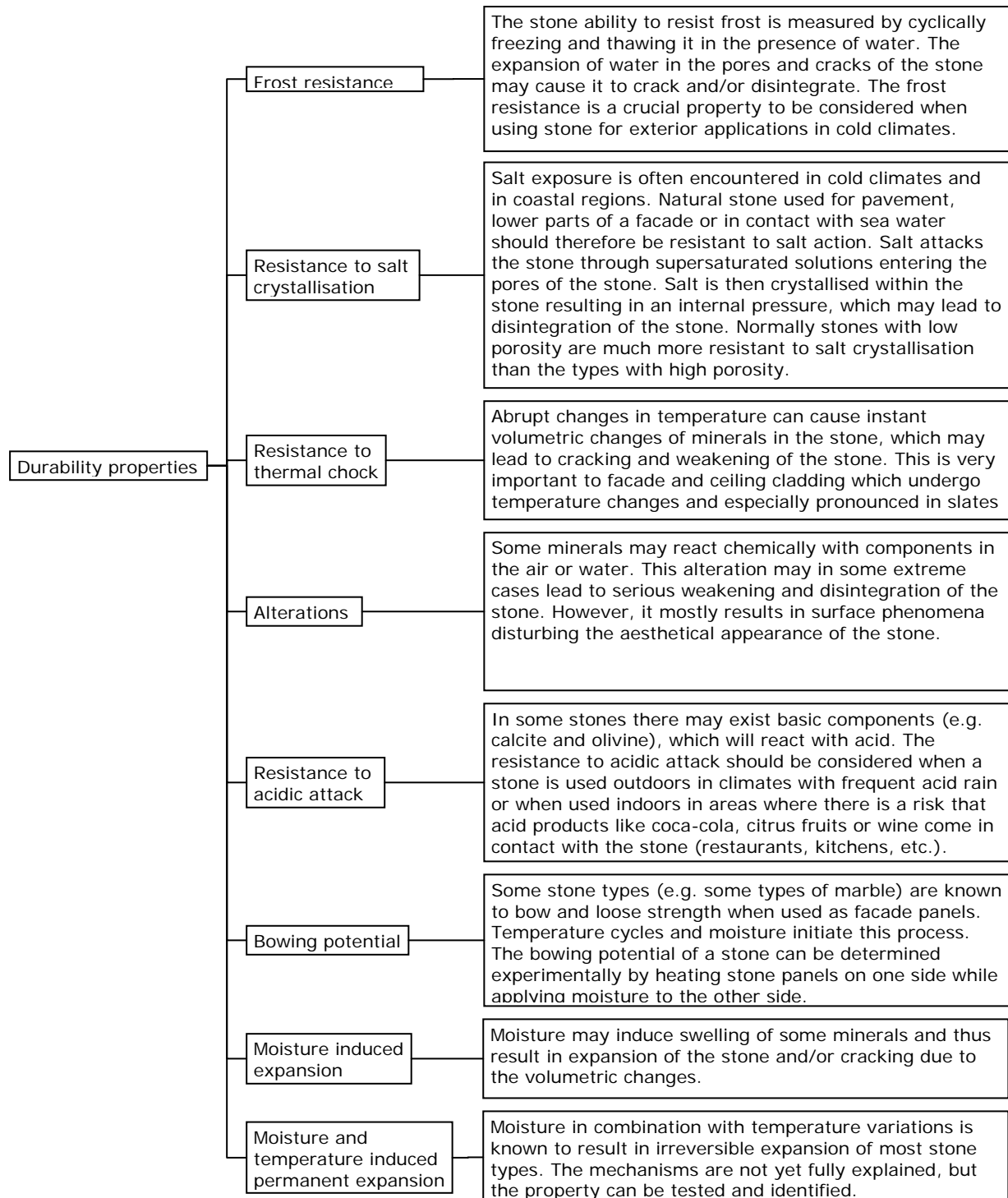


Figure 2. Durability properties

2.1. Frost (with and without salt)

In some countries, for example, Scandinavia, Canada and northern parts of the United States of America, frost is considered to be a very potent cause of decay. The damaging process of freeze-thaw cycles has long been known by researchers. Kessler, (Schaffer 1932) in 1924 noted that the Bureau of Standards calculated the weathering resistance of a building material in any given district by comparing the number of occasions on which heavy rain was followed by frost (recorded in the meteorological records of that district) with the number of repetitions of the freezing test which are found to be necessary to cause disruption of the material.

Most of the building stones in common use have relatively low water saturation, i.e. the stone is seldom sufficiently saturated by rain to be badly damaged by frost. But in unprotected applications like cornices and parapets, where thorough soaking by rain or groundwater is more frequent, freezing may cause disintegration. In retaining walls, the seepage of water behind the wall may also cause the stone to become excessively saturated with water and frost damage may follow. Similarly, in stone paving and in the surroundings of fountains, failure by spalling, quite independently of the bedding, is not infrequent under specific weather conditions. The laying of stone paving on an impervious foundation may also amplify the effect of frost.

2.1.1. Freeze-thaw parameters

Freeze-thaw action of water in the pores of natural stone may, under certain conditions, damage the stone. The type of damage is mostly surface scaling, exfoliation and cracking, which are often associated with loss of strength.

Frost action on porous solids is complex and includes several mechanisms that may interact. Powers (1945) mentions volumetric expansion of freezing water, pressure by growth of ice crystals and hydraulic pressure caused by freezing of water as some of the most recognised theories presented in literature. The amount of finer pores is crucial for the freeze thaw durability of natural stones (Sims and Brown, 1988).

Accidental combination of circumstances, such as severe frost following upon heavy rain, may result in frost damage; frequent fluctuations of temperature about the freezing point, is normally considerably more damaging than continuous severe frost. The physical properties of the material and its position in the building are other factors, which determine its liability to damage by frost.

The most common (and simple) explanation of frost action is that of volumetric expansion. A volumetric expansion of approximately one-tenth occurs when water freezes to ice. Hence, when water freezes in a confined space, a considerable pressure is developed. The freezing of water in the pores of building materials may develop sufficient pressure to cause disruption if the tensile strength of the stone is exceeded. However the degree of damage, which may result from frost action, depends on the conditions of temperature (variations) and moisture (availability) to which the material is exposed. Moisture reaches a porous building material from the ground by suction of ground water, by rain and snow, or by diffusion of vapour from the air (Wessman, 1997). Furthermore, water sources may also result from the interior of buildings, where periodic water spill or high water vapour concentrations may penetrate the stone constructions. In climates with many freeze-thaw cycles stone decay due to frost action occurs more often (Hirschwald, 1908).

Chatterji and Christensen (1979) studied frost damaged limestone nodules in gravel pits in Denmark. They found that nodules smaller than 8 to 10 mm in size were not damaged. Larger nodules were either fractured into a few, comparatively large pieces or they were surface

pitted. The results from the fractured nodules gave rise to a theory regarding the development of hydrostatic pressure during freezing. The theory states that hydrostatic pressure develops when the outer surface of a porous, wet material is initially frozen. As freezing continues, ice also forms in the inner parts of the material, but since the outer shell is sealed with ice, it cannot expand. If the hydrostatic pressure thus developed exceeds the tensile strength of the ice-limestone composite in the shell, the material will eventually break down.

2.1.2. Saturation coefficient

Several studies have shown that the amount of water present in the pore space tends to be of vital importance for frost damage to occur. Since an expansion of approximately 10% occurs upon freezing, damage by frost should not occur until about 90% of the available, interconnected pore space in the material is filled with water. The influence of the degree of pore saturation has been established by the experiments of Hirschwald (1908). He found that materials, which are practically unaffected by freezing when saturated by simple immersion in water, are rapidly disintegrated after saturation in a vacuum.

In accordance with Hirschwald, Fagerlund (1972) found that critical degrees of water saturation existed for all porous, brittle materials. In his study he tested various kinds of brick, lime silica brick, cellular concrete, asbestos cement and cement mortar. Fagerlund showed that samples with a degree of water saturation higher than a certain critical value were all damaged, whereas samples with less water contents were almost undamaged.

The ratio between the natural capacity of a stone to absorb water and its total porosity is defined as the saturation coefficient S :

$$S = \frac{w}{p}$$

where w = water absorption and p = total porosity (EN 1936).

Theoretically, a stone having a saturation coefficient of 0.9 should be insensitive to frost action (Figure 3). However, by observation on a large number of different building stones Hirschwald concluded that this figure is too high, and that in practice the limit should be placed at 0.8. He found, however, exceptions to the general rule. Certain stones with saturation coefficients as low as 0.7 disintegrated under frost action, while others with saturation coefficients above 0.8 were not affected (Figure 4). The disintegration of the former class was attributed to a special system of the pores (with certain shapes) and their interconnections, to an arrangement of the particles in parallel layers, or to a tendency for the binding agent to soften in water. The resistance of the latter class was attributed to the squeezing of the ice inside the pores. He showed that by freezing water in vessels of a suitable shape, ice could be extruded from the neck. He also showed that, with certain stones, ice can in a similar way be extruded from the pores. It is clear that the presence of totally closed pores, not accessible to water, will tend to indicate an inaccurate coefficient. Kreüger (1924) (in Shaffer 1930) reached a similar conclusion that a saturation coefficient of 0.80-0.85 represents the practical limit above which materials are liable to be damaged by frost.

A saturation coefficient of 0.75 has been regarded by the former German standard DIN 52106 as a practical (upper) limit for frost resistance of porous stone materials. For stone material with higher saturation coefficient it is recommended to carry out a freeze-thaw test, the results of which are closer to the actual frost resistance of a stone in practical use. McBumey (1929) preferred to measure what he termed as "Schurecht's ratio," which is the ratio between the water absorption occurring as a result of 48 hours immersion in cold water and that occurring

as a result of 5 hours boiling in water. McBumey regards this ratio as a useful measure of frost resistance, but states that it is not sufficiently reliable to form a basis for classification.



Figure 3. Porous limestone with very high water saturation coefficient (>95%) and severe frost damages (cracking and spalling) on a building facade in Copenhagen, Denmark.

The results of laboratory tests with respect to predicting the frost resistance of natural stones have become more reliable today, but some uncertainties still exist. Fitzner & Kalde (1991) and Wessman (1997), stressed that freeze-thaw tests carried out using pure water does not attack the stone in the same magnitude as when a small concentration of salt is present in the water. The dynamics of the freezing process including salt in solution are complex, but several studies show, that even small amounts of salt cause a significant increase in the damage of frost susceptible rock types.



Figure 4. A yellowish, permeable granite with relatively low water saturation coefficient (<80%) showing frost damages (surface spalling) on a building in Copenhagen, Denmark. The stone is however also exposed to de-icing salt.

The freezing temperature of a salt solution is lower than that of pure water. The reason is basically the same as that of the freezing point depression in a small pore; the ions or molecules of the solute attract the water molecules in the same qualitative way that the pore wall does. The solubility of a salt normally decreases with decreasing temperature, and salts can form various hydrates (described later in section 4.2.1.).

When a salt solution is cooled below the freezing point many small ice-crystals, caused by heterogeneous nucleation, are formed (Hobbs, 1974) and a salt solution with a higher concentration than the original one is trapped in the cavities between the crystals. The reason for this is that foreign substances, such as salts, are normally not incorporated into the crystal structure of ice.

It is known (Laugesen, 1996) that materials like concrete are more damaged by salt solutions than by pure water when they are frozen and thawed, and that weak solutions cause more damage than stronger ones do. No theory is yet fully established to explain this phenomenon.

Several interactions can occur between the phases present when a salt solution freezes in a porous solid. Three main phases exist:

- Ice, which does not incorporate salt in its crystals.
- Salt solution, consisting of water and solved salt ions (the salt does not normally crystallise because of the low concentrations).
- The solid, porous material.

This complex system makes it difficult to describe quantitatively in detail what is actually happening when a salt solution freezes inside or on top of a porous solid and thus to explain the occurrence of a minimum salt concentration.

Goudie & Viles (1997) stress the complexity of frost action in the presence of salts, where different salts act in different ways in freezing solutions. Some salts, such as magnesium sulphate (Jerwood et al. 1990a and 1990b), are actually known for having a moderating effect on frost action. Williams & Robinson 1991 lists a range of possible mechanism, which may explain why, under some conditions, salts can accelerate frost weathering.

Table 2. Possible mechanisms that may explain why salts under some conditions lead to accelerated frost action (Williams & Robinson 1991).

<p><i>Surface sealing.</i> Salts that have been accumulated on the outer layers of a rock surface as a result of surface evaporation could block pores and seal the surface. Water beneath such a sealed surface may be less able to escape by extrusion during freezing, thus increasing the stresses created within the rock.</p>
<p><i>Combined growth of salt and ice-crystals.</i> The combined action of salt crystal growth and frost action may be greater than they would be individually. Moreover, as salt crystals form they may tend to reduce the amount of pore space available for ice formation.</p>
<p><i>Osmotic pressure.</i> The growth of ice-crystals tends to expel solutes included in water and they diffuse into the unfrozen portions of the rock creating osmotic pressures, which may be sufficient to cause damage in rocks with a certain micro pore structure.</p>
<p><i>Expansion of ordered water.</i> If frost damage of sorption-sensitive rocks results from the expansion and concentration of absorbed, ordered water on clay surfaces then, due to the presence of salts freezing delays, there will be a greater amount of ordered water that can undergo expansion and, as the temperature falls, there is consequently more damage in the presence of saline solutions.</p>
<p><i>Greater saturation.</i> Because of the hygroscopic nature of some salts, rocks containing salts can take up more moisture from the atmosphere than rocks that do not contain saline solutions. The presence of larger amounts of moisture in the rock pores could make them more susceptible to frost weathering.</p>
<p><i>Increased water mobility.</i> Low concentrations of dissolved salt may increase the rate at which water moves to ice-crystals on freezing. This could facilitate crystal growth and increase the crystallisation pressure.</p>
<p><i>Leapfrogging on the freezing front.</i> The rejection of salts by growing ice-crystals may cause them to accumulate beyond the advancing freezing front, thereby depressing the freezing point. In the zone where salts become concentrated freezing may be temporarily prevented so that the freezing front may jump this zone, reforming on the other side. An unfrozen layer may be expected to experience pressure as the adjacent frozen layer expands.</p>
<p><i>Reduced rate of freezing.</i> If the freezing of a dilute salt solution is slower than that of pure water solution, then the resulting ice-crystals may be larger than usual and thus more effective at causing rock disintegration.</p>
<p><i>Corrosion.</i> The corrosion effects of salts may, especially in carbonate rocks, act in a multiplicative manner with frost to produce rock disintegration.</p>

2.1.3. Loss of strength

Frost action causes loss of strength in frost susceptible natural stone, and this knowledge is also incorporated into most modern tests on frost resistance (e.g. EN 12371). Frost damages are not necessarily visible to the eye but may also cause interior cracking and damages of the pore structure (e.g. Wessman 1997). This should normally cause some loss of strength, but to the knowledge of the authors no systematic study has ever been performed on this aspect on natural stones. Some researchers (Kessler, 1919) have found an increase in flexural strength after frost test for certain limestone and marble types.

2.2. Salt weathering

Salt weathering has a strong destructive effect similar to that of frost action. It is widely recognised as one of the primary parameters in the deterioration of historical and archaeological structures and buildings (Schaffer, 1932). Salt weathering has also a serious degradation effect on newly built (modern) buildings, especially in environments where porous building materials are exposed to both moisture and salt. Damages typical for salt actions are scaling, deep cracking, and uniform expansion, micro-cracking, granular disintegration and delaminating (Doehne, 2002). However, chemical alteration of stones may also be caused by salt (Figure 5).

In temperate climates, it can be difficult to determine, with the naked eye, if damage has occurred due to freezing, salt crystallization or through a combination of both of these. Although salts are of chemical origin, the crystallization damage is of a mechanical-physical nature.

Table 5.1. Mechanisms of salt attack
Physical changes
Crystallisation
Hydration
Thermal expansion
Electrical slaking double layer effects associated with hygroscopicity
Chemical changes
Silica mobilisation under alkaline conditions
Etching of calcite under acid conditions
Changes to concrete mineralogy
Corrosion of incorporated iron and steel
Moisture-related chemical weathering associated with hygroscopicity
Gypsum/silicate replacement

Figure 5. Mechanisms of salt attack (Goudie & Viles, 1997).

However, salts can damage stones and other building materials through a range of mechanisms, such as differential thermal expansion, osmotic swelling of clays, hydration pressure, and frequent wetting-drying cycling caused by deliquescent salts (Goudie & Viles 1997). Despite a lot of investigation in this field, many issues related to salt weathering remain unsolved, ranging from details on the damaging mechanisms to the interactions between the substrate, environment and salt type (Doehne, 2002). Numerous properties, factors and behaviours in the salt crystallisation process must be considered in each case of salt crystallisation (Figure 6). The interactions between all these possible parameters may be highly complex. Some of the salt “behaviours”, such as salt creep and efflorescence, may not be of destructive nature to the stone, but merely to the surface, i.e. of an aesthetical importance.

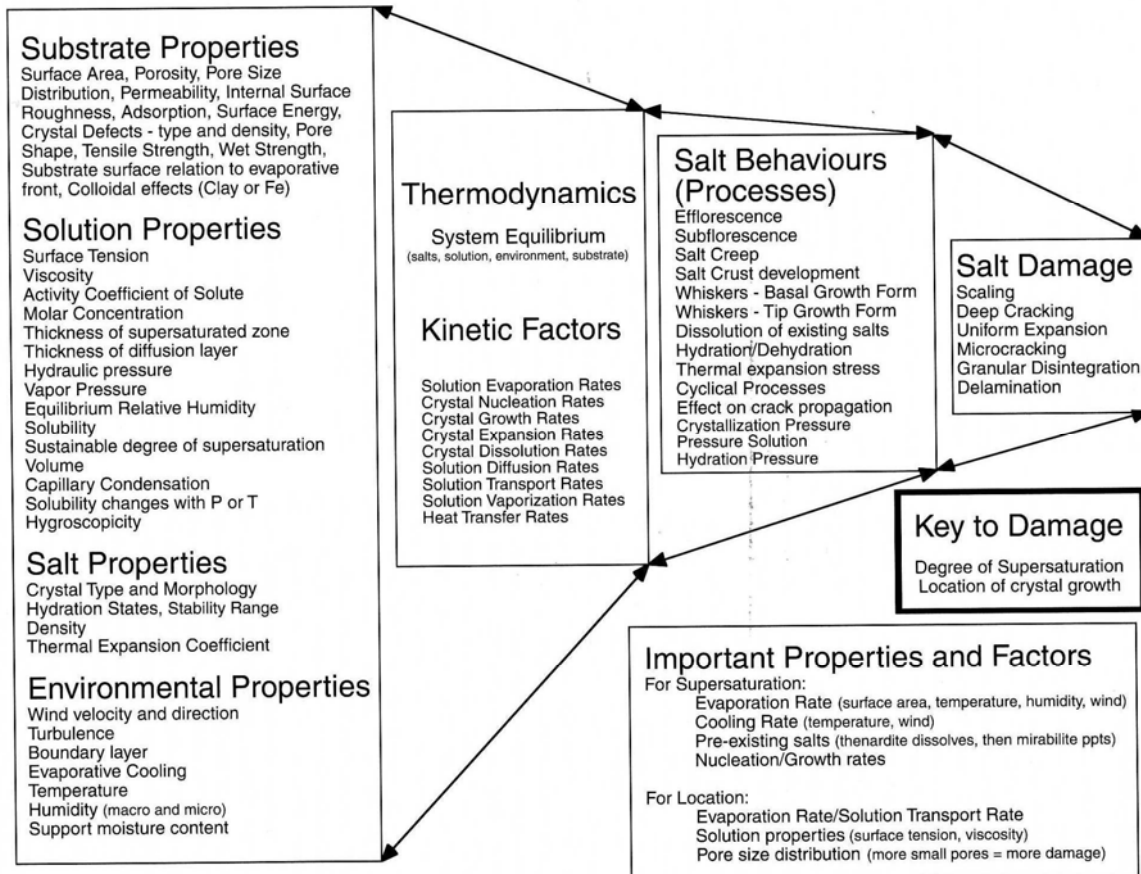


Figure 6. Diagram of properties, factors and behaviours in the salt crystallisation process (Doehne, 2002).

2.2.1. Salt pressure mechanisms

Pressure crystallisation is the most important decay mechanism that occurs during salt crystallisation, which depends mainly on the degree of super-saturation and the pore size.

Doehne (2002), states that “it has long been known that the solution in pores must be supersaturated, in order for salt crystallisation to damage porous materials”. What has been unclear until recently is how, in a material with abundant nucleation sites, such a supersaturated solution was created and maintained.”

Several mechanisms on this aspect have been presented in literature, and they may reflect different properties of the various salts. A generally accepted pathway to super-saturation is the rapid cooling of salt with a high dependence of its solubility to temperature. Rapid evaporation has also been put forward as a cause for super-saturation. Chatterji & Jensen (1989) described another pathway, where pre-existing, unhydrated salts dissolve rapidly in a supersaturated solution leading to rapid crystallisation of hydrated salt (e.g. the thenardite-mirabilite relationship, Chatterji 2005).

Table 5.4. Material strengths and salt pressures

(A) Tensile strengths of materials in MPa	
Extremely high strength rocks ¹	> 10
Very high strength rocks ¹	3–10
High strength rocks ¹	1–3
Medium strength rocks ¹	0.3–1
Low strength rock ¹	0.1–0.3
Very low strength rocks ¹	0.03–0.1
Extra low strength rocks ¹	< 0.03
Concretes (typical values) ²	2–4
(B) Pressures produced by salt processes in MPa	
Expansion of steel reinforcements on rusting ²	Up to 30
Crystallisation pressures of gypsum ³	28.2–19.0
Crystallisation pressures of halite ³	5.54–373.7
Crystallisation pressures of thenardite ³	29.2–196.5
Hydration pressures of gypsum ⁴	Up to 254
Hydration pressures of MgSO ₄ ⁴	Up to 42
Hydration pressures of Na ₂ SO ₄ ⁴	Up to 48

Sources: ¹Bell (1992); ²Murdock et al (1991); ³Winkler and Singer (1972); and ⁴Kirchner (1996).

Figure 7. The tensile strength of some materials and possible salt pressures (Goudie & Viles 1997).

Salt pressure is also believed to happen through hydration of salt. Some salts may incorporate water into their structure at certain moisture and temperature conditions, leading to volume increase. Non-hydrating salts, like NaCl, can therefore be excluded as causing damage by hydration. However, NaCl may react with CaCO₃ (calcite) at 37°C and form Na₂CO₃, which subsequently may hydrate and lead to the formation of Na₂CO₃·10·H₂O. The presence of NaCl may, in this way, lead to salt crystallisation damage in limestone.

Crystallization can also occur under a compact surface. A component in the stone has then generally been dissolved chemically and built-up a dense gypsum containing surface layer.

The crystal structure of some salts also change when there are changes in atmospheric humidity and temperature. Salt, which is in the surface layer of the stone, follows the changes in the atmospheric humidity and gives rise to different structures or becomes dissolved. Due to this large variation in the structure of different salts, the combination of salt - water can cause serious frost damage, especially in small porous and layered materials.

2.2.2. Sources of salt

Salt presence in a stone can be of many origins. Rising ground moisture which contains salt, water which penetrates the cracks and/or leaking coping and releases salt from the masonry, old surface treatments or cleaning processes and air pollutants are some of the sources of salt in stone. It can also emanate from activities inside a building such as keeping animals or a tannery. Salt can even cause damage to stone indoors. The salts can be de-icing salts brought indoors with shoes, onto the floor or splashed up on pavement surfaces, kerbstones and facings. The salt solution subsequently penetrates the surface pores of the stone. When the water evaporates the salts accumulate in the surface pores and cause decomposition or bursting of chips in the surface layer of the stone. When the moisture is widely spread, salt can even be released from the cement in the fixing mortar and concrete, carried to the surface and cause the same type of splitting. Sandstone and clay-containing layered limestone floors are particularly susceptible, but with a high load of salt, damage can occur to other types of stone too. Examples of buildings where some natural stones have been subjected to such critical environments have often resulted in costly restoration projects (e.g. the terrace of The National bank of Denmark), (Figure 8).



Figure 8. Spalling due to salt crystallisation on the terrace of the National Bank of Denmark.

2.3. Thermal and moisture variations

Moisture may induce swelling of certain minerals, especially clay containing stone types, and thereby result in expansion of the stone and/or cracking due to the volumetric changes.

This part will be completed further on in the project. Results from outdoor exposure sites will then be incorporated.

2.3.1. Bowing and expansion

Moisture in combination with temperature variations is known to result in irreversible expansions of certain rock types. The mechanisms are not yet fully explained, but the property can be tested for.

Kessler (1917) was one of the first scientists to observe the deteriorating behaviour of marble. He noted that gravestones made of marble bowed and expanded significantly, and he argued that these deformational features were related to cyclic temperature variations. Today it is known that bowing of marble takes place all over the world. Most cases of bowing involve Italian marble types from the Carrara area (Figure 9), simply because it is the most commonly used marble type. However, it has been observed that marble from other areas all over the World also exhibits durability problems (e.g. Portugal, Norway, Poland, and USA) (TEAM 2005).



Figure 9. Facade clad with Carrara marble on a building in Göttingen, Germany

Deterioration of marble panels involves several parameters and mechanisms. Bowing is the most obvious phenomenon but bowing is followed by volume changes, i.e. the marble expands. However, the most serious deterioration feature is the loss of strength, which may progress all the way to total loss of cohesion (granular de-cohesion) between the grains. The three features mentioned above, may cause cracking of panels, spalling in connection with anchor points (and in the worst of cases, detachment of the panel).

Petrographic studies have showed that the microstructure is strongly connected to the bowing potential. It has been shown from bowing test like NT Build 499 and from the numerous other tests on marble samples (TEAM, 2005) that calcitic marbles with interlobate grain shapes have low bowing potentials and that marbles with granoblastic-polygonal grain shapes have a much higher bowing potential. The influence of the mineral properties and the micro-structure on the bowing and expansion potentials is described in detail by Åkesson et al (2004).

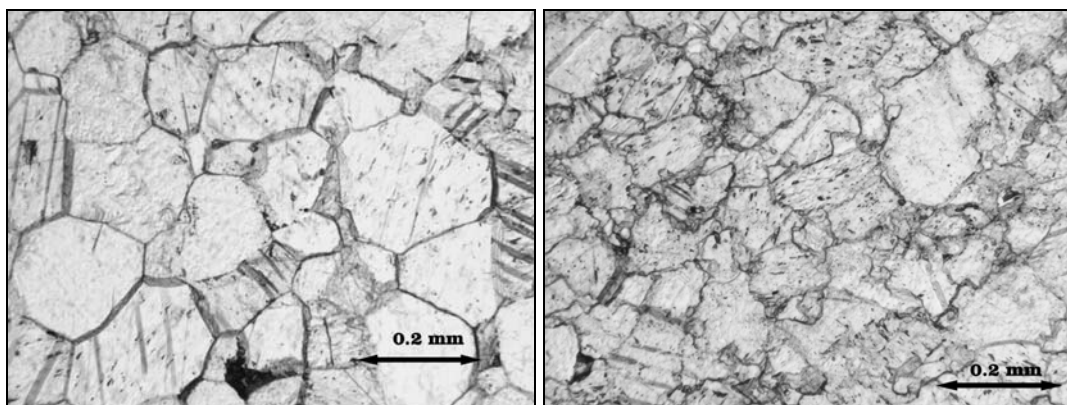


Figure 10. Marbles with granoblastic (left) and inter-lobate (right) crystal/grain structure.

The microstructure of a marble with typical interlobate grain shapes is shown to the right in Figure 10 and the microstructure of a marble with typical granoblastic-polygonal grain shapes is shown to the left in Figure 10. The terms granoblastic-polygonal and interlobate grain shapes are used in accordance with Passchier et al. (1996) and Spry (1983). It is important to note that it is not only the grain shape that is important but also the fact that marbles with a more complex micro-structure also have a considerably wider grain-size distribution! In addition, the granoblastic marble types often have a high inter-granular porosity.

2.4. Thermal shock and fire safety

Damage to stone by fires and high temperatures has been studied by many researchers both in the rural and on urban buildings.

All minerals expand when heated. Very high temperatures can have a severely damaging effect on stone. Most affected stone types are granites, sandstones, limestone and marbles. Heating of rock-forming minerals in e.g. granite, results in uneven expansion of the minerals. The phase change of quartz at 573°C from low to high quartz is accompanied by a nearly 4.5% volume expansion which very disastrous (cracking and spalling) to a quartz-containing stone product, e.g. all granitic rocks.

Also lower elevated temperature, equal to solar heating-cooling cycles, can lead to disruption (cracking, spalling and bowing) of thin stone panels (paragraph 4.3).

Toxic gasses from the stone may be in some cases emitted at high temperatures (fire). Natural stones are in general categorised considering fire as Class A1 following the Commission Decision 96/603/EC, unless the stone or stone products contain significant amounts (> 1 %) of asphalt, organic material or whenever the processing of the stone involves the use of organic patching, fillers or other similar products. In that case the natural stone or stone product shall be tested in accordance with EN13501-1 (ref. EN 1469:2004 Natural Stone products - Slabs for cladding).

The strength stability of the stone during fire should also be considered, especially in cases where the stone is used as load bearing element, or in cases where it can fall from great heights.

2.5. Abrasion resistance

A measure of abrasion hardness can be given by 8 minutes abrasion using a load of the 2000 g plus the weight of the specimen (W_s). The Dorry equation defines the abrasion resistance:

$$H_A = \frac{10 \cdot G \cdot (2000 + W_s)}{2000 \cdot W_A}$$

where W_s =weight of the specimen, W_a =the loss of weight and G = the bulk specific gravity.

Dense rock, such as fine grained limestone, records high values because the grains loosen more easily than coarse-grained varieties. By this method, the abrasion resistance can be evaluated for stones used for floorings or steps, where the wear is due to foot traffic (Figure 11). Quartz sandstone with the weaker calcite-cemented quartz grains record abrasion resistance close to that of calcite, the strength of calcite determining whether the quartz grains will twist out of the stone or not. Winkler (1997) emphasizes that the true abrasion resistance does not depend on the average mineral hardness and on the interface bond.



Figure 11. Soft limestone floor in a public library in Copenhagen.

The Dorry test is in principle very similar to the European standard Methods B and C (Böhme and Amsler, ref. EN 14157). The reference method A: Wide wheel, is fundamentally different due to the simple fact that the testing conditions change during the actual test. The pulling force of the counterweight, about 14 kg, initially works on the line of contact between the wheel and the stone specimens. During the test, the line gradually changes into a wider and wider groove whereas the pulling force of the counterweight gradually decreases. This is in contrast to the weight applied on top of the specimens in the Böhme and Amsler methods (and Dorry test). There the weight remains the same throughout the entire test. The abrasion resistance analysis will be completed further on in the project, including results from the I-STONE test site.

2.6. Harmful components

Minerals in the rock may react chemically with components in the air or water which come in contact with the stone. The alteration may in some extreme cases lead to serious weakening and disintegration of the stone. However, in most cases it is confined to the surface, changing only the aesthetical appearance of the stone.

Experimental studies have shown that in order to assess the risk of staining due to iron bearing minerals, specific tests have to be applied depending on the composition of the specific mineral. When a natural stone contains visible (size in the order of millimetres to centimetres) iron bearing minerals, the most adequate tests to check the liability of developing rust coloured stains are probably the thermal shock test and/or the oxidation test.

The iron bearing minerals are mainly iron sulphides (pyrite, marcasite), iron carbonates (siderite) and ferromagnesium-silicates (biotit, hornblende) and iron oxides (hematite, goethite, limonite, amorphous $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$). These accessory minerals are dispersed throughout the stone or concentrated to the presence of veins in the stone. Iron is leached from biotite, mica and hornblende and transported by water to the surface of the stone, where it initially spreads across the surface of the stone as greenish or black soluble ferrous iron. It readily oxidizes to an insoluble brown or yellowish iron hydroxide (limonite). This kind of staining develops after placement of the stone elements (Figure 12).

The discolouration affects not only the appearance of stone but it can also result in physical damage. Fissures may result from volume expansion of oxidised and hydrated minerals. Such stains are often non-soluble and therefore difficult to remove.



Figure 12. A facade clad with yellowish Chinese granite. Some of the panels are discoloured due to iron bearing minerals has been leached out from the panels and precipitated on the surface.

In other cases, these ore minerals are not visible by the naked eye, but are only visible under the microscope. Their size is in the order of micrometers. To create the typical yellow-brown discoloration on the stone (Figure 13), one has to expose the stone to an accelerated oxidation test (with an alkaline solution). BBRI is responsible for Subtask 5.1.3, which aims to develop a procedure for an “Accelerated oxidation stain test”. This test is especially developed for light coloured marbles but will be tested on other project stones too.



Figure 13. A wall with a magmatic stone type showing rust stains due to the precipitation of iron bearing minerals on the surface.

3. CLIMATE

This part will be included further on and completed from a previous deliverable [D5.2 Different uses of natural stone products in different application and climatic conditions in Europe].

4. CONCLUDING DISCUSSION

The durability of a stone is depending on many factors, e.g. the type and degree of weathering that it is exposed to. Some stone types may be resistant to one kind of weathering but sensitive when exposed to another kind. For example, some marbles do not show significant signs of degradation when exposed to frost action, but may lose a lot of strength when exposed to high temperature variations.

The position of the stone in the building is also an important aspect to consider regarding frost action. If the stone is in contact with the ground it is more likely to be saturated with water, and it is therefore more susceptible to frost damage. Furthermore, a horizontally placed stone is more exposed to water saturation than a vertically to the ground oriented one, because of the difference in runoff. Thus, different environmental classes of stone positions should also be considered in context of frost action.

For a given climate, a classification for the intensity of the frost action on the different external parts of a building can be the following (from the highest to the lowest):

- 1) paving and flooring;
- 2) elements in direct contact with the floor, e.g. base course, plinth and foundation;
- 3) non-vertical parts in elevation and all elements sticking out of the façade, e.g. cornices, mouldings, windowsills;
- 4) solid masonry units, e.g. non-ventilated walls, i.e. with no possibility of drying from the back face of the stone units;
- 5) wall cladding units or cavity wall units with ventilation allowing for drying from the inner face;

The climate is another very important aspect in the weathering of stone. Frost action is much more likely to occur in wet climates with many freeze-thaw cycles. On the contrary, frost damages are not as frequently observed in colder climates with heavy frost and only a few freeze-thaw cycles whereas they are absent in climates with no frost. Any climatic condition between these extremes constitutes intermediate levels of frost action, and they can be differentiated into a climatic classification.

The relevant parameters that define the severity of a climate with respect to the frost action are:

- the intensity of the rain fall during the winter period
- the number of freeze/thaw cycles during one winter

However, there is no official classification of the climatic zones in Europe until now concerning the frost action. By combining these two parameters, it is possible to define a critical climatic event as “a frost period preceded by a certain quantity of rain, which is likely to affect the durability of the exposed material when repeated” (I-STONE, D 5.2 section 3.4).

Yet another aspect of significant importance is the combined effect of salt and frost, because freeze-thaw cycling in saline environments increases the frost damages. Common salt sources are marine water and especially de-icing salts which are often used in aggressive, cold climates. Since only a very small concentration of salt is needed to enhance the magnitude of frost damages, freeze-thaw tests including a saline component should be considered for stones in such harsh climates. The European Standard EN 12371 does not require a salt solution to be absorbed by the stone before the stone freeze. This has probably led to some misuse of stone types that have passed the frost test only to perform poorly in real use. However, the

European standard for frost testing of concrete (CEN/TR 15177) is based on both pure water and saline solution (3 weight % NaCl), which will test the material much more aggressively. The latter test could provide the criteria for mild and aggressive climates respectively. In the standardisation of frost testing of aggregates in severe freeze-thaw conditions (EN 1367-1) a recommendation is to use 1% NaCl solution. This concentration is also included in the I-STONE project for evaluation of test results from previous national standards like the German DIN 52 104, the Belgian standard NBN B27-009 & TV 228 and the new EN 12371.

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