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TESI DI LAUREA

Multiscale models of diffusion and production of defects in porous materials

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Abstract

Questo lavoro di tesi vuole mettere a punto un modello fisico per la descrizione dei fenomeni di diffusione all'interno dei materiali porosi che sono comunemente utilizzati nei beni di interesse archeologico, storico e artistico. La tesi prende innanzitutto in esame i principali fenomeni di trasporto di umidità e calore che avvengono all'interno e attraverso la struttura porosa. Infatti l'esposizione agli agenti atmosferici, e all'acqua in particolare, causa un inevitabile degrado della struttura. L'acqua entra in contatto in forma liquida e di vapore con la struttura porosa e viene quindi trasportata all'interno del mezzo; un primo step è dunque una descrizione dal punto di vista fisico-matematico di tali meccanismi. Dato che la presenza d'acqua influenza anche le proprietà termiche della struttura, si è poi rivolta l'attenzione al trasporto di calore, ottenendo quindi un modello con due equazioni accoppiate per il trasporto simultaneo di calore e umidità.

Inoltre, un aspetto particolarmente interessante concerne lo studio del trasporto e dell'interazione dell'idrossido di bario. Quest'ultimo composto viene applicato come parte fondamentale di un metodo, chiamato per l'appunto metodo del bario, con lo scopo di ottenere una duplice azione desolfatante e consolidante all'interno di strutture soggiate affreschi e pitture murali. Grazie a questo metodo, la superficie degradata dal fenomeno della solfatazione viene ripristinata tramite il consolidamento della matrice costitutiva dell'affresco. Sebbene il metodo del bario sia vastamente utilizzato, esso non è mai stato studiato prima d'ora dal punto di vista teorico. Uno degli scopi principali della tesi è, dunque, proporre un modello che ne permetta la descrizione e, in futuro, la simulazione numerica per poter capire effettivamente ciò che accade.

Oggi risulta più che mai chiaro che il solo monitoraggio dei beni culturali è insufficiente, ma è invece necessario intervenire su più fronti con un approccio multidisciplinare. In tal senso, i modelli fisico-matematici possono dunque offrire un valido aiuto alla conservazione del patrimonio artistico e culturale.

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Chapter 1

Introduction

Porous building materials used in historical architecture, such as brick, natural stone and mortars, are subjected to an inevitable environmental and anthropogenic deterioration processes. These phenomena modify the original micro-structural characteristics of the materials, altering the physical and chemical properties.

In order to counteract these degradation actions, two treatments are possible: consolidation and protection. The first process is a highly critical process and includes a series of treatments that allow to reestablishing the cohesion between the grain, while the latter permits to increase stone resistance to aggressive action of water. [1]

A particular case of study concerns the preservation of the fresco or the wall painting. They are particularly susceptible to degradation processes because of their porous structure permits the absorption of water in which dangerous substance are presented.

Historically, restoration has developed as an empirical technique, without the development of theoretical or methodological models. In the of frescoes, for instance, it took a long time to become aware of the material composition and, therefore, how to correctly act. The first practices used to restore frescoes, were those used for paintings on canvas or boards. Of course, this approach did not consider the physical nature of what lies below a few microns of the paint film that is totally different of canvas or boards. Moreover, as an alternative to these techniques, wall paintings or frescoes were directly detached of wall and often irretrievably damaged. [2]

Over the years it has become clear that the techniques for the treatment of the frescoes must be specific, and multi-disciplinary skills are involved. This thesis would analyze, from physical point of view, a method used to consolidate frescoes and wall painting. This method, called the barium method, was developed in order to dealing with the damage caused by the disastrous flood in Florence in 1966. Since then, the method has been used several times, but its effects and its diffusion within the material have not been studied in the long term. This work moves a first step in this direction.

Outline of the thesis

Three main parts can be identified in the thesis: chapter 2 describes the moisture storage and transport in porous materials, chapter 3 deal with the heat storage and transport while chapters 5 and 6 are focused on the barium method.

In chapter 2 the moisture storage and transport is analyzed: because of the porous structure of the materials used, water, in liquid and vapor form, is absorbed, storage and transported inside the structure. The main processes and their relative driving potentials are taken into account in order to write a balance equation for the moisture content.

In chapter 3 the emphasis is on heat. The water inside pores influences the thermodynamical properties of the material and it has to be considered. Heat is studied in term of enthalpy of both dry material and water and the heat transport is, therefore, studied as enthalpy flow. Phase change and heat due to reactions that occur inside of the porous structure are taken into account.

In chapter 4, the balance equations for heat and moisture are summarized. These are coupled equations since they influence each other. Moreover the main boundary conditions are shown.

In chapter 5 the degradation processes involved in the damaging of cultural heritage are summed and the so-called barium method is explained. This method allows to consolidate the structure of frescoes that are damaged by pollutants, reconstituting in situ the binder. Since this method has never been studied from the theoretical point of view, in chapter 6, the equations for the transport of the barium hydroxide used in the method are developed, taking into account the reactions that occur.

Chapter 2

Moisture storage and transport

Exposure to atmospheric agents causes an inevitable degradation of all materials, whether natural or artificial. The timing of degradation depends on the materials and it is usually long but in recent decades the process of degradation has accelerated in many cities due to the increased level of pollution. Both modern and historical buildings are subjected to deterioration mechanisms, but the latter are more susceptible because of their age and the materials with which they are built. If the world Heritage is not properly protected, it will be irreversibly damaged.

Industry, transportation and heating emit into the atmosphere pollutants such sulphur and nitrogen oxides that causes acidity in the air ¹.

Sulphur and nitrogen oxides, for example SO_2 and NO_3 compounds, react with calcium carbonate stone to form sulphates and nitrates which are soluble in water and can be drained away or, if the stones are protected from rain, may produce crusts. [3] Moreover, if there are frescoes or painting on the surface of the wall, the formation of sulphates and nitrates inside the surface can cause mechanical stresses and then liftings, cracks, fissures and opacification. In order to cope with this problem, a process based on barium hydroxide has been invented fifty years ago and yet used today to consolidate wall paintings and frescoes ².

The chemical deterioration is mainly expected to occur when the surface is wet, hence one is concerned with the moisture storage and transport in a porous medium as first step. Water penetrates into the materials and it is basically transported thanks to pressure or relative humidity gradient. This process creates not only structural damage, but also formations of mold, therefore causing a double problem, i.e. the safety of the structure and the health of people. Water can come in contact with the structure in liquid form, for example as rain or moisture, or as water vapor that condenses on the surface or within the structure. [4]

In general construction materials have a porous structure which allows the infiltration and the penetration of water inside the medium.

¹Nitrogen and sulphur oxides, respectively, are transformed through complex reactions into gaseous nitric and nitrous acids and into acidic sulphates as suspended particles.

²It is known as Barium method and it is described in chapter 5.

On a microscopic scale, a porous material is a body consisting of a solid matrix with void spaces (pores) of irregular shape, different size and random distribution. Its configuration depends on different factors as density, dimension, distribution of molecules, their shape and how they are bonded together.

Cavities are filled with one or more fluids. Typically some pores are interconnected and other disconnected. If pores are interconnected, heat and mass transfer occur and fluid flows through them and this process implies heat transfer into the solid matrix. [5] The following picture is useful to get an idea of a structure of porous media:

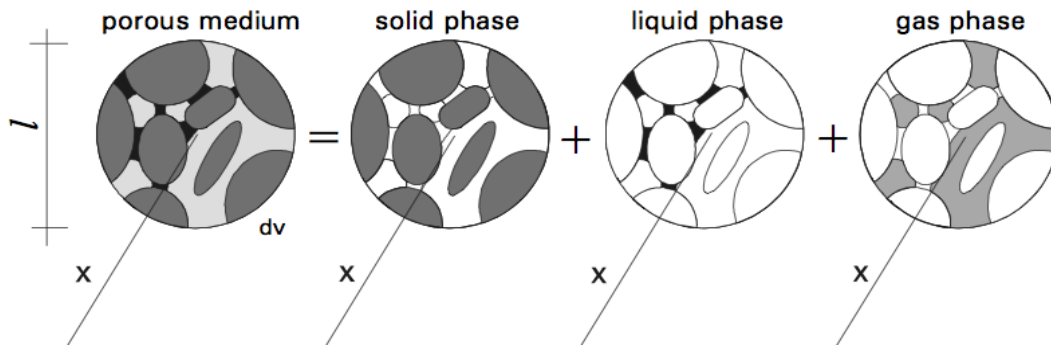


Figure 2.1: Schematic representation of a porous structure: solid matrix together liquid and gas phases are present. [6]

Of course, the real structure of a porous medium is more complicated. The following images show an example of scanning electron photographs of aerated concrete:

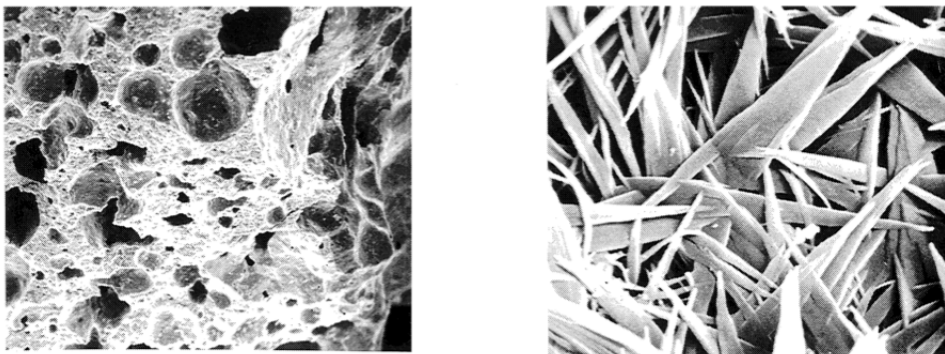


Figure 2.2: Scanning electron microscope photograph of aerated concrete: 22x magnification (left), 11'000x magnification (right). [7]

Usually pores are divided in open and close pores: the first ones are connected with the external surface and are accessible to ions and molecules, while the latter are not connected to each other. Closed pores do not contribute to determine the properties of adsorption and permeability of the materials, but are important to provide the mechanical properties.

A further distinction can be made between the blind pores (B in fig. 2.3), the interconnected ones (I) and those which are open on both sides (the through pores, T). [8]

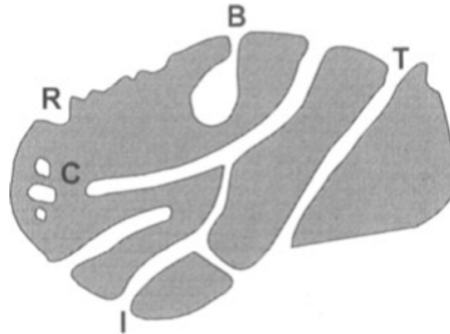


Figure 2.3: Schematic representation of the possible configuration of pores. [8]

Finally, the *International Union of Pure and Applied Chemistry* (IUPAC) classifies pores according to their size:

- Micropores: the diameter is less than 2 *nm*.
- Mesopores: the diameter is between 2 and 50 *nm*.
- Macropores: the diameter is greater than 50 *nm*.

The pore size is important because it plays a key role in the transport of moisture.[8]

In general, to take into account porosity, it is defined a variable based on volume of void of the material used. In particular we can defined the porosity φ as:

$$\varphi = \frac{\text{volume of void}}{\text{total volume}}. \quad (2.1)$$

2.1 Moisture storage

Before considering the moisture storage, it is appropriate to recall some basic concepts.

At environmental temperatures in the air, a small amount of water is always present and this determines the humidity of air.

Together with the main components of the atmosphere (nitrogen (78%), oxygen (21%), noble gases, carbon dioxide (0.3%)), water vapor is an important component of the air we breathe.

Each component exerts a pressure and the total pressure is given by the sum of the partial pressures of the individual components. Recalling the Dalton's law:

$$P_g = \sum_i p_i, \quad (2.2)$$

where:

P_g : total gas pressure.

p_i : partial pressure of the i -th species.

A crucial quantity is the humidity, i.e. the amount of water present in the air. In particular, the absolute humidity, ρ_v , is determinate by the partial pressure of water vapor and it is simply the amount of water vapor present in one cubic meter of air.

The amount of water vapor, ρ_v , that can be held by air is not unlimited. The upper limit is called the saturation concentration of water vapor, ρ_{vs} , and it depends on temperature.

Another useful quantity is the relative humidity, Φ : it indicates the percentage of water vapor in the air compared to its maximum value:

$$\Phi = \frac{\rho_v}{\rho_{vs}} \quad \text{or, in terms of pressure:} \quad \Phi = \frac{p_v}{p_{vs}}, \quad (2.3)$$

where:

p_v : water vapor pressure,

p_{vs} : saturation vapor pressure.

When humid air is cooled, the amount of water vapor is conserved, while the amount of saturation vapor decreases and hence the relative humidity increases.

If the saturation threshold is exceeded, the excess of water condenses. The limit temperature at which moist air saturates and water starts to condense is called the dew point temperature. For example condensed water can be found on surfaces. This occurs when the surface temperature is lower than the dew point temperature of the air in the relevant environment.

The dependence of the saturation vapor pressure on temperature is shown in fig. 2.4. Referring to the figure, one sees that from point Q, there are many possibilities to reach saturation. By an isothermal change of state, the system moves parallel to pressure axis and will block in Q'; extra vapor will condense. By an isobar change of state, the system moves parallel to temperature axis and will block in Q'' on saturation curve. Real changes of state consist of a combination of isothermal and isobaric. [9]

When water, in liquid or vapor form, permeates a material we talk about moisture. In fact this term, otherwise from humidity, indicates the amount of water present in a material.

A building is defined dry when it does not contain water or it contains only chemically bound water molecules. When the structure comes in contact with humid air, it can behave in two different way:

- non-hygroscopic: the material does not absorb water and remains dry.
- hygroscopic: the material collects water molecules on the inner surface of the network of pores until the equilibrium with humidity of surrounding environment is reached.

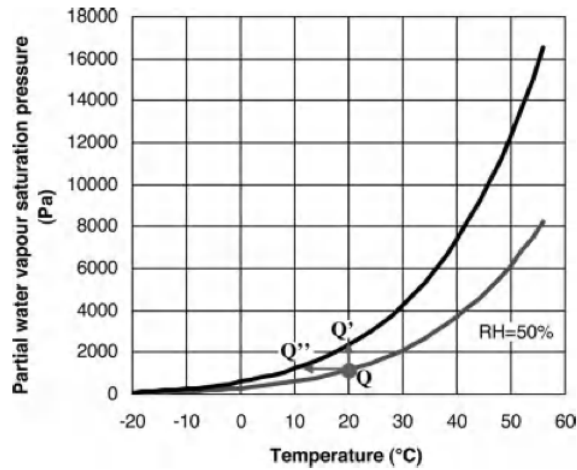


Figure 2.4: Vapor saturation pressure as function of temperature (black line), line of 50% relative humidity (grey line). [9]

Depending on the percentage of moisture (Φ) present in the structure, one can distinguish three different regions (see table 2.1 and fig. 2.5 or 2.6) :

Region	Moisture range
Hygroscopic	$0 < \Phi < 95\%$
Capillary	$\Phi > 95\%$
Supersaturated	100%

Table 2.1: The three regions of moisture storage as a function of the relative humidity.

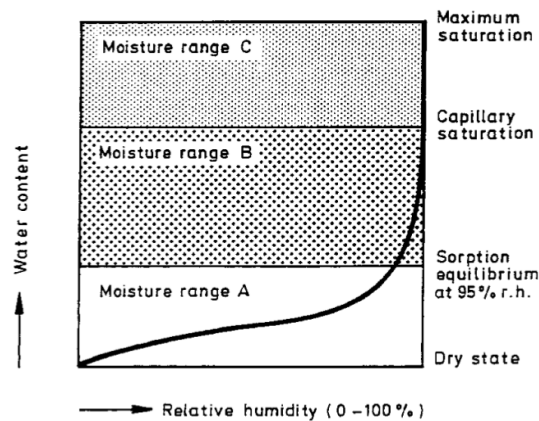


Figure 2.5: Diagram of the moisture storage function. The different regions are shown. [4]

In the next paragraphs, water behavior in the three different regions is described.

2.1.1 Sorption moisture region or hygroscopic region

This region ranges from the dry state to an equilibrium moisture of about 95% relative humidity. In fact when hygroscopic building materials are in contact with moist air, they reach an equilibrium moisture which is determined by the relative humidity of the environment. [4]

When a porous material is exposed to moist air, moisture is adsorbed at the inner surface of the pores, resulting in an increase of the weight of the material. [6]

This sorption process can be summarized by two phenomena:

1. Molecular surface adsorption in the lower relative humidity range.
2. Capillary condensation in the relative humidity range above 40-50%.

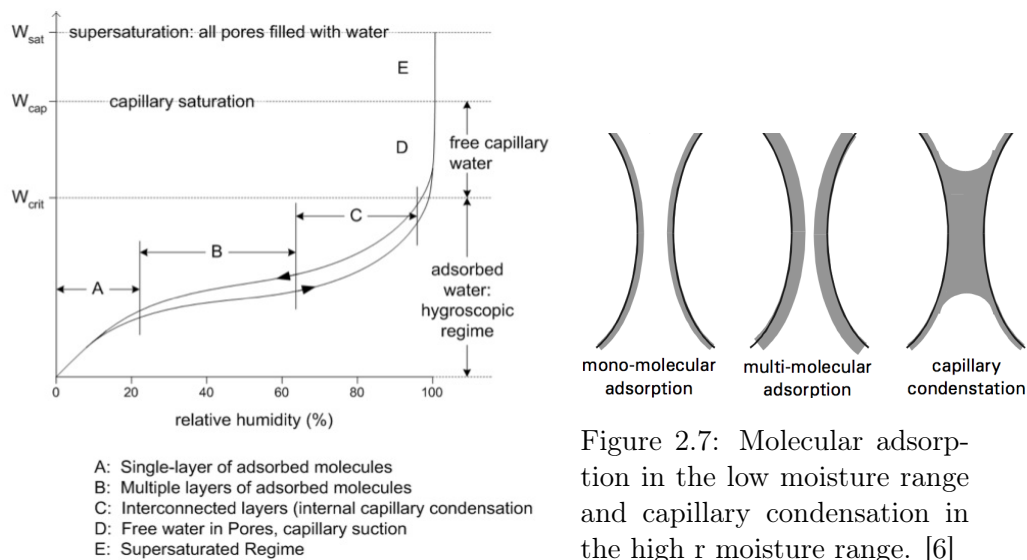


Figure 2.6: Diagram of the moisture storage function: the hysteresis between sorption and desorption is evident. [10]

Molecular surface adsorption

The process of accumulating water molecules on the surface of the porous medium is called adsorption and through this phenomenon a thin film is formed. The opposite process, i.e. when water molecules are released from the surface to the dry air, is called desorption.

As figure 2.6 shows, the hysteresis between adsorption and desorption is not very pronounced, and generally the adsorption isotherm is enough to characterize the moisture storage. If the hysteresis is more distinct a sufficient accuracy is obtained by averaging the adsorption and desorption curves.

As described in fig. 2.7, the adsorption process can be subdivided in two steps:

1. Mono-molecular adsorption: gas molecules liquefy on a solid surface as a result of surface force attraction. Bonds formed between molecules and surfaces are usually weak and due to hydrogen bond or Van der Waals forces.

The layer becomes filled at a relative humidity of approximately 25%.

2. Multi-molecular adsorption: as relative humidity increases more layers adhere, although the first few layers are more strongly attached.

If the pores are large enough, the adsorbed layer reaches a thickness of five molecules at 99% relative humidity.

Capillary condensation

Capillary condensation starts when layers of water molecules grow to such a size that they begin to interact and interconnect.

The surface tension forces the water molecules to change to a more stable arrangement and a meniscus, which separates liquid (l) and gas phase (g), is formed.

Clearly the beginning of capillary condensation depends on the sizes of the pores.

When $\Phi > 95\%$ the sorption isotherm rises very sharply and the system passes in the capillary water region. [7]

2.1.2 Capillary water region

When a capillary-active material is placed in contact with liquid water, it absorbs water until it reaches free water saturation value, w_f . [4] At this point, an equilibrium relationship exists among the relative humidity, the liquid water saturation and the capillary pressure in the pores. The capillary pressure (often called suction pressure) is defined as the macroscopic pressure difference between gas phase and liquid phase [6]:

$$p_c = P_g - P_l, \quad (2.4)$$

with

p_c : capillary pressure,

P_g : gas pressure,

P_l : liquid pressure.

The isothermal thermodynamic equilibrium at the meniscus can be expressed through the Kelvin's law, which describes the relationship between the relative humidity, Φ , and the capillary pressure, p_c , in the pores:

$$\Phi = e^{-\frac{p_c}{\rho_l R_v T}}, \quad (2.5)$$

with

ρ_l : density of liquid water,

R_v : gas constant for water vapor,

T : absolute temperature.

Also in this case, the process could present a hysteresis between wetting and drying but some studies show that, almost for all mineral building materials, in the capillary water region hysteresis is no more pronounced than in the sorption moisture region and assumption of a single storage function for wetting and drying is a reasonable approximation. [4]

Figure 2.8 shows the relative humidity over a water surface in dependence of the capillary suction stress in water for two different temperatures.

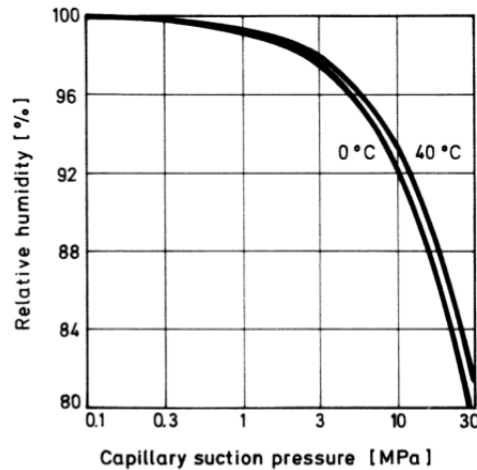


Figure 2.8: Relative humidity over a water surface as a function of capillary suction pressure for two temperatures. [4]

The capillary pressure depends on the pore size. If one assumes a cylindrical capillary tube, the relation between the capillary pressure and the pore radius is expressed by the Young-Laplace's equation that represents the mechanical equilibrium:

$$p_c = \frac{2\sigma_w}{r} \cos \theta, \quad (2.6)$$

where:

σ_w : surface tension of water,

r : capillary radius,

θ : contact angle.

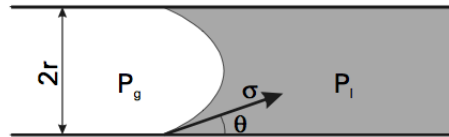


Figure 2.9: Scheme of a cylindrical capillary. [6]

In the equation (2.6) appears the contact angle, θ . As fig. 2.9 shows, θ is the angle between meniscus and surface. As fig. 2.10 shows, its value determines if the pressure is positive or negative and therefore if the meniscus rises (capillary ascension) or drops (capillary depression) respectively. In fact, if θ ranges within $0^\circ < \theta < 90^\circ$ the capillary pressure is positive and the cylindrical pore sucks water and the liquid is said to preferentially wet the solid. On the contrary, if contact angle ranges within $90^\circ < \theta < 180^\circ$ the capillary pressure is negative and the cylindrical pore does not adsorb the fluid. This occurs, for instance, for fluids like mercury.

For water on a plain solid surface, it is assumed that $\cos \theta = 1$.

In general, the pore system of a building material is very complex and the cylinder capillary model seems unsuitable; for that reason it is more practicable to determine the suction stress directly and not via that model.

It is interesting to note that the capillary pressure depends on the inverse of the pore radius: if capillaries of different radii are connected with each other, the smaller ones have greater suction forces and draw moisture out from the larger capillaries until their meniscus has the same radius of curvature or until the capillary is empty. This is schematically shown in fig. 2.11.

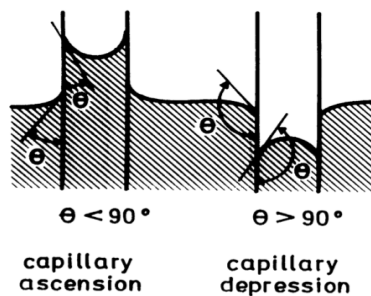


Figure 2.10: Capillary ascension or depression according to the curvature of the meniscus. [7]

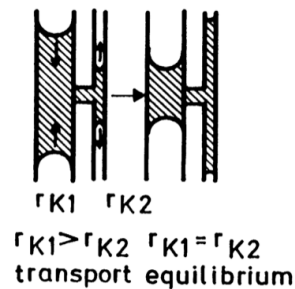


Figure 2.11: Capillaries of different radii connected to each other. ($r_K = r / \cos \theta$) [7]

If a hygroscopic material comes in contact with another hygroscopic substance, there is a moisture exchange until equilibrium is reached. This equilibrium is due to the fact that equal capillary pressure in the two materials exists. When the two materials have not the same pore size distribution, the moisture contents of the two buildings will be different. [7]

2.1.3 Supersaturated region

In this region the relative humidity always amounts to 100%.

Capillary saturation can only be exceeded applying external pressure, removing trapped air or forcing a condensation process. Therefore, steady-state moisture equilibria cannot occur under natural condition.

From a mathematical point of view, the moisture storage function between free water saturation, w_f , and maximum saturation, w_{max} , has an infinitely rise and, consequently, can be only described by a moisture storage capacity, Δw .

$$\Delta w = w_{max} - w_f. \quad (2.7)$$

Since wetting beyond capillary moisture saturation rarely happens, at least under natural physical conditions, the supersaturated region is ignored in the following considerations.

2.1.4 Experimental method to determinate moisture storage: Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a technique based on the spin of nuclei and their magnetic moment.

In the last fifteen years, techniques based od NMR have been applied in the field of Cultural Heritage to study the pore size distributions and their changes due to decay. [11] It can be seen as a direct and non destructive method to determinate the water content in building material. Thanks to the knowledge of water content distribution during liquid transport, the liquid transport coefficients can be calculated. [7]

The following paragraph briefly describes the basic principles of NMR.

Nuclei can be divided in three groups depending on their number of protons (Z) and neutrons (N), and their nuclear spin \vec{I} :

- Nuclei with both N and Z even: all proton spins are paired and all neutron spins are paired. Resultant nuclear spin I is zero and these nuclei are invisible to NMR.
- Nuclei with both N and Z odd: there is a odd number of unpaired protons and odd number of unpaired neutrons. In this case I will be a nonzero integer. These nuclei can be seen by NMR.

- Nuclei with odd N and even Z , or vice versa: all proton spins are paired and there is an odd number of unpaired neutron spins, or viceversa. I will be an odd integer multiple of $\frac{1}{2}$.

Total number of possible spin states in complex nuclei is called multiplicity and it is determined by I . In fact there are $2I + 1$ states and each of these states has its own magnetic spin quantum number, m , that ranges $m = -I, -I + 1, \dots, +I$.

All nuclei with $I = \frac{1}{2}$ have a spherical distribution of charge and the magnetic and electric field surrounding the nucleus are isotropic. If $I > \frac{1}{2}$, nuclei have a non-spherical distribution of charges and this implies an electrical quadrupole moment of the nucleus that can complicate the NMR investigation.

When a nucleus is immersed in a magnetic field, the Hamiltonian (H) of the system that describes the interaction between nuclear magnetic moment, $\vec{\mu}$, and external magnetic field, \vec{B}_0 , is:

$$H = -\vec{\mu} \cdot \vec{B}_0, \quad (2.8)$$

where:

$$\vec{\mu} = \gamma \frac{h}{2\pi} \vec{B}_0,$$

and γ is the gyromagnetic ratio, characteristic of each isotope.

Thus, the presence of an external magnetic field, \vec{B}_0 , causes the splitting of each energy level, in fact this is the essence of the nuclear Zeeman effect.

In this case the energy of the i -th spin state of a nucleus in a magnetic field of strength B_0 depends on m :

$$E_i = -m_i \frac{\gamma h B_0}{2\pi}. \quad (2.9)$$

Largest value of m corresponds to the lower, and hence more stable, energy state.

Magnetic moments of nuclei are forced to remain at a certain angle with respect to \vec{B}_0 and this causes a precession motion. The magnetic moment vector precesses with a characteristic angular frequency called Larmor frequency (ω_L), which is a function of \vec{B}_0 and γ :

$$\vec{\omega}_L = \gamma \vec{B}_0. \quad (2.10)$$

In units of radians per second Larmor frequency (ω_L) becomes $\nu_L = \frac{\gamma B_0}{2\pi}$.

Larmor frequency is independent of m and hence all spin orientations of a given nucleus have the same frequency in a fixed magnetic field.

Suppose to take 1H nuclei³. In this case only two states are possible: the lower energy state relative to $m = +\frac{1}{2}$ and higher energy state relative to $m = -\frac{1}{2}$.

³Since the degradation of building materials is closely connected to moisture, it makes sense to focus on 1H in order to identify water.

It is known that for any system of energy levels at thermal equilibrium, there will always be more particles in the lower state energy than in the higher level. Boltzmann distribution describes the population of each state:

$$\frac{P_{(m=-1/2)}}{P_{(m=+1/2)}} = e^{-\frac{\Delta E}{kT}}, \quad (2.11)$$

where:

$$\Delta E = E_{(m=-1/2)} - E_{(m=1/2)},$$

k : Boltzmann's constant,

T : absolute temperature.

Therefore, in presence of an external field, ΔE is not zero and the populations of the two states are different. The difference in populations of 1H spin states is very small (of the order of 20 *ppm*) but it is enough to allow a NMR signal to be detected. In fact the excess results in a macroscopic nuclear magnetization \vec{M} that is the sum of all the nuclear magnetic moments:

$$\vec{M} = \sum_i \vec{\mu}_i. \quad (2.12)$$

\vec{M} results parallel to the external field \vec{B}_0 as can be see in fig. 2.12 (configuration *a*), where \vec{B}_0 is in z -axis direction.

To induce the spin flip, a radiation frequency that exactly matches the precessional frequency can be used. Hence a resonance phenomena happens.

Thus NMR can be used for quantitative and selective mapping of several chemical elements in materials, because the resonance condition of a certain type of nucleus depends on the gyromagnetic ratio. [12]

In order to do this, one applie an external alternating radio frequency magnetic field, \vec{B}_1 , perpendicular to \vec{B}_0 and oscillating at exactly the same frequency as the nuclear magnetic moment, i.e. the Larmor frequency. Now the nuclear magnetization is disturbed by a high energy pulse.

In this case all the individual magnetic moments become phase coherent and form a precessing "bundle". Nuclear magnetization \vec{M} is not parallel to \vec{B}_0 but forms an angle α and starts to precess with the characteristic Larmor frequency (configuration *c* in fig. 2.12).

The flip angle α is determined by the power and the duration of the irradiation \vec{B}_1 .

An important quantity to be introduced is the spin-lattice (or longitudinal) relaxation time T_1 .

When a system is immersed in an external field, the achievement of a new equilibrium is not infinitely fast and the rate at which it is established is T_1 . The name of relaxation time derives from the fact that T_1 is the time that magnetization takes to return to its maximum value along z -axis (i.e. longitudinal). It also gives the speed at which the measurements can be conducted.

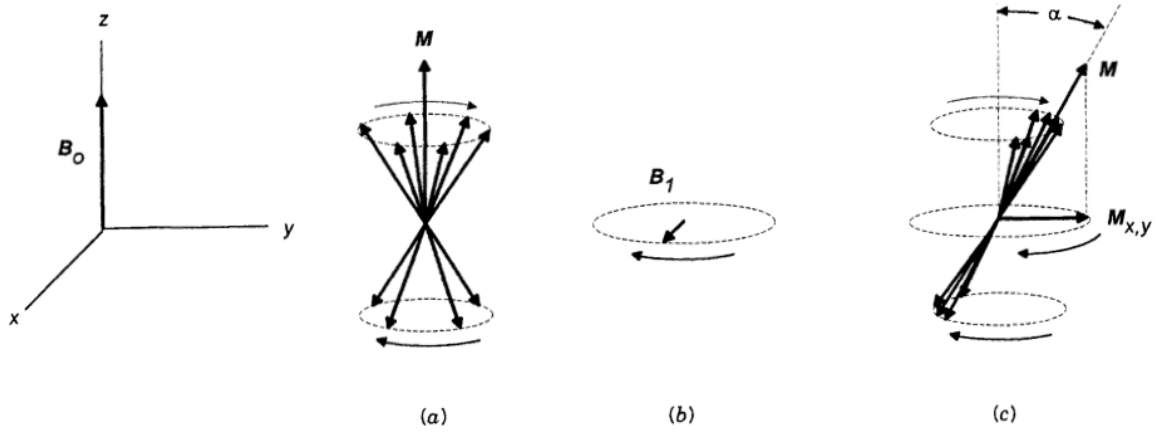


Figure 2.12: Precession of a collection of $I = 1/2$ nuclei around an external magnetic field \vec{B}_0 (a); precession of the same nuclei after the irradiation by \vec{B}_1 (c). [13]

In term of population, it follows that:

$$\frac{P_{eq} - P_t}{P_{eq} - P_0} = e^{-\frac{t}{T_1}}, \quad (2.13)$$

where:

P_{eq} : population of a given state at equilibrium,

P_t : population at time t ,

P_0 : population at time $t = 0$.

In term of nuclear magnetization:

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}, \quad (2.14)$$

with:

\vec{M}_0 : magnetization at time $t = 0$,

M_z : magnetization on the axis z at time t .

The NMR signal will be generated from the oscillation of \vec{M} , so that the maximum signal intensity will be when $\alpha = 90^\circ$.

When irradiation ceases and \vec{B}_1 disappears, the population of the two states revert to Boltzmann distribution and nuclear magnetic moments return out of phase. This latter process is called spin-spin (or transverse) relaxation and it causes the transversal magnetization ($\vec{M}_{x,y}$) decay at a rate T_2 . This particular time is the so called spin-spin (or transverse) relaxation time. The name means that T_2 is the time required by transverse magnetization to become zero and hence it controls the time behavior of $\vec{M}_{x,y}$:

$$\frac{dM_{x,y}}{dt} = -\frac{M_{x,y}}{T_2}. \quad (2.15)$$

Usually T_2 is much shorter than T_1 . [13]

Because transverse relaxation occurs more rapidly than longitudinal one, the time behavior of the measuring signal is essentially determined by this latter process and it shows an exponential decline. Calling *FID*(free induction signal) the signal measured, the relation will be:

$$FID = FID_0 e^{-\frac{t}{T_2}}, \quad (2.16)$$

where:

FID: measuring signal,

*FID*₀: measuring signal immediately following the pulse.

T_1 and T_2 depend on physical and chemical bonding of the nucleus. If there are different components with various T_2 , the signal will be composed of the overlapping exponential curves of single components. Separating measured curve into individual curves, the relative contents can be estimated.

Since T_1 and T_2 depend on physical bonds of the water in pore space, and hence on pore space-size, it is plausible that determining them is a way to gain information about relative content of bound/free water or kind of pore size distribution. [7]

NMR is therefore a valid method that allows to detect the water content and, in general, can be used for a quantitative and selective mapping of several chemical elements in materials thanks to the fact that the resonance condition of a certain type of nucleus depends on the gyromagnetic ratio. [12]

An example of NMR analysis: the Civic Tower in Ravenna

In this brief section an analysis of the Civic Tower in Ravenna carried out in winter 2010/ spring 2011 is reported. The authors of the work analyzed some samples through SEM (scanning electron microscopy), chemical microanalyses and NMR in order to estimate the porosity and the behavior the humidity of the bricks of the tower. Here only the results concerning NMR are described.

The Civil Tower, also called Tower of the Butchers, is situated in the Ravenna's historical center (Via Paolo Costa). The Tower is an example of medieval architecture, in fact the works of its construction started in the eighth century and ended in the twelfth century. Regarding its function, the Tower was probably used to control and to defend a strategic hub of the city.

Over the century, the Tower has undergone several changes; for example it has been noted the reworking of curtain walls, or the fact that the upper part presents bricks of primary use, as the finding of the same bricks in buildings of the thirteenth century has evidenced.

The Civic Tower has a square base, is about 38 meters high and, depending on the height, the walls have different thickness.

Ravenna is situated in a seismic zone and, in particular, the tower is located in an area prone to seismic risk. Therefore the tower presents steep slope due to differential settlement, subsidence and problems. Moreover bad state of conservation of materials, occurrence of major billing and vibrations due to the vehicular traffic (so that the municipality has taken steps to ensure the nearby zone became a limited traffic zone) contribute to the degradation of the structure.

The surface of the exterior and interior walls show chemical, physical and biological degradation products such as salt efflorescence and leaching of mortar; they are deeply eroded and present furrows of several inches, often reconstructed with unsuitable binders⁴.

The following figures show the tower and a particular of the wall where degradation can be see.



Figure 2.13: The Civic Tower of Ravenna. [14]



Figure 2.14: A detail of the Civic Tower in Ravenna: deposition of pollutants and black crusts are evident. [14]

NMR analysis was performed on three samples taken from the Civic Tower of Ravenna in order to study the effects of climate. It was possible to investigate until the depth of 2.85 *mm* in each sample, probing the porous matrix with a resolution of less than 200 μm .

The approach with NMR can be very powerful for the evaluation of the state of fine arts materials: not only water saturation and the porosity of the material can be evaluated, but information on material pore-size distributions can be obtained from distribution of relaxation times T_1 and T_2 .

⁴A more complete explanation of causes of degradation can be found in chapter 5.

If pores are small and viscosity of the fluid is low, an approximation can be made: relaxation times T_1 and T_2 are proportional to pore diameter and pore size distribution is obtained by inverse Laplace transform of the relaxation curve.

Three samples of brick from the Tower are taken at different heights, i.e. 2 (sample 1), 8 (sample 2) and 38 meters (sample 3). Every sample is 3 *cm* height, 3 *cm* width and 3 *cm* depth. The brick is a ceramic material consisting mainly of clay, formed by silica in varying percentages around 50%, a 20-30% of calcium carbonate, a small percentage of around 2% of iron oxide and a percentage of 4-6% of water.

The samples were placed in condition of capillary absorption for 120 minutes in order to verify the hydrophobic porous matrix of the samples themselves. The pulse sequence adopted, allows to obtain a measure of the intrinsic spin-spin relaxation time, T_2 , of the system.

Reliable estimate of the size of the porous matrix can be obtained by the following relation:

$$\frac{1}{T_{1,2}} = \rho_{1,2} \frac{S}{V}, \quad (2.17)$$

with:

$T_{1,2}$: relaxation time (T_1 or T_2),

$\rho_{1,2}$: constant having the dimension of a velocity ($\mu\text{m/s}$),

S : surface of the pore,

V : volume of the pore.

As example, fig. 2.15 are reported; the charts show the trend of the density signal as a function of spin-spin relaxation time T_2 . From this parameter, distribution of pores in the porous matrix is estimate.

From the graph of the first sample, one can deduce a predominance of small to medium sized pores. This is because the values of T_2 are thickened between 0.2 *ms* and 50 *ms*. Sample 2 shows a distribution of relaxation times similar to the sample 1. These two samples were in the lower parts of the tower and both felt less the effect of ageing caused by climatic phenomena. Bottom of the tower is essentially affected by infiltration of rising damp.

Sample 3, that is the highest, shows pores smaller than the previous ones. Its high location makes it more prone to windy and rainy weather. In fact recrystallization inside of the pore space occurs and produces a reduction of pore space as well as a reduction of the interconnections between the pores.

As this example shows, NMR analysis (together with complementary techniques as optical microscopy, SEM and microanalysis) allow to obtain meaningful and important data necessary for an eventual restoration and consolidation. [14]

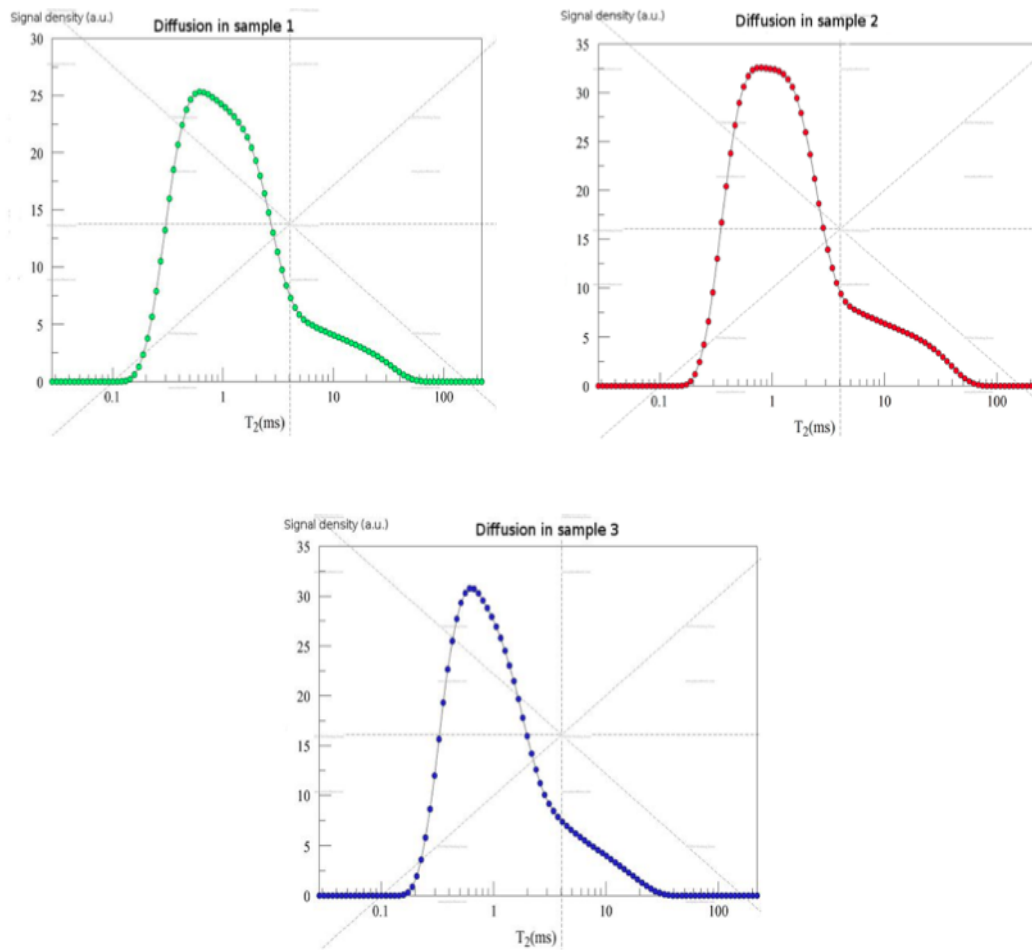


Figure 2.15: Density signal for sample 1 (green), sample 2 (red) and sample 3 (blue). [14]

2.1.5 Experimental method to monitoring historical building: Infrared Thermography

Infrared thermography is a qualitatively technique that allows to observe water content in historical building. Thanks to the fact that it is quite simple to perform and not invasive, it is often use in monitoring historical building.

Infrared thermography is based on the detection of electromagnetic radiation emitted by any physical body with a temperature above absolute zero. In a usual temperature range, a material emits radiation with wavelengths in the infrared region of of electromagnetic spectrum and, due to this fact, the thermal camera systems are designed to detect this infrared radiation. [15]

Infrared radiation region is positioned among microwave and visible part of the electromagnetic spectrum and the wavelength ranges from 0.75 to $1000\mu m$.

In thermal radiation theory, a blackbody is defined as hypothetical object which absorbs all incident radiations and radiates a continuous spectrum according to Planck's law as follow:

$$M_{b\lambda}(\lambda, T) = \frac{C_1}{\pi\lambda^5 \left[\exp\left(\frac{C_2}{\lambda T}\right) - 1 \right]}, \quad (2.18)$$

with

$M_{b\lambda}$: power radiated by the blackbody per unit surface and per unit solid angle for a particular wavelength,

λ : wavelength of the radiation,

C_1 : first radiations constants,

C_2 : second radiations constants,

T : temperature in absolute scale.

Integrating over all frequencies, Stefan-Boltzmann's law is obtained:

$$\frac{q}{A} = \varepsilon\sigma T^4, \quad (2.19)$$

with

q : rate of energy emission,

A : area of the emitting surface,

ε : emissivity of the emitting surface for a fixed wavelength and absolute temperature T ,

σ : Stefan-Boltzmann's constant.

The wavelength of the peak of the emission spectrum is related to the absolute temperature of the emitting surface by Wien's displacement law, which is expressed as follows:

$$\lambda_{max}T = 2,8977nm \cdot K. \quad (2.20)$$

Infrared radiation emitted by a body is detected by an infrared detector and using Stefan-Boltzmann's law, the temperature of the body can be obtained.[16]

Through this technique temperature differences are detected and measured. Interpretation of thermograms temperature field, and specifically of the thermal anomalies, can be very informative. In fact the temporal response of a material to thermal stress depend on the intrinsic thermal properties of the material, its appearance (for example color and surface) and its morphology. In the case of porous materials it has been shown that this response depends on some internal parameters such as porosity, water content, internal temperature distribution but also the nature and density of the granulate.

One problem to keep in mind is that the thermography measures are very sensitive to atmospheric boundary conditions: wind, humidity and sunshine are three important parameters to take into account before any action. [15]

The following fig. 2.16 is an example of a thermography measure.



Figure 2.16: Example of thermographic measure of a facade of a building. [15]

Thanks to the high value of the latent heat of water (each gram of water evaporating absorbs 2500 J and cools the surface very effectively), thermography allows also to estimate the evaporation rate of a wall. If the boundaries conditions are the same, moist areas result colder than dry ones. [17]

2.2 Moisture transport

The most important moisture transport mechanisms in building physics are water vapor diffusion and liquid transport through capillary forces.

The effect of gravitation, electrical fields and ion concentration gradient can be neglected in first approximation. For example gravitation only begins to affect liquid transport at pore radii larger than $1\mu m$.

Basically two processes occur:

1. Water vapor diffusion that, depending on the size of the pore, is divided in:
 - (a) Knudsen diffusion,
 - (b) Diffusion.
2. Liquid transport that is divided in:
 - (a) Surface diffusion,
 - (b) Capillary conduction (namely, viscous flow)

These processes are summarized in fig. 2.17:

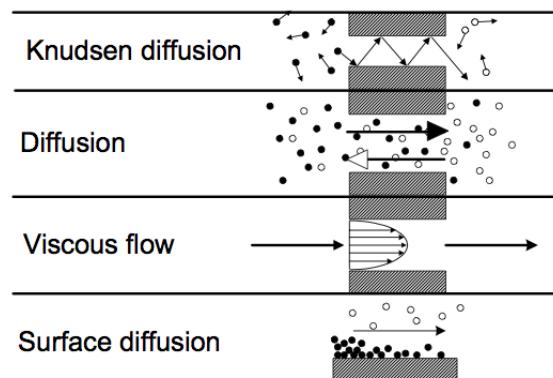


Figure 2.17: Summary of the main processes with regard moisture transport. [18]

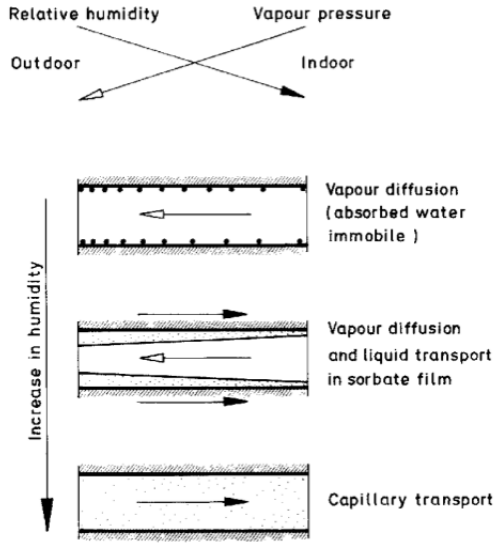
Figure 2.18 graphically shows the behavior of water transport in building components as vapor and liquid flows. In particular, the picture takes into account moisture transport in winter conditions with gradients of vapor pressure and relative humidity running in opposite directions.

Table 2.2 summarizes the relevant quantities, i.e. temperature (T), vapor pressure (p_v) and relative humidity (Φ) comparing internal and external environments.

If building component is dry, vapor diffusion takes place only from inside to outside and water absorbed in the wall remains immovable because of high adhesive forces.

When total moisture rises, a sorbate film is created on the pore walls: it is thicker on the outside and thinner on the inside because of the gradient of relative humidity. This different thickness implies that water molecules become more mobile and begin to move. This is the so-called surface diffusion and its driving gradient is precisely the relative humidity. This process is part of liquid transport.

Moisture transport in capillary pores



	Outdoor	Indoor
T	T_{out}	T_{in}
p_v	$p_{v(out)}$	$p_{v(in)}$
Φ	Φ_{out}	Φ_{in}

Table 2.2: Summary of temperatures, pressures and relative humidities inside and outside, in reference to the figure on the left.

Figure 2.18: Schematic diagram of moisture transport: vapor pressure and relative humidity run in opposite directions (winter condition). [4]

When total humidity increases again, the onset of capillary conduction inverts the moisture transport from inside to outside. In fact, if the surface diffusion reduces the moisture transport from inside to outside, then the capillary conduction reverses the flow.

It is important to emphasize that the prerequisite for this model is the assumption that vapor and liquid transports do not influence each other. This assumption applies in the sorption moisture region, since vapor diffusion takes place mainly in larger pores, while liquid transport occurs via the micropores and on the pore walls. [4]

2.2.1 Water vapor diffusion

As fig. 2.17 shows, vapor diffusion is divided into two processes depending on the pore size, i.e. Knudsen diffusion and diffusion.

In general vapor diffusion as well as effusion may occur as a result of difference in partial pressure.

In order to split the processes, it is possible to introduce the Knudsen factor K_n :

$$K_n = \frac{L}{2r}, \quad (2.21)$$

where:

L : mean free path,

r : pore radius.

Knudsen diffusion

Knudsen diffusion, also known as effusion, dominates the molecular movement if the mean free path is greater than the pore diameter, i.e. $L > 2r$, or $K_n > 1$.

In this case, the diffusion process is governed by collisions of the molecules with the pore walls.

Under normal conditions the mean free path L for gases and water vapor is of the order of $10^{-8}m$ and hence the effusion occurs in pore with radius $r < 5 \cdot 10^{-9}m$, that is in the micropore region.

For effusion through cylindrical capillaries, the following transport equation can be introduced:

$$g_E = -\frac{8}{3}r\sqrt{\frac{M}{2\pi RT}}\nabla p_v, \quad (2.22)$$

where:

g_E : effusion flux density,

M : molecular weight,

R : universal gas constant,

T : absolute temperature,

r : capillary radius,

p_v : partial pressure of water vapor.

As can be seen from equation (2.22), the process is governed by the pressure gradient. [7]

Diffusion

The kinetic gas theory describes the diffusion of molecules in multi-component gas mixture through equations which include three different diffusion driving parameters: mass fraction, temperature and total pressure.

When it is applied to physics of building, the total pressure gradient can be neglected and one obtains the following relation:

$$g_v = D_m\nabla m + D_T\nabla T, \quad (2.23)$$

where:

g_v : vapor diffusion flux density,

m : mass fraction of water vapor related to the total mass of vapor and air mixture,

D_m : mass related diffusion coefficient,

D_T : thermodiffusion coefficient.

The diffusion caused by mass gradient fraction is the well-known Fick's diffusion, while the thermodiffusion based on temperature gradients, also referred as Soret effect, is negligible in building components.

Since in a ideal gas there is a proportional relation between mass fraction and its portion of total pressure, the diffusion equation can be rewritten as a function of the partial pressure gradient:

$$g_v = -\delta \nabla p_v, \quad (2.24)$$

where:

g_v : vapor diffusion flux density,

δ : water vapor diffusion coefficient in air,

p_v : water vapor partial pressure.

According to [4], the water vapor diffusion coefficient in air (δ) can be calculated by means of the the following relation:

$$\delta = 2,0 \cdot 10^{-7} \frac{T^{0,81}}{P_L}, \quad (2.25)$$

where:

T : absolute ambient temperature,

P_L : ambient air pressure.

Another quantity often used to calculate diffusion, in place of vapor partial pressure, is the vapor concentration, C_v :

$$C_v = \frac{p_v}{p_{air}}. \quad (2.26)$$

In the case of non-isothermal conditions, this last assumption is not allowed. [4]

In building materials there is often a pore size spectrum which covers all three regions of radii and a clear separation of the two transport phenomena is not possible. Moreover, in the transition zone of pore size, the two transport mechanisms are intermixed.

It is worth noticing that the driving force for both kinds of transport mechanisms is partial water vapor pressure. For that reason the effects of the micro structure and the interaction of Knudsen and Fick's diffusions on water vapor transport through porous media can be described by a common diffusion coefficient.

In practice, a water vapor diffusion resistance factor, μ , characteristic for each material, is introduced. It is the ratio of the diffusion coefficient of water vapor in air and

in the building material and it is independent of temperature, but it depends on water content.

Keeping in mind these considerations, equation (2.24) becomes:

$$g_v = -\frac{\delta}{\mu} \nabla p_v, = -\delta_p \nabla p_v. \quad (2.27)$$

Then, defying the ratio between δ and μ as a unique coefficient, $\delta_p = \frac{\delta}{\mu}$, the vapor diffusion flux density, g_v , becomes:

$$g_v = -\delta_p \nabla p_v. \quad (2.28)$$

This equation is valid until $p_v < 10\%$ of the total pressure, otherwise convection phenomena occur. If temperature is below $40^\circ C$, this condition is always met. Higher temperatures are allowed if relative humidity is lower than this value. [4]

In the sorption moisture region, the diffusion resistance can be considered constant and it is physically plausible that liquid and vapor transports are independent from each other. The issue is that it is not completely clear if these assumptions are valid also in capillary region. [4] [7]

Some experiments have demonstrated that the vapor flux is higher than expected. Philip and de Vries developed a microscopic model to account for this enhancement. They suggested that in a porous material, when relative humidity increases, water islands are formed due to capillary condensation.

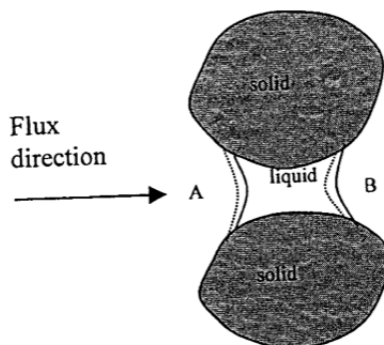


Figure 2.19: Water island within a solid matrix. [19]

If there is no temperature gradient, radii at sides, A and B, of the island are equal and there is not a increase of vapor flux. In fig. 2.19 this configuration is represented by continuous black line.

On the other hand, if a vapor (and hence a temperature) gradient is present in the direction of the arrow, vapor will condensate at one end of this island. At the same time water at the other side has to evaporate in order to maintain equilibrium. Looking at dashed lines in fig. 2.19, vapor condensates on the "cool" side (A) of the liquid island and evaporates on the "hot" side (B). The curvature of the meniscus decreases at A

and increases at B, causing capillary transport of the liquid from A to B. This process continues until the capillary flow equals the rate of condensation and evaporation at points A and B.

The process of condensation of water vapor molecules is instantaneously balanced by evaporation of water molecules on the other side and thus a travel time of vapor molecules through liquid island is put equal to zero. [19] By this way, water passes the island through a faster mechanism and as a consequence, the diffusion coefficient will increase. [20]

Other authors argue that the lowering of vapor diffusion resistance is to be found in surface diffusion occurring in parallel to the vapor transport. It would seem more likely to assume that when water is absorbed, it is deposited as an adsorbed film on walls of the porous material and in particular in wedge-shape spaces between crystals. As humidity rises, these wedge shaped spaces are capable of absorbing a great deal of water which is highly mobile with respect to a film with a thickness of only few molecules.

The formation of a gradient of absorbed moisture leads liquid transport and the equilibrium is reached more rapidly compared to that achieved when only diffusion occurs. This fact could causes the increase of water vapor permeability.

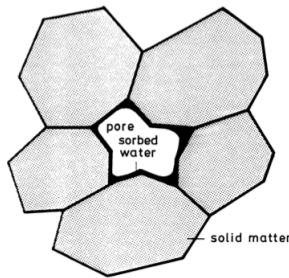


Figure 2.20: Sorbate film inside a porous with a wedge form. [7]

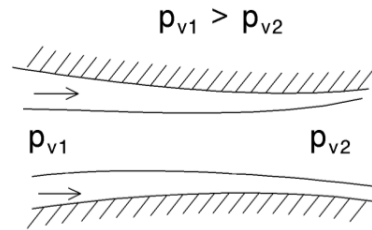


Figure 2.21: Surface diffusion of water along the pore wall. [20]

Since this phenomenon occurs when capillary conduction dominates over vapor diffusion, it seems reasonable to assume that vapor diffusion does not depend on moisture. [4]

2.2.2 Liquid transport

Treating the phenomenon of liquid transport, it is necessary to distinguish between moisture sorption region and capillary water region. In the first region, surface diffusion takes place, while in the latter capillary conduction dominates. [7]

Actually capillary conduction and surface diffusion can occur simultaneously in liquid transport and there is not a sharp point where one stops and the other begins.

Surface diffusion

Surface diffusion is defined as moisture transport in the water molecule layers adsorbed at the pore walls of hygroscopic materials. [4]

It does not happen for every type of condition, for example in sandstone it begins at about 60% of relative humidity.

The thickness of the film becomes greater with the rising of relative humidity and with the increase of the thickness there is also an increase of mobility of the water adsorbed molecules. Differences in layer thickness of the film are the starting point for mass transport in the liquid film.

The driving potential of surface diffusion is the relative humidity and not the vapor pressure as in the case of diffusion seen before. One way to explain this fact is depicted in fig. 2.22, where the graphs show the dependence of measured moisture fluxes (here indicated as G) through a paper membrane: there is an opposite behavior with respect to temperature, when we relate the moisture flux with vapor pressure difference, Δp , (top) and relative humidity, $\Delta \Phi$, (bottom). In the first case moisture flux increases with the decreasing of temperature, in contrast to the gas diffusion law. In fact, remembering equation (2.25), water vapor diffusion coefficient, δ , rises with temperature. This implies that partial pressure cannot be the driving potential.

Instead, by relating surface diffusion flow with relative humidity, one notes that higher flow results when temperatures are higher. This suggests that the relative humidity is the driving potential.

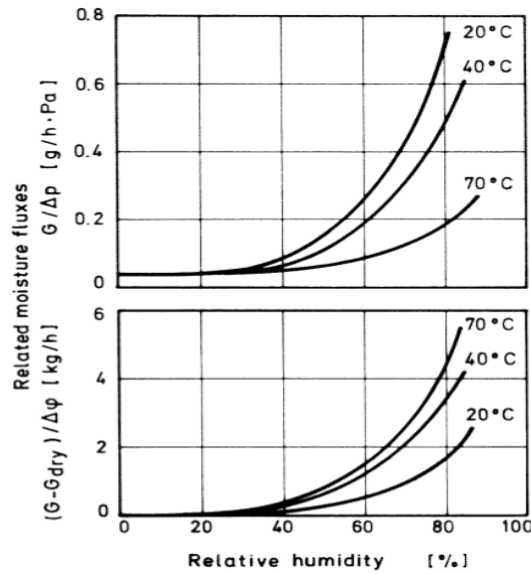


Figure 2.22: Dependence of the measured moisture fluxes, G , on the mean relative humidity; it is related to pressure difference (top) and difference of relative humidity (bottom). [4]

It may be assumed that mass flow in surface diffusion is proportional to the layer thickness and thus to the concentration gradient. If w is the water content, the surface diffusion flux density, g_s , can be described by the following equation:

$$g_s = D_s \nabla w, \quad (2.29)$$

with D_s surface diffusion coefficient.

Capillary conduction

Capillary conduction in porous building materials is a very complex phenomenon because of the complicated cavity structure of the materials themselves.

If one assumes the model of single cylindrical capillary, the position of the meniscus (s) that moves in time during suction process can be expressed by Hagen-Poiseuille's law:

$$s = \sqrt{\frac{\sigma_w r \cos \theta}{2\eta} t}, \quad (2.30)$$

where:

σ_w : surface tension of water,

r : capillary radius,

θ : contact angle,

η : viscosity of water,

t : suction time.

The amount of water, m_w , absorbed (in kg/m^2) is:

$$m_w = A\sqrt{t}, \quad (2.31)$$

with A water absorption coefficient.

The time square root dependence assumes a precisely defined water front which penetrates the building material, but this hypothesis is not true in actual building material where there is a water content gradient due to interconnection of pores of different size.

The formation of water content profiles can be explained with the help of the following fig. 2.23.

In a pore there are two opposite effects: acceleration by capillary tension and slow-down because of flow resistance. The first one, reminding equation (2.6), is proportional to the inverse of the radius, while the latter is proportional to the inverse of the square of the radius.

This means that larger pores have a lower drawing power but they also lower flow resistance and therefore larger capillaries have, overall, greater suction power. For this reason there is a continuous decline in water content as the fig. 2.23 shows.

Many authors usually describe suction by a diffusion equation, although the process is a "flow" [4]:

$$g_w = -D_w(w)\nabla w, \quad (2.32)$$

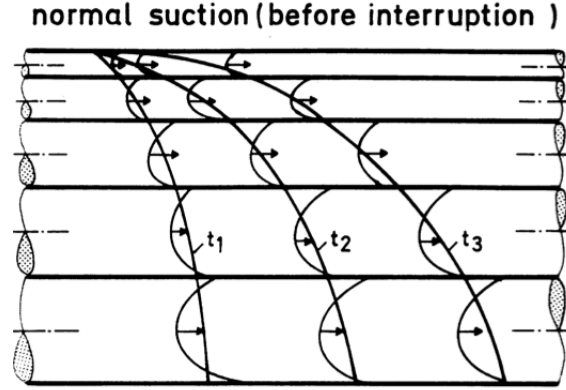


Figure 2.23: Capillary transport phenomena: due to the lower flow resistance, the larger pores draw at higher rate. [7]

with g_w liquid flux density, and

D_w capillary transport coefficient.

The capillary transport coefficient, D_w , is strongly dependent on the water content.

Equation (2.32) can lead to a good approximation of suction process under certain conditions; some studies show that the \sqrt{t} dependence can be reproduced, regardless of the form of D_w .

However this approach, and thus equation (2.32), cannot apply to water transport in the following cases [7]:

1. water transport without water content gradient: in this case the transport coefficient would have to be infinitely large.

This situation rarely occurs because it involves total saturation of sizable area.

2. water transport with discontinuous water content gradient: the transport coefficient would have to be zero at the discontinuous point.

This case has not been observed in miner building materials as for water content regions of interest.

The capillary transport coefficient, D_w , also depends on temperature. In fact, both surface tension, σ_w , and viscosity, η , of water are affected by temperature. As fig. 2.24 shows, variation of surface tension, σ_w , is negligible compared to viscosity, η .

Therefore temperature dependence of D_w can be written through dependence of η .

$$D_w(T) = \frac{\eta_{ref}}{\eta(T)} D_{w,ref}. \quad (2.33)$$

It is practical to select $20^\circ C$ as reference temperature.

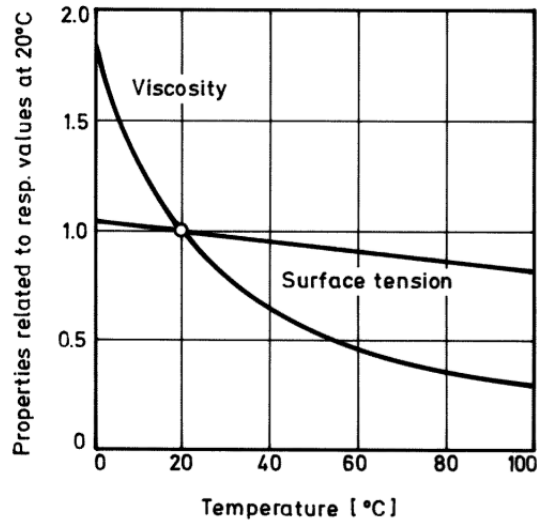


Figure 2.24: Viscosity and Surface tension as a function of temperature. [4]

Another important aspect that should be taken into account is the dependence on boundary conditions. This becomes clear when the suction process is interrupted and redistribution phenomena starts (fig. 2.25).

When supply of water is cut off, the movement of fluid is due to smaller pores that are not yet filled and have a great suction power; therefore they suck up water from the larger one. As soon as water is removed, menisci are curved until the suction forces of these menisci and those in the water front region cancel each other.

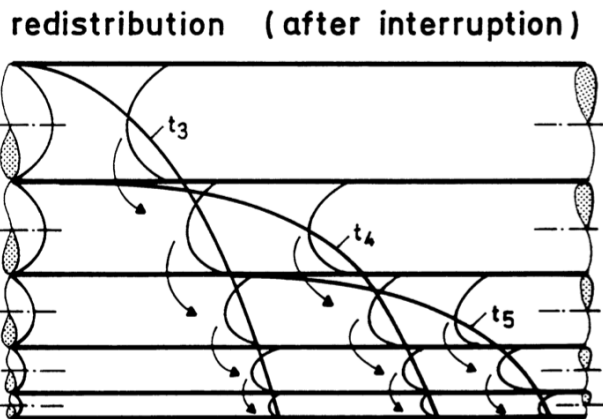


Figure 2.25: Capillary transport phenomena: after the interruption of the water supply, smaller capillaries, not yet filled, suck dry the larger pores because of their greater drawing power. [7]

However, this process is slower than liquid transport during adsorption process and

it is necessary to apply different capillary transport coefficients for liquid transport.

Experimental results with various building materials show that capillary transport coefficients determinate during redistribution can be smaller by more than one decimal power compared with the coefficient observed during suction process.

For that reason two different coefficient should be introduced to characterize the capillary liquid transport. [4]

From a physical point of view, it is more plausible to describe liquid transport in porous media through a flow model. In hydraulic engineering, for water saturated porous materials, the Darcy's formula is often used and the liquid flux density, g_w , can be written as:

$$g_w = K_1 \nabla p_c, \quad (2.34)$$

where:

K_1 : permeability coefficient,

p_c : capillary pressure.

For flow in water saturated porous materials, the permeability coefficient, K_1 , is approximately constant, but in general, below free water saturation level, the permeability is very dependent on moisture content. [21]

From Kelvin's relation (2.8), capillary pressure, p_c , can be obtained:

$$p_c = -\rho_l R_v T \ln \Phi. \quad (2.35)$$

Substituting in equation (2.34) the just found expression for p_c , one has that:

$$g_w = -K_2 \nabla (T \ln \Phi), \quad (2.36)$$

and hence:

$$g_w = -K_2 \frac{T}{\Phi} \nabla \Phi - K_2 \ln \Phi \nabla T. \quad (2.37)$$

The second term in equation (2.37) is smaller than the first one and, under practical condition, can be disregarded.

Introducing a unique coefficient, D_Φ , incorporating all terms before $\nabla \Phi$, it follows that:

$$g_w = -D_\Phi \nabla \Phi, \quad (2.38)$$

and

$$D_\Phi = D_w \frac{dw}{d\Phi}. \quad (2.39)$$

Equation (2.38) contains a material independent moisture transport potential that is continuous also at boundaries of layers.

Supersaturated region

In supersaturated region the relative humidity is always 100% and in principle liquid transport doesn't take place.

Experimental researches seem to confirm this fact, indeed in supersaturated water region the moisture profile remains unchanged and only when the amount of water falls below free water saturation a defined relationship develop between moisture potential and water content. [4]

2.2.3 Moisture transport below the freezing point

Ice formation can block vapor diffusion. Until 60% of the pores are filled, the diffusion resistance is little affected by frost formation because the diffusion flow dominates in large pores with few branches. These pores are filled only when the water content is high.

Frost affects the liquid transport more than the vapor transport. Below 0°C there is no capillary suction, but the water in micropores freezes only at lower temperatures. So even below zero celsius degrees liquid transport can occur with little interference from ice formation in large pores. [4]

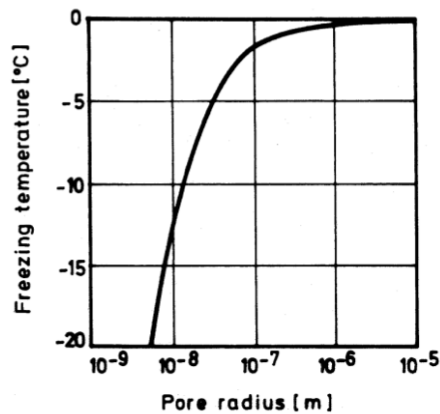


Figure 2.26: Freezing temperature as a function of the pore radius. [4]

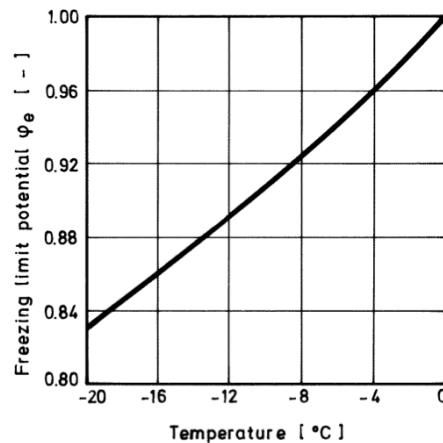


Figure 2.27: Trend of the freezing limit potential as a function of temperature. [4]

The relative humidity over the menisci just above freezing, calculated by means of Kelvin relation (2.8), is called freezing limit potential (Φ_e) and its dependence on temperature is shown in fig. 2.27.

2.2.4 Moisture transport in organic polymers

Moisture transport in organic polymers are called solution diffusion and, for completeness, it is shortly mentioned in this paragraph.

Often organic polymers are used in buildings for seals or coating in the form of vapor barrier. The mechanism of water transport is quite different respect of mineral material, because in this case water molecules creates its own pore spaces by attaching itself to the macromolecules and this cause swelling. The movement of water is coupled to the movement of polymer molecules.

Diffusion flux, g_{op} , for solution diffusion of gases and vapors can be calculated as follow:

$$g_{op} = -D_L L_s \nabla p, \quad (2.40)$$

with

D_L : solution diffusion coefficient,

L_s : solubility,

p : partial pressure.

Solubility of the polymer for water depends on the polarity or non-polarity of the macromolecule and it decreases exponentially with temperature. On contrary, the solution diffusion coefficient increase with temperature and depends on the structure of polymer.

However temperature dependence can be generally disregarded while the moisture content plays an important role. In fact there is a pronounced decrease in diffusion resistance of hydrophilic polymer with the increase of moisture. [4]

2.3 Brief summary

Figure 2.28 summarizes the moisture behavior. It illustrates moisture permeability as a function of capillary pressure and the corresponding filling of the pore space for a fictitious material. Shaded areas correspond to the material matrix, the white areas represent pores filled with air and the black areas correspond to pores filled with liquid water. [6]

- **(a)-(b)**: At low moisture content, liquid water is present only as a thin film on pore walls. It is practically immobile because it is strongly adherent to the pore walls. Moisture transport is dominated by molecular vapor diffusion whose driving potential is partial pressure.
- **(c)**: As the moisture content rises, the film becomes thicker and water molecules start moving. In addition capillary condensation begins and liquid water fills the smaller pores. Liquid water transport in water-filled regions is governed by water content and it is far more efficient; this results in an apparent increase of the experimentally observed water vapor flow.

- (d)-(e): As the moisture content further increases, the water filled regions expand and coalesce. At the critical moisture content, a continuous liquid water phase is formed and permeability increases significantly.

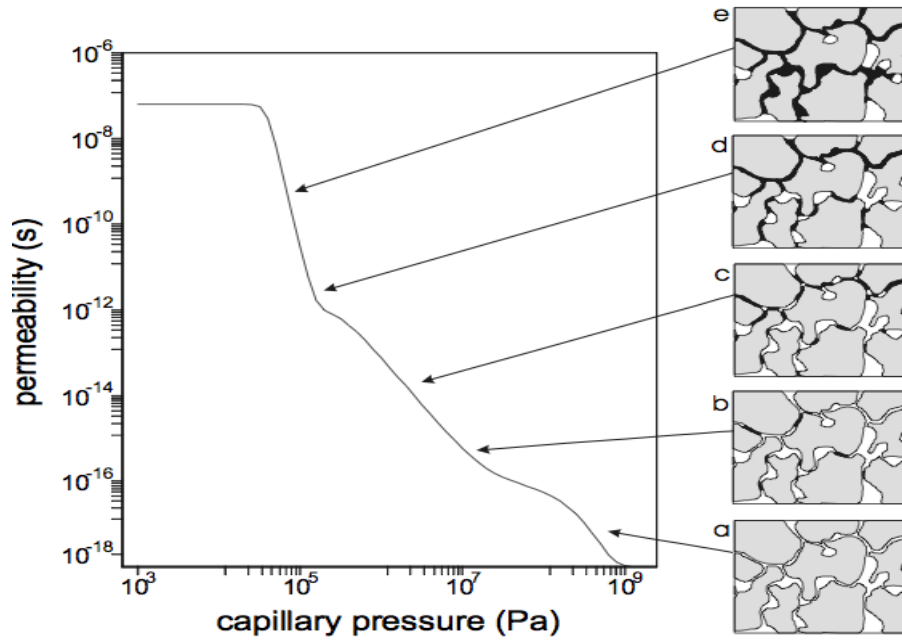


Figure 2.28: Moisture permeability as a function of capillary pressure and the corresponding filling of the pore space for a fictitious material. [6]

Chapter 3

Heat storage and transport

The effects of heating can be very important with regard to the mechanism of deterioration of the stone. Thermal stresses can induce anisotropic deformation of the crystals and micro-cracks occur. These facts imply an increase of porosity with a shift of pore size distribution towards larger pore and, consequently, an increase of water absorption. [1]

In this chapter the main issues regarding heat are summarized in order to develop an equation of heat transport. A key role is played by the moisture that is present inside the pores and this fact will lead to a coupled equations for heat and moisture.

3.1 Heat storage

3.1.1 Basics of thermodynamics

In general system can be divided in:

- Isolated: systems can exchange neither energy nor matter.
- Closed: systems can exchange energy but not matter.
- Open: system can exchange both matter and energy with the exterior.

The principle of conservation of energy postulates the existence of a function of state, called the energy of the system, E , such that its change per unit time is equal to some flow from the surrounding. This is the first principle of the thermodynamic and it takes the usual form:

$$dE = dQ - pdV, \quad (3.1)$$

with

p : pressure of the system,

V : volume of the system.

For a closed system, the term dQ in equation (3.1) represents the heat exchange with surrounding environment.

For an open system, instead of the simple heat transfer, the resultant energy, due heat transfer and matter exchange, must be taken into account. [22]

Walls or buildings, for instance, are examples of open systems.

Another useful thermodynamic function to introduce is the enthalpy of the system, H ; it is the proper thermodynamic potential to deal with heat issue in porous media. It is defined as follow:

$$H = E + pV, \quad (3.2)$$

and the specific enthalpy, h , can be obtained dividing all terms of equation (3.2) for the mass of the system. The specific enthalpy will be a function of specific energy, e , and density, ρ :

$$h = e + \frac{p}{\rho}. \quad (3.3)$$

The principle of conservation of energy in term of enthalpy can be written as:

$$dH = dQ + Vdp. \quad (3.4)$$

In isobaric condition, the exchanged heat is equal to the enthalpy change.

Developing dH or dE as total differential in term of variables p , T or V , important thermodynamical quantities can be found. For example, specific heat, that is the amount of heat required to change the temperature of a mass of $1kg$ by 1 Kelvin degree, can be obtained. In particular the specific heat at constant volume, c_V , and the specific heat at constant pressure, c_p , can be respectively derived from the specific energy and the specific enthalpy as follows [22]:

$$c_V = \left(\frac{\partial e}{\partial T} \right)_V \quad \text{and} \quad c_p = \left(\frac{\partial h}{\partial T} \right)_p. \quad (3.5)$$

3.1.2 Enthalpy of porous materials

In physics of building, the stored thermal energy usually equals the so-called internal energy that consists of the kinetic energy of the molecules. For gases, the mechanical energy resulting from a volume change at constant pressure (volume-work) and condensation of water vapor (latent heat), has to be considered. Enthalpy equals the sum of the internal energy, the latent heat and the volume-work. [23]

Starting from the equation of specific heat at constant pressure, eq. (3.5), the general relation between enthalpy of a material and its temperature can be derived ¹.

$$\frac{\partial H_s}{\partial T} = \rho_s c_s, \quad (3.6)$$

¹From now on, the subscript p , that stands for constant pressure, will be omitted.

with

H_s : enthalpy of dry material per unit volume,

ρ_s : density of the dry building material,

c_s : specific heat capacity of the building material at constant pressure.

In the temperature range of building physics, the relation among enthalpy and temperature is approximately linear:

$$H_s = \rho_s c_s T. \quad (3.7)$$

The presence of moisture affects enthalpy of the building materials, in fact heat and moisture transport processes in buildings are usually strongly coupled. Therefore, enthalpy of the water that is contained in the media must be added to equation 3.7.

One problem that derives from the presence of water inside the medium, is the dependence of enthalpy on the physical state of water itself.

The following figure, fig. 3.1, shows the development of the enthalpy of ice, liquid water and saturated vapor inside a porous material as a function of temperature:

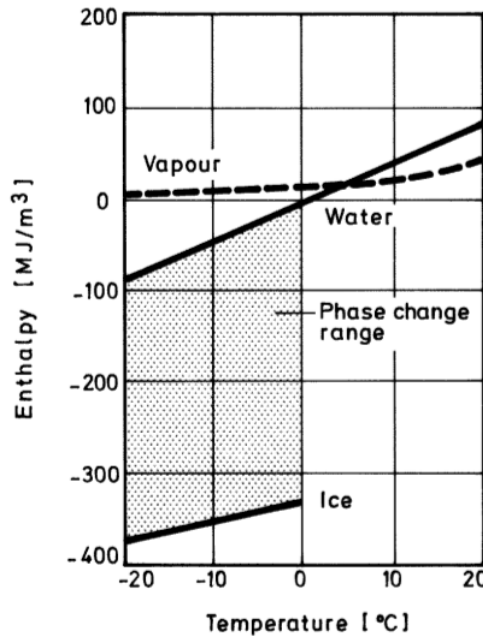


Figure 3.1: Enthalpy of various water physical phases at normal pressure as a function of temperature.[4]

The dashed line represents the enthalpy change of water vapor under saturation condition, taking into account the latent heat effects to maintain the state of saturation.

It is negligible compared to enthalpy variation of liquid water. Shaded area shows the enthalpy of phase change of liquid water to ice. As can be seen, this latter fact plays an important role.

In order to determinate exactly the enthalpy of a phase mixture, it is necessary to know the pore radii distribution or the moisture storage function of the building material, but this knowledge is often difficult to obtain.

However the enthalpy of moisture, H_w , in the building material can be summarized in a unique equation, in according to [4], as follows:

$$H_w = \left[(w - w_e)c_w + w_e c_e - h_e \frac{dw_e}{dT} \right] T, \quad (3.8)$$

with

w : total water content,

w_e : content of frozen water,

c_e : specific heat capacity of ice,

c_w : specific heat capacity of liquid water,

h_e : specific melting enthalpy.

Keeping in mind the considerations about enthalpy of dry material and water, the total enthalpy, H , will be the sum of equations (3.7) and (3.8):

$$H = H_s + H_w = \rho_s c_s T + \left[(w - w_e)c_w + w_e c_e - h_e \frac{dw_e}{dT} \right] T. \quad (3.9)$$

3.2 Heat transport

In order to take into account the effect of localized water on the heat transport, the thermal conductivity depending on the water content is introduced.

Thermal conductivity is a very important quantity because, for a porous material, it takes into account the effect of radiation, convection and conduction; these events, in fact, often happen jointly [23].

Therefore the heat conduction equation will be introduced to described heat transfer in porous materials and boundaries conditions are added later to consider what happens at surface, for instance radiation.

Moreover, heat transport is also influenced by evaporation and condensation of transported moisture. In general it is difficult to described these processes in practical terms by means of the thermal conduction equation and hence they are described as a source, or sink, terms.

In addition, if few reactions occur inside the porous material, the heat involved in these processes has to be considered. Since it has a local character, also this term will be considered as a source term.

3.2.1 Heat conduction

The relationship between heat flow and the temperature gradient is governed by Fourier's law of conduction. It is true for a homogeneous, isotropic², solid in steady state. It can be written as follows [24]:

$$\vec{q} = -\lambda \nabla T, \quad (3.10)$$

where:

\vec{q} : heat flux density,

λ : thermal conductivity.

Thermal conductivity λ

The thermal conductivity, λ , is a property of the conducting material and it depends on the state of the material itself. It is also called a transport property because, for a given temperature gradient, heat flux is directly proportional to thermal conductivity.

In moist material, thermal conductivity λ is influenced by water content, w , and it can be written as follows:

$$\lambda(w) = \lambda_0 \left(1 + b \frac{w}{\rho_s} \right), \quad (3.11)$$

where:

λ_0 : thermal conductivity of dry material,

b : thermal conductivity supplement.

The thermal conductivity supplement, b , is a percentage value that describes the thermal conductivity increase per mass percent of moisture. In general it depends on the type of building material, but, in case of hygroscopic materials, it is largely independent of their bulk density. [4]

The following fig. 3.2 shows the increase in heat conductivity of three different building materials as a function of their moisture content. While the heat conductivity of porous materials, such as cellular concrete, increases linearly with moisture content, the heat conductivities of polystyrene foam or mineral wool show a slightly progressive increase. These two latter materials are, in fact, often used for the insulation.

²An isotropic materials presents a diffusion coefficient that is independent of the direction.

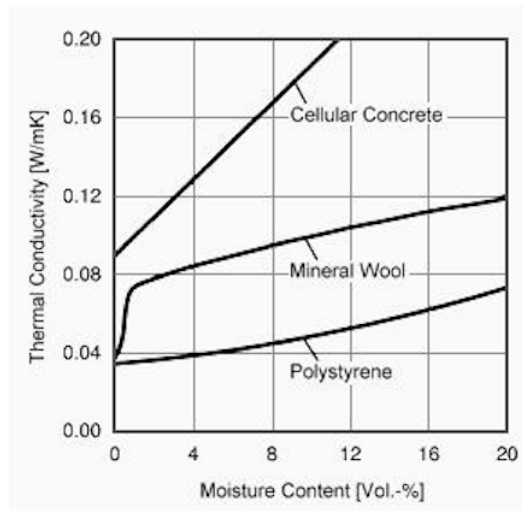


Figure 3.2: Effect of moisture on measured thermal conductivity of different building materials.

3.2.2 Heat transport through enthalpy flows with phase change

Heat transport can be described as enthalpy flows connected to a flowing medium. These media are diffuse water vapor and liquid water moved through capillary pressure.

In the following paragraph a particular case is shown, by way of example, in order to underline the importance of enthalpy flows and to realize which flows are important and which are negligible.

Changes of phase are considered because, in order to get the evaporation, heat is needed and, at condensation, heat is released. If in a porous material this phase change occurs, a heat source will be present.

Supposing to consider a western exposed wall in winter condition: it is plausible that the building material will be subject to high moisture load in presence of temperature gradient.

In table 3.1 averaged values under winter months at foothills of the Alps are reported.

	Outdoor	Indoor
Temperature ($^{\circ}C$)	2,0	20,0
Radiation (W/m^2)	40	/
Total driving rain (kg/m^2)	200	/

Table 3.1: Temperature, radiation and driving rain averaged values.[4]

The exchanges of heat are shown in the following table:

Heat transferred from inside to outside (W/m^2)	8,5
Heat transferred by radiation (W/m^2)	28
Heat released to the surrounding (W/m^2)	36,5

Table 3.2: Heat flows between inside and outside by caused by radiation. [4]

In order to simplify the situation, just to understand the scale of flows, one can assumes that the driving rain hits the wall, then it is completely absorbed and evenly distributed over the rain screen. Eventually the moisture introduced by the rain dries out and this leads an evaporative cooling:

Heat transfer rate by rain (W/m^2)	<0,2
Heat loss by evaporative cooling (W/m^2)	32

Table 3.3: Heat flows caused by water absorption and evaporative cooling. [4]

The assumption adopted above about rain is quite drastic, but this example shows an important matter: heat loss by evaporative cooling, that is an enthalpy flow connected to phase change, is in the order of the heat gained by solar radiation, instead enthalpy flow due to liquid transport is negligible. Therefore latent heat can have important effects.

Some studies test the fictitious thermal conductivity of dry mineral slabs between moistened blotting paper or cellular concrete. They have demonstrated that among heat conductivity and vapor diffusion flux there is a linear relationship, as shown in fig. 3.3. The change in the thermal conductivity is attribuite solely to latent heat effect through phase change.

This enthalpy flow has nothing to do whit heat conduction and they must be taken into account by separate equation. Therefore the interaction of vapor diffusion and phase change is taken into account as a source or sink term, S_h , in the heat balance equation.

$$S_h = -h_v \nabla g_v, \quad (3.12)$$

with

h_v : latent heat of phase change,

g_v : water vapor diffusion flux density.

In equation 3.12 the latent heat of phase change appears. It consists of the specific evaporation enthalpy of pure water and the material-dependent sorption enthalpy. However the latter term can be disregarded in the moisture range above 50% relative humidity, which is the important range of physics of building for most materials. [4]

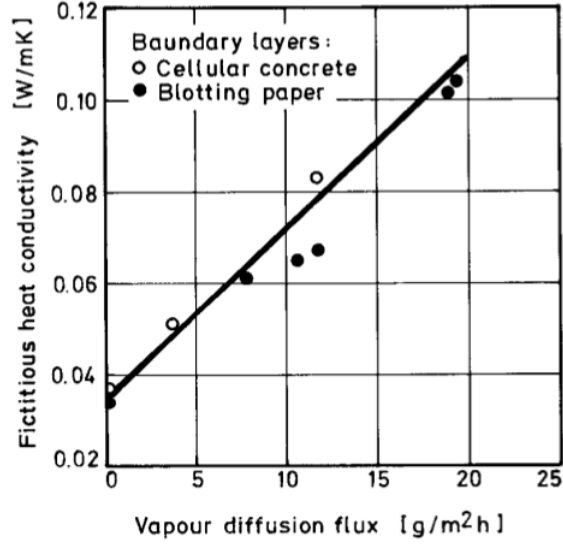


Figure 3.3: Relationship between the thermal conductivity of mineral fibre and water vapor diffusion flux density. [4]

3.2.3 Heat released by reactions

If some reactions occur inside a porous materials because a fluid infiltrates inside the pores, they can contribute to heat balance. The heat associated with the reaction has a local character and it is not possible to predict a priori where heat will be released. Therefore, in order to take into account the enthalpy variation due to a reaction in the heat balance equation, one can introduce a source term.

In general form, one supposes to have a multicomponent reacting mixture of N chemical species in which each species is characterized by a density ρ_i . According to reference [25], the enthalpies for each species, h_i , for an arbitrary temperature, T , are obtained starting from the enthalpy, $h_{i,0}$, at standard temperature, T_0 thanks to the following equation:

$$h_i = h_{i,0} + \int_{T_0}^T C_{p,i}(s) ds, \quad (3.13)$$

with

h_i : enthalpy of species i at an arbitrary temperature T ,

$h_{i,0}$: heat of formation for species i at standard temperature T_0 ,

$C_{p,i}$: specific heats at constant pressure.

The heat flux for each species due to reaction can be written as follows:

$$\vec{q}_i = -Dh_i \nabla \rho_i, \quad (3.14)$$

where the term D is the diffusion coefficient.

Therefore, the total heat flux due to reaction will be the sum of the heat fluxes, \vec{q}_i , :

$$\vec{q}_r = - \sum_{i=1}^N Dh_i \nabla \rho_i. \quad (3.15)$$

In order to include this term in the heat balance equation, one needs a source term. Such term can be written in the following form:

$$S_r = -\nabla \vec{q}_r = \nabla \left(\sum_{i=1}^N Dh_i \nabla \rho_i \right). \quad (3.16)$$

Chapter 4

Heat and moisture coupled equations

The moisture and heat transports are strongly interrelated and coupled. For example, air flows cause heat and moisture transfers, temperature differences cause differences in relative humidity that cause moisture transfer, evaporation and condensation and these facts influence the heat balance. Moreover moisture content influences thermophysical properties of building construction materials. Fortunately for building physics many simplifications are permitted because the processes happen at atmospheric pressure, at a relatively small temperature range and low flow velocities [23] [24].

4.1 Differential equation of moisture transport

In the first chapter the processes concerning moisture have been described. Now the goal is summarize all processes in a balance equation for the moisture content, w .

The two processes that occur and their relative driving potential are summarized in table 4.1:

Process	driving potential	flux
Vapor diffusion	vapor pressure p_v	$g_v = -\delta_p \nabla p_v$
Liquid water diffusion	relative humidity Φ	$g_w = -D_\Phi \nabla \Phi$

Table 4.1: Summary of the processes and their driving potentials in moisture transport.

Therefore, the continuity equation of moisture transport is written as follows:

$$\frac{\partial w}{\partial t} = -\nabla \cdot (g_w + g_v) + S_w. \quad (4.1)$$

In principle, in equation (4.1) a source term, S_w , is introduced in order to take into account possible moisture sources. However it is very rare for moisture sources to occur

in a building components and they can be neglected in first approximation.

Therefore, the governing continuity equation is:

$$\frac{\partial w}{\partial t} = \nabla \cdot (D_{\Phi} \nabla \Phi + \delta_p \nabla p_v). \quad (4.2)$$

Given that $p_v = \Phi p_{sat}$, equation 4.2 can be rewrite as:

$$\frac{\partial w}{\partial t} = \nabla \cdot (D_{\Phi} \nabla \Phi + \delta_p \nabla (\Phi p_{sat})). \quad (4.3)$$

Another way to write the previous equation is through the water retention curve, $(\partial w / \partial \Phi)$, that describes the relationship between the water content and the driving potential.

$$\frac{\partial w}{\partial \Phi} \frac{\partial \Phi}{\partial t} = \nabla \cdot (D_{\Phi} \nabla \Phi + \delta_p \nabla (\Phi p_{sat})). \quad (4.4)$$

Equation (4.4) is the moisture balance equation: the left hand side represents the moisture storage, while in the right hand side there are the transport terms. [26]

4.2 Differential equation of heat conduction

Heat conduction is a temporary phenomena in buildings. In fact it is strongly influenced by boundary conditions which are in general affected by the outside condition. Energy conservation's law implies that the rate of heat storage equals the rate of heat entering plus the rate of heat generation:

$$\rho c_p \frac{\partial T}{\partial t} = -\nabla \cdot \vec{q} + \sum_i S_i, \quad (4.5)$$

where:

S_i : source term.

A source term, S_i , can be, for example, the latent heat due to phase change described by equation (3.12) or the source term connected to the heat due to chemical reactions, given by equation (3.16).

Introducing the source terms, S_h and S_r , and the Fourier's equation for heat flux (3.10), the equation 4.5, written in term of enthalpy, becomes:

$$\frac{\partial H}{\partial T} \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) + S_h + S_r. \quad (4.6)$$

Again, as equation 4.4, equation 4.6 is the heat balance equation: on the left side there is the stored heat, while the terms on the right side are the heat flows. The latter are given by the the sum of the divergence of heat conduction, the latent heat term (that is the specific latent heat multiplying the divergence of vapor flow) and the heat associated with reactions. [26]

4.2.1 Considerations about enthalpy and open irreversible systems

In section 3.1.1 the first principle of thermodynamics has been set out. Now the attention is placed on the second principle and irreversibility.

Irreversibility occurs in all natural processes such as conduction of heat, chemical reactions and diffusion. In accordance with the second law of thermodynamics, irreversibility is the phenomenon which prevents from extracting the most possible work from various sources. In other words, in all the natural processes, a part of work, called W_λ , is lost due to irreversibility. This work can be related to the entropy generation through Gouy-Stodola theorem¹, and the Lagrangian formalism is introduced in order to develop an analytic approach to the thermodynamic analysis of open irreversible system. The goal is to extend the results to enthalpy.

Definition 4.1. The work lost W_λ for irreversibility is defined as:

$$W_\lambda = \int_0^\tau \dot{W}_\lambda dt,$$

where:

$$\dot{W}_\lambda = \dot{W}_{max} - \dot{W}. \quad (4.7)$$

The term \dot{W}_{max} , in equation (4.7), is the maximum work transfer rate, which exists only in the ideal limit of reversible operation, while \dot{W} is the effective work transfer rate.

Definition 4.2. The entropy of the whole system, composed by the open system and the environment, is defined as:

$$\Delta S = \int \left(\frac{\delta Q}{T} \right)_{rev} = \Delta S_e + S_g.$$

The term ΔS_e is defined as the entropy variation that would be obtained exchanging reversibly the same heat and mass fluxes throughout the system boundaries, while S_g is the entropy generation due to irreversible processes. The latter term is defined as:

$$S_g = \int_0^\tau \dot{S}_g dt. \quad (4.8)$$

With the introduction of the previous quantities, the Gouy-Stodola theorem can be introduced.

Theorem 4.1 (Gouy-Stodola Theorem). *In any open system, the work lost for irreversibility, W_λ , and the entropy generation, S_g , are related each another as:*

$$W_\lambda = T_a S_g,$$

where T_a is the ambient temperature.

¹The original documents can be found in references [27] [28].

Another important theorem gives the relationship between the Lagrangian, \mathcal{L} , and the work lost, W_λ :

Theorem 4.2. *The thermodynamic Lagrangian is:*

$$\mathcal{L} = W_\lambda.$$

At the stationary state, the work lost for irreversibility is an extremum. This can be demonstrated starting from the action, \mathcal{A} , and applying the least action principle:

$$\mathcal{A} = \int_0^\tau \mathcal{L} dt = \int_0^\tau W_\lambda dt, \quad (4.9)$$

and considering the least action principle it follows that:

$$\delta\mathcal{A} \leq 0 \quad \Rightarrow \quad \delta\mathcal{L} \leq 0 \quad \text{or} \quad \delta W_\lambda \leq 0. \quad (4.10)$$

This also implies that $\delta S_g \leq 0$. This point of view is from inside the system. If it is considered from the environment, the behavior of entropy will be opposite and hence $\delta S_g \geq 0$. Therefore the entropy generation is maximum if it is evaluated from the environment and minimum if it is evaluated from the inside of the system. [29] [30] [31]

In the case of open system with constant pressure and temperature, the state function that must be considered is the Gibb's energy. This function, also called free enthalpy, connects the enthalpy and the entropy of a system in the following way:

$$G = H - TS. \quad (4.11)$$

For every spontaneous process, the following relation must hold:

$$\Delta G = \Delta H - T\Delta S \leq 0 \quad \Rightarrow \quad \Delta H \leq T\Delta S. \quad (4.12)$$

Therefore the Gibb's energy tends to its minimum value, and this rule governs all natural processes.

In the best case it holds that:

$$\Delta G = 0 \quad \Rightarrow \quad \Delta H = T\Delta S. \quad (4.13)$$

In analogy with entropy, the enthalpy can be write as follows:

$$\Delta H = \Delta H_e + H_{irr}. \quad (4.14)$$

The term ΔH_e refers to the enthalpy that would be obtained exchanging reversibly the same heat, while H_{irr} refers to the enthalpy due to irreversibility.

From equations (4.12) and (4.13), the variation of entropy due to the irreversible processes, i.e. S_g , can be connected to the variation of enthalpy due to the irreversible processes, H_{irr} , as follows:

$$H_{irr} = TS_g \quad \text{or in a general case} \quad H_{irr} \leq TS_g. \quad (4.15)$$

Following the reasoning previously adopted and using the results obtained in equations (4.15), it holds that:

$$W_\lambda = T_a S_g \Rightarrow W_\lambda = H_{irr} \quad \text{or in a general case} \quad H_{irr} \leq W_\lambda. \quad (4.16)$$

Recalling the last action principle previously applied, the condition for enthalpy is:

$$\delta W_\lambda \leq 0 \quad \Rightarrow \quad \delta H_{irr} \leq 0. \quad (4.17)$$

This result must hold for every irreversible process.

In the particular case of this theses, there is another point to keep in mind: as seen in the previous chapters, the enthalpy depends on the water content, w . The water which may be withheld in a porous material is not infinite but has a maximum limit, i.e. the free water saturation, w_f ; for this reason a bond must be introduced:

$$\int_V (w_f - w) dV = 0 \quad (4.18)$$

In summary, the fact that irreversible processes occur, imply the entropy generation has to be taken into account. The expansion of Gouy-Stodola theorem to enthalpy, allows to apply this principle to enthalpy. The bond on water content is introduced by usual Lagrange's multiplier and it can be calculated only numerically.

Therefore, the final conditions are:

$$\begin{cases} \delta H_{irr} \leq 0, \\ \int_V (w_f - w) dV = 0. \end{cases}$$

4.3 Boundary conditions

Differential equations indicate the way in which the dependent variables depend on the independent ones. To obtain a solution, the boundary conditions are important factors that have to be specified. In fact any particular physical circumstance implies a set of boundary conditions that designates the temperature, moisture or the flows at the boundaries of the domain. Additional equations are given in which temperature and heat flow or moisture and water flow compare. [24]

Boundary conditions can be classified in three categories:

1. First kind, or Dirichlet: these conditions are satisfied when ambient and surface conditions are the same, therefore when temperature and humidity are fixed at boundary surface.

In the case of moisture these conditions occur only when the building component is in contact with water or the earth. In the case of liquid transport, these happen when surface is completely wetted.

2. Second kind, or Neumann: this case occurs when the flows on boundary surface are specified.

When there are constant flows of mass or heat on the surface, as in the case of solar radiation and the uptake of rain until the surface is not completely wetted, these conditions are satisfied.

3. Third kind boundary: these conditions are also known as mixed or convection condition and are a mixed situation of the first and second conditions.

An example is the heat exchange by convection with prescribed ambient temperature. These kind of conditions are the most frequent.

When two conditions occur in the same time, an appropriate source term is used. [4]

On the external side of the room, walls, roof, doors and windows are exposed to solar radiation, convection heat transfer and rain. The following paragraphs summaries the most common situations that may occur.

4.3.1 Solar radiation

Speaking about radiation a specification is necessary. When one refers to solar radiation, the term usually adopted is short-wave radiation, while heat emitted by the wall or received from the surroundings is called the heat exchange by long-wave radiation.

This can be explained recalling Planck's equation, eq. (2.18), and Wien's relation, eq. (2.20). Solar and visible radiation ($3nm < \lambda < 3000nm$) are short-wave radiation, while radiation emitted by surfaces with temperatures between about 260 and 350 K is called long-wave radiation ($\lambda > 3000nm$).

Fig. 4.1 shows the spectrum of short and long-wave radiation: sun, that can be considered as a Planckian emitter with a temperature of approximate 5800 K , has a maximum wavelength of about $\lambda_{max} = 500nm$, while the maximum wavelength for a surface at temperature $T = 290K$ is approximately $\lambda_{max} = 10^4nm$, that is in the infrared part of the spectrum. [23]

The two type of radiation, i.e. short and long-wave, are usually taken into account in different way. Long-wave radiation, according to [4], is considered together with heat exchange by convection.

To quantify all relevant radiation terms affecting an exterior surface, a complete balance of all these terms is set up [32]:

$$I = a_s I_s + \varepsilon I_l - I_e , \quad (4.19)$$

with

I_s : short wave solar radiation incident onto the component's surface,

a_s : short-wave absorptivity,

I_l : long wave radiation incident onto the component's surface,

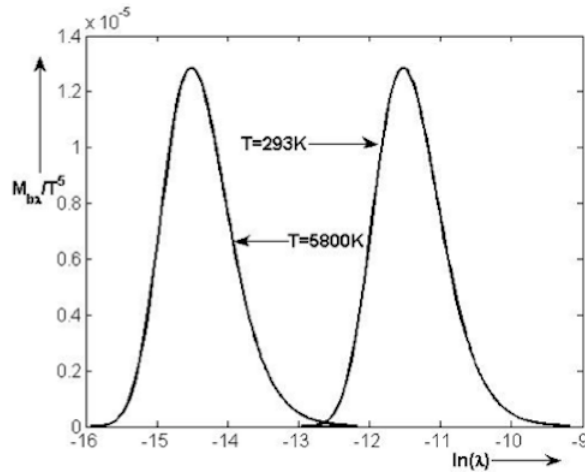


Figure 4.1: Spectrum of a short and a long-wave radiation. [23]

I_e : long wave radiation emitted by the component's surface,

ε : long wave emission coefficient (=absorption coefficient) of the component's surface.

The long wave radiation incident onto the component's surface is the sum of the atmospheric long-wave counterradiation, the terrestrial long-wave counterradiation and the atmospheric long-wave counterradiation reflected by the ground.

The long-wave emission from the component's surface depends on the temperature of the component's surface (T_e) according to the Stefan-Boltzmann relation (2.19):

$$I_e = \varepsilon \sigma T_e^4 . \quad (4.20)$$

Solar radiation shows a pronounced diurnal variation and can be taken into account as boundary condition of second kind. The heat flow from the sun, q_s , can be calculated as follows:

$$q_s = a_s I_s , \quad (4.21)$$

The short-wave absorptivity, a_s , indicates the fraction of the total incident solar radiation which is absorbed. It depends on the material and can be determined from the brightness reference values.

The solar radiation vertical to the building component surface can be calculated from the direct and diffuse solar radiation ² to horizontal surface, depending on the inclination and the orientation of the surface. [4]

²Diffuse solar radiation taken into account the sunlight that has been scattered by molecules and particles in the atmosphere but arrive to the surface of the earth.

4.3.2 Convection and longwave radiation

Heat exchange by convection and long-wave radiation depends on the difference in temperature between air ambient and surface.

Heat flux density can be calculated as follows:

$$q_c = \alpha(T_a - T_s) , \quad (4.22)$$

with

T_s : surface temperature,

T_a : ambient temperature.

The heat transfer coefficient α that appears in equation (4.22), takes into account convection and long-wave radiation:

$$\alpha = \alpha_c + \alpha_r , \quad (4.23)$$

with

α_c : convective heat transfer coefficient,

α_r : radiative heat transfer coefficient.

In principle the heat transfer coefficient, α , depends on local air flow condition, the temperature and the geometry of the building component and it is quite complex to calculate. However, in first approximation, it can be assumed constant. Obviously it differs from inside and outside and it depends on the climate condition of the place where the building is built.

4.3.3 Vapor flow

Water vapor flow, g_v , can be described in similar way of heat transfer by convection. In this case the flow depends on the difference between ambient water vapor pressure and water vapor pressure on the surface.

$$g_v = \beta_p(p_a - p_s) , \quad (4.24)$$

with

β_p : water vapor transfer coefficient,

p_a : ambient water vapor pressure,

p_s : water vapor pressure on the building component surface.

The water vapor transfer coefficient, β_p , is connected to convective heat transfer coefficient, α_c , by means of the following relation:

$$\beta_p = 7 \cdot 10^{-9} \alpha_c . \quad (4.25)$$

4.3.4 Rain

The rain or the driving rain on an external wall is a boundary condition for the density of moisture flow rate. Its value depends mainly on the horizontal rain intensity and the wind speed near the surface; in general, determining the rain load by a building component surface is more difficult than estimate solar radiation. The prediction of the amount is still an important research topic.

Wind plays an important rule in the estimation of driving rain load. In fact, one possibility to estimate rain is based on the knowledge of normal rain, wind velocity and wind direction. An reasonably linear relationship exists between vertical wind velocity multiply by normal rain, and the driving rain load of a wall section, as fig. 4.2 shows.

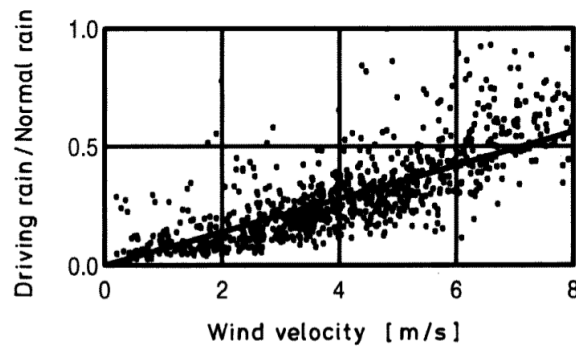


Figure 4.2: Correlation between the ratio of driving rain and normal rain and the wind velocity perpendicular to the facade. [4]

In particular, the relation is:

$$R_s = r_s v R_N , \quad (4.26)$$

with

R_s : driving rain load of the wall section,

R_N : normal rain,

r_s : site specific driving rain coefficient,

v : wind velocity.

The better way to determine the site specific driving rain coefficient, r_s , is through the measuring of the driving rain for a short period at the site in question.

When the rain, or the driving rain, load of a building component surface is known, the surface liquid flux, g_w , can be calculated in a mathematical similar way to the heat flow due to solar radiation:

$$g_w = a_r R_p , \quad (4.27)$$

with

a_r : precipitation absorptivity,

R_p : precipitation load vertical to building component.

The precipitation absorptivity, a_r , allows to take into account the fact that a part of the rain water impacting on vertical surface splashes off again. In the case of horizontal building components, it is about one because the splashing rain water drops again onto the surface. Moreover, the absorptivity depends on the type of material and in particular depends on the roughness of the surface. Finally also the kind of precipitation influences the absorption of water; for example for hail or snow the precipitation absorptivity is approximatively zero.

Flows due to rain can be considered as boundary condition of second kind until the surface is completely wetted. In this latter case, one passes from a condition of the second kind to one of the first kind because there is more rain than the maximum water that the surface can take up and the relative humidity at the surface is set to one. [4] [23]

Chapter 5

The barium hydroxide method

In recent years it has been observed that wall paintings decay more rapidly and increasing air pollution often plays a key role in such accelerated deterioration.

During past decades, many techniques to preserve paintings have been developed. Wall paintings, together with monuments and many other things, contribute to constitute the cultural heritage and are a legacy from the past; it is essential to understand chemical and physical processes damaging wall paintings and frescoes, and the conditions under which decay occurs in order to prevent or to intervene in an appropriate way and to avoid further damage.

The method described in this chapter is a technique that permits to consolidate internal structure of walls.

5.1 Degradation of works of art

Porous materials, that often compose built heritage, are subjected to deterioration caused by mechanical, physical, chemical, and biological processes. Usually different processes act at the same time and identifying the causes of decay is seldom easy and often requires an interdisciplinary study. [33]

The following paragraphs describe the deterioration processes. They are divided into two categories, i.e. mechanical and physical actions. The first one is briefly described while the latter will be studied more in depth because it is the part most inherent in this work.

5.1.1 Mechanical deterioration

Tensile stress

Porous materials are formed by atoms connected by strong covalent bonds that are directional and do not allow a plastic deformation of the crystals. This feature makes the medium hard, rigid, and brittle.

Tensile stress acting on a material usually depends on the point where it acts on the structure; for example all horizontal parts are subjected to such problems. Tensile stress

is never equally distributed across the sections of a block of material but it is, rather, concentrated in some particular points. If a stress cannot be redistributed by plastic deformation, the overstressed point fails and this determines the failure of the whole block. [33]

Thermal expansion

Porous materials, as well all materials on earth's surface, absorb solar radiation in the course of the day and expand. Then they give off energy by emitting infrared radiation.

Thermal cycles, both diurnal (day-night) or annual (summer-winter), cause periodical changes of dimensions and stresses arise in all constructions exposed to the earth's environment.

Stone, that are constituted of large crystals, undergo to a progressive weakening of their structure due to the exposure to the thermal cycles. This occurs because crystals have an anisotropic thermal behavior: they expand in one direction (usually main axis) and contemporaneity contract along other axis (usually perpendicular to the main axis). This causes a progressive detachment of some crystals and the cleavage of others; porosity increases and there is a loss of cohesion.

Another problem derived from the fact that different materials, with different thermal behavior, are often connected to each other without an interposed expansion joint [33].

Even the presence of organic material in pores can be a problem. They are used, for example, when a polymeric consolidant is applied or there is a material originating from biological sources. Such materials may expand significantly faster than the stone on wetting. For this reason it's important that consolidats have thermal expansion properties similar to the substrate being treated. [34]

Iron and steel corrosion

Sometime metal is inserted inside stone or concrete. When a film of water is deposited on an iron surface and stays there for some time, an electrochemical process starts and causes the transformation of part of the metal into rust.

This process leads an increase of volume respect to the volume occupied by the metal and a destructive stress is produce.

Human action and traffic vibrations

Chisel work on surfaces, cleaning by sandblasting, cleaning with rotating discs or metal brushes and addition of different materials to repair the structure, are some of the actions that can cause damages instead of protection.

Moreover, vibrations induced by road traffic can cause mechanical stresses in nearby buildings. The intensity of the stresses depends on the irregularities of the pavement and the weight and speed of the vehicle.

Vibrations are transmitted through the soil, but their magnitude drops rapidly with distance. Hence only constructions that are very close to roads are affected.

Damage are mostly produce when resonance occur.

In reality, the actions of traffic vibrations are unlikely to cause large movements of entire structure of a building, but they are important when single parts of a construction are take into account. For example ceilings, parts of walls made of weakly cemented rubble, peaces insufficiently adherent to walls, roof tiles and decorations are sensible to traffic vibration and they can be seriously damaged. It must be noted that the probability of damage is closely connected to the state of repair of a construction as the number of loose components increases with the progress of decay. [33]

5.1.2 Physical and chemical deterioration

This section is essentially reserved to salt formation and air pollution. They are the most important causes of stone decay.

Air pollution

Air pollution is one of the main cause of stone decay. Limestone, marble, lime mortars, and carbonate-cemented sandstones are the most vulnerable to acidic pollution, even if soiling from atmospheric particulates is a universal problem for all types of stone.

The term air pollutants identifies the sum of particulates, biological molecules, or other harmful materials introduced into Earth's atmosphere. The most common products are sulfur oxide (SO_x), nitrogen oxides (NO_x), carbon oxide (CO_x), particulates and so on. Emitted substances are transmitted over short or long distances, arrive in a certain local environment and are deposited as wet or dry particles and gases on wet or dry surfaces with variable reactivities [35]. Wet deposition, i.e. by rain, or dry deposition, i.e. by condensation of water vapor, occur and air pollutants are deposited on the surface.

The direct effects of acidic pollutants on stones depend very much on the surrounding environment. If the stone is in an exposed position and regularly washed by rain, the reaction products are washed away and the surface of the stone gradually recedes. If, however, the stone is in a relatively sheltered position, the reaction products accumulate and may form dense black crusts on stone surface [34]. Moreover these crust are porous and hence aggressive gaseous and liquid products can still penetrate and reach crystals underneath.

Many studies on the black crusts were performed. For example a study about some stones present in Milan (see reference [36]) analyzes the formation of black crusts in a urban area. The case described is very significative because samples of crust were collected in 1991 from two sculptural groups, made with white Carrara marble, placed in 1937 on the front of Milan General Hospital and never restored. Therefore the stones had been exposed to Milan environment for 54 years.

The two sculptural groups were exposed to rain, but the presence of rather deep undercuts protected some parts. In the parts that rain could not reach, thick black crusts had been formed, while washed surfaces showed corroded pattern produced by the solvent action of rainwater.

Analyzing the samples, it was found that black crusts, forming at rate of $2\text{-}5 \mu\text{m}/\text{years}$, are composed mainly of gypsum, carbonaceous particle and iron oxides; moreover their formation seems to be strongly influenced by slightly different condition that may exist in the different parts of the statues.

The responsible of the black crusts on built heritage in urban areas worldwide are sulfates. They are very common and dangerous salts that produce the largest damage compared to other salts.

In practice the phenomena can be summarized in a three steps process and it is briefly described below.

1. Dust deposition.

It is demonstrated that dust has a high capacity for fixing atmospheric SO_2 as sulfates in the presence of humidity. Dust is composed by high level of iron, Fe , lead, Pb , chrome Cr , nichel, Ni , and cobalt, Co , forming a part of atmospheric pollution. Moreover there are carbonaceous particles, with an entirely different morphology and composition, that play a driving role in surface soiling and black crust formation. [37]

Some studies show that carbonaceous and aluminosilicate particles are the two main typologies of particles identified by scanning electron microscopy at all the sites. [38]

Due to its mineralogical composition and high porosity, dust can retain a high humidity while at the same time prevent quick evaporation of the water penetrating through to the surface of the underlying porous limestone. In addition limestone (or other construction materials) has a high surface roughness and open porosity and this aggravate deposition.

2. Catalytic oxidation of SO_2 in the presence of particulate matter and humidity. This stage, in turn, is composed of three steps:

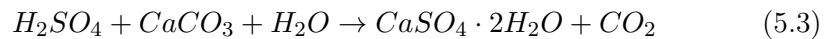
(a) Oxidation of SO_2 on the surface:



(b) Hydration process: in the presence of water, hydrolysis reaction applies. It is necessary for the formation of sulfuric acid (H_2SO_4):



(c) Gypsum formation: gypsum nucleation points are formed as a consequence of the sulfuric acid attack on the calcite in the limestone.



3. Gypsum growth and final development of the black crust.

The gypsum formed in previous step is initially poorly crystalline, but then it is involved in dissolution and reprecipitation processes on both the surface and within the porous system of the stone.

This last step leads to the formation of a crust. The black color is due to the incorporation of carbonaceous species. [37]

The crust grows and forms a discontinuous layer between itself and the unaltered calcareous substrate, producing the loss of entire slabs of crust and limestone. Sandstones, limestones and marbles are particular sensitive to the effect of sulphur dioxide. The formed crust has different physical and chemical characteristics from the underlying structure and these facts increase the velocity of degradation. The main reasons can be summarized in three points:

- Volume variation: a mechanical stress is caused by the bigger volume of gypsum compared to calcium carbonate (the first is about twice the latter).
- Different thermic expansion: black crust absorbs more radiation with respect to white surface.
- Reduction of permeability: this causes water retention in the stone. [39]

These effects, together with other degradation processes¹, can occur in every carbonate-based works of art. A example of the effect of pollutants is shown in fig. 5.1.

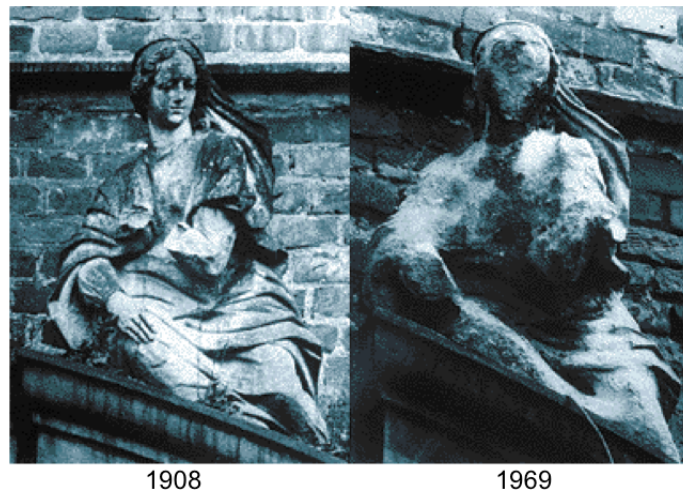


Figure 5.1: Effects of the aggression of pollutants on sandstone statue of 1702 (Castle Herten, Westphalia). [39]

¹For instance, degradation due to the presence of bio-organisms, such as fungi, mold, lichens and bacteria, leads to the dissolution of mineral substrates through mechanical and chemical processes. [40]

Crystallization process inside pores

The crystallization process can produce damages if it is caused by both salt formation and freezing.

When the temperature drops below 0°C and ice formation inside a wet porous solid occurs, serious damage can be produced.

Crystals in general, and ice crystals in particular, grow easily in the large pores when the conditions for crystallization are reached; inside smallest pores, it is more difficult to form the seed of a crystal due the fact that molecules of the liquid are strongly attracted to the solid walls.

However most of the damages occur when material has a large proportion of capillary pores: they represent a reserve of water stored when porous material is wet. In fact ice crystals start growing using the water available around them in the large pores, but, when this becomes scarce, they suck water out of the capillary pores. If there are more small pores than large one, stress is determined because the space is not enough for all the crystals of ice that can be formed.

After that the crystal is grown and filled the space available in large pore, it keeps attracting water by capillarity in the gap between its edges and the wall and, by this way, exerts a pressure. The increase of volume because of ice formation contributes to the magnitude of stress, but it is not the deciding factor.

Water inside a wet porous material often contains dissolved salts and, when evaporation occurs, crystallization process starts. Salts can have different origin: they can be present in building materials (usually sulphate of potassium, calcium, magnesium), rise from the ground (usually nitrates of sodium, potassium, calcium), came from wrong material used for restoration or they can came from the atmosphere. [2]

As in the previous case, the growth of crystals takes place inside the large pores, while the capillary ones store the liquid and feed it to the growing crystals.

Crystallization does not occur immediately after of evaporation of water because the solution has to reach the saturation concentration. Otherwise ions are attracted to the polar surfaces of the hydrophilic material and tend to resist the shift to a new position to form a crystal nucleus. [33]

When supersaturation condition is reached, crystallization takes place very rapidly. This process can occur on the surface or inside the medium: in the first case it is known as efflorescence and salt crystals are visible, the latter case is the most damaging process and it is called subefflorescence. If one imagines that crystals are formed inside the pores or at the interface between the paint layer and the plaster underlying, it is easy to understand that this process causes mechanical stresses and then lifting and detachment of the paint layer, or cracks and fissuring of the plaster. [40]

The following figures show salt efflorescences on pictorial surfaces of mural paintings in the archaeological site of Ixcaquixtla in Mexico. The detachment of the paint layer caused by mechanical stress is evident.

Surrounding environmental condition can favor evaporation and hence crystallization. Slow evaporation occurs when temperature are low or moderate, humidity are medium



Figure 5.2: Salt efflorescence effects on a pictorial surfaces of site of Ixcaquixtla, Mexico. The detachment of the paint layer due to the mechanical stress of salt crystallization is manifest.[40]

or high and air velocity are low; in this case efflorescence is favored. A warm, windy, dry climate favors subefflorescence and deeper damage.

Wind action accelerates evaporation and sets up the subefflorescence process that results in the formation of small cavities that modify the pore size distribution. If these cavities, in order to restore the structure, are filled with strong, low-porosity material, the water in the pores is deflected to evaporate on the nearby surfaces and cause damage there. This one the cause that explain the importance of compatibility between materials used in conservation and the original ones.

Obviously salt damages do not take place only in an outdoor environment, where the stone is subjected to cycles of rainfall and subsequent drying, but it can occur also indoors through the hygroscopic action of the salts.

Moreover salts can even cause damage by stress due to differential thermal expansion. For example sodium chloride expands at about five times the rate of calcite at surface temperatures. [34] [33]

One important example of deteriorating cultural heritage is the case of wall paintings: the reactions described, and in particular the formation of gypsum, can produce lifting and detachment of the paint layer, or cracks and fissuring of the plaster.

One of the first methods used to resolve the problem of degradation of wall painting is the so-called detachment or *stacco*. It consists in a drastically removing of the paint layer with a part of plaster layer or directly the entire piece of wall. Obviously this procedure is very dangerous for the art work which was often damaged during the intervention.

Another procedure is through the tearing, or *strappo*, of the paint layer. In practice a canvas impregnated with animal glues is pasted on the painting and then it is torn. By this way the fresco remains attached to the canvas and then it is placed on another support.

This method was appreciated because after the paint layer was removed, the sinopia became visible and so fresco and its underpainting could be confronted and exposed.

Both techniques are very invasive and often dangerous and harmful. According to the *International Council on Monuments and Sites* (ICOMOS), «detachment and transfer are dangerous, drastic and irreversible operations that severely affect the physical composition, material structure and aesthetic characteristics of wall paintings. These operations are, therefore, only justifiable in extreme cases when all options of in situ treatment are not viable.» [41]

The techniques that involve consolidation are more advantageous. The common practice in consolidation of immovable artworks is based on the use of synthetic organic materials. These materials have, however, different physical-chemical properties with respect to the carbonate based artworks and their application can cause effects that are contrary to the expectations. By this way, degradation phenomena such as salt crystallization are enhanced and hence dramatic effects such as cracking, severe flaking and detaching of the surface layer are caused; these occur even in short periods (10-50 years depending on the environmental conditions). In fact, in presence of polymer film, salt crystallization processes involve deeper areas, with stronger decohesion until the complete powdering of the painting. The polymer closes the pores surface, generating mechanical stresses towards the paint layer. An example is presented in fig. 5.3. [42] [40]

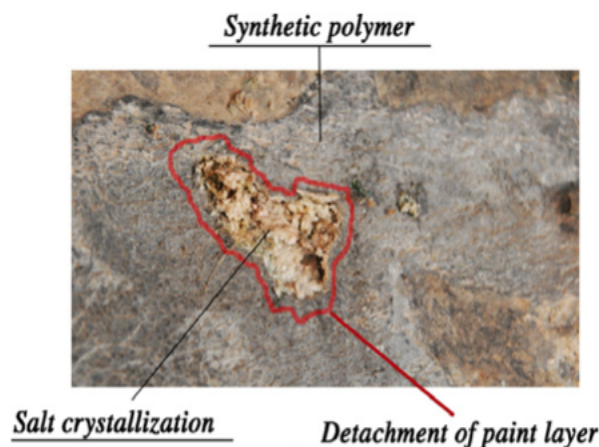


Figure 5.3: An example of polymer layer on wall paintings of the archeological site of Tulum, Mexico. The different physico-chemical properties of the organic polymer with respect to the inorganic substrate enhance detachment of paint layer. [40]

For the above reasons, the use of inorganic consolidants, compatible with wall painting and works of art, is recommended and it minimizes the risk of damage, preventing unexpected side effects. Inorganic consolidants are highly chemically stable and preserve the wall painting porosity, so ensuring long-lasting consolidation effects. [42]

5.2 Structure of a fresco

Before dealt with the consolidation method of the barium hydroxide, the general structure of a fresco is briefly described in this paragraph.

The term *fresco* indicates a technique of mural painting executed upon freshly laid lime plaster (*intonaco*).

A schematic idea of the structure of a painting on wall can be provided observing the fig. 5.4.

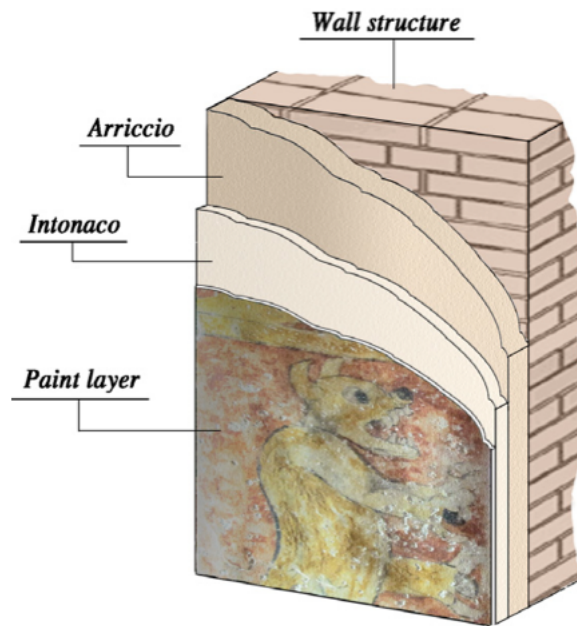
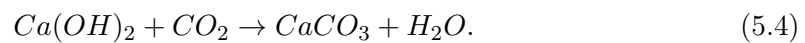


Figure 5.4: A schematic figure of the stratigraphy of a fresco wall painting. [40]

Four different layers, whose main structural component is calcium carbonate, can be observed.

Calcium carbonate ($CaCO_3$) is formed by the reaction of lime ($Ca(OH)_2$) with atmospheric CO_2 via the carbonation reaction:



Sand is added to lime as a filler, to prevent shrinkage and cracking during and after drying; moreover it increases the mechanical strength of the plaster. [40]

- **Wall structure:** It is made of stone or brick. Actually this layer is not part of a fresco, but it is the basis on which the next stratum is lying.
- **Arriccio:** It is made of lime with the addition of large particles of river sand or

pozzolana². It is rich in sand, in fact the volume ratio is one part of lime every three of sand. The thickness is about 1cm.

- **Intonaco:** It consists in a plaster that usually contains an equal amount of lime and sand. In this case the sand used is much finer than the sand used in the previous layer.
- **Paint layer:** It is a thin film, of about 50 – 500 μ m thick, made by a mixture of pigments and calcium carbonate. Pigments must be oxides because they must not interact with the carbonation reaction. In the so-called *buon fresco* technique, the pigments, dispersed in lime water, are directly applied on the wet intonaco layer and, upon carbonation, are embedded into the crystalline carbonate network forming a smooth surface.

The pigments can also be applied on the dried intonaco ("*a secco*" tonaco), by using organic binder such as egg, milk or vegetal extractives. Often mixed fresco and secco techniques were widely used by artists, for instance by Michelangelo in the Sistine chapel. [43] [40]

The paint layer is at contact to surrounding environment and it is strongly susceptible to degradation caused by the mechanical stresses deriving from salt crystallization.

5.3 The method with Barium hydroxide

In the mid-sixties of last century, the chemist of the University of Florence Enzo Ferroni, in collaboration with the restorer Dino Dini, developed a method to achieve a good consolidation of wall painting. He studied a solution to deal with the conservation issues of frescoes following the disastrous flood of Florence in 1966. [40] [42]

The approach found is therefore called Ferroni-Dini method and it was applied for the first time by Dino Dini during the restoration of the fresco *La Crocifissione*³ between 1967 and 1974. Dini refused to apply the traditional tear-off method because of the vastness of the fresco and the particular fragility of the surface attacked by sulphates.

The method consists in applying ammonium carbonate ($(NH_4)_2CO_3$) and barium hydroxide ($Ba(OH)_2$) aqueous solution loaded on poultices, in a two-step procedure: first ammonium carbonate turns gypsum into soluble ammonium sulfate and then the application of an excess of barium hydroxide leads to a stable consolidation effect.

The main feature of this method is the chemical and physical compatibility.

In particular, the process occurs through four reactions.

²It's a siliceous and aluminous material which reacts with calcium hydroxide in the presence of water at room temperature. In this reaction insoluble calcium silicate hydrate and calcium aluminate hydrate compounds are formed possessing cementitious properties. The name pozzolana derived from one of the primary deposits of volcanic ash used by the Romans in Italy, at Pozzuoli.

³It was painted by Beato Angelico in 1442 in the convent of San Marco (now the National Museum) in Florence.

1. After the painting has been properly cleaned with deionized water, the ammonium carbonate ($(NH_4)_2CO_3$) is applied, for example, through cellulose poultice or materials that have high absorbing capacity; this to ensure a prolonged contact and to preserve the painting from the abrasive action of paintbrushes and sponges. [44]



The ammonium sulphate ($(NH_4)_2SO_4$) is water soluble, so it is mostly absorbed by cellulose poultice used to apply the ammonium carbonate.

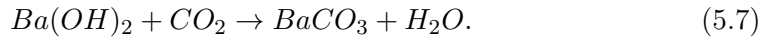
The calcium carbonate ($CaCO_3$) produced is in form of powder and does not form a binder.

2. Then a solution of barium hydroxide ($Ba(OH)_2$) is applied:



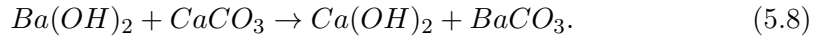
Barium sulphate ($BaSO_4$) is a inert and insoluble salt that crystallizes and remains in the cavity. Ammonium hydroxide (NH_4OH) decomposes in NH_3 and H_2O and both by-products evaporate.

3. The excess of barium hydroxide ($Ba(OH)_2$) inside the matrix reacts with carbon dioxide and produces barium carbonate ($BaCO_3$). This process forms a new lime that undergoes to slow carbonation reaction that enhances the mechanical strengthening of the paintings,

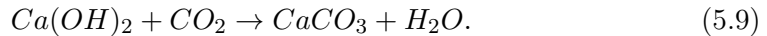


Barium carbonate ($BaCO_3$) gradually falls between the crystals of $CaCO_3$ and solders them. Thermic dilatations of $BaCO_3$ and $CaCO_3$ are very similar and their solubility in water is very low.

4. A second consolidating action derived from reaction between barium hydroxide ($Ba(OH)_2$) and calcium carbonate ($BaCO_3$) which is not bound to the plaster,



Through this reaction, a new lime is formed in situ and a slow process of carbonation starts and the consolidation action is completed,



The following figures, 5.5 and 5.6, are an example of the effects of the application of Ferroni-Dini method. It has to be noted that this method is consolidant and not protective. [43] [44] [45]



Figure 5.5: A detail of the painting before the application of the method.



Figure 5.6: A detail after the application of the method.

Figure 5.7: A detail of "*S. Domenico in adorazione del Crocifisso*", Beato Angelico.[43]

5.3.1 Limits of the method

This method has, however, a few limits. The following paragraphs summarize the major criticisms that have been raised for this method.

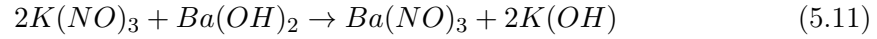
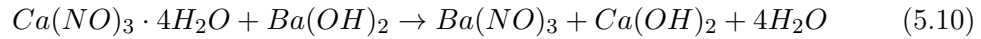
Scale of consolidation

The barium method is not a technique that is correct for every situation. In fact it is useful when impaired cohesion of the materials occurs at microscopical level given that the gaps that can be welded must have a width of maximum $50 \mu m$. Keeping this in mind, it is clear that the method is useless if there are macroscopic structural impairment and detachment of large elements due to degradation.

Moreover the method is unusable if there are problems of adhesion of element of small, but visible to eye, dimension. Barium hydroxide does not have adhesive properties like natural resins and synthetic polymeric materials, but it has a consolidating property and it restores the cohesion of materials.

Presence of substances that do not allow the application of the method

Barium hydroxide ($Ba(OH)_2$) cannot be applied if there are soluble salts and in particular if nitrates are present. In this case a barium nitrate ($Ba(NO_3)_2$) is formed:

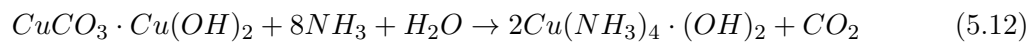


It is a soluble salt that has the tendency to crystallize and this fact could lead to efflorescences. If salt formation occurs in the surface of the painting, nitrate can be removed by a paintbrush, but if it is formed inside, it will cause dangerous damage. For this reason an accurate cleaning is necessary before the application of the solutions.

If the painting is made with temperas, some problems due to alkalinity of barium hydroxide can occur. In fact alkalinity could cause hydrolysis and hence partial depolymerization of tempera. These facts imply softening, swelling and solubilization.

Nevertheless practical experiments show that tempera painting tolerates the barium method because, in most of cases, the organic material used originally as binder is practically not longer present. With the passage of time, organic material has undergone to gradual processes of mineralization that have turned it into new inorganic products.

An other limit can be the presence of copper pigments, in particular the malachite ($CuCO_3Cu(OH)_2$), that gives green color, and the azurite ($Cu_3(CO_3)_2Cu(OH)_2$), that gives azure/blu color. They are sensible to solvent action of ammonia. For example the reactions for malachite are the following:



The product $2Cu(NH_3)_4 \cdot (OH)_2$ is soluble and hence there could be a partial solubilization of painting film. The action is considerably less on azurite. [46]

Whitening of the surface

Whitening of the surface can occur if the method is not correctly applied. This happens for two main reasons:

1. Incorrect execution of the application of ammonium carbonate. In this case reaction (5.5) can occur on the surface and it forms a whitish permanently film.
2. Too much fast transformation of barium hydroxide ($Ba(OH)_2$) into barium carbonate ($BaCO_3$). This process is quite slow because it is characterized by spontaneous interaction of $BaCO_3$ and CO_2 of air. If the process does not occur correctly, the reaction (5.8) takes place mostly near or on the surface an this form whitish film. [44]

Finally the barium hydroxide is toxic and hence it must be handled with care.

Although the results obtained with this method are very good, it is necessary to keep in mind that this method was proposed and used as provisional remedy in a emergency situation, namely the flood of Florence in 1966.

The method is now often used but it has never been studied in the long term. This work would take the first steps in this direction.

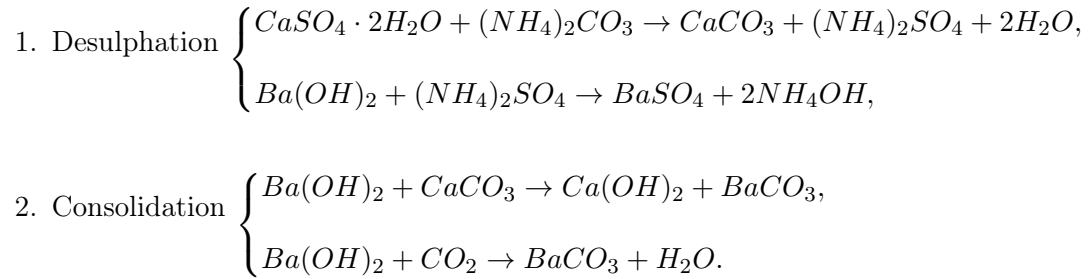
In the next chapter the reactions of barium hydroxide, $Ba(OH)_2$, with carbon dioxide, CO_2 , and calcium carbonate, $CaCO_3$, are taken into account. In order to obtain a mathematical-physical model, the equations for barium hydroxide transport and interaction are developed.

Chapter 6

Barium hydroxide transport

The goal of this chapter is to develop a model that allows the description of the behavior of barium hydroxide inside porous media.

The reactions involved when the method of barium hydroxide is applied are briefly summarized and divided into two subgroups, i.e. desulfation and consolidation:



In this chapter the attention is focused on the consolidation process. The two reactions described above are different, not concatenated and occur in different time. For example, carbonation reaction takes place in a few months.

For these reasons the chosen approach is to treat separately the two reactions and deduce two different diffusion equations for the barium hydroxide.

6.1 Basic of chemical kinetics

Suppose to have a multicomponent reactive mixtures of N chemical species. The continuity equation can be used to described the conservation of mass for every species $i = 1, \dots, N$:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \vec{V}_i) = \dot{r}_i, \quad (6.1)$$

with

ρ_i : total density of i -th species,

\vec{V}_i : fluid velocity of i -th species,

\dot{r}_i : rate of production or consumption of i -th species.

It is important to note that the concentration, ρ_i , is called total because it is defined with respect to the total volume, considering both solid and fluid materials. In general it depends on position (x) and time (t).

With regard to the rate of production, if the system is closed, the following equation must hold:

$$\sum_{i=1}^N \dot{r}_i = 0. \quad (6.2)$$

Denoting the mass of single molecules with m_i , the stoichiometric coefficients of the reactants with ν_i and of the products with ξ_i , the rate of production (or consumption) of i -th species, \dot{r}_i , can be written as:

$$\dot{r}_i = m_i(\xi_i - \nu_i)\omega, \quad (6.3)$$

with ω : rate of the reaction.

One assumes that ω is proportional to the concentration of each reactant and hence it can be written as:

$$\omega = A \prod_{i=1}^N \left(\frac{\rho_i}{m_i} \right)^{\nu_i}. \quad (6.4)$$

The proportionality constant A can be derived from the Arrhenius' law¹:

$$A = B_0 T^\alpha e^{-\frac{E_a}{RT}}, \quad (6.5)$$

with

E_a : activation energy,

B_0 and α : constants.

The term R , in the previous equation, is defined as:

$$R = R_0 \sum_{i=1}^N \frac{y_i}{m_i}, \quad (6.6)$$

with

¹In the literature, there is not a unique treatment of the term A . Some authors, for example [25], set $\alpha = 0$ since T^α reflects a weak temperature dependence; other authors, for example [47], neglect the dependence of A on temperature and on the activation energy. In this case no particular assumptions have been adopted.

R_0 : universal gas constant,

y_i : mass fraction of i -th species.

Instead of the total concentration (ρ_i), another useful quantity can be used: it is the concentration calculated with respect to the volume of pores. Using the definition of the porosity (equation (2.1)), φ , a connection between total concentration, ρ_i , and porous concentrations, C_i , of a generic molecule i , can be established:

$$\rho_i = \varphi C_i. \quad (6.7)$$

It is also important to specify another matter regarding the velocities.

In the continuity equations the fluid velocities, \vec{V}_i have been introduced. This velocity is defined with respect to the concentrations inside the pores and hence it is an average velocity taken with respect to a volume element of fluid, \mathcal{V}_f . It is an intrinsic velocity that differs from the seepage, or Darcy, velocity, \vec{v}_i . This latter quantity is defined as the average velocity taken with respect to a volume element of the materials, \mathcal{V}_m , considering both solid and fluid components.

The two velocity, i.e. \vec{V}_i and \vec{v}_i , are related through the Dupuit-Forchheimer relationship:

$$\vec{v}_i = \varphi \vec{V}_i. \quad (6.8)$$

Henry Darcy studied the flow of a fluid through a porous medium and his law has been used in the second chapter talking about moisture transport. Practically, his law states that there is a proportionality between flow rate and the applied pressure difference. In particular, he introduced the following relationship for the seepage velocity:

$$\vec{v}_i = -\frac{\vec{\kappa}}{\eta_i} \cdot \nabla p_i, \quad (6.9)$$

with

$\vec{\kappa}$: specific permeability or intrinsic permeability of the medium,

η_i : viscosity of the fluid,

p_i : pressure of the fluid.

The permeability coefficient is independent of the type of fluid but it depends on the geometry of the medium. In general it is a tensor but, for an isotropic medium, it is a scalar quantity. In this case the previous equation simplifies to [48]:

$$\vec{v}_i = -\frac{\kappa}{\eta_i} \nabla p_i. \quad (6.10)$$

6.2 Study of the reactions

Keeping in mind the considerations made above, in this paragraph the reactions of consolidation process are studied.

Before to proceed with the study of the reactions, a specification is necessary: the total concentration of barium hydroxide, that is a known experimental parameter, is divided as follows:

$$\rho_{Ba,tot} = \rho_{Ba,1} + \rho_{Ba,2} + \rho_{Ba,3}, \quad (6.11)$$

with

$\rho_{Ba,tot}$: total concentration of barium hydroxide,

$\rho_{Ba,1}$: partial concentration of barium hydroxide that reacts with $(NH_4)_2SO_4$,

$\rho_{Ba,2}$: partial concentration of barium hydroxide that reacts with $CaCO_3$,

$\rho_{Ba,3}$: partial concentration of barium hydroxide that reacts with CO_2 .

6.2.1 Reaction $Ba(OH)_2 + CaCO_3 \rightarrow Ca(OH)_2 + BaCO_3$

The set of continuity equations for each species of the reactions taken into account are:

$$\frac{\partial \rho_{Ba,2}}{\partial t} + \nabla \cdot (\rho_{Ba,2} \vec{V}_{Ba}) = \dot{r}_{Ba}, \quad (6.12)$$

$$\frac{\partial \rho_C}{\partial t} = \dot{r}_C, \quad (6.13)$$

$$\frac{\partial \rho_{Ca}}{\partial t} + \nabla \cdot (\rho_{Ca} \vec{V}_{Ca}) = \dot{r}_{Ca}, \quad (6.14)$$

$$\frac{\partial \rho_B}{\partial t} = \dot{r}_B, \quad (6.15)$$

with

$\rho_{Ba,2}$: total concentration of barium hydroxide $Ba(OH)_2$,

ρ_C : total concentration of calcium carbonate $CaCO_3$,

ρ_{Ca} : total concentration of calcium hydroxide $Ca(OH)_2$,

ρ_B : total concentration of barium carbonate $BaCO_3$.

It is assumed that calcium carbonate, $CaCO_3$, and barium carbonate, $BaCO_3$, are fixed and hence their fluid velocities are set to zero.

The rates of production satisfy the following relation:

$$\dot{r}_{Ba,2} + \dot{r}_C + \dot{r}_{Ca} + \dot{r}_B = 0. \quad (6.16)$$

Recalling equation (6.3) for the rate of production and noting that all stoichiometric coefficients are equal to one, we have that:

$$\dot{r}_{Ba,2} = -m_{Ba}\omega_1, \quad \dot{r}_C = -m_C\omega_1, \quad \dot{r}_{Ca} = m_{Ca}\omega_1, \quad \dot{r}_B = m_B\omega_1, \quad (6.17)$$

$$\text{with } \omega_1 = A_1 \left(\frac{\rho_{Ba,2}}{m_{Ba}} \right) \left(\frac{\rho_C}{m_C} \right). \quad (6.18)$$

Another interesting feature to note is about equation (6.13) and (6.15). In fact, by dividing each equation for the relative mass of the involved molecule, they become:

$$\frac{\partial}{\partial t} \left(\frac{\rho_C}{m_C} \right) = -\omega_1, \quad (6.19)$$

$$\frac{\partial}{\partial t} \left(\frac{\rho_B}{m_B} \right) = \omega_1. \quad (6.20)$$

Summing the previous equations we obtain that:

$$\frac{\partial}{\partial t} \left(\frac{\rho_C}{m_C} + \frac{\rho_B}{m_B} \right) = 0, \quad (6.21)$$

and finally

$$\frac{\rho_C}{m_C} + \frac{\rho_B}{m_B} = \frac{\rho_{C0}}{m_C} + \frac{\rho_{B0}}{m_B}, \quad (6.22)$$

where the subscript 0 means that the value is referred to initial time, $t = 0$.

The relation just found can be useful to link the density of calcium carbonate and barium carbonate.

In order to obtain a set of diffusion equations, it is worth to employ the relations introduced in the previous section.

Exploiting equation (6.7) to connect total and porous concentration, we have that:

$$\rho_{Ba,2} = \varphi C_{Ba,2} \quad \text{and} \quad \rho_C = \varphi C_C. \quad (6.23)$$

In addition the Darcy's law for barium hydroxide is written as:

$$\vec{v}_{Ba} = -\frac{\kappa}{\eta_{Ba}} \nabla p_{Ba}. \quad (6.24)$$

Introducing equations (6.23) and (6.24) in the continuity equation of barium hydroxide, (6.12), we get:

$$\frac{\partial}{\partial t}(\varphi C_{Ba,2}) - \nabla \cdot (C_{Ba,2} \frac{\kappa}{\eta_{Ba}} \nabla p_{Ba}) = \dot{r}_{Ba,2}. \quad (6.25)$$

Finally, inserting the rate of production for barium hydroxide, we obtain:

$$\frac{\partial}{\partial t}(\varphi C_{Ba,2}) - \nabla \cdot (C_{Ba,2} \frac{\kappa}{\eta_{Ba}} \nabla p_{Ba}) = -\frac{A_1}{m_C} \varphi C_{Ba,2} \rho_C. \quad (6.26)$$

For calcium carbonate, the equation is simpler because the term relative to Darcy is missing:

$$\frac{\partial \rho_C}{\partial t} = -\frac{A_1}{m_C} \varphi C_{Ba,2} \rho_C. \quad (6.27)$$

6.2.2 Reaction $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$

The set of continuity equations for each reactants of the reactions taken into account in this paragraph are the following:

$$\frac{\partial \rho_{Ba,3}}{\partial t} + \nabla \cdot (\rho_{Ba,3} \vec{V}_{Ba}) = \dot{r}_{Ba,3}, \quad (6.28)$$

$$\frac{\partial \rho_{Co}}{\partial t} + \nabla \cdot (\rho_{Co} \vec{V}_{Co}) = \dot{r}_{Co}, \quad (6.29)$$

with

$\rho_{Ba,3}$: total concentration of barium hydroxide $Ba(OH)_2$,

ρ_{Co} : total concentration of carbon dioxide CO_2 .

Recalling equation (6.3) for the rate of production and noticing that all stoichiometric coefficients are equal to one, one obtains that:

$$\dot{r}_{Ba,3} = -m_{Ba} \omega_2, \quad \dot{r}_{Co} = -m_{Co} \omega_2, \quad (6.30)$$

$$\text{with } \omega_2 = A_2 \left(\frac{\rho_{Ba,3}}{m_{Ba}} \right) \left(\frac{\rho_{Co}}{m_{Co}} \right). \quad (6.31)$$

Through equation (6.7), total and porous concentration are connected as follows:

$$\rho_{Ba,3} = \varphi C_{Ba,3} \quad \text{and} \quad \rho_{Co} = \varphi C_{Co}. \quad (6.32)$$

The Darcy's velocity for barium hydroxide can be written as in the previous paragraph:

$$\vec{v}_{Ba} = -\frac{\kappa}{\eta_{Ba}} \nabla p_{Ba}, \quad (6.33)$$

and the continuity equation for barium hydroxide is similar to equation (6.26) for the reaction considered before:

$$\frac{\partial}{\partial t}(\varphi C_{Ba,3}) - \nabla \cdot (C_{Ba,3} \frac{\kappa}{\eta_{Ba}} \nabla p_{Ba}) = -\frac{A_2}{m_{Co}} \varphi C_{Ba,3} \rho_{Co}. \quad (6.34)$$

In order to deal with carbon dioxide, a specification is necessary. In fact one assumes that air infiltrates in the porous structure and carbon dioxide, that is contained in the air together with other molecules, diffuses in the air and reacts with barium hydroxide in order to complete the carbonation reaction. Then, one can assume that air infiltrates with a Darcy's velocity given by the following law, (6.35), where the subscript a means that the quantities are referred to air:

$$\vec{v}_a = -\frac{\kappa}{\eta_a} \nabla p_a. \quad (6.35)$$

Moreover, the air concentration inside porous materials can be seen as the sum of concentration of carbon dioxide, C_{Co} and the concentration of the remaining molecules, C_R . Among the remaining molecules, even water produced by the reaction will be considerate.

$$C_a = C_{Co} + C_R, \quad (6.36)$$

and multiply by the seepage velocity, one obtain:

$$C_a \vec{v}_a = C_{Co} \vec{v}_{Co} + C_R \vec{v}_R. \quad (6.37)$$

Carbon dioxide diffuses in the air with a relative velocity, \vec{u}_{Co} , that is:

$$\vec{u}_{Co} = \vec{v}_{Co} - \vec{v}_a. \quad (6.38)$$

This diffusive velocity is obtainable by the Fick's law as follows:

$$C_{Co} \vec{u}_{Co} = -D \nabla C_{Co}, \quad (6.39)$$

where D is the diffusion coefficient.

Starting from equation (6.39), and using equation (6.38), one obtains:

$$C_{Co} (\vec{v}_{Co} - \vec{v}_a) = -D \nabla C_{Co}, \quad (6.40)$$

therefore, using equation (6.35):

$$C_{Co} \vec{v}_{Co} = -C_{Co} \frac{\kappa}{\eta_a} \nabla p_a - D \nabla C_{Co}. \quad (6.41)$$

In the continuity equation of carbon dioxide, eq.(6.29), appears the divergence of $\rho_{Co} \vec{V}_{Co}$. Recalling the connection between the fluid velocity and Darcy velocity, one gets:

$$\rho_{Co} \vec{V}_{Co} = C_{Co} \vec{v}_{Co}, \quad (6.42)$$

that is the term that has just been found in equation (6.41).

Summing all the results together, the continuity equation of carbon dioxide becomes:

$$\frac{\partial}{\partial t}(\varphi C_{Co}) - \nabla \cdot (D \nabla C_{Co}) = \nabla \cdot (C_{Co} \frac{\kappa}{\eta_a} \nabla p_a) + \dot{r}_{Co}. \quad (6.43)$$

The rate of consumption of the carbon dioxide, \dot{r}_{Co} , will be:

$$\dot{r}_{Co} = -\frac{A_2}{m_{Ba}} \varphi \rho_{Ba,3} C_{Co}. \quad (6.44)$$

Therefore, the continuity equation for the carbon dioxide assumes the following form:

$$\frac{\partial}{\partial t}(\varphi C_{Co}) - \nabla \cdot (D \nabla C_{Co}) = \nabla \cdot (C_{Co} \frac{\kappa}{\eta_a} \nabla p_a) - \frac{A_2}{m_{Ba}} \varphi \rho_{Ba,3} C_{Co}. \quad (6.45)$$

In order to close the system of equations, it is necessary an equation for the air pressure, p_a . To obtain this equation, one can start from a continuity equation for air without carbon dioxide, i.d. how C_R evolves.

$$\frac{\partial \rho_R}{\partial t} + \nabla \cdot (\rho_R \vec{V}_R) = \dot{r}_R, \quad (6.46)$$

or equivalently:

$$\frac{\partial}{\partial t}(\varphi C_R) + \nabla \cdot (C_R \vec{v}_R) = \dot{r}_R. \quad (6.47)$$

Recalling equation (6.37), one gets:

$$C_R \vec{v}_R = C_a \vec{v}_a - C_{Co} \vec{v}_{Co}, \quad (6.48)$$

and using equation (6.38) to find the seepage velocity of carbon dioxide, \vec{v}_{Co} , in terms of the diffusion velocity, \vec{u}_{Co} , one obtains:

$$\vec{v}_{Co} = \vec{u}_{Co} + \vec{v}_a. \quad (6.49)$$

Inserting equation (6.49) in (6.48), the term $C_R \vec{v}_R$ is expressed as function of v_a and u_{Co} :

$$C_R \vec{v}_R = C_R \vec{v}_a - C_{Co} \vec{u}_{Co}. \quad (6.50)$$

This latter term can be substituted in equation (6.47), where also the rate of production can be explicated. In detail, the rate of production will be:

$$\dot{r}_R = +\frac{A_2 m_R}{m_{Co} m_{Ba}} \varphi \rho_{Ba,3} C_{Co}, \quad (6.51)$$

and the continuity equation becomes:

$$\frac{\partial}{\partial t}(\varphi C_R) - \nabla \cdot (C_{Co} \vec{u}_{Co}) = -\nabla \cdot (C_R \vec{v}_a) + \frac{A_2 m_R}{m_{Co} m_{Ba}} \varphi \rho_{Ba,3} C_{Co} \quad (6.52)$$

Summing this equation with the continuity equation of carbon dioxide written in the following form:

$$\frac{\partial}{\partial t}(\varphi C_{Co}) + \nabla \cdot (C_{Co} \vec{u}_{Co}) = -\nabla \cdot (C_{Co} \vec{v}_a) - \frac{A_2}{m_{Ba}} \varphi \rho_{Ba,3} C_{Co}, \quad (6.53)$$

one gets that:

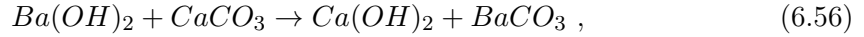
$$\frac{\partial}{\partial t}(\varphi C_a) = -\nabla \cdot (C_a \vec{v}_a) + A_2 \frac{m_R - m_{Co}}{m_{Ba} m_{Co}} \varphi \rho_{Ba,3} C_{Co}. \quad (6.54)$$

Assuming the incompressibility of the the total air fluid², the concentration of air, C_a , is considered constant and, introducing the equation for the seepage velocity of air, \vec{v}_a , the equation for the air pressure, p_a , is reached:

$$-\nabla \cdot (C_a \frac{\kappa}{\eta_a} \nabla p_a) = A_2 \frac{m_R - m_{Co}}{m_{Ba} m_{Co}} \varphi \rho_{Ba,3} C_{Co}. \quad (6.55)$$

6.3 Sets of transport equation

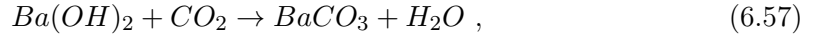
In order to summarize, the sets of equations obtained is briefly reported. The first examined reaction is the following:



and the relative set of equations are:

$$\begin{cases} \frac{\partial}{\partial t}(\varphi C_{Ba,2}) - \nabla \cdot (C_{Ba,2} \frac{\kappa}{\eta_{Ba}} \nabla p_{Ba}) = -\frac{A_1}{m_C} \varphi C_{Ba,2} \rho_C, \\ \frac{\partial}{\partial t} \rho_C = -\frac{A_1}{m_C} \varphi C_{Ba,2} \rho_C. \end{cases}$$

The second examined reaction is the carbonation reaction:



and the relative set of equations are:

$$\begin{cases} \frac{\partial}{\partial t}(\varphi C_{Ba,3}) - \nabla \cdot (C_{Ba,3} \frac{\kappa}{\eta_{Ba}} \nabla p_{Ba}) = -\frac{A_2}{m_{Co}} \varphi C_{Ba,3} \rho_{Co}, \\ \frac{\partial}{\partial t}(\varphi C_{Co}) - \nabla \cdot (D \nabla C_{Co}) = \nabla \cdot (C_{Co} \frac{\kappa}{\eta_a} \nabla p_a) - \frac{A_2}{m_{Ba}} \varphi \rho_{Ba,3} C_{Co}, \\ \nabla \cdot (C_a \frac{\kappa}{\eta_a} \nabla p_a) = -A_2 \frac{m_R - m_{Co}}{m_{Ba} m_{Co}} \varphi \rho_{Ba,3} C_{Co}. \end{cases}$$

These sets of equations represent the model that describes the barium hydroxide interaction and transport inside a porous material. This is a starting point to understand and predict its behavior.

²This assumption is adopted in according to works about the aggression of porous material by SO_2 that is contained in air, for instance reference[47].

Chapter 7

Conclusions and perspectives

The object of this study is the development of a physical model for the description of diffusion phenomena in porous media. Porous materials are very important and common; for instance they are present in the most of cultural heritage, from the frescoes to the architectural structures. In this work, a particular attention is placed on frescoes and wall paintings for which the method of the barium hydroxide was proposed. This is a consolidating method that was conceived and applied, for the first time, after the flood of Florence in 1966. It is a method still widely used with excellent results but it has never been studied before from a theoretical point of view.

In order to develop a model, three main arguments are analyzed and taken into account: moisture storage and transport, heat storage and transport, barium hydroxide transport and interactions.

Moisture inside porous material is very important because its presence can cause damages. Moisture storage is divided into three regions depending on the moisture content, namely hygroscopic, capillary and supersaturated region. The first region is characterized by sorption of moisture inside pore structure up to 95% of relative humidity; it is followed by capillary region in which the equilibrium moisture depends on capillary suction stress in water-filled pores. These two regions cover the range of water content from zero up to free water saturation. The third region cannot be reached under normal conditions but only in laboratory; in this case the water content reaches its maximum value.

With regard the moisture transport, two basic physical mechanisms are considered: vapor diffusion and liquid transport. The first process is essentially described as a transport due to vapor pressure gradient with moisture-independent water vapor diffusion resistances. The latter one takes into account surface diffusion and capillary transport: a priori these two processes are distinguished, in fact the driving potential of surface diffusion is the relative humidity, while capillary conduction is driven by capillary pressure. However, this latter quantity is connected to relative humidity and this allows to described liquid transports as a unique process. Moisture movements due to gravitation and electrokinetic are, instead, do not taken into account.

Moisture transport is strongly coupled with heat transport. Moist porous structure

is an example of an open system and hence the thermodynamic potential used is the enthalpy. Both the dry material and the water inside pores contribute to the construction of enthalpy function. Water content also affects the conductivity of the materials, in fact it is assumed a linear relationship between the thermal conductivity of a material and the water contained inside. Heat transport due to vapor diffusion with phase change is also taken into account as a source term; it is considered separated because it does not occur in proportion to the temperature gradient. Moreover, the heat associated with reactions is added as another source term.

Summing these considerations, two coupled equations for moisture and heat are obtained and the main boundary conditions, such as rain or solar radiation, are specified. They take into account the main possible climatic situations as boundary conditions of the first, second or third kind.

In addition, some considerations about enthalpy are proposed, using the Gouy-Stodola theorem. This theorem was developed for entropy generation that occurs when irreversible processes take place; in this work the use of this theorem, together with the least action principle, is proposed to deal with enthalpy of irreversible processes. In fact, all the considered processes, such as diffusion, conduction or chemical reactions, are real irreversible processes and this imply a bond on enthalpy.

In the last part of the thesis, the attention is focused on the barium method. First, a general overview of the degradation of works of art shows the main causes of damages and, in particular, the focus is on the effects of air pollution and salts. Then the method is presented: basically it acts in a twofold manner because it has a desulphating and consolidating action. The first action is obtained applying ammonium carbonate and barium hydroxide, while the latter action is due to the reactions of the excess of barium hydroxide with calcium carbonate and carbon dioxide. As specify before, this method is applied with good results on wall painting or frescoes, but nobody know the long-term behavior. For this reasons the equation for barium hydroxide transport and interaction with carbon dioxide and calcium carbonated are proposed. The continuity equations achieved, contain the Darcy's seepage velocities, based on pressure gradient, and Fick's diffusion, based on the concentration gradient.

This work would move the first steps for the creation of a theoretical model that allows simulations for cultural heritage. In recent years, in fact, it is became clear that the only monitoring of cultural heritage is not enough and simulations can predict what will happen and constituted an important tool to understand how to intervene. This first analysis is a part of a more general european project that wants to follow this direction.

Appendix A

Numerical method used in preliminary work

From numerical and simulation points of view, some preliminary work has been done in collaboration with researchers of the Keldysh Institute of Applied Mathematics of the Russia Academy of Sciences in Moscow. New effective methods of solution of complex mathematical models, such as those object of this thesis, are today available by means of progressive numerical approaches on parallel computers. For instance, vacancy - gas pores and cracks into crystal lattices - problems discussed in previous chapters - can be modeled as phase transitions of first kind. Therefore, the investigation of initial state porosity due to fluctuation of thermodynamical parameters of the system "atmosphere - sample stone" was performed by using algorithms for numerical solution of the Kolmogorov equation describing non-equilibrium initial stage of the phase transition. Since nucleation of defects into crystal lattice, for instance, led to more easy penetration for pollutants as well as degradation of its qualities, these results are useful to define the initial and boundary conditions for our set of equations, previously introduced. In fact, these calculations, even preliminary, provide the possibility to know mechanisms of nucleation into lattices and determine initial rates of degradation in buildings' materials. Analogous numerical approaches and algorithms will be used to solve the system of equation describing the time evolution of degradation on the surface and in the bulk of stones of historical buildings.

Appendix B

List of symbols

Symbol	Meaning	Unit
Roman symbols		
A	water absorption coefficient	$(kg/m^2s^{1/2})$
a_r	precipitation absorptivity	$(-)$
a_s	short-wave absorptivity	$(-)$
b	moisture related thermal conductivity supplement	$(-)$
B_0	external magnetic field	(T)
B_1	external oscillating magnetic field	(T)
c_e	specific heat capacity of ice	(J/kgK)
c_s	specific heat capacity of dry building material	(J/kgK)
c_w	specific heat capacity of water	(J/kgK)
C_i	porous concentration of species $i = Ba, Ca, Co, \dots$	(kg/m^3)
D_L	solution diffusion coefficient	(m^2/s)
D_m	mass related diffusion coefficient	(kg/ms)
D_s	surface diffusion coefficient	(m^2/s)
D_T	thermodiffuion coefficient	(kg/msK)
D_w	capillary transport coefficient	(m^2/s)
D_Φ	capillary transport coefficient in term of Φ	(kg/ms)
FID	free induction decay signal	(V)
FID_0	free induction decay following pulse	(V)
g_E	Knudsen flux density	(kg/m^2s)
g_s	surface diffusion flux density	(kg/m^2s)
g_v	vapor diffusion flux density	(kg/m^2s)
g_w	liquid flux density	(kg/m^2s)
h_e	specific melting enthalpy	(J/kg)
h_v	latent heat of phase change	(J/kg)
H_s	enthalpy of dry building material	(J/m^3)
H_w	enthalpy of moisture in building material	(J/m^3)
I_l	long-wave radiation incident onto surface	(W/m^2)

Symbol	Meaning	Unit
I_s	short-wave solar radiation	(W/m^2)
I_ε	long-wave radiation emitted from the surface	(W/m^2)
κ	permeability of the medium	(m^2)
K_n	Knudsen factor	$(-)$
K_1	permeability coefficient	$(kg/msPa)$
L	mean free path	(m)
L_s	solubility	(kg/m^3Pa)
m	mass fraction of water vapor	$(-)$
M	macroscopic magnetic magnetization	(T)
M	molecular weight	(kg/mol)
m_w	amount of water absorbed	(kg/m^2)
p_c	capillary pressure	(Pa)
P_g	total gas pressure	(Pa)
p_i	partial pressure of species i	(Pa)
P_l	liquid pressure	(Pa)
P_L	ambient air pressure	(Pa)
q	heat flux density	(W/m^2)
r	capillary radius	(m)
\dot{r}_i	rate of production/consumption of $i = Ba, Ca, Co, \dots$	$(-)$
R	universal gas constant	$(J/molK)$
R_p	precipitation load vertical to the surface component	(kg/m^2s)
R_N	normal rain	(kg/m^2s)
R_s	driving rain load of the wall section	(kg/m^2s)
r_s	site specific driving rain coefficient	(s/m)
R_v	gas constant for water vapor	(J/kgK)
s	position of meniscus	(m)
S_r	heat source due to reactions	(W/m^3)
S_h	heat source due to phase change	(W/m^3)
T	absolute temperature	(K)
T_1	spin-lattice relaxation time of a nucleus	(s)
T_2	spin-spin relaxation time of a nucleus	(s)
v	wind velocity vertical to the wall	(m/s)
V_i	intrinsic velocity of fluid $i = Ba, Ca, Co, \dots$	(m/s)
v_i	Darcy velocity of fluid $i = Ba, Ca, Co, \dots$	(m/s)
w	water content	(kg/m^3)
w_e	content of frozen water	(kg/m^3)
w_f	free water saturation	(kg/m^3)
w_{max}	maximum water content	(kg/m^3)
Greek symbols		
α_c	convective heat transfer coefficient	(W/m^2)
α_r	radiative heat transfer coefficient	(W/m^2)

Symbol	Meaning	Unit
β_p	water vapor transfer coefficient	(kg/m^2sPa)
γ	magnetogyric ratio	(rad/Ts)
δ	water vapor diffusion coefficient in air	$(kg/msPa)$
ε	long wave emission coefficient	$(-)$
η	viscosity of water	(kg/ms)
η_{ref}	reference viscosity of water	(kg/ms)
η_i	viscosity of the fluid $i = Ba, a$	(Pl)
θ	contact angle	$(^\circ)$
λ	thermal conductivity of building material	(W/mK)
λ_0	thermal conductivity of dry building material	(W/mK)
μ	nuclear magnetic moment	(MeV/T)
ρ_i	total concentration of species $i = Ba, Ca, Co, \dots$	(kg/m^3)
ρ_l	liquid water density	(kg/m^3)
ρ_s	density of dry building material	(kg/m^3)
ρ_v	water vapor concentration	(kg/m^3)
ρ_{vs}	saturation concentration of water vapor	(kg/m^3)
σ_w	surface tension of water	(N/m)
Φ	relative humidity	$(-)$
φ	porosity	$(-)$
ω_i	rate of reaction ($i = 1, 2$)	(Pl)
ω_L	Larmor frequency	(rad/s)
Constants		
k	Boltzmann's constant	$1,380 \cdot 10^{-23} J/K$
σ	Stefan-Boltzmann constant	$5,670 \cdot 10^{-8} W/m^2K^4$
Subscripts used in the description of barium hydroxide transport		
$Ba, 1$	portion of $Ba(OH)_2$ which reacts with $(NH_4)SO_4$	/
$Ba, 2$	portion of $Ba(OH)_2$ which reacts with $CaCO_3$	/
$Ba, 3$	portion of $Ba(OH)_2$ which reacts with CO_2	/
B	barium carbonate $BaCO_3$	/
C	calcium carbonate $CaCO_3$	/
Ca	calcium hydroxide $Ca(OH)_2$	/
Co	carbon dioxide CO_2	/
a	air (inside porous materials)	/

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Sebbene siano gli anni più tosti, un lato positivo c'è: si capisce veramente di che pasta si è fatti e come si reagisce quando si è messi alla prova. La cosa bella è scoprire che, anche se si devono affrontare le prove personalmente, non si è veramente soli. Da ciò, nasce l'esigenza di scrivere queste ultime righe.

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