

Why Pore Size Is Important in the Deterioration of Porous Stones Used in the Built Heritage

/ DAVID BENAVENTE (1,2*)

(1) Departamento de Ciencias de la Tierra y del Medio Ambiente. Universidad de Alicante. 03080 Alicante (España)

(2) Laboratorio Petrología Aplicada. Unidad Asociada CSIC-UA. Universidad de Alicante 03080 Alicante (España)

INTRODUCTION.

Porous stone is widely employed as building and sculpture material in much of our cultural heritage, including archeological and architectural monuments. The term "porous stone" will be here applied to stone with porosity values higher than ~10%, which include a wide array of stone used in the built heritage, such as sandstone, travertine, carbonate tufa, oolitic and other clastic limestones, volcanic tuff, etc. This paper highlights the role of pore size on different factors and mechanisms of deterioration of porous building stone. For that purpose, pore structure is addressed in terms of pore connectedness; the role of moisture is emphasized and linked to pore size and stone deterioration; and finally salts and ice crystallization are related to pore size, taking into account the environmental conditions that porous stone undergoes in a monument. There are other deterioration mechanisms that will not be addressed in detail in this paper and in which pore size becomes important, such as in chemical dissolution and biocolonization, or where its influence on deterioration is minor as thermal expansion.

POROSITY AND PORE SIZE.

Porosity quantifies the pore space volume and also contains pore connectedness information. Pore connectedness is related to the coordination number of the pore space skeleton, and increases with porosity. A simple view of the porous structure can be described as a bundle of pore throats (entrance) and chambers where the pore chamber is placed between the pore throats (by definition, the pore throat is smaller than the pore chamber). Two porosity intervals can be distinguished with different porosity-stones property relationships in porous stones. For

porosity values lower than 10%, pore chambers and throats evolve differently; the throats shrink considerably and are eventually destroyed. In stones with porosity higher than 10%, the reduction of the water transport coefficients and the increase of salt and ice stress and water condensation are due almost entirely to the gradual reduction of the throat dimensions (Benavente et al. 2007).

Pore sizes in porous building stone can form a continuum from nanometers to millimeters. Sometimes pore chamber and pore throats (entrance) are overlapped. For instance, a well sorted sandstone may present a monomodal pore-throat distribution family (which can be measured using mercury intrusion porosimetry) but also a different monomodal pore chamber distribution (which can be observed under scanning). This explains why a stone with an overall monomodal size distribution can be deteriorated by salt crystallization (crystallization pressure occurs when a crystal growing within a pore chamber is connected to a small pore throat).

The presence of very large pores can have an impact on stone deterioration depending on how the pores are connected. This is found in travertines and carbonate tufas, where fenestral, coated bubbles or plant cast porosity presents a variable connection (García-del-Cura et al., 2011). In this sense, during the last decades, Lucia (2007) developed an interesting classification for carbonate sedimentary rocks to understand the influence of each type of porosity on permeability. Lucia demonstrated that pore spaces located between grains (intergranular porosity) and between crystals (intercrystalline porosity) are petrophysically similar. They are known as interparticle porosity. Vuggy porosity is pore space that is

within grains or crystals or that is significantly larger than grains or crystals; that is, pore space that is not interparticle. Vuggy porosity is divided into two classes based on the manner in which the vugs are connected. Separate vugs are interconnected only through the interparticle porosity. Touching vugs form an interconnected pore system of significant extent (see details in Lucia, 2007).

Pore size therefore becomes the most important pore structure parameter in terms of stone deterioration and the effectiveness of each deterioration process depends on whether a specific pore size interval is present in a particular stone type. Fig. 1 summarizes the pore size intervals that define the different processes involved in the deterioration of porous stones in a monument. These intervals should be considered as an approximation, since most models are constructed by assuming a cylindrical pore geometry and, therefore, they are in poor agreement with the real pore structure.

MOISTURE.

Salt and ice crystallization, biocolonization, chemical weathering or swelling do not damage the stone by themselves as they require the presence of water. The amount of water condensed onto an exposed built stone surface depends on the difference in vapor pressure (and temperature) between the stone surface and the air. However, in porous stone, effective condensation occurs below to saturation (because of the presence of the pore system). At very low RH, the only transport mechanism is vapour transport. With rising air humidity, the number of layers of water molecules on the surface increases. Within those multimolecular layers of water, surface flow occurs as a secondary and more

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efficient transport mechanism (Rose, 1963). For RH values between 75-85%, the water layers merge into the small pores due capillary condensation, which is effective up to some 10^{-7} m ($0.1 \mu\text{m}$) pore radius. When the RH exceeds 85%, capillary condensation starts to be important and a significant increase in water content in the stone is produced. Capillary condensation continues until the pores with radius $\sim 1 \mu\text{m}$ are filled.

Variations in the thermo-hygrometric conditions and the presence of this pore size interval therefore determinate the amount of water within stone. In this situation, stone is partially saturated in (liquid) water but yet it provides an excellent context to its deterioration: (1) supply of water to the development of microorganisms, salt and ice crystallization, clay swelling and chemical deterioration; (2) decrease in diffusivity of gases (H_2O_v , CO_2 , ^{222}Rn , etc.) since condensed water obstructs the direct passage of gases (Cuezva et al., 2011); (3) reduction in mechanical strength (stone softening); (4) enhancement of swelling, when water invades the pore structure, and shrinking when negative capillary pressures act during drying (for instance, in advance stages of drying, a negative capillary pressure of -10MPa can be reached in pores with a size $0.014\mu\text{m}$ considering a meniscus with a wettable surface).

The occurrence of liquid water in porous stone is enhanced by the presence of rain and capillary waters, which are transported by capillarity forces. This process is active for a pore size up to $0.1 \mu\text{m}$, although the pore size interval between $1 \mu\text{m}$ and 1mm promotes high water absorption rates. Applying Jurin's Equation for a wetting liquid, the

capillary height for a pore radius of 1mm is $\sim 1.5 \text{mm}$, indicating that fluid movement by capillarity is negligible, and the most important mechanism would be gravitational. If the large pores are not spread throughout the porous network (i.e. they behave as separate vuggy porosity), the smaller pores will fill with solutions, and the larger ones will remain empty, because they do not have enough capillary suction to drain liquid from the smaller pores. In such a case, for example, only the small pores will contain salts.

SALT AND ICE CRYSTALLIZATION.

It is generally accepted that crystallization of salts and ice is a major deterioration mechanism in built heritage. Although the crystallization of salts and ice presents obvious chemical differences, the crystallization pressures are equivalent, including the influence of pore size on crystal growth (Steiger et al., 2011). The effectiveness of salt and ice deterioration is linked to capillary solution transport and both unfortunately are very active in the same pore size interval. Thus for porous stones, the effectiveness of crystallization stress generated by salt growth may be considered for the pore throat size interval between 0.1 and $10 \mu\text{m}$. A crystal requires a considerable degree of saturation to penetrate into the pore fraction below $0.1 \mu\text{m}$. Such salt saturations are not frequent in building stones, although they can be reached during salt crystallization standard tests. In contrast, entry pore throats up to $10 \mu\text{m}$ act as sinks, consuming the high supersaturations caused by the growth of large crystals that does not produce sufficient stress to damage these building stones. Consequently, the large pores do not

contribute significantly to salt weathering (Benavente et al., 2011). This effect explains why built heritage stones with large pores, as some travertines (with separate vuggy porosity) or tufas and lumachellas (with touching vuggy porosity), are more resistant to salt and ice deterioration than porous stones with thin pores as some sandstones, dolostones or calcarenites.

As described in this paper, deterioration of porous stone is a complex process. The factors and mechanisms of stone deterioration seldom occur on their own in the built heritage. The observed damage is the result of their interaction whether they act simultaneously or sequentially, and it is here where pore size becomes a key factor with a not very-well-known role.

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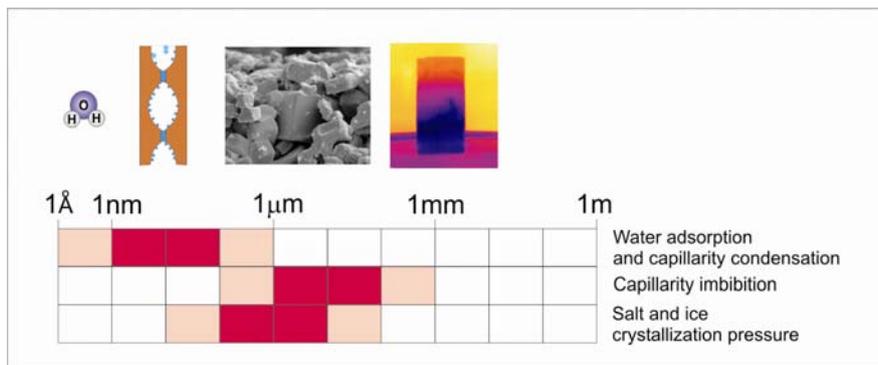


fig 1 Pore-size ranges and different processes involved in stone deterioration, including water adsorption and capillarity condensation, capillarity imbibition, and salt and ice crystallization pressure.