

Chapter 9.2

A CRITICAL APPROACH TO SURFACE AND POROUS STONE ANALYSIS METHODS

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Abstract: The aim of this paper is to give a correct interpretation to contact angles values that are obtained on porous surfaces by applying different methods. First a brief description of the physical meaning of the contact angle value is given, then a new methodology for the contact angle analysis by using the Wilhelmy balance is presented. Finally some limitations in the use of the Washburn's equation are shown.

Key words: wettability; porous materials; contact angle; Washburn's equation.

1. INTRODUCTION

It is well known that protection operations have the purpose to slow down or to make less probable the inevitable transformation processes every monument suffers and that are provoked by the aggressive environment where the work of art lives. Particularly, with the protection one wants to operate both on the alteration causes, correlated to the environmental factors and on the caused processes. Regarding the protective agents, today the most frequent problem consists in the use of new chemical products, which are not sufficiently experimented and whose effects are not known in a middle and long term. At the base of a balanced intervention it is therefore important to know both the materials and the techniques very well. Insofar it is necessary to analyze in every single case the most opportune treatment, appraising advantages, disadvantages, risks and probabilities to achieve a positive result, also effecting appropriate laboratory tests on the material-produced system.

The surface and porosity analysis to obtain characteristics of the stone as wettability and water absorption ability have a very long tradition. In fact the theories and the equations on which some common methods are based have been discovered even in the XIX century. Here reference is made to the application of Young's and Laplace's equations^{1,2} and to the Washburn's equation³ in the sessile method or in the Wilhelmy⁴ technique for the determination of the contact angle and in the liquid absorption measurements for the determination of the stone porosity.

In the case of the stone protection by applying polymeric agents the evaluation of wettability modification or water absorption have an important practical and theoretical role. Notwithstanding this long tradition of experimental and theoretical results there is a long debate about the validity of the results and even about the exact meaning of the experimental results⁵.

In the present paper it will be briefly shown how the evaluation of surface stone wettability and porosity may be considered in the light of recent experimental results. Initially attention is focused on the static angles and it is explained why these values do not well correlate with the liquid absorption. It appears that the wettability properties may be easily modified without decreasing the effective liquid absorption, while the real trouble is hidden in the real meaning of static contact angle. Only the use of the advancing and receding angles may overcome this misunderstanding; on a rough and heterogeneous material these angles may be attributed to the effect of both of these properties and so it is not correct to correlate the high advancing contact angles with the chemical composition of the material itself. When a stone is protected against the water absorption through the use of a polymeric agent in some way distributed on its exposed face the presence of the polymer induce an immediate increase of the advancing angles, due to its reduced wettability, while the portion of stone not covered allows in any case a significant absorption of water. Only when the increase in the concentration or in the final mass of the deposited polymer reduces the non-covered stone surface the absorption of water is really reduced; this phenomenon is followed by using the receding angle, which is generally connected with the most easily wettable portion of the surface.

This kind of measurement can be led using a Wilhelmy balance but the absorption of the test liquid often makes this evaluation difficult and introduces a systematic error in the final values of the contact angles. In this case a mathematical model of the absorption has been developed, which uses a Washburn-like approximation to calculate from the absorbed liquid mass and the interval time of the experiment, the speed of the imbibition; introducing this adjustment in the original data the experiment is corrected in an acceptable way. Moreover if the experiment is made on a porous and so on a reasonably rough material, it can be performed in a perfectly wettable liquid to recalculate the Wenzel ratio of the material; as a final result the contact angle of the wet solid is easily obtained.

Finally the mechanism of the absorption itself, described by the Washburn equation appears not well related to the size pores obtained by other methods and does not give values of the contact angles in agreement with those obtained through direct surface analysis.

2. MATERIALS AND METHODS

Two different porous materials were analyzed: the Noto Stone, an organogenic calcarenite coming from the caves of Palazzolo (Siracusa, Italy), largely employed in the local historical buildings and a ceramic material having a controlled porosity.

Specimens for the absorption and contact angle measurements had a size of 10x3x30 mm while ceramic samples of sizes 5x2.5x30, 10x2.5x30, 25x4.5x30 and 25x7.6x30 mm were used for the study of the dependence of the absorption parameters on the geometrical shape.

3. THE PHYSICAL MEANING OF THE CONTACT ANGLE

In the field of monument protection the use of contact angle has a long tradition⁶⁻⁸; notwithstanding this tradition it is often difficult to accept the approach which is used in papers or even in procedures proposed by official norms; in fact the actual application of the contact angle may be shortly expressed as the use of the static or of advancing angles on surfaces which are always heterogeneous and rough, i.e. non-ideal. Obviously this can be performed if and only if the intrinsic limits of this approach are known and explicitly considered.

These limits may be easily conceived referring to the concept shown in Figure 1 in which one can compare the profile of surface free energy of an ideal and of a real interface versus the contact angle. The first one presents only one minimum, corresponding to the Young angle, while the second one shows many minima in a wide interval of values; each one of these minima being a metastable minimum, produced by the roughness or heterogeneity, which may be found as the result of a contact angle measurement in different experimental conditions.

In a given experimental condition, the highest one corresponds to the advancing angle and the lowest one to the receding angle; note that the curve is not necessarily symmetric; however it is possible, using modern experimental methods as VIECA^{9,10}, to evaluate the angle corresponding to the energy minimum, e.g. the Wenzel angle for the rough surfaces; this angle does not necessarily corresponds to the Young angle.

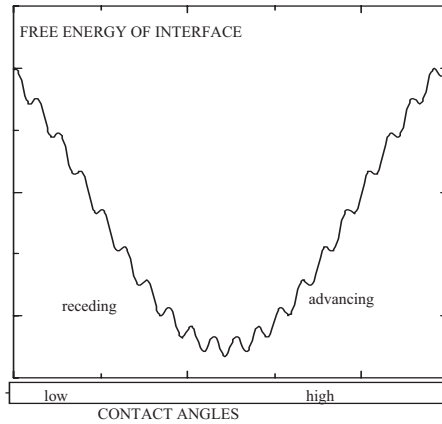


Figure 1. The surface free energy of the triphase system versus the experimental contact angle; the shape of the local minima is important in its effect on the real mobility of the meniscus.

The general correlation among all the angles may be captured by Figure 2 for a moderately rough surface. It appears clear that the current use of the static or advancing angle is often misleading. In order to obtain practical indications from the experimental results one should be fully aware of the real meaning of the angle which is measured.

The surfaces evaluated in the case of monument protection are among the most complex ones, because they may be rough, heterogeneous and porous. The effect of porosity will be analyzed in the following using a new mathematical model; the effect of heterogeneity has been already analyzed in literature; on a flat, but heterogeneous surface, one will obtain the so-called “hysteresis graph”¹³ which allows to assign the advancing angle to the lowest energy portion of the surface and the receding one to the highest energy portion. The correlation is not linear, as clearly evidenced in Figure 3: a low percentage of hydrophobic surface can increase the advancing contact angle.

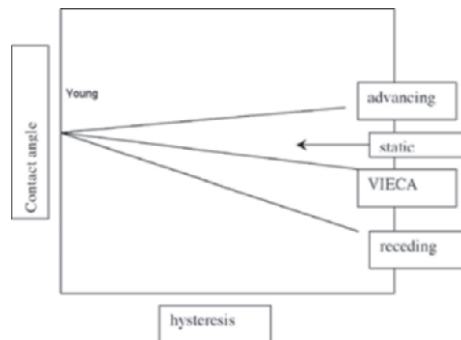


Figure 2. The variation of advancing, receding and VIECA contact angles with the surface roughness, which is generally correlated with a hysteresis. The Young angle may be only obtained by extrapolation^{11,12}.

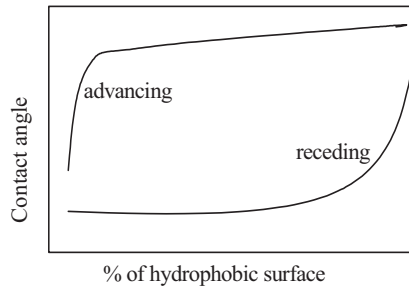


Figure 3. The Cassie Baxter Contact Angle and the hysteresis on a heterogeneous surface.

The conclusion may be that on a moderately rough surface, even neglecting the effect of roughness, the advancing angle is monitoring the lowest energy portion of a surface; as a consequence the use of the contact angle to check the efficacy of a polymer used as protective agent is misleading; its increase may simply confirm the mere presence of the protective and not its efficacy; a more efficient way to check the efficacy of the protective is to follow the evolution of the receding angle which increases with the percentage of the protective agent as shown in Figure 4.

A second point to stress is that it is common to find very high advancing angles on protected surfaces, often higher than the values characteristic of the flat protective agent alone. This experimental finding may be strongly misleading, inducing to accept the conclusion of the enormous efficacy of the used material, a fact which is difficult to reconcile with the contemporaneous water absorption; water cannot be absorbed when the contact angle is above 90°. The reason of this is in the eventual formation of a “composite” surface (today named “superhydrophobic”), already revealed by the traditional lite-

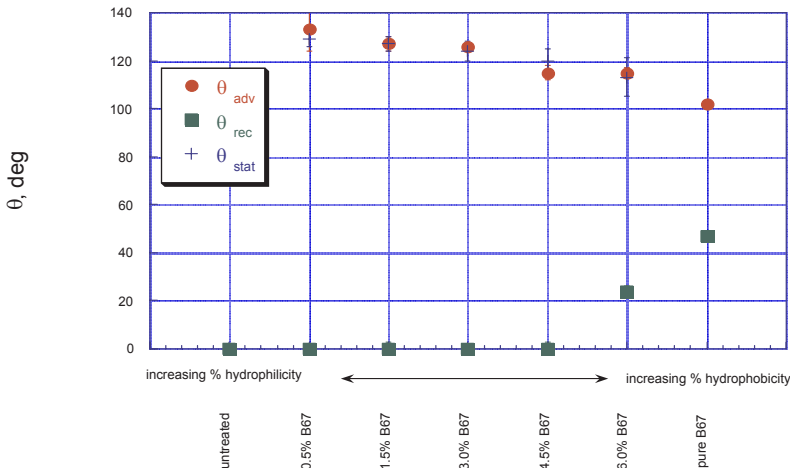


Figure 4. The advancing and receding contact angles of water on Noto stone protected with solution of Paraloid B67 of increasing concentration.

perature, which may transform a strongly rough surface in a heterogeneous one, using the air captured in pores as well as in the case of aquatic birds feathers. This situation is valid on the protected portion of the surface only, and for this reason appears as strongly metastable.

A last point to mention is the consequence of time-ageing of the protective agents; the effect of UV radiation and weathering may induce the formation of newly chemical functions, oxidizing the protective and altering its continuity; the final effects are very complex and difficult to understand in terms of surface properties only. A general decrease of the contact angles, may reveal this alteration, but it is necessary to use other techniques to understand the situation.

4. MODELING THE WILHELMY EXPERIMENT ON A POROUS MATERIAL

In order to correctly use the Wilhelmy experiments on porous samples it is necessary to model the mechanism of liquid absorption. The mass of the porous sample at the beginning and at the end of a typical Wilhelmy experiment are not the same, as also the slope of the force/immersion depth curve does not correspond to the buoyancy coefficient $-\rho g A$ expected for a sample with constant cross-sectional area A immersed in a liquid of density ρ . Therefore, appropriate corrections are needed.

The main idea of the model is that liquid penetration follows a Washburn-like law and defines empirically a mean absorption coefficient α as follows:

$$\alpha = (m_B - m_A) / \sqrt{t_B - t_A},$$

where m_A and m_B are the initial and final mass of the sample for a typical Wilhelmy run of duration $t_B - t_A$, the dependence on the square root of time being just suggested by Washburn law. α can be easily calculated from the experimental data. At any time t larger than t_A , which corresponds to the zero depth of immersion, the total force measured by the microbalance will be corrected by subtracting the mass of the absorbed liquid:

$$F_{corr} = F_{original} - \alpha \sqrt{t - t_A} \quad (1)$$

It is understood that whenever full absorption takes place in a time shorter than the duration of a Wilhelmy cycle, the above correction must be referred only to the absorption time interval, by introducing a constant weight correction in the rest of the measurement. In any case the liquid advances on a solid surface already wetted, owing to the absorption process, and this could be a serious limit of the model when the contact angle is nonzero.

Another important effect to take into account in the analysis of a Wilhelmy experiment on a porous sample is the liquid evaporation from the solid surface. This phenomenon can be reasonably modelled by assuming that evaporation takes place at a constant rate per unit time and area and thus expressing the mass loss of the sample due to evaporation by the formula

$$\Delta m_{evap} = \int_A^B \beta \cdot S(t) dt \tag{2}$$

where $S(t)$ denotes the evaporation area as a function of time and β is a mean evaporation coefficient per unit time and area. Such a coefficient can be empirically calculated by prolonging the final stage of the Wilhelmy measurement, when the sample is completely withdrawn from the liquid and the evaporation area is constant, so that the sample mass decreases linearly with time. $S(t)$ typically increases with the height of the liquid within the sample and therefore with the square root of time, owing to the absorption phenomenon. Such a conjecture can be experimentally verified by checking (through a set of digital images) that the height of the liquid in the sample follows a square root law versus time and subtracting the height of the liquid meniscus. A height of the liquid less than the meniscus or negative must be regarded as a zero contribution to evaporation. A law of the form $S(t)=\sigma(t-t_A)^{1/2}$ is in good agreement with the experiment and introduces a new empirical constant σ which can be interpreted as the evaporating area one second after the ZDOI time t_A . The sum of the masses evaporated per second, $\beta \cdot S(t)$, provides the total amount of evaporated liquid, which is then summed up to the amount of absorbed liquid previously measured to recalculate the new absorption coefficient, α' . By setting $\beta'=\beta\sigma$ the corrected force at time t takes then the following form:

$$F_{corr} = F_{original} - \alpha' \sqrt{t - t_A} + \beta'(t - t_A) \sqrt{t - t_A} \tag{3}$$

where the prime indicates that the absorption coefficient has been recalculated as explained and the evaporation coefficient incorporates the variation of evaporating surface.

5. WICKING ANALYSIS

Absorption measurements are often used for the determination of the contact angle of a porous material, notwithstanding the explicit limitations of the Washburn equation³ and of the models derived from its application. This equation provides a kinetic model of the rise of a liquid in a cylindrical capillary and is written in the form:

$$h^2 = \frac{1}{2} r \frac{\gamma_{liq} \cos \theta}{\mu} t \quad (4)$$

with r the radius of the capillary, h the height of the meniscus at time t , γ_{liq} the surface tension, μ the dynamic viscosity of the liquid and θ the contact angle of the liquid on the solid. In the original paper of Washburn an equation for a porous system was obtained, simply considering the case in which the porous body "can be taken as equivalent to the penetration of n cylindrical capillary tubes of radii r_1, \dots, r_n "³ otherwise, in the opinion of Washburn, the applicability of its equation "could only be determined by experiments"³. The finding that during the first part of the imbibition, not the whole porosity is used by the liquid¹⁴ was an important improvement but as it is shown in this work other strong limitations still exist. Some experimental absorptions and contact angle measurements on two different calcareous and silicates porous media are here reported. Each absorption measurement with different liquids has been performed by collecting the mass of the sample and height of the liquid versus the imbibition time. The model applied is given by Washburn's equations for the mass absorbed and the height reached by the liquid as a function of time:

$$H_w(t) = h_1 \sqrt{t} \quad \text{with} \quad h_1 = \sqrt{\frac{\bar{r} \gamma_{liq} \cos \theta}{2\mu}} \quad (5)$$

$$M_w(t) = m_1 \sqrt{t} \quad \text{with} \quad m_1 = \sqrt{\frac{(\rho \varepsilon A)^2 \bar{r} \gamma_{liq} \cos \theta}{2\mu}} \quad (6)$$

Once the parameters m_1 and h_1 have been derived, the effective porosity and the equivalent capillary radius can be determined by means of the following relationships:

$$\varepsilon_{eff} = m_1 / \rho_{liq} A h_1 \quad (7)$$

$$r_{eq} = \frac{2h_1^2 \mu}{\gamma_{liq}} = \left(\frac{m_1}{\varepsilon A \rho} \right)^2 \frac{2\mu}{\gamma_{liq}} \quad \text{with} \quad \cos \theta = 1 \quad (8)$$

The calculation of the contact angle θ_{nw} , for the non wetting liquid, can be done finally applying the simple relationship:

$$\frac{r_{eq-nw}}{r_{eq-w}} = \cos \theta_{nw} \quad (9)$$

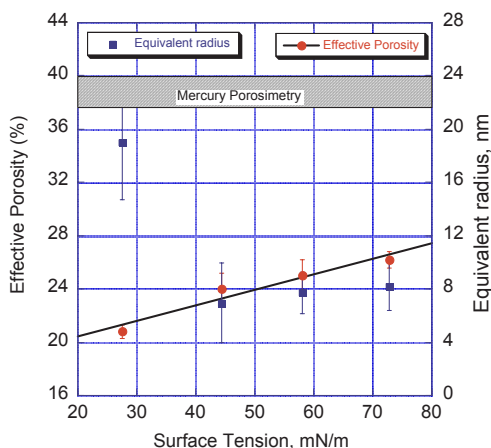
where r_{eq-w} and r_{eq-nw} are the equilibrium radius calculated using a perfectly wetting and non wetting liquid and knowing that in the first case $\cos\theta_w=1$ ($\theta_w=0^\circ$ for its definition). The values of effective porosity and equivalent radius for 4 different liquids found on Noto Stone are presented in Figure 5. The equivalent radius determined in this way turns out to be at least two orders of magnitude smaller than the average pore radius deduced from mercury porosimetry.

A qualitative explanation of this behaviour is that the meniscus spends the majority of time in the largest segments, where the capillary driving force is the smallest and the volume to fill is the greatest. On one hand this fact explains why only a part of the porosity is used, on the other hand it points out that this value does not have a physical meaning. As it is expected the final result reflects all the limitations of the too raw model and that the so determined contact angles of water on calcite are widely scattered and meaningless.

It is possible to note in Table 1 that the contact angle for water, found applying the Washburn procedure by using the n-Hexadecane radius is not so far from the same value found using the corrected Wilhelmy approach. Instead the results calculated starting from 1-Bromonaphtalene and Formamide radii are totally different: this can mean that the reference radius refers to a non-complete wetting fluid, but the measurements confirm that the contact angle of those liquids on Noto Stone is zero.

Table 1. Contact angle for Water/Noto Stone as calculated from the absorption results of other wetting liquids using the equivalent radius approach.

Employed liquid	Contact angle of water
n-Hexadecane	65.1±7
Formamide	<u>0-23</u>
1-Bromonaphtalene	<u>0-27</u>



One of the reasons explaining why contact angle values are often meaningless, is the dependence of the parameters obtained by the application of the Washburn model on the sample shape. This limitation is due to the fact that in the Washburn's study the replaced fluid (air in this case) resistance is not considered; this approximation could be acceptable in a multi-capillary system, where the displacing liquid enters from a side and the air exits from the opposite side. On a porous system the situation is totally different because the porosity is a complex network and the removed fluid need to follow pathways different than just a simply capillary tube.

By applying Eqs.(5, 6) one must calculate the parameters h_1 , m_1 and ϵ_{eff} for samples of ceramic material having different transverse sections in water and in heptane. Notice that, the parameter m_1 , increases linearly with the sample area (Figure 6a), as correctly indicated by the Washburn's model (see Eq.6). The parameter h_1 shows instead a maximum (Figure 6b) or in any case a variation with the sample section whereas its mathematical model does not include such a dependence (see Eq.5).

The factors, which affect the absorbed mass in time and, respectively, the rate of propagation of the liquid front as measured by the front height, are therefore different. It is important to stress out that the weighted mass corresponds to a value independent on the size and shape of the sample, while the height is relative to the external faces of the parallelepiped sample. It is quite reasonable to assume that the height of the liquid front, as it is visible on the lateral surface, does not correspond to the analogous height reached by the liquid in the whole section of the sample, as supposed in the application of Washburn's model.

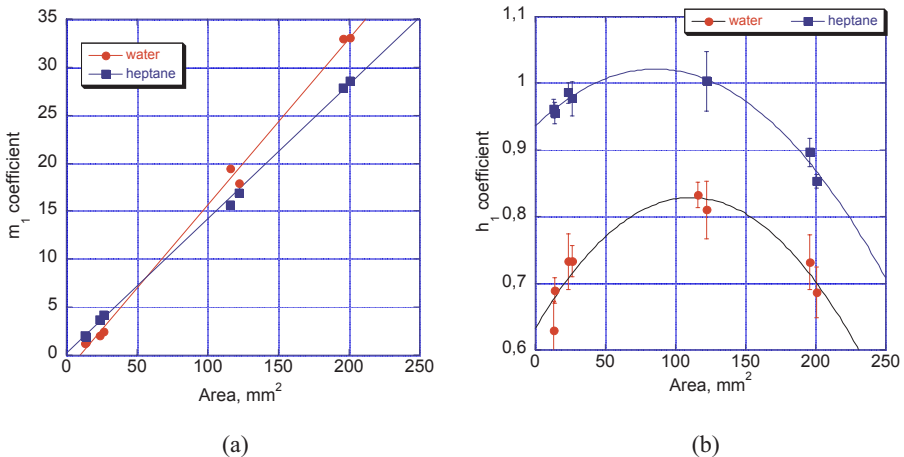


Figure 6. (a) The dependence of the parameter m_1 of the Washburn's equation on the size of the sample. (b) The dependence of the parameter h_1 of the Washburn's equation on the size of the sample.

6. CONCLUSIONS

1. The use of the contact angle in the field of monument protection should be made with reference to its meaning on rough and heterogeneous surfaces; the advancing angle only is not able to show the ability of a protective agent but only to reveal its presence; receding angles or a more general view of the wettability properties of the material should be considered.
2. Obtaining contact angles of porous materials, as stones, through standard techniques is possible applying a suitable model to the obtained data; in the case of Wilhelmy experiment a model has been proposed to this direction.
3. The use of the Washburn equation to follow the liquid penetration in a porous material is certainly useful; the direct calculation of the contact angle from the results of a Wicking experiment, on the contrary, does not appear a good strategy.

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