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Application of mercury porosimetry to the study of xerogels used as stone consolidants

María J. Mosquera [a,*], Josefa Pozo [a], Luis Esquivias [b], Teresa Rivas [c], Benita Silva [c]

[a] *Departamento de Química-Física, Facultad de Ciencias, Universidad de Cádiz, P.O. Box 40, 11510 Puerto Real, Spain*
[b] *Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Spain*
[c] *Departamento de Edafología, Facultad de Farmacia, Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain*

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Abstract

Alkoxysilanes, low-viscosity monomers that polymerize into the porous network of stone by a sol–gel process, are widely used in the restoration of stone buildings. We have used the mercury porosimetry technique to characterize changes in microstructure of three granites following their consolidation with two popular commercial products (Wacker OH and Tegovakon V). The suitability of this technique is questioned because a surprising increase of stone porosity is observed. In order to investigate the feasibility of porosimetry, we analyze the behavior of xerogels prepared from the two commercial products, under mercury pressure. Gels are basically compacted and not intruded by mercury. Thus, the increase of stone porosity after consolidation can actually be associated with gel shrinkage. Mercury porosimetry, therefore, has been found unsuitable for characterizing the microstructure of consolidated rocks. However, it can be employed usefully to evaluate shrinkage of gels under mercury pressure, which permits the behavior of a consolidant during the process of drying in stone to be predicted. It is a key factor because many problems of consolidants are related to their drying process within the stone. Gels under study exhibit a high rigidity and an elastic behavior, as consequence of their microporous structure. Finally, the reduction in the porous volume of gels after the porosimetry test demonstrates that the shrinkage mechanism is based on pore collapse.

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1. Introduction

In recent decades, an apparent acceleration in the rate of stone decay and the growing worldwide interest in preserving historic structures are promoting a significant increase in the number of studies of restoration. Deeply penetrating materials with the ability to re-establish the cohesion

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[*] Corresponding author. Tel.: +34-956 016 331; fax: +34-956 016 288.
E-mail address: mariajesus.mosquera@uca.es (M.J. Mosquera).

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between particles of deteriorated stone are commonly used in these interventions. Alkoxysilanes, such as tetraethoxysilane (TEOS), are regarded as the most promising of the commercial products available at the present time [1,2]. Alkoxysilane monomers have extremely low viscosity, permitting their deep penetration into porous stone. In addition, they polymerize upon contact with moisture in the stone, producing a strong, resistant consolidant. After a drying and ageing process, a stable xerogel with silicon–oxygen backbone similar to the stone binder is achieved. The drawback is that contradictory reports regarding the performance of alkoxysilane consolidants proliferate in the literature. The reasons for these contradictions are basically related to variations in composition and structure of stones that can substantially modify consolidant–stone interaction. Moreover, the effects of drying and ageing within stone and the mechanisms of adhesion are still unknown.

It is clear that consolidant products should be selected on the basis of a correct understanding of their behavior. Their compatibility with any particular stone and the characteristics of the deterioration process it sufferers must be known. Therefore, the development of preliminary tests in the laboratory that evaluate the efficacy of the consolidant on the specific stones is extremely important. In fact, many standard test methods for the selection of a suitable consolidant [3,4] are available. Basically, observed changes in appearance, strength, and porosity in stone after the consolidation, are used to evaluate the performance. Since the porous structure of stones plays a key role in their deterioration process, characterization of changes in porous network is especially important for correct consolidant selection. Depending on the range of pore sizes presented by particular stones, mercury intrusion porosimetry (MIP) is the usual technique for these studies [4]. Porosimetry is based on the fact that mercury is a non-wetting liquid. Thus, mercury penetration into pore spaces exclusively occurs exclusively when pressure is applied. Then pore size distribution can be obtained according to the radii calculated using the Washburn equation, where pore radius is inversely proportional to the applied pressure.

Contradictory results in respect of changes in stone porosity after consolidation, are found in the literature. In some studies, a decrease of microporosity is reported, with a consequent increase in the percentage of larger pores [5]. In other cases, authors report a relative increase of both the smaller and larger pores after consolidation [6]. In a preliminary study [7], we observed a surprising increase of porosity in granitic rocks after the consolidation process. This finding was associated with the development of stress greater than the resistance of the stone, within the gel during drying. However, we believe a study in depth of this explanation is required, because the suitability of mercury porosimetry for characterizing stone microstructural changes after consolidation must be questioned.

In fact, several interpretations of mercury porosimetry as applied to dry gels have concluded that the compressive effect of pressure does not allow intrusion of the mercury because these materials present a small pore size together with a low bulk modulus [8–13]. Scherer et al. [8] calculated the pressure at which intrusion should occur, assuming that the pore size decreases roughly in proportion to compressed volume. In the cases reported of aerogels [9–13], calculated pressure always exceeds the porosimeter pressurization range. Therefore, porosimetry cannot be used to measure pore size distribution in these materials. However, volume shrinkage of the porous network occurring during experiments with mercury pressure may be used to estimate their bulk modulus. In all these studies, aerogels exhibited low bulk moduli. On the other hand, these gels, which are known to be elastic, showed linear elasticity at low strains, followed by yielding, and then displayed irreversible shrinkage corresponding to plastic behavior. The compaction process is a consequence of pores collapse [9,14] resulting in the formation of siloxane bonds that increase the network connectivity [11–13]. Recently, the mechanical structure–property relationship in gels has been described by a theoretical model [15], which confirms that the connectivity network controls the gel rigidity.

In this paper, we apply mercury porosimetry to examine changes in the pore structure of three granites consolidated with two commercial products. As contradictory results are found, we evaluate the response of monolithic xerogels prepared from the two consolidants to isostatic pressure provided by mercury porosimetry. The first objective of the paper is to determine the suitability of porosimetry for characterizing the porous structure of the stone after consolidation. We find that gel networks are compressed and the mercury hardly intrudes at all into the gel pores; consequently we use porosimetry to evaluate shrinkage behavior of the gels. Our second objective is thus to examine gel strain under mercury pressure. This enables us characterize gel behavior during the drying process within the stone. Finally, data of nitrogen adsorption isotherms of the xerogels are analyzed to determine the nature of the compaction process occurred.

2. Experimental

Components of the two commercial products under study are summarized in Table 1. In both cases, the products contain pre-polymerized TEOS mixed with non-aqueous solvents. In these conditions, the amount of atmospheric water inside the stone, which cannot be controlled, is not a limiting factor in the condensation; the water exclusively activates the total polymerization process. An organotin catalyst is also included in the products.

First both consolidants were applied to samples of three granitic rocks (Roan, Baleante and Axeitos) widely used in historic construction in Northwest Spain. The 36 test specimens (six cubes of 125 cm^3 for each granite and consolidant) were totally immersed in each of the consolidants for 24 h. The samples were then removed from the product and any consolidant remaining on the surface was eliminated. The amount of product absorbed was determined. Samples were then left for a period of 30 days at room temperature to allow polymerization. The amount of polymerized material was determined by the weight gain of the samples. For these two measurements, the arithmetic mean and standard deviation for the six cubes of each test are shown in Section 3.

Table 1
Composition of the two commercial consolidants used

Product	Alkoxysilane	Catalyst
Wacker OH	Partially polymerized TEOS (<50%)	Dibutyldinlaurate
Tegovakon V	Partially polymerized TEOS (>75%)	Dibutyldinlaurate

Runs of MIP measurement were carried out on two compatible instruments, for the low-pressure (up to 400 kPa) and high-pressure (maximum 400 MPa) ranges. Three samples, with an average size of 2 cm^3, of each type of granite with each consolidant, were cut by low speed sawing from the cubes used in the consolidation. Sawing was performed close to the surface, in order to ensure that the specimen had been correctly penetrated by the product. Samples were washed in an ultrasonic bath, dried at 60 °C and then analyzed. Next the porosity accessible to water of the six initial samples was evaluated following the RILEM procedure [16]. The porosity determination is essentially very simple: the specimen mass, dried until of constant weight, is measured (m_d). Then it is placed under vacuum and immersed in distilled water until all open pores are completely filled with water. Then its mass is measured both under water (m_w) and normally in air (m_m). Using Archimedes's law, the open porosity can be found from

$$P(\%) = \frac{m_\mathrm{m} - m_\mathrm{d}}{m_\mathrm{m} - m_\mathrm{w}} 100$$

All the tests were carried out on both untreated and treated stones. Three samples were tested in each case. Again, arithmetic mean and standard deviation of specimens tested are shown.

In order to evaluate the response of the consolidants submitted to mercury pressure, monolithic xerogels of the two commercial products were prepared. Synthesis was developed as follows: separately, 10 ml of each commercial products were mixed with 1.6 ml of water in Wacker OH and 2.4 ml of water in Tegovakon. To ensure the complete polymerization of the products, water was added in molar ratio (4:1). In both cases, 5 ml of ethanol was added for dilution. Next the solution was homogenized by magnetic stirring, and then the mixture was poured into plastic tubes and hermetically closed. The samples gelled at room temperature in a few days. The gels were aged and dried at room temperature for three weeks. In order to obtain monolithic gels, the evaporation rate was controlled at a slow rate. To guarantee the total water elimination, gels were dried in an oven at 50° until no change of weight was observed. Mercury porosimetry was then performed on the xerogels. Three specimens of each gel were tested. For the MIP run, Hg pressure was varied between 0.1 and 400 MPa. The corresponding depressurization paths of the experiments were also recorded. We take as apparent density the value measured at atmospheric pressure. In a first stage, monolithic specimens were put inside a rubber membrane to prevent mercury intrusion. A rotary vacuum pump was used to extract the air. Control specimens were run without the membrane for comparison. Sample weight was checked before and after the run to ascertain whether any mercury was retained within the network. In addition, the Wacker OH xerogel was subjected to sequential pressurization–depressurization cycles with maximum pressures of 150, 200, 250, 300 and 350 MPa. Finally, nitrogen adsorption–desorption isotherms at 77 K of the gels before and after porosimetry tests were obtained.

3. Results

As shown in Table 2, the relatively small amount of consolidant absorbed in all the cases suggests a poor penetration of product, limited to the surface region of the rocks. Despite this low penetration, associated with the low porosity of granites, an increase of the rocks' resistance to salts crystallization has been reported [17]. This finding indicates that the consolidants develop a protective film within the porous network of the granite. Durability to salts crystallization was evaluated by artificial tests in the laboratory based on the RILEM procedure. Specimens are subjected to alternate phases of absorption of sodium sulphate solution and subsequent evaporation at 50 °C and 40% RH. Mass lost of specimens and changes in porosity accessible to water after 20 cycles determine the resistance of the rocks evaluated. According to the sol/gel ratio (see Table 2 caption), the gel remaining inside the rock was the highest in Axeitos granite, indicating that the polymerization reaction was more efficient in this granite, at least initially. In all granites, the sol/gel ratio was lower for Tegovakon than for Wacker OH, implying that the polymerization process was more efficient after the treatment with Tegovakon.

Table 3 shows the porosity accessible to water as well as to mercury. In the case of untreated specimens, MIP porosity data were close to those obtained by the RILEM test. The good agreement obtained in these stone leads us to conclude that porosity data obtained by mercury porosimetry in untreated specimens are correct. As we have reported previously [18], pore size distribution of untreated granites (Fig. 1) is clearly bimodal. This presents a first linear segment of the intrusion curve corresponding to trans-granular fissures and a second segment corresponding to inter- and intra-granular fissuring. Trans-granular fissuring is a significantly higher proportion in Axeitos (90%) than in the other granites (40%).

After consolidation, porosity accessible to water is reduced in all cases, while porosity measured by MIP is surprisingly increased in several specimens (Baleante and Axeitos after Wacker OH consolidation and Roan after both treatments). At

Table 2
Amount of sol uptake (g/m^2) (sol), amount of gel in the rock (g/m^2) (gel), and ratio between these parameters (sol/gel) after the treatment with the two consolidants

Granite	Tegovakon			Consolidant OH		
	Sol	Gel	Sol/gel	Sol	Gel	Sol/gel
Roan	156 (32.6)	76 (13.4)	2.05	158 (25.3)	74 (9.2)	2.13
Baleante	189 (13.2)	41 (5.6)	2.19	211 (21.7)	94 (11.3)	2.24
Axeitos	75 (22.3)	41 (19.9)	1.82	79 (54.2)	42 (27.5)	1.88

Data are mean values measured in six specimens of each type. Standard deviations are shown in brackets.

Table 3
Mean values of porosity accessible to water and total porosity obtained by MIP, expressed in volume (%) for each of the granites, before and after application of the two consolidants

Granite	Porosity accessible to water (%)			MIP porosity (%)		
	Untreated	Tegovakon	Wacker OH	Untreated	Tegovakon	Wacker OH
Roan	2.11 (0.21)	1.65 (0.15)	1.59 (0.18)	2.10 (0.12)	2.58 (0.16)	3.14 (0.25)
Baleante	2.78 (0.20)	2.34 (0.25)	2.20 (0.66)	2.80 (0.15)	2.40 (0.24)	3.52 (0.40)
Axeitos	1.94 (0.33)	1.68 (0.18)	1.80 (0.22)	1.50 (0.17)	0.80 (0.32)	1.59 (0.42)

Standard deviations are shown in brackets.

first sight, the increase of volume, basically observed at high pressures (Fig. 1), is associated with an increased porosity of the stones after the treatments. The superficial penetration of the two consolidants into the rocks could indicate that MIP data are more reliable because they correspond to the zone closer to the surface where the product has penetrated, while RILEM porosity corresponds to the total volume of the specimen.

Fig. 2 shows the behavior of monolithic gels made from Tegovakon V and Wacker OH submitted to a maximum pressure of 400 MPa. In the case of gel from Wacker OH, the compression curves with and without rubber membrane are

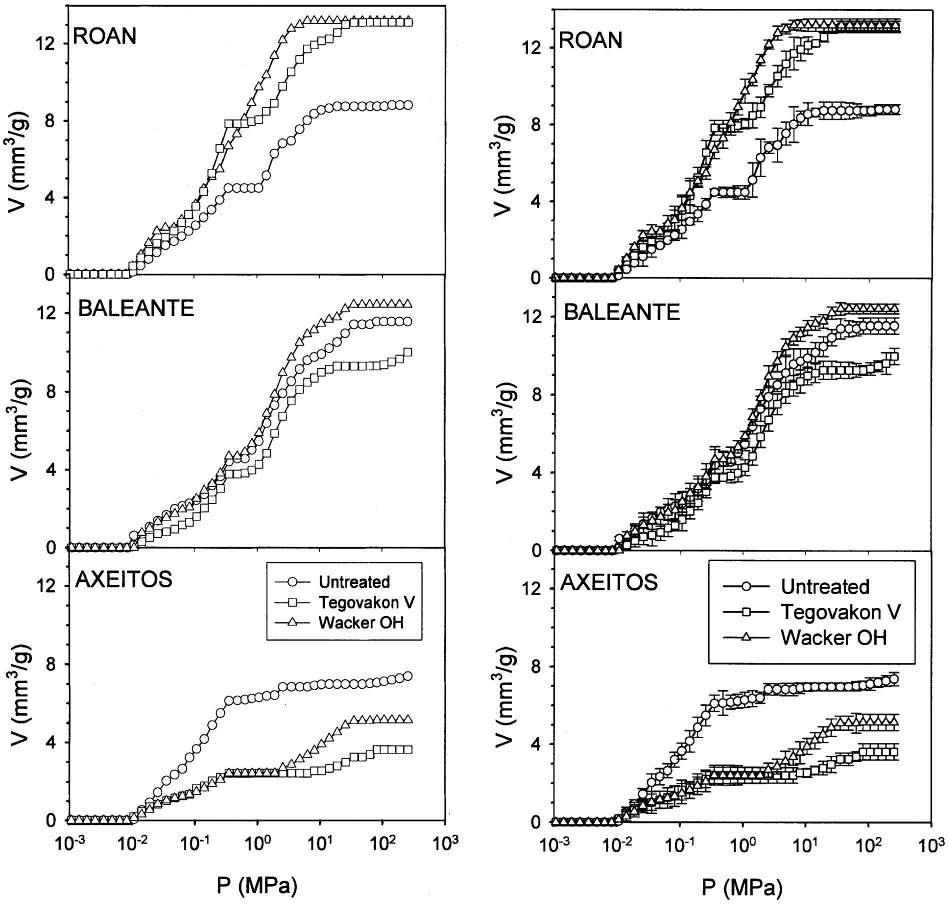

Fig. 1. Mercury porosimetry curves, volume vs pressure, for granites studied.

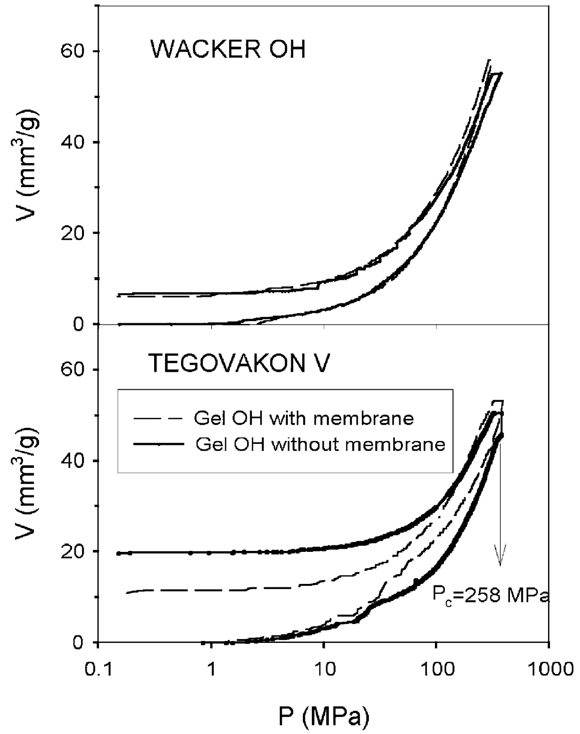

Fig. 2. Mercury porosimetry curves, volume vs pressure, for monolithic gels.

identical and gel weight is not altered after MIP runs (Table 4). Consequently, there is no mercury intrusion into the Wacker OH gel in any of the cases. Volume lost is exclusively due to the strain resulting from the applied stress. For gel made from Tegovakon V (Table 4), a weight increase (20%) is observed after test in specimens without membrane, while it is not altered in gel with membrane. This behavior indicates that mercury intrusion occurs in Tegovakon. In addition, we can easily distinguish a slope change in the pressurization curve without membrane (P_c in Fig. 1) indicating mercury intrusion above this pressure (258 MPa). This is confirmed by the test without membrane, in which weight remains constant and no slope change is observed. However, volume lost is basically due to material shrinkage because intrusion occurs at high pressure and the curves obtained with and without membrane are similar. As has previously been reported for aerogels [8–13], xerogels prepared from these two commercial consolidants are compacted and mercury is not intruded under pressure. Therefore, porosimetry cannot be used for the characterization of porosity and pore size distribution of these materials. However, it is a suitable tool for predicting mechanical properties of gels.

Compression curves for both gels (Fig. 2) show strain is practically negligible until a pressure of around 10 MPa is reached, then above this the deformation curve is concave, reaching similar volume shrinkage in both gels (Table 4). When the pressure is released, the volume retrieved after depressurization is 88% of the total in Wacker OH and 80% in Tegovakon, which in practice means the behavior of the gel is elastic. Fig. 3 shows the curves obtained in the sequential compression experiment. The initial volume is almost completely retrieved after each depressurization cycle, confirming reversibility and, accordingly, an elastic response of the network. When pressure is increased again, the curve nearly retraces the previous one, just showing a slight deviation associated with the small volume not retrieved. In Tegovakon V gel without membrane, the retrieved volume

Table 4
Mean results of mercury porosimetry curves

Gel	M (%)	V_{Hg} (mm^3/g)	V_R (mm^3/g)	V_R (%)	P_c (MPa)
Wacker OH					
With rubber	0 (0.0)	55.06 (2.80)	48.46 (2.07)	88	–
Without rubber	0 (0.0)	58.10 (2.32)	51.50 (1.65)	88	–
Tegovakon V					
With rubber	0 (0.0)	50.43 (1.96)	30.81 (1.14)	81	–
Without rubber	20 (1.5)	53.10 (1.76)	42.78 (1.78)	61	257.9 (3.56)

M (%) is mass variation of specimen after test. V_{Hg} is lost volume of mercury at maximum pressure. V_R is retrieved volume after depressurization. P_c is pressure at which mercury begins to intrude into the gel. Standard deviations are shown in brackets.

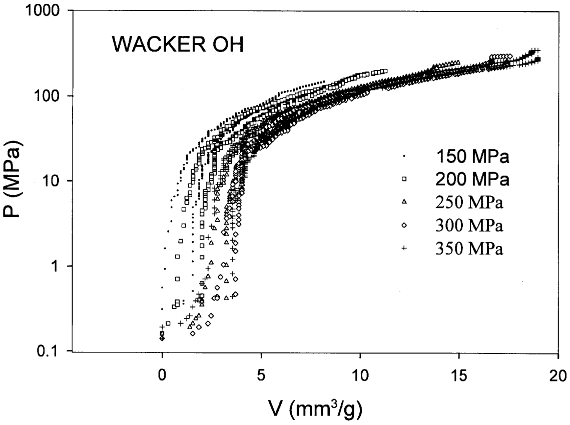

Fig. 3. Sequential pressurization/depressurization, volume vs pressure. Symbols indicate highest pressure reached in each cycle.

decreases (to 60% of total) and hysteresis is observed in the cycle. This irreversible process is associated with mercury intrusion into the porous network of the gel, as was previously reported by Pirard et al. [19] in xerogels of low density.

In the absence of irreversible deformation, the volumetric strain $\mathrm{d}V$ shows a linear response to pressure increase $\mathrm{d}P$. The slope defines the bulk modulus, K, according to the relationship: $\mathrm{d}P = -K(\mathrm{d}V/V)$ where V is the initial volume of the specimen. For both xerogels (Fig. 4, Table 5), a constant modulus ($r > 0.99$) during the complete pressure cycle is obtained. Both gels exhibit high bulk moduli due to the low strain of materials under mercury pressure. The slight increase in modulus of Tegovakon gel is related to its higher density.

As shown in Fig. 5, nitrogen adsorption isotherms of the two gels are close to standard microporous material isotherms (type I according to BDDT classification). For Wacker OH, its pore size distribution is below 10 Å, on the threshold of the equipment. Tegovakon V gel shows a higher amplitude in its pore size distribution, its maximum pore radius being close to 30 Å (Fig. 6). After

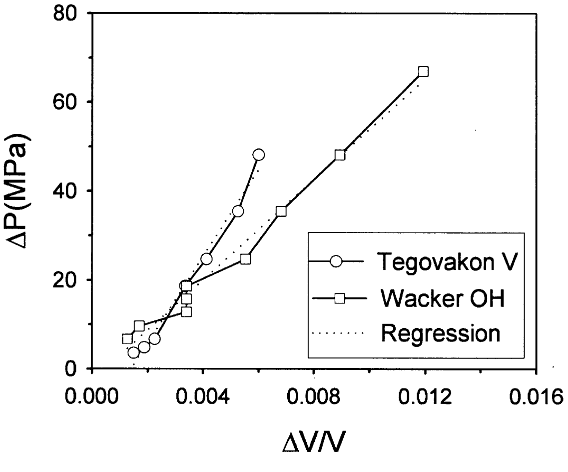

Fig. 4. Curve of volumetric deformation ($\Delta V/V$) vs pressure increase (ΔP) for gels studied. Curve slope is bulk modulus (K).

Table 5
Fitting parameters to stress–strain curve

Gel	ρ (g/cm³)	K (MPa)	r	V (cm³/g)
Wacker OH	1.392 (0.05)	5502 (332.3)	>0.99	0.22
Tegovakon V	1.627 (0.10)	7579 (257.4)	>0.99	0.52

ρ is bulk density before compaction. K is bulk modulus. r is linear correlation coefficient. V is porous volume of gels obtained by nitrogen adsorption test. Bulk density and bulk modulus data are mean values in three specimens of each type.

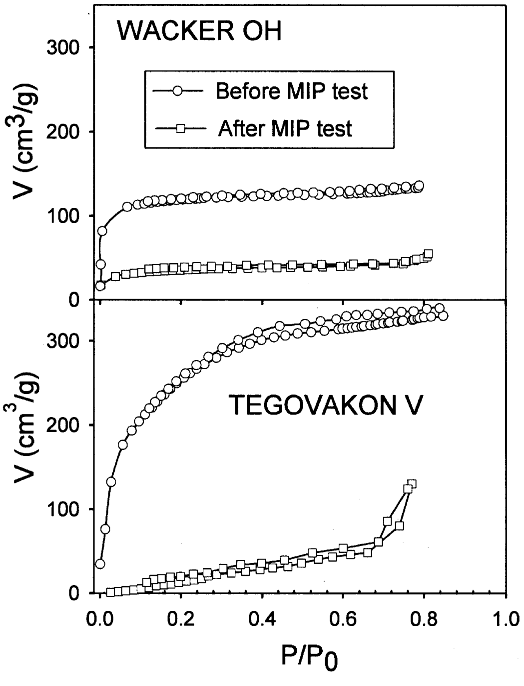

Fig. 5. Nitrogen adsorption isotherms at 77 K.

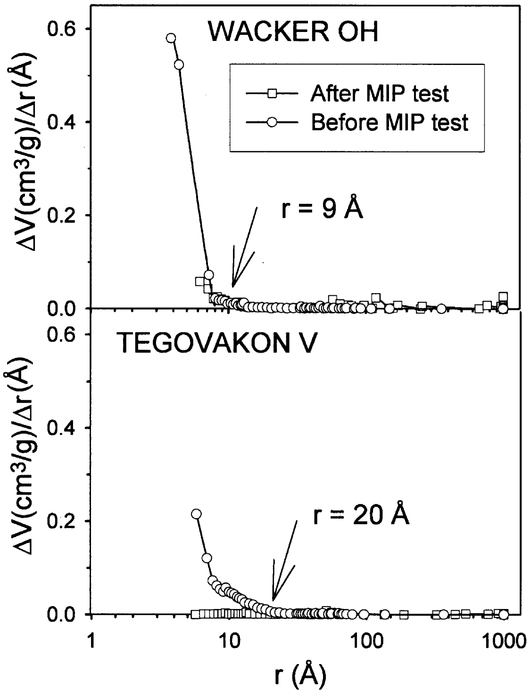

Fig. 6. Pore radius distribution of gels, volume variation ($\Delta V/\Delta r$) vs pore radius (r), obtained from nitrogen adsorption isotherms.

MIP test, a clear decrease of the adsorbed nitrogen volume in the microporosity range is observed in both gels.

4. Discussion

The first point to consider is the suitability of mercury porosimetry experiments for characterizing changes in the porous structure of rocks caused by consolidation. When xerogels prepared from Wacker OH consolidant are pressurized, their porous network is compressed, but mercury is not intruded into the pores. In Tegovakon V xerogels, a similar shrinkage occurs until a pressure of 258 MPa is reached. Above this value, pressure does intrude mercury into their porous structure. Consequently, the classical data interpretation based on intrusion of mercury fails and this experiment cannot characterize the gel porous structure. Therefore, the increase in volume lost of mercury observed in the granites after consolidation (Fig. 1) cannot always be interpreted as an increased porosity of the stone's network. It could actually be related to gel shrinkage on subjection to mercury pressure. Mercury porosimetry thus is not a suitable tool for predicting microstructural changes in consolidated stones.

In Roan and Baleante granites consolidated using Wacker OH, there is a larger volume increase than in these granites consolidated using Tegovakon (Fig. 1). This difference could be due to Wacker OH having a lower modulus, and thus a higher strain under pressure. In addition to the intrusion of mercury under high pressure into the network of Tegovakon gel, its higher modulus explains the smaller volume increase or even the volume reduction in these stones.

In the case of Axeitos granite, the decrease in volume lost of mercury observed after application of these consolidants can be related to the anomalous porous network of this rock. Its porosity distribution consists practically completely of macropores (90%) where mercury is intruded at such a low pressure that the gel does not deform. In this case, interpretation of results could be based on the assumption that mercury penetrates into the macroporous structure of the stone. Thus, the reduction of volume lost after treatment can be associated with the presence of the consolidant.

To explain the reason for mercury intrusion into the Tegovakon network at high pressures, we analyzed the intrusion conditions as a function of modulus and pore size of gel. This analysis is based on the equations developed by Scherer et al. [8], who assumes that pore size decreases roughly in proportion to the contraction of volume, so in the elastic regime:

$$\frac{2\gamma\cos\theta}{r_{\mathrm{BT}(0)}K_0} = \left(\frac{V_0}{V}\right)^{-1}\ln\left(\frac{V_0}{V}\right),$$

where γ and θ are the surface tension and contact angle, respectively, for mercury; $r_{\mathrm{BT}(0)}$ represents the minimum pore radius which the gel network should have to allow mercury intrusion; K_0 is the bulk modulus of the gel; V_0 and V are the initial specific volume and the specific volume at a certain pressure P, respectively.

Using this equation, we found that when maximum pressure is 400 MPa, in Wacker OH no mercury penetration occurs if $r_{BT(0)}$ is below 14 Å. For Tegovakon V, no intrusion takes place if $r_{BT(0)}$ is below 12 Å. Our findings are supported by nitrogen adsorption data (Fig. 6), because in the Wacker OH gel, where there is no intrusion, pore radius is below 9 Å. Conversely, Tegovakon gel, where intrusion is possible at high pressures, has a porous network with a maximum pore radius of 20 Å. Although gel shrinkage may perfectly explain the increase in lost mercury volume measured by the porosimeter, an increase in the porosity of the stone after consolidant drying cannot be completely discounted.

Regarding the study of the shrinkage behavior of the xerogels under isostatic pressure, both gels show small strain under the pressures applied. As the bulk moduli are constant across the pressure range (Fig. 4, Table 5), the process is practically reversible and hence, elastic. However, it is should be taken into account that a small volume is not retrieved after depressurization (12% in Wacker OH and 19% in Tegovakon V). This is clearly seen from sequential pressure cycles applied to Wacker OH, where a slight and progressive densification of gel with each cycle can be appreciated (Fig. 3).

From the comparison of our data with those of aerogels and xerogels reported in the literature [9–13,19], an anomalous behavior of gels made from commercial consolidants can be reported. For aero- and xerogels, large and irreversible shrinkage is observed, while in the products under study the shrinkage is small and mostly reversible. We associate this anomalous behavior with the unusual pore size distribution of their network. Specifically, while TEOS gels are known to be mesoporous materials with pore size ranging widely from 1 to 10^3 nm, the gels prepared in this study exhibit pore sizes of less than 30 Å. The presence of unspecified additives in these commercial products could be responsible for this unusual pore distribution. As Pirard demonstrated [9,14], the compaction mechanism is based on the preferential collapse of the larger pores of the gel. Thus, a direct relationship between pore distribution and mechanical performance of the gel is established. Therefore, the high rigidity of gels made from the commercial consolidants studied and their anomalous elastic behavior are related to the low microporosity of their networks. Further, the reduction of the porous volume of these gels after compaction (Fig. 5) corroborates the mechanism of collapse described by Pirard.

Finally, the shrinkage of a gel under mercury pressure can be used to characterize its behavior during the process of drying in stones, as Scherer has reported [10]. When a consolidant dries inside a stone, the gel network contracts developing tensile stress, which could cause cracking [20]. Therefore, characterization of the drying process is a key factor in the consolidation process. The small pore size of gels from commercial consolidants and their high rigidity implies the development of high capillary pressures during drying. This feature confirms previous experimental results showing that alkoxysilane consolidants form brittle and highly cracked gels within the stone [21–23]. In a forthcoming article [24], we investigate the drying behavior of gels made from the commercial consolidants studied here.

5. Conclusions

Xerogels from two commercial stone consolidants pressurized in mercury porosimetry are compacted and thus little or no mercury intrusion into the gel network occurs. This indicates that porosimetry is not a suitable tool for predicting microstructure changes in consolidated stones. The reason why mercury intrusion does not occur is the small pore size of the gel network. In fact, at maximum porosimetry pressure, intrusion occurs only with Tegovakon gel because it exhibits higher pore radii than Wacker OH gel. Pore size distribution in stones is a key factor for predicting the validity of MIP results, because consolidants are not compacted at low pressures. Therefore, when stones exhibit large pore sizes, mercury volume lost is due to intrusion into stone pores while for stones with low pore size, volume lost after high pressure MIP is related to gel strain.

However, since the gel is compacted, mercury porosimetry can be used to characterize gel shrinkage under mercury pressure. For the two commercial consolidants tested, high values of the bulk moduli, which imply a high rigidity of gel network, are observed. This is a consequence of the low microporosity of gels. Finally, the reduction of micropores following MIP confirms that gel shrinkage occurs through pore collapse.

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