Journal of Sol-Gel Science and Technology 26, 1227–1231, 2003

Stress During Drying of Two Stone Consolidants Applied in Monumental Conservation

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Abstract. The object of this paper is to evaluate behaviour during drying of two stone consolidants: Wacker OH and Tegovakon V, containing tetraethoxysilane. During drying, the gel network contracts due to capillary pressure generated by solvent evaporation. When the consolidant dries inside the stone porous structure, the shrinkage is constrained in all three dimensions. In these conditions, the dried gel suffers a high stress that could cause it to crack. When there is a free surface, as for a consolidant layer on the surface of a pore, the stress can relax in the direction normal to the surface. In this case, the stress is controlled by network rigidity.

The rigidity of the gel network has been evaluated by mercury porosimetry, while pore size, which controls capillary pressure, has been determined by nitrogen adsorption. The shrinkage of gels under mercury pressure is characterised by high moduli. This fact suggests a high rigidity of the networks. The small pore radii found in the network (<3 nm) indicate that high capillary pressures are generated within the gel network.

Keywords: consolidants, drying, porous structure, mercury porosimetry, mechanical behaviour

1. Introduction

Alkoxysilanes, such as tetraethoxysilanes (TEOS), are commonly applied as stone consolidant in the restoration of monuments. The product, which is applied as a low viscosity monomer, can penetrate deep into the stone, and polymerise homogeneously to give a stable consolidant with silicon-oxygen backbone similar to typical rock minerals [1]. However, the drawback is that the characteristics of consolidants when applied within stone are highly sensitive to modifications of the conditions of the sol-gel process. Therefore, the evaluation of the different stages through which a consolidant passes to reach full gelation is critical for selecting the most suitable product for a particular application. Although hydrolysis and polymerisation have been studied, aging and drying processes of gel have not been properly considered.

As Scherer and Wheeler previously reported [2], when the liquid solvent evaporates during consolidant drying, a liquid-vapour meniscus below 90° is formed, and thus a negative pressure is generated in liquid. This tension is balanced by the shrinkage of gel. If gel shrinkage is constrained in all three directions, the stress in the gel network is equal to capillary pressure, p_c. In the case of gel filling the cylindrical pores of a stone, p_c is:

$$\partial_r = \partial_z = -p_c = \frac{2\gamma_{LV}\cos\theta}{r_p} \qquad (1)$$

where ∂_r and ∂_z are the radial and axial stresses, γ_{LV} is the liquid-vapour interfacial energy, θ is the contact angle, and r_p is the pore radius in the gel.

When a layer of gel drying on the exposed surface of stone, it is free to shrink in the direction perpendicular

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to the surface. In this case, the stress is lower and depends on the rigidity of the gel network. If the gel is compliant, all its pores could collapse. In rigid networks, shrinkage stops before the pore collapse. Stress in the plane of the surface σ_x is:

$$\partial_x = \left(\frac{1-2v}{1v}\right)p \tag{2}$$

where v is Poison's ratio for the network.

Scherer and Wheeler [2] evaluated the visco-elastic properties of wet gels from Conservare OH (the commercial name of Wacker OH in USA) by a beam-bending experiment. From this experiment, they calculated gel permeability, which permitted a calculation of the network pore size. They concluded that the small radius of network pores (around 3.6 nm) gives rise to high capillary pressures. However, the gel is so compliant (Young's modulus of 1.1 MPa) that it could collapse completely under stress.

In a previous study [3], we analysed the behaviour of xerogels prepared from two commercial consolidants: Wacker OH and Tegovakon V under the isostatic pressure of a Mercury Porosimeter. Gels were prepared by the classical sol-gel process (water/TEOS ratio 4:1). As other authors have reported for aerogels [4, 5], we observed that the gels were compacted and mercury was hardly intruded at all. As a result, we concluded that porosimetry data is suitable for predicting the shrinkage of gels, which is a key factor in the evaluation of how a consolidant dries within a stone. The two gels showed an elastic behaviour with small strain, which suggested a high rigidity of networks. Such rigidity was associated with the low microporosity of the two gels.

The purpose of this paper is to characterise the drying process of these commercial consolidants. We have measured the pore size of dried gels by nitrogen adsorption; this permits the calculation of capillary pressures that are responsible for stress in gels consolidated into stone. By evaluating gel behaviour under isostatic pressure provided by mercury porosimetry, we have characterised the rigidity of gel networks, this being a key factor in the drying of a consolidant gel on the surface of a stone.

2. Experimental

Wacker OH (Wacker) and Tegovakon V (Goldsmith), two popular commercial consolidants used in monumental restoration, are evaluated in this paper. Hydrolysed and pre-polymerized tetraethoxysilane (TEOS), is contained in the two commercial products (proportions: $<50\%$ and $>75\%$, respectively). As TEOS is hydrolysed and pre-polymerised, atmospheric moisture is not a limiting factor in the polymerisation process.

Xerogels were prepared in the laboratory by exposure of commercial products to an environment with relative humidity of 50% and temperature of 20°C. The samples gelled in 2–3 days. The gels were aged and dried at room temperature until no change of weight was observed (2–3 weeks). In order to make the samples monolithic, the evaporation rate was controlled to be slow.

Runs of Mercury Intrusion Porosimetry (M.I.P.) were carried out over a pressure range of 0.1 to 400 MPa. The corresponding depressurisation paths were also recorded. The apparent density of specimens was measured at atmospheric pressure. Initially, the samples were enclosed in a rubber membrane using a rotary vacuum pump, to avoid mercury intrusion. MIP was performed on a second batch of specimens without the membrane for comparison. In order to ascertain whether any mercury was retained within the gel network, sample weight was checked before and after the run.

Textural features of the gels were evaluated by physical adsorption of nitrogen on their free surface. Samples were previously evacuated, using a rotatory pump to remove the liquid from the pores, at 75°C. Pore size distribution, specific surface area and porous volume values were obtained. Analysis of adsorption-desorption isotherms enabled the determination of pore size distributions, using the Horvath/Kawazoe method.

3. Results and Discussion

The behaviour of gels under mercury pressure is shown in Fig. 1. In both cases, a slight weight increase was observed after tests in gels run without membrane, while weight was not altered after tests with membrane (Table 1). Consequently, mercury intrusion did occur in the two gels tested without membrane. However, we observed that the volume lost during pressurization is basically due to material strain, because the curves are very similar. Therefore, mercury porosimetry results can be used for predicting the shrinkage of gels.

In both gels, the strain is significant at pressures over 100 MPa (Fig. 1). The depressurization curves

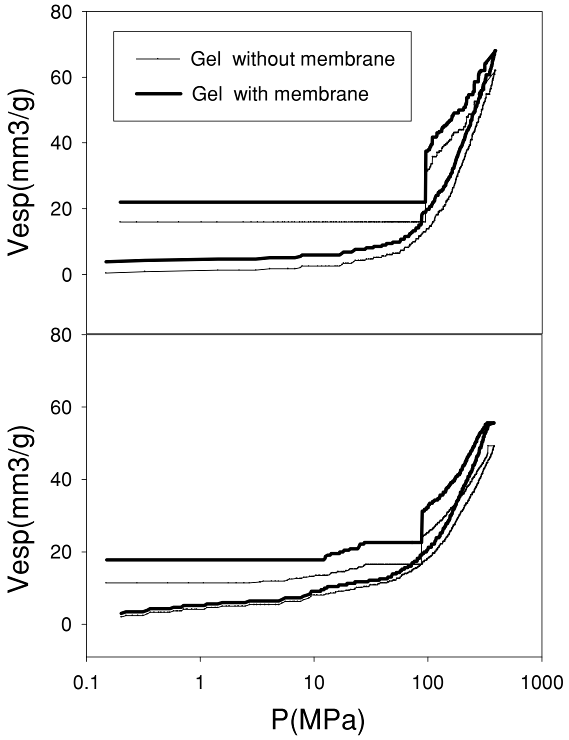

Figure 1. Mercury porosimetry curves, volume vs pressure, for monolithic gels.

show an abrupt volume change at 100 MPa. This is associated with the extrusion of mercury previously intruded into the network pores, or confined by the membrane. Since the major proportion of the initial volume is retrieved after the depressurization cycles (Table 1), the shrinkage can be considered basically reversible, which means in practice that the gel presents an elastic behaviour. In the absence of irreversible deformation, the volumetric strain dV shows a linear response to pressure increase dP [4]. Therefore, the bulk moduli were calculated according to the relationship: $dP = -K(dV/V)$, where V is initial volume. Both gels exhibit high moduli as a consequence of the low strain occurred (Table 2).

Table 1. Mercury porosimetry curves results.

GEL		M (%)	V_{Hg} (mm^3/g)	V_{R}(%)
WACKER OH	With rubber	0.0	55.6	68
	Without rubber	3.4	49.3	79
TEGOVAKON V	With rubber	0.0	68.1	68
	Without rubber	3.9	62.1	75

M is mass increase after test. V_{Hg} is lost volume of mercury. V_{R} is retrieved volume after depressurisation.

Table 2. Gels characteristics.

GEL	ρ (g/cm^3)	K (MPa)	r	V (cm^3/g)	S_{BET} (m^2/g)
WACKER OH	0.786	5945	0.98	0.29	318
TEGOVAKON V	0.473	5789	0.98	0.40	525

ρ is bulk density before compaction. K is bulk modulus. r is linear correlation coefficient. V is porous volume measured by nitrogen adsorption. S_{BET} is BET surface area.

Figure 2 shows the adsorption-desorption isotherms that correspond to mesoporous materials of IUPAC type IV. Nevertheless the hysteresis loop due to capillary condensation is associated with the H4 loop of the IUPAC classification, which characterises isotherms with closed shape as corresponding to microporous solids (type I). A high adsorption takes place for low relative pressure values, indicating that the average size of pore in the network is small. At higher relative pressures, a plateau in the curve reveals that additional adsorption is very limited and, consequently, the proportion of larger pore sizes in the two gels is low. However, the hysteresis loop in the plateau region indicates the existence of mesoporosity, in both xerogels.

Pore radius distributions obtained from desorption branch data are plotted in Fig. 3. Average pore radius is around 1 nm in both distributions. Wacker OH presents pore radii of up to 1.5 nm, whereas in Tegovakon V, a wider pore size distribution is observed with radii up to 3 nm. In both cases, distributions range across the limits between micro and mesoporous regions.

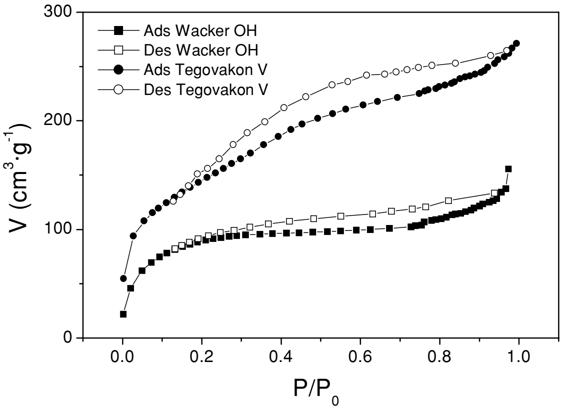

Figure 2. Nitrogen adsorption isotherms at 77 K.

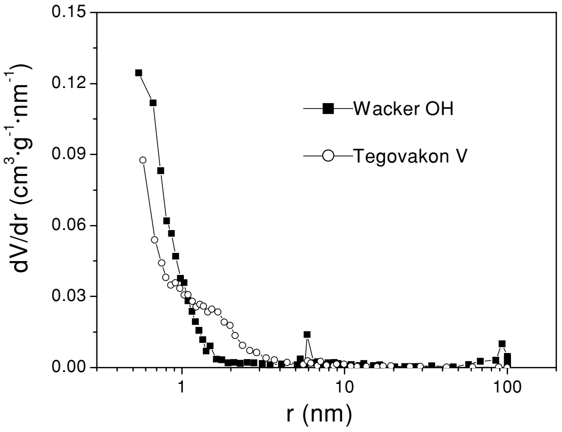

Figure 3. Pore radius distribution of gels, volume variation ($\Delta V/\Delta r$) vs pore radius (r), obtained from nitrogen adsorption isotherms.

In comparison with classical aerogels, the xerogels studied exhibit a lower porous volume (Table 2) and smaller pore radii. These characteristics could explain their different behaviour under pressure. Aerogels, typical mesoporous materials, show large and plastic strains under mercury pressure [5–7]. As plastic strain is the consequence of a collapse of the pores in the network [5], the low microporosity of the gels evaluated would be responsible for the high rigidity of the material. The small volume not retrieved after depressurization could be the result of pore collapse.

Furthermore, from the comparison of the shrinkage of gels tested in this paper with that of gels from the same precursors but prepared by the classical sol-gel process [3], we observe a similar behaviour. The slight differences appreciated are associated with modifications in the microstructure. As expected, the use of acid water in the classical process [3] slightly reduced the pore size and the porous volume of their network. This explains why in the earlier paper the pore radius distribution of Wacker OH gel exhibited slightly lower values (below 1 nm) than those obtained in this study (below 1.5 nm). For Tegovakon gels, the porous volume of specimens tested is significantly lower (0.40 cm^3/g) than that of the earlier work (0.52 cm^3/g). These values explain the significantly reduced value (around 2000 MPa) obtained for its modulus.

Finally, we used the microstructural data and shrinkage behaviour of gels together to evaluate their behaviour during drying. In the case of drying inside the stone, capillary pressure, which is inversed to the pore size of the network, controls the process. We calculated capillary pressure using equation 1 given in the Introduction. For an average pore radius of 1 nm, a high value of capillary pressure (around 40 MPa) is obtained. This high pressure could cause network cracking. This conclusion is confirmed by previous experimental results, which have shown that TEOS consolidants form brittle and highly cracked gels inside stone [8].

In the case of gel that forms on the surface of stone, stress is controlled by gel rigidity. As consequence of the high rigidity of networks, a high stress, equal to the capillary pressure, would occur. The small pore radius of wet gels from Wacker OH, around 3 nm, obtained by Scherer and Wheeler [2] confirms that only limited shrinkage occurs during drying.

4. Conclusions

Mercury porosimetry is a suitable tool for predicting shrinkage of gels made from commercial consolidants. The high values of the bulk moduli of the network and their elastic behaviour are consequences of their low porosity.

Pore size of the dry gels is estimated to be low. Such small pores give rise to high capillary pressure during gel drying inside the stone pore structure. In gels formed on the surface of stone, the high rigidity of networks implies that stress would be also controlled by capillary pressure.

Acknowledgments

The present study was supported by the Spanish Government: Ministerio de Ciencia y Tecnología as part of the Project MAT2001-3805. The authors are grateful to Goldsmith España, S.A. and Wacker Química Ibérica, S.A. for supplying commercial consolidants, and to Dr. R. Litrán for helping in nitrogen adsorption experiments.

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