



DRYING METHODS PRESERVING THE TEXTURAL PROPERTIES OF GELS

G. Pajonk

► To cite this version:

G. Pajonk. DRYING METHODS PRESERVING THE TEXTURAL PROPERTIES OF GELS. Journal de Physique Colloques, 1989, 50 (C4), pp.C4-13-C4-22. 10.1051/jphyscol:1989403 . jpa-00229478

HAL Id: jpa-00229478

<https://hal.science/jpa-00229478>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DRYING METHODS PRESERVING THE TEXTURAL PROPERTIES OF GELS

G.M. PAJONK

*Université Claude Bernard Lyon I, Laboratoire de Thermodynamique et
Cinétique Chimiques, CNRS UA-231, 43 bd du 11 novembre 1918, F-69622
Villeurbanne Cedex, France*

Résumé - Il est possible de préserver plus ou moins la texture des gels au cours du séchage grâce à trois procédés principaux qui diffèrent en gros par le domaine des températures et des pressions qui les caractérise. Dans l'ordre croissant des températures et des pressions on peut distinguer : la cryodessiccation qui permet d'obtenir des cryogels (basses températures et pressions) - le séchage classique conduisant aux xérogels (températures et pressions habituelles ou faibles) et enfin le séchage dans les conditions supercritiques qui donne les aérogels (températures et pressions élevées).

Abstract - To preserve more or less the gels textural properties during their drying step three main methods can be applied which differ roughly by the temperature and pressure range in which they are conducted. In increasing temperatures and pressures ranking one may distinguish : i) the freeze drying process giving "cryogels" (low pressures and temperatures), ii) the ordinary drying method leading to xerogels (ordinary or low pressures and temperatures) and finally, iii) the supercritical drying method producing aerogels (high pressures and temperatures).

1 - INTRODUCTION

The sol-gel technique has become a widely used method in order to obtain highly divided solids (powders, monoliths, microspheres, etc...) having textural properties very well developed (surface area, porous volume, etc...). The dried gel is generally a precursor such as in the fabrication of glasses, catalysts, ceramics, adsorbents, composites whose properties are essential with respect to the final desired product /1, 2, 3, 4/.

As a gel is usually regarded as a semi-solid having immobilized the solvent (mostly water) in a network of fine capillaries the drying conditions (nature of solvent, rate of heating or method of evacuation of the liquid part, duration, final temperature, etc...) are important factors that influence the texture of the dried solid (generally named xerogel after the greek word for dried).

Figure 1 depicts the sol-gel transformation leading to a hydrogel for instance /1, 3/.

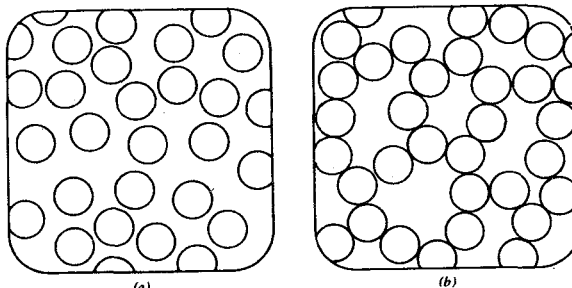


Fig. 1 - a) sol, b) gel.

Now in order to preserve the porous texture of the wet gel surface tension forces developed by the liquid-vapour interface menisci in the fine capillaries (or pores) must be counterbalanced if shrinkage is to be avoided. This shrinkage process is at the heart of the drying problem and the following methods described below give instructions how to "escape" pore collapse and surface area decrease phenomena taking into account that in this paper hydrothermal treatments modifying for instance surface areas (or particle size) will not be described.

A general picture of the drying step of a wet gel into a dried one is given on figures 2 for a ceramic body and 3 for clay as examples /5/.

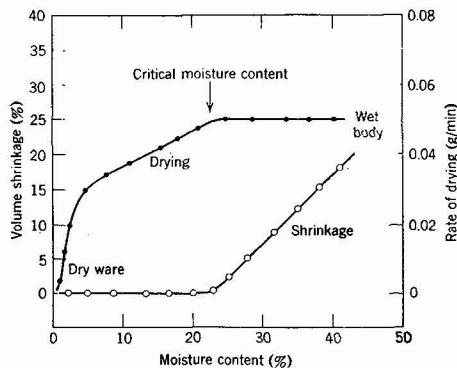


Fig. 2 - Rate of drying and drying shrinkage for a ceramic body. At a critical moisture content which corresponds to the solid particles coming into contact, the rate of drying begins to decrease and the shrinkage stops.

It can be seen here that the shrinkage is almost completed in the constant rate drying period (figures 2 and 3). At the critical point the rate begins to decrease continuously. The first rate period corresponds to the rate of evaporation of "free" water films while the decreasing rate period belongs to water being removed from the interior of the body to the surface.

A more detailed comment is given below when the case of silicagel is considered (see figure 6).

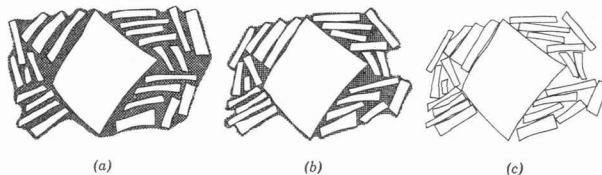


Fig. 3 - Drying process for a clay body showing (a) wet body, (b) critical point and (c) dry ware.

A good representation of how the surface tension forces are acting on the pore walls is given in Figure 4 /1/.

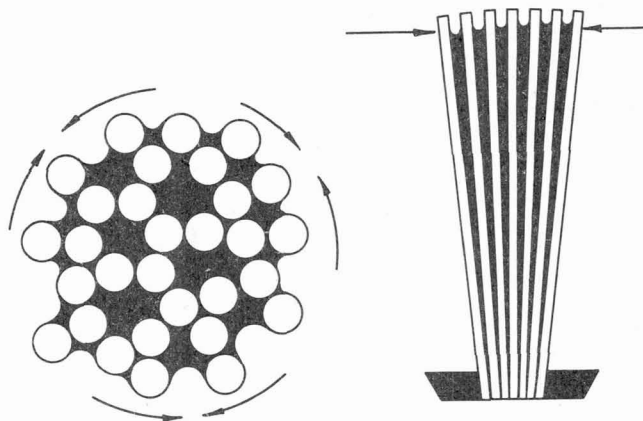


Fig. 4 - The forces that cause silica gel to shrink during drying resemble those that cause wet plates of glass to draw together.

For instance if the pore width is of the order of 1.5 nm the capillary compression exerted will be equivalent to 10^4 psi and higher for smaller pores.

Finally as silica gels are one of the most frequent gels Figure 5 describes the hydrogel-xerogel transformation in details /1/.

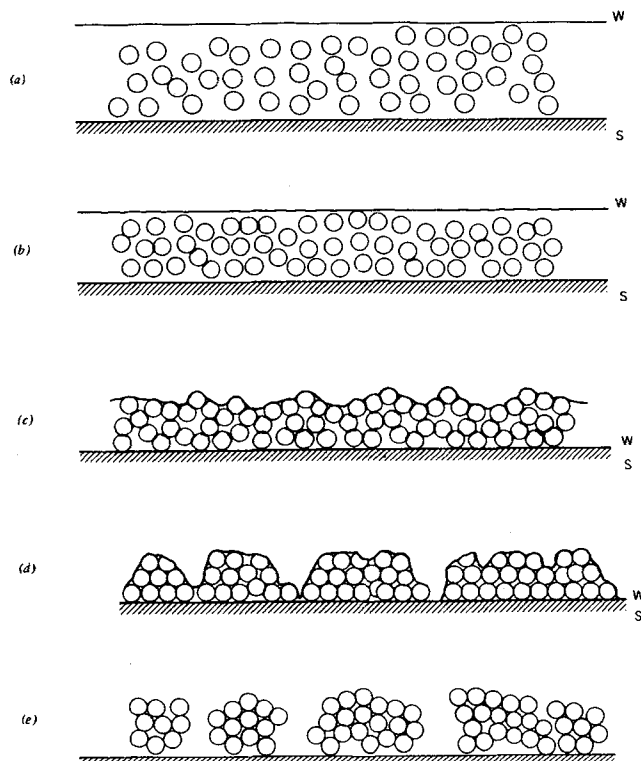


Fig. 5 - Evaporating film of silica sol to gel and drying-schematic cross section. (a) Sol ; (b) concentrated sol-beginning of aggregation ; (c) gel compressed by surface tension ; (d) fracturing of gel by shrinkage ; (e) dried loose gel fragments. W = water surface, S = solid substrate.

A complete set of data concerning the drying of a hydrogel is represented in Figure 6 for silica and can be generalized for other wet gels as well /6/. In this figure step I (constant rate period) is related to the decrease of volume of the "still" hydrogel while step II shows the effect of capillary compressive forces counterbalanced by the resistance of the actual framework of the gel. Then step III corresponding to the decreasing drying rate occurs now without appreciable volume change and is accompanied by the hysteresis exhibited by the adsorption-desorption isotherm of water by the gel. This means that water is removed from the pores, the larger ones being emptied first. The smaller the pores the slower the drying rate. Finally step IV represents evaporation of water from contact points between the silica particles.

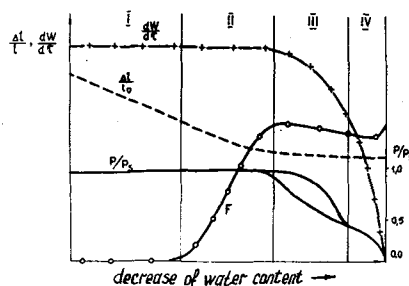


Fig. 6 - Drying steps and the formation of the framework of xerogels, dW/dt = drying rate, $\Delta l/l_0$ = relative deformation, P/P_s = relative vapor pressure, F = contraction force.

The pore volume and pore radius modifications of a gel during the drying step are summarized on figure 7 /3/.

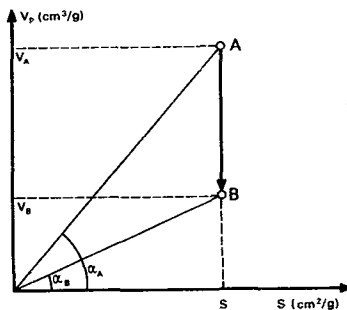


Fig. 7 - V_p : porous volume, S = surface area, $R = 2 V_p / S = 2 \tan \alpha$ = pore radii
 A^p corresponds to the hydrogel, B corresponds to the dried gel.

As the most encountered way of drying gives xerogel, the obtention of xerogels will be treated first, followed by aerogels and finally by cryogels.

2 - XEROGELS

According to Barby /7/ the drying method of gels can have five major influences.

First when water is present the hydrogel can be to some extent hydrothermally treated (steaming) and it can loose surface area and it increases its pore volume as pictured in figure 8 for silica.

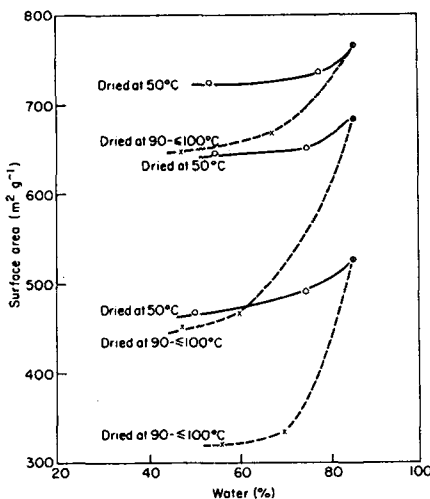


Fig. 8 - Drying hydrogels

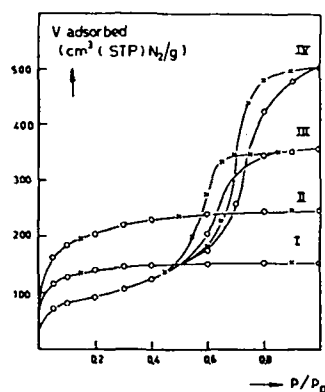
Thus it is possible now to distinguish between "hot" and "cold" drying under these conditions. For instance lowering the drying temperature impedes gel breakage, this result can be also obtained by increasing the relative humidity or reducing the air-flow across the gel /2/. Ternan et al /8/ prepared highly porous alumina xerogels using the low temperature drying method while when drying at higher temperatures ($T > 333$ K) pore collapse occurred due to pressure and temperature effects. They concluded that the low drying temperature influence is to remove water from the large pores.

Steaming occurs when the water vapor is not removed from the drying system as fast as it is generated. It has been observed that if this process builds up in the constant rate step then the silica gel exhibits large surface area and pore volume. Now if steaming proceeds during the decreasing rate step then the surface area as well as the pore volume decrease while cracks developed in the gel /2/.

It has also been shown that predrying treatments of silica gels at $T < 393$ K result in a decrease of pore volume with decreasing predrying temperatures but does not vary the surface area and the hydroxyl content /9/. Results are shown on table 1 and figure 9.

pH of formation	Predrying temp. in °C	BET m ² /g	Pore volume cm ³ /g	OH content in %
3.2	20	555	0.25	5.6
	40	630	0.28	6.0
	80	670	0.35	6.1
	120	675	0.38	6.1
7.0	20	330	0.59	3.7
	40	395	0.71	3.6
	80	345	0.78	3.6
	120	330	0.85	3.5

Table 1 -

Fig. 9 - N₂ adsorption isotherms.

- I. Silica prepared at pH = 3.2 predried at 20°C
- II. Silica prepared at pH = 3.2 no predrying
- III. Silica prepared at pH = 7 predried at 20°C
- IV. Silica prepared at pH = 7 no predrying.

Secondly the rate of drying is an important parameter because it can affect the particle size to a great extent /2/. In particular in order to prepare monoliths considerable drying times are necessary /10/. Drying times may vary from hours to weeks as in the case of lead-titanate monolith /11/ at 307 K or months as for TiO₂ monolith /12/ at room temperature.

It is well known at least for silica gels that step I of figure 6 determines the total porosity of the xerogel while step II imposes the pore size distribution. The surface area is a function of step III /13/. Thus by a rapid drying of the gel during step I and a smaller one during step II it is possible to prepare bimodal porous silica gels.

In general a rapid drying increases both pore volume and pore size distribution (pore size distributions are broadened). This is also confirmed for silica gels made from alkoxides /12/.

Thirdly it has been observed that if the drying rate is such that water is evaporated more rapidly than it can be removed then there is a decrease of gel shrinkage /2, 7/.

Fourthly it is well agreed that the degree of shrinkage is a function of the surface tension properties of the solvent. The smaller the liquid surface tension the lower the degree of shrinkage /2, 7/. This remark opens the field of nonaqueous drying. Water may be replaced by an organic liquid of lower surface tension or by using the same organic solvent instead of water for the gelation step. Alcohols are commonly used in this application.

A zeolitic texture type of alumina was prepared through the sol-gel method using methanol as solvent and the alcogel was dried at room temperature and under vacuum /14/. This type of alumina exhibited a unique microporous texture (Langmuir N₂ isotherm for instance) and a very high surface area $\approx$ 600 m²/g).

An interesting drying process which can be related to non aqueous drying involving DCCA (drying control chemical additive) is described in the paper of Wang and Hensch /15/. Addition of formamide in the $\text{Na}_2\text{O-SiO}_2$ sol preparation prevents fracture of the xerogel. It is believed that the amine groups build up hydrogen bonds between the hydroxide groups of the silica particle surface thus improving the strength of the gel. The main result is that with DCCA the critical shrinkage rate (leading to cracks when overcome) is substantially higher than without thus allowing higher drying rates and subsequently shorter drying times without cracking effects.

Uranium spheres UO_2 were also prepared by internal gelation and dried according to two ways : steam or air drying. The resulting xerogel spheres showed densities depending upon the drying conditions /16/. For example steam drying at 373 K gave microspheres with densities varying between 0.7 to 1 g/cm³ while air drying at 293 K led to densities comprised between 1.3 to 1.6 g/cm³.

3 - AEROGELS

To preserve at most the original texture of a wet gel the surface tension forces which develop in the pores when the solvent is evacuated giving a liquid-vapor meniscus must be completely eliminated during the drying stage. This is achieved by supercritical drying which gives "aerogels" instead of common xerogels. Details can be found in reference /17/. Water as solvent must be discarded because due to its high critical constants ($T_c = 647 \text{ K}$, $P_c = 218 \text{ bars}$) the gels are always recrystallized showing poor textural properties. Water is used only as a reactant partner in the sol step. Generally alcohols are preferred as solvents or CO_2 /18/ ($T_c = 304 \text{ K}$, $P_c = 73 \text{ bars}$). The supercritical drying method is the best way up to now to prepare monoliths without cracks and of large dimensions. Again here the heating rate of the autoclave and the venting rate are important factors controlling the quality of the aerogels /19/. A typical supercritical procedure is described on figure 10.

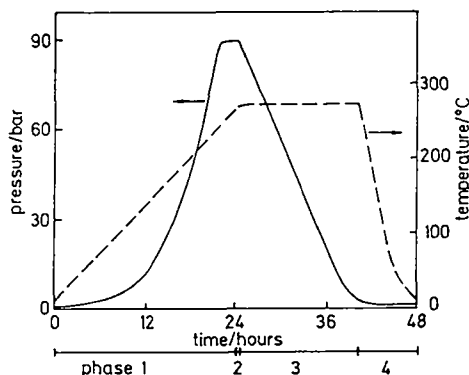


Fig. 10 - Autoclave cycle with the four phases : 1 = heating, 2 = equilibrium, 3 = vapour outlet, 4 = cooling.

Improvement of the aerogel drying method have been claimed by Mulder and van Lierop who applied a prepressure of 80 bars of N_2 prior to the heating step of the autoclave /20/ in order to avoid shrinkage. Table 2 shows the influence of the pressure upon the shrinkage. Moreover this last method does no more require to introduce extra alcohol in the autoclave to maintain the saturation pressure of the liquid (here ethanol for instance) and it shortens the time of the whole procedure as it can be seen on figure 11.

N_2 pressure (bar)	Specific density (g/cm ³)	Shrinkage (%)
0	0.49	73 (cracked)
10	0.27	52
40	0.14	7
80	0.13	0

Table 2 - Initial N_2 Pressure and Corresponding Density and Shrinkage of a Gel

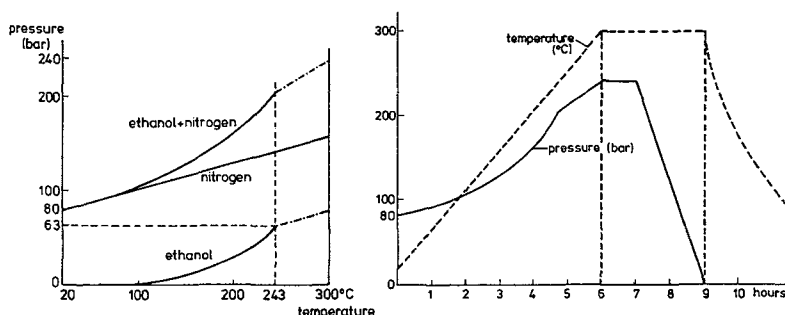


Fig. 11 - (a) Pressure of ethanol from room temperature to 300°C.

(b) Temperature and total pressure during a drying process, starting with 80 bar N_2 and a heating rate of 50°/h. After reaching 300°C decompression follows and finally the vessel is cooled down.

Other fluids can be used in supercritical drying such as the Freons 13, 23 or 116 but they are more expensive than CH_3OH , C_2H_5OH or CO_2 .

The supercritical drying method gives large size monoliths and very large pore volume aerogels under the form of monoliths, powders or granules and the general rules given for the aerogels also apply for aerogels.

4 - CRYOGELS (OR FREEZE-DRIED GELS)

The same reason of choosing the supercritical drying method can be involved in this process which consists to freeze the solvent (mainly water) and then to sublimate it under low pressure. Again the direct solid-vapour transformation can be achieved without the formation of a meniscus in the pores. The term cryogel is proposed by the author to distinguish the so dried gels from aerogels, though the resulting solids should be a priori comparable.

Figure 12 shows the pressure-temperature diagram for water. In this picture AB represents the curve for subliming ice. (Note that C is the critical point for water). Now when a salt is dissolved in water the pressure temperature diagram for the system is represented on figure 13. The freezing point of the system is depressed as is the water vapour pressure. At saturation an invariant point Q exists where four phases are in equilibrium: ice, anhydrous salt, saturated salt solution and water pressure. Q is often called the cryohydric point /21/. At pressures below this point water can be removed by sublimation until the anhydrous salt remains in a freeze-dryer as shown on figure 14 schematically.

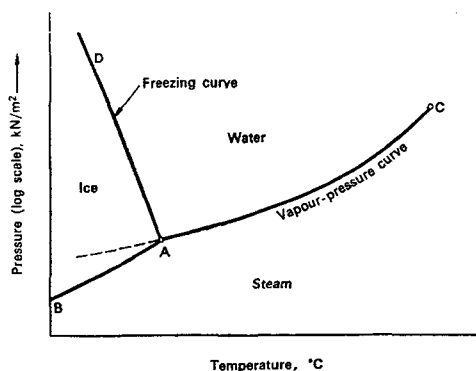


Fig. 12 - Pressure-temperature diagram for water.

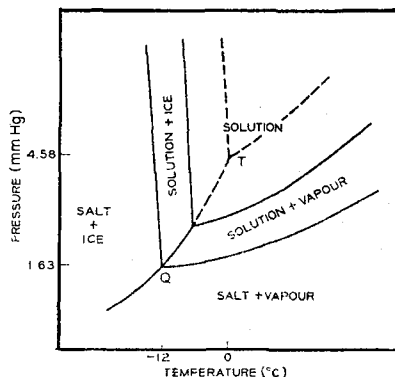


Fig. 13 - Temperature-pressure relations in a salt-water system. The dotted lines pertain to pure water (or solvent).

The main drawback of this drying method is the time required to sublimate the ice (or the frozen solvent). So heat is supplied from an external source to accelerate (without melting) the sublimation step, for instance via an infra red lamp /22/. It was shown that the time required to sublime 100 g of ice was reduced from 40 h to 4 h when heat was supplied by a i-r lamp, all other conditions being the same /23/.

It has been checked that cryogels such as Li doped NiSO_4 /22/, aluminium sulfate /24/, ammonium paratungstate /25/ are more developed from the textural point of view than their corresponding xerogels.

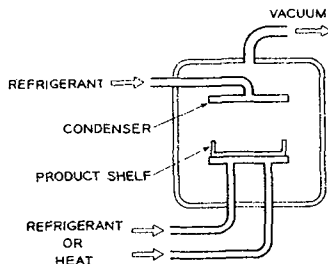


Fig. 14 - Schematic diagram of a freeze dryer.

The main parameters controlling the textural properties of the final cryogel seem to be the rate of freezing, the temperature of freezing and the nature of the solvent (which also determines the rate of sublimation).

For instance if a silica gel is frozen very quickly an extremely porous honeycomb material can be obtained, if the freezing rate of the gel is lowered chunks of porous silica cryogel are prepared as described by Mahler and Chowdhry /26/.

The temperatures of freezing as well as the drying temperatures seemed to exert an influence on the BET area of samples of pulpwood fibres according Swanson /27/. Table 3, shows that for a constant drying temperature decreasing the freezing temperature results in increasing the surface area, the same effect applies also when for a constant freezing temperature the drying temperature is decreased.

Freezing temperature °C	Drying temperature °C	BET area ($\text{m}^2 \text{g}^{-1}$)
- 20	- 5	1.20
- 80	- 5	1.62
- 80	- 20	1.81
- 195	- 20	3.17

Table 3 - Surface areas of fibres dried by sublimation of water

Finally Beyer et al. /24/ observed that the rates of subliming ice in aluminium sulfate -ice system gave different results. For instance using the long duration sublimation (70 up to 122 h) led to a mixture of amorphous and cristallized phases while using an infra-red lamp to accelerate the sublimation (33 up to 49 h) of the same mixture gave a quite complete amorphous cryogel. Due to processes of ovulation or spheroidization occuring when water separates into channels /24/ a macroporosity developed in both types of cryogels during sublimation. A difference was however observed : the high rate sublimed cryogel showed smaller average pore diameter, particle size and surface area than the other one (without heat supplied by the i-r lamp).

A comparison of drying a mixed oxide $\text{NiO-Al}_2\text{O}_3$ either by the supercritical process giving an aerogel or by freeze-drying is discussed in paper n° 23 in this Symposium /28/. The main difference between the two gels is in relation with their respective macropore volumes.

5 - MISCELLANEOUS

Two other drying modes are worthy to be mentionned here.

Spray drying is widely used to obtain microspheres of xerogel. The particle size depends upon the drying rate among other parameters. Spray drying is considered as a fast drying method.

Freeze-thawing /26/ is an interesting drying process leading to fibrillar gels developing porosity and high surface areas such as silica and zirconia fibers. This morphology seems to be due to the ice structure playing the role of a mould. As the solvent is not sublimed here surface tension forces build up during the thawing step, therefore it is advantageous to replace water by a lower surface tension liquid such as acetone in order to develop the total porosity of the final gel. Figure 15 demonstrates the effect of substituting acetone to water on the total porosity as well as on the pore size distribution.

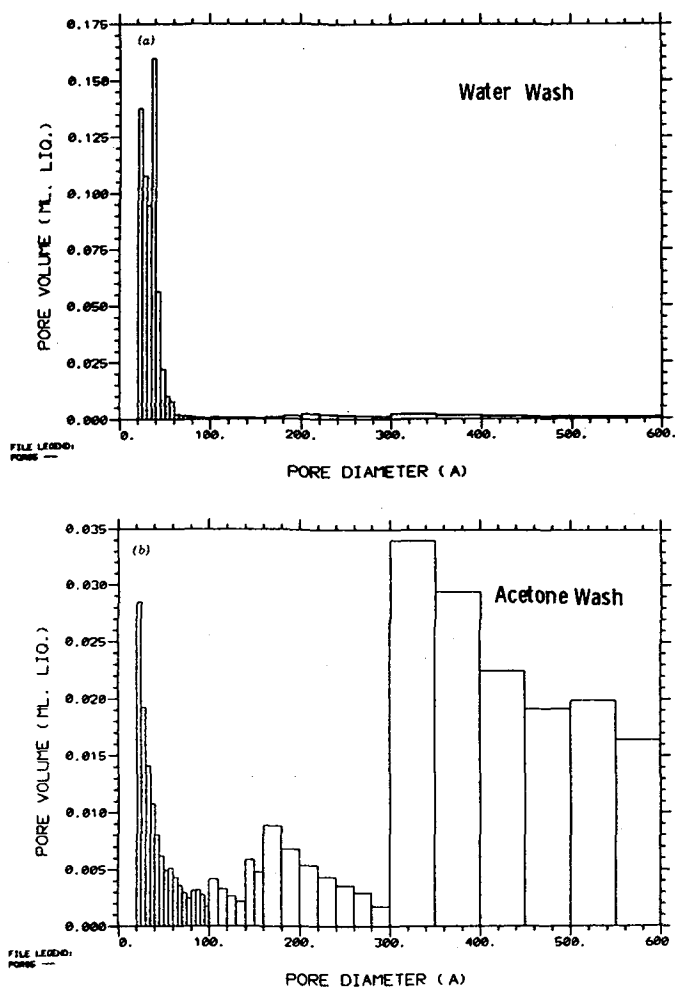


Fig. 15 - Effect of washing medium on pore size distribution of freeze-thawed silica.

6 - CONCLUSIONS

To summarize the many drying methods surveyed in this paper it is convenient to keep in mind primarily what is to be avoided in the final gel rather than what properties are expected because these characteristics depend on the three important previous stages of the sol-gel, process principally : hydrolysis, condensation and ageing.

In other words careful drying processes are to be used in order to preserve the general texture of the wet gel. In particular if cracks and/or shrinkage are not wanted a general rule seems to apply whatever the precise drying method to be finally choosen : if water is present as a solvent it may be important to replace it by a lower surface tension medium. Moreover combination of water (even as a reactant if in excess) and high temperatures are quite always detrimental towards the textural properties of the dried gel with respect to those characterizing the still soaked one, at least for silica /29/.

In 1972 R.B. Keey wrote in his book /5/ "The word drying is commonly used to describe any process in which water (or solvent) is removed from a substance" and adds he : "Drying is a commonly practised art but a neglected science".

The sol-gel process which is now increasingly developed to fabricate high technology materials has been an incentive to look at the drying step in more details since though not considered as a central or key step it may well determine the final properties exhibited by the end material.

REFERENCES

- /1/ Iler, R.K. in "The Chemistry of Silica", John Wiley, New-York 1979.
- /2/ Winyall, M.E. in "Applied Industrial Catalysis" Bruce E. Leach Ed., Academic Press, New-York, Vol. 3, 1984.
- /3/ Le Page, J.F. in "Catalyse de contact" Ed. Technip Paris, 1978.
- /4/ "Ultrastructure Processing of Ceramics Glasses and Composites" L.L. Hench and D.R. Ulrich Eds, John Wiley, New-York, 1984.
- /5/ Kingery, W.D. in "Introduction to Ceramics" John Wiley, New-York, 1960 and Keey R.B. in "Drying, Principles and Practice" Pergamon Press, New-York 1975.
- /6/ Boreskov, G.K. in "Preparation of Catalysts", B. Delmon, P.A. Jacobs and G. Poncelet Eds., Elsevier, Amsterdam, 1976.
- /7/ Barby, D. in "Characterization of Powder Surface", G.D. Parfitt and K.S.W. Sing Eds, Academic Press, New-York, 1976.
- /8/ Ternan, M., Packwood, R.H., Buchanan, R.M. and Parsons, B.I., Can. J. Chem. Eng., 60 (1982) 33.
- /9/ Okkerse, C. and De Boer, J.H., J. Chimie Physique, 57 (1960) 534.
- /10/ Zarzycki, J. in op cit ref. 4, p. 27.
- /11/ Gurkovich, S.R. and Blum, J.B. in op cit, ref. 4, p. 152.
- /12/ Prassas, M. and Hench, L.L. in op cit ref. 4, p. 100.
- /13/ Fenelonov, V.A., Gavrilov, V. Yu and Simonova, L.G. in "Preparation of catalysts III", G. Poncelet, P. Grange and B. Delmon Eds., Elsevier, Amsterdam, 1983, 665.
- /14/ Tournier, G., Lacroix-Repellin, M., Pajonk, G.M. and Teichner, S.J. in "Preparation of catalysts IV", B. Delmon, P. Grange and G. Poncelet Eds., Elsevier, Amsterdam 1987, 333.
- /15/ Wang, S.H. and Hench, L.L. in Mat. Res. Soc. Symp. Proceed, vol. 32, 71, North Holland, New-York, 1984.
- /16/ Haas, P.H., Begovich, J.M., Ryon, A.D. and Vavruska, J.S., Ind. Eng. Chem. Prod. Res. Dev., 19 (1980) 461.
- /17/ Teichner, S.J. in "Aerogels", p. 22, J. Fricke Ed., Springer Verlag, Berlin, 1986.
- /18/ Tewari, P.H., Hunt, A.J. and Lofftus, K.D. in op cit ref. 17, p. 31.
- /19/ Henning, S. in op cit ref. 17, p. 38.
- /20/ Mulder, C.A.M. and Van Lierop, J.G. in op cit ref. 17, p. 68.
- /21/ Schnettler, F.J., Monforte, F.R. and Rhodes, W.W. in "Science of Ceramics" Vol. 4. The British Ceramic Society, Stoke on Trent, 1968, p. 79.
- /22/ Kelly, J., Hibbert, D.B. and Tseung, A.C.C., J. Mat. Sci., 13 (1978) 1053.
- /23/ Hibbert, D.B. and Tseung, C.C., J. Mat. Sci., 14 (1979) 2665.
- /24/ Beyer, L.A., Kalnas, C.E., Roy, D. and Lloyd, I.K., Am. Ceram. Soc. Bull., 66 (1987) 1647.
- /25/ Sale, F.R. in "Fine Particles", W.E. Kuhn and J. Ehretsmann Eds. The Electrochemical Society, Princeton, 1974, p. 283.
- /26/ Mahler, W. and Chowdhry, U. in op cit ref. 4, p. 207.
- /27/ Swanson, J.W. in "Characterization of porous solids", S.J. Gregg, K.S.W. Sing and H.F. Stoeckli Eds, Society of Chemical Industry London, 1979, p. 339.
- /28/ Klvana, D., Chaouki, J., Repellin-Lacroix, M. and Pajonk, G.M., 2nd International Symposium on Aerogels ISA 2 - Montpellier 21st-23rd sept. 1988.
- /29/ Gavrilov, V. Yu, Karnaukhov, A.P. and Fenelonov, V.B., Kinet. i Katal., 19 (1978) 1549, (english translation).