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Synthesis of glasses from gels: the problem of monolithic gels

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The synthesis of glasses from gels has recently aroused considerable interest both from the theoretical and practical standpoint. The conditions of gel formation which determine the structure of the wet gel are first examined. During the drying process, which is a decisive step in the obtention of monolithic gels, an essential role is played by capillary forces. It is shown that, among the various methods of obtaining monolithic gels, that based on the hypercritical evacuation of the solvent is the most reliable.

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1. Introduction

The synthesis of glasses from gels is being actively investigated in many laboratories as the increasing potential importance of this method of preparing glasses is more and more recognized.

Essentially, in this process the required ingredients are reacted at low temperatures to constitute a gel which is then dried and densified to massive glass (Fig. 1). The gel route is attractive because glasses can be prepared at much lower temperatures than those required in direct fusion and quench of the liquid, and a high degree of homogeneity is readily attained on a molecular scale. Furthermore, the process lends itself not only to the preparation of massive pieces but also of thin coatings or fibres, interesting for sophisticated optical applications.

Classically, two ways are being explored, which differ in the starting compounds.

(1) Destabilization of a silica sol, type "Ludox"®; other ingredients, e.g. salt solutions, may be added which supply the required cations (Method I).

(2) Hydrolysis and polycondensation of mixtures or organometallic compounds in the presence of a limited amount of water (Method II).

The gel → glass process has been sucessfully applied to silica and a number of binary and ternary systems involved SiO_2. The main examples are given in Table I.

It must be recognized that, at the present time, while the final step, i.e. densification, is fairly well understood, the other steps, i.e. gel formation and especially the drying stage, have received much less attention. Densification is essentially a *sintering* process by which the pores of a dry gel are eliminated and the material converted into clear, massive glass. The driving force in this process is supplied by the surface energy of the porous gel. It tends to decrease the interface thus eliminating the pores, the collapse being governed in the case of glasses by Newtonian viscous flow. Extra pressure, as in hot-pressing techniques, may be applied to speed up the process.

The gel being densified will, at the same time, tend to devitrify. The successful conversion of gel into glass therefore depends on a competition between phenomena which lead to densification and those which promote crystallization. A detailed study of devitrification behaviour of SiO_2 gels was made using TTT (time–temperature–transformation) diagrams. It has led to the conclusion that a heterogeneous nucleation mechanism is operating here, associated with larger specific surface of the gel and also trace impurities [16, 17]. In particular the differences observed for SiO_2 gels prepared respectively from Ludox® and organometallic compounds were shown to be linked with the traces of Na^+ ions which prevent gels prepared from Ludox® being sintered to glass without devitrification [14].

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Figure 1 The gel → glass process.

For a gel of a given composition it thus appeared that the possibility of converting it into glass depends on its mode of preparation and the final impurity level. The mode of preparation determines the texture of the wet gel. This may, however, be further modified by the drying process leading to the dry gel required for densification process.

It is, therefore, interesting to discuss in more detail those two steps which condition the gel → glass procedure. In particular, if massive pieces of glass are to be obtained without the use of hot-pressing techniques, which have the disadvantage of limiting the specimen size, massive pieces of gels, not in particulate form, are required. The obtention of *monolithic* dry gels is thus an essential prerequisite. This seems to have provoked a lot of attention but the process has not been discussed and the solutions obtained so far have led to rather limited dimensions, of the order of 1 cm^3.

2. Gel formation

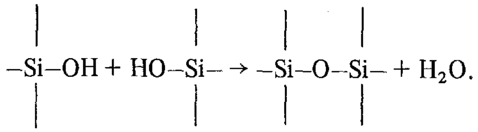
The formation of a pure silica gel involves a polymerization mechanism in which three essential stages may be distinguished (Fig. 2):

(a) polymerization of monomer to form primary particles;

(b) growth of the particles;

(c) linking of these particles together in chains, then into three-dimensional networks.

The polymerization reaction is based essentially on the condensation of silanol groups:



$$-\overset{|}{\underset{|}{Si}}-OH + HO-\overset{|}{\underset{|}{Si}}- \rightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O.$$

This reaction intervenes both in the primary particule formation steps as in their growth and subsequent linking.

TABLE I Binary and ternary systems involving SiO_2 studied for gel → glass transformation

Systems	References
Binary	
SiO_2–B_2O_3	[1, 2]
SiO_2–Al_2O_3	[3]
SiO_2–TiO_2	[4–6]
SiO_2–ZrO_2	[7]
SiO_2–SrO	[8]
SiO_2–CaO	[9]
SiO_2–Na_2O	[10, 11]
Ternary	
SiO_2–Na_2O–Al_2O_3	[12]
SiO_2–La_2O_3–Al_2O_3, SiO_2–La_2O_3–ZrO_2	[13]
Li_2O–Al_2O_3–SiO_2, Na_2O–B_2O_3–SiO_2	[14, 15]
Na_2O–ZrO_2–SiO_2	[7]

In *aqueous* solutions, monosilicic acid is stable at 25° C for long periods if its concentration is less than 100 ppm. For greater concentrations the monomer polymerizes by condensation to form dimer and higher molecular species (oligomers).

Above pH = 2 the rate is proportional to the concentration of OH^- ions, below pH = 2 to the H^+ ion. The tendency is to produce a maximum of Si–O–Si bonds and a minimum of uncondensed Si–OH groups, resulting in the formation of ring structures, then linking these cyclic polymers to larger three-dimensional molecules. The condensation leads to a most compact state, the Si–OH groups being placed at the outside of the condensate.

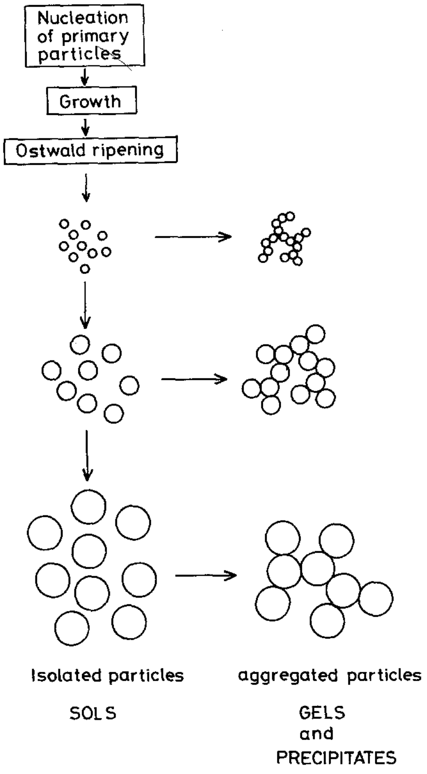


Figure 2 Polymerization steps leading to the formation of sols and gels.

These amorphous spheroidal groupings of about 1 to 2 nm are formed by a *nucleation* process in a similar way as in the case of the formation of crystalline precipitates. Because of the size differences. Ostwald ripening mechanism then sets in (Fig. 3). The smaller particles which have a higher solubility dissolve and the silica is redeposited on the larger ones, the total number of particles decreasing.

At low pH, particle growth stops once the size of 2 to 4 nm is reached. Above pH = 7 particle growth continues at room temperature until particles of about 5 to 10 nm diameter are formed, then it slows down. At higher temperatures particle growth continues, especially for pH > 7.

For the pH range between 6 and 10.5 the silica particles are negatively charged and they repel each other – the growth continues without aggregation resulting in the formation of stable *sols*. If, however, salts are present, aggregation and gelling occur.

At low pH the particles have little ionic charge; they can collide and form by aggregation continuous networks leading to *gels*. This process may involve primary particles of different sizes according to the pH condition and the presence of salts.

It is possible to destabilize a sol by change of pH and to provoke gel formation by *aggregation*. This conversion of sol into gel is progressive, the growing aggregates (microgel) invading, progressively, the whole volume. The local concentration of silica and water remains, however, the same. A gel has the same density as the sol.

When about half of the silica has joined the gel phase a rapid increase in viscosity is noted.

The mechanism of interparticle bonding leading to microgels and gels involves the attachment of two neighbouring silica particles via the formation of Si–O–Si bonds. Neutral $-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH}$ and ionized $-\overset{|}{\underset{|}{\mathrm{Si}}}-\bar{\mathrm{O}}$ groups on the surface condense to form Si–O–Si linkages by the same mechanism as in the primary particle formation. However, the presence of soluble silica or monomer near the points of contact may contribute to the cementing together of the particles.

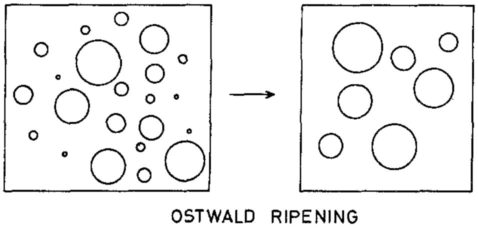


Figure 3 Ostwald ripening.

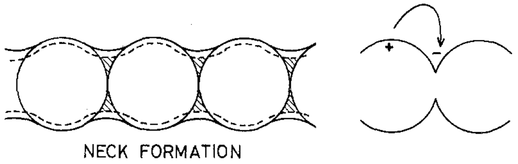


Figure 4 Strengthening of particulate chains by the deposition of silica at the necks.

A further step is the *strengthening* of the network of the particles by a mechanism involving the partial coalescence of the particles. The negative radius of curvature at the neck joining the two particles implies that the local solubility is less there than near the surface of the particle. A transport and deposition of silica occur there preferentially leading to the thickening of the neck (Fig. 4). This occurs in ageing treatments where chains of particles may be converted into more or less "fibrillar" structures by this rearrangement mechanism.

The sol → gel transition should be distinguished from a *precipitation* (or floculation) mechanism in which separate aggregates are formed in contrast to the continuous three-dimensional particle network (Fig. 5).

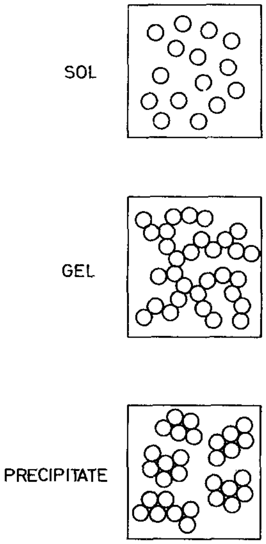


Figure 5 Differences between gel formation and precipitation from a sol.

Colloidal particles will form gels only if there are no active forces which promote coagulation into aggregates with a higher silica concentration than the original sol. Metal cations, especially the polyvalent ones, may lead to precipitation rather than gelling.

Particle size in sols may be increased by adding "active" silica in the form of particles less than 2 nm or even smaller polymer species; they redissolve in the presence of larger particles and redeposit on them. This "nourishment" of particles forms the base of the so-called "build-up process" (Fig. 6).

Commercial sols are stabilized by an ionic charge in the presence of alkali at optimum pH and are concentrated to maximum concentration.

The above discussion is based on work relative to aqueous solutions; very little is known about mechanisms in other media but the formation of primary particles and their subsequent bonding seems general.

The structure of silica gels was initially thought to consist of a cross-linked network of chains of polysilicic acid. Carman [18], in 1940, proposed the structures made up of ultimate spherical particles. The particulate theory of gel formation was described by Iler in 1955 [19]. Gels formed in aqueous solutions are termed *hydrogels* or *aquagels,* those in alcoholic media *alcogels;* their pores are filled with the corresponding liquid.

3. Drying

The drying process consists in eliminating the interstitial liquid phase. When a "wet" gel is dried the following sequence of events is generally observed on a macroscopic scale:

(a) progressive skrinkage and hardening;
(b) stress-development;
(c) fragmentation.

3.1. Capillary forces

When a liquid evaporates from a porous material the solid phase is subjected to forces due to capillary phenomena at the liquid–gas–solid interface. The capillary pressure, Δp, developed across a curved interface with principal radii R_1 and R_2 is given by Laplace's formula:

$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right),$$

where γ is the surface tension. For a cylindrical capillary of radius r and a liquid having a wetting angle θ this pressure is:

$$\Delta p = p_r = \frac{2\gamma\cos\theta}{r}.$$

The height of the capillary rise, h, of the liquid in a vertical capillary of radius r is determined by Jurin's formula:

$$h = \frac{2\,\gamma\cos\theta}{r\,g\,(\rho_L - \rho_v)}$$

where ρ_L and ρ_v are the densities of liquid and vapour and g is the acceleration due to gravity.

The behaviour of a liquid in different capillaries can be characterized by the *capillary potential* defined as the potential energy of the field of capillary forces per unit mass of liquid. By analogy with the potential of the field of gravity, the capillary potential, ψ_c, for a cylindrical capillary is, for $\rho_L \gg \rho_v$:

$$\psi_c = gh = \frac{2\gamma\cos\theta}{r\rho_L}.$$

A wetting liquid will tend to occupy a position with the highest capillary potential and a non-wetting liquid a position with the lowest potential. A wetting liquid moves spontaneously from a wide into a narrow capillary.

In a drying gel there are capillary pores and gaps of different sizes and shapes; the value of the capillary potential differs at different points of the system. The liquid will tend to occupy positions ensuring the minimum energy of the system as a whole.

A wetting liquid preferentially forms cups (menisci). Capillary forces act on the curved liquid–gas surfaces and on the three-phase liquid–solid–gas contact lines pulling or pushing apart neighbouring particles.

The magnitude of capillary forces depends on the size of the particles in the system and generates stresses that may reach considerable values. Stresses developed by the capillary forces depend in the first place on the capillary pressure $p_r = 2\gamma\cos\theta/r$. Fig. 7 shows variations of p_r as a function of r for (a) water with $\gamma = 0.073\,\mathrm{N\,m^{-1}}$,

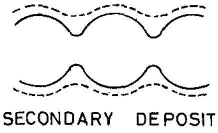


Figure 6 Strengthening of chains during ageing.

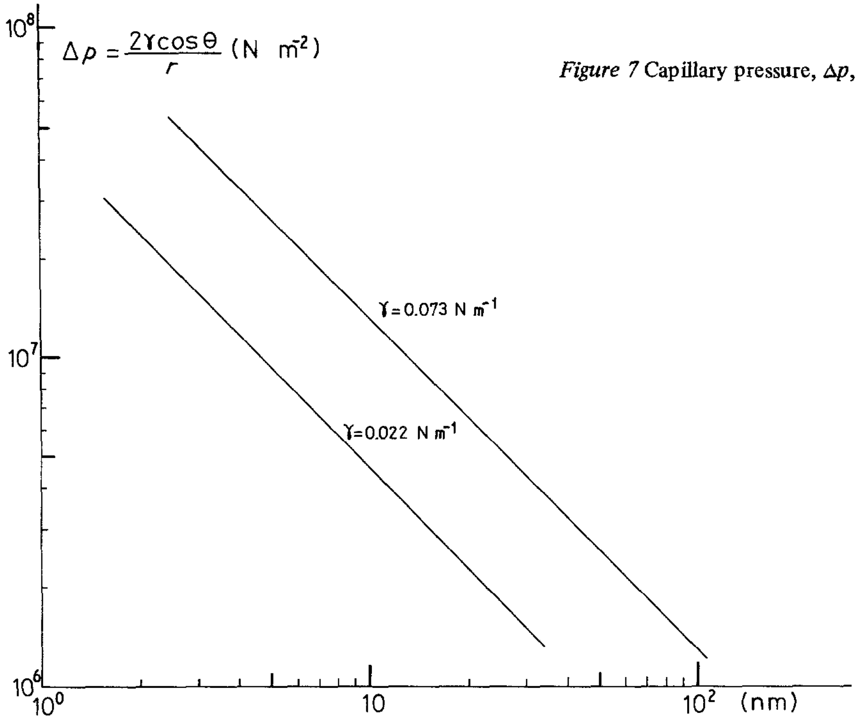


Figure 7 Capillary pressure, Δp, as a function of pore radius, r.

and (b) methyl alcohol, $\gamma = 0.022\,\mathrm{N\,m^{-1}}$ (the wetting angle taken was $\theta = 0$).

At the beginning the volume decrease of the material is equal to the volume of evaporated liquid. There is enough liquid to fill the pores and no liquid–air interface is present – no capillary forces are operating. During the second stage the volume is reduced by an amount smaller than the volume of the water lost, numerous menisci are formed in the pores and capillary attraction presses the particles together (Fig. 8). For particles in contact the volume reduction may result either in an elastic deformation of the system or, for a rigid system, a further collapse may occur during drying. The larger the dimensions of a single gel mass the greater the shrinkage.

Consider, for instance, two idealized adjacent pores of radii $r_1 > r_2$ embedded in liquid (Fig. 9a). When evaporation has progressed so far that menisci appear (Fig. 9b) the unequal capillary pressures will set up differential stresses, $\sigma_1 < \sigma_2$. If the stress difference $\sigma_2 - \sigma_1$ locally exceeds $\sigma_{\mathrm{th}}/\beta$ where σ_{th} is the cohesive theoretical stress and β a stress concentration factor, a crack will result.

The local variation of p_r across the structure and stress-concentration effects due to porosity make a detailed calculation difficult but an estimate can be obtained from the curves of Fig. 7 of the admissible pore size for a given rupture stress.

3.2. Structure of dried gels

The gel consisting of a three-dimensional network of particles or short chains is essentially inelastic and as it dries the network folds or crumples.

The capillary forces press the grains together provided the surface of the solid is wetted by the liquid (zero contact angle). The shrinkage proceeds until the mechanical strength can withstand the pressure exerted by the surface tension of the

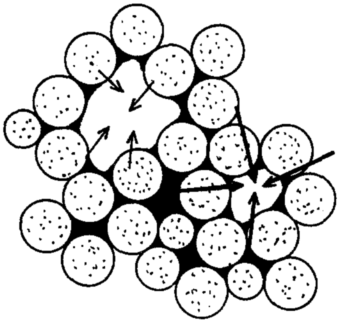


Figure 8 Capillary forces during drying of a wet particulate material.

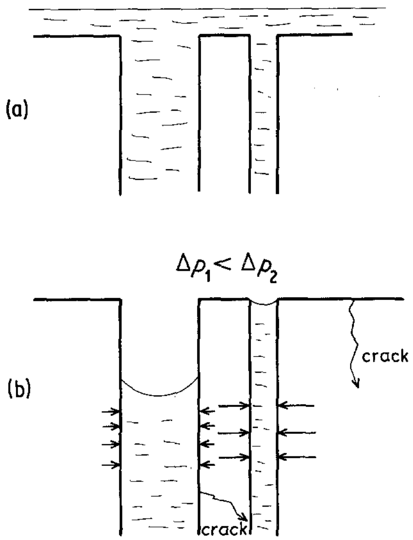


Figure 9 Formation of differential strains at the pores during drying: (a) before, and (b) after the onset of capillary forces.

liquid along the boundary of the gel. As the structure shrinks a certain number of particle-to-particle bonds will break because the structure is inelastic. If the structure is compact and brittle it will shatter. Only if the packing density is low and the gel soft and flexible can the gel shrink without cracking. The irreversibility of the shrinkage means that during collapse new bonds may be formed.

The final gel structure will depend on the structure of the gel originally formed in solution but it will be a contracted or distorted version of the latter.

The models proposed comprise (Fig. 10), (a) aggregates of particles of approximately the same size, essentially massive in nature; (b) aggregates of particles formed by primary particles (with macropores); (c) aggregates of a more complex nature in which three levels of particles can be distinguished.

According to the packing geometry, the systems present different porosity and specific surface.

The final characteristics of a dried gel are determined by the physico-chemical conditions at every step of the preparation:

(1) the size of primary particles at the moment of aggregation;

(2) the concentration of particles in solution;

(3) the pH, salt concentration, temperature and time of ageing or other treatment in the wet state;

(4) mechanical forces during drying;

(5) condition of T, pH, pressure, salt concentration and surface tension of the liquid medium during drying;

(6) temperature, time and atmosphere during drying.

3.3. Monolithicity

Very few indications exist in the literature on how to obtain monolithic gels. Essentially empirical, the majority concern pure silica.

By very slow drying (about two weeks) of the gels obtained by hydrolysis and polycondensation of tetramethoxysilane (TMS), Yamane *et al.* [20] obtains discs free from fissures and of small dimension (~ 1 cm). The dry gels have an apparent density of 1 to 1.5 g cm^{-3}; the average pore diameter is 2 to 5 nm.

Similarly, Nogami and Moryia [21] obtain monoliths of small dimensions. Their density is 1.8 and 0.8 g cm^{-3} and the pore radius between 2 and 7 nm.

Shoup [22] prepared, by the sol–gel process, silica monoliths of appreciable dimensions. The process uses sols containing Na$^+$ and K$^+$ ions. Adding polar solvents, such as formamide or ethyl acetate, the gelling is obtained at pH > 10. To eliminate traces of alkali ions the humid gel is washed with acid solution. The dry gels have a uniform open porosity with a pore diameter ~ 200 nm. The monolithicity is attained if pore diameter exceeds 60 nm.

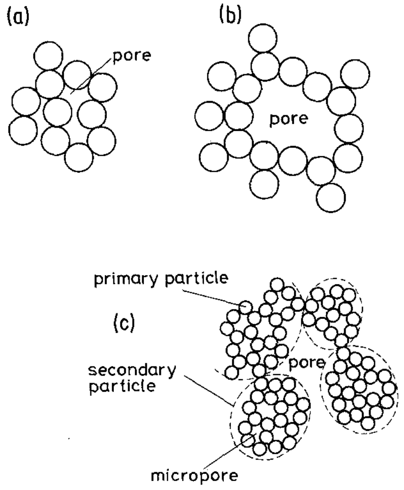


Figure 10 Different structural models of dried gels. (a) Massive aggregates; (b) aggregates with macropores; (c) secondary aggregates of primary particles.

Yoldas [23] obtained monolithic transparent aluminas in three stages:

(1) hydrolysis of aluminium alkoxide $Al(OR)_3$;

(2) peptization of the hydroxide and formation of a transparent sol;

(3) gelling of the sol.

Insufficient detail is given about the drying stage. The author determines a critical acid concentration in stage 2 necessary to retain monolithicity: it is 0.03 to 0.1 mol (mol alkoxide)$^{-1}$. There is no discussion of the causes of fracture.

The preceding analysis of the phenomena accompanying drying has shown the importance of capillary forces and of differential stresses which operate during shrinking. All actions which tend to minimize these stresses and increase the mechanical resistance of the network should enhance the probability of monolithic gel formation. The following are possible:

(1) strengthening the gel by reinforcement;

(2) enlarging the pores;

(3) reducing the surface tension of the liquid;

(4) making the surface hydrophobic;

(5) operating in hypercritical conditions where the liquid–vapour interface vanishes;

(6) evacuating the solvent by freeze-drying.

The use of solvents with small surface tension is only efficient when the gel presents large pores; it is complicated by the necessary compatibility of the liquids in the initial mixture to ensure homogeneous polymerization. The role of such solvents in the porosity of silica gels has been investigated [24].

Tensioactive substances which lower the surface tension of the liquid may be used as well as substances which diminish the wetting of the solid phase. Ammonia and its organic derivatives have been proposed to decrease the wetting of silica particles [25].

The increase in the radius of pores may be obtained by varying the conditions of hydrolysis or by the addition of foreign substances [26].

Enhancement of the mechanical resistance of the gel may be obtained before drying by an ageing process or the addition of "active silica" during the gelling process. Numerous examples exist of the favourable results thus obtained [22, 27].

The increase in the mechanical resistance of the gel is continuous during drying. For a silica gel with 60% TMS the solid phase represents 10% in volume of the initial solution. In the first instants of evaporation the solid phase is in the form of an open network and presents very slight mechanical resistance. The capillary forces then draw the particles together and new Si–O–Si bonds strengthen the solid network. For this humid gel the stresses originating in micropores can bring about fragmentation during the first drying stages; it is necessary to evacuate the solvent trapped in the larger pores without provoking evaporation in the smaller ones. This can be done only if a pressure of the solvent is maintained over the gel, a pressure slightly lower than the saturation pressure.

The most efficient way of eliminating the destructive (noxious) action of the surface tension of the liquid is to suppress the liquid–vapour interface, operating in *hypercritical conditions*. This method has been used by Kistler [28] to obtain gels with a large pore volume (aerogels). To avoid the peptizing effect of water at high temperature, water was first replaced by alcohol. Nicolaon and Teichner [29] have used this method directly on alcogels. However, aerogels obtained in this way were synthesized for application in catalysis and no attention has been given to monolithicity. It should be noted that the structure of the aerogels closely resembles the structure of the wet gels as the compression and collapse of the structure during drying have been avoided.

A systematic study of the conditions for obtaining monolithic gels has been performed in our laboratory [30]. The aim was the synthesis of monoliths of fair dimensions, attention being given to the rapidity of the method, a good reproducibility and the conservation of the monolithicity during thermal treatment for densification without crystallization. Only a few examples will be given here – a fuller account of these studies will be given later.

Three different procedures were tested for silica gels produced by hydrolysis of tetramethoxysilane (TMS):

(1) slow drying;

(2) addition of surfactants during gelling;

(3) hypercritical evacuation.

Gels were prepared from solutions of TMS in methanol. Hydrolysis was obtained by introducing a quantity of distilled water slightly higher (4.65 mol (mol TMS)$^{-1}$) than that required from stoichiometry. The mixture was stirred for ½ h then transferred to Pyrex containers. For Method 2 a solution of surfactants was added (8 vol %). The slow drying conditions were obtained in

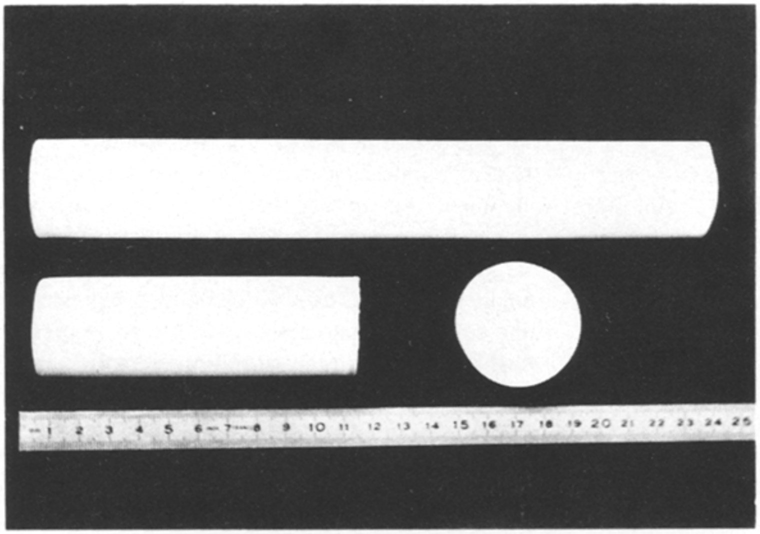


Figure 11 Example of gels produced by hypercritical solvent evacuation.

Methods 1 and 2 by covering the gel with a plastic film to slow down solvent loss by evaporation. Holes were pierced in the film to control the speed of evaporation. The speed of evaporation was evaluated from the weight loss of the sample.

The hypercritical evacuation of the solvent (Method 3) was obtained by placing the tube containing the gel in an autoclave into which a certain quantity of methanol was added to attain hypercritical conditions. The heating was done electrically.

When a temperature well above the critical temperature of methanol was attained, a slow evacuation (3 to 4 h) followed by flushings with dry argon eliminated the last traces of alcohol. The dried gel is removed once the autoclave has cooled down.

Experiments have shown that in the case of Method 1 for gels, 60% TMS and a speed of drying between 0.03 and $0.08\,\mathrm{g\,h^{-1}}$, monolithic gels are obtained with 100% certainty. If the speed is increased to $0.2\,\mathrm{g\,h^{-1}}$ about 50% of the specimens develop 2 to 3 cracks, the rest of drying not introducing supplementary cracks. However, if this drying is preceded by an ageing for 50 h the resulting gels are again systematically monolithic.

All these gels show a uniform shrinkage, their apparent density is 80% of vitreous silica. This shows that by controlling the speed of evaporation it is possible to obtain monolithic silica gels. The disadvantage of Method 1 is the length of time of drying: about 400 h for an evaporation surface of $8\,\mathrm{cm^2}$. This is considerably increased for larger specimens.

The risks of adhesion of gel to the container which may induce cracks are lessened by using polythene or teflon containers or an ageing process. The geometry of the sample plays a role in the uniformity of shrinkage, important in avoiding crack initiation.

Method 2 enabled us to obtain monolithic gels which differ from Method 1 by their greater porosity. These gels, however, have a greater tendency to devitrify during densification heat treatment.

The only reliable method of obtaining monolithic gels proved to be by hypercritical evacuation in an autoclave (Method 3). By carefully optimizing different parameters monolithic gels of large dimensions (see, for example, Fig. 11) were obtained reproducibly. Porosity varied from 84% to 91% with a specific surface between 250 and $600\,\mathrm{m^2\,g^{-1}}$. These figures can be varied by modifying TMS concentration.

4. Conclusion

The conditions of gel preparation determine the structure of the wet gel which undergoes further modifications during ageing and drying steps. The possibility of direct conversion of the gel into massive glass by sintering implies the production of monolithic gels. These can be obtained by solvent evacuation in hypercritical conditions.

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