# SUPERCRITICAL CO$_2$ DRYING OF SILICA AEROGELS SYNTHESIZED IN 2-PROPANOL

**Yasmine Masmoudi\*, Arnaud Rigacci, Patrick Achard and François Cauneau**

Centre d'Energétique, Ecole des Mines de Paris,
Sophia Antipolis-Les Lucioles, BP 207, 06 904, France

E-mail : Yasmine.masmoudi@ensmp.fr , Fax : 33 (0)4.93.95.75.35

Drying of silica gels is a critical step to obtain monolithic and crack-free aerogels. It is known that drying under supercritical (SC) conditions of CO$_2$ avoids densification and occurrence of cracks resulting from the capillary stresses appearing during the "conventional" sub-critical evaporative drying. However, one of the limitation of this process is the SC "washing" phase which consists in replacing the interstitial solvent (here 2-propanol) by the SC CO$_2$. In fact, this phase is generally governed by molecular diffusion mechanisms of the interstitial solvent in the surrounding CO$_2$ and is limited by the low permeability of the nanostructured gel network. Furthermore, an incomplete washing can damage the final properties of the aerogels (because of re-condensation during depressurization).

The present paper focuses on our first experimental investigations for the determination of the criterion of the end of the SC washing step. The evolution of the propanol concentration in the autoclave was followed "on-line" with a "micro" gas chromatograph and compared with analytical estimations obtained from a bibliographic model. Current work is using the experimental results obtained in order to estimate the effective coefficient of diffusion of the propanol.

## INTRODUCTION

Silica aerogels result from drying of gels elaborated through a sol-gel process. They are monolithic, very light (< 0.2g/cm$^3$) and nanoporous materials. Their porosity is opened and can exceed 90 % of their whole volume [1].

Thanks to the combination of their high porosity and the nanometric size of their pores (generally 1-100 nm), silica aerogels have thermal conductivities lower than that of air (< 20 mW/mK [2]) and are classified among the best potential thermal super insulators.

Besides, these materials have good optical properties with a transparency higher than 90% in the visible range [3] which make them very interesting to be used in double-windows and more precisely to be introduced between two glass sheets to replace the "standard" air layer. The feasibility of the elaboration of flat monolithic and crack-free 60×60×2 cm$^3$ aerogel plates with good thermal and optical properties has been already demonstrated in a previous European project (acronym : HILIT) [4]. However, this kind of samples requires SC drying to avoid densification and occurrence of cracks associated to" conventional" sub-critical evaporative drying.

Nevertheless, the SC drying still represents a crucial and limiting phase. It is crucial because it must be carried out "softly" to obtain monolithic aerogels. It is limiting because it is time-consuming. Regarding to an industrial process, it is consequently important to reduce the duration of this phase while preserving the good thermal and optical properties of the final material. This is one of the main objectives of the current European project HILIT+ within the framework of which is carried out the present work.

In this paper, we focus on the degree of advancement of the SC "washing" step. We have initiated the quantification of the duration of this phase in the case of a low Reynolds SC extraction (*i.e.* without any turbulence phenomena) by following experimentally the concentration of extracted solvent with a micro gas chromatograph (µCPG). We have then compared the results to estimations coming from a mass –transfer bibliographic model.

## I – MATERIALS AND METHODS

### 1 – Gel Synthesis

Wet gels are synthesized through a two catalytic steps, according to a previous patented elaboration route [5]. The first step consists in preparing the pre-polymerized silica precursor so-called Polyethoxydisiloxane (PEDS-Px) (PCAS, France[1]). These precursors are synthesized by pre-polymerizing Tetraethoxysilanes (TEOS) monomers under acidic conditions ($H_2SO_4$) in 2-propanol (IPA) according to the following chemical scheme :

$$TEOS + n^*H_2O \rightarrow PEDS\text{-}Px \quad (x = \frac{n^*}{2}*1000) \tag{1}$$
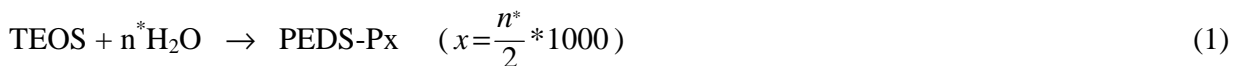
The second step is based on the gelation - at room temperature - of a sol composed of PEDS-P750, IPA and HF (21N) in the following respective proportion 49vol% : 49vol% : 2vol%.

At room temperature, two parallelepipedic gels ($5.5 \times 5.5 \times 1$ cm$^3$) were prepared in Teflon moulds and then aged in a pure IPA bath for 11 days in order to strengthen them and to obtain the maximum rate of shrinkage before drying [9].

### 2- Drying Process

The gels elaborated as previously described were dried under the SC conditions of $CO_2$ using the experimental loop schematically presented at Figure 1.

The two gels were firstly introduced vertically in the autoclave and were covered with an excess of IPA in order to avoid the evaporation of the interstitial solvent during the pressurization phase in order to avoid any risk of cracking of their "fragile" texture. The system was then heated to 40°C and then isothermally pressurized with $CO_2$ up to 80 bars in order to exceed the critical conditions of $CO_2$ (31.06°C and 73.8 bars).

After removing the excess of solvent, interstitial IPA was dynamically extracted in order to replace it with SC $CO_2$. This phase is called the "washing phase". During this extraction phase, the SC $CO_2$ mass flow rate was about 5 kg/h, and the Reynolds number in the vicinity of the gels was lower than 413. Consequently, the washing phase was governed by molecular diffusion phenomena of the interstitial solvent to the surrounding $CO_2$ through the porosity of the gels.

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[1] PCAS, BP 181 – 91 161 Longjumeau Cedex (France)

These phenomena are limited by the nanometric size of the pores (1-100 nm) and therefore by the low permeability of the gels (D < 20 nm² [6 ; 9]) which increases significantly the duration of the washing phase. In order to detect the criterion of the end of SC washing, IPA concentration in the autoclave was followed "on-line" with a µCPG (Figure 1). The detection limit of the chromatograph corresponds to an IPA concentration of $10^{-4}$ kg/m$^3$. This concentration is considered as the experimental criterion of the end of the washing phase. In order to avoid any risk of IPA condensation, the line connecting the µCPG to the autoclave was heated and thermally isolated.

When all the interstitial solvent is considered to be extracted, $CO_2$ was isothermally vented out to avoid any condensation phenomenon. This is the depressurization phase. It must be performed at low depressurization rate to avoid the appearance of mechanical stresses[8]. In fact, in the case of a too rapid depressurization, and because of the low permeability of silica gels, the fluid can not flow out of the network at a comparable rate, and the gel is therefore submitted to high tensile stresses. Because of their poor mechanical properties (modulus of rupture in compression lower than 0.3 Mpa [8 ; 9]), silica aerogels can crack and break. Consequently, during our SC extractions, the depressurization rate used was of 1.5 bars/h.
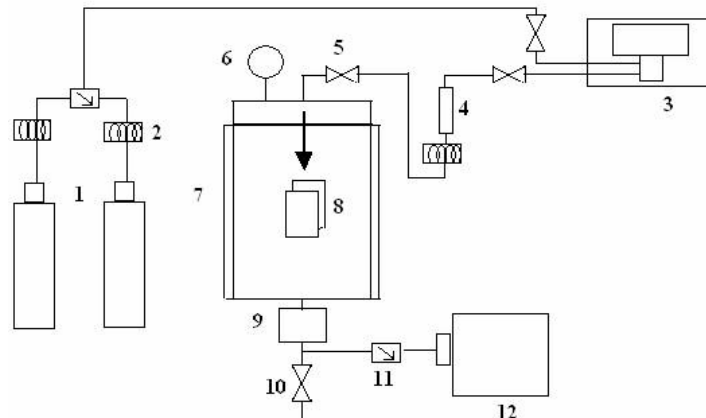


Figure 1: Schematic representation of the supercritical drying loop: (1) gaseous $CO_2$, (2) Heater (3) Air Compressor, (4) Buffer, (5) Alimentation valve, (6) Pressure Gauge, (7) Autoclave (1 litre), (8) Gels, (9) Pneumatic depressurization valve, (10) Security valve, (11) Pressure reducer, (12) µCPG

## III- RESULTS AND DISCUSSION
### 1- Experimental Results
In order to estimate the criterion of the end of washing, two series of extractions have been carried out.

During the first series (Armines_1), the dynamic washing phase lasted about 16 hours, which is the experimental duration usually used at the laboratory for extractions in the same conditions. The evolution of the IPA concentration of the fluid extracted was followed on line with the µCPG. The fluid is supposed to be a binary mixture composed of IPA and $CO_2$.

As showed by Figure 2, after about 10 hours of dynamic washing, no longer IPA was detected with the µCPG. This duration seems to be sufficient to extract the totality of the interstitial solvent contained in the $SiO_2$ mixture.

The aerogels obtained were monolithic and have low densities (0.17 and 0.18 g/cm$^3$ ± 0.01).

The second series of extractions (Armines_2), has also been performed in the same conditions, but has been stopped after about 12 hours in order to confirm the results of the first series. The aerogels obtained were also monolithic (Figure 3) and their densities were comparable to those of series Armines_1. In order to compare the washing efficiency, the evolution of the aerogels properties has been followed after drying. It has been noticed from both series that no cracks appear in the aerogels and that the densities have not been significantly modified. This means that there was no longer IPA in the pores of the gels at the end of drying. Otherwise, the IPA evaporation would have induced capillary stresses, and the gels would have been densified and even cracked.

From these results, it can be considered that in our specific experimental conditions, a SC washing duration between 10 and 12 hours is sufficient to obtain dry materials.
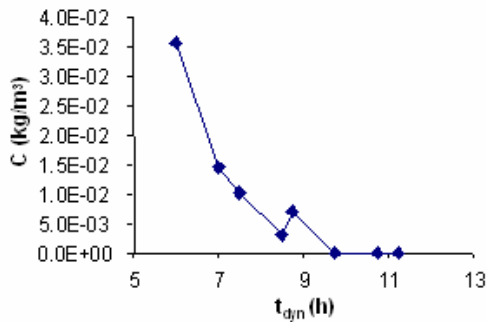


Figure 2: Evolution of the IPA concentration in the autoclave (C) with the duration of the dynamic SC washing (t$_{dyn}$)
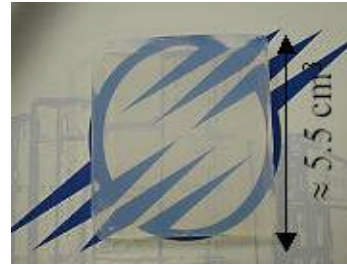


Figure 3: View of Ecole des Mines logo through monolithic silica aerogels from extraction Armines_2

**2- Analytical Results**

In the autoclave, the wet gels are surrounded by SC $CO_2$. During the dynamic washing phase, a constant flux of $CO_2$ is entering the autoclave. The solvent contained in the gel is then extracted from the pores according to an unsteady-state three dimensional diffusion process. It leaves the autoclave mixed with $CO_2$. In order to estimate analytically the evolution of the washing phase, the model described by Wawrziniak et al. was used [10]. This model is based on a mass conservation model assuming an instantaneous IPA/$CO_2$ mixing outside the gel :

$$\frac{dQ(t)}{dt} = \frac{dC(t)}{dt} V + F\, C(t) \qquad\qquad (2)$$

where Q (kg) is the mass of the interstitial solvent diffusing from the gels at t, C (kg/m$^3$) the mass concentration of the solvent in the fluid surrounding the gels at time t, V (m$^3$) the free volume of the autoclave and F (m$^3$/s) the flow rate of $CO_2$.

The mass of IPA/$CO_2$ solvent diffusing out of the gels was estimated by the formulation used by Delhomme et al. [11] for modeling the extraction of paraffins from a porous medium. It is based on the resolution of the Fick's equation for plate gels [12].

So, assuming that the solvent extracted is mainly composed of IPA, and that it is instantaneously evacuated from the surface of the gel and mixed with SC $CO_2$, the formulation of Q (t) is :

$$1-\frac{Q(t)}{Q_0}=\frac{512}{p^6}\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty}\frac{\exp(-a_{i,j,k}\,t)}{((2i+1)(2j+1)(2k+1))^2} \tag{3}$$

with $\alpha_{i,j,k}$ determined by the following equation : $a_{i,j,k}=\frac{p^2 D_{eff}}{4}\left[\frac{(2i+1)^2}{(\frac{L}{2})^2}+\frac{(2j+1)^2}{(\frac{l}{2})^2}+\frac{(2k+1)^2}{(\frac{e}{2})^2}\right]$ $\qquad$ (4)

where L (m), l (m) and e (m) are respectively the length, the width and the thickness of the gel, $Q_o$ (kg) the initial amount of interstitial solvent and $D_{eff}$ (m²/s) the effective diffusion coefficient of IPA in $CO_2$.

The resolution of the equation (2) leads to the formulation of the mass concentration of IPA in the fluid surrounding the gels at time t :

$$C(t)=K1\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty}\left(\frac{a}{a+K2}\right)\left(\frac{\exp(K2.t)-\exp(-a_{i,j,k}\,t)}{((2i+1)(2j+1)(2k+1))^2}\right) \tag{5}$$

where $K1=\frac{512\,Q_0}{p^6\,V}$ and $K2=-\frac{F}{V}$.

Experimental parameters used for the resolution of the equation (5) are V = 1.039 $10^{-3}$ m$^3$ and F = 4.93 $10^{-6}$ m$^3$/s (i-e. 5 kg/h) while $D_{eff}$ = 1.7 $10^{-9}$ m²/s as determined by the empirical equation [10]:

$$D_{eff} = D_0\frac{e}{t^2} \tag{6}$$

where $\tau$ is the tortuosity of the gel and $\varepsilon$ its apparent porosity ($\varepsilon$ = 1- ($\rho/\rho_{SiO2}$), with $\rho_{SiO2}$ = 2.2 g/cm$^3$ and $\rho$ (g/cm$^3$) the apparent density of the aerogel). The diffusion coefficient $D_0$ (m²/s) of IPA in SC $CO_2$ was determined using the semi-empirical relation of Wilke and Chang [13]. The resolution of the equation (5) leads to the following analytical curve (Figure 4):
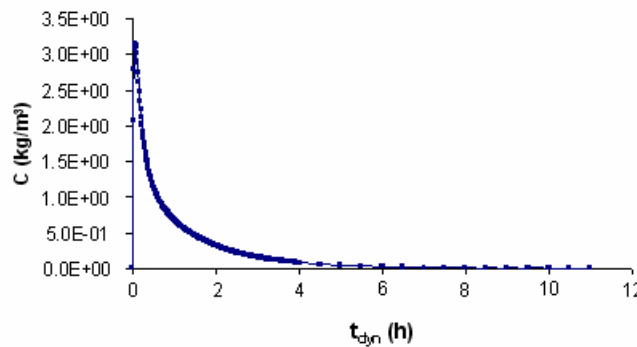


Figure 4 : Evolution of the IPA concentration in the autoclave
with the duration of the dynamic SC washing phase ($t_{dyn}$)

The calculations have been stopped when the IPA concentration reached the minimum value detectable in the autoclave *i.e.* $10^{-4}$ kg/m$^3$. According to this criterion, the analytical calculations show that 10 hours of dynamic SC washing seem sufficient to extract the totality of IPA from the gels. This first estimation is in good agreement with the experimental order of magnitude.

## CONCLUSION

During the supercritical drying of aerogels, the washing phase is critical because, on the one hand, it strongly influences the final properties of the material, and on the other hand it is time–consuming.

In this work, we have initiated the optimization of this SC drying step from a duration point of view in simple laminar conditions. The first experimental results permit to estimate the time necessary to obtain dry materials and were consistent with the analytical calculations. Complementary work should, nevertheless, be accomplished in order to go further.

Next objective is to reduce the SC washing duration by modifying experimental conditions, like introducing turbulences.

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