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Drying of silica gels with supercritical carbon dioxide

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Results of drying experiments of aerogels with supercritical carbon dioxide are reported. In addition to the results of experiments with a pilot extracting apparatus, a preliminary design is also given of a large-scale supercritical carbon dioxide extraction plant to be used for drying of aerogels. From the experiments it was found that crack-free aerogels could be obtained when drying with carbon dioxide under supercritical conditions. The lowest temperature and pressure at which crack-free aerogel samples were obtained was at 35 °C and 85 bar, respectively. The temperature had a minor influence on the drying time. It was also found that the diffusion of ethanol into the aerogel pores limits the drying time. This limitation implies that the thickness of the aerogel tiles will have a large influence on the cost of drying of an aerogel.

1. Introduction

Silica, as well as other metal oxide aerogels, can be produced as monoliths with extremely high porosities and very high specific surface areas [1–3]. As a result of the high porosity, silica aerogels are very good thermal insulators. They are, depending on their structure, also able to withstand temperatures up to 1000 °C and can be highly transparent for visible light [1–3]. For application as insulating material, it is necessary to produce aerogel tiles or plates of considerable size (> 0.1 m^2), thickness (> 1 cm) and strength.

Silica aerogels can be prepared from ethoxysilanes by a two-step sol–gel process [1,4], resulting in a silica gel skeleton immersed in ethanol. Monolithic silica aerogels can then only be produced when the ethanol is removed in the absence of capillary forces in the gel pores, because even small capillary forces will result in a collapse of the gel skeleton and will crack the gels [1–3]. This removal can be achieved by placing the wet gel in an autoclave and heating the autoclave above the critical temperature of ethanol ($T_c = 243$ °C) [1–3, 5–7]. At this temperature, ethanol is slowly removed by releasing the pressure (depending on the degree of filling of the autoclave, typically 80–120 bar after heating to temperatures between 250 and 300 °C) to 1 bar and the monolithic silica aerogel is obtained. It is clear that this is a very tedious procedure because the autoclave has to be heated to temperatures above 250 °C. Another way to produce a monolithic silica aerogel is by replacing the ethanol by carbon dioxide [1–3, 8–11]. Most of the literature reports procedures in which the alcohol is replaced by liquid carbon dioxide. Monolithic silica aerogels are obtained by slowly raising the temperature of the carbon dioxide-filled gels until supercritical conditions are obtained and then slowly releasing the carbon dioxide pressure to 1 bar.

In this paper a procedure is described in which the complete alcohol–carbon dioxide exchange is carried out under supercritical conditions. Compared to the high-temperature autoclave drying procedure, the carbon dioxide drying procedure has the advantage that only relatively low temperatures (35 °C) are necessary. Owing to this low temperature at which the process is operated, equipment costs can be low and the drying time will be shorter because it is not necessary to heat and cool the autoclave. Because of these advantages a process using supercritical carbon dioxide will be much cheaper and thus more attractive for the production of large quantities of the monolithic silica aerogel.

The effects of pressure and temperature on the aerogels produced are investigated and compared with aerogels which are dried with a high-temperature autoclave process. Finally, the structure and economics of a large-scale commercial production process for the preparation of monolithic silica aerogel plates with a thickness of 3 cm are discussed.

2. Experimental procedure

2.1. Gel preparation

The complete hydrolysis–condensation of TEOS requires a minimal amount of 2 mol water per mol TEOS [12]. For our investigations, gels were prepared from a mixture with a final molar ratio TEOS/ethanol/water of 1:2:2. The amount of water was divided in an acidified fraction (0.5 mol/water/mol TEOS) added in the first step of the two-step sol–gel process, in

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order to catalyse the hydrolysis reactions and a basic fraction (1.5 mol water/mol TEOS). A base was used to enhance the polymerization reactions. In the acid step, an HCl concentration of 10^{-2} M in water and in the basic step an NH_4OH concentration of 6×10^{-2} M in water was used. Both water fractions were diluted with equal weight amounts of ethanol to avoid immiscibility during the addition [12]. The rest of the ethanol was used for the initial TEOS/ethanol mixture.

The reactions started the moment the acidic water–ethanol mixture was added drop by drop to the initial TEOS–ethanol mixture that was vigorously stirred and maintained at a constant temperature of 50 °C. Including the time spent for addition of the acid fraction, the total hydrolysis time was chosen at 30 min. This time is beyond the point at which a maximum hydrolysis degree is obtained [12].

The basic fraction was then added in less than 5 min to the well-stirred mixture which was maintained at 50 °C. Before gelation occurred, the solution was poured into test tubes, with an internal diameter of 1.5 cm and a length of 18 cm. The inner wall of the test tubes was coated with a two-component silicon rubber in order to prevent adhesion of silica gel to the glass. After gelation at 50 °C the samples were aged at 60 °C for 48 h [13]. Finally, the gels were dried with supercritical carbon dioxide or with the high-temperature autoclave process [14, 15].

2.2. Supercritical carbon dioxide drying

The supercritically carbon-dioxide-dried silica aerogel rods were produced with the equipment shown in Fig. 1. At the beginning of the drying experiments it is essential to minimize the evaporation of the ethanol from the gel rods. The wet gel rods were carefully taken out of the coated glass tubes and immersed in pure ethanol. The extractor (1), with a volume of 600 ml, was then completely filled with cold ethanol to avoid the occurrence of cracks during pressure build-up. Subsequently a wet gel was taken from the ethanol and inserted quickly into the extractor. A specially designed steel wire construction was used to keep the gel rod vertical in the centre of the extractor and to ensure that the complete rod surface was in contact with the supercritical carbon dioxide.

During most of the experiments the carbon dioxide was taken directly from a gas-bottle (4) and not recycled through the equipment to ensure that no residual amounts of ethanol were present. The carbon dioxide was first liquefied at − 15° (3) and then pumped (6) to a pressure above the critical pressure of carbon dioxide (73.8 bar).

Before entering the extractor, the carbon dioxide is heated to a chosen temperature above its critical temperature (31 °C) by a hot-oil circuit. After closing, the extractor is pressurized with carbon dioxide until the desired operating pressure is reached. Fig. 2 shows a *PT*-projection of the binary system ethanol–carbon dioxide around the critical point of carbon dioxide (73.8 bar and 31 °C) [16, 17]. In the figure, a homogeneous liquid region where ethanol and carbon dioxide are completely miscible, is depicted. During our experiments, the carbon dioxide flow to the extractor (depending on the experiment, typically 1.0–1.3 kg h^{-1}) is controlled independently of the pressure by adjusting the pump stroke length and measured with a micromotion flowmeter. A pressure-control valve is used to maintain the extractor pressure at the desired operating pressure by releasing small amounts of the ethanol carbon dioxide mixture from the extractor into the separator (2). During most of the experiments the separator was operated at 1 bar and 0 °C to separate almost all the ethanol from the carbon dioxide. The carbon dioxide was vented. After several hours the ethanol in the extractor had been replaced completely by supercritical carbon dioxide (Fig. 2) and the pump was stopped. The pressure in the extractor, which was heated with an oil jacket was slowly released (Fig. 2) at a rate of 2–3 bar min^{-1} and the dried aerogels could be taken out of the extractor.

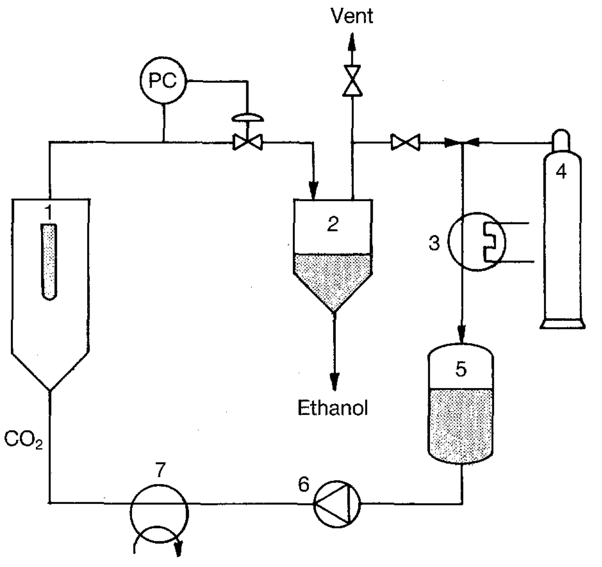

Figure 1 Schematic representation of the supercritical carbon dioxide drying equipment. (1) Extractor, (2) separator, (3) condensor, (4) CO_2 bottle, (5) buffer, (6) pump, (7) heat exchanger.

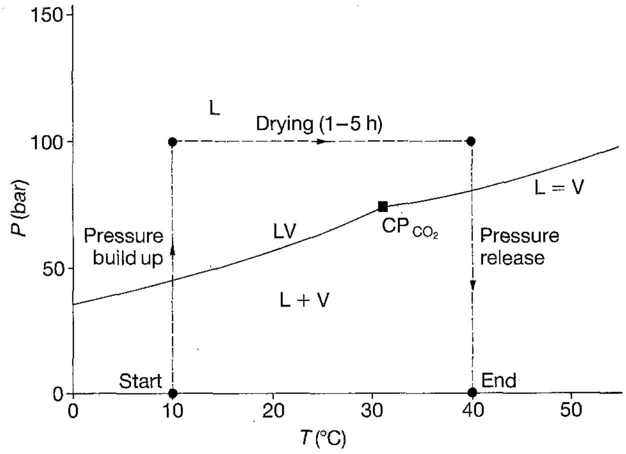

Figure 2 Schematic representation of the supercritical carbon dioxide drying procedure in a *PT*-projection of the binary system ethanol–carbon dioxide [16, 17]. (■) CP_{CO_2}; Critical point of carbon dioxide. L = liquid, V = vapour.

2.3. Autoclave drying

The procedure we used for the drying of the silica gel rods in an autoclave has been discussed in more detail elsewhere [14]. After inserting the wet gel rods, the autoclave is filled at room temperature with nitrogen gas up to a pressure of 80 bar. This nitrogen pressure was intended to prevent boiling during the evaporation of ethanol present in the gels and to diminish temperature gradients during heating. Next the autoclave is heated with a linear heating rate of 50 °C h^{-1} to 300 °C or higher temperatures, and kept at this temperature for a short time. The autoclave is then decompressed to 1 bar in about 1 h and subsequently cooled to room temperature.

3. Results and discussion

3.1. Supercritical carbon dioxide drying conditions

The results of the supercritical carbon dioxide drying experiments at various pressures and temperatures are presented in Table I. A clearer view of these results can be obtained by plotting the occurrence of cracks in the aerogel rods in a *PT*-projection of the binary system ethanol–carbon dioxide as illustrated in Fig. 3. It can be seen that at combinations of pressure and temperature above the binary critical curve (L = V) crack-free aerogel rods were produced, while at combinations of pressure and temperature below the binary critical curve (L = V), severe cracks occurred. This cracking can be understood when it is recognized that above the binary critical curve, carbon dioxide and ethanol are completely miscible, while below the binary critical curve, a vapour (CO_2) and a liquid (ethanol) phase are present. The presence of a vapour and a liquid phase will result in capillary forces that may cause the gel rods to crack as a result of internal stresses. Above the binary critical curve only one phase will be present and no capillary forces will occur. From our experiments (Fig. 3) it can be concluded that the monolithic silica aerogels rods can best be dried by using conditions at a combination of pressure and temperature above the binary critical curve instead of subcritical conditions.

TABLE I Results of the drying experiments of the aerogel rods with an overall composition TEOS–ethanol–water of 1:2:2. Samples 1–9 were dried with supercritical carbon dioxide over a period of at least 4 h with a carbon dioxide flow between 1.0 and 1.3 kg h^{-1}. Sample 10 was dried in an autoclave (*A* is the specific surface area)

Sample	*P* (bar)	*T* (°C)	Cracks	Weight loss (%)	*A* (m^2 g^{-1})
1	85	35	No	18	
2	80	40	Yes	18	520
3	90	40	No	17	520
4	85	50	Yes	–	–
5	100	50	No	18	520
6	150	50	No	15	
7	200	50	No	18	540
8	125	70	Yes	19	630
9	140	70	No	–	–
10	150	310	No	13	511

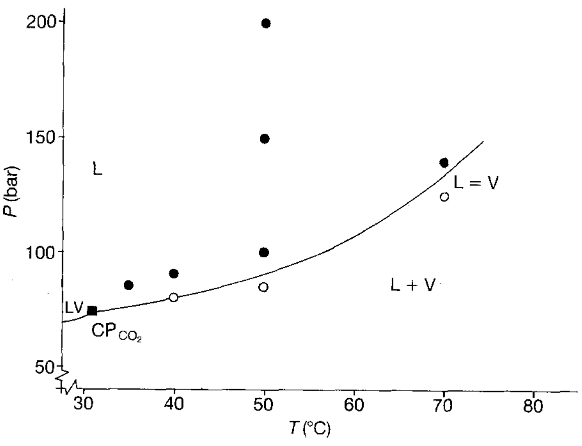

Figure 3 Occurrence of cracks ((O) yes, (●) no) in aerogel rods dried with supercritical carbon dioxide for at least 4 h as a function of pressure and temperature plotted in a *PT*-projection. (■) CP_{CO_2}: Critical point of carbondioxide.

In addition to the pressure and temperature, when using a constant flow the drying time is also an important process parameter. For each chosen temperature a process for drying of monolithic silica aerogel will be most economical at the lowest possible operating pressure. This condition means that for each temperature a pressure just above the binary critical curve of the binary system ethanol–carbon dioxide should be used. To determine the required drying time several experiments were performed at one combination of pressure, temperature and carbon dioxide flow with only the drying time as a variable. These experiments showed that the ethanol was removed more quickly from the extractor than from the gel rod. This means that the diffusion of ethanol in the silica gel pores limits the required drying time. Furthermore, it was found that at least six extractor volumes (6 × 600 ml) of supercritical carbon dioxide were required to remove all the ethanol from the extractor.

The effect of the temperature on the drying time is illustrated in Fig. 4. It can be seen that about 3 h are required to replace the ethanol in the silica gel rods with a diameter of 1.5 cm by supercritical carbon dioxide. The required drying time decreases only slightly with increasing temperature. Because the aerogel rods contain pores with radii that vary from a few nanometres to 60 nm [1], it is expected that both Knudsen diffusion and surface diffusion are the main mechanisms by which the ethanol and carbon dioxide molecules are transported through the silica gel material [18–20]. This explains roughly why the drying process is hardly dependent on the temperature. However, more work has to be done to elucidate the respective contributions of both mechanisms to the drying process.

The decrease in weight of the samples between the aerogel samples before and after a vacuum treatment at a temperature of 250 °C, was determined and is presented in Table I, as well as the specific surface area, *A*, which was determined using a Carlo Erba sorptomatic with nitrogen at liquid nitrogen temperatures and calculated according to the BET method. Before measuring the specific surface area, the samples

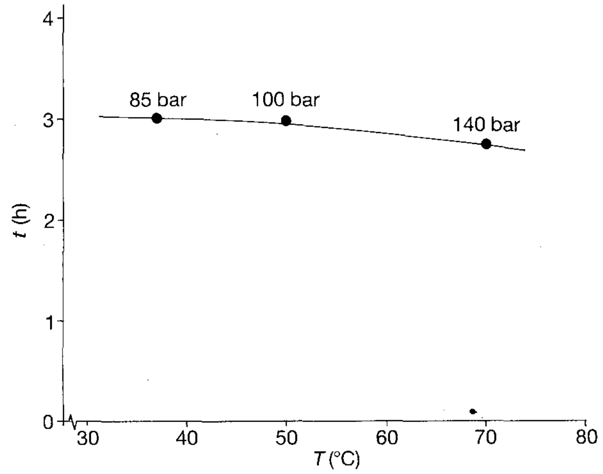

Figure 4 Required drying time for silica aerogel rods with a diameter of 1.5 cm as a function of temperature.

were degassed at a temperature of 200 °C for 24 h in order to remove the physically adsorbed impurities.

The results of a high-temperature autoclave drying experiment at a drying temperature of 310 °C are also listed in Table I. From this table it can be concluded that the specific surface area of the autoclave-dried aerogel sample is only slightly lower than the samples dried with supercritical carbon dioxide. Only when higher temperatures (> 400 °C) are used will a sintering of the primary particles occur, resulting in a lower specific surface area [21].

Also, the weight reduction in the supercritical carbon dioxide dried samples is slightly higher than in the autoclave dried samples. This is ascribed to higher water contents in the samples dried with supercritical carbon dioxide. Only the alcohols are extracted from the gels with supercritical carbon dioxide; any nonreacted water present in the gels will be removed during the vacuum treatment at higher temperatures.

These observations coincide with those reported in the literature [2].

4. Process design

In the following sections the design and economics of a drying process with supercritical carbon dioxide for the large-scale production of silica aerogel plates with a thickness of 3 cm are discussed. The design was based on a process in which five extractors with a volume of 2 m^3 are used because these are already commonly used in other supercritical carbon dioxide extraction processes. Instead of venting, the gaseous carbon dioxide from the separator is liquefied and recycled to the extractors.

4.1. Operating conditions

From Fig. 4 we concluded that the required drying time was nearly independent of the temperature. This means that the silica gel plates should be dried with supercritical carbon dioxide at the lowest possible temperature because the use of higher temperatures would result in higher pressures in the extractors and more expensive equipment. For this reason we selected a temperature of 35 °C and a pressure of 85 bar in the extractors. The extracted ethanol is separated from the carbon dioxide by pressure and temperature reduction. The operating pressure of the separator was chosen to be 50 bar to enable the use of a normal, cold-water producing cooling machine for liquifying the gaseous carbon dioxide. A temperature of 20 °C was used in the separator because at this temperature the mixture of carbon dioxide and ethanol separates into a vapour and a liquid phase, while the ethanol concentration in the vapour phase is minimal. If a lower temperature was selected, phase separation would no longer occur and the ethanol would no longer be separated from the carbon dioxide that is recycled to the extractors. The selection of a higher temperature would result in a higher vapour pressure of ethanol and therefore a higher concentration of ethanol in the carbon dioxide that is recycled to the extractors. It is expected that at 20 °C and 50 bar only 0.1–0.2 wt % ethanol remains dissolved in the gaseous carbon dioxide from the separator [22].

To check whether monolithic silica aerogels can be produced at the chosen process conditions, an experiment was performed with the supercritical carbon dioxide drying equipment available at the Technical University of Delft (Fig. 1). A silica gel test rod was dried with supercritical carbon dioxide for 3 h at the chosen process conditions. During the experiment the carbon dioxide was recycled instead of vented to the atmosphere. The dried test rod was found to be free of cracks, proving that an industrial process can operate at the chosen process conditions with a carbon dioxide recycle.

4.2. Flowsheet description

A simplified flowsheet of the process designed for the production of silica aerogel plates with supercritical carbon dioxide is shown in Fig. 5. The process uses parallel extractors with an internal diameter of 1 m, height of 3 m and a volume of 2 m^3, that are operated cycle wise. At the beginning of each cycle the extractor is opened and a cylinder containing the silica gel plates immersed in cold ethanol (10–20 °C) is placed in the extractor. Subsequently the extractor is closed and pressurized with supercritical carbon dioxide until the operating pressure of 85 bar is reached. The carbon dioxide is first liquefied at 50 bar and 5 °C and then pumped up to 85 bar. Before entering the extractors, a hot-water circuit is used to heat the carbon dioxide to 35 °C. The ethanol–carbon dioxide mixture is separated at 20 °C by pressure reduction to 50 bar. The gaseous carbon dioxide is liquefied again and recycled to the extractor, while the ethanol is drawn off from the separator. When the ethanol in the gels has been completely replaced by supercritical carbon dioxide, the carbon dioxide flow to the extractor is stopped and the pressure is first reduced to 50 bar to recover the major part of the carbon dioxide present in the extractor. Finally the pressure is reduced to 1 bar by venting the remaining amount of carbon dioxide, and the cylinder with the dried aerogel plates is removed from the extractor.

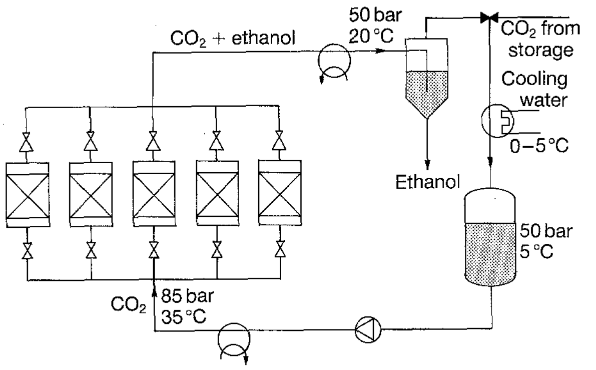

Figure 5 Flowsheet of the designed process for the production of silica aerogel plates with supercritical carbon dioxide.

4.3. Cycle time

The time required for each drying cycle includes the replacing of the cylinder with silica gel plates, the pressure build-up, the replacing of ethanol by supercritical carbon dioxide and the reducing of the carbon dioxide pressure in the extractor to 1 bar. It is expected that replacing the ethanol with supercritical carbon dioxide will make a major contribution to the cycle time. An estimate of the time required for this step can be made by using the theory for penetration into plates and rods [23]. From this theory it follows that the same degree of drying (ethanol replacement) is obtained for rods or plates with a different diameter when the Fourier number is constant

$$F_0 = \frac{Dt}{d^2} \tag{1}$$

where D is the diffusion coefficient in the gel material ($m^2 s^{-1}$), t is the contact time (s) and d is the plate thickness or rod diameter (m).

In order to obtain the same degree of drying of the different aerogel dimensions, the Fourier number should be kept constant. Because, at a constant pressure and temperature, the diffusion coefficient will remain constant, the time t, required for replacing the ethanol is related to the plate thickness or the diameter d, by

$$\frac{t_2}{t_1} = \left(\frac{d_2}{d_1}\right)^2 \tag{2}$$

In our experiments we have only measured the required drying time for silica aerogel rods with a diameter of 1.5 cm. This means that a second correction has to be made for drying plates instead of rods. For large Fourier numbers the mass transfer coefficient, k, in a plate or a rod will remain constant during the drying process because the shape of the concentration profile remains the same [23]. When a rod and a plate with the same diameter are considered, the ratio of the mass transfer coefficients is equal to [23]

$$\frac{k_p}{k_r} = 0.85 \tag{3}$$

This means that the ratio of the time required for replacing the ethanol by supercritical carbon dioxide in a plate t_p, and a rod, t_r of the same diameter is equal to

$$\frac{t_p}{t_r} = \frac{1}{0.85} \tag{4}$$

Combining Equations 2 and 4 results in the total time required to replace the ethanol by supercritical carbon dioxide in a plate when the required time, t_1, for a silica gel rod with diameter, d_1, is known

$$\frac{t_2}{t_1} = \left(\frac{d_2}{d_1}\right)^2 \left(\frac{t_p}{t_r}\right) = \frac{1}{0.85}\left(\frac{d_2}{d_1}\right)^2 \tag{5}$$

In Fig. 4 we have shown that 3 h are required to replace all the ethanol in a silica gel rod with a diameter of 1.5 cm at 85 bar and 35 °C. This means that about 14 h are required to replace the ethanol by supercritical carbon dioxide in plates with a thickness of 3 cm. Furthermore it is clear from Equation 5 that the plate thickness has a large effect on the cycle time. For example, a plate with a thickness of 1 cm will require only 1.5 h, whereas a plate with a thickness of 2 cm will require 7 h.

In addition to the time required to replace the ethanol, the decompression of the extractor to 1 bar will also require a considerable period that depends largely on the thickness of the plates. For plates with a thickness of 3 cm we expect that the pressure can be reduced at a rate of about 1 bar min^{-1}. Including the time for replacing the cylinder with wet gel plates and pressure build-up, we expect that about 2 h are required between two drying periods. This means that each cycle for the production of plates with a thickness of 3 cm will take 16 h.

5. Conclusions

An experimental procedure has been developed to produce monolithic silica aerogels by supercritical carbon dioxide drying. It was found that a combination of pressure and temperature above the binary critical curve of the ethanol–carbon dioxide system is required to obtain crack-free silica aerogel rods, plates or tubes. For rods with a diameter of 1.5 cm, a period of 3 h was required to replace all the ethanol with supercritical carbon dioxide. This drying time was found to be almost independent of the temperature (if above T_c of carbon dioxide).

From the experiments it was concluded that the most economical design will be obtained at a temperature of about 35 °C and a pressure of about 80 bar. At these conditions, a process was designed for the production of silica aerogel plates with a thickness of 3 cm.

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