Properties and applications of porous glasses from foamed glasses and gel-derived glasses to allophanes

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Porous glasses can be synthesised by different methods: in the conventional ways such as foaming (foamed glasses) or phase separation and leaching process leading to the Vycor glass, and also by the sol-gel method (sintered xerogel and aerogel), or by geological alteration process of volcanic materials (allophanes). In this paper we will discuss different features of these porous materials related to their properties, and their possible applications such as biomaterials (foamed glasses), host matrices for nuclear wastes (Vycor and sintered gels), precursors for special glasses (xerogels and aerogels), and mitigation of the greenhouse gases by carbon sequestration (allophanes).

Keywords: Porous glasses, sol gel process, allophanes.

Los vidrios porosos pueden sintetizarse por diferentes vías: por las tradicionales, tales como el espumado (vidrios espumosos) o la separación de fase seguida de lixiviación, (con lo que se produce el vidrio Vycor), y también mediante otras de desarrollo más reciente como el método sol-gel (geles) o de procesos de alteración geológicas de materiales volcánicos (alofanos). En este artículo discutimos diferentes características de estos materiales porosos y la relación de éstas con sus propiedades y las posibles aplicaciones como biomateriales (vidrios espumosos), matrices de almacenamiento para desechos nucleares (Vycor y geles), precursores de vidrios especiales (xerogeles y aerogeles), y en la disminución del efecto invernadero por secuestración de carbón (alofanos).

Descriptores: Vidrios porosos, sol gel proceso, alofanos.

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1. Introduction

The physical and chemical properties of conventional glasses have been analysed for a long time, and their applications are well known. Glasses are used obviously in the field of optical materials and containers, but also as fibres for reinforcement, and in some “exotic” applications such as nuclear waste storage. More recently, new kinds of glasses have been studied and synthesized for a specific application: the porous glasses. There id general agreement that porous glasses exhibit a physical behaviour similar to that of dense glasses, more or less affected by the porosity. For example, porous glasses have a brittle behaviour, and their mechanical characteristics (strength, elastic constant, toughness) diminish due to the porosity and to the associated lower network connectivity [1].

Porous glasses can originate from different processes. The first way was from conventional melting and quenching process which is modified to produce bubbles in the melt or pores in the dense structure. In the last decades a new kind of porous glasses has been extensively studied in literature. These amorphous materials are no longer prepared using the classical melting and refining processes but by the sol-gel method [2]. The porous structure of these materials results from the aggregation of oxides like SiO_2, Al_2O_3, ZrO_2, B_2O_3, TiO_2... The aggregation mechanism does not allow to fill the entire space, leading to a porous and amorphous material.

Another exotic porous “glasses” are the natural amorphous aluminosilicates, such as allophanes, known as weathered volcanic ash and glass [3]. Allophanes are widely present in volcanic soils called Andosols.

In this paper we will describe the different properties and possible applications of these different porous and amorphous structures. We will more specially detail the interest of sol-gel method and the associated problems.

2. Porous glasses obtained from conventional glass.

Foamed glasses

Usual glasses (window glass and other silicates) are generally made through a multiple steps process including the melting of different oxides at a temperature higher than their melting point, followed by the refining and finally quenching. The last step causes the freezing of the amorphous structure of the melt. This step is often followed by an annealing treatment which relaxes the thermal strain.

A first possible way to prepare porous glasses is to nucleate bubbles inside the melt and then quench it. The resulting glasses are generally called “foamed glasses” [4]. The bubbles are obtained, for instance by the decomposition of carbonates during the melting. An example of application of the foamed glasses is biomaterials for bone prosthesis. Calcium-phosphate glasses have a chemical composition close to that of the apatite, the mineral part of the natural bone, and consequently are well accepted by the human body. This kind of material is suitable to be used as bone implant, and the spongy texture similar to the natural bone is obtained by the decomposition of $CaCO_3$. After the foaming, the glass is heat-treated and crystallizes to the apatite form. The size of the interconnections between pores (30–40 μm) ir high enough to allow the growth of new bone inside the porosity. The development and maturation of bone inside the porosity improve the sealing between the natural bone and the implant [5].

A leaching process of heterogeneous glasses

Another example of porous glass obtained in the classical way is the microphase separated and leached ⟨⟨Vycor⟩⟩ glass [6]. In this process, sodium borosilicates glasses are heat treated in order to obtain to a phase separation. One of the phases is rich in silica and the other rich in boron. An acidic corrosion treatment will dissolve the "weak" borate phase and create a continuous porosity in the silicate phase. By controlling the composition and the heat treatment, it is possible to adjust the pore size in the range of 10 nm. The application of such a process is to prepare a silica rich glass at low temperature. This porous glass can be further sintered in vitreous silica glass at a temperature close to 1000°C, instead of the 2000°C required in the classical way [7] .This elegant method has also been proposed to confine nuclear wastes in the porosity, before sintering [8].

The corroded surface of oxide glasses can also be considered as a porous glass, the porosity is created by an aqueous corrosion effect. Corrosion starts in an initially dense glass, by the extraction of ions having a high mobility, like Na, Ca or B. The corrosion process leaves a skeleton with a chemical composition essentially based on the glass formers such as silica and alumina. The consequence of glass long time corrosion has been studied in two different kinds of materials: buried ancient glasses and nuclear glasses. Archeologists are interested to preserve the exhumed ancient glasses altered by the burying soil [9].In the case of nuclear wastes glasses, researchers have to be aware of a possible release of radioactive chemical species, if the glass structure is destroyed by a corrosion process [10].

3. Porous glasses obtained by the sol gel process

The classical procedure for making glasses includes a step at elevated temperature which ensures that the raw materials are dissolved and have reacted. Then the liquid structure is preserved by quenching the melt. In the sol - gel route this high temperature step is avoided. The homogenization is achieved in the solution at room temperature, and cross-linking and preservation of the liquid structure is accomplished by the gelling step. Further heat treatments only serve to remove organic species, hydroxyls and porosity.

The challenge of the sol - gel process is to obtain a solid, mineral, and amorphous material from a room temperature liquid (not a melt) which is generally organic. Several transformations of the liquid compounds are necessary. The first step is the formation of a gel from the solution, and generally involves the hydrolysis reaction of an organometallic compound ($Si(OR)_4$) dissolved in alcohol in the presence of water.

$(OR)_3$ Si - OR + H_2O →$(OR)_3$ Si - OH + ROH

By condensation reactions, two silanol groups give rise to siloxane bonds Si - O - Si.

$$(OR)_3Si - OH + HO - Si\,(OR)_3 \rightarrow (OR)_3Si - O - Si\,(OR)_3 + H_2O$$

These two reactions lead to non-crystalline materials containing substantial amounts of water and organic species [2].

Xerogel

After gelation, we obtain a gel which is a two-phase medium containing the solid network and the liquid (alcohol + water). Then, a drying treatment can be carried out at ambient temperature, taking into account that during this drying stage considerable shrinkage occurs converting the wet and soft gel into a dry and hard porous solid (xerogel). The drying procedure is crucial and must be performed extremely slowly because it induces capillary phenomena which can destroy the gel network and lead to the breaking up of the solid network. Various alternatives drying methods involve a favorable compromise between the capillary forces and the mechanical resistance of the gel network (strengthening the gel by reinforcement, reducing the surface tension, enlarging the pores. . .).

In summary, xerogels samples can be synthesized by a careful control of the drying parameters. They are porous glasses with relative density ranging from 0.3 to 0.7 containing essentially micropores due to the collapse of the larger pores, during drying.

Aerogel

The goal of supercritical drying (SCD) is to eliminate these capillary forces. The magnitude of these stresses dependens on the interfacial energy γ of the liquid, and it is possible to suppress γ if the pressure and the temperature exceeds the critical point of the liquid. The supercritical solvent is, then, isothermally evacuated by condensation outside the autoclave. After supercritical drying, the gel (which is called "aerogel") becomes a solid, amorphous, and extremely porous material, (80 to 99 % of porosity). The small angle scattering technique gives information on the structure and compactness of the cluster forming the gel network. The aerogel network can be described as an assembly of clusters ($\sim$50 nm). The clusters can be fractal (Df$\sim$2) built by the aggregation of small particles ($\sim$1-2 nm) [11,12]. The porosity is totally open and spans over the range of the micro to the macroporosity.

Although the xerogel or aerogel networks are rather far from that of the silica glass, Raman, infrared and RMN spectroscopy, which characterize the molecular structure, provide evidence for vibration bands identical to those observed in vitreous silica. These two kinds of porous materials can be considered as porous glasses, in spite of the very different ways attaining the "glassy" state.

The potential applications of these very porous materials are: as catalytic insulator [13–16], and as a glass precursor. By a sequence of sintering treatments, the silica gels can be easily transformed into silicate glasses [17,18], and ceramics glass [2].

Another possible interesting aplication of these porous materials is as a host matrix for the synthesis of multi-phase materials. The large pore volume is used as a sponge to incorporate chemical species in order to get a two phases material. However, the counterpart of this porosity is the poor mechanical properties and the consequence is that very porous glasses crack during filling, once again because of capillary forces. Another important parameter is the permeability. High permeability is generally an advantage because it means that the fluid and thus the chemical species of interest migrate easily in the porous network and we can expect a homogeneous repartition of the chemical species. However because micropores are very numerous, the permeability is poor and the impregnation time could be long. In summary, mechanical properties, capillary forces, and permeability are the most important parameters for the filling of the porous gel network.

One way to control the mechanical properties is through sintering. Depending on the duration of the heat treatment, the microporosity is progressively eliminated [18], and partially sintered samples can be obtained in the range of relative density between 0.15 (classical aerogel), and 1 (silica glass). The sintering has several effects: it increases the connectivity in the whole material and closes the smallest pores. So, sintering improves the ability of the porous network to resist a liquid filling.

It is generally admitted that an inclusion of particles or fibers in the material could improve the mechanical properties. In previous works, we have shown that it is possible to adjust the apparent density, the mechanical properties and the permeability by adding silica powder (aerosil) in the monomer solution, just before gelation [19]. The aerosil addition also affects the aggregation process and the structure is made of two imbricate networks, the polymeric, and the aerosil networks. For aerosil weight percent increasing from 0% to 70%, the mechanical performance increases by a factor 5, the mean pore diameter and the permeability increase too and this porous material is able to resist the capillary stresses during the pore filling by a liquid.

These different kinds of gel-derived porous glasses have been used as host matrix for very different applications. Guest molecules are deposited on the surface of the skeleton when the liquid is further evaporated. The tailoring of the mean pore size and of the pore size distribution are needed to facilitate an homogeneous dispersion of doping molecules within the texture. If the sintering is carried out inside a gradient furnace, graded porous volume with graded pore size is obtained. Doping will result in a graded property material.

The control of the chemical species diffusion inside the porosity has been done to synthesize gels and glasses showing graded properties such as gradient refractive index [20].

Impregnation by rare-earth ion solutions has also been successfully applied to synthesize doped silica glasses interesting for their Faraday effect. These glasses contain Er, Mn and Dy with a different Verdet constant [21]. For these optical applications, the very pure optical quality of the silica network issued from the sol gel route is one of the important parameters.

In a completely different domain, the containment of nuclear wastes, the impregnation of gel derived porous glasses has also been proposed. In this case, the important key is the very high chemical durability of the silica matrix which traps the nuclear wastes and protects them against water corrosion. After the soaking treatment, the host matrix is dried, then sintered. The resulting material is a composite constituted by nuclear waste crystals embedded into a silica matrix. The initial dissolution rate of such a composite in water is 10^2 times lower than that of the nuclear classical glasses [22].

Silica gels with very important porosity $(> 95\%)$ are also applied in space research as a capture medium for cosmic dusts. These hypervelocity particles enter the fine structure of the aerogel which dissipates their kinetic energy. Consequently particles having a few micron size are captured intact and can be easily located within the transparent network of the gel. [23].

4. A geological porous "glass": Allophane

The upper surface layer of volcanic soils often comprise weathering products such as imogolite and allophane originating from the sedimented volcanic ash and volcanic glasses. These components contain a significant proportion of humus substances. These soils are referred as the "Andosol" in pedological classification [3,24]. Under a high humidity climate, a leaching process of Ca, Mg, Na and K rapidly transforms volcanic glass and ash in allophane and other secondary products rich in Si and Fe. However, a detailed characterization of the reaction schemes leading to the formation of imogolite and allophane is missing. Allophane exists for young volcanic soil, and is finally transformed into halloysite by exposure to the weather.

Allophane are amorphous alumino silicate with Al/Si ranging between 1 and 2; the unit cell appears as hollow spheroids with diameter between 3 and 5nm [25]. The wall structure of allophane is porous with micropores of 0.3- 0.5 nm diameter [26]. From a structural point of view, static light scattering data demonstrate that allophane aggregates have a fractal geometry and the fractal dimension 1.8 implies that the structure of allophane aggregates can be described as clusters formed by a diffusion limited aggregation [27]. These alumino silicates have a bulk density close to 0.5 g/cm^3 [28], and develop a specific surface area as high as 700 m^2/g [25]. Because of their high reactivity, these small colloidal particles are involved in the geocycling of metallic ions such as Cu^{2+} and Co^{2+} [29]. The OH ions located at the surface of the wall and inside the particles are available for exchange by other ions and give origin to several allophane possible applications.

Silver is known to have a wide antibacterial spectrum and when loaded, then released by design from a carrier, it can be used as a disinfectant and sterilizing agent . Allophane samples are good carriers and sterilizing allophanic specimens showed immediate effect for bacterial activity (of *Escherichia Colli* and *stapphylococcus aureus*) when co-loaded with phosphorus and silver[30]. Another application of allophane is as deodorant and gas treatment. It has been shown that it is more effective than the commercially available active carbon [31].

In the field of research, allophane could have an important impact in regard to the greenhouse gas emission. It refers to the environmental function of soils for organic carbon sequestration [32]. The sequestration of carbon in the soil system is the carbon directly or indirectly removed from the atmosphere and stored in the soil. For a given texture, allophanic soils exhibited higher organic carbon concentration (by a factor 4) than other clay soils (kaolinic or smectitic)[33]. This behavior is attributed to a very stable humus - Al , Fe- complexes which may be protected from bacteria and enzyme in micro-aggregates [34]. The water content of the soil is also related to the sequestered carbon but the reason of this relationship is not yet understood [28]. A complete understanding of the sequestration mechanism in allophane will contribute to identify the factors which influence organic matter storage. For that, the acquisition of pure allophane is required, but it is not easy to get natural allophane, because of the difficulty in its separation from the impurities. Another way could be to artificially synthesize the allophane particles. For this purpose the sol-gel process seems to be a new and interesting method based on the co-hydrolysis of Al and Si precursors [35].

5. Conclusion

Porous glasses can be obtained by different ways, and have different properties and applications. The large spectrum of applications is, in fact, related to the possibility to synthesise a porous matrix having very different textural properties and chemical compositions.

The flexibility of the glass science allows to prepare porous glasses with a large and continuous domain of composition, which is not the case for crystalline compounds such as mesoporous materials (zeolite, MCM 41…). In addition to the flexibility on the chemical composition, the sol-gel process also allows a great liberty to control and adjust the pore features. The association of these two sets of advantages allows to tailor the physical and chemical properties of the porous solid to attain specific objectives and applications.

By the sol gel process, if gelling and sintering are correctly controlled, it is possible to vary the pore volume of the porous glasses between 0 and 99.5% (it must be noted that although the gels have not been melted nor quenched, the physical properties of the fully dense samples have the same physical properties than vitreous silica). These porous glasses are of interest for technological application, but also for theoretical research. Gel-derived porous glasses are ideal materials in the sense that the evolution of physical properties in relation to the structure can be experimentally studied over the whole range of porosity, and the small size of the pores could lead to specific behavior of molecules in a confined media, such as for helium superfluid. More recently, gel-derived porous glasses with tailored textural properties have also been used to investigate the polymorphism of liquid crystals in a confined structure [36].

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1. R.W. Rice, *Porosity of Ceramics*, Materials Engineering 12, Marcel Dekker, Inc (1998).
2. J. Brinker, G.W. Scherer, *Sol-Gel Science*, Academic.Press, Inc (1990).
3. K.H. Tan, *Andosols*, Van Nostrand Reinfold Company Inc. Benchmark paper in soil sciences , vol.4, (1984).
4. J.G. Zwissler and M.A. Adams, *Fracture Mechanics of Ceramics*, R.C. Bradt, A.G. Evans, D.P.H. Hasselman, and F.F. Lange, Plenum Press, (1983) p. 211.
5. F Pernot, J Zarzycki, J. Bonnel, J.F. Baldet, and J. Mater. *Sci.* **14** (1979) 1694.
6. P. Debye and R.L. Cleland, *J. Appl. Phys.* **30** (1959) 843.
7. K Kuhne and W Skatulla, *Silikattechn* **10** (1959) 105.
8. J. H Simmons, P.B.Macedo, A.Barkatt, and T.A Litovitz, *Nature* **278** (1979) 729.
9. C. Maquet, J.H. Thomassin, and T. Woignier, *J. of Sol-Gel Sci. and Techn.* **2** (1994) 285.
10. B. Granbow, *Mat. Res. Symp. Proc.* **44** (1989) 15.
11. W. Schaeffer and K.D. Keefer, *Phys. Rev. Lett.* **56** (1986) 2199.
12. R. Sempere, D.Bourret T. Woignier J. Phalippou, and R. Jullien , *Phys. Rev. Lett. 71* (1993) 3307.
13. G.A. Nicolaon and S.J. Teichner, *Bull. Soc. Chim. France* **5** (1968) 1906; US Patent N°.3,672,833, (1972).
14. S.J. Teichner, G.A. Vicarini, and G.E.E. Gardes, *Adv. Coll. Interface Sci.* **5** (1976) 245.
15. M. Gronauer and J. Fricke, *Acustica* **59** (1986) 169.
16. J. Fricke, *J. Non-Cryst. Solids* **147** (1992) 356.
17. T.Woignier, J. Phalippou *“Glasses: Sol-Gel Method “*, (Encyclopedia of Materials science: Science and technology,2001) p. 3581.

18. T. Woignier, J. Phalippou, and M. Prassas, *J. Mater. Sci.* **25** (1990) 3117.
19. J. Reynes, T. Woignier, and J. Phalippou, *J. Non-Cryst. Solids* **285** (2001) 353.
20. M. Yamane and M.Imani, *J. Non-Cryst. Solids* **147** (1992) 606.
21. J. Bouaziz, D. Bourret, and R Sempere, *J. Non-Cryst. Solids* **82** (1986) 225.
22. T. Woignier, J Reynes, J.Phalippou, and J.L.Dussosoy *J. Sol-Gel Sci. and Tech.* **19** (2000) 835.
23. P. Tsou, *J. Non-Cryst. Solids* **186** (1995), 415.
24. P. Quentin, J. Balesdent, A. Bouleau, M. Delaune, and C .Feller, *Geoderma* **50** (1991) 125.
25. L. Denaix, I. Lamy, J.Y. Bottero, *Colloids and surfaces A :Physicochem. Eng. Aspects* **158** (1999) 315.
26. Y. Onodora *et al.*, *Applied Clay Sci.* **18** (2001) 123.
27. Y. Yasuhisa and J. Karube, C*olloids and surfaces A :Physicochem. Eng. Aspects* 151 (1999) 43.
28. C.Feller *et al.*, *Nutrient cycling in agroecosystems* **61** (2001) 19.
29. C.J. Clark and M.B. Bride, *Clays Clay miner* **32** (1984) 300.
30. Y. Onodora *et al.*, *Applied Clay Sci.* **18** (2001) 135.
31. H. Morimoto, K Maeno, and T. Yamada, *US Patent* **5611853** (1998).
32. C.Feller and M.H.Beare, *Geoderma* **79** (1997) 49.
33. K.J. Wada, *The distinctive properties of Andosols* Springer Verlag (1985)
34. J.P. Boudot, B.A.B Hadj, and T. Chrone, *Soil Biol. Biochem.* **18** (1986) 457.
35. S.I. Wada, A. Eto, and K. Wada, *J. Soil Sci.* **30** (1979) 347.
36. C. Fehr *et al.*, *Phys. J. E* to be published in European.