



High resolution monitoring, real time visualization and reliable modeling of highly controlled, intermediate and up-scalable size pilot injection tests of underground storage of CO<sub>2</sub>

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## Executive summary

Optimal sealing of sol-gel fluids is examined in term of pore filling potential and permeability reduction potential by means of laboratory experiments. To this end, specific equipment has been designed and installed (ICARE SRRIS rig). It allows reproducing storage conditions in large size cores while measuring the permeability drop due the reactive fluid injection. Post mortem analyses of the cores using 3D electronic microscopy techniques have been used to investigate the sealing mechanisms and to assist the optimization of the fluid formulation (composition, retardant products, rheology, ...) and injection protocol (flow rate, alternative use of different fluids, temperature, volume,...) according to the local hydro-thermo-chemical properties of the sandstone reservoirs.

The first part of the report summarizes the state-of-the-art concerning the sol-gel preparation, properties of the final silica material and known applications for geo-material consolidation, for instance. The second part present and discuss the experiments performed for testing the application of sol-gel to decrease sandstone reservoir permeability, specifically in the frame of the application to leakage remediation test at the Heletz site (Israel). Results

Keywords	CO <sub>2</sub> geological storage, leakage mitigation, laboratory experiment, sol-gel
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## 1. Foreword

This document reports the research works done in WP6, Task 6.2, by CNRS. The objectives of Task 6.2 are to determine the optimal fluid formulations and uses according to the local hydro-thermo-chemical properties of sandstone reservoirs. The preliminary phase consisted in testing the sealing potential of different types of fluids (ionic solutions, light slurries and sol-gels) in porous media and fractured media. Only light slurries and sol-gels have been selected for detailed investigations. This document focusses on the use of sol-gels for leakage remediation and reports the first set of experiments from which we decided to design a second set of experiments that will be performed in 2015, in order to explore 1) the use of low grade (low cost) silica precursor and 2) optimized aging/drying methodology.

## 2. Introduction

It was in the early 1845 that the French chemist Ebelmen reported for the first time that the metal alkoxide synthesized from  $\text{SiCl}_4$  and alcohol gelled on exposure to the atmosphere [1][2][3][4][5][6][7]. Observing the formation of transparent solid by slow hydrolysis of the mentioned silicic ester, he wrote: *"it is permitted to hope that it could be used in construction of optical instruments"* [4].

Nowadays sol-gel technique is an attractive method to obtain high performant materials as for example hybrid materials (organic-inorganic) and nanocomposites for: optic, electronic, metallurgy, catalysis, stone consolidation and nuclear fields [3][4][5][6][7].

The advantages of the technique - widely accepted by material science community- could be summarized as it follows [4]:

1. Low temperature process.
2. High homogeneity and purity of resulting materials.
3. Possibility of various forming processes.

## 3. Characteristics of a Sol-Gel

Definition: - sol: dispersion of particles of specie M within a liquid

- gel: solid tridimensional interconnected network, expanded through a liquid medium.

### 3.1 "Sol" state

Sol is defined as a solution containing a monomer specie M and solvent. In function of the size of the specie in solution, it will be called true sol (molecular specie); or colloidal solution (particle of the order of hundreds of Å). Solvent molecules surround species in solution, forming a solvation envelope. The stability of the sol characterizes the quality of dispersion of particles, in the medium. A sol is stable if there is no formation of aggregates during the time. So, interactions between solvated species and molecules are stronger than interactions between species themselves preventing in this way, any aggregation, precipitation or flocculation [1][2][5].

There are three kinds of interactions[5]:

- **Electrostatic:** Coulomb forces between charged species.
- **Chemicals:** Hydrogen bonds with complexation of the solute and solvent.
- **Physical:** Weak bonds of Van Der Waals between neutral species.

Until that the gel state is reached, system is in liquid state: it is constituted by a mixture of colloidal oligomers, small macromolecules and, in function of the progress of the polymerization reaction, of different partially hydrolyzed monomers. This liquid solution is called "*Sol*". The time needed by the sol to transform itself in "gel" is the gel time (or gel point), noted  $t_g$  [1][2][5].

## 3.2 "Gel" state

Although the term "gel" had received numerous definitions in literature, it is generally admitted particularly in "sol-gel community", that the gel is characterized by an oxide network inflated by the solvent, with chemical bonds ensuring the mechanical cohesion of the material, giving it a rigid and not deformable structure (gel could present an elastic character, but not a macroscopic viscosity). A gel is defined as a biphasic system in which solvent molecules (water, alcohol) are trapped in the solid network. In function of preparation conditions, the nature of the cohesion between particles constituting the material, changes. So we distinguish two kinds of gels:

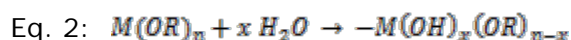
- **Physical gel:** the system is fixed by electrostatic interactions. Under the effect of a mechanic action (stirring for example), bonds between particles can be broken to recover the sol state [5].
- **Chemical gel:** particles constituting the solid network are bonded by chemical bonds; gel state is irreversible but could deform itself and recover the form [5].

The distinction between these two systems it is not always easy. In fact, electrostatic and chemical interactions can occurs at the same time and combine them in the sol. During the aging of gel, reticulation leads to a material shrinkage and to the expulsion of the solvent: this is the syneresis phenomena. Independently of it, it is possible to dry the gel in atmospheric conditions or in supercritical conditions. In both cases we obtain a more or less dense structure without solvent, called *xerogel* if drying is carried out in atmospheric conditions; and *aerogel*, if system had undergoes a drying in supercritical conditions. Sol-gel transition takes place suddenly when an enough amount of monomers aggregate, forming macroscopic clusters occupying all of the sol volume [1][2][5].

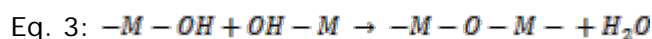
## 3.3 The Sol-Gel process

A sol-gel process can be carried out by the destabilization of colloidal solution or by the polymerization of molecular species [5][6]. By the control of both hydrolysis and condensation reactions, the latter method can be more easily controlled compared to the colloidal one [6][7]. It is admitted that reactions characterizing the polymerization method of sol gel process are [1][2][5][6][7][8][9]:

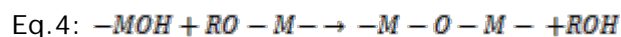
- Hydrolysis:



- Condensation:

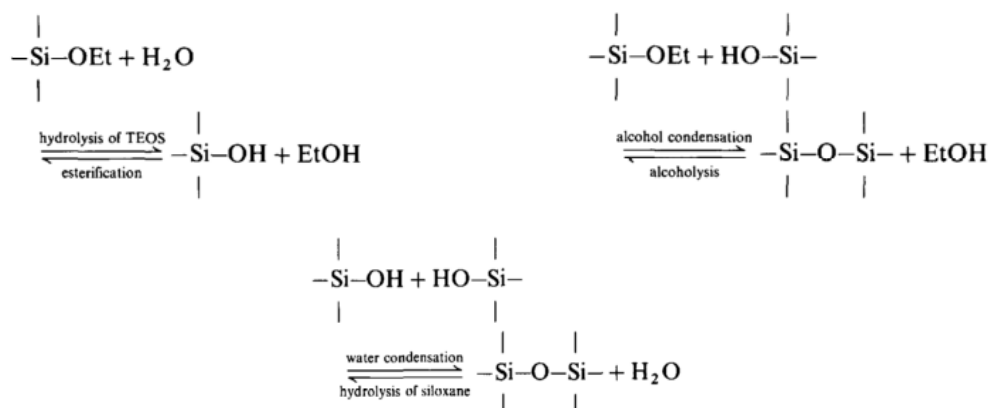


- De-alcoholization/Drying:



## 3.4 Sol gel chemistry of silica







In polymeric route (chemical gel), the silicon alkoxide ( $Si(OR)_4$ ) is the main used precursor. The most common commercial silicon precursors are trimethoxysilane  $Si(OCH_3)_4$  (TMOS) and triethylethoxysilane  $Si(OC_2H_5)_4$  (TEOS) in their associated alcohols. In our work we choose TEOS, as silica precursor which transformation in silica gel takes place in a water-ethanol medium, following the reactional mechanisms presented below:



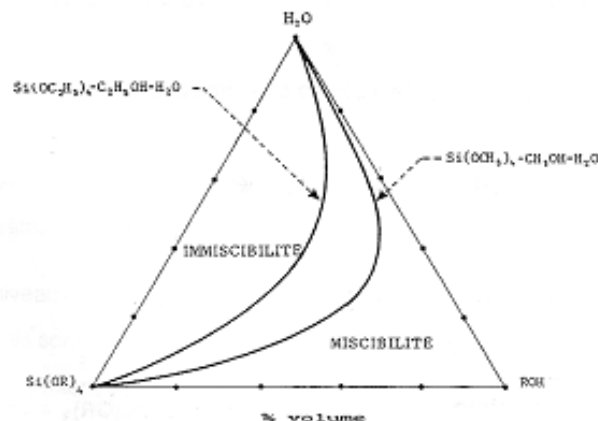
**Figure 1:** Reactional mechanism of transformation of TEOS into silica gel[10][11]

In the course of this conversion a wide range of intermediates is formed which belong to ethoxysilanes, ethoxysiloxanes, ethoxyhydroxyloxanes. Their structures and molecular weight determine the properties of intermediate phase ( $SiO_2$  sol) or of final product ( $SiO_2$  gel). It depends of the statement of hydrolysis and condensation processes [10]. A complete hydrolysis is obtained when stoichiometric molar ratio water: $Si(OR)_n$  (R) is 4 so, any intermediate is considered the result of partial hydrolysis [7]. Under most conditions, condensation can start before a complete hydrolysis but by the control of reactional parameters such as pH,  $H_2O/Si$  molar ratio and the presence of catalysts, we can force complete hydrolysis before condensation begins [1][5][7][12]. Silica network and its properties result from alkoxides polymerization and/or from silica clusters aggregation in both alcohol and aqueous solutions. Extensive studies of condensation and re-dissolution of silica in water were carried out by Iler [13]. It depends of the probability of aggregation during the contact of two species (reactivity), of the diffusion of the main specie and of the growth of clusters (effects of dilution, viscosity and temperature). Models proposed are stipulated considering that "growing" is the limiting mechanism: limited diffusion of growth of monomer-cluster or cluster-cluster, limited reaction of monomer-cluster or cluster-cluster. Generally speaking, clusters or aggregates have a fractal structure (or hierarchical) for scales higher than the primordial unity (see Figure 2) [1][5].

Due to the immiscibility of the alkoxides and water (cf. Figure 3), a mutual solvent -an alcohol- is used as homogenizing agent to facilitate the hydrolysis process [1][5][7][14]. Thus the rates of hydrolysis and polycondensation determine the structure and instantaneous properties of the products of the TEOS-water reaction. These rates depend on the reaction conditions and can be acid or basic catalyzed.

	REACTION-LIMITED	BALLISTIC	DIFFUSION-LIMITED
MONOMER-CLUSTER	EDEN  $D = 3.00$	VOLD  $D = 3.00$	WITTEN-SANDER  $D = 2.50$
CLUSTER-CLUSTER	RLCA  $D = 2.69$	SUTHERLAND  $D = 1.95$	DLCA  $D = 1.80$

**Figure 2:** Aggregation model.  $D$  is the fractal associated dimension [1][5]



**Figure 3:** Ternary diagram of miscibility of Water-Alcohol-Water system [1][5][7][14].

Under acid-catalyzed conditions, the hydrolysis kinetic is favored instead of the condensation, which generally starts when hydrolysis is completed. In alkali-catalyzed reactions, condensation is faster than hydrolysis, resulting in a highly condensed species that may agglomerate into fine particles [7][9][15]. Compared to the transition metal alkoxides, TEOS is known to be less sensitive to hydrolysis, due to Si which is less electropositive [7]. Thus, in the case of silicon alkoxides, a change of surface charge can be easily carried out by changing pH using acid or alkaline catalyst to enhance the hydrolysis and condensation reactions [1][5][7][10][16]. At  $\text{pH} = 2.2$  we reach the isoelectric point of Si (surface charge is null). In this way, particle-to-particle interaction is limited and no aggregation or agglomeration takes place [7][10][13]. By pH change or if the particle-to-particle distance is reduced by solvent evaporation, the surface charges are decreased and gelation takes place. In the case of sol-gel systems based on oxides, the particle-to-particle interactions are strong so that, especially after drying, the agglomeration is irreversible. It is known that for TEOS under acid conditions (with  $R=4$ ), condensation rate is minimized at  $\text{pH}=2$  and maximized at intermediate pH values for various types of acid. Unlike, hydrolysis phenomenon has a maximal rate at low pH and a minimal rate at  $\text{pH}=7$  [7][10][16].

The pH also affects the dissolution of silica [7][13]. At high pH values, where particle may have a high solubility in the sol, more porous structures are obtained. At low pH values fine pore networks and dense structure are obtained due to low dissolution-reprecipitation rate [7]. A lot of studies show that final properties of sol-gel prepared material depends also on the nature of the choose catalyst [1][2][7][10].

Temperature, Aging and Drying are others three important parameters affecting directly the final structure of obtained material. The aging of the gelled structure before the drying step, gives the statement of polymerization process (clusters size) and so, the texture of resulting solid. Drying, then, strongly affects the porosity of synthesized material. In fact, under atmospheric conditions, it involves the loss of water, alcohol and other volatile components. This leads to gel shrinkage causing internal stresses which, if they are not stopped, make cracks happened creating in this way additional random porosity, deformations and breaking of the structure. Heating at relatively high temperatures is carried out to remove the organic species and leads to formation of covalent Si-O-Si bonds [1][2][5][7][8][10][16][17][18][19].

## 3.5 Use of alkoxylane for stone consolidation - Performance criteria

The earliest attempt to use silicic ether or ethyl silicate for stone conservation was in an 1861 meeting of Royal Institute of British Architect by A. Hoffmann for the treatment of the Houses of Parliament of London. Around the time of World War II, the improvements relating to the organosilicon industry were rapid. Partially polymerized ethyl silicate such *Ethyl silicate 40*, began to be widely marketed and experimental studies with various chemical formulations of ethyl silica were carried out in United States. Although some contradictory observations emerged, global results have pointed out that alkoxysilanes and related compounds are still the most promising consolidants [11][20][21][22].

### 3.5.1 Performance requirement for consolidants

Performance requirements for stone consolidants have gradually emerged as understanding of the factors controlling their performance has improved. The most significant criteria which must be taken into account are[11][20]:

- **Consolidating value:** The primary requirement of a stone consolidant is to restore physical integrity and mechanical properties of the decayed stone to an acceptable level by re-establishing the bonds between adjacent grains. A consolidant may perform this function through the deposition of new and durable binding agent within the pores of stone.
- **Durability of consolidated stone:** The treated stone is expected to be as durable as the untreated stone. It is very important that the aging of solidified injected compound don't leads an accelerate degradation of the existent porous media.
- **Depth of penetration:** The consolidating substance should have the ability to penetrate easily and deeply into stone porous structure. There are many factors affecting penetration of the consolidant. They are related to the properties of the treating agent including its surface tension, viscosity, rate of evaporation and gel rate, as well as the characteristics and temperature of the porous material to which it is applied. Low viscosity and high surface tension of the impregnating fluid are desirable to achieve good penetration (role of surfactant).
- **Compatibility of consolidant with stone:** Consolidant should not form by-products which can be harmful to the stone. Many of the inorganic consolidants are precipitated as a result of the reaction between two dissolved salts. In addition to the precipitate, at least one soluble salt is formed, much of which is deposited in the stone as the water evaporates. These soluble salts can damage the stone through recrystallization processes and/or produce unsightly efflorescence on the treated surface of stone.
- **Stone consolidants**  
We have already mentioned the difference between the polymeric and colloidal route. We will show below, the result of their use in consolidation stone field.

### 3.5.2 Inorganic Materials

This kind of compounds has been widely studied since they are cheaper than organic compounds and less toxic so, easier to manipulate in the most of cases. For the consolidation of historical monuments stones, inorganic materials has a little success and in some case, their use has greatly accelerated stone decay. Some of the reasons given for the poor performance of inorganic consolidants are their tendencies to produce shallow and hard crusts because of their poor penetration abilities (Precipitation processes are often so rapid that precipitates are formed before inorganic compound can appreciably penetrate the stone), the formation of soluble salts as reaction by-products, growth of precipitated



crystal, and the questionable ability of some of them to bind stone particles together. The most widespread of inorganic mixtures are obtained from nonstoichiometric dispersion of silica in sodium or potassium hydroxide and are often associated to acids solutions as for example hydrochloric acid, sulfuric acid, arsenic acid... Resulting by-products are often hydrophilic and react with elements present in pores environment and which cause, in most of cases, an acceleration of stone deterioration by unsightly efflorescence, salt dissolution and re-crystallization anisotropic crystal growth[11].

It is interesting to highlight that, numerous sealant technologies applied in oil field, are based on these inorganic materials (cements or not) and their annexed problematics as specified by some field operator : once in contact with weakened or cracked rock, these compounds are effectiveness only at shallow layers due to the difficulty in control their solidification behavior [23]–[26].

### 3.5.3 Alkoxides based compounds

As specified, the use of alkoxysilanes for consolidating stone is not a recent development. It has been commonly used since around 1960 in Germany. Nowadays, alkoxides (silicon-based or not mixtures) still considered by stone conservators as promising stone consolidating materials for both siliceous and calcareous stones. The main reasons are their abilities to penetrate deeply into porous stone and the fact that their polymerization can be delayed until deep penetration has been achieved. In addition, in function of the chemical composition of the mixture, they polymerize and then solidify producing material similar to the binder. So, it is possible to fill stone porous media and make polymerization happens inside them. Water and catalysts needed for the hydrolysis process can be injected separately or be already present in the rock pores. It presents a net advantage make the penetration of depth and the rate of reaction, perfectly controllable [8][11][17][19][20][22][27][28][29].

Recent studies confirm these theories and show that the utilization of TEOS based material increases significantly the properties of degraded stone. In its work, Sassoni [28] compared the effectiveness of TEOS based consolidant and one synthesized starting from diammonium hydrogensulfate and calcite to form hydroxyapatite (HAP). Treated samples were two different sandstones: highly porous calcareous sandstone (Giallo Terra di Siena (GS)); and quartzitic sandstone (Pietra Serena (PS)). He observes that PS stone treated by TEOS based consolidant presents an important diminution of pore size distribution (62,6 %). On the other hand, a slightly modification was obtained for GS (18,8% only). An increasing of hydrophobicity and then, decrease of water absorption were also recorded for samples treated by TEOS based solution. This was attributed to the presence of residual ethoxy groups given that these results were not recorded for HAP treated samples. For both treatments, a considerable enhancement in Young modulus and tensile strength were observed. Results obtained for TEOS based consolidants are in accord with those obtained by Ludovico-Marques and Chastre [27].

The poor chemical affinity between calcite and silica molecules formed after hydrolysis and condensation was evoked. However, Ksinopoulous [30] by the absence of difference of thermal expansion coefficient between TEOS-treated and untreated carbonate stones affirms that good affinity exists between silica based consolidant and carbonate substrate. For the extension of underground application in carbonated reservoir, this aspect will have to be more deeply studied.

One of the reasons for which TEOS was not considered for massive injection use is its price which is due in part, by its high degree of de-hydration process. For these reasons, numerous studies were carried out in order to replace this component by cheaper ones. In the next paragraph we will focus on the case of Ethyl Silicate 40.

## 3.6 Use of ethyl silicate 40 (ETS40) [31]

Ethyl silicate 40 (ETS40) is produced by the reaction of silicon tetrachloride with ethanol and water, or by partial hydrolysis and condensation of tetraethyl-orthosilicate (TEOS), which is also called ethyl silicate 28. These two silicates contain an equivalent amount of about 40 wt% and 28 wt% of  $\text{SiO}_2$  respectively. On this basis, the molecules of the ethoxysiloxanes in ETS40 are assumed to contain an average of five Si atoms.

In 1992, Cihlár carried out a study on the influence of temperature, catalyst concentration, water concentration, solvent amount, ETS40 concentration, and the number of Si atoms in the ethoxysiloxanes molecule on the hydrolysis and condensation processes.

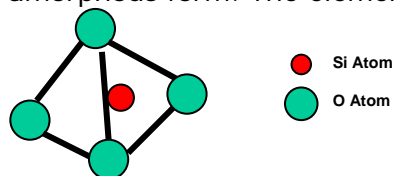
The reaction of ETS40 with water was performed in a stirred laboratory batch reactor at temperatures between 20 and 50°C over a period of 2-5h. The ETS40 behavior were rigorously compared to TEOS one. The author observed that ETS40 hydrolysis and condensation take place according to the same mechanisms as TEOS hydrolysis and condensation.

The difference between these components as regards hydrolysis rate, condensation rate and the structure of the products of hydrolysis and condensation were due to the difference in structure of the two ethyl silicates. The lower hydrolysis rate and higher condensation rate of ETS40 are related to its composition which, in contrast to TEOS, is a mixture of TEOS and ethoxysiloxanes with linear, branched and cyclic structures. Steric parameters characterizing these polymers make difficult the nucleophilic attack of  $\text{H}^+$  to hydrolyse the chains. The larger ethoxyhydroxysiloxane molecules, formed during ETS40 hydrolysis and containing 14-20 Si atoms, were responsible for the more rapid condensation of ETS40 hydrolysates, compared to TEOS one. As for the latter compound, hydrolysis and condensation are very influenced by the pH value. Strong acid catalyzer appeared to be more efficient than weak acids.

So, ethyl silicate 40 seems have the same behavior as TEOS with respect to hydrolysis and condensation processes. Its longer time of hydrolysis with respect to TEOS could present net advantages for our specific applications. Moreover, its high concentration in  $\text{SiO}_2$  could give denser and more effectiveness solid matter filling pores of stone matrix. A depth study on its rheological properties and the controllability of sol-gel technic parameters at hydrothermal conditions in presence of such component must be carried out; as an anteriority research on patents already existing, the extension of their applications and met problematics.

## 3.7 Silica and glasses structure

Silica is by far the major component of the earth's crust. It is the basic constituent of glass and ceramic materials and can exists under both three crystallographic forms (quartz, tridymite and cristobalite) and amorphous form. The elementary unity of all silicates is tetrahedral  $\text{SiO}_4$  structure (Figure 4).

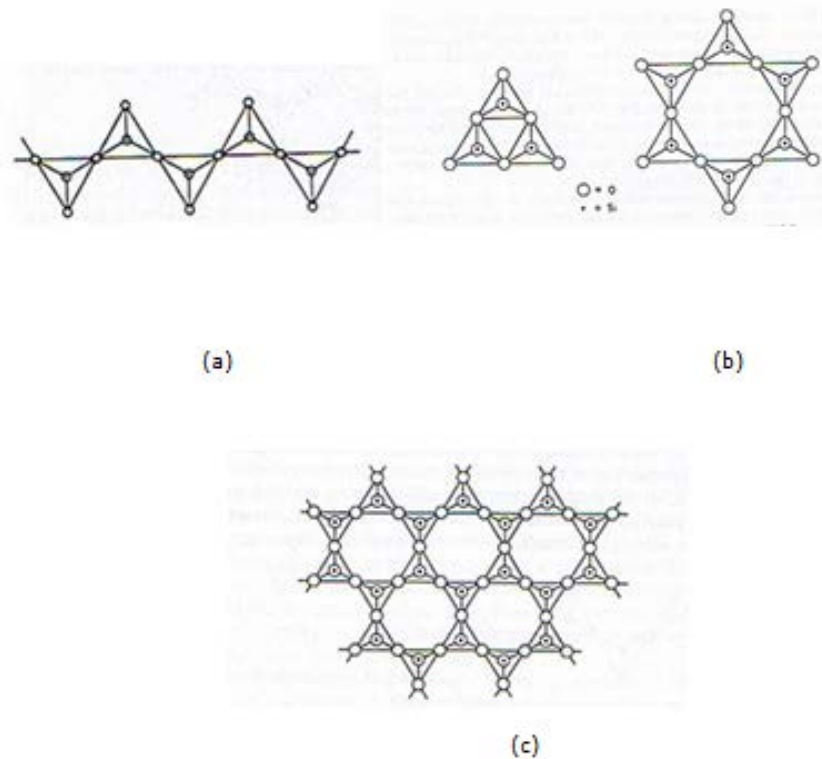


$\text{SiO}_4$  Tetrahedron

**Figure 4:** Silica tetrahedron [32].

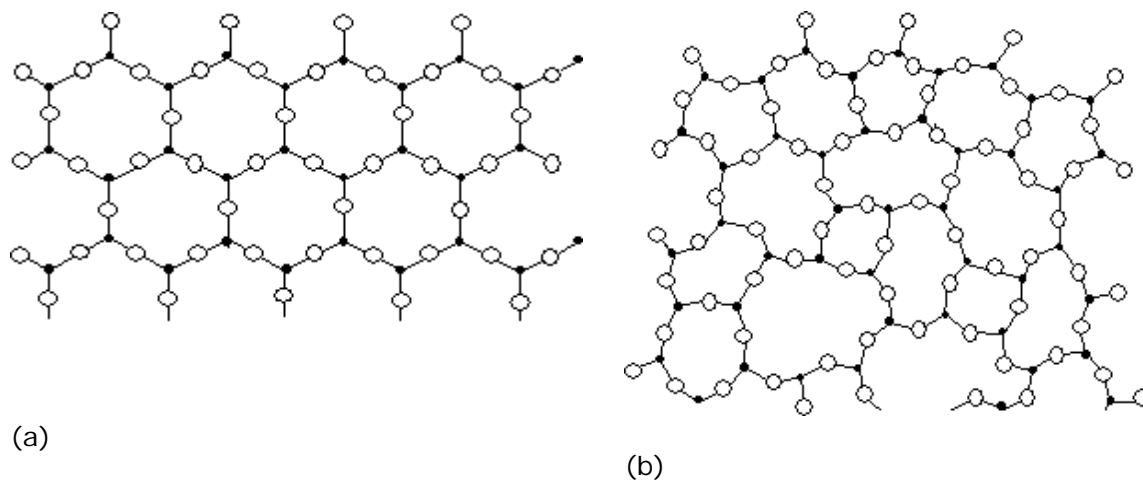
The bindings between oxygen atoms of these tetrahedrons (also called bridging oxygen) contribute to the formation of chains, sheets or cycle as shown by Figure 5; and are responsible of the flexibility of

formed structures. In crystalline ones, these tetrahedral unities are superposed orderly (Figure 6a) while, in amorphous ones as glass structure arousing our interest, tetrahedrons are superposed randomly (Figure 6b).



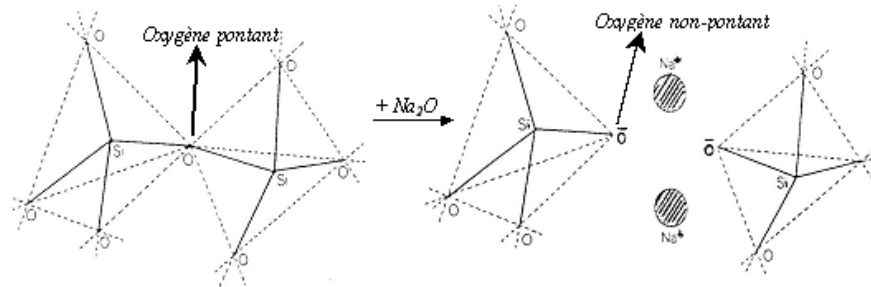
**Figure 5:** Arrangement of silica tetrahedrons[33] : (a) As chain (b) as cycles (c) as sheets

In tetrahedrons, the bond energy between silicon and oxygen is of 368 KJ/mole[34]. The Si-O bond measures 1.62Å while O-O bond 2.7 Å [35].



**Figure 6:** Bi-dimensional representation [36] (a) Cristobalite (b) Vitreous silica

Vitreous silica based glass often contains other cationic elements playing an important role on vitrification process. In '30s, Zachariasen separated these elements into two categories: "*formers*" and "*modifiers*". *Formers* (*F*) as boron oxide ( $B_2O_3$ ); phosphorous oxide ( $P_2O_5$ ); germanium oxide ( $GeO_2$ ) and arsenic oxide ( $As_2O_3$ ); have a coordinance of 3,4 and 5; and form  $FO_4$  or  $FO_3$  polyhedral structures, linked by their summit oxygen constituting the glass network as shown in Figure 7. On the other hand, *modifiers* are alkaline or alkaline-earth elements, giving ionic bonds which can produce the breakage of Si-O-Si bridges. (Figure 7). It was already specified that the bridge between tetrahedral structures assured by Si-O-Si bonds, confers to the material its mechanical properties.



**Figure 7:** Breakage of Si-O-Si bridge by addition of  $Na_2O$  modifier molecule [37].

Tab.1 presents a classification of oxides in function of their aptitude to form glass. [36].

<i>Formers</i>	<i>Modifiers</i>	<i>Intermediates</i>
$SiO_2$	$Li_2O$	$Al_2O_3$
$GeO_2$	$Na_2O$	$PbO$
$B_2O_3$	$K_2O$	$ZnO$
$P_2O_5$	$CaO$	$CdO$
$As_2O_5$	$BaO$	$TiO_2ZrO_2$
$V_2O_5$		

**Tab1.** : Classification of oxides in function of their aptitude to form glass

## 3.8 Mechanical properties of silica and silica based glasses

It is known that silica and glasses are brittle materials. They have a very small thermal expansion coefficient ( $5.5 \times 10^{-7} / ^\circ C$ ) with respect to steel one ( $12 \times 10^{-6} / ^\circ C$ ) for example; and are characterized by brittle breaking.

In order to apprehend the relation between intrinsic properties of silica based material and their mechanical properties, we will focus on the definition of the main mechanical characteristics allowing the mechanical evaluation of studied material.

## 3.8.1 The Young's modulus

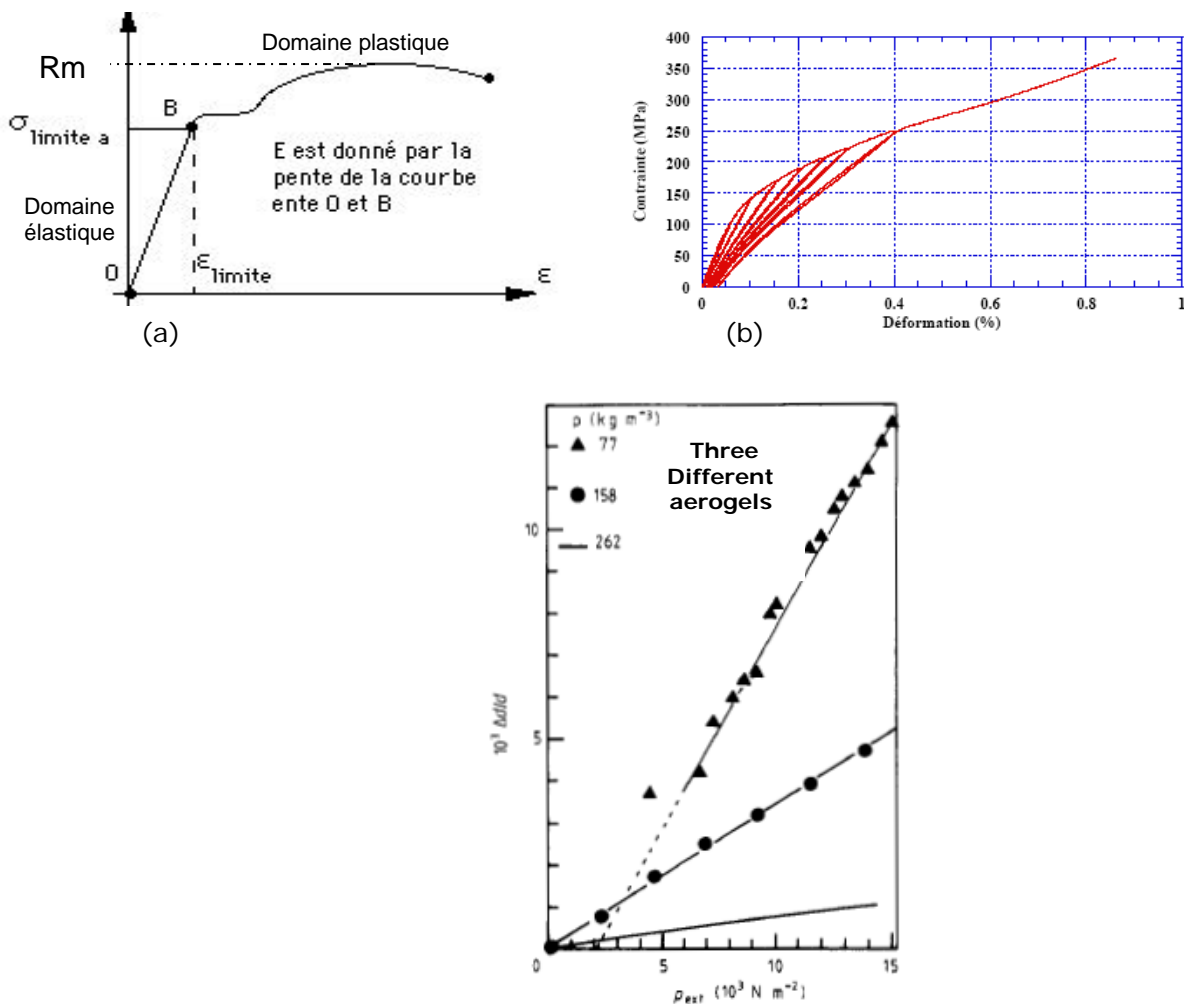
The relation between stress and strain of an isotropic and homogeneous material is given by the Hooke law

$$\sigma = \varepsilon E$$

With:  $E$ : Elastic modulus or Young's modulus (MPa)

$\varepsilon$ : Deformation (without unity)

Figure 8, presents stress-strain curves of three different materials.



**Figure 8:** Stress-strain curve of (a) metal, (b) SiC based composite material [38] and (c) three different specimens of silica based aerogels [39].

We can observe that unlike metal which presents both elastic and plastic mechanical properties; silica based aerogels is characterized by brittle breakage. No plastic behavior is appreciable at macroscopic scale for this material.

### 3.8.2 Brittle breaking

In accord with Benson [40], the rupture of material is its separation into two or more parts. Brittle fracture as glass one, unlike ductile one, is characterized by the absence of plastic deformation at macroscopic scale and then, by the very fast cracks propagation with a weak energy consumption. The relationship between breaking stress ( $R_m$  or  $\sigma_{Th}$ ), Young's modulus ( $E$ ), the surface energy created during breaking ( $\gamma$ ), and the distance of atoms in free strains conditions ( $x_0$ ), is given by the following relation:

$$\sigma_{Th} = R_m = (E\gamma / 4x_0)^{1/2}$$

For glass, the really breaking stress is lower than theoretical stress ( $/200$ ). It is due by the fact that glass always presents surface defects. Breaking happened when defect reach a critical dimension defined by Griffith relation:

$$\sigma > \sqrt{\frac{2\gamma \cdot E}{\pi \cdot a}} \text{ with } \gamma: \text{ surface energy and } a: \text{ critical size of defect}$$

### 3.8.3 Relation between structure and mechanical properties

As already specified, in sol-gel synthesis, cracking phenomenon is due by the drying stresses that are generally attributed to large capillary forces generated in very small ( $\leq 10\text{nm}$ ) pores of as formed gel [41]. This phenomenon can be minimized by several ways including very slow, controlled drying over the course of weeks or months, by increasing the average pore size through the introduction of colloidal silica seed particles, by adding surfactant, by supercritical drying, by freeze-drying or by the use of "drying control chemical additives" (DCCAs) such as glycerol, formamide, and oxalic acid [41]. For this purpose, numerous studies were carried out in order to correlate the glass composition and its mechanical properties.

### 3.8.4 Introduction of nanoparticle and polymeric elements in stone consolidants

Into two recent studies in stone consolidation field, two solutions were proposed to avoid shrinkage and cracking phenomena of consolidant within porous structure of substrate. In the first one [30], author proposed the introduction of nanoparticles of titanium oxide in TEOS based consolidant. It is highlighted that an increase of viscosity of applied sol is recorded with the increase of particle oxide amount in starting mixture. Moreover, the effectiveness of consolidant is not the same for the two studied carbonate stones which had different pores distribution and sizes. A better penetration of consolidant was recorded in stone presenting the higher porosity and smaller pore size. In this work, the sol-gel synthesis was *base catalyzed* and the poor chemical affinity between calcite and silica molecules formed after hydrolysis and condensation was evoked.

In the second study, Luo et al. [19] proposed the introduction of polydimethylsiloxane (PDMS) (silicon oil particularly known for its unusual rheological properties) with nano-sized hydroxyapatite (n-HA) or micro-sized hydroxyapatite (m-HA) particles. A cracks-free solid were obtained in glass crystallizer for TEOS-PDMS-(n-HA) prepared sample. If only PDMS were added to TEOS based sol, shrinkage and cracking phenomena happened as for sols in which m-HA were added instead of n-HA. A hydrophobic character seems appear for TEOS-PDMA-(n-HA) treated samples. No penetration depth measurements



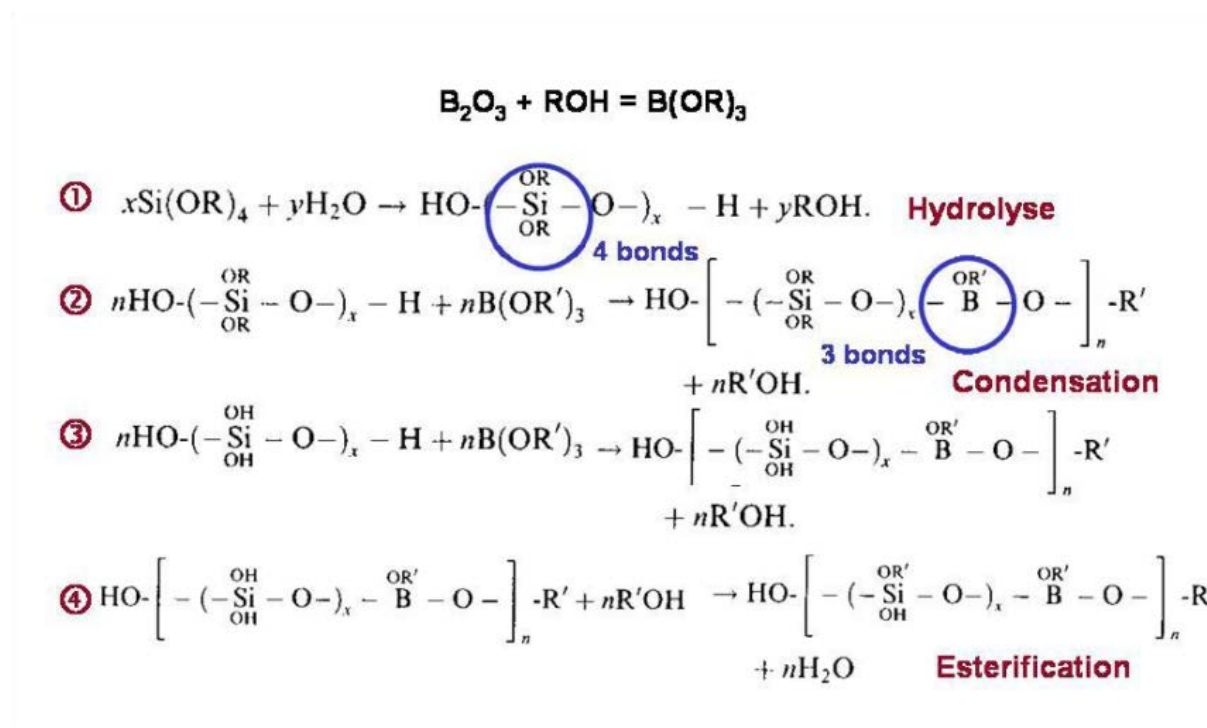
were performed and, the slight difference of pore size distribution between treated and untreated samples allow us to suppose that no depth penetration within porous matrix have taken place.

So, what emerges of these studies is that the addition of nanoparticles or polymeric elements in TEOS based sols, can implicate an increase of its viscosity avoiding a good filling of porous matrix of substrate.

In the next paragraph, we will focus on the effect of the addition of boron oxide in silica matrix, and its repercussions on its mechanical properties.

### 3.8.4.1 $\text{Bi}_2\text{O}_3$ - $\text{SiO}_2$ binary system

Boron is a trivalent element used as boric anhydride ( $\text{B}_2\text{O}_3$ ). By its introduction in reaction field in which silicon alkoxide undergoes hydrolysis, boric anhydride and alcohol react in situ to form boron oxide precursor - of type of boron alkoxide - able to leads to its incorporation into in-formation silica matrix. The reaction of boron introduction is described in Figure 9.



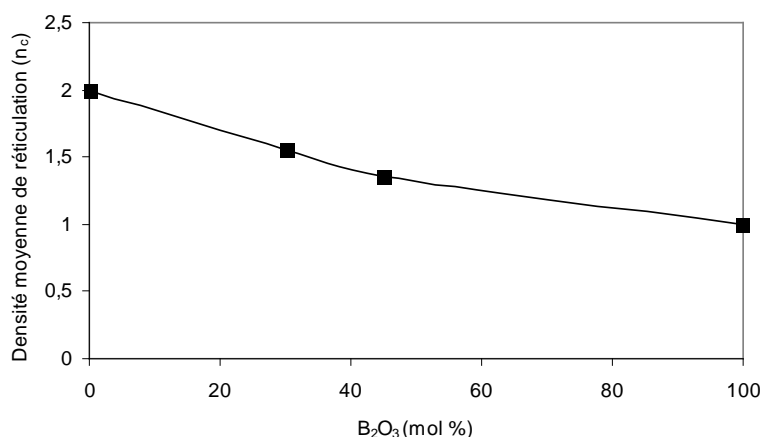
**Figure 9:** Reactional mechanism of insertion of boron anhydride in silica matrix [5]

The B-O bond energy evolves between 560 and 790 KJ/mole [34] for  $\text{BO}_4^-$  and  $\text{BO}_3$  respectively. B-O distance in  $\text{BO}_4$  is of 1.476 Å while, in  $\text{BO}_3$  is of 1.37 Å only. The bond between boron and oxygen is stronger than those existing between silicon and oxygen. So, boron element inserts itself in silica network forming directly borosilicates as tetrahedrons linked with oxygen atoms by Si-O-B bonds, between the two kinds of tetrahedrons. Figure 10 shows the structure of datolite constituted of silica, boron oxide and calcium oxide.



**Figure 10:** Example of datolite structure:  $(\text{CaBSiO}_4(\text{OH}))$

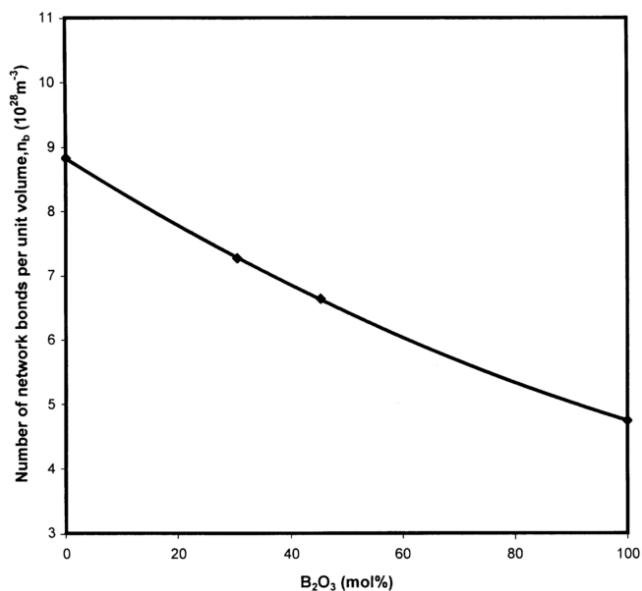
A.Abd El-Moneim [42] studied the influence of addition of boron oxide on silica network parameters (cross-link density, number of network bonds per unit volume of the glass and atomic ring size). He treated the case of borosilicates exempt of stabilizer elements as alkaline ones; and shown that the introduction of  $\text{B}_2\text{O}_3$ , reduces the number of bonds between silica tetrahedrons (cross-link density) as shown by the Figure 11. This phenomenon increases with boron oxide amount.



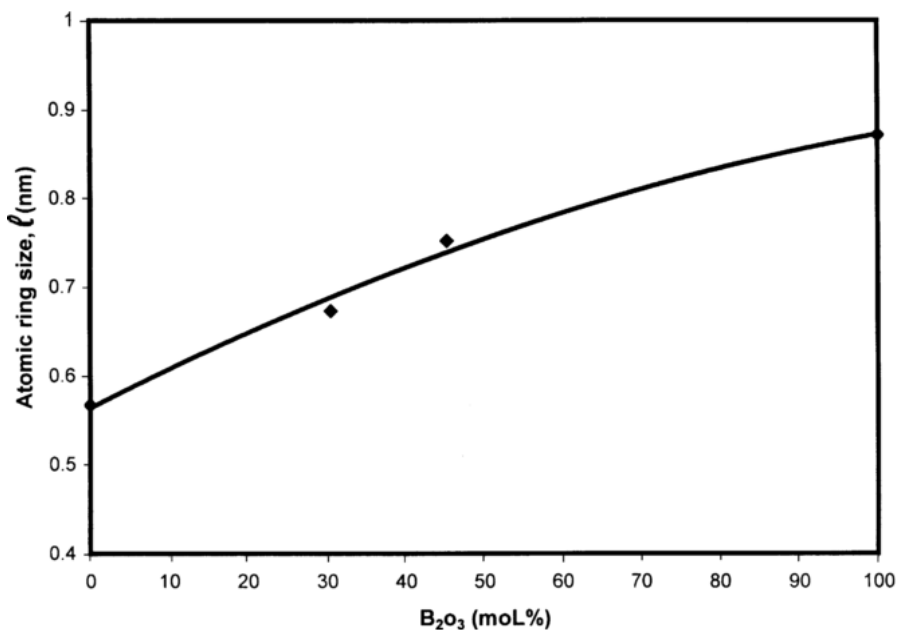
**Figure 11:** Variation of the average cross-link density with  $\text{B}_2\text{O}_3$  concentration in the  $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  glass system. [42]

He also showed that this enhancement of non-bridging oxygen atoms leads to the decrease of network bond per unit volume and it is associated to the increase of atomic ring size of the silica intrinsic structure (Figure 12 and Figure 13 respectively).





**Figure 12:** Evolution of network bond in function of boron oxide concentration

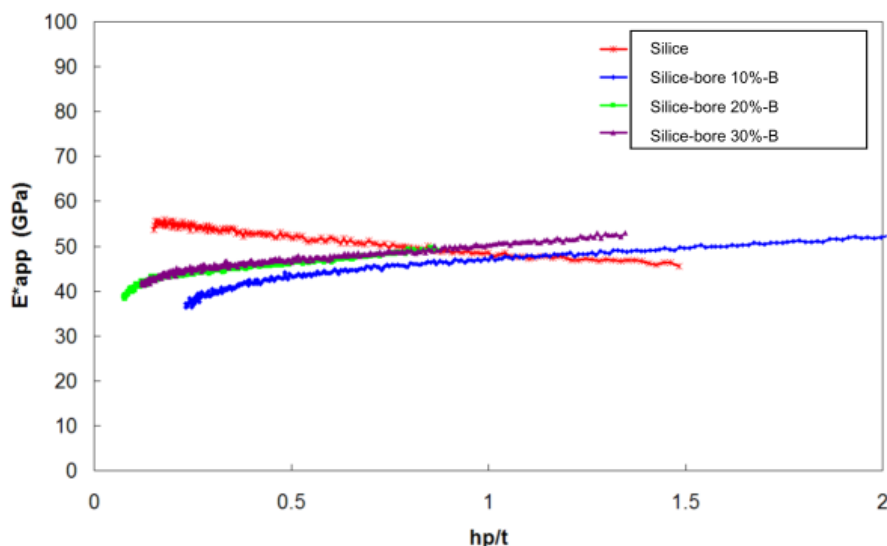


**Figure 13:** Evolution of atomic ring size in function of boron oxide concentration

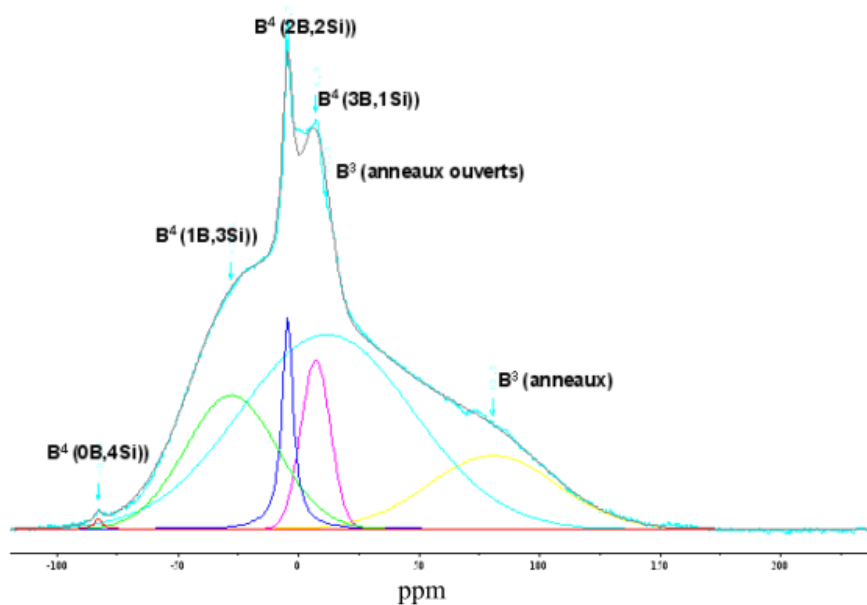
Sala [43] in her studies on sol-gel prepared helium selective membranes, observed the decrease of Young's modulus of silica based layers in function of rise of boron oxide concentration within it (Figure 14). Moreover, the thermal expansion of the same layers increased from  $5,5 \times 10^{-7}$  to  $2,6 \times 10^{-6}$ . So,

obtained layer are more elastic and follow better deformations. It leads to the obtaining of cracks-free boron silicate layer with thicknesses of the order of hundreds of nm.

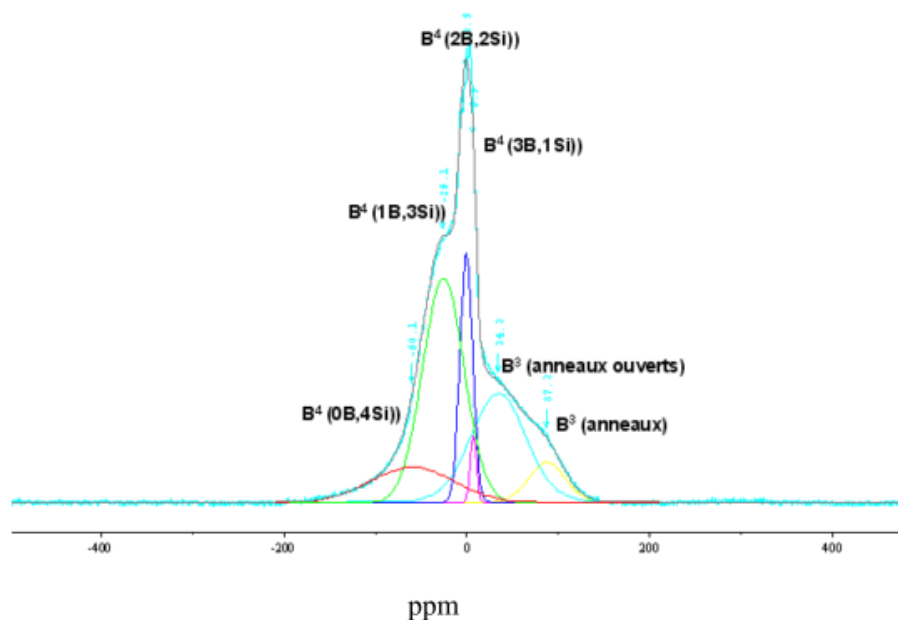
RMN analysis of these borosilicates containing different amounts of boron anhydride (Figure 15 and Figure 16) prove the fact that, at low temperature, boron has a trivalent character while, during calcination (550°C) it acquires tetravalent structure. The substitution of silicon atom (tetravalent) with boron one (trivalent) leads to the decrease of reticulation in silica based network - also observed by Moneim – which can explain in part, the softening of the structure especially during drying step.



**Figure 14:** Young's modulus of silica doped with different amount of boron anhydride



**Figure 15:** RMN spectra. 10% B<sub>2</sub>O<sub>3</sub> – 25°C



**Figure 16:** RMN spectra. 10% B<sub>2</sub>O<sub>3</sub> – 550°C

So, the introduction of boron oxide in silica gel precursor mixture is a good solution for our application for reasons specified below:

- Boron oxide is soluble in TEOS-Ethanol mixture;
- Once boron anhydride is dissolved in binary mixture, the viscosity of latter is kept unchanged;
- $B_2O_3$ , by interaction with silica matrix, confers it some elastic properties avoiding cracks during shrinkage phenomenon which characterize the drying step of sol-gel synthesis.

It represents a net advantage with respect to the utilization of organic polymer for the obtaining of hybrid material having elastic or some plastic properties, in function of required applications. In fact, as pointed out by Novak [41] and others researcher teams, the need of specific polymer solvent, the need of good functionalization of polymer to increase and control silica-polymer interfacial reactions, the delicate task of the control of polymer dispersion within silica matrix and the sensibility of these organic precursors at temperature (which lead degradation of matrix and hole formation), make the synthesis of such materials by the sol-gel technic quite complex and restrain considerably the number of eligible polymers for our specific application (Filling of a porous structure at hydrothermal conditions).

### 3.9 Hydrothermal synthesis and supercritical drying

Generally speaking, sol-gel synthesis at hydrothermal conditions leads to an aerogel, which is a nanostructured material with high specific surface area, high porosity (pores of the order of nanometer), low density, low dielectric constant and excellent heat insulation properties. With a meticulous control of synthesis parameters, all of these characteristics can be optimized in function of specific applications for which material is required. For example, Z. Li et al. [44] affirm that, by a hydrothermal treatment, grain size, particle morphology, crystalline phase, and surface chemistry can be controlled via processing variables such as sol composition, pH, reaction temperature and pressure, aging time, and nature of solvent and additive.

As for ambient temperature and pressure synthesis conditions, hydrothermal one can be divided into three general steps:

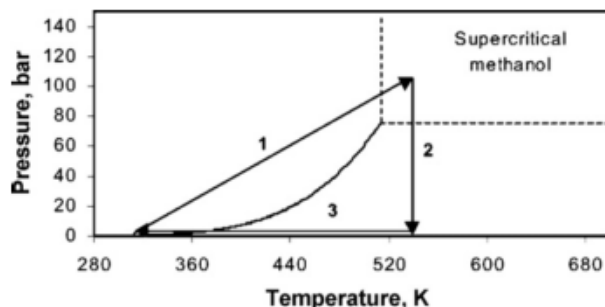
1. Gel preparation
2. Aging of the gel
3. Drying of the gel

It is proved that the aging step also influences the structure and so, the final properties of synthesized material. But for many specialists field, one of the major obstacles for wide-scale application of silica aerogel is the drying step of as formed gels.

Drying is characterized by shrinkage, which is driven by capillary pressure developing capillary tensions that may reach 100-200 MPa [14]. In supercritical drying (SCD) method the pore liquid is removed above the critical temperature ( $T_c$ ) and critical pressure ( $P_{cr}$ ) of the concerned liquid. At this point, there is no liquid-vapor interface and, thus, no capillary pressure. This is not the case at ambient pressure at which, the surface tension between liquid and vapor, cannot be avoided. There are two different methods of supercritical drying: high temperature (HTSCD) and low temperature (LTSCD).

*High temperature supercritical drying (HTSCD)*

Kistler firstly carried out this method of drying aerogel in 1931. The process occurs in three steps as resumed in Figure 17 below:



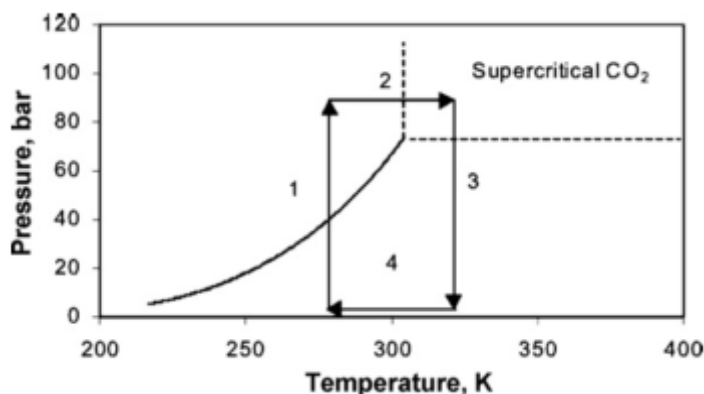
**Figure 17:** Schematic procedure of high temperature supercritical drying.

1. The wet gel, together with a sufficient amount of solvent is placed in autoclave and the temperature is slowly raised. This causes a pressure increase. Both the temperature and pressure are adjusted to reach values above the critical points of the corresponding solvent. On attaining the set temperature and pressure, the conditions are kept constant for a certain period of time.
2. The fluid is then slowly vented at constant temperature, resulting in a pressure drop.
3. When ambient pressure is reached, the vessel is cooled to room temperature. Thus, the phase boundary between liquid and gas is not crossed during the drying process.

### 3.9.1 Low temperature supercritical drying (LTSCD)

In this alternative method suggested in 1985, the solvent present in the gel before drying (generally alcohol) is replaced by liquid having a critical point close to ambient temperature. Liquid CO<sub>2</sub> was found to be the most practical choice. The experimental procedure is as follow:

1. The gel containing excess amount of solvent is placed in an autoclave. The vessel is sealed and liquid CO<sub>2</sub> is pumped in at 4-10°C until the pressure reaches about 100 bar. The outlet valve is then opened so that the solvent extracted by the liquid CO<sub>2</sub>, is able to flow out. When the solvent is completely replaced by CO<sub>2</sub>, the pump is turned off; the temperature is raised to 40°C (I.E. above the critical temperature of CO<sub>2</sub>, T<sub>c</sub> = 31 °C) and the pressure is kept constant at 100 bar.
2. On reaching 40°C, and thus ensuring the transition of CO<sub>2</sub> into the supercritical state, the system is slowly depressurized under natural flow.
3. When ambient pressure is reached, the system is cooled down to the room temperature. Aerogels obtained by this method are hydrophilic.



**Figure 18:** Schematic procedure of low temperature supercritical drying.

Even these two methods are still largely used for the synthesis of aerogels, they present some disadvantages. For example, both high pressure and temperature characterizing HTSDC are often not easy to combine to confer at the system optimized conditions for organic solvents. In fact, the risk of flammability, or secondary reactions -as rearrangements of gel network - could be occurring due by the instability of solvents at these conditions. Moreover, the second and third steps (heating to reach the supercritical point of solvent, ventilation and cooling) for both HTSDC and LTSDC considerably limit the range of application field of the synthesized material (as for example the other one).

### 3.10 Supercritical CO<sub>2</sub> drying

Van Bommel and de Haan proposed in 1995 [45], a drying process involving a supercritical CO<sub>2</sub> instead of liquid CO<sub>2</sub>. They affirm that by the use of the first one, the heating and cooling steps can be eliminated. Even they also admit that solvent extraction step is still to be a delicate phase governed by the diffusion of supercritical CO<sub>2</sub> (the diffusion coefficient of CO<sub>2</sub> in the sample is unknown in most of cases which make difficult the prediction of drying duration); they showed that by a combination of pressure and temperature above the binary critical curve of the ethanol-CO<sub>2</sub> (1MPa-14MPa and 343,2K-363,2 K respectively [46] it is possible obtain crack-free aerogel rods, plates or tubes. It is important to note that, if the duration of diffusion is not long enough, cracking of aerogel occurs due by the internal strains caused by non-homogeneous solidification process within sample.

## 4. Experimental investigations

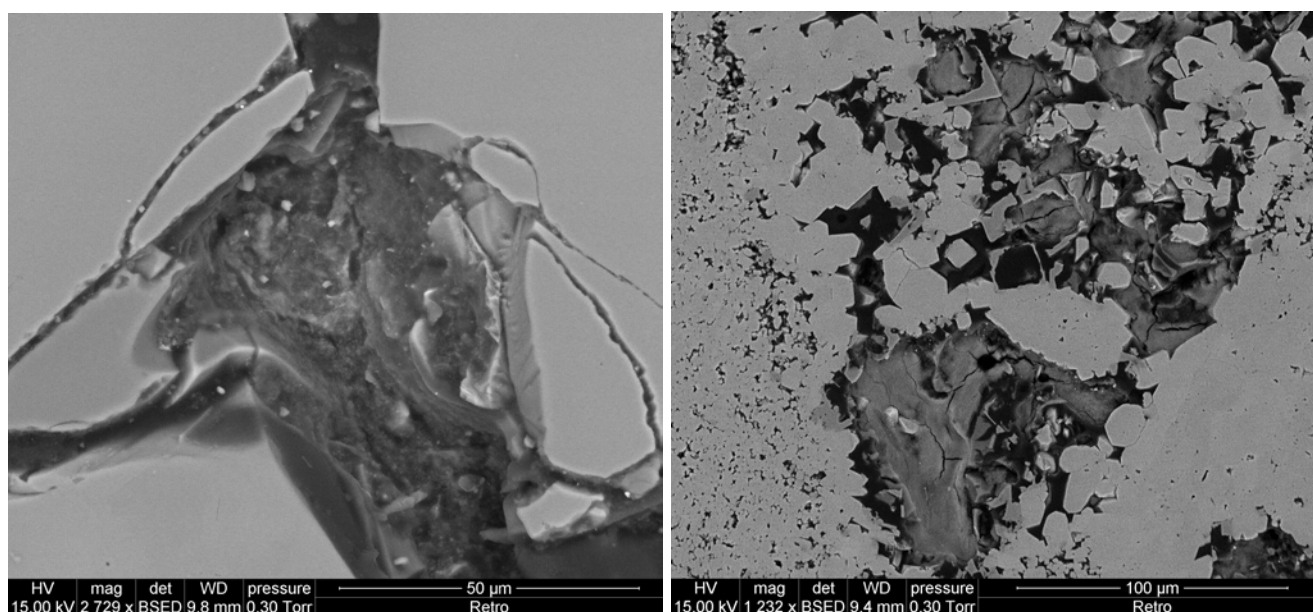
### 4.1 Preliminary tests

The objectives of preliminary tests performed at room temperature were:

- Verification of the capacity of TEOS- ethanol-water to undergoes gelation and solidification within porous structure of different kind of rocks.
- Observation of the influence of synthesis duration (improvement of sol viscosity) or the temperature at which it was carried out.
- Verification of the capacity of the rocks to absorb sols, making the mixture with previously acidified water possible, which should lead to its hydrolysis and condensation.



**Figure 21:** tests at room temperature.



**Figure 22:** Solidified silica gel in Fontainebleau sandstone (left) and limestone (right)

Generally speaking the comparison of the untreated structure of rocks and the ones put in contact with *sol+acidified water* by both introduction of sample in mixture and capillarity, allow us to affirm that sol penetrated in stone porous matrix undergoing gelation and solidification within them. Unfortunately, the EDX analysis which was supposed confirms it, turned out to be imprecise for the tests which we carried out. The presence of resin and the same elements as in solidified sol (mainly C; Al; O; Si) in the environment in which it was injected, surely made the analysis difficult. Moreover, it is known that boron mark in EDX spectra has almost the same than the carbon one. It surely makes its detection difficult given that, mainly for embedded in resin, there is big percentage of carbon in observed sample. However, Sassoni, among others, in its experiences [28] observed that TEOS based consolidants penetrate into stone matrix as water. It supports our affirmations.



The faster gelation and solidification of sol put in contact with carbonate stone samples can be attributed to the fact that the latter, is more sensitive to acid solutions than sandstone. Its dissolution once in contact with prepared acid mixture could accelerate aforementioned phenomena introducing some rock particle which could speed aggregation and so, gelation. The difference of effectiveness of TEOS based solution as consolidant for carbonate stones and sandstones, has been evoked by E. Sassoni and its team in recent study [28]. The study of its effectiveness in carbonate porous media must be deep.

Sol cracks and shrinkage observed at the outside of sample stone matrix was observed in all of our experiments and are well known by sol-gel community. Considering B. Sala works cited in bibliographic paragraph, this phenomenon is certainly due by the addition of an insufficient amount of boron oxide in TEOS based sol. Tests for sol composition optimization are envisaged.

No sol cracks were observed at the inside of the sample porous structure. Two explanations could be advanced: no solvent evaporation taken place (We observed gel); or stone matrix plays an unknown role.

The synthesis carried out at 60 °C instead of 40°C seems to not significantly influence properties of resulting sol and gels as its longer duration. In fact the latter test has not led to a more viscous sol.

Finally, the presence of so small amount of observed solid matter within pores could be attributed to the too small volume of injected sol.

## 4.2 Injection at reservoir conditions

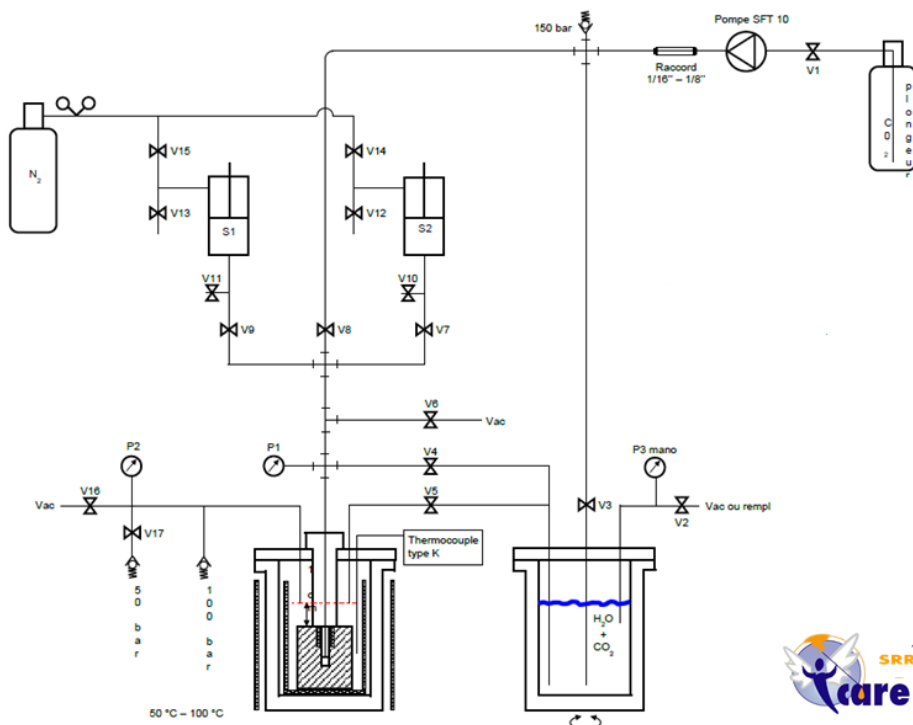
The aim of the experiments performed at CNRS is the study and improvement of TEOS based sol behavior in sandstone at hydrothermal conditions. In order to reproduce at laboratory scale real reservoir conditions, all experiments were carried out in cylindrical steel autoclave. Machined samples were put in teflon beaker to protect internal walls of the autoclave. Centered cylindrical drilling constitutes them, and reach the half of their height (see Figure 20), having the same diameter and shape as injection probe, which is introduced within them to assure that injection happens at the sample core. This configuration reproduces, at smaller scale, the injection from a well in a confined reservoir.

Once the autoclave is closed, brine (0,8 mol/L NaCl) initially stored in second reservoir (stirred), was pumped into the sample until the solution overflow and covers the sample. The brine solution is saturated in supercritical CO<sub>2</sub> which confers it a pH value about 3. Autoclave temperature and pressure were 75°C and 9 MPa respectively. The sample was kept at these conditions during 24h before the remediation fluid injection.

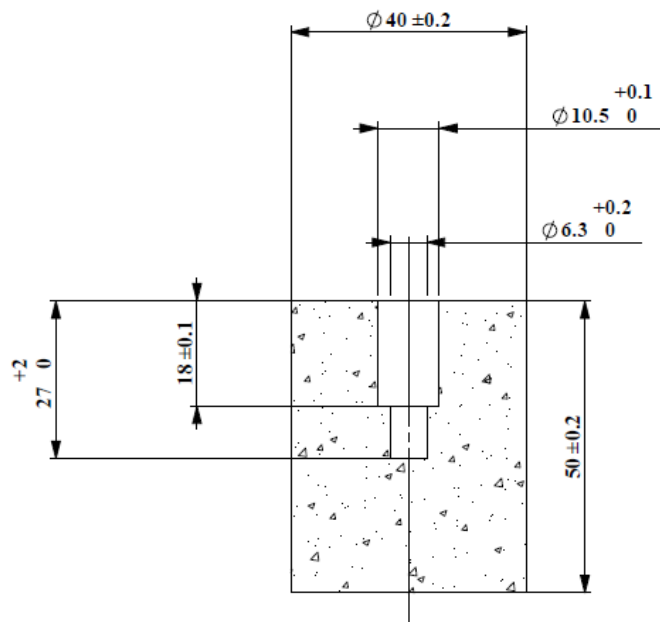
Sol for the injection was prepared by refluxing at 40°C and room pressure. The duration of sol synthesis is about 40 min. Once sol is ready, it is injected in the sample and the system is kept at these conditions during the time needed to form the final material. This time is function of the injected fluid composition (see tables 2 and 3).

The mixture of acidified water and sol within rock pore structure should trigger hydrolysis and condensation processes and leading to a borosilicate aerogel. According to Smirnova [47], the presence of supercritical CO<sub>2</sub> in solution filling pores of the rock matrix, favors the condensation step. In her studies she observed that the gelation time decreases considerably when supercritical CO<sub>2</sub> concentration increases in water solution at hydrothermal conditions.





**Figure 19:** Scaled Radial Injection Simulator (SRRIS)



**Figure 20:** Sample description.

Reactants	Amount (g)
TEOS	6
Boron oxide	0,196
Ethanol	5,202

**Table 2:** Sol without Ti

Reactants	Amount (g)
TEOS	7,5
Boron oxide	0,278
Ethanol	7,4
Titanium isopropoxide	1,137

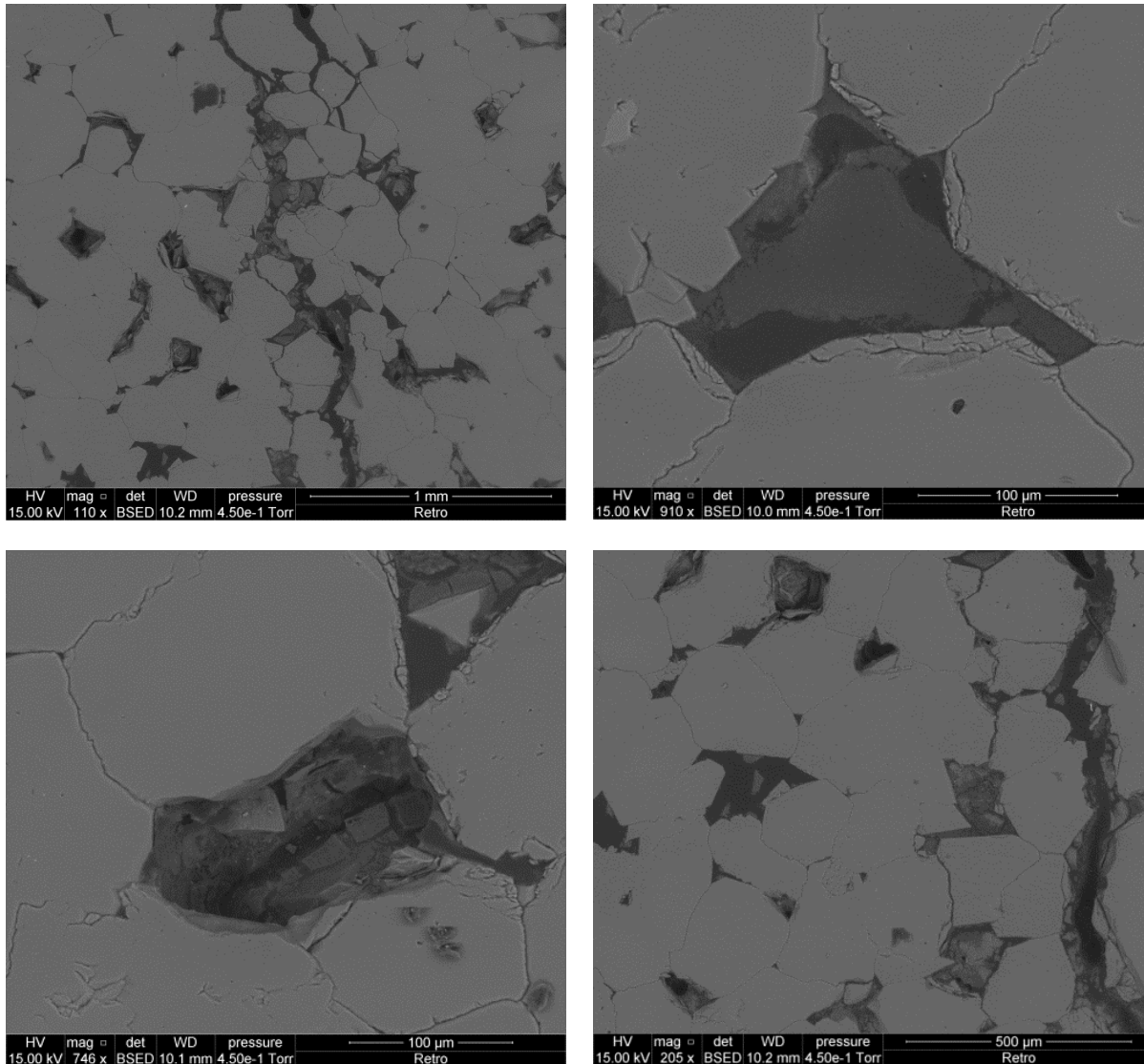
**Table 3:** Sol with Ti.

## 4.3 Experiment n° 1

Preliminary tests showed, as expected, a shrinkage phenomenon during the sol-gel process. Accordingly, we decided to perform two consecutives injections with a delay of one week between each one. In this experiment, injections were performed into a Fontainebleau sandstone sample (GF1).

In this experiment, the volume of injected sol is the equivalent of pore volume corresponding to about 1/3 of the sample volume. One week after, we repeat the same injection. The mixture which was injected in this time contains a little amount of titanium oxide (Tab. 3) in order to make the differentiation possible during the ex-situ SEM and EDX analysis. An augmentation of pressure of the system was recorded at this step attesting for the initial reduction of permeability due to the first injection.

The system was kept at these conditions one week long and then removed from the autoclave and dried at room conditions (during about one week). In order to observe the extension of injection (starting from the injection point), sample was cut, embedded in resin and its surface was polished. SEM observations were carried out by environmental SEM associated with chemical analysis. Even latters have not given any exhaustive results: both boron and titanium oxides were no significantly detected or were detected in analyzed portions in which both boron and titanium there should not be present; we can affirm that some analogy exists between images observed and those obtained for preliminary experiences. It allows us to suppose that injected sol penetrated into stone porous structure and interacted with brine already filling it, undergoing hydrolysis and condensation processes. Figures 23 shows solidified injected sol within some pore of stone matrix. The injected volume does not enough to fill pores and only zone near the injection was imbued.



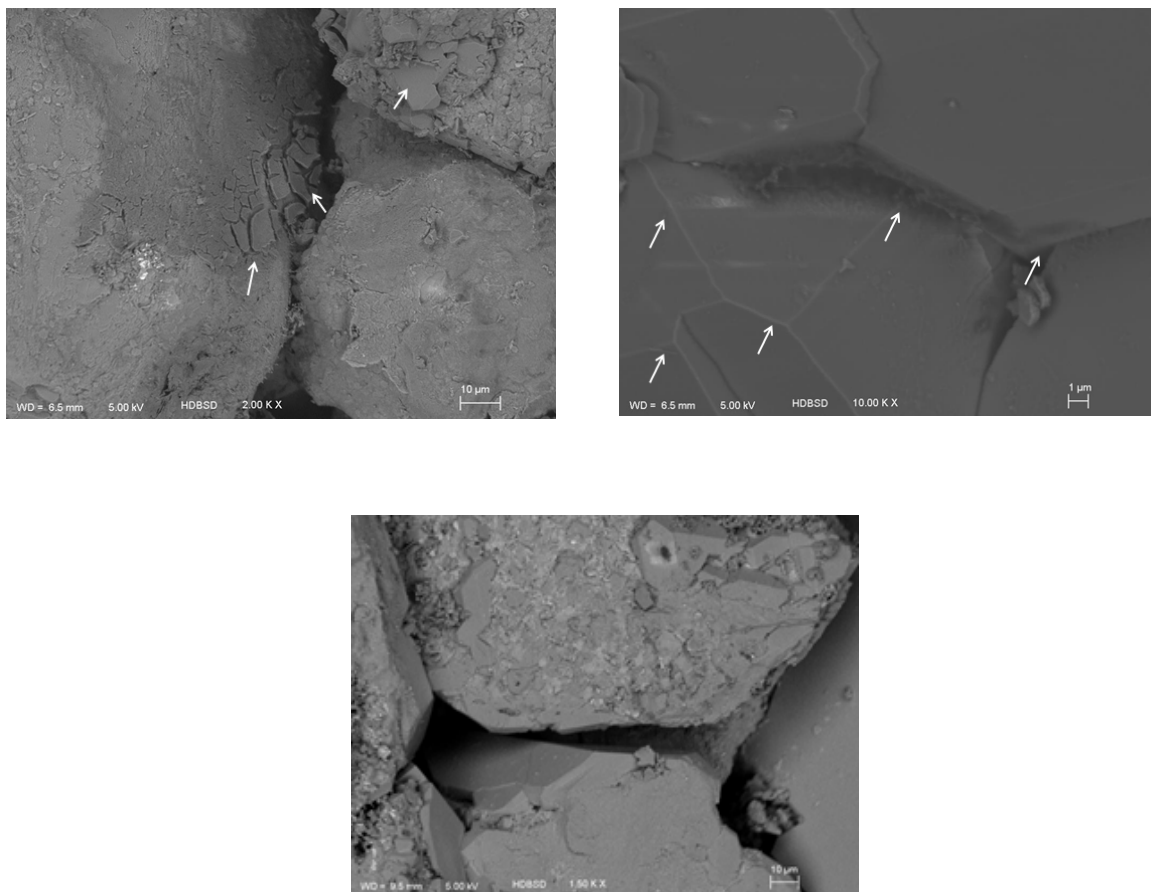
**Figure 23:** Solidified sol within pores in the vicinity of the injection zone. Embedded and polished sample.

## 4.4 Experiment n° 2

The same protocol as in the first experiment was followed but the injection was carried out in a Berea sandstone of initial permeability ranging from 500-1000mD; porosity around 19% (Table 4). At this time the equipment for preparing the sample for the environmental SEM observation was impracticable and followed an alternative protocol, actually widely used in the field of ceramic studies: the sample was hammer broken and its surface was Platinum (Pt) metallized in order to observe and analyze the injected zone with classic SEM. In Figure 24, we can see solid veil recovering silicic grains of the observed sandstone. As for in the first experiment, chemical analysis results were not very informative.

<b>Silica</b>			93,13
<b>Clays and Feldspars</b>	Alumina	( $\text{Al}_2\text{O}_3$ )	3,86
	Ferric Oxide	( $\text{Fe}_2\text{O}_3$ )	0,11
	Ferrous Oxide	( $\text{FeO}$ )	0,54
	Magnesium Oxide	( $\text{MgO}$ )	0,25
	Calcium Oxide	( $\text{CaO}$ )	0.10%

**Table 4:** Berea sandstone composition



**Figure 24:** Solid veil recovering silicic grains. Classic SEM observation.

## 4.5 Experiment n° 3

In this experiment, sol was injected in Berea sandstone (same as experiment 2). The injected volume (single injection experiment) was twice the volume in experiment 2 instead of performing successive injections. Boron based mixture previously prepared, contains the same proportion of titanium oxide as introduced in the sol synthesized for the second injection of experiment 2. After injection, the sample

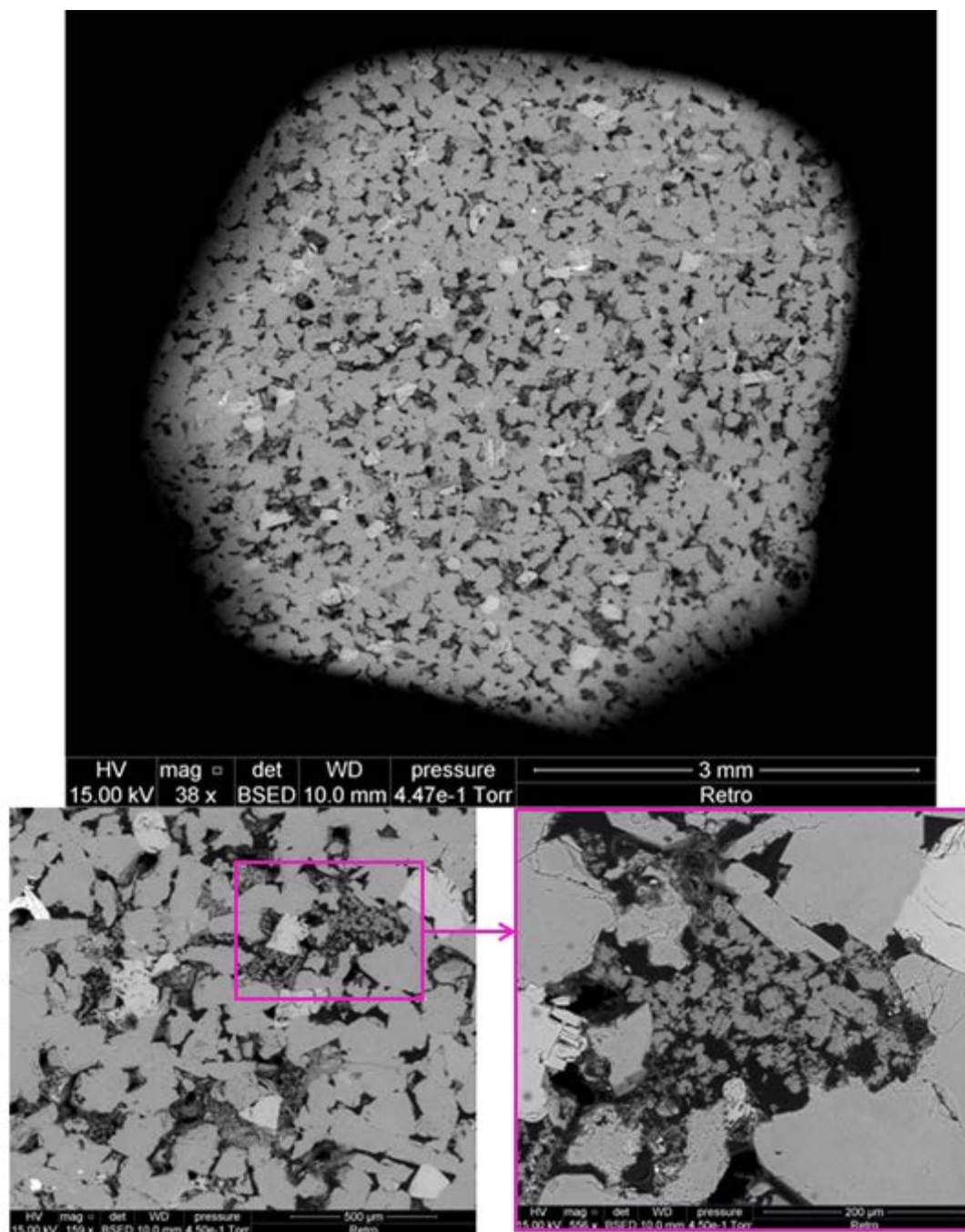
was kept at experimental conditions ( $P = 9 \text{ MPa}$ ;  $T = 75^\circ\text{C}$ ) during almost two months and was then removed and dried, at room conditions. Two observation methodologies were performed:

- One half of sample was cut, embedded into resin structure and its surface was polished. Observations were carried out with an environmental SEM.
- The other half part of sample was hammer broken and the surface was Pt metallized. No polishing had been performed. Observations were carried out with classic SEM.

We can observe that more matter than in previous experiments are present within pores of stone structure (Figure 25). This supports the idea that the expected sol-gel process happens into porous matrix of stone.

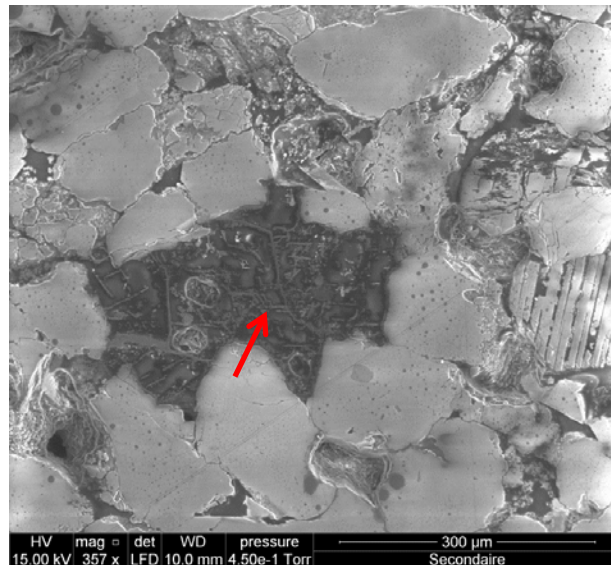
The solid veil recovering grains is appreciable in Figure 24 and Figure 25. SEM obtained images are comparable with some published by some consolidation stone field author [18][28]. As specified by E.K. Kim et al [18], it is difficult to make the difference visually, between a TEOS treated stone and the untreated stone. This is explicable by the fact that we are looking for an as-formed product which is mainly composed by the exactly same elements as which present in stone matrix. Ksinopoulou also affirmed this, in article published during the 12<sup>th</sup> international congress on stone deterioration and treatment [30].

The chemical analysis of solid recovering grains, shows in this time, the presence of little amount of titanium. It was not detected in matrix structure (Figure 28).

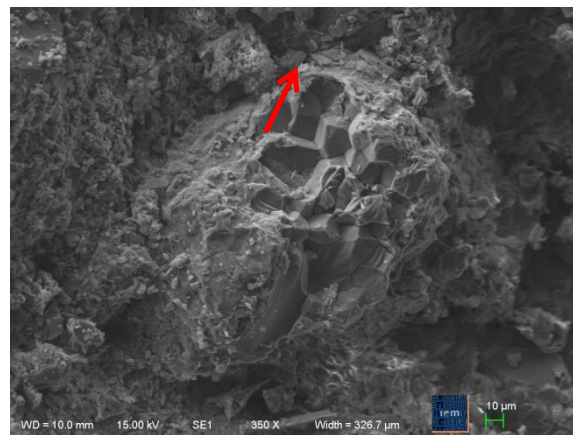
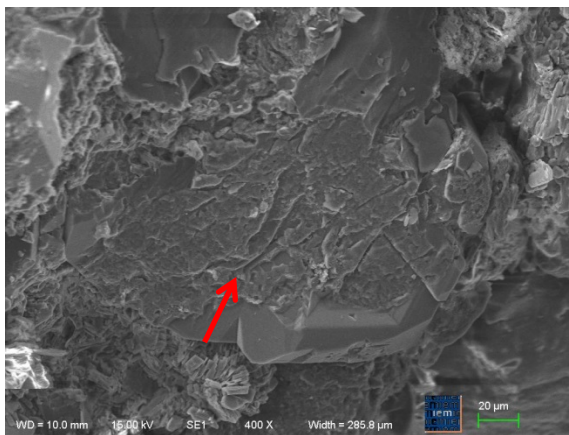


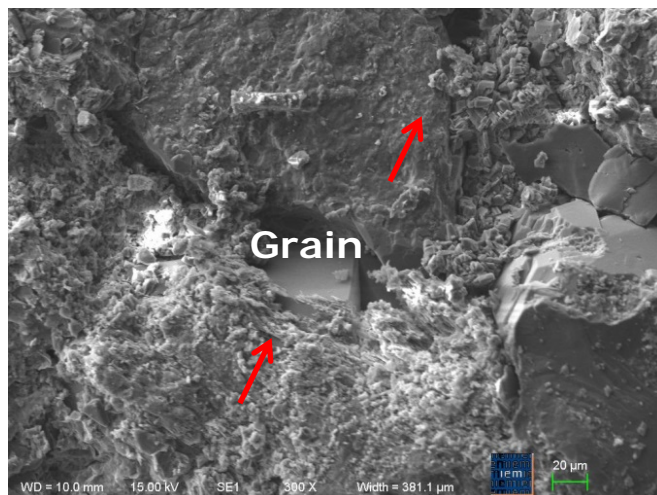
**Figure 25:** Solidified injected sol within pores. Environmental SEM Observation.



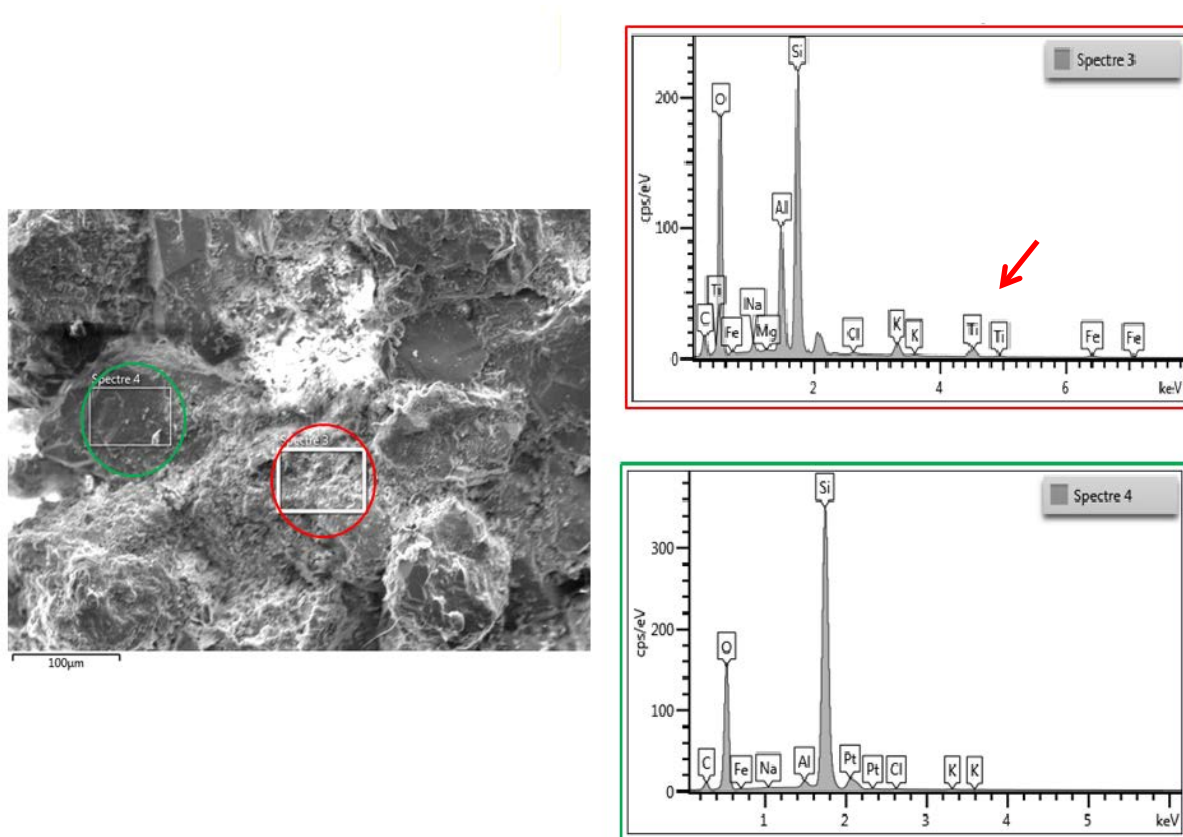


**Figure 26:** Solid veil recovering grain structure. Environmental SEM analysis. Secondary diffusion.





**Figure 27:** Matter recovering grain. Classic SEM observations. Metallized sample



**Figure 28:** Chemical analysis of matter recovering grain. EDX Analysis



## 4.6 Experiment n° 4

During the previous experiments, the sample was kept aging at hydrothermal conditions all the test duration, then removed from the autoclave after a variable duration and dried at room conditions. In accord with sol-gel process theory, we believe that only polymerization (gel formation) occurs in-situ while solidification resulting from the drying of gel, happened after the removal of the sample from the autoclave (Figures 29a and 29b). Accordingly, experiment 4 was set up for studied the method for drying the material in situ. In-situ drying was performed by a slow flow of supercritical CO<sub>2</sub>, after a given gel aging time. Moreover, it was pointed out, that in order to characterize the effect of injected sol on rock sample and the statement of sol-gel steps, it is necessary perform more tests than a simple visual observation associated to EDX analysis.

So, in accord with numerous authors (recent or not) of consolidation stone field, mercury porosimetry [11][19][20] are planned. Protocol steps followed to reach this purpose can be appreciated below:

- Sol: Only boron silicate based mixture was prepared. No titanium was added.
- Sample: BERE A sandstone (500-1000 mD)
- Injection: The volume injected was 3 times the total pore volume. Before the immersion of the sample in reservoir brine, it was put under vacuum during 24 hours in order to extract all residual humidity within it and then it was weighed.

Once it was immersed in SRRIS reservoir and put at experimental conditions, we injected CO<sub>2</sub> through sample in order to have a reference of pressure. Once sol was injected, to remove all amount of sol eventually remained in machine tubes; we injected their equivalent volume of dry CO<sub>2</sub>. Gel resulting from injected sol aged for 1 months at experimental conditions. After that, a continue flow of supercritical CO<sub>2</sub> through sample was applied for 6 weeks.



**Figure 29a:** As removed sample



**Figure 29b:** Sample after one week of drying at room conditions

## 4.7 Discussion and concluding remarks

The SEM observation of pore structures of stone samples for experiments assessed at high pressures and high temperature (hydrothermal conditions), could be compared to those obtained for the preliminary ones. So, we can affirm that injected sol penetrated into stone matrix and interact with brine already present within it. This is in accord with Aparicio [48] which obtained a good TEOS based sol penetration in a porous silica matrix previously prepared under an isostatic pressure applied on the sample. In his studies the author recorded a weight increase going from 20%-65% depending on the initial porosity of the substrate.

The same difficulty for the detection of boron and titanium as for sample of preliminary experiments was met.

The fact that the drying step of sol-gel synthesis occurs at room temperature and pressure once sample is removed from the autoclave, gives us non-representative results. In fact, in field application, the injected sol will must hydrolyzes, condensates and dryings (solidifies) at hydrothermal conditions. The supercritical CO<sub>2</sub> assisted drying (Experiment 4 which is ongoing) seems to be the most viable technic for such purpose. At least it allows the elimination of heating and cooling steps of supercritical drying which could not carried out in our field application. In accord with authors met in our bibliographic study, this drying method is still a critical step. Indeed, the control of processes and phenomena driving it is still a delicate operation, which needs meticulous study of all parameters characterizing experimental conditions.

So, in function of results of experiment 4, complementary analysis must be envisaged as for example, DRX tomography (for which new composition of sol and its synthesis process are being studied). Furthermore, simulations could also be carried out in order to optimize drying conditions (cyclic injections of solvent, combination of supercritical CO<sub>2</sub> with dry air ...). The possibility of in-situ following of sol-gel process steps would be very useful. The study of permeability behavior of sample in function of supercritical CO<sub>2</sub> flow could be a plausible and realistic approach.

Once both borosilicate sol composition and drying process will be optimized, the interaction between injected sol and substrate must be studied (By interphase study, chemical analysis, thermal expansion coefficient analysis...). Moreover, the omnipresence of water and known difficulty of its removing process in porous structure (especially at our temperature and pressure conditions), and the presence of elements such oil residues and crystallized salts, are parameter which must be taken into account for the effectiveness of our stone treatment process.

The next step required for the industrial application (minimize cost of injection process) is to the study in detail the use of the ethyl silicate 40. This will be done in the second part of this study and will be presented in a second report.

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