An Investigation into the Acoustic Properties of Alcogels

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Background

Aerogels are ultra low density solids, with obtainable porosities up to 99.7%. They are composed of chains of silicon atoms with lengths between 1 and 100 nm, which become entangled and form a solid[1]. At lower densities (and thus greater porosities), they are transparent with a bluish tint. They have surface areas as large as 1600 square meters per gram [2] while having extremely low densities (~3 mg/cm^3)[3]. Their thermal conductivity is very low, with an average of 0.01 W/(K*m) [4]. They also have a low refractive index of about 1.01 [5]. Currently, they are not heavily used in industry, but work is being done to take advantage of their potential as an insulator by including them in windows to block heat transfer between panes, and to make refrigerators more efficient by preventing heat contamination [6]. The possibility of utilizing their high surface area to store hydrogen and other gases is also being investigated [7] They are also used frequently in ultra low temperature physics, where they are included in systems containing superfluid ^3He as their inherently fractal nature make them contrast well with the superfluid's ultra-low entropy nature[7].

There are many different procedures that can be used to produce silicon aerogels, but the simplest is a "one step" method (meaning that all that is needed to prepare the substance is to mix the chemicals) that produces between 94% and 98% porosity depending on the concentration of methanol (CH_3OH), the liquid medium, used. Tetramethyloxylsilicate (TMOS) is combined with H_2O, CH_3OH, and NH_4OH. The TMOS and the H_2O combine according to the following reaction:

$$Si(OCH_3)_4 + nH_2O \rightarrow Si(OCH_3)_{4-n}(OH)_n + n(CH_3OH)$$

The methanol acts as a liquid medium which will later be removed during the supercritical drying process while the ammonia hydroxide acts as a catalyst for the reaction [8].

Once the solution has been mixed, the gelation process begins – at this point the mixture is known as an alcogel. The length that the substance should be allowed to rest at room temperature and gel before proceeding with the next step of heating the sample is debatable, but it is known that the length of time plays a significant role in the formation of the gel and its final properties, including mechanical strength, transparency, and texture [9]. Even when the alcogel appears to be a solid gel and no longer moves within its container, it still continues to undergo further structural shifts. Identically made samples of different ages produce audibly different frequencies when they are mechanically excited. This phenomenon has been studied by mechanically exciting an acid-catalyzed gel and performing light scattering tests upon it. It was shown that the gel's structure changes the most during the period from initial gelation to twice the gelation time, where gelation time is defined as the length of time necessary for the sample to become solid to the point that it bonds with the container walls and no longer appears to flow when handled. However, the gelation of acid catalyzed gels is very different from that of base gels, with the latter containing less well defined resonant frequencies [10].

After the alcogel has been allowed to gel, it is placed inside an autoclave where it is heated to ~300ºC and pressurized to ~1500 PSI so that the methanol enters a supercritical phase, meaning that the substance disregards the capillary forces within it, and the solution becomes a highly porous solid [11]. The substance is kept in this state for

a period of approximately one hour, then allowed to slowly cool and depressurize over the course of approximately four hours and removed from the autoclave.

The reliable production of aerogels for use in industrial and scientific endeavors is still not a precise science. They will often have significantly shrunkand be riddled with cracks. One hypothesized reason for this is that the alcogels are in a constant state of gelation up until the point that they are super-critically dried. One known method for decreasing this shrinkage is to allow the substance to gel properly before processing it.

The purpose of this experiment is to characterize the gelation of silica based ninety-eight percent porosity alcogels produced using the one step procedure. This is done by investigating the acoustic response of the alcogels. It had been previously observed by the author that any mechanical excitation of alcogels in sealed glass containers that are allowed to oscillate freely will produce an audible frequency of sound. The sound increases in pitch as time progresses; thus the principle frequency of the alcogel can be examined over time. The stiffness of the gel could be determined by this, as the higher the resonant frequency, the stiffer the gel.

Experiment

The experiment was designed to measure the acoustic responses in alcogel over time. Two different samples were investigated, a 98% porosity one-step procedure and a 95% porosity. They were stored in cylindrical glass containers with a diameter of .517" and a height of 1.754". The alcogel was prepared by combining 38.1 grams methanol with 12.0 grams TMOS in a beaker and mixing. In a separate beaker, 27.0 grams methanol, 2.9 grams H_2O and 135µl NH_4OH were combined. They were mixed together and stirred thoroughly, then poured into two containers (the second container's purpose

was to monitor the viscosity of the liquid and to act as an emergency backup in case of problems). A Piezoelectric transducer with a width of 5mm and length ~3mm (not a straight edge) was affixed to the side of the glass container using super glue. The transducer's purpose was to convert the mechanical excitations of the alcogel into an electrical signal. This was then connected to a preamplifier, which was in turn connected to an oscilloscope, which was connected to a computer. When the alcogel was excited, the vibrations would be converted into a current which would go through the preamp. The oscilloscope would read the current and produce a graph of voltage versus time. The computer would then save the data for further analysis.

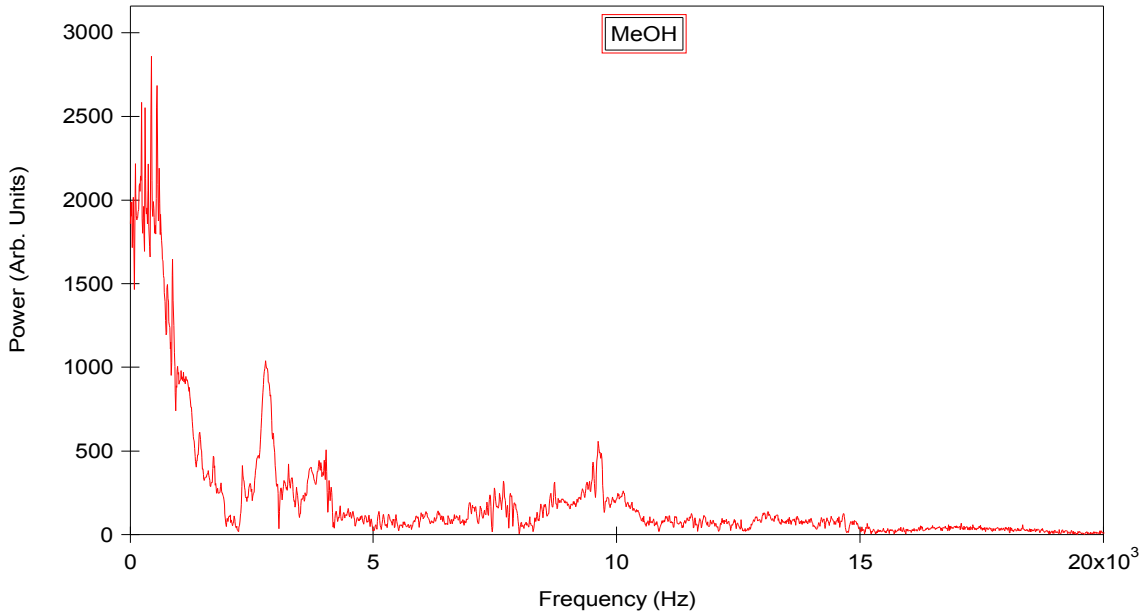
The alcogel sample was clamped opposite the transducer to a mechanical vibrator whose purpose was to excite the sample. This device takes a signal from a function generator and propels a metal rod forwards and backwards based on the amplitude and frequency of the signal. The function generator was set to produce a square wave with a frequency of .319 Hz and had its amplitude set so that the mechanical vibrator oscillated with an amplitude of .9 cm. To take a data set, the function generator was turned on and allowed to hit the sample until a steady graph was displayed on the oscilloscope of voltage versus time (this took two hits). 3 sets of data were taken and stored on the computer. Data sets were taken approximately every half an hour initially, then more frequently once the viscosity increased in the second container. When the sample had completely jelled, data sets were taken every five minutes. This rate was then reduced as time went on. Each data set produced a graph of time versus voltage, ranging from -8 to 8 volts, and 0 to 100 ms, which was then Fourier transformed so that frequency could be compared with amplitude.

Results

The first three graphs (Figures 1, 2 and 3) are plots of Fourier transformed data taken from a 98% porosity sample at two points during the gelation process, one shortly after the initial gelation occurred at 168 minutes after the preparation of the gel and one 402 minutes after its preparation. The amplitude of the y-axis is in terms of an arbitrary unit of power, however it is internally consistent. The frequencies are plotted from 20 Hz to 20 KHz, the range of the human ear.

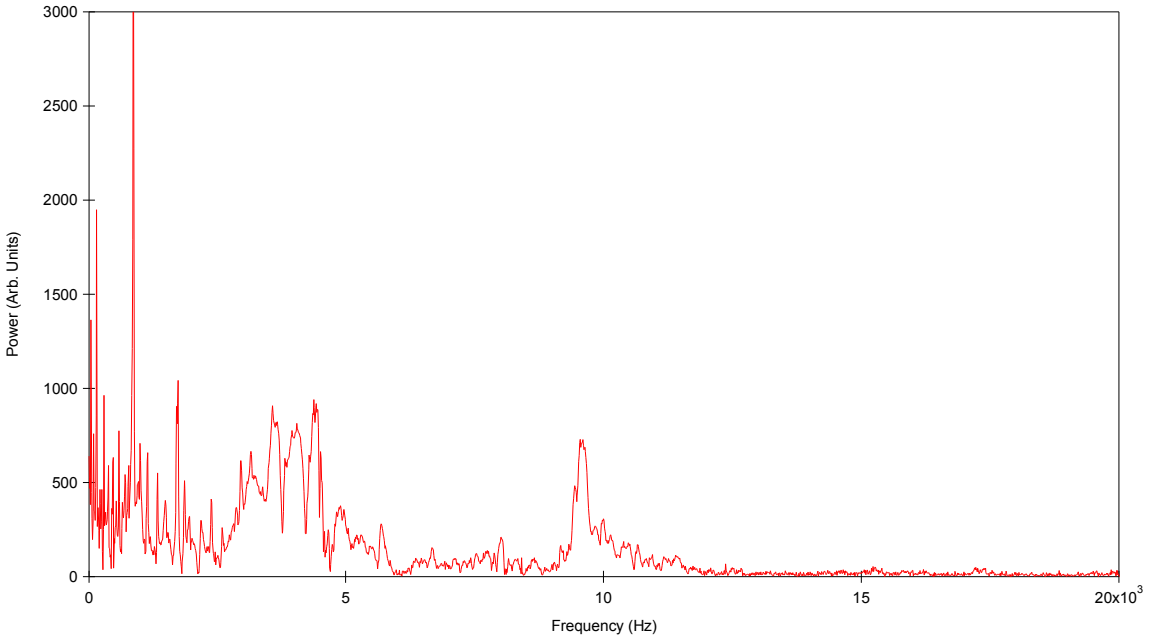
The fourth and fifth graphs (figure 4 and 5), plotted on the same scales, shows the 95% sample. The earliest time shown in figure 5 occurred after the substance had gelled, which was defined as a viscosity such that the fluid had no noticeable motion when rotated, could not be observed when felt. The final graph (figure 6) shows a magnified view of the lower frequencies, and has more data sets. The data point taken at 168 minutes had gelled, but not to the point that it could be tactically sensed.

Figure 1



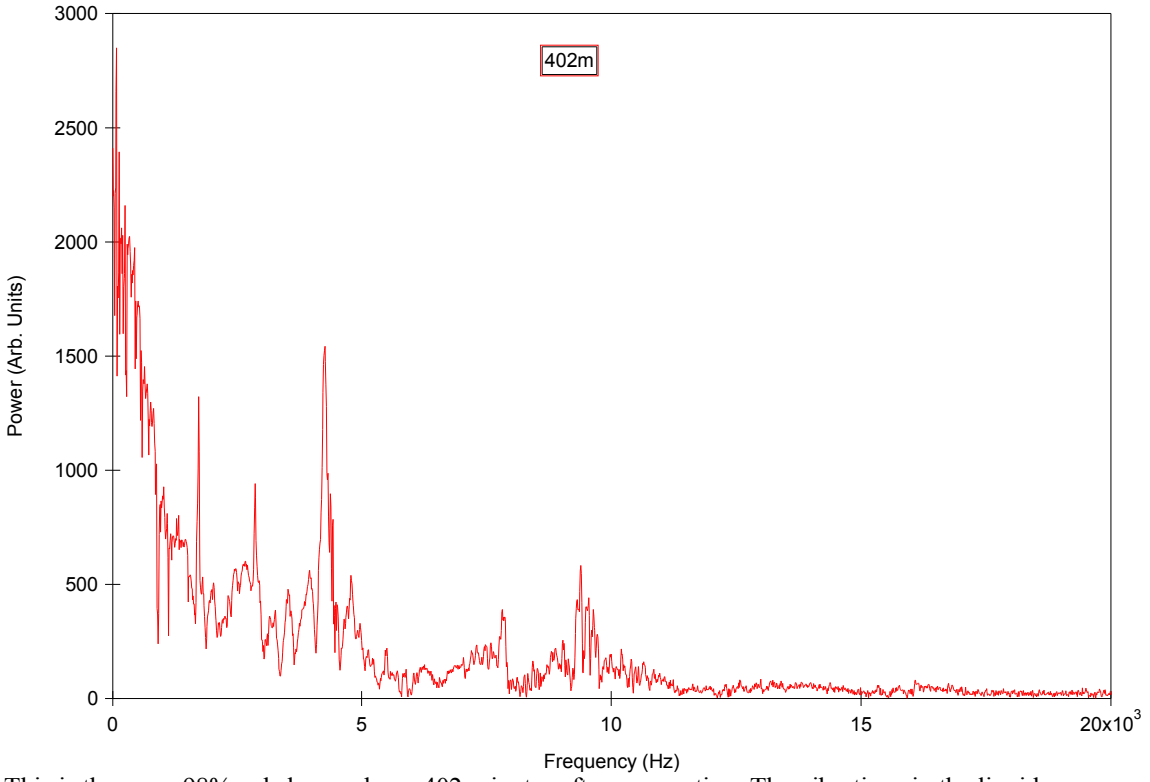
A Glass container identical to the ones used for the alcogels was filled with methanol and excited. The same clamping and transducer conditions were kept. This sample was taken just prior to the 98% gel was prepared.

Figure 2



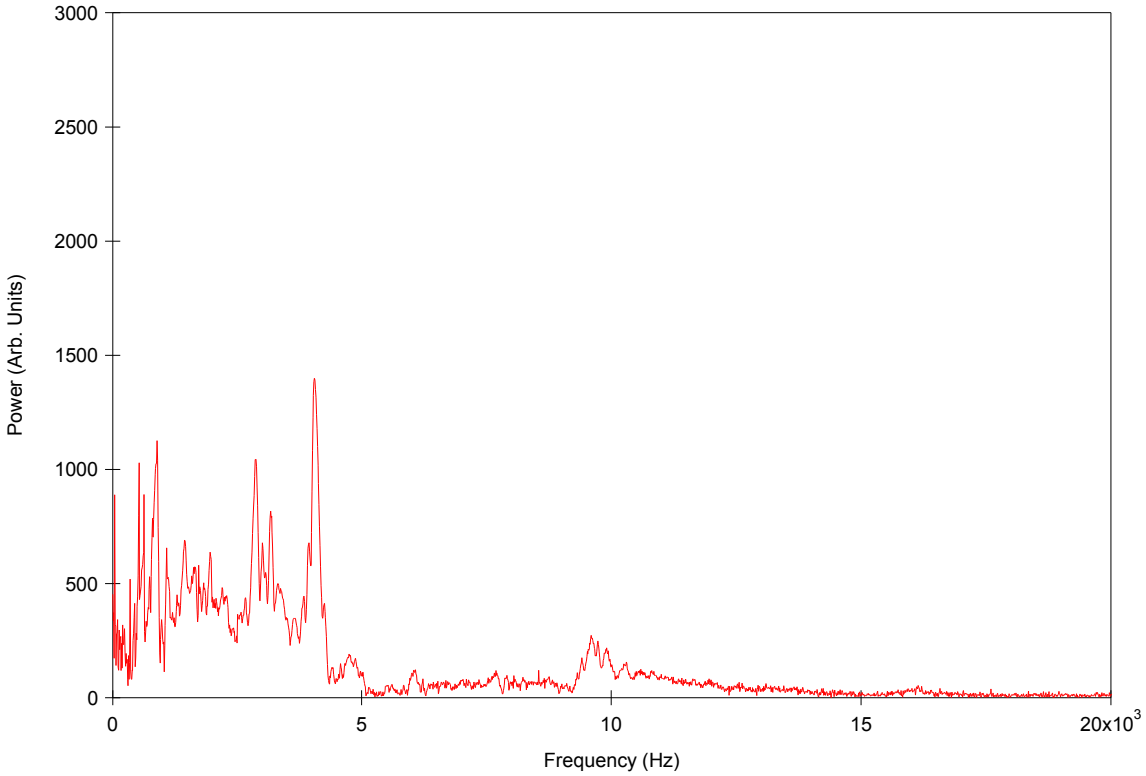
This is a 98% gel data set taken 168 minutes after the sample was prepared. This set was taken once the liquid appeared to have completely solidified when visually examined, but vibrations could not be sensed when felt. It is in an identical container and uses the same clamping and transducer conditions as used in the control.

Figure 3



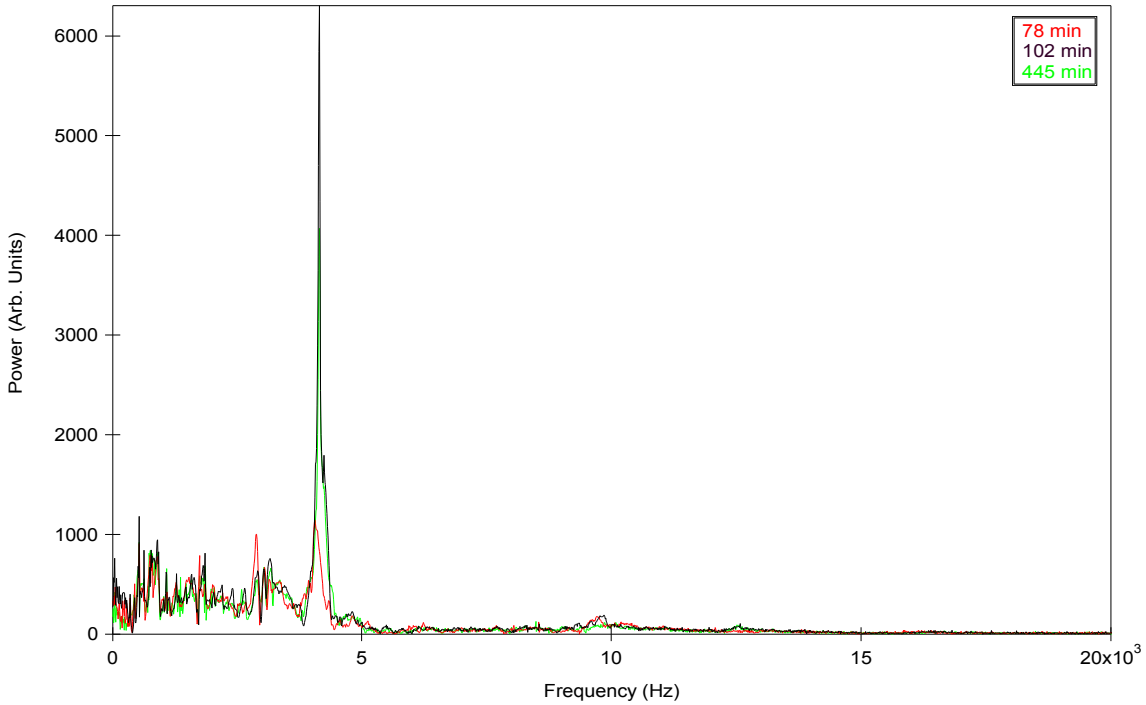
This is the same 98% gel shown above 402 minutes after preparation. The vibrations in the liquid were obviously discernable when the sample was felt, and had been since 184 minutes had passed.

Figure 4



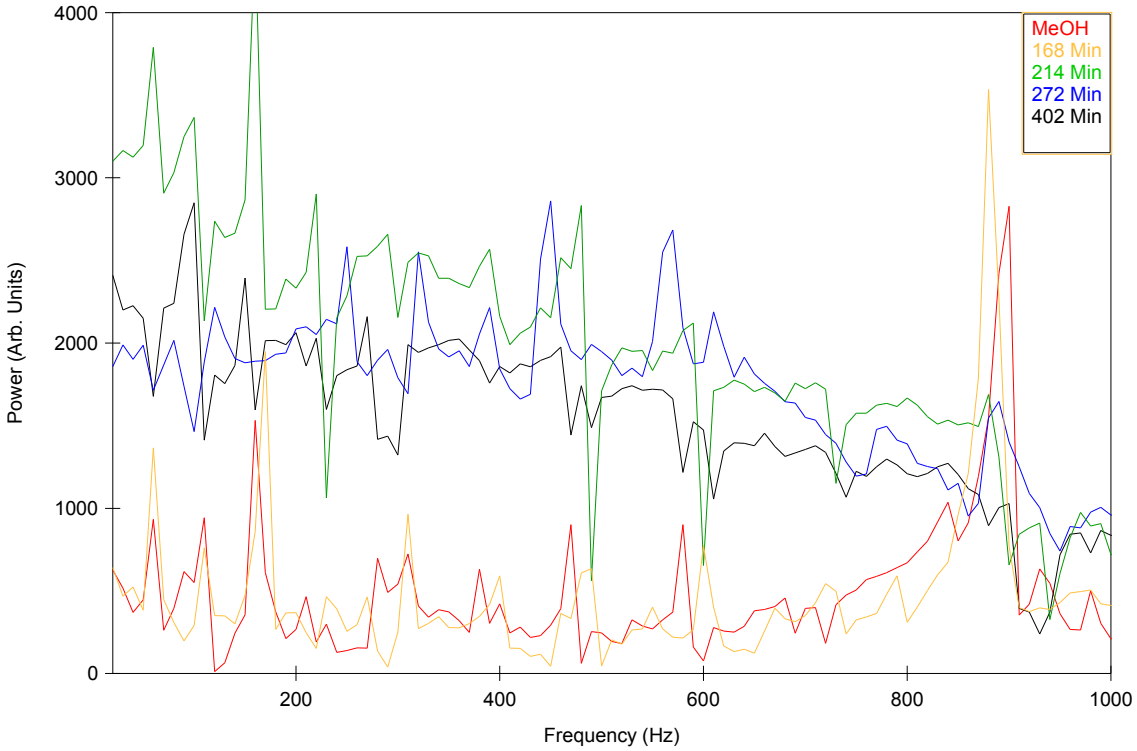
This is the 95% sample observed immediately after preparation, when it still maintained the same viscosity as pure methanol.

Figure 5



This is the 95% sample beaker with an identical setup and the same transducer as used by the control and 98% sample. After 78 minutes, the liquid appeared totally gelled, but it wasn't until 83 minutes that vibrations could be felt.

Figure 6



This is a graph of 4 different data sets taken from the 98% sample at various point in time, along with the control. At 168 minutes, the gelation had finished, but the sample was not yet vibrating (this occurred at 184 minutes).

Discussion

The observations of the acoustic responses of base-catalyzed silica alcogels provides valuable information on what the resonant frequencies of the gels are. Comparing the control with the 98% alcogels show that a different definition of gelation should have been adopted, defined at a point in which the resonant frequencies of the sample differ from that of a methanol filled container. If this definition were to be adopted, a definite trend of smaller amplitudes in the lower frequencies (<1 KHz) becomes apparent (see figure 5). Closer examinations of higher frequencies and comparisons to the control reveal either white noise or static frequencies when various points in time are view.

The 95% gel graphs did not show the same differences as exhibited by the 98% sample. They appear to be much more simplistic in nature, with the only difference

between them being the massive peak at around 3400 Hz. This clear resonance is most likely the frequency observed when the sample is physically handled. The low power levels under 100 hz in all the samples can most likely be attributed to some accidental change in the setup of the problem, as it is exhibited even in the newer control, but not in the control taken earlier, when the 98% sample was made.

Future Research

There are many further studies concerning alcogels that can be performed. This study was performed using a single chemical makeup, but there are many other variables to explore, such as different porosities, different catalysts, or even a different liquid medium, such as Acetyl Nitrile – the liquid medium used in the two step process. This experiment was also only concerned with one set of boundary conditions (the glass vial) which involved a glass-alcogel interface. The boundary conditions could be changed, investigating a longer or wider cylinder, or even something completely different like a prism. The container could be composed of a different material, such as nalgene plastic or brass.

Another potential avenue of research would be to perform the same measurements while the alcogel was being heated. This would show information about the transition between alcogel and aerogels. The resonant frequency could be measured as a function of temperature, pressure, or time. This would provide very interesting data about the drying process of alcogels and aerogels. Another potential test would be to perform the same acoustic measurements on a container filled with alcogel and a container filled with aerogel. Both of these experiments would provide information on the nature of aerogels and their creation.

A final avenue of research would be to investigate the effects of various gelation times on the aerogels produced. This would allow a link to be established between alcogel nature and aerogel composition. It would help refine the process of making alcogels, making them easier to manufacture and thus increasing their potential as an industrial material.

References:

[1] P.H. Tewari, A.J. Hunt and K. Lofftus, in: Aerogels, ed. J. Fricke (Springer, Berlin, 1992) p. 31.
[2] C.A.M. Mulder and J.G. Van Lierop, in: Aerogels, ed. J. Fricke (Springer, Berlin, 1992) p. 68.
[3] L.W. Hrubesh, report, ucrL-21234 Ilnl (Livermore, 1989).
[4] J. Fricke, in: Aerogels, ed. J. Fricke (Springer, Berlin, 1992) p. 24.
[5] S. Henning and L. Svennson, phys. Scripta 23 (1987) 687.
[6] G. Carlson, JoNCS-186 (Livermore, 1995).
[7] Ibid.
[8] P. Wawrzyniak, JoNCS-285 (Łódź, 2001).
[9] Personal Communication with Dr. John Poco, Lawrence National Laboratory, 2004.
[10] A. Hunt and M. Ayers, JoNCS-285 (Berkeley, 2001).
[11] Personal Communcation with Johannes Pollanen, Northwestern University, 2003.