RADON ADSORPTION ON AN AEROGEL

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ABSTRACT OF THE DISSERTATION

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Radon is an important radioactive gas, responsible for environmental exposures and subsequent impact on human health. It is a Noble gas and under most circumstances is not chemically reactive. Its physical properties and resultant behavior, however, may not be simple in all cases, especially where barriers to free diffusion are present, or when encountering materials with special properties. The importance of radon comes from its radioactivity, by imparting energy in material after decay, with resulting damage to living tissue. Transport in the environment is controlled by its physical properties, since it is chemically inert. Aerogels made of silica glass are a relatively new material with the unique property of having a very large surface area, on the order of hundreds of m² per gram, compared to the exterior surface of the bulk volume of typical solid materials. Insight may be gained into the behavior of both radon and unique materials by observing how radon interacts with such materials.

Silica aerogel monoliths with bulk densities of approximately 0.25 g cm⁻³ were manufactured and exposed to radon gas diffusing freely into the gel using a closed chamber. Measurements were taken while allowing the gas to diffuse out of the gel. Radon is found to diffuse out of the sample chamber at about the same rate when a gel material is present as from an empty chamber. Long-term measurements show radioactivity (from progeny) remains present leading to the conclusion that, the radon may have penetrated some distance into the gel. This leaves open the possibility of applying aerogels as a radon detector.

The aerogel manufactured in this study did not preferentially absorb radon. Some evidence suggests that radon may have penetrated the surface however, based on increased long-term radioactivity.

Doping the gel with cerium salts, known to cause glass produced by melting processes to scintillate when exposed to ionizing radiation did not produce observable light signal distinguishable from Cerenkov radiation, thereby excluding the hypothesis that the cerium will scintillate in the current arrangement.

PREFACE

This research was performed as part of a doctoral project in Rutgers Graduate School, the Environmental Sciences Department, the with the assistance of the School of Engineering and the Environmental and Occupational Sciences Institute, a joint institute of Rutgers, the State University of New Jersey and The University of Medicine and Dentistry of New Jersey. The intent of the work was to determine how radon behaves in a confining material, in this case an aerogel. Aerogels have large surface areas with an open internal structure that may allow radon to access the material bulk and are also relatively translucent, allowing light generated within to be detected. The scope of the investigation included determining basic protocols for manufacture of a gel monolith, observing bulk radon transport in and out of the gel by observing the signal from progeny, and whether simple doping of the gel was feasible with respect to gel synthesis and radiation detection.

Radon remains an important concern to human health, representing approximately two-thirds of total effective dose from natural sources and about half of that from all sources (1). Its ubiquity in the environment means it will remain a concern for the foreseeable future, and therefore is worthy of continued investigation. However, radon sampling and analysis present unique challenges. Gas sampling methods have the requirements of capturing and retaining an analyte, which then may be measured while within a chamber or media or after desorption. In passive applications, capture and analysis are usually performed in sequence. As new materials become available they can be tested for utility in various applications such as sequestration or detection. An aerogel takes advantage both of its porous property, allowing radon to enter, and translucency, allowing light created after decay events to be observed. The latter property would allow detection of light created by ionizing radiation, unlike for example charcoal or molecular sieve. This would increase sensitivity and simplify instrumentation.

Aerogels of two basic compositions were synthesized: one based only on a silicon dioxide backbone, and the second contained a dopant of cerium salt. Both were synthesized at ambient room temperature and pressure. Gels tend to collapse during manufacture under the intense molecular forces created as solvents exit the pores. A silylation reagent was used with these gels to prevent free hydroxyl moieties from condensing, thereby preserving the open gel structure. This was important in creating monolithic gel structures, on the order of centimeters in size. An advantage of this process is that the gel surface becomes hydrophobic, which should enhance its stability in ordinary environments. Another potential advantage of aerogels is that, being a manufactured material, chemical and dimensional uniformity is more likely to be better, as compared to charcoal, a common absorbent used in radon analysis.

Experiments in this work consisted of exposing the gels to radon gas, then stopping the exposure and allowing the gas to exit as the radiation signal was observed.

Aerogels tested were as follows:

- 1. Blank gel, an aerogel consisting only of silicon dioxide,
- 2. Cerium-doped aerogel, with fabrication identical to (1) but including the addition of a cerium dopant,
- 3. Blank gel monolith, chemically identical to (2) but which was tested as a whole, intact gel,

In (1) and (2) above, the bulk gels were crushed to pieces on the order of 1 to 2 mm in order to make each as similar in physical dimensions. Experiment (1) examined the behavior of the gel to radon. Experiment (2) addressed the question whether simple addition of a dopant demonstrates any promise of a useful in-situ detector. Experiment (3) investigated whether desorption is sensitive to the bulk size of the gel. The presence of any light output from the radon-exposed aerogel was measured as part of each experiment.

This thesis focused on evaluating how this type of aerogel responds when exposed to radon. It is hoped that interest will be generated for follow-up work in the area of gas transport and scintillation properties.

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I. INTRODUCTION

The properties of radon and aerogels and the importance of radon to human health are briefly discussed in the following sections. It also provides information of how radon might interact with a unique material such as an aerogel (e.g. porosity, surface area, tortuosity) and the potential utility of the aerogel. Background on how radon is measured in practice is included for the purposes of understanding the desire to develop an aerogel detector. The objectives of the thesis work are delineated, including the goal of creating gel monoliths determining how radon interacts with the aerogel, and a dopant may affect one particular property of the gel, namely light emission.

A. Properties and Characteristics of Radon

Radon is a colorless, essentially inert gas at STP, discovered by Fredrich Ernst Dorn in 1900. It belongs to the Noble elements, and has a completely filled outer 6p-electron shell. Radon (CAS # 10043-92-2) is the heaviest of the known elements in Group VIII of the Periodic Table and the heaviest known mononuclear gas at 298 K. ¹ There are 33 known isotopes of radon (atomic number 86) ranging from mass number 195 to 228. All are radioactive (2). Only ²²²Rn and ²²⁰Rn are of potential consequence to health in the earth's environment. These are supported respectively by ²³⁸U and ²³²Th. Only one other radon isotope, ¹¹⁹Rn, exists in some quantity in nature (supported by ²³⁵U) but its half-life is very short (4 s) so that it decays before transporting any significant distance and therefore presents very little threat to health. There are 24 other exotic radon isotopes

¹ The heaviest known gas is tungsten hexafluoride at 12.9 kg m⁻³. (9)

Half Life	Mass No.	Nuclide	Atomic No.	Decay Mode
4.7 E9 y	238	U	92	Alpha
24 d	234	Th	90	Beta
70 s	234m	Pa	91	Beta
2.5 E5 y	234	↓ U	92	Alpha
7.7 E4 y	230	Th	90	Alpha
1.6 E3 y	226	★ Ra	88	Alpha
92 h	222	▼ Rn	86	Alpha
183 s	214	♥ Po	84	Alpha
27 m	214	♥ Pb	82	Beta
20 m	214	Bi	83	Beta
1.5 10 ⁻⁴ s	214	♥ Po	84	Alpha
20 y	210	▼ Pb	82	Beta
5.0 d	210	♦ Bi	83	Beta
138 d	210	▼ Po	84	Alpha
Stable	206	▼ Pb	82	None

Figure 1.1 Main Branch of the ²³⁸U Decay Series

with mass numbers ranging from 200 to 226. Radon in solid form at 202 K (-71 C) is reported to exhibit brilliant phosphorescence that turns yellow as the temperature is lowered and becomes an orange-red at 79 K (-194 C), the temperature of liquid air. Selected properties of radon are given in Table 1.1.

The isotope ${}^{222}_{86}$ Rn (CAS # 14859-67-7) is formed from the radioactive decay of ²²⁶Ra by alpha particle emission. ²²⁶Ra is a member of a uranium decay series, which begins with the primordial radionuclide ²³⁸U and ends after a series or "chain" of decay events at ²⁰⁶Pb, which is a stable element. The chain of nuclear decay is given in Figure 1.1. The serial transmutation has important consequences, both in the environment and in selection of detection methodology. Detection usually relies on measurement of either an alpha particle or a gamma photon, since these are monoenergetic and lead to a confirmation of the emitting radionuclide. However, since the progeny generally have half-lives that are fairly short in comparison to the time frame at which measurement is usually desired, the simplest method for detection is to establish an equilibrium. This approach provides the opportunity for all radionuclides in the portion of the chain that is of interest have an equal activity level. Then, the measurement of any one nuclide allows for the inference that equal activity exists for the others. By allowing the radon generator to equilibrate (radon production from ²²⁶Ra equals the rate of physical decay) a constant amount of radon is available for the exposure to a detector, including a gel. Once ²¹⁴Bi has equilibrated with ²²²Rn, the ²¹⁴Bi decay rate matches the ²²²Rn decay rate, e.g. in equilibrium, assuming ²²²Rn does not escape the system. If the activity levels of ²¹⁴Bi decrease faster than the ²²²Rn activity, then it may be inferred that ²²²Rn is exiting the

	Chemical	
Melting Point	-71 C	
Boiling Point	-61.8 C	
Density (STP)	9.73 kg m^{-3}	

 Table 1.1.
 Selected Radon Chemical Properties and Radon-222 Radiological Properties

		Radiological (²²² Rn)	
Half life		3.825 d	
Specific Activity		$1.3 \ge 10^{27} \text{ Bq g}^{-1}$	
Radionuclide		Types of Major Radiations	
		Gamma	<u>Alpha</u>
	²²² Rn	None	5.0 MeV
Progeny:			
	²¹⁸ Po	None	6.0
	²¹⁴ Pb	0.352 MeV, 0.295 MeV	None
	²¹⁴ Bi	0.609 MeV, 1.74 MeV, 1.12 MeV	None
	²¹⁴ Po	None	7.7 MeV

system by means than physical decay, e.g. transport via gaseous diffusion or flow. The ²¹⁴Bi activity then said to be "unsupported."

The chemical properties of some elements in the chain play an important role in transport during the time the other members of the chain decay. Each decay event in the sequence creates a different element, so therefore the chemical properties of each successive progeny will also change. For example, radon becomes a health concern because as a gas it easily exits the subsurface soil and water where it is formed and is transported by diffusion of soil gas. The pressure-driven flow can lead to the movement of radon into breathable air in areas inhabited by people, such as commercial buildings and residences. Radon is the most likely cause of lung cancer among non-smokers, and according to Environmental Protection Agency it is estimated, to be responsible for 21,000 lung cancer deaths every year. (3)

The radioactive emissions given off by the uranium series decay progeny include alpha, beta and gamma emissions. Because ²²²Rn may transport into, and either decay or leave an area, the detection of radiation from its progeny, which are not as mobile, allows an inference of the presence of ²²²Rn at some time earlier. In most cases, the beta and gamma radiations from ²²²Rn are not measured directly. First, alpha detection requires close proximity of the incident radiation and the detection medium (on the order of microns). Second, the one other type of radiation emitted by ²²²Rn, a gamma photon at 0.510 MeV has very low abundance (0.078 %.) Gamma detection schemas therefore typically rely on detection of one or more of the progeny. Measurement of gamma rays is

the most convenient. Gamma rays easily penetrate most media and containers, so a chemical separation step is often not required to detect them, and further interactions and absorption within the medium are minimal. Measurement can be done at some distance from the sample, simplifying handling procedures. An additional advantage is the monoenergetic nature of gamma rays that allows measurement of the specific radionuclide that is emitting the radiation. In some cases the detector measures several gamma photons emitted by the radionuclide. Usually, unless not critical to the application, correction must be made for the state of the decay chain equilibrium.

The decay sequence of ²²²Rn in Figure 1.1 shows four short-lived radioactive progeny (²¹⁸Po, ²¹⁴Pb, ²¹⁴Bi, ²¹⁴Po) created in quick succession. For practical purposes this is the end of the chain since the next element, ²¹⁰Pb, has a half life 20.4 y, long enough on the laboratory time scale for its activity, once created, to remain essentially constant. The chain does continue with the decay of elements ²¹⁰Bi and ²¹⁰Po until an atom of stable ²⁰⁶Pb is formed. (There are also three side chains where minute quantities of ²¹⁸At, ²¹⁰Tl and ²⁰⁸Pb are created and decay in turn, but these are generally unimportant analytically.) Because the first four progeny have half-lives significantly shorter than ²²²Rn, their activity can build up, and become equal to the ²²²Rn activity. Equilibrium is maintained when the rate of production of a radionuclide is balanced against its rates of removal and decay: when the two rates are equal, the activity remains constant. Careful correction for time-dependent phenomenon is usually necessary if activity of a progeny radionuclide is out of equilibrium or if the parent has decayed, when the decay rate is then a function only of the decay constant of the radioanalyte. In practice measurement strategy is to take measurements when equilibrium exists, or when equilibrium is

changing slowly relative to the time period of the measurement. The volatile nature of radon can result in its transport out of a medium or container in the time frame on the order of the decay rate of the short-lived progeny. Therefore, care must be taken to contain radon or make appropriate time-based corrections.

B. Radon in the Environment

The earth's crust and underlying plastic mantle are the ultimate sources of radon, which emanates after the decay of 226 Ra, one of the sub-series of the 238 U chain. 226 Ra may be present in ore deposits, or in soils. The 1620-year half-life of 226 Ra is sufficiently long for transfer to the hydrosphere, and subsequent movement away from the original ore body. Radon may enter the atmosphere directly from soil gas or be released from water. 222 Rn entering the soil pore volume has a concentration of 2 x 10³ Bq m⁻³ (500 pCi L⁻¹) per ppm 238 U at equilibrium. (4)

Most soils in the United States have some ²²⁶Ra in soil from which ²²²Rn may emanate. Concentrations typically range from 0.5 to 1 pCi g⁻¹. Concentrations higher by two to three orders of magnitude are possible from process wastes, such as phosphate or uranium mining. (5) The average radon concentration in outdoor air is about 37 Bq (100 pCi m⁻³⁾ and may range up to ten times that in localized areas. However, can be even higher levels found in areas proximate to process wastes such as uranium mill tailings. Progeny activity is typically within 60% of equilibrium. The term 'equilibrium' refers to the constant activity level of a member of a radioactive decay chain that occurs when the rate of production of a nuclide equals the rate of decay. In a closed system where no mass transport changes the mass amounts of the nuclide or it's parent present in the system the time to achieve equilibrium depends only on the starting quantities and the half-life of the progeny. It is assumed in this type of equilibrium, also called 'secular' equilibrium that the parent has a half-life much longer than the progeny as is the case with both the ²²⁶Ra/²²²Rn and ²²²Rn/progeny pairs. When either or both parent and progeny may exit the system, then the equilibrium must also consider those respective rates of transfer. If the rates are comparable, equilibrium might be established; otherwise the activity levels never reach equilibrium. When progeny activity reaches a maximum, constant value, equilibrium is said to have been achieved.

Radon is found naturally in soil, ores and subsurface water. Transfer across the soil-air boundary is relatively slow. (6) The relatively short half-life of 3.8 d for ²²²Rn results in a half-infinite depth concentration depth of 1.06 m. This means radon in the air, which is released from soil due to direct diffusion is from only a relatively thin surface layer. Most radon transported from the soil to air results from active mechanisms, such as a pressure differential, or transport in (ground) water rising to the surface. Radon entry into buildings is driven by a lower than-atmospheric pressure in the enclosed spaces where radon can accumulate, or "build up," rather than dissipating into the atmosphere. However, in many cases it may not present an exposure problem since the radon can decay in the time it takes for the gas to reach inhabited areas. Industrial and commercial

activities can play a significant role in increasing radon levels. For example mining activity release radon to well water, and radon present in natural gas can all contribute to the proximity of radon to people. Thus, the source will be an additional contributor to exposure. Radium sulfate can precipitate onto surfaces of equipment in contact with oil production waters from oil wells because it is relatively insoluble, and subsequently release radon. Phosphate mining is an example of how radium can be separated during ore processing and refinement, and result in the release of radon. Radon that is present close to the surface can also be drawn into basements and living areas by heating systems and atmospheric pressure differentials if there is an actual pathway through the building foundation (e.g., cracks in foundation).

C. Radon and Health

When radon is present in air people can breathe, it results in a radiation exposure and subsequent dose delivered to lung tissues. The median radon air concentration found in US homes is 2.5×10^{-2} Bq L⁻¹ (0.67 pCi L⁻¹.) Ionizing radiation from radon itself contributes only a small part of total radiation dose. The progeny (²¹⁸Po, ²¹⁴Pb, ²¹⁴Bi and ²¹⁴Po) are electrically charged upon formation and then attach themselves to particles in the air thus becoming deposited in the lung during inhalation, and thereby affecting biological processes. Radiation dose is then delivered to the lung during decay. Breathing rate and exposure time also are important. Radon is a well-recognized cause of lung cancer in miners working underground and is the second leading cause of lung cancer in the U.S., with about 15,000 lung cancer deaths per year. The most important biological target is the lung although other malignancies such as leukemia and some types of solid cancers have been reported. (7)

The process by which progeny attach to aerosols is complex. Many physical and biological factors influence exposure and dose. As progeny are generated by decay, they begin not as free atoms, but rather small clusters of molecules. (6) These are referred to as the "unattached fraction." Subsequent deposition onto aerosols creates a second fraction, whereby the progeny become "attached" to the particles. The size of the particles on which this fraction becomes attached determines deposition in the lungs. Particles less than 10⁻⁶ m in size can remain suspended in the air for a long period of time.² Unattached progeny have higher mobility and are more likely to reach the respiratory tract and deliver dose.

D. Properties and characteristics of Aerogels

An aerogel is a material with an internal structural continuity or 'monolithicity' in a solid but porous form with at least 50% open space by volume. The term 'monolithicity' refers to the continuous nature of the material, which is a property typical of a solid, liquid or glass. While the aerogel can be categorized as a glass, it differs from typical glasses is that its structure is porous. Typical aerogels are more than 90% open space that is usually air with densities from 3 to 1900 kg m⁻³. By comparison, typical fused silica has a density of 2200 kg m⁻³. Because much or all the internal material is available to the outside environment (unlike a solid where the internal portion is blocked

² A quantitative definition of "long" is not provided. See reference (6) page 179.

by the exterior surface) an aerogel may be described as being "all surface" or of having an "internal surface." A comparison can be made to the structure of a sponge. Silicon dioxide is the most common material used to make an aerogel. Other metal oxides, metal chalcogenides (a compound of an element in group VIB or VIA in the periodic table with a more electropositive element), organic polymers and other inorganic polymers have also become a common aerogel material. Samuel Kistler synthesized the first aerogel in 1931. (8) In addition to its very low density, aerogels have several other unique properties, among them an extremely low thermal conductivity (0.003 W m⁻¹ K⁻¹) (9), a large surface area per unit mass, optical transparency and high structural strength for its mass, which are useful properties for a detector.

Kistler's method to produce aerogels used acidic condensation of aqueous sodium silicate followed by salts removal by rinsing with water, then alcohol, followed by removal of the alcohol under supercritical conditions. Later, Stanislaus Teichner developed a method that did not use salts (which tended to re-dissolve the gel) and did not need a rinsing step where a silica precursor such as tetramethylorthosilicate is hydrolyzed in a solution of methanol to produce a gel. (10) This came to be known as the "sol-gel" process, where silicon dioxide precursor sols are gelled by hydrolysis and condensation. A colloidal suspension, the sol, is produced and then forms into a continuous network or gel. It is converted to glass by removal of solvent without using the high-temperature melting required during the manufacture of typical glass. The original method of solvent removal was used to create supercritical conditions whereby the solvent (methanol) is above its thermodynamic critical point. The supercritical solvent is then no longer either a liquid or gas and may be removed from the pores of the gel using a pressure differential without huge hydrostatic pressures that could cause the gel to collapse.³ This method is still common but some processes use safer reagents such as supercritical carbon dioxide.

Prakash, Brinker, Hurd and Rao (11) reported on a method that did not require supercritical conditions to remove the solvent. This was accomplished by modifying the surface of the gel prior to drying. By capping the hydroxyl moieties on the gel surface with a sylyl moiety, the gel is protected from complete collapse under the huge hydrostatic pressures that develop with liquid solvent (typically an alcohol) as it is removed and replaced by a gas. Brinker's approach used trimethylchlorosilane (CAS # 75-77-4) as the silylation reagent.

Although aerogels need not be made of only one material, pure silicon dioxide makes up the gel matrix used in the present study. Composite materials are possible, when additives are chosen to modify bulk properties, such as flexibility, or change transparency. An additive may also be a dopant, where it plays no role in modifying the bulk properties, but may have other functions. Cerium (3+) in nitrate form was added as a dopant in the present study to investigate the possibility of increasing the optical activity from ionizing radiation. Cerium probably does not participate in the gel structure, but could become trapped by occlusion or hindered transport after the gel synthesizes. Jean-Marie Nedelec, et al, (12) showed that photosensitive Ce(3+) doped aluminosilicate

³ During sub-critical evaporation the receding liquid menisci results in a pore liquid capillary pressure approaching 100 bar, which collapses the gel framework.

waveguides for optical applications could be produced using a sol-gel process. In that work, the glass was increased in density at 1173 K (900 C) was followed by a hydrogen atmosphere treatment at 723 K (450 C.) However, the densification of the gel collapses its pores.

E. Porous Glasses

A porous glass has several advantageous properties for use as a radiation collector or sensor. While technically a liquid, glass at STP has some solid-like properties. For example it does not deform and, maintains a given shape. Composite glasses maintain short-order structure unlike a liquid where additives might redistribute. The many smaller pores have the potential of providing radon a surface distribution of pores (inside the glass) of various sizes available for trapping, some are optimally positioned for allowing radon to enter the bulk material and then trapping the radon. Subsequently, it may be released more slowly than radon would before the pores surface, which would be in contrast to a release from a larger void. Materials other than aerogel such as activated carbon, silica gel and molecular sieve have been used in radon detector or capture studies. Of these, activated carbon shows the most affinity for radon. The others are not considered good radon adsorbents. Molecular sieves with larger pore sizes show a somewhat larger increase in radon adsorption. (13)

Additionally, even if the aerogel does not preferentially adsorb radon, the porous nature of aerogels would cause progeny to become trapped, rather than remaining entrained in air after exiting the gel's porous structure. Similar to activated charcoal,

radioactive decay that occurs while within the bulk aerogel results in deposition of the progeny that will remain in place within the gel. Progeny would subject to movement only after recoil that could occur during subsequent decay events. Thus, when ²²²Rn decays to ²¹⁸Po, the recoil nucleus is likely to remain within the gel medium. Subsequent decay to ²¹⁴Pb, ²¹⁴Bi, etc. will also remain entrapped. Given the solid-like structure, and scale of the gel and its tortuous surface-laden pathways, even recoil would be unlikely to release progeny back to the surroundings. In contrast to activated charcoal however, the prospect of gel transparency opens new possibilities for detection methodologies, namely the use of optical methods. Of particular interest would be a process whereby alpha particles causes, with sufficient efficiency, a detection signal proportionally to the energy imparted by the decaying radon. This would provide nuclide identification analogously to the semiconductor detector methods in gamma energy detectors, and liquid scintillation technology. For radon this would allow a direct determination of the amount of radon, and the fraction of progeny in equilibrium if successfully employed it may even act as a long-term average measurement methodology.

The distribution of pore sizes in aerogels is adjustable with the appropriate chemistry. Unlike a thin filter, the contiguous, tortuous inter-connected pores result in too high a pressure drop to effectively as a typical filter; so this may be a disadvantage for certain applications, e.g., large volume air-sampling. However, possibilities exist for creating gels of various shapes, such as plates, where radon might be exposed only to one side, or by coating the inside of chambers (or various constructs where the gel itself creates the wall of one or more chambers.) Where large-volume airflow is desired,

sintered powders of aerogel fragments would provide aerogel properties but with a macro-structure typical of a filter; air could then easily enter the macro-spaces, but still have access to the interior of the gel medium.

An intact, monolithic gel, unlike a filter, would tend to exclude progeny generated external to the gel, whether as an attached or unattached moiety, but retain those created within the gel boundary. Additionally, a gel might have the capability of retaining radon, unlike a filter, thereby providing a longer window for analysis, since the progeny decay faster than radon itself. Note that this is the principle behind charcoal filter measurements, although charcoal is not actually a filter in the strict definition of the term but rather is an adsorbent. Most filters would allow radon to pass through but accumulate progeny, depending on the filter mesh, particulate size and other parameters, such as humidity. A thin filter might capture only some progeny, as secondary decays are swept out by air flowing out of the filter.

Glass is generally inert and structurally strong, inexpensive and can be chemically tailored for specific uses. Proper treatment can result in a hydrophobic surface that should stabilize its behavior in ordinary atmosphere. Translucency is another important property of glasses. A solid glass transmits light, but lacks porosity. Therefore the radon can reach only the surface, which represents a very small fraction of the total mass. If the glass were a viscous liquid allowing radon to permeate the bulk, such as occurs in water for example, radon might be able to better interact with the material. One common example is liquid scintillation fluid. But, liquid must be contained, and often has volatile fractions that limit usefulness over time. A powder configuration is possible, but these are often fragile, and pore size can be difficult to control. Also, powders tend to be opaque, which would defeat the concept of being able to detect light generated within the gel material. Glass fibers, as mentioned earlier would also be an interesting avenue of study since they have a high surface to volume ratio and since these remain more translucent than powder and can be made quite small in size.

Aerogels take the concept of increasing ratio of the total surface area to total volume to a theoretical maximum. Thus, they are just short of a gaseous state, and still maintain structural rigidity, in a solid rather than liquid state. Additionally, the gel preserves an acceptable degree of translucency. The properties of high surface area per unit volume and an open, accessible structure to a glass-like material that allows light to pass though also will provide the opportunity to construct a simultaneous collector-detector.

Ideally, one would also require the material to be luminescent, whereby ionizing radiation interacting within the sensor can generate light. This would allow radon detection to occur within the same volume of material as radon is collected, and possibly at the same time. Scintillation is the preferred mechanism, because of the relatively fast time constant, and because the amount of light can be related to the amount of energy deposited, thereby giving information on the type of radiation being measured. However, other energy deposition and other rerelease processes may be useful, for example phosphorescence or Cerenkov interactions. The latter are possible in glass, and are commonly observed. For example, phosphorescence might be achieved by incorporating a photoactive material within the gel. Cerenkov detectors are a common application of aerogels for the detection of high-energy particles. Aerogels have been found useful for Cerenkov detection of high-energy particles because their index of refraction is inbetween that of gases and condensed matter. The emission spectrum of Cerenkov radiation for particle energies emitted by radon progeny (a few MeV) is close enough to the ³H spectrum in LS fluid commonly utilized for LSC applications. For example, a common LSC application is detection of the 1.7 MeV (maximum) energy beta particle from ³²P without the use of liquid scintillation fluid. The light is generated in the wall of the LS vial. No attempt is made here to determine what fraction of Cerenkov light originates within the aerogel versus the glass wall of the vial.

F. Questions on Radon Behavior

Il Sik Kim's research with glass fibers has shown promise as a radon sensor. (14) Kim has shown that bundles of scintillating glass fibers 5×10^{-5} m in diameter could be used to detect the alpha radiation from radon and progeny. The fibers were packed together to form a cylindrical bundle, in what could be considered a porous glass construct. Because the fibers were tightly packed the space between them may be considered to be like pores in that gas can enter and exit, and larger particulates are excluded, or trapped on the exterior surface. Kim estimated that approximately 1/3 of the bundle volume was open space. Because of the geometry it is likely that the space was entirely contiguous. The air spaces between fibers allowed radon to enter, and would also trap progeny.

Similarly, an aerogel also allows radon to enter, but exclude progeny created outside the bulk and trap progeny generated inside. However, aerogel can have tortuous connections between the pores, which may play a role in radon transport. Its finer scale structure could preclude any progeny generated outside the bulk, whereas the fiber bundle may allow some progeny to enter and move some distance into the structure.

G. Radon Measurements, Detector Design and Technology

Radon measurements often require precise separation of the radiation signal from the mix of alpha, beta and gamma radiation. Alpha and gamma radiation are the preferred radiations to detect because they are mono-energetic, and therefore can lead to identification of the emitting nucleus. Liquid scintillation counters (LSC) can be used to detect alpha radiation and can distinguish between light events produced by alpha and beta/gamma energy, by observing the time it takes for the light pulse to decay, or by the time it takes for post-pulse processing. (The method varies by instrument manufacturer.) The LSC typical application uses fluors to capture the energy. This has the advantage of preserving the information of the emitted energy, e.g. if a known fraction of the energy of a pulse is collected, conclusion can be made about the impinging energy. In this study, no fluor was used. However, the LSC was used instead as a spectrophotometer, observing the spectrum of light output. This mode of operation is used sometimes for high-energy beta (for example ³²P) studies without liquid scintillation, where the Cerenkov radiation is measured. Gamma spectrometers detect and record the photon energy that interacts with the active area of the detector element. Both scintillation and semiconductor detectors are commonly used for gamma spectrometry. Both have the advantage, with proper instrumentation, of simultaneously counting photons (depending on the time constant of the detector) of different energy and providing the distribution, or spectrum of photon energies. In this study, a high-purity germanium spectrometer was used to observe the energy region corresponding to events created by interactions of 609 keV photons from ²¹⁴Bi with the detector. When energy is deposited from a photoelectric event inside the detector volume, all the energy of the photon is converted to a pulse, and the emitter can be identified based on the fact that photons are mono-energetic, corresponding to specifically allowed energy levels within the nucleus. The time sequence of other photons from the various progeny can sometimes be used to determine radon activity, or even the state of the equilibrium.

One ideal is to combine collector technology and detector technology so that the separate step of intermediate processing is not needed for analysis. For example, radon monitoring with charcoal detectors involves collecting radon in canisters of activated charcoal media, transport to the laboratory, and then waiting for the radon and progeny to reach equilibrium. The charcoal serves only as a collector; detection occurs in the gamma detector instrument. In liquid scintillation, the detector (the liquid scintillation fluid) is intimately mixed with the sample. This work with aerogel might be considered as taking a similar approach, in using a collector (the aerogel) and seeing if it can also be used as a detector. Note that the term 'detector' is variously used depending upon the context to

mean either a single module, e.g. an active element which light is created upon response to incident radiation and an ensemble, such as an instrument composed of a detector and sensing electronics such as an amplifier or photomultiplier tube. This work makes some small steps toward that goal: if a gel that is essentially a solid can collect radon or progeny, and is also sufficiently translucent to allow light to reach a photomultiplier this might form the basis for a simple, portable detector.

H. Research Objectives

The research objectives of this thesis were defined to demonstrate the following:

1). Bulk aerogel can be manufactured in ordinary laboratory conditions. e.g. at temperatures under 373 K (100 C) and at atmospheric pressure by preparing monolithic aerogels exceeding 4 mm thickness in each of three dimensions.

2.) Radon adsorbs to bulk aerogel.

2.1. Radon adsorbs to the bulk aerogel by conducting an experiment that exposes the aerogel to a fixed amount of radon gas in air and measuring the change in radon content, as compared to an empty chamber.

2.2. How fast the radon/progeny signal fades after the radon exposure is terminated, by observing the rate of decay of the radon signal.

3.) Cerium dopants within the bulk aerogel scintillate in response to exposure to ionizing radiation by observing light-output response in radon-exposed cerium-doped aerogel using the photomultiplier tubes in a liquid scintillation counter, as compared to aerogels without cerium.

I. Hypotheses

The hypotheses of this thesis are:

1) Bulk aerogel can be manufactured in ordinary laboratory conditions, e.g. at temperatures under 373 K (100 C) and at atmospheric pressure,

2) Radon adsorbs to bulk aerogel:

 H_0 : MA(Rn) = M(Rn) H_a : MA(Rn) ≠ M(Rn)

where MA(Rn) is the mass of radon which is retained by the bulk aerogel, and M(Rn) is the total mass of radon in the closed container to which the aerogel is exposed,

and

3) Whether Ce dopants placed within the bulk aerogel scintillate in comparison to aerogels without a dopant in response to exposure to ionizing radiation.

$$H_0: IA(Ce) = I_A$$

H_a: IA(Ce)
$$\neq$$
 I_A

where I_A (Ce) is the amount of light (or LSC counts observed) from radonexposed cerium-doped aerogel and I_A is the amount of light observed for radonexposed aerogel without cerium.

II. METHODS

A. Gel Manufacture

1. Reagents and Materials

Reagent grade chemicals were used to synthesize gels. Sols were synthesized with tetraethyl orthosilicate (TEOS) from Fisher Chemicals. Deionized water (>18.3 M Ω cm.) was used in all dilutions and rinses. Hydrocholoric (HCl) acid was use to hydrolyze the TEOS. Ammonium hydroxide (NH₄(OH)) in ethyl alcohol (EtOH) was used to neutralize the sol, and allow the gel formation to begin. Pure EtOH was used to rinse wet gels, to remove all water. (A 'wet gel' refers to a gel in either aqueous or organic liquid, such as alcohol or hexane.) Hexane (Fisher H303-4, Hexanes UN1208) Optima grade was used to rinse out the EtOH and later, the Trimethlycholosilane (TMCS) from Fluka Chemika 92361, purum >98% (<2% hexamethyl disiloxane) which was used to cap hydroxyl moieties on the silica surface. Cerous nitrate hexahydrate was used to dope selected gels with cerium. Some test runs used variously, sodium nitrite, toluene, 2,5-diphenyl oxazole (PPO), La(NO₃)₃·6H₂O, or benzene (HPLC grade 99.9+ % from Sigma Chemicals #27070-09).

Disposable glass pipettes were used for dilutions, and for transfer of reagents and sols to the vials. Acid and base reagents were measured and diluted in borosilicate beakers or graduated cylinders, and used within a few hours. Dry reagents were transferred using a Teflon®-coated spatula. Sols were created in 500 ml Pyrex® borosilicate beakers by hydrolyzing TEOS and adding dopants, if any, and stirred gently using Teflon® stirring bars on a standard magnetic laboratory hotplate. A glass

thermometer was used to monitor the temperature of the sols during hydrolysis. pH indicator paper was used to test sols prior to gelation. Measured volumes were transferred via pipette to glass or polyethylene vials, which were the gelling containers.

Gels were formed in a standard laboratory oven at 50 C, in 5 ml high-density polyethylene vials (1 cm diameter) with a loosely placed polyethylene screw cap. Gels were allowed to age, and then each was transferred from the 5 ml vial to a 20 ml borosilicate glass vials, having aluminized and plastic-coated cap interiors for rinsing and surface treatment. Transfer was performed quickly into an alcohol bath in order to prevent the newly formed gel exterior surface from drying. Vials were kept tightly capped during rinsing and opened only during the actual exchange of liquids. Disposable polyethylene pipettes and borosilicate beakers were used to deliver alcohol and hexane rinses, depending on the rinse volume. Initial rinses were performed with pipettes, to keep the hydrostatic pressure between phases comparable. Disposable polyethylene pipettes were used for TMCS transfers.

Surface-treated gels were initially dried slowly at room temperature, while capped loosely within the vial. A standard laboratory oven was used to finally dry the gels to 80 C. All other operations not performed on the hot plate were performed at laboratory ambient temperature, approximately 20 C.

The masses of the gels were measured using one of three balances: an Ohaus balance, portable advanced Model CT6000; a Metlar Toledo Model PB1502; and a

Metlar Toledo Model AX205 Delta Range balance. For convenience, most reagent solutions were weighed rather than delivered volumetrically. Liquid volumes under 200 µl were dispensed using an Eppendorf® repeating pipette.

2. Gel Synthesis

Gels were made in batches since experience was needed in determining the optimal conditions for obtaining a monolith. Preparing several gels at the same time, and moving a few forward to the next processing step saved time and materials. For example if drastic conditions cracked the gel, the remaining gels could be processed more carefully and prevent cracking. If too much solvent was added at once, especially in the initial rinse steps, invariably the monolith cracked. An initial run was performed to test basic parameters such as reagents amounts, order of addition, evaporation rates, time factors, logistics and so on. The first run created five batches, labeled 1A, 1B, 2A, 2B, and 2C, as illustrated in Figure 2.1. Each batch had one or more replicates to evaluate reproducibility and allow for errors. Parallel sets were made in glass and plastic vials. The glass vials provided good visibility of the sol-gel physical state, while the plastic vials provided gels in the target dimension of 1 cm diameter. Each "route" is comprised of a sequence of procedures used to create a gel. Some routes differ in only the order that reagents are used; other use differing reagents.

Batch 1 followed the most direct route: acid hydrolysis in the presence of cerium, followed by neutralization and gelling. Batch 2 tested whether cerium dopant could be added before or after neutralization. Figure 2.2 shows batch 3 where various other additives and dopants (toluene, aniline, phenylphenoxazole and lanthanum nitrate) were



Figure 2.1 Test of Gel Synthesis Routes








tried using synthesis route 2B; and batch 4, where various types of plastic containers were tested using synthesis route 1A. Figure 2.3 shows syntheses paths for batches 5 through 8, with varying levels of alcohol. Gels from batches 7 and 8 were taken to surface treatment and solvent removal to produce dry aerogels.

B. Radon Exposure Chamber

1. Reagents, Materials and Configuration

A 21.5 kBq ²²²Rn source (Pylon® Electronics Inc., Canada) was used to provide radon. The manufacturer reports the calibration error as ± 4 %. The generator was used in static mode, e.g. no airflow was passed through the generator so that all of the radon remained within the apparatus. The generator active volume is 1.06 x 10⁻¹ L. The volume of the exposure chamber (a liquid scintillation vial) is 0.020 L. The final volume of the connected apparatus was about 1.27 x 10⁻¹ L considering the additional volume of the leading tubing minus dead space from the brass fitting. Therefore, the radon concentration in the exposure chamber was 170 kBq L⁻¹, not considering the volume of the aerogel.

This was the only size available when experiments were started, and the same source was used for all experiments in order to keep experimental variability at a minimum. The source unit is a proprietary configuration of ²²⁶Ra in a "dry powder" form (not specified by the manufacturer) and contained within an aluminum housing, with a valve at each end. Opening either valve allows radon to exit the apparatus. The source may be used to provide radon either a continuously or intermittently. The manufacturer

states that 100 % of radon generated within the device can exit the source, with a calibration accuracy of 4% (1 σ confidence level). The operating range for temperature is 0 to 50 C and for humidity 0 to 90 % under non-condensing conditions.

The radon gas passes through a 25 mm diameter glass fiber filter with pore size 0.8×10^{-6} m in a polypropylene filter assembly that was positioned immediately past the brass outflow valve via a threaded connection. A ¹/₄-inch ID copper tube, 8 cm long (to pass through the lead brick shielding) was connected to the nipple of the filter housing with at ¹/₄-inch ID Tygon® polyvinyl chloride tubing fastened tightly with a steel hose clamp. The copper tube was connected at the other end to a Swagelok[®], brass fitting and sealed with a metal ferrule. This fitting was threaded to another brass fitting with a compression joint and which was inserted in a ¹/₂-inch hole drilled though the center of the plastic cap, and the cork and aluminized plastic liners, thus forming a seal with the liner. Screwing the glass vial tightly onto the cap threads made an airtight seal to the rim of the glass vial. The copper is somewhat flexible, durable, malleable, seals well to brass and is impermeable to radon. The 20 ml glass vial served as the exposure chamber. The end of the Pylon® radon source was kept closed. A block diagram is provided in figure 2.4. The goal of the apparatus is to provide a constant radon air concentration in the glass chamber in which the aerogel is placed by providing a sealed environment between the source and sample.

2. Procedures

A radon exposure session began by completely opening the outflow valve. When radon exposure ended, the outflow valve was closed, the glass vial disconnected from the

Figure 2.4 Diagram of Exposure Apparatus



exposure apparatus, the vial was left open for 60 seconds to allow any radon in the chamber air to exit and the vial was capped with a new, intact plastic cap. This cap was removed during off-gassing and replaced during sample transport and radiation counting. During each exposure, the progress of radon transfer from the radon generator to the sample chamber was monitored using a 1-inch NaI(Tl) detector, (Model 44-2 Ludlum Instruments, Texas) positioned at a fixed location relative to the exposure chamber so that the exposure conditions and were the same for each sample. The purpose of this measurement was to continuously monitor the presence of radon (via progeny) to establish that a continuous, constant activity level was maintained within the chamber, which remained at a fixed distance to the NaI detector. All exposures utilized the same geometry. The detector was held at a potential of 890 V, connected via a coaxial cable by a scaler (Model 2000, Ludlum Instruments, Texas.) The count rate was observed over time in order to observe the progress of radon transfer into the exposure chamber. The total beta-gamma signal was recorded to determine the status of mass transfer and radiological equilibrium, e.g. when and whether the radon concentration stops rising and becomes and remains constant. Counts were collected for either 1-minute or 10-minute time intervals. Background counts were collected before and after the exposures.

Prior to each exposure a ¹³⁷Cs "button" check source was used to confirm correct operation of the NaI detector by placing the check source within two inches of the detector active volume, and then confirming that counts were observed when the check source was present. This was a non-quantitative test to confirm that the detector is responding to gamma radiation. A counting efficiency calibration was neither needed nor practical, since the only purpose of this apparatus is to indicate that radon is present and reaches a constant activity level within the chamber. The count rate is a sum (with their separate counting efficiencies) for all progeny beta and photon radiations present and does not indicate the location of the radon or progeny, e.g. whether within the chamber volume or on or within the aerogel bulk. The radon generator is shielded behind a 0.05 m thickness lead brick. Therefore, all counts are due to the presence of progeny within the sample chamber.

A cave of lead bricks shielded the radon source in order to minimize laboratory exposure, and to eliminate scatter and sky shine from the source to the detector. A hole slightly larger than ¼ inch was drilled through one brick in the cave wall. The copper tube passed through this hole to the exposure chamber, which was housed in a contiguous cave of lead bricks. The detector was placed in a fixed position in the corner of this second cave, off of the source-chamber centerline. The lead brick wall between the caves shields photons coming directly from the source, thereby preventing them from contributing signal to the NaI detector. With the lead shield in place, all counts registered in the detector are due to progeny present in the exposure chamber. Without the lead, the tubing leading to the chamber could have been 2 inches shorter, but the radon still diffused to the chamber. The tubing length was arbitrary, but it was made as short as possible for maximum efficiency of transfer. The entire assembly was housed in a chemical fume hood. C. Gamma Counter

Gamma photons were counted using a 50% relative efficiency hyper-purity germanium (HPGe) detector with digital spectrometer, EG&G Ortec Model DSPEC. The detector was housed in a "low-background" graded lead-tin-copper shield, and cooled with liquid nitrogen via a remote cryostat, in an up-looking J-configuration. The industry term "low-background" in referring to shielding material refers to either or both of the use of lead cast before atomic weapons were tested, or to tested and certified materials which do not have ambient levels of naturally occurring radioactive materials as contaminants. The counter was kept continually cooled during the period of work. Samples remained in the glass vial, which was placed directly on top of the detector can, positioned in the center. The apparatus was housed in a modular steel building on a concrete slab. Background counts were collected before and after the exposures. ¹³⁷Cs and ⁶⁰Co "button" check sources were used to confirm correct operation. Energy calibration was accomplished using mixed gamma sources. Energy resolution was about 0.5 eV per channel.

D. Liquid Scintillation Counter

The liquid scintillation counter (LSC) used was a Model 2770 TR/SL from Packard Instruments, Connecticut. Samples were counted in the glass vials used as the exposure chamber, the same procedure as with the gamma counter. The LSC operation was confirmed as stable by using the manufacturer-provided calibration standards, which consisted of a sealed liquid scintillation ¹⁴C standard and an internal ¹³³Ba source. The procedure also included following the manufacturer "normalization" protocols with each

run. No scintillation fluid was used for the aerogel studies, rather, the light created from radiation impinging on the aerogel and glass vial (exposure chamber) was observed. Routinely, standards made from NIST traceable ⁹⁰Sr and ²²⁶Ra solutions were also run, these standards being in liquid scintillation fluid, which ensured that the LSC was operating properly, using standard protocols. While the LSC was calibrated using a ²²⁶Ra standard in liquid scintillation fluid, giving about 1 keV per channel for beta particles, less light per unit energy is created and detected without liquid scintillation fluid, so the LSC was used as a sensitive, but uncalibrated spectrophotometer. Counts are recorded according to energy (wavelength) because the equipment self-calibrates during the normalization operation; it is calibrated in eV/channel. But, the fraction of energy deposited and the fraction converted to light are not known with the aerogels under the current arrangement. Events recorded in the alpha channels are those that are above 300 keV, since this roughly corresponds to the minimum energy deposited by alpha particles in liquid scintillation fluid. This may be an arbitrary cut-off value in the counter software.

E. Safety

Standard chemical and radiological laboratory practices were followed during the completion of experiments. All chemical operations were performed while wearing vinyl gloved, laboratory coat, and safety goggles. Chemistry operations were performed in a laboratory chemical fume hood, with a nominal laminar face velocity of 100 CFM. Weighing was performed in sealed containers, except for reagent preparation. Radon exposures were performed in the fume hood. Radiation dosimetry badges were worn while working with radioactive material. All safety training was kept current. The

radiation safety committee approved radiological protocols. Regular wipe radiation surveys were conducted each month, and after each exposure experiment.

F. Measurements

The masses were of the reagents and gels were determined on calibrated scales to the precision specified by the scale display. Reagent volumes were dispensed based on the calibrations marked on the glassware (typically 5% error unless otherwise specified. Micropipettes were checked by delivering a volume of deionized water that was then weighed on a scale of appropriate sensitivity.

Sol pH was determined using pH sensitive paper with gradation of +/- 1 and a range of pH 1 to 8 to ensure that sol pH was close to neutral or slightly acid, so a gel would form. Temperatures during gel synthesis and oven drying were measured using a glass laboratory thermometer, with a range 0 - 100 C (error $\pm 2 \text{ C}$) with 1 C gradations.

The radiation counts were recorded as total counts within the count time for the NaI(TI) counter. No corrections for dead time were performed in these experiments. The gamma counter recorded counts in each of 2000 channels from approximately 60 keV to 2 MeV for the specified counting period. Liquid scintillation measurements were recorded in the open window (all channels) as counts per minute (CPM) for the selected counting period. In some cases data was recorded in each of the 2000 channels corresponding to the light energy detected by the LSC's photomultipliers.

Visual observations were recorded in the logbook. State (liquid or solid), color transparency, geometric arrangement and any notable features were recorded as observed to the eye under laboratory lighting conditions (fluorescent lights.) Selected observations were documented with photographs using a digital camera, Kodak, Model DC265.

G. Analysis

1. Observable Signal

Radioactivity (gamma, and energetic beta from progeny) during radon exposure was monitored with the NaI(Tl) detector, indicating the presence of radon, and, when a constant activity level was achieved, indicated equilibrium. This was the experimental balance between radon decay and diffusion back and forth between the generator and the exposure chamber, or through leakage.

For the off-gas experiments, the presence of ²²²Rn was determined by the HPGe detector observing gamma photons from the progeny, primarily ²¹⁴Pb and ²¹⁴Bi decaying respectively, with half-lives of 26.8 and 19.9 minutes. Because these half-lives are much shorter than the 92-hour half-life of ²²²Rn, equilibrium was reached within about 3 hours, and the apparent decay rate of the progeny is the same as ²²²Rn. If all the ²²²Rn was removed, the progeny activity would be "unsupported" and the radiation would quickly decay away. The presence of progeny for period of time longer than would be expected based solely on decay rates is evidence of retention of ²²²Rn in the sample.

Radioactivity measured by the LSC during the off-gas experiments indicated the

presence of beta and/or gamma radiation from progeny retained in the gel. Determination of the presence of alpha radiation was not attempted in this study.

2. Background

Repeated backgrounds were taken for each type of radioactive measurement, to include backgrounds taken before and after each measurement as reported in section III.A. The appropriate background was subtracted for each gamma count, based on the Compton continuum in the region of interest (ROI) for each photopeak. A peakedbackground correction was determined not to be necessary based on the short time frame of the counts. Backgrounds were determined for each detector configuration, and longterm measurements were also conducted.

3. Minimum Detectable Level

The minimum detectable counts for each photopeak (or gross count) was determined according to the formula (15, 16)

 $MDA = 3 + 3.29 * (BACKGROUND)^{1/2}$

4. Interferences

Radon variations in the laboratory can fluctuate based on local ambient radon levels. The building ventilation plays a role by exchanging air that carries radon progeny. Counts acquired with the NaI(Tl) detector and the LSC were performed in a modern laboratory environment, with a state-of-the-art high volume air conditioning system. No interference from radon progeny was expected. The HPGe counts were performed in a building with minimal air conditioning, e.g. a large room, with a wall-mounted air conditioner. A difference in progeny background count rate was detected, but was not corrected for, since it was small, about 50% ($1.6 \times 10^{-3} \text{ c s}^{-1}$ compared to $1.0 \times 10^{-3} \text{ c s}^{-1}$.

5. Calibration

The NaI(Tl) detector was used with the factory calibration. A "button" check source was used to confirm positive detector response to gamma radiation.

The LSC was calibrated with the standard calibration set provided with the instrument using a manufacturer-provided ¹⁴C standard. The instrument self-calibration protocol includes the use of a ¹³³Ba internal standard. NIST-Traceable standards (in liquid scintillation fluid) were made using a ⁹⁰Sr/⁹⁰Y beta standard. An activity of 6.1 d s⁻¹ gave 9.9 c s⁻¹ The standard is in transient equilibrium (e.g. both ⁹⁰ Sr parent with a 28.5 y half life and ⁹⁰Y progeny with 64 h half life decay essentially at the same rate. The counting efficiency (with liquid scintillation fluid) is 0.75 c d⁻¹ (per beta) for high-energy beta. A ²²⁶Ra standard gave 5.5 c s⁻¹ alpha radiation (using the alpha discrimination feature of the counter, also with liquid scintillation fluid.) Since ²²⁶Ra decay with progeny at equilibrium to ²¹⁴Po has 4 alpha particles per decay, ²²⁶Ra the counting efficiency is 0.82 c d⁻¹ (per alpha.) The standard was six years old and stable in its response over the entire time of use. Count rate vales are net (from background) and the counter backgrounds were 0.05 c s⁻¹ and 0.22 c s⁻¹ for alpha and beta regions, respectively.

The HPGe detector was energy-calibrated using a NIST-traceable mixed-gamma standard. A counting efficiency calibration was performed using the ²²⁶Ra LSC for the

alpha radiation calibration vial centered on top of the detector housing in the same configuration as the vial containing the aerogels. The 1.68 d s^{-1 226}Ra calibration standard yielded 945 net counts for a 43,200 s count, for an absolute counting efficiency of 0.013 c d^{-1} for the 609 keV photon from ²¹⁴Bi, at equilibrium.

6. Replicates

Gels were produced in sets, with one or more samples proceeding to the next in step synthesis. Since certain parameters such as time-to-gel, rate of solvent exchange, and rate of surface modification were unknown and dependent upon sample configuration, each step was taken first with one gel, followed by the remaining gels. For example, addition of too much hexane during the first stages of solvent exchange caused the gel to crack. If a gel was damaged this way, the procedure was adjusted to prevent this. Then, the production process proceeded with the remaining gels. So, small amounts were added incrementally at first, followed by increasingly larger additions of solvent or reagent.

Several gels were completed through the drying step, to make final aerogels for use. Two were selected for the exposure experiment: one having cerium added, the other a "blank" gel, without cerium. These were broken to give several pieces of irregular shape, but which collected uniformly at the base of the vial for counting. (Aerogels were on the side of the vial during exposure, since the vial was rotated 90 degrees; see Figure 2.5, exhibiting a typical configuration of gel within the exposure chamber (removed from the apparatus to facilitate photography.) One gel, a "blank" was kept as a monolith for the radon exposure. Ideally, a single monolith would be best for comparison but since one





sample (8-4A) had cracked, allowing more direct access to the interior which made the exterior bulk surface area more similar, it was felt that it was best to have gel 7-1A approximately in the same configuration. The air space above the gel is a result of the volume of the gel being smaller than the chamber volume. It has the advantage of not impeding the diffusion of radon around the gel, allowing access to the exterior surfaces of the each gel fragment. Since the monolith is fragmented into pieces, there would be more interaction with radon, so this would represent the best-case scenario (e.g. more radon might be expected to penetrate the gel, and more deeply) as compared to a true monolith, where there might be some depth at which the radon does not penetrate into the gel structure.

Precision and accruing of replicates radioactivity counts were performed at some points during the radon exposure, but were not generally necessary, since a pattern was exhibited of increasing counts up to stabilization. Replicate measurements of counting precision (e.g. determined by replication) were not necessary, as the monitoring was done watch the progress of radon ingress to the chamber and to ensure radon was present and reached equilibrium, and because the count rates were high enough for good counting statistics, and also because count rates were rising or falling smoothly until equilibrium was reached. Replicates of gamma counts were not performed during the off-gassing due to the short decay-time of radioanalytes within the exposed samples. LSC counts were not replicated in the initial stages due to the short decay-time of radioanalytes within exposed samples. Long-term LSC counts were performed at periods after the runs to observe residual activity.

H. Experimental

Aerogels were alternately exposed to radon, and observed for radioactivity, as radon was allowed to exit the aerogels. Radon was allowed to diffuse into the gels, for as long as necessary to reach a static state as determined by a steady counting rate response from the NaI detector. Ideally, the off-gas experiment would then have consisted of simply closing off the valve from the source and opening another to allow off gassing, while observing the radiation detected. Since co-location of the exposure apparatus and the LSC and gamma counters was not possible, the off-gas experiments proceeded in stages, alternately off gassing, transporting and counting as described below.

1. Study Design

Four radon exposure and off-gas experiments were conducted in the study. The first involved allowing radon to diffuse into an empty chamber and the next three involved exposing an aerogel to radon in an identical chamber constructed for the experiment. During each experiment, the exposure continued until the count rate remained constant for an extended period, to ensure that radon transport had been completed, especially considering the possibility of a slower transport phenomenon, within the gel matrix or trapping phenomena. Closing the valve from the radon generator then stopped the exposure, and the vial was removed from the exposure assembly. The open vial was placed in the fume hood for 60 seconds, and then capped with a new, intact cap.

The closed vial was then off-gassed and counted in a three-part cycle. First, the vial was transported to the HPGe counter and counted. Then, the vial was transported and counted in the LSC. Finally, the vial was taken to the fume hood and opened for 20 minutes. Then, the cycle was repeated. A cycle took about an hour, since it included transport between buildings across campus during which the vial remained closed and then increased, as more count time was needed to achieve confidence in detection. Long-term counts were conducted in the LSC to follow any trend in residual radioactivity, and radon was allowed to reach equilibrium in the generator before starting the next experiment.

2. Samples

Three aerogels as shown in Figure 2.6 were selected for radon exposures, as follows:

a.) Sample 7-1A, a cerium-doped aerogel, in pieces

b.) Sample 8-4A, a blank aerogel, in pieces

c.) Sample 8-2, a blank aerogel, essentially a monolith (plus three larger pieces)

3. Background

An empty vial was used during one experiment to determine how much radon/progeny might adhere to the surface of the exposure chamber itself. This allowed direct comparison to results of the aerogel exposures. The protocol followed was exactly the same, except that the aerogel is not present. By having these background measurements, any contribution of radioactivity caused by the progeny plating out onto the walls of the



7-1A

Figure 2.6 Aerogels



8-4A



8-2

chamber was compared to the results obtained with an aerogel present. Also, the result provided information on how much radon enters the chamber. Since there was no gel present there were no interactions attributable to a large surface area or porous medium represented by the aerogel.

III. RESULTS

A. Exposures

Four separate radon exposure experiments were conducted in the exposure chambers, using a new glass vial as the chamber each time. The first exposure run utilized an empty chamber, and it lasted 3155 hours. During that time the gross count rate was monitored With the NaI counter. The results showed that the count rate was stable after an initial rise and fall from about hour 635 onward. Exposures to gels were held for shorter periods of 503, 1271 and 585 hours for gels 7-1A, 8-4A and 8-2 respectively, but in each case long enough for a plateau to be evident (indicating constant presence of radon.) The data is summarized in Table 3.1

All exposures, including empty chamber and gel experiments, showed the same pattern of initial rapid rise in count rate, followed by a fall-off and approach to a plateau as equilibrium is reached. The presence of a plateau was important to demonstrate that the radon and progeny had reached a constant concentration within the apparatus. Any radon moving e.g., by diffusion, across an interface within the chamber, such as between the air space and the gel or the walls would be balanced by radon moving in the opposite direction. The constant level of radon at a given position constant within the gel and within the chamber also means that progeny levels are constant. Since the radon is not measured, but rather the progeny, the constant signal from the (less mobile) progeny allows the inference of constant radon concentrations.

	Plateau Begin	Exposure Duration	Maximum Count Rate†	Plateau Count Rate†
Sample	(h)	(h)	$(c s^{-1})$	$(c s^{-1})$
A202, empty chamber	996	3155	96 ± 2.5	82 ± 2.3
7-1A, Ce-doped gel	244	503	112 ± 2.7	71 ± 0.7
8-4A, undoped gel	487	1271	78 ± 2.3	47 ± 0.6
8-2, undoped gel (monolith)	585	585 *	142 ± 1.0	112 ± 0.9

Table 3.1 Exposure Duration and Count Rates

† Error is at 95% confidence level* Exposure terminated due to scheduling requirements

For each exposure experiment the count rate at the plateau was different. The plateau value was taken as the last data point collected. The broken aerogels had a lower number of counts than the empty chamber. In contrast, the intact aerogel had higher count rates. Counts were collected in 1-minute increments while the count rate was changing and 10-minute increments when the count rate was steady during the counting interval.

Figure 3.1 shows the count data during the earliest stage part of the exposure period, from 0 to 3 h, which was when the count rate was rising. In this and subsequent figures, the error bars on the ordinate marl the 1σ counting error at the 95& confidence interval, based on the total number of counts. With radioactive decay, this is approximated by the square of the total count, and propagating for error based on the background count, and the time of data collection for both the gross and background counts. No error bar is visible when the data symbol itself is larger than the scale allows. Bars on the abscissa represent the width of the counting interval. No bar is visible when the data symbol itself is larger than the scale allows. The time-of-count data is centered on the mid-point of the collection interval in all cases.

Figure 3.2 shows the count rate during the subsequent time period, to 30 h. Gels 8-4 and 8-2 reached peak count rate at about the 25-hour mark. Gel 7-1A reached a peak at an earlier point in time (between 13 and approximately 18 hours.) Although data were not collected during the preceding time frame by 25 hours, 7-1A had fallen to the plateau level, and remained there. For the blank run data was not collected during the peak period. The background ranged from 115 c min⁻¹ to 198 c min⁻¹, and was subtracted to



Figure 3.1 Count Rate During the Radon Exposure, (0 – 3 h)



Figure 3.2 Count Rate During the Radon Exposure, (0 - 30 h)

give net count rate for each run. The standard deviation of the background measurements ranged between 6.0% and 12% relative error (n=7.) Figure 3.3 shows monitoring data for the entire exposure period for each run, showing the total length of exposure for each gel and the, at first changing, then stabilization of count rate from progeny seen by the monitoring detector, indicating the presence of radon over time.

When the radon exposure was stopped, the exposure chamber (vial) was removed from the apparatus, and radon was allowed to off-gas in the chemical fume hood. The vial was then capped and taken to the gamma counter for counting, and subsequently for analysis in the LSC. Gamma counts were collected during intervals that would provide reliable counting statistics, but still allow time for further off-gassing. Count times were 60 s "live time" and at three hours post-exposure were increased to 120 s, then 180, 300, 600 and 900 s for successive count periods. The following day, two counts were conducted, for 1200 s and 1800 s. The increasingly longer counts were needed because the radioactivity level had decreased, becoming closer to counter background by the second day. Table 3.2 gives the off-gas net count rate data for the ²¹⁴Bi 609 keV photopeak for all runs. Figure 3.4 shows the first 9 hours of the data in Table 3.2, illustrating the decrease in count rate. Negative count values are truncated in the figure since the count rate is on a logarithmic scale; these values are not statistically significant.



Figure 3.3 Count Rate During the Radon Exposure

7-1A, Ce-doped Gel		8-4A, Undoped Gel		8-2, Undoped Gel,		
			monolith		monolith	
Time	Rate	Time	Rate	Time	Rate	
(h)	$(c s^{-1})$	(h)	$(c s^{-1})$	(h)	$(c s^{-1})$	
0.72	23 ± 0.70	0.69	3.4 ± 0.21	0.38	34 ± 0.66	
2.0	5.2 ± 0.26	1.9	3.2 ± 0.20	1.8	7.1 ± 0.30	
3.5	0.59 ± 0.087	3.3	0.49 ± 0.056	3.3	0.74 ± 0.097	
4.8	0.070 ± 0.021	4.6	0.050 ± 0.018	5.1	0.07 ± 0.030	
6.8	0.0067 ± 0.0053	6.1	0.0084 ± 0.0052	6.4	0.012 ± 0.0070	
22	0.0089 ± 0.0031	7.8	0.0054 ± 0.0027	8.2	0.0031 ± 0.0018	
		23	0.0025 ± 0.0017	25	0.0039 ± 0.0021	
Background	0.0017 ± 0.00029		0.0017 ± 0.00020		0.0015 ± 0.00017	

Table 3.2 Off-gas Data for 609 keV Photopeak

A202, E	mpty Chamber
Time	Rate
(h)	$(c s^{-1})$
0.77	17 ± 1.1
1.1	12 ± 0.86
1.5	6.7 ± 0.67
2.3	2.5 ± 0.41
3.0	1.1 ± 0.18
3.4	0.55 ± 0.11
4.0	0.17 ± 0.047
4.8	0.060 ± 0.021
5.9	0.013 ± 0.0079
21	0.0017 ± 0.0057
25	0.00012 ± 0.0034
Background	0.0010 ± 0.00010



Figure 3.4 Off Gas Count Rate (609 keV photopeak)

2. Off-gassing the cerium-doped Gel (7-1A)

The off-gas counting followed the same protocol as the empty chamber experiment. The LSC count was conducted first generally for logistical reasons. The pattern of alternately counting in the gamma counter and LSC counter, with off-gas periods in-between was followed. Gamma count times were, for each successive count period 180, 300, 300, 600 and 900 s. One count was conducted on the following day for 3600 s. Gamma count rates above 0.01 c s⁻¹ are at the MDA at the 95% confidence interval

B. Off-Gassing Experiments: Gamma Counts

1. Off-gassing the blank (empty chamber)

. Repeat counts of gel 7-1A were conducted after the off-gas experiment was conducted. The gel was counted 69 times for 1200 s each set, while the vial remained closed. The gross counts, net and error are displayed in Figure 3.5. The net count rate average is 4.4×10^{-3} c s⁻¹ with a counting error of 3.2×10^{-3} c s⁻¹. The gross count rate is $1.2 \times 10^{-2} \pm 0.3 \times 10^{-2}$ c s⁻¹. The last (70th) data point on the graph is the average of each set of 69 data points.

2. Off-gassing the Blank Gel (8-4A)

The off-gas counting of each gel followed the same protocol as the empty chamber experiment. The LSC count was conducted first for logistical reasons. The pattern of alternately counting in the gamma counter and LSC counter, with off-gas periods in-between was followed. Gamma count times were, for each successive count



period 296, 298, 597, 597, 1195 and 2985 s. One count was conducted on the following day for 3581 s. The reason for the odd count times was the inadvertent selection of "real time" rather than "live time" during the experiment. "Live time" is used in all analyses.

3. Off-gassing the blank Gel, Monolith (8-2)

The off-gas counting followed the same protocol as the empty chamber experiment. The LSC count was conducted and counts were completed alternately using the gamma counter and the LSC counter, with off-gas periods in-between. The gamma count times were, for each successive count period 300, 300, 300, 300, 925 and 3600 s. One count was conducted on the following day for 3600 s. Increasingly longer counts were needed because the radioactivity level had decreased, becoming closer to counter background by the second day.

C. Off-Gassing Experiments: Liquid Scintillation Counter

Liquid scintillation counter data collected during the off-gassing experiment is given in Table 3.3. The count rate indicated refers to counts seen in the ³H region of the counter, which corresponds roughly to the Cerenkov region (0 – 18.6 keV.) The LSC data was taken alternately with the gamma counter data, as indicated:

- 1. Off-gassing the blank (empty chamber)
- 2. Off-gassing the cerium-doped Gel (7-1A)
- 3. Off-gassing the Blank Gel (8-4A)
- 4. Off-gassing the blank Gel, Monolith (8-2)

Figure 3.6 shows the first 10 hours of the LSC off-gas data from Table 3.3, showing a fall-off over three orders of magnitude of the count rate. This range is one



	Empty		7-1A		8-4A		8-2
Time	Rate	Гime	Rate	Time	Rate	Time	Rate
(h)	$(c s^{-1})$	(h)	$(c s^{-1})$	(h)	$(c s^{-1})$	(h)	$(c s^{-1})$
0.2	1066±5.8	0.3	313±3.2	0.4	183±1.4	0.2	505±5.7
0.8	443±3.8	1.5	82.5±1.6	1.5	58.9±0.87	1.5	145±3.0
1.2	295±3.1	3.2	10.1±0.46	3.3	13.9±0.42	3.0	16.2±1.0
1.6	186±2.0	4.3	2.37±0.17	4.3	8.03±0.32	4.6	1.65±0.015
2.3	67.9±1.2	6.2	0.967±0.064	5.7	6.93±0.30	6.2	0.400 ± 0.074
3.1	26.6±0.75	23.8	0.817±0.051	7.3	6.98±0.17	7.8	0.300±0.036
3.5	14.8±0.44	24.2	0.833±0.051	22.6	7.00±0.17	27.1	0.317±0.026
4.2	7.70±0.22	77.9	0.817±0.029				
5.1	4.95±0.18						
6.2	4.05±0.13						
21.5	3.77±0.090						
25.8	3.90±0.091						
Backgro	ound 0.098±0.0	015	0.108±0.0	011	0.095±0.0	013	0.100±0.009

Table 3.3 Off-gas Data for LSC Counts (0 - 18.6 keV)



Figure 3.7 Ratio of Count Rates, Cerenkov/Alpha

order less than the gamma counter data owing to less specificity in the radiation types observed, and a difference in background between the two different systems.

Table 3.3 provides the off-gas data for the LSC counter and Figure 3.6 graphically displays the results.

Figure 3.7 gives the ratio of count rate in the Cerenkov channels for each sample to the count rate in the alpha channels. Alpha particles have high linear energy transfer (LET) compared to electrons. When depositing energy in liquid scintillation fluid they create post-track pulses that can be analyzed by the software, which can identify them as distinct from a typical Compton interaction caused by photons or electrons. In aerogel, the energy imparted and converted to light visible by the detector will be different than within the liquid scintillation fluid. Nevertheless, the results show some counts in these regions when glass or gels are used. Whether this is an important phenomenon is not clear. There is some crosstalk between channels where alpha events are interpreted as beta events, and vice-versa. Selection of the energy and post-pulse processing parameters must be optimized in typical liquid scintillation operation, but evaluation of this aspect without a liquid fluor (from liquid scintillation fluid) was beyond the scope of this study. Since it did not appear that events in the alpha region were due to alpha, it appears unlikely that the gels trap radon preferentially. Any radon in the gels is probably more likely in proportion to the air space in the interior.
D. Backgrounds: NaI, Gamma and LSC

1. Background During Exposure Monitoring

The NaI counter background with the Radon generator present within the shield was measured for each exposure run. The backgrounds were 2.57, 1.97, 2.03, 3.30 c s⁻¹ (n=7,7,1,4) over the course of the experimental sets. The standard deviations were 0.15, 0.22, NA, 0.18 c s⁻¹ (corresponding to 6.0, 11, NA and 5.7%.) This background is sufficiently low to measure radon progeny reliably during the course of the experiment.

2. Gamma Counter Background

Gamma background data was collected to allow evaluation of counter performance in its environs and to watch for contamination. Background as reported in Table 3.1 is the net counts in the photopeak region, and based upon the results peak-background subtractions were not made to off-gas data. Background count times for the empty chamber was 2.70000×10^5 s, and for gels 7-1A, 8-4A, and 8-2 were respectively, 1.83560 x 10^5 , 4.2944 x 10^4 , and 5.4000 x 10^4 s. Net count values were determined by the gamma counter software, which applies a peak-search algorithm to identify the region of interest and subtracts the Compton background based on the counts on either side of the peak. The (net) peak background in the 609 keV photopeak region for the empty chamber, gels 7-1A, 8-4A, and 8-2 were respectively, 1.0×10^{-3} , 1.7×10^{-3} , 1.7×10^{-3} , and 1.6×10^{-3} c s⁻¹. The per-channel Compton background in the photopeak region was respectively 3.1×10^{-4} , 5.7×10^{-4} , 5.5×10^{-4} , and 5.5×10^{-4} c s⁻¹.

Long-term background counts gave $0.0017 \text{ c} \text{ s}^{-1} \text{ s}$ (net) peak and 0.59 c/channel/1000 seconds for an 183560 s count and $0.0035 \text{ c} \text{ s}^{-1}$ (net) peak and 0.59 c/channel/1000 seconds for a 2.70000 x 10^5 s count. A series of 64 repeated backgrounds at RSB was conducted. The counts in one hour for gross, net and error are displayed in Figure 3.8. The net count rate average is 2.7×10^{-3} counts s⁻¹ with a counting error of 1.9 x $10^{-3} \text{ c} \text{ s}^{-1}$. The gross count rate is $1.14 \times 10^{-2} \pm 0.21 \times 10^{-2} \text{ c} \text{ s}^{-1}$. The right-most data point gives the average for each data set.

3. LSC Background

A long-term background was taken with an empty glass vial. A counting time of 4.3200×10^4 s gave 1.09×10^{-1} , 1.15×10^{-1} and 4.83×10^{-2} c s⁻¹ for the regions CPMA, CPMB and CPMa respectively. A spectrum of the entire counting region is shown in Figure 3.9. The background of the liquid scintillation counter using an empty glass vial was measured during each exposure run and is reported with each data set.

E. Repeated Liquid Scintillation Counts

An opportunity was taken to measure residual radiation with the LSC after the main data set was collected from each sample. The reason was that if any radioactivity was seen, it might be because it was supported by radon retained within the gel, and the supporting progeny. Thirteen days after the off-gas experiment for gel 7-1A repeat LSC count data were collected in a series of 50 sequential 1200-second counts. Repeat counts were again collected at 50 days post-off-gas.



Eighty-three days after the 8-4A off-gas experiment was conducted, and 188 days after the completion of the 7-1A off-gas experiment, a series of 20 sequential 1200-second LS counts were performed.

The day of each count after the end of the off-gas experiment was recorded for each count completed on a sample. Counts were performed in series, and 1200 s was allocated for repeat by each count. Table 3.4 summarizes the data. The number of counts varied as indicated is based on the time available. The notations CPMA, CPMB and CPMa refer to, respectively, counts where the energy deposited falls within the energy range from 0 to 18.6 keV, counts from 0 to 2000 keV, and counts recorded in the "alpha" category. A similar data set was not taken on the gamma counter. The data shows significantly elevated count rate at a time significantly past when radon would have completely decayed. The levels are comparable to those at the end of the off-gas counts, indicating a long-term source, probably ²¹⁰Pb.

1. Unexposed gels

Gel 7-3 is a cerium-doped gel produced in the same batch as sample 7-1A. Gel 8-2 is a gel with no cerium dopant, produced in the same batch as sample 8-4A. Unexposed gels have LSC count values indistinguishable from background.

2. Exposed

Gel 7-1A, a cerium-doped gel, was counted at three different times post-exposure. Gel 8-4A is an exposed gel without dopant. Exposed gels had elevated radioactivity, even





	Ce	Days		Count	CMPA	CPMB	СРМа
Gel	Doped	Post-		time	$x \pm s$	$x \pm s$	$x \pm s$
	?	Off-gas	n	(s)	$(c s^{-1})$	$(c s^{-1})$	$(c s^{-1})$
7-1A	Yes	13	31	1200	0.87 ± 0.02	0.88 ± 0.02	0.0073 ± 0.0028
7-3	Yes	NA	14	1200	0.10 ± 0.01	0.11 ± 0.01	0.0060 ± 0.0023
8-2	No	NA	14	1200	0.10 ± 0.01	0.10 ± 0.01	0.0052 ± 0.0018
MTGV	NA	NA	14	1200	0.10 ± 0.01	0.11 ± 0.01	0.0053 ± 0.0028
7-1A	Yes	50	50	1200	1.1 ± 0.02	1.1 ± 0.02	0.0088 ± 0.0028
MTGV	NA	NA	50	1200	0.10 ± 0.01	0.11 ± 0.01	0.0055 ± 0.0027
8-4A	No	83	20	1200	7.1 ± 0.09	7.1 ± 0.09	0.0093 ± 0.0033
7-1A	Yes	188	20	1200	1.5 ± 0.04	1.5 ± 0.04	0.0062 ± 0.0025
MTGV	NA	NA	20	1200	0.10 ± 0.01	0.10 ± 0.01	0.0043 ± 0.0020

Table 3.4 LS Count Rate After Off-Gas Experiment

CPMA = counts in 0 to 18.6 keV energy region CPMB = counts in 0 to 2000 keV energy region

CPMa = counts meeting alpha criteria

= Not Applicable (not exposed) NA

MTGV = empty glass vial

after all radon is allowed to exit the gel. ²¹⁰Pb and subsequent progeny may account for increasing activity with time for gel, 7-1A. For 8-4A gel the activity was significantly elevated compared to the exposed gel, 7-1A.

3. Empty Glass Vial

An empty glass vial was included in three of the counting runs (see Table 3.4), to obtain a background. Rows in the table marked MTGV ("empty glass vial") exhibit typical LSC background values. The LSC spectrum for gels 7-1A and 8-4A (for the measurements in the last three rows of Table 3.4) are provided below. The spectrum was collected over 59880 s (the maximum acquisition time of the counter.) Figure 3.10 displays the alpha spectra and Figure 3.11 displays the spectra in the beta region, showing how the energy of all the counting events is distributed. The alpha energy events reported is probably crosstalk from a much larger number of beta events. The beta energy distribution is consistent with a Cerenkov spectrum.

G. Observations on Gel Synthesis and Character Post Drying

When fully dried, gel 7-1A had a mass of 0.88 g cm⁻³, a diameter of 1.1 cm and a height of 3.4 cm. Using the formula density = mass / pi x radius² x height, the bulk density is calculated to be 0.28 g cm³. Similarly, the final bulk density of gel 8-4A is 0.26 g cm³.

Gels were made in batches with the leading samples processed first, so that errors or problems would have a minimal impact overall processing time. Where conditions





such as drying too fast or solvent exchange took place too quickly, damages occurred to the gel. The gels following were unaffected and could then be processed taking advantage of the experimental parameters. Figure 3.12 shows a set of early batches of wet gels in the oven.

As gels dried their bulk optical clarity progresses to become more opaque. Figure 3.13 shows a batch of gels in at various stages of drying. The wetter gels are on the right, and as the images proceed to the left, the monoliths are progressively dryer. At this stage in the procedural development, a smaller amount of TEOS was used, which resulted in a smaller final gel. The overall physical dimensions of shrinkage during drying were larger than with later gels, where more TOES was used per gel. Gels always cracked at the end stages, although it can be seen that the pieces can be considered monoliths. A set of dried gels is displayed in Figure 3.14. These gels are a little denser than the other sets, but are also clearer. The small size is due to a smaller TEOS molar ratio.

Figure 3.15 shows two gels from batch 7. Gel 7-1 was used in the exposure experiments, and is a cerium-doped gel. At this stage, the gels had been thoroughly rinsed with hexane. Gel 7-1 has just had a small, substoichiometric amount of TMCS added. Experience showed that all necessary TMC should not be added at once. During gelation and/or synuresis some (probably most) of the cerium salt is excluded from the gel matrix. The salt is evident in both of these gels at the top, which was the bottom of the gel during formation. (The gels are now 'upside-down.') The cerium oxidation state is probably unchanged at 3+ in gel 7-1, but becomes oxidized to 4+ after reacting with TMCS and



Figure 3.12 Early batches of wet gels in the oven

Figure 3.13 Early batches of gels at various stages of drying



3.14 Various gels from batch 3 at various stages of drying





Figure 3.15 Two gels from batch 7

Figure 3.16 Leading gel samples in batches 7 and 8





Figure 3.17 Close-up of gel fragment arrangement within the glass vial

Figure 3.18 Top View of the Exposure Setup



thus turns a yellow color. The intensity of the yellow indicates that an excess of cerium salt becomes excluded at the base of the gel. However, observation of the bulk gel 7-1 shows a yellowish opacity as compared to gel 7-2, which has not been contacted with TMCS. This indicates that some cerium remains within the bulk matrix.

After reaction with TMCS is complete the gels are slowly dried. Gels go through a stage where they are "sticky." After which they dry to an opaque state. The gels in Figure 3.16 are shown in the process of drying, which has occurred a little too fast. Immediately slowing the rate then allowed these to continue to dry and remain mostly whole. The increased opacity of gel 7-3 shows that some fine-tuning of method is necessary. Cracks that develop internally are as common as external cracks. These domains can be seen clearly in gel 8-2.

Figure 3.18 shows a top view of a gel in the chamber demonstrating the relative placement of equipment of the experimental setup, showing the radon source, surrounding shield (with the top removed) and detector.

IV. DISCUSSION

A. Observations on Aerogel Synthesis

There are a wide variety of formulae for synthesizing gels bases on orthosilicates. The tetraethylorthosilicate (TEOS) approach was chosen because it is a popular pathway leading to silica aerogels. There is also a large body of work on gels made of metal oxides other than silicon. Much of the interest in sol-gel work arises from the ability to better control the cost and chemistry of glasses. Most literature on sol gel science seems to be focused on optical properties. There is much interest in gels as films or coatings and as substrates or matrices for active moieties such as enzymes for glucose monitoring. In fact, the field is too wide to summarize adequately in a few sentences.

There was some uncertainty about what molar ratios would be optimum to achieve a useable density and gel structure. Experimental parameters such as rinsing rates and surface treatment regimens were selected during synthesis of batches 1 through 6. The amount of TEOS determines the final mass, while the amount of alcohol plays an important role in the final volume. As long as there is enough gel structure from TEOS, the gel is less likely to crack or collapse during drying. Too much alcohol would result in a longer gelation time, and can make the gel soft and "springy." More work could be done to test more precisely how higher TEOS: alcohol ratios work with respect to lighter gels, permeability and pore size, and how these attributes affect retention of Ce. Gels can be made of simple arbitrary shape and size on the order of a few centimeters using the method performed in this work. A practical limitation on size is the result of ambient conditions used – it should be possible to make larger structures with the help of pressure-supported solvent exchange or supercritical extraction. Cost factors also limited the study: small size helps keep down costs.

Cai Weiping, et al, (17) reported that no luminescence is observed with preformed mesoporous silica soaked with trivalent cerium ion (nitrate solution.) Their procedure involved drying the gel containing the cerium salts at 150 C. However, soaking with Ce(4+) (sulfate solution) did produce luminescence. They proposed that Ce(4+) can ion-exchange with Si⁴⁺ in the network while Ce(3+) cannot. Additionally, the Ce(4+) within the network can then be reduced by the O²⁻ ion in the OH group from water during drying. The simultaneous presence of both Ce(3+) and Ce(4+) was determined using x-ray photoelectron spectroscopy.

Some work has been started to create thermoluminescent dosimeter material (TLD) that was an attempt to create a sol-gel pathway for creating a gel material that was later densified, and not an attempt to create a permeable gel. However, it should be pointed out that a gel-material could be a useful pathway to a lower density TLD crystal that might be useful in dosimetry applications where electronic equilibrium is an issue.

The trimethylchlorosilane (TMCS) appears to have oxidized the Ce(3+) to Ce(4+) based on the yellow color that appears immediately after its addition. Cerium

was chosen both because it was available, but also because Ce is known to scintillate in glasses. Other lanthanides might also be tried. But perhaps a more important point is to understand the chemistry in this reagent system, to determine if there is a way to prevent or reverse the cerium oxidation. An additive might be found that keeps the cerium in a reduced state, but that does not interfere with the gel synthesis. Heating to 450 C in a hydrogen atmosphere might reduce available Ce, and not melt the silica structure. Silica microspheres doped with reduced Ce were added to the gel during synthesis (18), so that that the Ce is not accessible to oxygen or other oxidation reactions during gel preparation. The resultant gel has reduced porosity. The aerogel framework replaced the aluminum used in some melt glasses in its role of preventing clustering of Ce3+ ions. A Lanthanum salt was used in batch 3-E. But, this pathway was dropped because of the need to better understand the reagent ratios and processes to an intact monolith.

The list of materials that could be tried to develop doped gels is practically endless – ZnS, TLD powder, the primary and secondary fluors of liquid scintillation fluid, or any material that would scintillate. Even microspheres, quantum dots and enzymes are a possibility for future research.

The TMCS is a critical reagent, since it is necessary to cap the available hydroxyl groups with an ester bond $(-O-CH_3)$ so that the hydroxyl groups do not condense – otherwise the high pressures cause by solvent exiting the pores collapse the gel.

The simple equipment used resulted in a slow production process, but was quite safe. Better process instrumentation should allow faster manufacture. Hydrolysis was a fairly quick process, on the order of an hour. No attempt, however, was made to measure or confirm that hydrolysis was complete. Rather, time was kept the same as reported in the literature. Gelation generally took place after a few days, depending on the amount of alcohol. In early batches, where too much ethyl alcohol was used, the batch did not gel after few weeks and so was discarded.

Rinsing and drying are two steps that result in long processing times. The gels are not sensitive to the amounts of alcohol used to rinse any water present after gelation. But, the addition of hexane, the purpose of which is to remove the alcohol has to be initiated slowly, by adding only amounts that are miscible. Adding too much hexane creates too high a pressure differential within the gel and cracking occurs. Once enough time has occurred to exchange enough of the alcohol from the gel matrix with hexane, complete washes of pure hexane are possible.

Measurement of the degree of rinsing accomplished by the alcohol and hexane rinses were not performed. It would be helpful to measure the amounts reagents present with an instrumental method in order to optimize the procedure for a particular gel size and composition. However, since the goal is complete exchange, applying excess solvent and waiting a sufficient time period is an inexpensive option. Addition of the TMCS is a delicate step because not only is it likely there are pressure differentials across the gel structure; a reaction is occurring that is probably fairly energetic. Addition of TMCS only works if the amounts are initially small, on the order of 10 microliters. Fortunately, additional TMCS can be added a few minutes later, with the process repeating, increasing to a hundred microliters and so on, until milliliter amounts can be added. As with the rinsing steps, excess TMCS is used.

Drying is a critical step. Even though the surface of the gel and hopefully the bulk is treated with TMCS, the gel cannot be left open to air or cracking occurs immediately. The rate of liquid removal must be slow so the pressures can equalize. Additionally, the gels begin to shrink in size, and this compresses the gel, perhaps even bending linkages and breaking bonds and exposing non-reacted surfaces. By keeping the evaporation rate low there is a chance that many of these sites become capped. This may be conjecture, however, but it is clear that the evaporation rate must be kept slow when creating gels under ambient conditions. By replacing all the hexane with TMCS before evaporation, any sites that become available during shrinking can be reacted. Since the reaction with TMCS stoichiometrically releases a water molecule, final drying at 105 C in the oven to constant weight removes any remaining liquid. The final density of the gels (about 0.27 g cm⁻³) is approximately 1/3 that of typical silica gel (CAS No. 63231-67-4) used as a desiccant. The actual surface area and porosity was not measured.

Recent work by Land, et al (19) shows that an alternate method of protecting the silica surface using trimethylmethoxysilane (TMMS) provides even higher pore volume

than TMCS. While in this study the gel was broken up prior to solvent exchange, it would be interesting to see how monoliths behave with this treatment, since exchanging the solvent is not necessary. Also interesting to note, is that both TMCS and TMMS processes using drying at ambient conditions produces gels with more pore volume than critical point drying (using supercritical carbon dioxide.) They also provide a useful datum, namely, that washing with an aprotic solvent provides a significantly higher pore volume, which was the approach taken here, using hexane.

Cerium was retained in the finished gel. This was one of the objectives of the study. It is not known whether the cerium participates in the gel structure or is trapped during gel formation. Even if the cerium is not trapped, but its exit from of the gel is simply limited by diffusion, the yellow color shows that some quantity remains in the completed gel.

Cerous nitrate is a colorless salt, and is also clear in solution with water and alcohol and water. Addition of hydrochloric acid turns the sol yellow, an indication of oxidation of the cerium. Since in borosilicate glass it is the Ce(3+) that provides scintillation, it is unlikely that this phenomenon will occur in the gels as synthesized. Also, the cerium may not have the same electronic environment as with a melted glass. Further work is needed to see if the cerium can be reduced in situ, and if the proper electronic environment can be achieved.

The selection of the geometry of the monolith, a right-circular cylinder, was chosen partially because of the convenience of available plastic vials, but also to allow a similar structure as the glass fiber bundle in case research opportunities went in that direction. It also was selected because of the desire to show that a monolith could be created. An intermediate step of creating a plate or disk of some limited thickness could have been tried, but would have represented an extra path and associated effort. However, this should be a step to be performed by future researchers, as it will simplify optical experiments and may itself result in a useful detector.

Large gels are produced commercially via the supercritical process to obtain large monoliths that are used as Cerenkov detectors in high-energy particle detection. There is no information in the literature regarding interferences from radon progeny in these gels. This is not to say that radon and progeny are not present. It just may be that any signal seen is easy to discriminate and not otherwise of experimental interest.

As mentioned in the Reagents, Materials and Configuration Section (II.B.1) the size of the exposure chamber was determined by the availability of the glass and plastic vials, respectively 20-ml and 10-ml liquid scintillation vials. The vials had several advantageous features. The glass vial is designed for use in the LSC so gels could be counted after exposure and off-gassing without removal from the chamber. Its small size reduced the amount of reagents needed also used for surface chemistry, rinsing and drying, since it was also used as a reaction vessel. The glass wall does not allow Rn penetration (unlike plastics or rubber materials typically present in sealing materials.) It is

readily available and inexpensive. The threaded neck was sealable to contain Rn and prevent radioactive contamination. Caps with cork-backed tops (allowing a pressureseal,) with both aluminum and plastic coated versions were available. The aluminum version was used for "dry" applications and the plastic where caustic wet chemistry took place. All that was need was to construct a custom insert for an input port using some Swagelok® fittings. Trays were available, designed for their for transport and storage. Glass is chemically inert and allows light to pass through facilitating the gel to be seen while handling and enabling LSC counting. Both vial types used are relatively pure materials, which presumably helped avoid problems with the chemistry. For example, some plastic straws used in some early testing did not hold up well to the solvents. The size of the interior volume was probably an optimum match to the size of the gels. The gels were made using 10 m vials, of high-density polyethylene, suitable for the aqueous chemistry and ethyl alcohol chemistry. The glass vials were used for chemistry involving more volatile organic reagents and solvents. The resulting size of the gels fit easily into the glass vial/chamber, and still had about 75% of void space as air so that radon diffusion would be unimpeded. Smaller chambers might have resulted in dead spaces, and larger vials would have reduced radon concentration at the aerogel surface unnecessarily. A reduced neck diameter help ensure a tight seal in the glass chamber.

B. Radon Exposures

Since the gel is a monolith, it was decided to expose the gel to radon in a static mode, that is, at a constant concentration. Also, exposure by simple diffusion is simpler than a continuously flowing arrangement, which requires a reliable pump. Further, there is less chance for leaks using a passive method. The pressure drop across a monolith would probably be essentially infinite, so there is no point in attempting to draw the radon through the gel, at least until it is better characterized, and tests shown that gas can be drawn through a gel.

The interior of the chamber consisted of only glass, aluminum and brass surfaces. Radon can leak through many types of seals, and can penetrate the walls of more permeable materials. So, the first experimental run was performed (with no gel) for an extended period as the count rate was monitored. Once the radon and gamma emitting progeny had stabilized, the count rate leveled off and remained level for 3155 hours (Figure 3.2.) This shows that the radon concentration to which gels would be exposed in the experiment would remain constant. The result also implies that there are no significant leaks in the system. This is not a proof that there are no leaks at all, only that the leaks are constant, minimal, and less than the physical decay rate. A larger leak would have resulted in a continual drop to a very low count rate, resulting in a high peak:plateau ratio.

A leak in the apparatus may occur at several critical points. A good design will prevent or at least minimize leaks, and reduce the possibility of leaks caused by faulty construction. The seal between the vial's glass rim and the vial cap is pressure fit and so may allow a leak if damaged or incompletely tightened. This arrangement facilitiated replacement of the chamber between gels and minimized costs, but it would be an improvement to replace this feature with a seal acknowledged to be gas-tight. Another possible leak source is the hose fitting to the copper tube which should be replaced with a gas-tight component such as a ferrule or potting compound impervious to Radon. Lastly, the progeny filter housing if not completely locked down might allow some leakage, depending on procedure and also age of the component.

It is interesting to note that the count rate corresponding to equilibrium is not the same for each sample, and is different for the empty chamber as well. While it might be possible that each time the apparatus was set up there was a small but constant leak of different magnitude resulted in a different equilibrium point, it is probably more likely that there are geometry differences that may result in different counting efficiencies. Such differences are the result of the settling of the various gel fragments of differing shapes rather than the chamber-detector positioning, which is quite similar, being constrained by shims and the hole through the lead block. Geometry could play a larger role if a significant portion of the signal were from beta radiation, which would be more position-sensitive. Both of the broken gels (7-1A, 8-4A) showed lower count rates than the empty chamber (A202) during exposure but the whole gel (8-2) count rate was higher.

The gel's bulk volume of 3.2 cm^3 is about 15% of the chamber (vial) volume of 20 cm³. This might cause enough displacement to account for the lower count rate in the

case of the broken gels, for example gel 7-1A is shows a 15% lower count rate than the empty chamber but this is counter to the case of the whole gel, where the count rate is higher than the empty chamber and does not explain the higher count rate for gel 8-2A, although the behavior of an intact gel (see discussion regarding mass-transport below) may be working in opposition to this effect.

Most of the signal from the NaI detector comes from the radiations emitted by ²¹⁴Pb and ²¹⁴Bi. The sum of these two nuclides reaches a peak at about 3.6 hours, when in equilibrium with a fixed starting quantity of ²²²Rn, per Figure 4.1. (The count signal results from the sum of emissions from these two nuclides, with correction for counting efficiency.) Since the maximum count rate during exposure is reached between 15 and 30 hours after the start of the exposure a delay is evident. Some of this delay may be due to the time it takes for radon to diffuse and equilibrate in the chamber. However, as is evident in Figure 3.2 in all cases there is a rise in count rate followed by a fall to equilibrium, there is some other factor at play. This factor may be redistribution, plate-out of the progeny of the surfaces or even within the gel or possibly a slow leak of radon from the chamber.

There also may be a difference caused by the interaction of recoil nuclei between the wall of the glass vial (density nominally 2.2 g cm⁻³ and the wall of the gel, density of 0.27 g cm^{-3} .) If intermediate progeny become trapped, this would change the counting geometry.

Figure 4.1 Ingrowth of ²²²RnProgeny



The rise of the radiation signal during radon exposure and subsequent fall to a fixed level is an interesting if unexpected phenomenon. The purpose of the monitoring of the radon exposure with the Na I detector is to establish that equilibrium is reached. That equilibrium includes both radioactive equilibrium but also the mass transport of radon and possibly of progeny.

The radon exposure signal (Figures 3.1, 3.2 and 3.3) is a composite of gamma radiation and beta radiation and perhaps even Bremstrahlung, each with their attendant counting efficiencies. The alpha radiations do not contribute, and low energy beta radiation would not penetrate either the glass wall of the chamber or the detector housing. The experiment has no moving parts other than the valve opened at the beginning and closed at the end. Counting geometry was constant during the entire exposure and made as similar as possible between samples.

Movement of radon within the system contributes very little to the composite signal because its gamma radiation is of very low abundance (7.8 x 10⁻⁴ photons per disintegration) and its alphas are not be seen by this detector. Practically the entire signal arises from the gamma radiation from the progeny ²¹⁴Pb and ²¹⁴Bi each of which also have moderate and high-energy beta radiation that can contribute directly to the signal. Scintillation detectors will respond to beta radiation with sufficient energy to penetrate the detector housing. Some Bremstrahlung radiation is probably also produced since the energetic betas could reach the brass fitting, some could have been produced in the glass, and perhaps even the lead shielding. Detection of the beta radiation could have been

reduced or eliminated by changing the detector discriminator settings. This would have reduced the composite nature of the signal at little cost to sensitivity, since the signal was strong. This would have been a minimal adjustment, but would still have required a rerun of at least one sample since this phenomenon was not anticipated.

The exposure pattern in Figures 3.1 through 3.3 shows upon examination that the longest rise and slowest fall-off of radon progeny signal occurs in the monolith (sample 8-2.) This observation is consistent with the intact gel presenting a longer set of continuous pathways for the radon to enter, thereby retaining more radon. This sample also off-gassed more slowly, a mass transport phenomenon in agreement with this gel configuration. Interestingly this sample also showed the most remaining ²¹⁴Bi activity on the day following the off-gassing (Figure 3.4). The MDA for the gamma counter is approximately 0.01 c s⁻¹, but is a function also of the count time. For this longer count of 3600 s, the MDA is 11 counts (95%CI). This count resulted in 32 net counts and so therefore is above the MDA. Therefore, this sample has residual activity, indicating radon retention. The LSC data also support this conclusion since the count rate for this sample (Table 3.3) is 7.5 times the background, a definite positive result for LSC given the stable, reliable background of this instrument. Its LSC count rate continued to rise (Table 3.4) up to the last observation at 188 d. While this activity is not from radon and immediate progeny (which have long since decayed) it is indicative of a larger integrated radon exposure due to build-in of ²¹⁰Pb and its progeny.

Differences between sample positioning between gels and particularly in the difference between broken and whole gels may change the total signal and possibly the signal pattern (the rise and fall to a constant value.) However, the fact that the same pattern emerges shows that similar processes and counting efficiencies for the various radiations are the case for each sample, and the empty chamber as well. The difference in magnitude of the peak and the plateau may well be the result of different degrees of radon or progeny trapping or location of trapping, but could be confounded by another phenomenon such as plating-out of progeny, which might change the counting efficiency or a leak, where radon exits the apparatus. Nevertheless, the goal of the apparatus was met, namely to show long-term, consistent level of radon is present in the gel and chamber by observing the progeny signal.

It would have been preferable, and could have been made into part of this work by use of a gamma spectrometer at this stage of the experiments, but one was not available. Also this would have complicated the apparatus at an early stage in the investigation; if this were to be included in the experimental objectives it would be better to perform this type of measurement and analysis at a later stage, once this type of phenomenon is recognized. An advantage would have been to better isolate the sources of the radiation signal used to determine equilibrium so that a cause might become more readily apparent for those portions of the exposure curve that differ from the expected pattern.

A simple model may show how two processes, plate-out and radon leakage, might affect the shape of the exposure curve. Figure 4.2 shows a model prepared using the

SBModelMaker software, Version 2.0c, Cherwell Scientific Publishing. The first three compartments represent the radon generator, with its ²²⁶Ra material, and 'Source' being the radon present internal to the generator. Compartment C1 represents all subsequent progeny, which do not leave the generator because of plate-out and the filter at the outlet. The transfer coefficient F1 is the ²²⁶Ra decay constant while P0 is the ²²²Rn decay constant. Initially the valve remains closed, to allow ²²²Rn to build to radioactive equilibrium, until time t=1000 hours as shown in Figure 4.3. At that time, the valve is open and ²²²Rn diffuses to the exposure chamber, denoted AirRn222. The model allows for ²²²Rn to diffuse back to the generator, and the competing rates are balance by the Inflow and Backflow values. These are arbitrarily set to demonstrate a balance in the mass transfer between the two volumes. Activity is displayed, not concentration. While the total amount of ²²²Rn in the system does not change, it becomes distributed in a manner as depicted. Initially, the Leak coefficient is set to zero since a leak would only have an effect after the generator valve is open. P1, P2, and P3, the plate-out factors for progeny within the exposure chamber are also zero for Figure 4.3. The activity of ²¹⁴Bi, chosen as an example, begins to rise after the valve is open (at which time the Leak>0 for the 'have a leak" runs of the model) and reaches an equilibrium based on its production and decay rates as shown in Figure 4.4. The values for ²¹⁴Pb are similar, as is the shape of the curve. The precise shape of the curve is not strictly correct (see Figure 4.1) since this modeling software does not have enough numerical precision to calculate radioactive decay for the entire progeny series using this set of data in the simple configuration used, e.g. actual decay constants. However, this should not affect the analysis for the purpose of this discussion.



Figure 4.2. Model of Radon Source and Exposure Chamber



Figure 4.3 Radon Levels in Radon Generator and Exposure Chamber

Figure 4.4²¹⁴Bi Level in Exposure Chamber



If plate-out changes the counting geometry and reduces the radiation signal, then that would be apparent in the model when non-zero values are assigned to P1, P2 and P3, representing removal or plating out of these progeny. However, all values of these coefficients from almost no removal to almost complete removal had no effect on the shape of the activity curve; the vertical scale was the only change. However, incorporating a Leak coefficient at t=1000 changes the shape of the curve. (Contrast the shape of the curve on Figures 4.4 and 4.6.) The model assumes a one-way leak, since radon would exit the system via the fume hood. Figure 4.5 shows the effect on the ²²²Rn within the system, and Figure 4.6 shows the effect on the ²¹⁴Bi signal that should model the detector. Since the shape of the curve, with a sharp rise and fall off to an equilibrium matches what is seen during the exposure, it is reasonable to conclude that plate-out is not a contributing factor in this response, but that radon removal though a leak would explain the shape of the curve.

Another feature of the leak phenomenon is that the level of the equilibrium will change based on the size of the leak. But, as long as the leak is much less than the production rate the equilibrium will exist indefinitely. This would explain the equilibrium different levels in the aerogel samples and blank and provides the explanation that while tightly sealed, there is probably a leak at slightly different levels in each sample.

Radon entry into the aerogel is possible because of the open gel structure, and because the diameter of the radon atom is smaller than the pores of the gel. Radon's atomic diameter is estimated to be 4.6×10^{-10} m. (20) Comparing this with pore diameters



Figure 4.5 Radon Levels in Radon Generator and Exposure Chamber, With Leak

Figure 4.6²¹⁴Bi Level in Exposure Chamber, With Leak


of a typical aerogel leads to the conclusion that radon should easily penetrate the gel, which are composed of a distribution of pore diameters that vary continuously in the range from 1 x 10^{-9} m to 1 x 10^{-6} m. (21). It is usually convenient to describe them as existing in three domains: micropores being less than 2×10^{-9} m, mesopores from 2×10^{-9} $m - 5 \ge 10^{-8}$ m and macropores which are larger than $5 \ge 10^{-8}$ m. While each aerogel will be different, generally the mesopores constitute the majority, and micropores are the least common. The gel structure is comprised of chains of essentially uniform diameter, with varying degrees of branching. A scanning electron micrograph in reference (21) shows silica particles aggregated into filaments that are arranged into a three-dimensional, crosslinked structure. One fact worth noting is that the closeness of radon's atomic diameter to the size of the larger micropores and smaller mesopores might mean that radon could fit snugly into an appropriate size pore and not exit as quickly as it might from a material with larger pore spaces. Experiments were conducted in a sealed environment; without a pressure-driven flow no pressure differentials existed. Diffusion is the only important mechanism at play here, so that the net movement of radon would be from areas of higher to those of lower concentrations.

Hirst and Harrison (22) reported the radon diffusion coefficient to be $1.2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. The diffusion coefficients in air, by comparison, of O₂, CO₂ and H₂O (using the same units of $10^{-5} \text{ m}^2 \text{ s}^{-1}$) are respectively 2.0, 1.6, and 2.4 at ambient temperature and pressure. (23) Therefore it may be concluded that radon moves only somewhat slower than other gaseous constituents of air, and therefore should be able to diffuse to and enter the open pore spaces of an aerogel.

Radon diffusing from the generator exits though a filter having pores no larger than $2 \ge 10^{-5}$ m diameter. Once in the chamber, radon may diffuse in and out of the gel. Progeny generated by decay within the gel will be trapped due to the small dimensions, tortuous pathways and possibly also static interactions, thus plating out on the internal surface of the gel. Progeny generated by decay within the chamber but outside of the gel will either diffuse (or recoil) to the gel or walls of the chamber. Progeny may remain suspended for some time in the air of the chamber. Unlike radon in natural environments (areas such as structures or outdoors) there would be less suspended particles within the chamber to which the progeny could attach. However, the chamber air was not filtered initially, and so any particulates that might survive in still air for the time period of the exposure (days to weeks) would be available to create an "attached fraction" i.e. a portion of the progeny becomes attached to air-borne particles. These also might then plate out on the walls of the chamber or on the exterior surface of the gel, but are unlikely to enter interior portions of the gel since their size would be too large. Most progeny will attach to aerosol particulates in ordinary room air typically range in size from 1.5×10^{-7} to 2.5×10^{-7} 10^{-7} m. A small number (averaging 2% and ranging from 0 to 10%) was attached to particles on the order of 1.0×10^{-6} m. (24)

It is possible to draw radon into aerogels in a flow regime using a pressure driven process. (25) However, there will generally be a large pressure drop due to the tight structure of the aerogel, and interestingly it can take on the order of a few hours for the flow to reach a steady state for a given increment of increased pressure. This could be mitigated a number of ways – using a high input pressure, by creating a larger proportion of pore with larger diameters during gel manufacture, by breaking and re-compositing the gel, allowing a large airflow within smaller contiguous gel fragments, or reducing the thickness of the gel monolith, such that the pressure drop across the pieces is sufficient to allow flow. These are all worthwhile experiments, but add complexity of manufacturing, require pumping equipment (adds cost and possibility of malfunction and leaks) and increase the complexity of the experimental design slightly. A simpler diffusion-only experiment avoids these. One advantage of a flow-driven regime is that filters can be used to continuously scrub progeny, thereby exposing the gel to radon only. A useful experiment would be to compare the response with and without progeny-scrubbing filters.

A calculation may be performed using the equations provided by reference (25) relating bulk aerogel density, ρ (g/cm³), to the apparent permeability, K (cm²),

$$K = 8.86 \times 10^{-13} \rho^{-1.48}$$

and relating the average mesopore size, d (nm), to the apparent permeability, K,

$$K = 1.32 \times 10^{-13} d^{1.41}$$

and setting the equations equal to each other, and solving for pore diameter, d.

The result is an average mesopore size of 1.5×10^{-8} m, based on a bulk density of 0.28 g cm⁻³. Since carbon aerogels "are not as permeable as other "open cell foams" because of their much finer cell/pore structure" and given that it may be inferred that that the average silica aerogel mesopores are a little larger, therefore their size distribution should encompass the radon atomic diameter.

The importance of radon research, at least from a health perspective, is the biological impact of radon and progeny energy deposition during radioactive decay when present in lung tissue. The diameter of the smallest air sacs of the lungs are between 1.3×10^{-4} and 3.4×10^{-4} m. (26) Therefore, radon is available to all lung tissue. Radon can enter all body tissue because it is an inert gas and can diffuse freely, like other gases. However, as an inert gas radon is free to diffuse out of the body so that the residence time is much less than its half-life. Therefore, radon decay while in the body contributes fairly little to the total dose. (27) A long-term radon contribution, e.g. from a steady state concentration, would be required for radon to contribute radiation dose where radon itself contributes a consistent fraction of the total dose.

The progeny deposit most of the total decay chain's energy by virtue of their tendency to become trapped in the cell tissues and surrounding fluid, and particularly those attached to respirable particles, which are small enough to enter the lung, but large enough to become trapped rather than exhaled. Progeny attaching to such particles become entrained in cell excretions and fluids with the result that radiation energy can be imparted upon decay. Both radon (as a gas) and unattached progeny (behaving as a gas) can exit the lung upon exhalation, delivering less dose per unit activity. Dose to the lung from radon and progeny depends also on aerosol "carriers", such as dust, or other airborne material to which the progeny attach, and then become trapped within the lung, based on their physical characteristics that are unrelated to the radon and progeny properties. Also, the presence of water plays a role, since the natural environment usually has water present, and lung air is humidified. Radon entry into the lung is driven by inhalation. This fact, the presence of humidity, and lack of defined natural aerosols makes this aerogel study not applicable to as a lung model. Rather, since it is desirable under a research situation to simplify as much as possible, and study only one specific aspect of radon behavior, aerogels could provide an opportunity to observe how radon behaves in relation to pore sizes in a specific material.

Radon studies have used other manufactured materials that have found general application for gas adsorption. Activated carbon is a common adsorbent and has been used to trap radon, notably for environmental studies. (28) "Molecular sieve" also has been used to capture radon. (29) This material is a zeolite, composed of an aluminosilicate of an alkaline metal. Natural versions of these substances exist, but as with activated charcoal, tend to be impure or of varying composition which can lead to varying behavior or difficulties in applications or in interpreting responses although better source and manufacturing control has made activated charcoal a useful material. Zeolites are polar materials unlike the aerogels in this study, which have a hydrophobic surface. Use of synthetic zeolites for radon studies is potentially attractive because the pores in their ring-like structure can be made in the same size range as the radon atom. Haman,

et al. compared radon adsorption on activated carbon, silica gel and molecular sieve. (30) They used 13X molecular sieve, which has pore sizes of 1.0×10^{-9} m, about twice that of the radon atom diameter. The 13X molecular sieve showed higher affinity for radon than the 5X molecular sieve, postulated because of the larger pore size of the 13X. The data showed molecular sieve adsorbed about twice as much radon as silica gel. The activated carbon however, showed more radon adsorption than either the molecular sieve or the silica gel. The activated carbon surface was described as "heterogeneous," based on the isosteric heats of adsorption but that the sample used was different from other studies, reportedly because of the different surface characteristics between various charcoals. Silica gel and molecular sieve is reported as "not good adsorbents for radon" despite their "incidental removal of radon" being of "considerable value and interest." So, it appears that surface characteristics could play a role, as well as pore sizes. Aerogels are a unique material with a unique structure, surface characteristics and pore size distributions and therefore worth investigation.

One reason this study did not include a pressurized atmosphere was the desire to see if there was any interaction of radon with the gel without a driving physical force, as might be expected under pressure, or with a gaseous flow. Such interaction might take the form of simple geometric entrainment due to the tortuous pathways, a physical trapping of the radon atom due to the steric configuration of a pore surrounding an atom or perhaps the availability of an infinite range of pore sizes among which the radon atom may find higher affinity sites. Higher pressures should drive gas into the pores and should therefore increase the amount of radon present. The higher pressures may also cause interactions on the surface of the aerogel, where gas molecules adsorb to the surface in more than one layer. The composition of the carrier gas would be important in the process because a molecule with higher affinity for the surface (or its own kind on the surface) may trap radon by multiple absorbed layers.

The above discussion assumes that radon measurement takes place under higher pressure or forced flow. It is also possible that these physical regimens could be applied and then removed prior to counting. This could have the effect of the radon being carried off with the exiting gas. However, an isotherm would need to be conducted to verify the actual effect, since it is possible that the higher pressure could allow the radon to find a more stable attachment or arrangement that might not be reversible as the pressure is reduced.

Aerogels are known to experience pore collapse during standard porosimetry techniques, which are commonly used to determine isotherms, a measurement of the amount of adsorbate in the material being studied as the pressure is increased while keeping the system at a constant temperature. This may mean that radon behavior in the gel may be influenced if static pressures are very high since the structure and distribution of pore sizes changes. (21) Gel structures have been known to be physically destroyed by the addition of pressure too quickly or even static pressures at very high levels, as the structure deforms.

A successful flowing gas arrangement, as would be created by a pump or gas pressure would be more likely to be in a low to moderate pressure regime. The sample configuration would play a major role, in that gas flowing through a monolith or pieces may have greater access to the internal surface area. One would want to be able to distinguish between experimental configurations where the exposure gas contains radon only and whether significant amounts of progeny are present. A configuration where gas is forced into the gel but where the radon in that gas is "old" enough to have generated progeny (or not sufficiently filtered) will result in the progeny being "filtered" into the gel. This phenomenon would not be, strictly, a test of radon affinity but could be a useful configuration if the filtering effect is an acknowledged aspect of the design.

The pressure drop across the gels manufactured for the current study would be rather large; it would be better to have gels constructed in a plate configuration, which would require a mechanical support since the pressure differential would easily fracture the gel. One study (25) noted that pressure drops had to be supplied in small increments to avoid breaking the gel.

C. Off-gassing and Gamma Analysis

Despite the differences in the apparent radon level during the exposures, the offgassing gamma (²¹⁴Bi 609 keV) counts are quite similar in absolute activity. All show the same half-life of about 25 minutes. This is close to the 26.8-minute half-life of ²¹⁴Pb. Since the ²¹⁴Bi would be transiently supported by ²¹⁴Pb this would be expected. It also indicates that most of the radon is off-gassed quickly: if the significant amounts of ²²²Rn were retained the ²¹⁴Pb would be supported, resulting in a much slower decay curve.

The empty vial showed about the same radioactivity as the gels during offgassing. While each of the gels also had about the same amount of ²¹⁴Bi, slight, consistent differences between gels are apparent. For example, gel 8-4A always has the lowest activity (except at the very end, near the detection limit) and gel 8-2 generally shows the highest radioactivity. The gels with the lowest and highest apparent radon activity in the exposure vial also had respectively the lowest and highest ²¹⁴Bi activity during offgassing.

A regression of the linear portion of the count rate for each gel (Figure 3.4, gamma data) yields a value for the slope and y-intercept of each line. The intercept corresponds to the count rate immediately after the exposure is stopped (time = 0.) The slope corresponds to the decay constant. For A202, the empty chamber, the initial activity is 64 c s⁻¹ and the slope corresponds to an effective half-life of 29 minutes (R = 0.996). The intercepts for gels 7-1A, 8-4a and 8-2 are respectively 68, 50, and 64 c s⁻¹. The slopes give respectively, half-lives of 30, 29 and 31 minutes for the ²¹⁴Bi activity in these gels. (R = 0.997, 0.995 and 0.998.) The standard error of the slope for samples 7-1A, A202, 8-41 and 8-2 is 1.1, 1.0, 1.3 and 1.1 min respectively.

The same calculation performed on the linear portion of the data in Figure 3.6 (LSC data) yields a half life of the composite activity for the empty chamber A202,

When repeated counts of gel 7-1A were performed six days after completion of the off-gas experiment (Figure 3.5) a ²¹⁴Bi net count rate of 4.4 x 10⁻³ c s⁻¹ \pm 3.2 x10⁻³ was measured. The typical counter net peak background (Table 3.2) for the ²¹⁴Bi photopeak is 1.7 x 10⁻³ c s⁻¹ \pm 2.9 x 10⁻⁴ c s⁻¹ or about three times the background count rate. Taking all 69 counts together the MDA is 69 net counts. (The two '69's is just a coincidence.) Although the ²¹⁴Bi net count of 362 counts is 5.2 times the MDA, the 70% relative error (3.2 x10⁻³ divided by 4.4 x 10⁻³) results in such a wide confidence interval so as to overlap the background. Therefore the presence of any remaining ²²²Rn, as indicated by the presence of supported ²¹⁴Bi, cannot be concluded with the gamma counter since the statistical power of the signal is not sufficient to warrant confidence especially in light of systematic errors, such as the temporal rise in the background level observed in Figure 3.8. These types of variations in the system require a stronger count signal to prove detection for the more sensitive applications.

C. Off-gassing and LSC Analysis

During off-gassing measurements were also taken with the liquid scintillation counter. The counts in the ³H region were taken as a surrogate for Cerenkov emission. The magnitude of the counts is 1500 times greater that of the gamma counter, but the counts are less specific in their origin. The effective half-life is calculated to be 34 minutes. This is significantly difference than what was determined with the gamma

counter. This maybe explained by the fact that the gamma measurement is based on only one radionuclide, ²¹⁴Bi, and the counts in the LSC counter may arise from many sources, e.g., other radionuclides, and Compton interactions.

Another difference between the two data sets is that the gamma measurements are linear (on the log scale) for 7 hours, whereas for the LSC counter the data moves away from linearity after only 4 hours. (The linearity on a semi-log plot is consistent with a first-order exponential process, as observed with of radioactive decay.) This result is likely caused by the LSC count data being a "mixed" signal and not the unique signature of one radionuclide.

Repeated counts of gel 7-1 were conducted at three different times after the offgassing experiment, reported in Table 3.4. The typical counter background in the 0-18 keV region is 0.100 CPM s⁻¹, and a count of unexposed gel 7-3 confirms this at 0.102 c s⁻¹. However, the count rate of gel 7-1A increases at 13, 50 and 188 days post off-gas to 0.87, 1.07 and 1.47 c s⁻¹ respectively. Gel 8-2, shows no increased activity; this is a nonexposed gel. Gel 8-4A shows a large activity of 7.1 c s⁻¹. Why 8-4A is so high is not understood, but it should be noted that the off-gas activity curves for gel 8-4A level off earlier than the other gels. However, gel 8-4 showed the lowest activity of all the aerogels during exposure (Figure 3.2) and the lowest initially during off-gassing (Figure 3.5) The increasing activity of gel 7-1A (and perhaps also 8-4A) should be investigated to confirm whether this is due to in-growth of 210 Pb progeny.

The MTGV referred to in Table 3.4 is not the empty exposure chamber (labeled 'A202 empty chamber' in other sections) but rather a clean glass vial that was used to provide a count that would correspond to an instrument background. The purpose of this data set, which was collected opportunistically, was to see if long-term activity would be present. The LSC counter is quite sensitive for particle detection, but is unfortunately not very good at particle identification. Particularly in this instance where there is no liquid scintillation cocktail, it would be over-reaching to attempt a precise analysis. Lack of any counts above background would prove that no radon is retained. However, a positive signal is not necessarily an indication of radon if there are other possibilities. For example, ²¹⁰Pb is a longer-lived progeny; so after the ²²²Rn is removed, the decay chain will "slow down" because ²¹⁰Pb decays more slowly ($t_{1/2} = 20.4$ y.) The count rate would be very low after about a month, and all of any ²²²Rn trapped would have decayed, as well as all of the progeny to ²¹⁰Pb. For each entrained ²²²Rn atom that decays a ²¹⁰Pb atom would remain. For each progeny atom created in the chamber volume that plates out one ²¹⁰Pb would remain (either within or on the gel surface or the exposure chamber walls. Some small amount of progeny might recoil during decay and exit the chamber during off gassing, but this can probably be ignored at this level of analysis.

The radioactivity level would be much less, being the ratio of the decay constant for ²¹⁰Pb to that of ²²²Rn, or 1.55 x 10⁻⁹ / 2.10 x 10⁻⁶ = 7.4 x 10⁻⁴ or 1/1350 of the integrated ²²²Rn activity. Given the unknown counting efficiencies for the various radiations it is not likely that a numerically precise calculation can be made.) A Cerenkov counting efficiency is estimated at about 50% (31) since ²¹⁰Bi has an energetic beta that will generate Cerenkov radiation. Because ²¹⁰Pb has low energy photons and beta, these are also assumed to contribute to the signal and composite counting efficiency of 150 % is estimated. ²¹⁰Bi has a half-life of 5.0 days and reaches equilibrium about a month after all ²¹⁰Pb atoms are created. It should be noted that in Figure 3.6 the counts for sample 8.4A leveled off at about 7 c s⁻¹. By 188 days, the decay rate of ²¹⁰Pb is essentially constant. Since the off-gassed empty chamber (Table 3.3) has a count rate of 3.9 c s⁻¹ (at the 25.8 hour mark,) this might lead to the conclusion that half of the activity is plate-out on the walls of the exposure chamber. However the modeling analysis suggests a leak in the system. Correcting for this phenomenon leads to the conclusion that since the ²²²Rn exposure level of the empty chamber A202 was 1.7 times higher than the level for gel 7-1A (82 / 47) a background correction should be applied, such that the appropriate subtraction is 3.9 / 1.7 or 2.3 c s⁻¹.

The total number of ²¹⁰Pb atoms can be used as an "integrating signal" by using the ratio of the ²²²Rn and ²¹⁰Pb half lives, thus:

$$(7.1 - 2.3)$$
 c s⁻¹ / 1.5 c dis⁻¹ x 20.4 y x 365 d x 24 h / 91.75 h = 6.3 x 10³ Bq ²²²Rn

The exposure chamber contained 3.4×10^3 Bq 222 Rn (see section II.B.1.) So the above calculation implies that an extra 85% of radon was retained long enough for progeny to become trapped.

Sample 8-2 showed the highest 222Rn exposure values (Figure 3.3,) but had the lowest retention values (Table 3.3.) This sample is the monolithic gel so the simplest explanation is that mass flow by diffusion does not penetrate very far into the gel and that cracks and fissures, plus extra jagged surface areas created by breaking the gel might allow better gas entry.

Samples 8-4 and 8-2 are chemically identical. The main difference between them is that 8-4 was crushed and 8-2 kept as a monolith. Gel 7-1A had Ce salt added as a reagent, and this may have created some differences in the gel structure. During manufacture, yellow-colored cerium (IV) was observed to exit the gel during surface modification. Since it is likely that some cerium remained, perhaps occluding the gel pores, this might explain why gel 7-1A has a lower ²²²Rn retention than the other, chemically purer glass gels.

D. LSC Energy Spectrum

The spectrum of events recorded by the LSC is displayed in Figure 3.8. The spectrum is similar in shape as the non-exposed and exposed gels, indicating a Cerenkov phenomenon as the cause of the detected light. However, for the exposed gels the scale is larger (there are many more counts) indicating radioactivity from the progeny as the cause. Counts are observed in higher energy regions but these are not reported since the ratio of counts to the low energy region is about the same.

The response of the counter to events occurring in the alpha region is not understood. The counter discriminates not only energy, but also a uses a post-pulse timing mode to discriminate further between events producing light from alpha particles from that cause by beta particles. Since there is some beta-to alpha crosstalk, it's not known if this approach is valid. Clearly the counts in the alpha region increase with the overall count rate. Since no alpha peak appears it is likely that this data is only an artifact.

V. CONCLUSIONS

A. It is shown that aerogel monoliths can be made at ambient conditions. The low density (0.27 g cm^{-3}) is indicative of the material being an aerogel. The TMCS is an important reagent in that it prevents collapse of the gel during final drying. However, it probably oxidizes the cerium from 3+ to 4+.

B. Radon can enter aerogels and then leaves more slowly in the monolith aerogel. Some penetration and retention did occur, since some gels show radioactivity persisting long after all (99.999971%) ²²²Rn has decayed. Tests are needed in the future to see if this effect can be distinguished and quantified from ²¹⁰Pb and further progeny since once ²²²Rn decay occurs, subsequent progeny are likely to remain within the gel. Gel 7-1A showed a slight increase in ²¹⁴Bi one day after off-gassing thus suggesting that this progeny was beginning to build in within the gel, supported by remaining ²²²Rn.

C. The cerium added to the doped gel during synthesis does not appear to scintillate in response to ionizing radiation.

VI. RECOMMENDATIONS FOR FUTURE RESEARCH

Work is needed on the chemistry of the doped gels especially as it relates to dopant-structure interactions. Research is also needed to determine where the cerium resides, whether in the pores or adsorbed to the surface and whether it plays any role in the gel matrix itself.

An important experiment would be to reduce the cerium within the dry gel while, if possible, retaining the gel's porosity. Some post–processing of dry gels, such as hot hydrogen gas treatment as suggested by Dr. Klein (32) to reduce the cerium in situ. Other dopants such as scintillating particulates might be tried since the gel can be used as a substrate for holding active moieties. Other geometries could be tried, such as flatter gels, which might give a better geometry for analysis. Utilization of supercritical extraction might yield quicker production of gels.

TCMS appears to have reduced the cerium 3+ to 4+. If a substitute could be found that did not react with the cerium that would be worth investigating. One might also try reducing in situ or adding a protective agent that would not effect pH, such as a buffer, but would provide the reductive potential to prevent the Ce from oxidizing.

Another option for incorporating cerium could be using an organic chelate of the cerium that would impede its transport, and perhaps even protects its oxidation state. Some researchers report the ability to pull fibers from the sol; this aspect should definitely be pursued. Better characterization such as measurement of isotherms to actually measure pore size and surface area would be useful for gels that show promise in absorb radon.

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