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Controlled Permeation of Hydrogen Through Glass

Final Report

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Executive Summary

For many years, the concept of storing gaseous hydrogen inside of hollow glass microspheres has been considered feasible but fraught with significant technical and economic challenges. The primary attraction for considering this mode of storage over currently practiced options is driven by the desire to achieve greater weight density of stored hydrogen. Greater weight density generally equates to lower unit distribution cost. Other attributes that have been claimed include increased storage safety, low cost raw material, and commercial bulk powder containment for transport and shipping.

Storing hydrogen inside of hollow glass spheres requires that the gas permeate through the glass walls. Hydrogen permeation through glass is relatively slow and the time to charge a sphere or bed of spheres is dependent on many factors. Permeation processes are strongly temperature dependent with behavior that follows an Arrhenius function. Rate is also dependent on the pressure drop driving force across a membrane wall and inversely proportional to thickness. Once filled, glass spheres will immediately begin to leak once the pressure driving force is reversed. Practical systems would take advantage of the fact that keeping the glass at ambient temperatures can minimize outboard leakage even with significant internal pressures.

If hydrogen could be loaded and unloaded from glass microspheres with significantly less energy and particularly at near ambient temperature, some of the key barriers to commercializing this storage concept would be broken and further system engineering efforts may make this approach cost-effective. Following this premise, Praxair initiated a limited exploratory program to evaluate possible means to enhance glass permeation by the application of various field effects. The Glass Science Laboratory at Alfred University was contracted to look at several concepts.

There were four objectives presented in our proposal for this study:

1. To determine if hydrogen permeation rates through glass can, in fact, be accelerated and decelerated in a controlled manner.
2. To identify and characterize glass formulations and associated triggering mechanisms that show a definite potential for being able to switch permeability from high to low and low to high at rates and with an energy consumption practical for commercial fill and discharge systems.
3. To develop a preliminary technical and economic assessment of the viability of using the best candidate formulation and mechanism in a microsphere and/or other configuration for hydrogen storage and transport.
4. To develop a preliminary business plan for advancing the microsphere technology and introducing it into commercial hydrogen applications.

The first two objectives have been met with limited success. The third objective has been partially achieved so far as a technical assessment is concerned. We have concluded that it is too premature for a preliminary economic assessment or business plan at this stage.

Practical systems for storing high pressure hydrogen gas inside hollow glass microspheres have been quantified. Microsphere geometry and material permeability properties have been determined that satisfy commercial operating requirements for both maximum product withdrawal rates and minimum no-loss hold times for storage in contained beds.

Assuming that microsphere beds need to be heated to 300°C to release gas, activation energies for permeability through glass must exceed 57 kJ/mol and microsphere diameters must be smaller than about 80 μm . Common borosilicate glasses with activation energies around 40 kJ/mol would only satisfy these requirements if heated to over 600°C. Significant thermal energy would be needed at end-user sites to provide these temperatures and this is not practical. Clearly an alternative approach must be sought that provides enhanced permeability at low temperatures when gas withdrawal from microspheres is desired.

The Glass Science Laboratory at Alfred examined the effects of applying various types of energy fields to glass samples in the hope that some mechanism other than thermal activation could enhance hydrogen gas permeation through glass. A series of experiments was devised to evaluate the effects of microwave, ultrasonic, infrared light, ultraviolet light, radio frequency, and oscillating magnetic fields on the outgassing rates of pre-saturated glass specimens.

Hydrogen diffusion through borosilicate glass was found to be radically enhanced by application of radiation from a commercial infrared lamp. The glass must be doped with a transition metal such as iron or copper for this effect to occur. While the enhancement is partially due to heating of the glass by direct absorption of energy, a major portion of the effect must be due to some as yet unknown mechanism. The enhancement effect has been found to occur for inert gases (He, Ne, Ar) as well, with increases in outgassing rates of orders of magnitude above those obtainable from simple heating of the sample.

Other methods of applying energy to the sample have, at most, very small effects. Microwaves and ultrasonic waves only increase the release of gases from these glasses by 10 to 30%.

Further work beyond the scope of this effort would be needed to determine the viability of a glass microsphere storage system which would use infrared light to enhance and control hydrogen gas permeation. Significant issues remain regarding developing an appropriate means to expose a bed of microspheres uniformly, quantifying the minimum energy requirements for achieving enhanced effects, and determining the economic feasibility of supplying the required IR radiation at production and end-user sites.

1. Background

For many years, the concept of storing gaseous hydrogen inside of hollow glass microspheres has been considered feasible but fraught with significant technical and economic challenges. The primary attraction for considering this mode of storage over currently practiced options is driven by the desire to achieve greater weight density of stored hydrogen. Greater weight density generally equates to lower unit distribution cost. Other attributes that have been claimed include increased storage safety, low cost raw material, and commercial bulk powder containment for transport and shipping.

Storing hydrogen inside of hollow glass spheres requires that the gas permeate through the glass walls. Hydrogen permeation through glass is relatively slow and the time to charge a sphere or bed of spheres is dependent on many factors. Permeation processes are strongly temperature dependent with behavior that follows an Arrhenius function. Rate is also dependent on the pressure drop driving force across a membrane wall and inversely proportional to thickness. Once filled, glass spheres will immediately begin to leak once the pressure driving force is reversed. Practical systems would take advantage of the fact that keeping the glass at ambient temperatures can minimize outboard leakage even with significant internal pressures.

Currently practiced storage methods for the merchant hydrogen industry include the use of liquid hydrogen in double-walled, vacuum-insulated tanks or high pressure gaseous hydrogen contained in thick-walled steel tubes. Liquid hydrogen provides a great deal of distribution flexibility, reasonable weight density, and permits the use of low pressure containment vessels. Disadvantages include the high energy consumption needed for liquefaction and expensive, cryogenic transport and storage equipment to minimize heat input from the environment and avoid product boiloff. Similarly, high pressure steel tube trailers are not very weight efficient with the best designs containing perhaps 300 kg of product (< 1% of the Gross Vehicle Weight). The economic range for delivery to end-users is generally limited to less than 200 miles.

If hydrogen could be loaded and unloaded from glass microspheres with significantly less energy and particularly at near ambient temperature, some of the key barriers to commercializing this storage concept would be broken and further system engineering efforts may make this approach cost-effective. Following this premise, Praxair initiated a limited exploratory program to evaluate possible means to enhance glass permeation by the application of various field effects. The Glass Science Laboratory at Alfred University was contracted to look at several concepts.

2. Project Objectives

There were two key objectives for this effort. The first was to evaluate the application of hollow glass microspheres for merchant hydrogen storage and distribution and then determine the hydrogen permeation performance required for practical commercial use.

The second objective was to identify, through a series of fundamental experiments, a low energy, low temperature field effect that could significantly enhance hydrogen permeation through glass without application of heat. If such an effect could be found, hollow glass microspheres could be much more attractive for hydrogen storage or possibly gas separation applications.

3. Glass Microsphere Storage Assessment

As currently conceived, a complete use cycle for storing hydrogen in hollow glass microspheres includes: gas charging, transporting, storing, and gas discharging. Economics and environmental concerns dictate that depleted microspheres from large beds be recycled and recharged. Single-use cartridge concepts may be feasible in the long-term for very small consumers of hydrogen.

The performance of a microsphere storage system needs to be examined over the entire cycle to ensure that proper design could achieve both functional and safety requirements. Lacking proper system design could lead to failure in meeting end-user needs for product flow rate or pressure. Unsafe conditions might result from poor flow rate control, unintended product leakage, or creation of unexpected flammable mixtures.

Key to meeting expected performance is a thorough understanding of the microsphere operating modes. Practical gas transfer rates during charging and withdrawal along with minimum leakage during storage will bracket the requirements for permeation performance and determine the material characteristics necessary for the glass spheres.

3.1 Operational Modes

3.1.1 Gas Filling

Filling microspheres with high pressure hydrogen gas will most likely be a batch process that involves purging, gas compression, heating, temperature control, pressurization rate control, cooling, void space depressurization, and purging. Semi-continuous processes might be achieved through use of multiple beds or lockhopper systems.

Filling productivity and economics will likely be limited by the ability of the glass to permeate hydrogen at sufficiently high rates. Previous analysis¹ has demonstrated the need for the external pressurization rate to not exceed the ability of the thin-walled spheres to accept gas. In certain high aspect ratios of diameter-to-wall thickness (D/w), maximum pressure drops across the membrane walls must be limited during charging or the spheres can fail from elastic buckling. Lower aspect ratio microspheres may be able to take the full pressure drop without failure.

Sphere internal pressure buildup and gas transfer rates will follow time-dependent exponential relationships. A common method of characterizing filling performance is through use of time constants. From an analysis of mass transfer through spherical shells, the time constant for filling microspheres with hydrogen can be expressed as follows:

$$\tau_{filling} = \frac{r_1^2 w}{3Kr_2RT}, \quad \text{where } r_1 = \text{inside sphere radius}$$

r_2 = outside sphere radius

w = sphere wall thickness

K = hydrogen permeability through glass

R = Universal Gas Constant

T = absolute gas temperature

Further, the permeability of hydrogen through glass can be expressed as:

$$K = K_0 e^{-E_k/RT}, \quad \text{where } K_0 = \text{Pre-exponential Coefficient}$$

$$E_k = \text{Activation Energy}$$

Combining these equations, it can be seen that the time constant for filling spheres is highly dependent on glass temperature. Even though the sphere material, geometry, and temperature are somewhat within the designer's control, practical considerations seem to indicate that the filling time constants are on the order of hours for temperatures of about 300°C.

Figure 3.1 depicts a possible pressurization profile for microsphere filling where the rate of increase is limited to minimize the cross-wall pressure drop driving force. To attain final storage gas density, it is necessary to heat the bed of microspheres to at least 300°C and pressurize to approximately double the final settled pressure. The bed is cooled to ambient temperature before depressurizing the gas contained in the void space. The stored gas will be locked into the spheres as a result of much lower permeability.

Figure 3.1 Glass Microsphere Filling Process with Direct Bed Heating

If, on the other hand, we could devise a low temperature "switch" that would increase the glass wall permeability by several orders of magnitude, we might be able to accomplish the filling operation as shown in Figure 3.2. Since the final filling pressure would be at low temperatures, there is no need for overpressurization as in the heated case. Overall processing time should be reduced if heating and cooling steps could be eliminated.

Figure 3.2 Idealized Glass Microsphere Filling Process with "Permeation Switching"

3.1.2 Gas Storage

Once hydrogen gas has been loaded into the glass microspheres, we can now use them for long-term storage. Storage in this sense also includes the period of time needed to transport them from a filling facility to the end-user's location. Once there, additional requirements for the microspheres may be imposed before, during, and after gas is removed from the spheres and is consumed by the end-user.

Since we need to maintain purity of the hydrogen product for the consumer, we would generally store bulk quantities of microspheres in sealed containers. Gaseous hydrogen with a slight positive pressure would protect the spheres from contamination of air or moisture. If the microspheres leaked some hydrogen into the container during prolonged periods, this would be acceptable if the pressure buildup within the container was manageable.

In fact, this containment pressure buildup is a good measure of storage performance. We could define a measure-of-performance related to the length of time filled microspheres could be stored before container pressure rises to a relief setpoint. This "No Loss Hold Time" is analogous to the storage of liquid hydrogen in cryogenic pressure vessels. In fact, the U.S. Department of Transportation regulates the design and certification of liquid hydrogen transports to meet or exceed certain levels of No Loss Hold Time.

Practical requirements for No Loss Hold Time of microsphere storage will be discussed in Section 3.2.1. These requirements will determine the ambient temperature permeability of the glass.

3.1.3 Gas Withdrawal

Withdrawing pure hydrogen gas from a glass microsphere bed to meet a customer's demand requires several things. The bed of hollow microspheres must facilitate high permeation rates when called upon to satisfy product flowrate needs. The gas must be available at useful pressure levels (at least 100 psig). The delivery system must be capable of load-following without significant delays.

If direct heating is used to raise glass permeability to a level sufficient for a commercial supply system, bed temperatures must once again reach 300°C or greater as was the case for microsphere filling. The difference this time, however, is that this heating process places the glass in its highest stress state of all operating modes. The internal pressure within the glass spheres will likely double from normal storage levels assuming that the internal gas temperature will closely track the wall temperatures. Since void space pressures will remain approximately 100 psig, the membrane stresses in the glass walls will be much higher than during ambient storage. Ogden² has analyzed this situation and related the maximum sphere aspect ratio (D/w) which can be used as a function of filling pressure and glass strength.

As an example of a possible storage system, if we chose to store hydrogen gas at 3000 psig inside hollow microspheres, we must pressurize the gas to approximately 6000 psig while heating the bed to 300°C. To withdraw gas later, we once again heat the bed to 300°C. At that point, we create 6000 psig internally while keeping external pressure at 100 psig. The maximum strength of engineered microspheres using the fabrication technology developed at LLNL³ is about 150,000 psi. Assuming an optimistic safety factor of 1.5, the maximum aspect ratio can be determined as a function of filling pressure.

$$(D/w) < \frac{4\sigma_{\max} / F_s}{P_{\text{charge}}}$$

In this example,

$$(D/w) < \frac{(4)(150,000) / (1.5)}{6000}$$

$$(D/w) < 67$$

However, these same aspect ratio spheres could be filled to higher pressures (and greater storage densities), if the withdrawal operation could be accomplished at approximately ambient temperature. Or, the maximum sphere aspect ratio could be doubled ($D/w = 134$ instead of 67) and less glass could contain the same hydrogen pressure. In either approach, the weight efficiency of microsphere storage could be improved significantly.

Avoiding the need to reheat the microsphere bed at an end-use point is very desirable. Merchant hydrogen distribution today does not impose this burden. Most customers simply expect to open a valve or regulator and get a dependable supply of gas without providing some form of energy to the system. Developing 300°C for a large, bulky container using electrical resistance heating or a gas-fired heater would be cumbersome, costly and likely to be non-competitive with simple high pressure cylinder or receiver storage. Heating to 300°C or greater will also create substantial thermal inertia effects from the additional heat capacity of container walls and insulation systems. Controlling discharge rates and void space pressure will be problematic. Additionally, startup heat losses following each storage period detract from the efficiency of the supply system.

If we could create a low temperature "permeation switch" as discussed earlier, the use-point supply system might be much simpler, use less energy, and permit more efficient use of the glass.

3.2 Bed Performance Requirements

A microsphere storage system could be engineered to meet the demands of both prolonged storage and fast gas transfer as discussed earlier. As an example, we will examine a system that would be heated to a minimum temperature of 300°C for gas transfers as well as be exposed to a maximum storage temperature of 80°C (representative of a container "baking" in the hot sun). The glass material requirements and microsphere geometry will be sought to achieve practical levels of performance for these conditions.

3.2.1 Storage Requirements

If we continue with the previous hypothetical storage system for containing 3000 psig hydrogen within hollow glass microspheres with $(D/w) = 67$, we can determine the required material characteristics for practical storage. We will further assume that the spheres will be packed so that a bed void fraction of 40% will be achieved (60% packing fraction). A vessel with 100 psig working pressure will contain a small bed of these microspheres. Initially they will be loaded into the container and will be purged and sealed at essentially atmospheric pressure.

The time constant for gas leakage out of the spheres and into the container void space is slightly different from the filling time constant previously described in Section 3.1.1. Since the void space (sink) pressure rises with time, the pressure differential decreases more rapidly. The time constant can be derived as:

$$\tau_{storage} = (1 - PF) \cdot \tau_{filling}, \quad \text{where } PF = \text{sphere packing fraction}$$

$$\tau_{filling} = \text{filling time constant}$$

The void space pressure will rise as a function of the storage time constant and the initial conditions as follows:

$$P_{\text{void}} = P_0 + \Delta p_0 (1 - e^{-t/\tau_{\text{storage}}}), \quad \text{where } P_0 = \text{initial void space pressure}$$

$$\Delta p_0 = \text{initial sphere pressure drop}$$

$$t = \text{storage time}$$

One reasonable requirement for No Loss Hold Time (NLHT) would be something like a week (7 days) where the internal void space pressure would not exceed 100 psig due to internal microsphere leakage. If we impose that requirement for "hot" storage at 80°C (353°K), use spheres with $(D/w) = 67$ and 3000 psig internal pressure, we can find a relationship between glass permeability and sphere geometry that will satisfy $\text{NLHT} > 7$ days. This relationship is shown in Figure 3.3 which depicts a region that satisfies this need. The operating map defines the necessary combination of microsphere diameter and the activation energy for hydrogen permeability.

Figure 3.3 Operating Map for Microsphere Diameter and Activation Energy for Hydrogen Permeability (3000 psi Storage Pressure, $D/w=67$)

3.2.2 Gas Transfer Requirements

Also shown on Figure 3.3 is the region that would satisfy gas withdrawal at rates that empty the spheres relatively quickly (63% depletion in less than 4 hours at 300°C). This rate was chosen to be in the approximate range for fast consumption of compressed gas cylinders. Normal withdrawal rates may be considerably slower. As can be seen, the common area where both conditions are satisfied is limited (in this example) to microsphere diameters smaller than about 80 μm and an activation energy for permeation through glass of higher than about 57 kJ/mol. Imposing faster withdrawal time constants (or longer NLHTs) has the effect of requiring both smaller diameter microspheres and a glass composition with even higher activation energy.

However, activation energies for hydrogen permeation of some common commercial glasses fall in the range of 32 to 43 kJ/mol.⁴ If we wanted to work with these glasses, we would require heating the microsphere beds to much higher temperatures than 300°C in order to achieve $\tau_{\text{withdrawal}} < 4$ hrs. For example, to satisfy both $\text{NLHT} > 7$ days and $\tau_{\text{withdrawal}} < 4$ hrs. with a glass that has an activation energy of 40 kJ/mol, we would need to heat the bed to approximately 620°C. At the same time, we would need to use much larger glass spheres ($D \approx 2200 \mu\text{m}$ and $w \approx 34 \mu\text{m}$). This is not a practical solution to our problem and we must look to use both a glass composition with a higher activation energy and seek an alternative means of inducing higher permeation rates without heating the glass to such high temperatures.

4. Permeation Enhancement Experiments at Alfred University

4.1 Technical Approach

In an attempt to avoid heating beds of glass microspheres to temperatures of 300°C or greater and gain the required increase in gas permeation rates needed for effective transfers, alternative non-thermal approaches were sought that might achieve similar effects. The Glass Science Laboratory at Alfred University was contracted to explore a series of potential concepts involving various applications of energy fields to glass specimens. Although no direct permeation experiments were conducted, numerous tests on the diffusion of hydrogen either into or out of glass specimens were completed. If enhanced diffusion rates were observed while specimens were exposed to an energy field, these would directly apply to cross-membrane permeation as well.

The Alfred study addressed the possibility of improving glass permeation rates by increasing the permeation coefficients of the hydrogen molecules by the application of energy from an external source using acoustic or ultrasonic waves, microwaves, or light with frequencies ranging from the infrared to ultraviolet region of the spectrum. A number of other, far more speculative methods were also originally proposed, including the use of RF waves for glasses containing metallic colloids, oscillating magnetic fields for glasses containing a dispersion of magnetic crystals, and direct electrical heating of spheres coated with metals.

The majority of the work performed under this study, however, dealt with the use of microwaves, ultrasonic waves, and light from a 250 watt source with a high output in the infrared region of the spectrum. The results, which are described in detail below, indicate that ultrasonic and microwaves each have only a small, albeit positive, effect in accelerating hydrogen gas permeability under the appropriate circumstances, while light can accelerate the permeation of hydrogen (and other gases) by orders of magnitude for glasses doped with iron and other transition metal oxides.

4.2 Experimental Methods

4.2.1 Gas Measurements

Two different methods were used to study the effect of external fields on the rate of hydrogen (and other gases) outgassing from glasses. Choice of method was determined by the

ability to configure the experiment. These methods will be referred to using the terms "*in situ*" for samples outgassed directly into the mass spectrometer system and "*ex situ*" for samples which were treated outside the mass spectrometer system to release gas and then outgassed directly into the mass spectrometer system to measure the remaining gas. A number of variations on these basic methods were used in specific circumstances. The variations will be described as the results using that particular method are presented.

The *in situ* method was used for studies using light as the external field under study. Since the samples could be contained in a transparent vitreous silica tube attached to the vacuum system, the samples could be easily exposed to the external light source (a 250 watt bulb sold as an "infrared light" source - the light also produces a large amount of visible light). Samples were placed in the vitreous silica tube and the tube evacuated to a pressure in the range of 2×10^{-6} torr. A background level for the gas under study was obtained using the mass spectrometer and then the light was turned on. Mass spectrometer data were collected until the signal returned to the background level. The rate of gas entering the mass spectrometer portion of the system could be controlled by use of a metering valve, which was necessary for quantitative measurements (termed the quantitative mode) or could be controlled primarily by the rate of release from the sample with a more open access of the gas to the pumping system (termed the kinetic mode), which provides good kinetic data, but less useful data regarding the exact amount of gas released. This measurement system is depicted in Figure 4.1.

Figure 4.1 In-situ Sample Outgassing System

The *ex situ* method was similar to that used at Alfred in several prior studies of gas solubility in melts.^{4,5,6,7,8,9} This method allows one to treat the sample in an environment which can not be used *in situ* and then determine if the treatment had any effect on the gas content of the sample. In this method, each sample to be tested is first exposed to the desired gas at an elevated temperature (400°C was used throughout this study) at a known gas pressure for a sufficient time to saturate the sample (Figure 4.2). The sample is then outgassed into the mass spectrometer system, where the total amount of gas originally contained in the sample is determined. Outgassing is usually carried out by placing a tube furnace preheated to 400°C around the vitreous silica tube containing the sample and heating the sample to that temperature. In some later measurements, the sample was outgassed by use of the light source instead of the tube furnace.

Figure 4.2 Sample Saturation System

After determination of the base quantity of gas contained in the sample, the sample is returned to the saturation apparatus, reloaded with gas under the same conditions used in the base measurement, and then removed from the apparatus. In this case, however, the sample is immediately treated using some test method, e.g. exposure to microwaves for 10 minutes, before the outgassing measurement. If the method tested has no effect on the gas diffusion rate, the amount of gas obtained during the outgassing measurement will be the same as for the base measurement. If, however, the exposure to the method tested accelerated the diffusion of the gas, the sample will contain less gas than the base sample.

Results of a typical outgassing measurement for helium are shown in Figure 4.3. The area under this curve is directly proportional to the total amount of gas in the sample. Since the mass spectrometer does not provide absolute measurements, a calibration measurement must be made in order to provide quantitative data. The calibration measurement is made immediately after the sample is outgassed. In this case, the amount of gas released into the mass spectrometer system is fixed by filling a known volume container to a known pressure. The standard provides a curve similar in shape to that of the sample. The ratio of the areas under these curves, multiplied by the known amount of gas in the standard, yields the amount of gas in the sample.

Figure 4.3 Sample Outgassing Curves for Standard and Furnace Heated Sample

4.2.2 External Treatment Methods

Tests were conducted using microwaves from a commercial microwave oven and sound waves from a commercial ultrasonic cleaner. In the first case, the samples were placed in the oven and typically treated for 10 minutes. Very little actual heating occurred, with the sample reaching a temperature of $\approx 60^\circ\text{C}$. In the second case, the sample was placed in a beaker of water, which was placed in the cavity of the ultrasonic cleaner and again typically treated for 10 minutes.

Limited external tests for effects of the light source were carried out to determine the heating effect. Samples were placed 4 inches from the 250 watt infrared lamp on an insulating brick. The temperatures of a sample was determined as a function of time by a thermocouple placed on the sample immediately after turning the lamp off. Tests were made using both vitreous silica and several iron-doped glasses melted in our laboratory (iron radically increases absorption of infrared energy).

4.2.3 Glasses Studied

Three commercial glasses, i.e. vitreous silica, and code 7070 and code 7740 borosilicate glasses, provided the basis for most of this study. Both of the borosilicate glasses are produced by Corning, Inc. Code 7740 glass is the most commonly used of the group of glasses sold under the Pyrex® trademark.

A number of variations of the borosilicate glasses were produced by remelting ground samples of the commercial glass with either Fe_3O_4 or CuO . Since these glasses produce very viscous melts, the remelted, doped glasses were quenched, ground, and remelted repeatedly until their optical appearance indicated relatively good dispersion of the colorant into the glass.

A few other samples were made using a ternary potassium borosilicate glass melted in the laboratory. These samples were only used for preliminary testing of light absorption and were not used for the outgassing studies.

4.3 Experimental Results

The results of this study are quite complex due to the large number of combinations of methods tested, gases and glasses used, and variations in the details of the experimental measurements. Presentation in order of actual experimental chronology would be very confusing due to the continual revising of the actual order of study as unexpected results were found.

The initial experiments in this study, for example, dealt with the effects of microwave and ultrasonic treatments. The results were disappointing, with only small effects on hydrogen and helium mobility. Subsequent experiments using the light source yielded results which were much larger than anticipated. Since the effects of the light source as an accelerant for outgassing were by far the most interesting and exciting results of the entire study, they will be presented before the results of the other work. It should be noted, however, that some limited results obtained after expiration of the term of this study suggest that microwave effects in the iron doped glasses are not entirely negligible and may be worthy of future study.

4.3.1 Acceleration of Gas Diffusion by Use of Light Sources

Initial consideration of light sources for accelerating gas diffusion in glasses was based on the assumption that the light source would simply serve as a different agent for heating the glass, i.e. the light source might provide a more efficient method for increasing the temperature of the glass. The initial study, which involved glasses doped with 1, 2, or 3 wt% of Fe_3O_4 , dealt only with the determination of this heating effect. Iron oxide was used in this study because of the known high absorption due to Fe^{2+} in the near infrared. The results, which are shown in Figure 4.4, clearly demonstrated that a light source could indeed be used to heat the glass. These particular data were obtained by heating 1 mm thick plates of glass in air, with the glass placed on a refractory brick approximately 4 inches from the lamp. The vitreous silica sample, which has high transparency in the infrared region of the spectrum, was included as a reference.

Figure 4.4 Effect of Exposure Time on the Temperature of Iron Doped Borosilicate Glasses

Since heating by a light source was possible, a series of *ex situ* measurements were made in which a code 7070 sample doped with 2 wt% Fe₃O₄ were saturated with helium and then partially outgassed by exposure to radiation from the light source. Samples were exposed to the light for 10, 20, or 30 minutes using the same experimental arrangement used for the temperature rise measurements and then analyzed using the mass spectrometer to determine the amount of helium remaining in the sample. The results (Figure 4.5) were quite encouraging, with approximately 50% of the gas removed in 10 minutes and 85% removed after 30 minutes.

Figure 4.5 Effect of Exposure Time on Outgassing of Iron Doped Borosilicate Glasses in an *Ex situ* Measurement

The results obtained in the *ex situ* study, while encouraging, were somewhat unsatisfactory experimentally in that they were time consuming and did not provide a complete history of the rate of outgassing versus time. In order to provide more complete data, we attempted the direct measurements provided by the *in situ* method. (This method was not attempted originally because we did not know that the silica tube would transmit the appropriate wavelengths of light and because of safety concerns regarding the sudden application of intense radiation to the silica tube containing a vacuum.) The results of the *in situ* measurements have proven to be the best obtained in this study and clearly illustrate the various aspects of the acceleration of gas diffusion due to exposure to light from this particular source.

An illustration of the effect of light in accelerating helium diffusion from a 2 wt% Fe_3O_4 doped sample of code 7070 glass as compared to that from a vitreous silica sample is shown in Figure 4.6. All of the helium is removed from the 7070 sample in ≈ 1500 seconds as compared to several thousand seconds for the silica sample (which was still not entirely outgassed). This particular set of measurements were made using the quantitative mode of operation, where the actual pumping of the gas through the system limits the removal rate. As a result, the rate of release of gas is known to be somewhat faster than that shown here. Since the measurement was run in the quantitative mode, we were able to calculate a helium solubility in the 7070 sample. The value obtained was 2.2×10^{17} atoms/cm²-atm, which is roughly that expected from the literature⁴ for similar glasses.

Figure 4.6 *In situ* Outgassing Curves for Helium from Vitreous Silica and from the 2% Iron Doped 7070 Glass

Since the data shown in Figure 4.6 were known to be influenced by the choking of gas flow through the metering valve, an attempt was made to eliminate this effect by by-passing this valve and allowing the gas to enter the mass spectrometer portion of the vacuum system through

a partially-closed large diameter valve. This method, which is called the kinetic mode, yields data which are more representative of the actual release rate from the sample.

Results obtained for hydrogen and deuterium in the doped and undoped 7070 glass are shown in Figures 4.7 and 4.8. The results for hydrogen are complicated by the presence of a large background, which decays with time. It is, however, obvious that all of the hydrogen was removed from the sample within a period of a few minutes. The data for deuterium, where the background from the atmosphere is much lower, more clearly show the effect of the dopant on the outgassing curve. We can now state that essentially all of the gas is removed from the doped sample (1 mm thick) in ≤ 200 seconds, while gas is still evolving from the undoped sample after 1000 seconds.

Figure 4.7 *In situ* Outgassing Curves for Hydrogen in 7070 and Fe-doped 7070

Figure 4.8 *In situ* Outgassing Curves for Deuterium in 7070 and Fe-doped 7070

The results discussed thus far might possibly be explained by a simple heating effect. Calculation of the temperature which would be necessary to yield these results, however, suggests that the temperature must have been sufficient to melt the glass. No evidence of melting was found on the samples, which still contain obvious scratches generated during sample cutting and grinding to the shape desired for the measurements.

The effect of heating was studied by comparing the outgassing rates from identical samples where deuterium was driven out of the sample either by exposure to radiation from the light source or by placing the tube furnace (preheated to 400°C) around the sample tube. In this case, the 7740 glass used contains only 0.5 wt% Fe_3O_4 , which actually reduces the effectiveness of the light source as compared to the use of 2 wt% doped glass. It is obvious (Figure 4.9) that use of the light source yields much more rapid outgassing of the sample.

Figure 4.9 Comparison of Outgassing Rates for Deuterium from a 0.5% Fe-doped 7740 Sample Using Either the Lamp or the Furnace

Much stronger evidence that these results are NOT due to simple heating effects can be found by comparing the behavior of a sample containing deuterium with that of one containing helium (Figure 4.10). All studies⁴ of gas diffusion in glasses yield a faster diffusion rate for helium than for deuterium. No one has, to date, ever reported a case where deuterium can diffuse faster than helium in any glass. The results shown in Figure 4.10, which have been reproduced many times during our studies, with a number of variations on the basic experiment (and the use of hydrogen instead of deuterium) always indicate that hydrogen isotopes can be removed from the doped borosilicate glasses (both 7070 and 7740) at least as fast as, and usually faster than, helium during an *in situ* experiment where the sample is heated using the light source. While the mechanism responsible for this behavior is not known, it is obvious that the phenomena reported here lie outside the range of traditionally expected behavior for gas diffusion in glasses. There is

no doubt that this aspect of the finding of this study are among the most exciting results reported in recent years for studies of gas diffusion in solids.

Figure 4.10 Outgassing Curves for Helium and Deuterium Using the Lamp Instead of the Furnace

A number of experiments were carried out to determine the universality of the dramatic increase in outgassing rate found for hydrogen isotopes. Neon is known to have a diffusion coefficient less than hydrogen and orders of magnitude less than helium in borosilicate glasses.⁴ Results of an experiment using helium, deuterium, and neon in the 2% Fe-dopant 7070 glass (Figure 4.11) indicate that neon diffusivity is also dramatically increased. In fact, there is little difference between the outgassing rates for these three gases in our experiments, even though the diffusivities of these gases in this glass should vary by orders of magnitude at 400°C.

Figure 4.11 Outgassing Curves for Deuterium, Helium, and Neon Using the Lamp Instead of the Furnace

Since the rate of outgassing of neon could be accelerated by use of the light source, one might wonder if the rate of entry of neon into glass could also be accelerated by the same method. Samples of 7740 glass doped with 2 wt% Fe_3O_4 were exposed to neon at 400°C overnight to saturate the sample. Calculations using diffusivities from the literature indicated that ≈ 24 hours should be needed to saturate the sample. A second sample was placed in the saturation system and exposed to the same pressure of neon. In this case, however, the sample was exposed to radiation from the light source for only 15 minutes. Both samples were then outgassed using the light source. The amount of gas released from the sample which was treated overnight at 400°C was almost identical to that for the sample exposed to the light source radiation for only 15 minutes (Figure 10). These results indicate that the in-diffusion of neon is radically increased by the use of high intensity, broad spectrum light.

Figure 4.12 Effect of Method Used to Introduce Neon into the Sample on the Subsequent Lamp Outgassing Curve

An even more impressive result was obtained for argon uptake by a doped 7740 sample (Figure 4.13). Data for argon diffusion have only been reported for vitreous silica due to the extremely low values for glasses, which make traditional diffusion measurements difficult. Extrapolation from higher temperature data for argon diffusion in silica and assumption that the diffusivity should be similar for 7740 glass indicated that hundreds of hours should be needed to saturate a sample of 7740 glass with argon at 400°C . A sample of this glass was thus exposed to argon at 400°C for a week-end (89 hours). A second sample was placed in the same system, under the same argon pressure, and exposed to the lamp radiation for 15 minutes. A thermocouple placed next to the sample reached a temperature of 359°C at the end of the 15 minute exposure. Outgassing of the two samples using the light source (Figure 4.13) indicates that considerably more argon entered the glass during 15 minutes of lamp exposure than in 89 hours at 400°C . It should also be noted that the very fact that a large portion of the argon can be driven out of the sample in times measured in thousands of seconds instead of hundreds of hours

is also an indication of the enormous increase in diffusivity induced by use of the lamp for outgassing.

Figure 4.13 Effect of Method Used to Introduce Argon into the Sample on the Subsequent Lamp Outgassing Curve

4.3.2 Effect of Variables on Light-Induced Outgassing

A number of variables were found to influence the rate of outgassing using the light source. In the usual configuration, the lamp bulb almost touches the silica sample tube, so that the distance from the sample is slightly less than 1 inch. A series of measurements for identical samples containing helium were made as a function of the distance of the lamp from the sample (Figure 4.14). These measurements clearly demonstrate the effect of reducing the amount of radiation reaching the sample on the rate of outgassing. The distance of 5 inches roughly corresponds to the ≈ 4 inch distance originally used in the *ex situ* measurements of helium outgassing which lead to the decision to try the *in situ* method. It is interesting to note that an increase in distance between the sample and light source of as much 6 inches only reduces the maximum rate of outgassing by about a factor of 2.

Figure 4.14 Effect of Lamp Distance from the Sample on the Outgassing Curve

The thickness of the sample also affects the outgassing behavior. A set of samples of 2% Fe-doped 7070 glass with thicknesses of approximately 1, 2, 3, or 4 mm were treated to saturation with helium. These samples were then outgassed using the light source. While the larger samples required more time for complete outgassing, the time required to reach the maximum outgassing rate (the maximum in the curve) increased by only a very small amount with increasing sample size (Figure 4.15).

Figure 4.15 Effect of Sample Thickness on the Outgassing Curve

The results obtained from the two different borosilicate glasses are quite similar (Figure 4.16). A comparison for *in situ* outgassing of deuterium from 7740 and 7070 yield similar results, as would be expected from the results of prior studies⁴ of helium diffusion in these glasses. Although this particular set of results indicate that the outgassing rate for deuterium is a little faster for the 7740 samples, there may be small differences in the actual, versus nominal 2 wt% Fe_3O_4 dopant level, sample thicknesses, and other variables which cause a small difference in the apparent outgassing rates. It can certainly be stated that any differences, if real, are small.

Figure 4.16 Effect of Base Glass Identity on the Outgassing of Deuterium for Glasses Containing 2 wt% Fe_3O_4

The effect of the iron oxide dopant level on the outgassing of 7740 samples is quite strong, as shown in Figure 4.17. The rate of outgassing increases substantially as the iron oxide concentration increases.

Figure 4.17 Effect of Iron Dopant Level in 7740 on the Outgassing Curve for Deuterium

A very limited study of the effect of identity of the dopant on the outgassing rate indicates that CuO is about as effective a dopant as Fe_3O_4 (Figure 4.18). Cu^{2+} ions also create a strong absorption band in these glasses. The band is shifted toward the visible relative to that caused by Fe^{2+} . In both cases, however, the glass is very dark, with little transmission in the visible. Unfortunately, since we do not have access to an instrument for measuring the optical spectrum of the glasses in the near infrared, we cannot determine the details of the difference in optical absorption for the Cu and Fe doped glasses as a function of wavelength in that spectral region. The literature indicates that the iron doped glasses should absorb much more radiation in the region between 1 and 2 μm .

Figure 4.18 Effect of Dopant Identity on Outgassing Curves for Helium

4.3.3 Microwave Studies of Vitreous Silica

Preliminary tests suggested that a 10 minute exposure in a conventional microwave oven resulted in a $\approx 18\%$ reduction in the amount of hydrogen subsequently released during the outgassing measurement from vitreous silica (Table 4-1). These results suggested that study of the effect of the hydroxyl content and the size/shape of the sample might prove useful. Further testing, however, has shown (Table 4-2) that the early results were probably erroneous. Improvements in the precision of the tests with increasing experience have eliminated the apparent effect observed in the early work.

Table 4-1. Initial Test Results for 10-Minute Microwave, Infrared, and Ultrasonic Treatments

Test Conditions	H ₂ Conc. - molecules/cm ³	% Evolved by Treatment	He Conc. - atoms/cm ³	% Evolved by Treatment
Untreated	4.9×10^{17}	---	2.8×10^{17}	---
Microwave	4.0×10^{17}	18	2.6×10^{17}	7
Ultrasonic	4.9×10^{17}	0	2.8×10^{17}	0
Infrared	4.6×10^{17}	6	2.7×10^{17}	4

The original set of outgassing measurements were made using 1 mm thick pieces of commercial vitreous silica tubing containing a low concentration of hydroxyl. Tests of the effect of sample shape and diffusion path length were made using sections of 1 mm diameter rod. Since a much greater fraction of the volume of the rods is in the near-surface region, any effect on diffusion rate would be expected to be greater for rod samples. Results for rods are indicated in Table 4-2 by Test ID numbers preceded by the designation R. No effect of sample configuration was found.

It also seems reasonable to expect that the hydroxyl content of the glass may control the coupling to microwaves. Further tests were then made using 1 mm thick plates of a form of commercial vitreous silica containing ≈ 1200 ppmwt (≈ 0.4 mol%) of hydroxyl. Results are listed in Table 4-2 for samples with the designation SU. No effect of hydroxyl content was found.

A further series of tests were carried out to determine if application of a sol-gel coating on the surface of vitreous silica samples would enhance the coupling of microwaves to the sample. Since a sol-gel coating contains a very large concentration of hydroxyl, it appeared reasonable to expect some additional heating of the sample. Results are listed in Table 4-2 for samples with the designation SOL. Once again, however, no significance enhancement of the outgassing rate was found.

One other experiment was carried out using a soda-lime-silicate glass containing silver colloids and some other commercial glasses containing arsenic and antimony colloids. Since these glasses have very low permeabilities for any gas, we only attempted to determine if the presence of metallic colloids would cause heating in the microwave oven. No significant effect was found.

Table 4-2. Effect of Sample Configuration, Hydroxyl Content, and Sol-Gel Coatings on Residual Helium Contained in Vitreous Silica

Date of Test	Test ID Code	Microwave Treated ?	He Conc. $\times 10^{17}$ (atoms/cm ³ -atm)
May 22, 1997	RHY1	No	12.2
May 23, 1997	RHY2	No	8.5
May 27, 1997	RHY3	No	9.3
May 29, 1997	RHY4	No	6.9
May 30, 1997	RHY5	No	7.3
June 2, 1997	RHY6	No	6.7
June 11, 1997	RHY7	No	6.2
June 12, 1997	RHY8	No	3.2
June 13, 1997	RHY9	No	4.6
June 17, 1997	RHY10	No	6.4
June 3, 1997	RMHY1	Yes	6.1
June 4, 1997	RMHY2	Yes	5.2
June 5, 1997	RMHY3	Yes	---
June 6, 1997	RMHY4	Yes	6.6
June 9, 1997	RMHY5	Yes	4.9
May 28, 1997	SUHY1	No	12.0
May 30, 1997	SUHY2	No	10.9
June 2, 1997	SUHY3	No	9.4
June 10, 1997	SUHY4	No	5.7
June 11, 1997	SUHY5	No	3.4
June 12, 1997	SUHY6	No	5.6
June 17, 1997	SUHY7	No	12.0
June 3, 1997	SUMHY1	Yes	10.3
June 4, 1997	SUMHY2	Yes	7.5
June 5, 1997	SUMHY3	Yes	7.2
June 6, 1997	SUMHY4	Yes	9.2
June 9, 1997	SUMHY5	Yes	10.9
June 13, 1997	SUMHY6	Yes	8.3
June 16, 1997	SUMHY7	Yes	7.7
July 11, 1997	SOL1	No	2.7
July 14, 1997	SOL2	No	2.7
July 15, 1997	SOL3	No	2.9
July 16, 1997	MSOL1	Yes	2.7
July 16, 1997	MSOL2	Yes	2.6
July 22, 1997	MSOL3	Yes	2.4

4.3.4 Microwave Studies of Doped Borosilicate Glasses

Microwave studies were essentially abandoned after the initial lack of success for vitreous silica and the discovery of very large effects due to exposure to intense light. A few final experiments, however, have been made on doped borosilicate sample. The *ex situ* experiments involved exposure of hydrogen or deuterium saturated, iron doped samples in the microwave oven for 10 minutes, and outgassing using the tube furnace at 400°C to determine if any of the gas had been lost from the sample during the microwave treatment.

The results of these recent studies (Figures 4.19 and 4.20) indicate that some small amount of gas may be removed during a 10 minute treatment in the microwave oven. In each case studied, the outgassing curve for the treated sample indicated that the sample contained less gas than the identical sample without treatment. The differences are small, indicating that no more than 20% of the gas was removed during a 10 minute treatment.

Figure 4.19 Effect of 10-Minute Microwave Treatment on Subsequent Outgassing Curve for Hydrogen with Undoped Glass

Figure 4.20 Effect of 10-Minute Microwave Treatment on Subsequent Outgassing Curve for Deuterium with 0.5% Fe_3O_4 -Doped Glass

4.3.5 Ultrasonic Waves

Test have been conducted on vitreous silica using an ultrasonic cleaner as the source of energy. The results (Table 4-1) indicate no effect for either helium or hydrogen. Recent tests on the 0.5 wt% Fe_3O_4 doped sample of 7740 did reveal a somewhat larger effect, with evolution of 20 to 30% of the gas during a 10 minute treatment (Figure 4.20). It is not clear if an effect of this magnitude would yield a large enough effect for the thin walls of microspheres.

Figure 4.21 Effect of 10-Minute Ultrasonic Treatment on Subsequent Outgassing Curve for Deuterium with 0.5% Fe_3O_4 -Doped 7740 Glass

4.3.6 Studies Based on Spheres

A quantity of hollow borosilicate glass spheres was acquired from MOSCI in Rolla, MO. No outgassing tests were made on these spheres due to the difficulties in developing a non-metallic, porous container which can be heated to a few hundred °C. Attempts to use commercial porous Vycor® as a container were unsuccessful. Our preliminary attempts to seal these spheres into the tubes resulted in spalling of the glass from the tube and inability to form a seal.

5. Conclusions

- Practical storage systems must accommodate both fast gas transfer rates on demand and prolonged storage periods without gas losses or venting.
- Analysis of mass transfer and transient pressure containment for microsphere storage can determine both geometry and material characteristics necessary for practical systems.
- Practical requirements for gas transfer and safe storage dictate use of microsphere diameters $< 80 \mu\text{m}$ and a glass composition with activation energy for hydrogen permeation $> 57 \text{ kJ/mol}$.
- Use of common glass materials with activation energies ranging between 32 and 43 kJ/mol would necessitate heating to $> 600^\circ\text{C}$ to achieve acceptable transfer rates without compromising no-loss storage performance.
- Conventional direct heating methods are not practical approaches to achieve enhanced glass permeation.
- Limited exploratory testing to assess the exposure of borosilicate glass specimens to other forms of energy fields has identified infrared light radiation as one means to enhance hydrogen diffusion from glass without direct heating. Samples doped with transition metal ions and exposed to wide spectrum infrared light exhibit outgassing rates that are orders of magnitude above those obtainable from simple specimen heating. Other gases (helium, neon and even argon) exhibit similar enhanced permeability.
- Microwave and ultrasonic energy fields have minimal effect on enhancing hydrogen diffusion.

6. Recommendations for Future Work

- The mechanism behind the enhancement of gas diffusion due to high intensity infrared light should be determined through further fundamental research.
- Some possible avenues to pursue experimentally include:
  - + conducting a true permeation test on doped glass specimens exposed to IR radiation to confirm expected performance based on diffusion studies
  - + determining the radiation wavelength(s) for various transition metal dopants that creates the largest enhancement effect through use of bandpass filters
  - + determining the threshold and saturation levels of dopant concentration needed to achieve enhanced effects
  - + determining the transient nature of the enhanced effect by applying light wave pulses of varying time length

- Until the fundamental mechanism responsible is fully understood and the capability to optimize the effect in terms of dopant selection, transient response and energy efficiency is better quantified, no further effort to engineer a glass microsphere hydrogen storage system should be undertaken.
- Several issues remain regarding the viability of any glass microsphere storage system which would use infrared light to enhance hydrogen gas permeation. Future effort would be needed to:
  - + Evaluate and select most appropriate means to deliver IR radiation uniformly to an entire bed of microspheres. (*In-situ* system for a fixed bed or exposure through an IR-transparent, pressure-resistant window for a moving bed concept are possibilities.)
  - + Quantify minimum energy requirements for IR radiation to achieve gas release rates compatible with system flowrate requirements.
  - + Determine the economic feasibility of supplying infrared radiation at both production and end-user sites in the technically preferred manner and at the exposure levels required.

7. References

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