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# Porous Wall, Hollow Glass Microspheres

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Hollow Glass Microspheres (HGM) is not a new technology. All one has to do is go to the internet and Google™ HGM. Anyone can buy HGM and they have a wide variety of uses. HGM are usually between 1 to 100 microns in diameter, although their size can range from 100 nanometers to 5 millimeters in diameter. HGM are used as lightweight filler in composite materials such as syntactic foam and lightweight concrete. In 1968 a patent was issued to W. Beck of the 3M™ Company for "Glass Bubbles Prepared by Reheating Solid Glass Particles". In 1983 P. Howell was issued a patent for "Glass Bubbles of Increased Collapse Strength" and in 1988 H. Marshall was issued a patent for "Glass Microbubbles".

Now Google™, Porous Wall, Hollow Glass Microspheres (PW-HGMs), the key words here are Porous Wall. Almost every article has its beginning with the research done at the Savannah River National Laboratory (SRNL). The Savannah River Site (SRS) where SRNL is located has a long and successful history of working with hydrogen and its isotopes for national security, energy, waste management and environmental remediation applications. This includes more than 30 years of experience developing, processing, and implementing special ceramics, including glasses for a variety of department of Energy (DOE) missions. In the case of glasses, SRS and SRNL have been involved in both the science and engineering of vitreous or glass based systems.

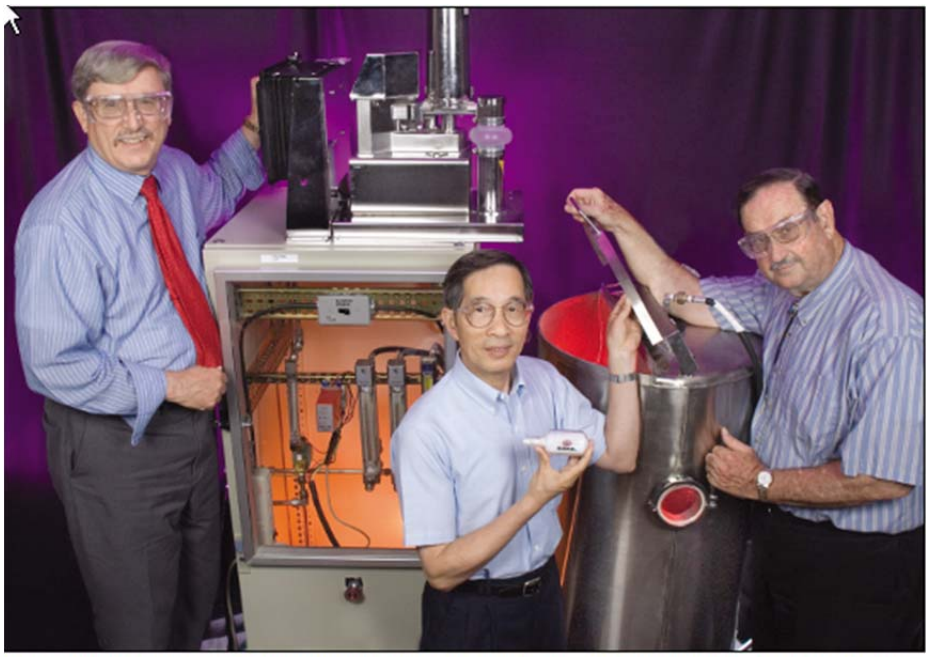
As a part of this glass experience and expertise, SRNL has developed a number of niches in the glass arena, one of which is the development of porous glass systems for a variety of applications. These porous glass systems include *sol gel glasses,* which include both xerogels and aerogels, as well as *phase separated glass compositions,* that can be subsequently treated to produce another unique type of porosity within the glass forms. The porous glasses can increase the surface area compared to 'normal glasses' of a 1 to 2 order of magnitude, which can result in unique properties in areas such as hydrogen storage, gas transport, gas separations and purifications, sensors, global warming applications, new drug delivery systems and so on.

One of the most interesting porous glass products that SRNL has developed and patented is Porous Wall, Hollow Glass Microspheres (PW-HGMs) that are being studied for many different

applications. The European Patent Office (EPO) just recently notified SRS that the continuation-in-part patent application for the PW-HGMs has been accepted. The original patent, which was granted by the EPO on June 2, 2010, was validated in France, Germany and the United Kingdom.

The microspheres produced are generally in the range of 2 to 100 microns, with a 1 to 2 micron wall. What makes the SRNL microspheres unique from all others is that the team in Figure 1 has found a way to induce and control porosity through the thin walls on a scale of 100 to 3000 Å. This is what makes the SRNL HW-HGMs one-of -a-kind, and is responsible for many of their unique properties and potential for various applications, including those in tritium storage, gas separations, H-storage for vehicles, and even a variety of new medical applications in the area s of drug delivery and MRI contrast agents.

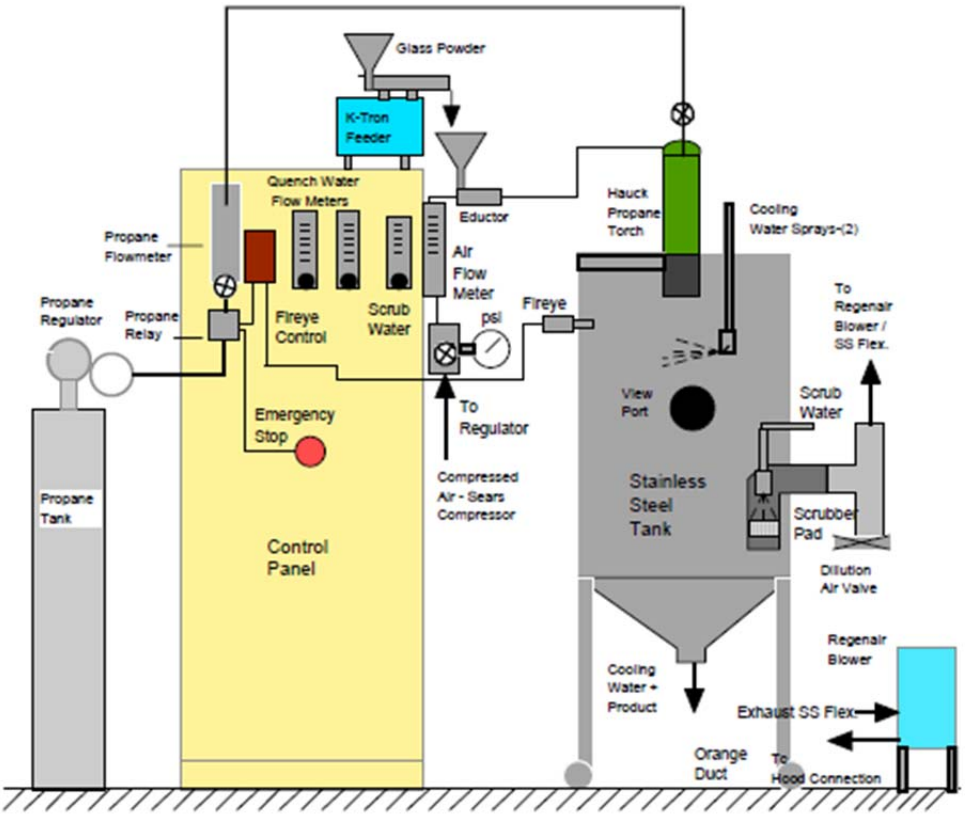
Figure 1. The Original SRNL Microsphere Team with Flame Former Apparatus.



The SRNL research and development team pictured here are Dr. George Wicks, Dr. Leung Heung, and Dr. Ray Schumacher. Also on the team, but not pictured are Dr. Steven Serkiz, and Dr. David Peeler.

SRNL Hollow Glass Microspheres, and subsequent, Porous Wall, Hollow Glass Microspheres are fabricated using a flame former apparatus. Figure 2 is a schematic of the apparatus.

Figure 2. Flame Former Apparatus

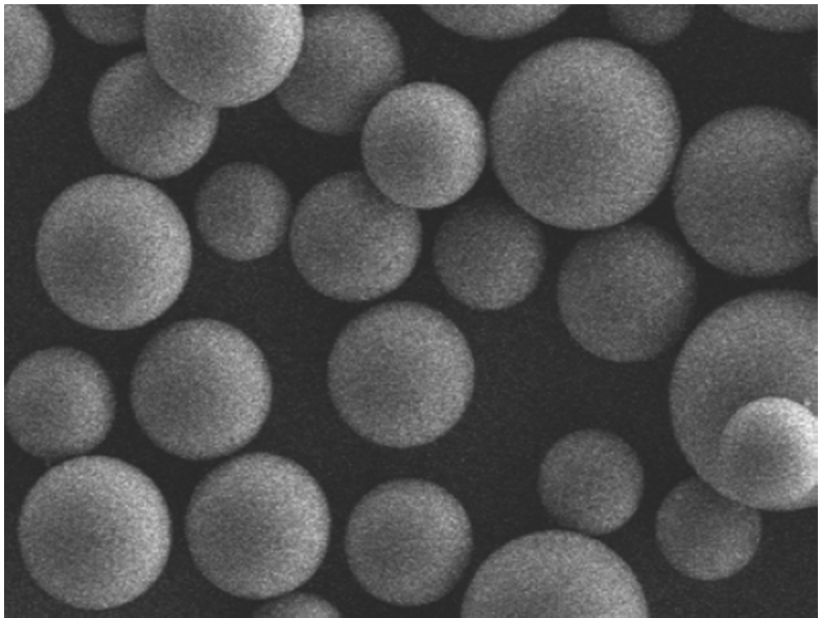



The flame former apparatus shown in Figure 2 consist mainly of a control panel and a combustion tank. The portable control panel houses the water, gas, and combustion controls. The stainless steel combustion tank contains the flame former, water spray and a collection basin. The apparatus is fueled by a portable propane tank and regulator.

The fabrication process starts by heating a glass powder ( ~20-40 microns) made up of Silica, Boron, alkali metal oxides, sulfur, and a small amount of various metal oxides along with a sulfate blowing agent. The heat zone is formed by a controlled gas-air flame from a modifiedHauck torch. During this heating phase the blowing sulfate agent becomes unstable and forms gas nuclei. As the spheres continue to be heated they expand and form hollow glass microspheres. Next ,the spheres pass through two water sprays that supply approximately 0.5 gallons per minute. These water sprays are used to quench the propane combustion flame to specific lenghts, to act as a coolant for the stainless steel tank and to capture the HGMs and glass particles in the quench water. The quench water exites

from the bottom of the stainless steel tank and is collected in plastic pails. The HGMs are collected by floation. Figure 3 below is a typical batch of SRNL microspheres.(Sizes 2-100µ with avg. dia. of ~50µ)

Figure 3. Typical batch of SRNL Microspheres



The HGMs collected are heat treated at 620° C for 18 hours before they are leached in a 4 molar hydrochloric acid (HCl) solution at 80° C for 4 hours. The heat treatment produces phase separation. The importance of this process is that it actually produces two different glass phases, one rich in silica and the other rich in sodium borate. The sodium borate phase is an interconnected worm-like morphology so when it is removed by the leaching process, it produces interconnect pores or channels that extend from the outside of the shell to the inside. Figure 4 offers a schematic representation of a SRNL microsphere and wall porsity. This phase sepatation is called spinodal decomposition. Vycor® 7930 (thursty glass) is also an example of this method. Figure 5 shows the similarities between the SRNL PH-WMs and Vycor®7930.

Figure 4. Schematic Representation of a SRNL Microsphere and Wall Porosity

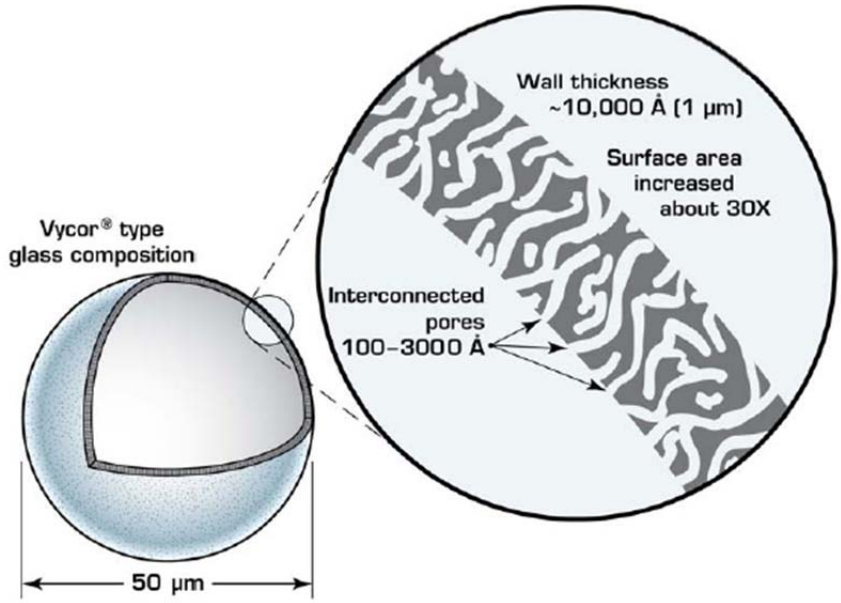
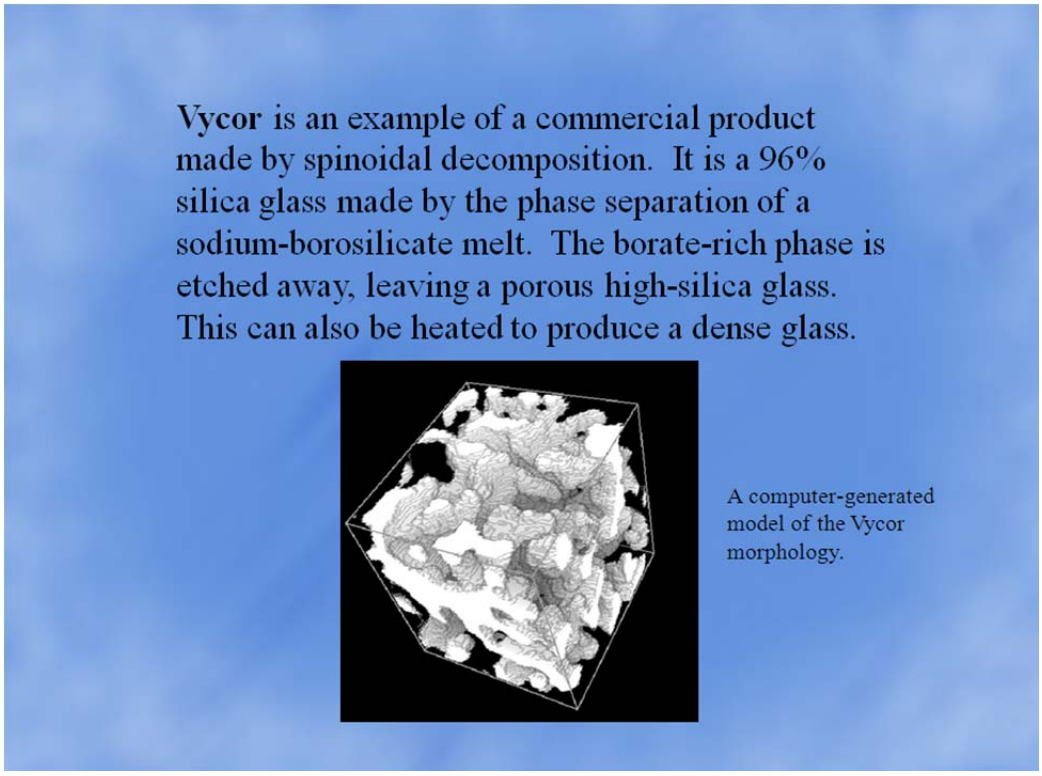


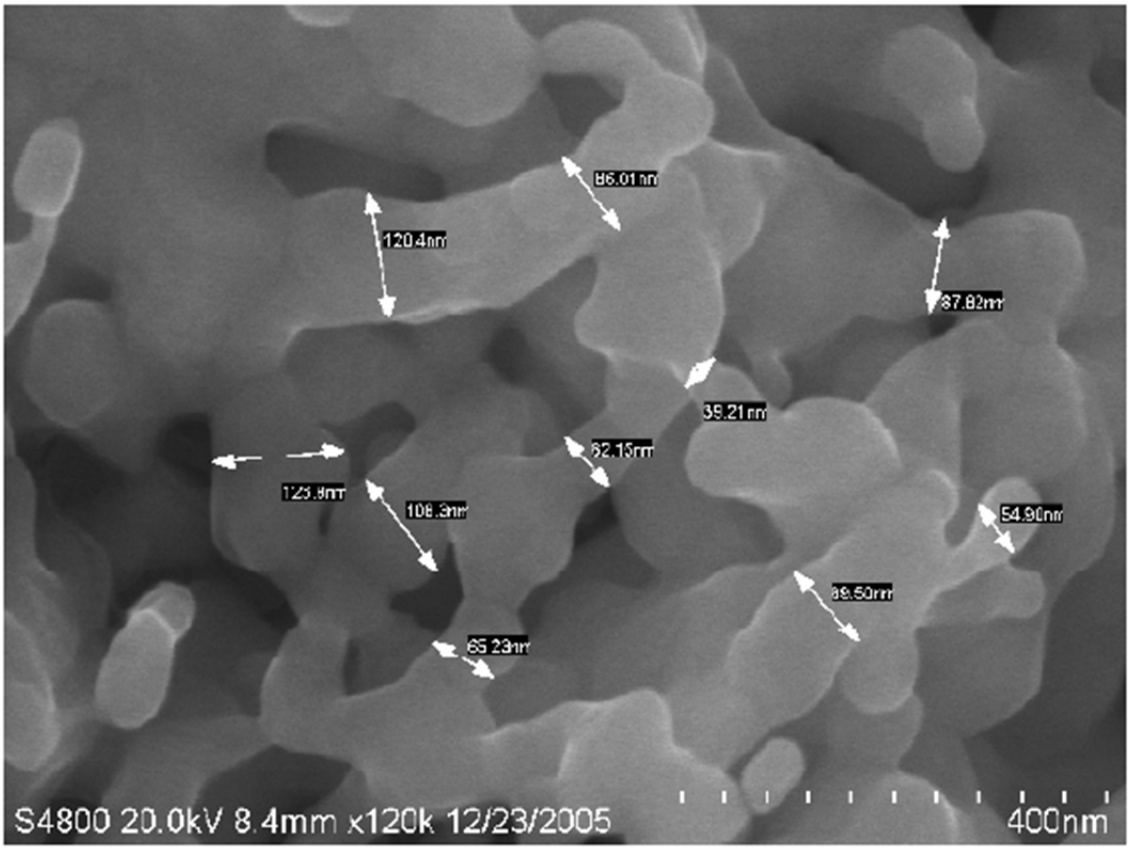

Figure 5. Spinodal Decomposition of Vycor

**(Slide taken from presentation, "Spinoidal Decomposition and Phase Diagrams", by Jason Bodson)**



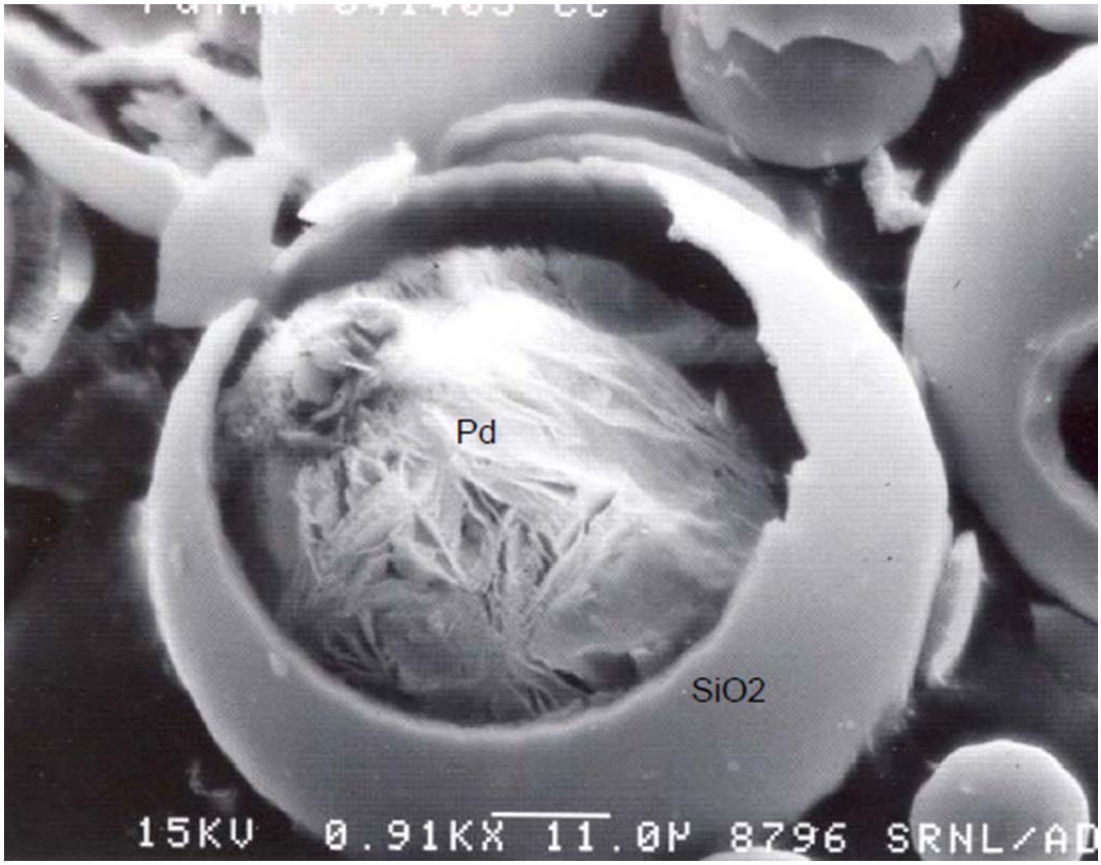
Leaching removes the soluble sodium borate phase of the glass and creates porosity through the microsphere wall. Figure 6 is an electron microscope view of the porous wall of a microsphere.

Figure 6. Unique Nano-scale Wall Porosity within the Microsphere Walls




Porosity is the key and the research team at SRNL used this porosity to fill the PW-HMs with special gas absorbents. Figure 7 is the first released micrograph of one of the microspheres after being successfully filled with Palladium metal which is used in the storage of radioactive forms of hydrogen. The wall porosity allowed the microsphere to be filled.

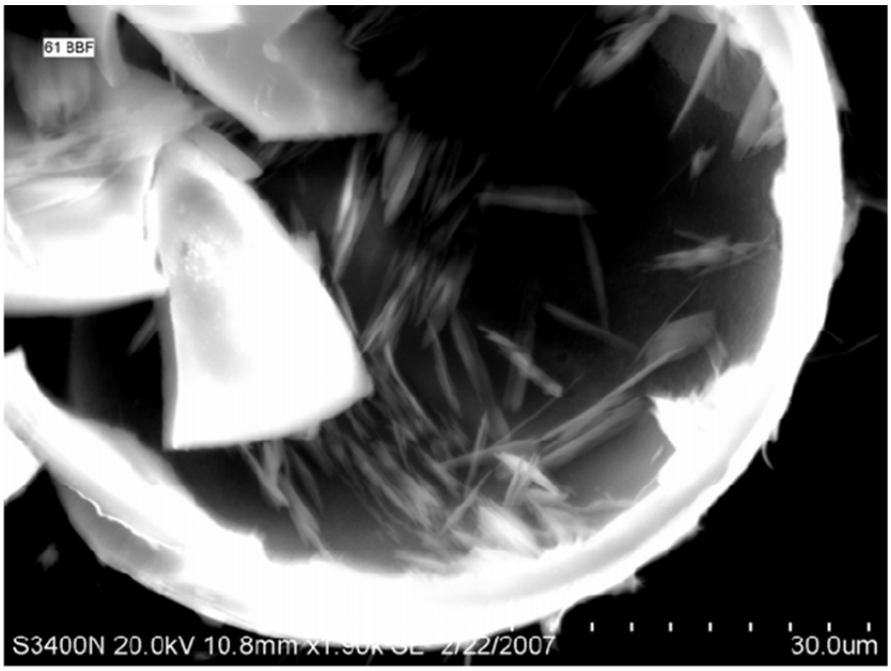
Figure 7. SRNL Microsphere Filled with Palladium (top of microsphere removed to view inside)




As part of a joint collaboration with Toyota, SRNL conducted test on filling the PW-HGMs with other special hydrogen absorbents. It was discovered very effective, but reactive absorbents could be filled and subsequently protected within the microspheres. This research could prove to be of major significance in the future of hydrogen fuel cells. In Figure 8 and 9, one of these nano-absorbent microspheres is shown for the first time. Bundles of nano-filaments were produced and noted, these bundles were observed on the outer as well as the inner walls of the microspheres.

Figure 8. Nano-Structure Absorbent Grown Outside PW-HGMs

Figure 9. Nano-Structure Absorbent Grown Inside PW-HGMs



Further work is needed to clarify these unique findings. As noted in Figure 8, the nano-structures can be produced on the outside of the microspheres. This information is not only relevant to absorbents of gases, but is also being investigated with the Medical College of Georgia, using protein and fluorescent indicators, for possible use in drug delivery systems and as new types of MRI contrast agents. An article has been published in the peer-review journal *Nanomedicine: Nanotechnology, Biology, and Medicine,* discusses a possible application of the SRNL PW-HGMs for the delivery of anti-cancer drugs.[1,2]

Porous Walled Hollow Glass Microspheres have potential for use in targeted drug delivery, hydrogen storage, and other applications. SRNL's partners in this winning technology include Toyota, the Georgia Health Science University (GHSU), and Mo-Sci Corporation, a specialty glass provider who has been licensed by SRNL to manufacture and market the microspheres. My special thanks to Dr. George Wicks of SRNL for his help and guidance in preparing this paper.

REFERENCES

[1] Savannah River National Laboratory, "SRNL Unique Porous Wall, Hollow Glass Microspheres (PW-HGMs) For Hydrogen Storage, Separation and Other Applications", G.G. Wicks, L.K. Heung, and R.F. Schumacher and all references within.

[2] "Encapsulation of Palladium in Porous Wall Hollow Glass Microspheres", L.K. Heung, G.G. Wicks and R.F. Schumacher Savannah River National Laboratory presented "Materials Innovations in an Emerging Hydrogen Economy", Feb. 24-17, 2008, Cocoa Beach FL, and published in proceedings (2008) and all references within.