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Design Strategies for Optically-Accessible, High-Temperature, High-Pressure Reactor Cells

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Design Strategies for Optically-Accessible, High-Temperature, High-Pressure Reactor Cells

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ABSTRACT

We have developed two optical cell designs for high-pressure and high-temperature fluid research: one for flow systems, and the other for larger batch systems. The flow system design uses spring washers to balance the unequal thermal expansions of the reactor and the window materials. A typical design calculation is presented showing the relationship between system pressure, operating temperature, and torque applied to the window-retaining nut. The second design employs a different strategy more appropriate for larger windows. This design uses two seals: one for the window that benefits from system pressure, and a second one that relies on knife-edge, metal-to-metal contact.

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Introduction

There are a variety of new research avenues in thermophysical science and engineering technology development that require optical access to high-temperature and high-pressure environments. Applications of these techniques are contributing to materials synthesis research, pressurized water reactor studies, and supercritical fluids research. However, the successful application of optical and spectroscopic methods in high temperature fluids at elevated pressure requires reliable window design that can typically withstand repeated thermal and pressure cycling.

This report addresses certain aspects of the design of optical cells suitable for environments where pressures and temperatures can exceed 8000 psia (55 MPa) and 1100 °F (600 °C). Such cells can be prone to sporadic leaks and cracked windows due to the mismatched thermal expansion characteristics of window materials, such as sapphire or fused silica, and the metallic alloy used for the construction of the pressure vessel. Over the past several years we have developed design improvements to two basic optical cell strategies, yielding two reliable reactors for our high pressure research. One system is a flow reactor which houses a flow optical cell. The other vessel is significantly larger and is equipped with a mechanically driven stirring mechanism. It is best suited for studying batch processes. Both systems accommodate the mismatch in the thermal expansion characteristics between high pressure alloys and optical materials and can maintain a high pressure seal over a wide range of conditions.

The flow optical cell design depends on spring washers to accommodate the thermal expansion mismatch between the cell body and the window material. The design is patterned after that of Abdullah and Sherman (1980) for Raman spectroscopy at high pressure in cryogenic systems. A cell design based on this principle has been reported recently by Bowers et al. (1995). The design presented here has the advantage of a much simplified gold gasket and has the flexibility to be inserted into a preexisting flow apparatus. Most importantly, in this paper, design calculations are provided to permit application of this window sealing strategy to other cell configurations and dimensions. Despite the small changes in dimensions in this example due thermal expansion, a quantitative evaluation of the design parameters is in good agreement with the actual operating characteristics of the cell. The design of our second reactor, the stirred optical cell, is based on the design of Schilling and Franck (1988). The design relies on two seals: the window seal which takes advantage of system pressure to press the window against its gasket, and the main seal that relies on an easily maintained, knife-edge contact between two metal parts.

Flow optical cell

Our flow optical cell is designed to fit into a 9/16-in (1.42 cm) OD, 3/16-in (0.477 cm) ID high-pressure chemical flow reactor. The optical cell can be inserted at any point in the 3-m reactor, allowing optical access to the flow over a wide range of reaction times. That system is described in detail elsewhere (Rice et al., 1996) (Hanush et al., 1995).

The cell, illustrated in Fig. 1, provides direct optical access to a high-temperature and high-pressure fluid flow. It is constructed of Inconel 625 and has three ports located at 90° intervals. The ports are fitted with Hemex CSI Ultra-VUV-grade sapphire windows shaped as coned cylinders, 0.375 in (0.952 cm) in diameter. The taper on the cone is 30° and is truncated to form a 0.079-in (0.20 cm) flat window. The length of the window is 0.437-in (1.11 cm). They are procured from Crystal Systems, Inc. The cell is heated by two Watlow, 175-W, resistive band heaters and is insulated with alumina blanket insulation.

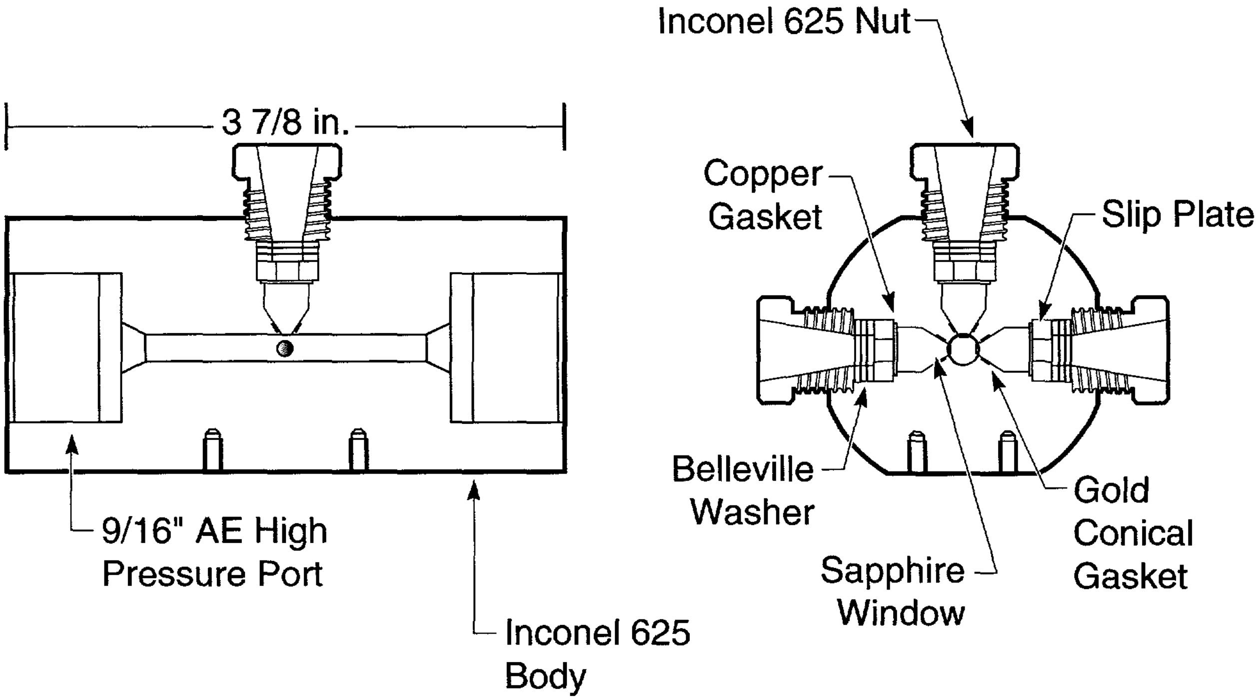

Figure 1. Cross-sections of the flow optical cell.

The design of the window seal in the cell, shown in detail in Fig. 2, relies on a balance between the force exerted on the window by the pressure within the cell and the force applied to the window by the compression nut. The actual seal is achieved with a gold gasket placed between the window and the cell body. This gasket is originally a flat washer, 0.13 in (0.33 cm) ID, 0.25 in (0.63 cm) OD, EDM cut from 0.010-in (0.025 cm)–thick pure gold foil that is deformed into a cone when the window is pressed into the assembly. An oxygen-free copper gasket is placed between the slip plate and the window to assure even distribution of force across the window. The slip plate also serves to prevent the compression nut and spring washers, described below, from turning the window in its seat and damaging the gold gasket.

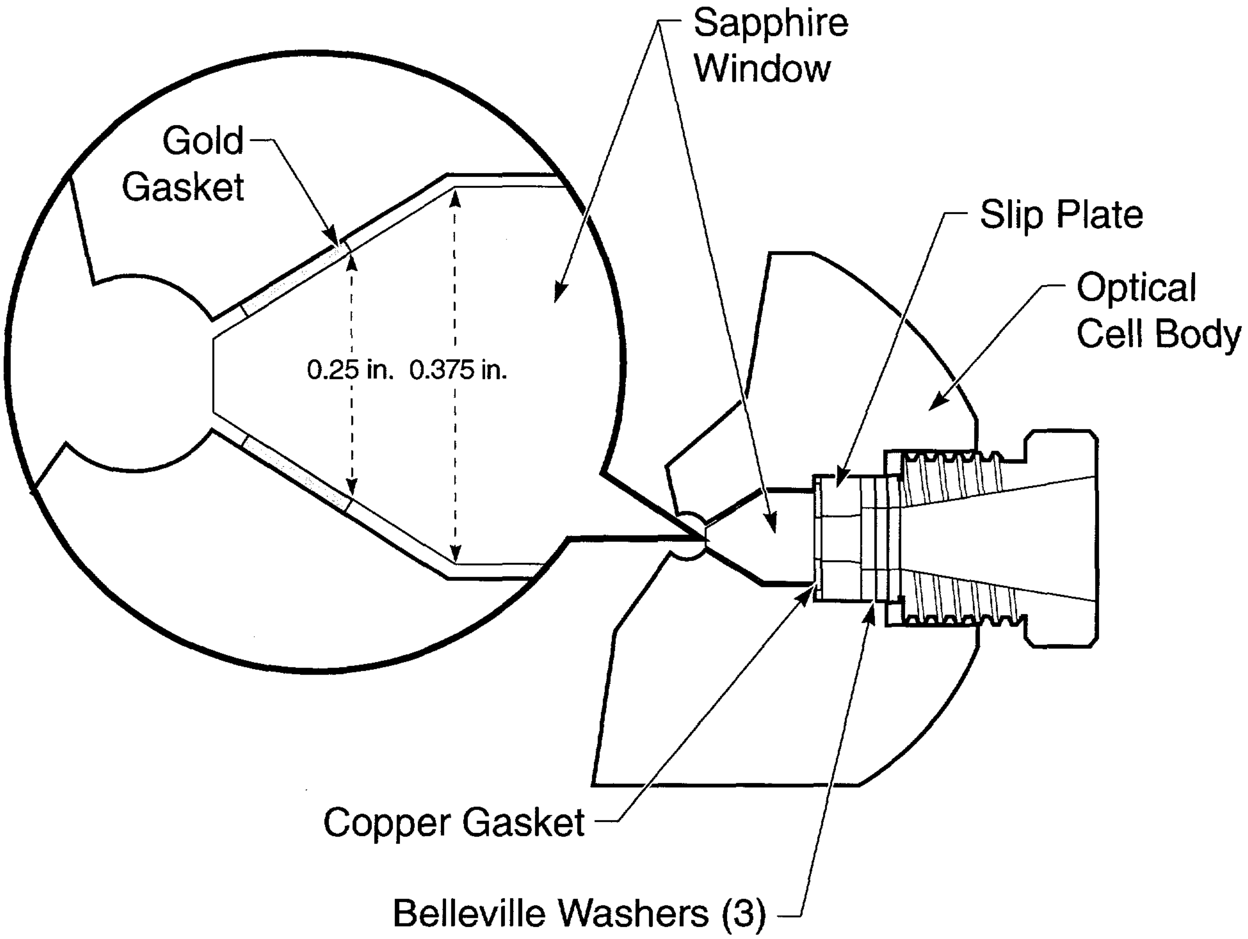

Figure 2. Detail of the flow optical cell window seal and Belleville washer spring assembly.

Three Belleville washers, Fig. 3, serve as a spring to maintain sufficient force on the windows as the cell dimensions change relative to the window during thermal expansion. For the cell (Inconel 625), the coefficient of thermal expansion, μ, is 7.1×10^{-6} in/in-°F at ambient temperature (Mankins and Lamb, 1990) and 7.7×10^{-6} in/in-°F at 1000 °F (Stoloff, 1990). Taking μ for the sapphire window as 4.3×10^{-6} in/in-°F, yields an average $\Delta\mu = 3.1 \times 10^{-6}$ in /in-°F for the mismatch in thermal expansion. If sealed at ambient conditions, a gap between the slip plate and the window develops when heated to a typical operating temperature of 1000 °F, $\Delta T = 925$ °F (500 °C). The gap is given by

$$\Delta l = (\Delta\mu)(\Delta T)l = 0.00125 \text{ in } (0.0032 \text{ cm}), \qquad (1)$$

where l is the length of the window, 0.437 in (1.11 cm). In addition, the diameter of the cell body at the sealing point changes relative to the sapphire diameter by 0.00072 in, requiring the 30° tapered cone sapphire to move by 0.00062 in. Without Belleville washers, the pressure in the cell would push the window away from the gold gasket into the expansion gap and break the seal. To maintain compression on the gold seal, the Belleville washer assembly expands while still balancing the force on the window from the high-pressure fluid inside the cell.

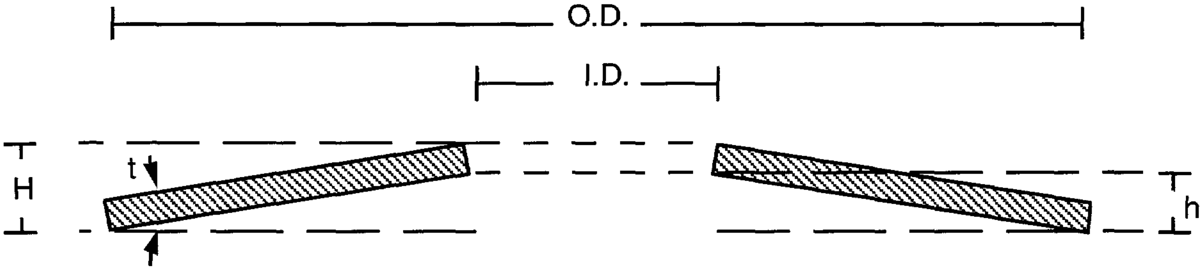

Figure 3. Cross-section of a Belleville washer showing the dimensions referenced in the text.

Belleville washers can be obtained in a wide variety of diameters, force constants, and dish dimensions. The force constant, k_W, of the washers used in our design is approximately 8.0×10^4 lbf/in (1.4×10^7 N/m), with an unloaded dish dimension, h, of 0.005 in (0.012 cm). The washer displacement, d, is defined as the amount h is reduced when the washer is loaded. Washers designed for high loads and small deflections deflect linearly with load. At full compression (flat), the displacement equals the full dish dimension, h, resulting in a force on the washer of $F_W(\max) = 400$ lbf (1770 N) from

$$F_W = k_W\, d. \tag{2}$$

When the cell is heated to operating conditions ($\Delta T = 925$ °F) , the window cavity expands more than the window according to Eqn. 1 permitting the washer to relax 0.00187 in (0.00475 cm) such that $d = 0.0031$ in (0.0079 cm) and $F_W = 248$ lbf (1100 N). The force on the window from the fluid is simply

$$F_f = PA, \tag{3}$$

where P is the pressure in the cell and A is the effective wetted cross sectional area of the window. If the wetted perimeter is conservatively estimated to be located at the OD of the gold gasket, 0.25 in, then A= 0.049 in^2 (0.32 cm^2) and F_f = 196 lbf (860 N) at an operating pressure of 4000 psia (27.6 MPa).

The modulus of elasticity of Belleville washer material, Inconel 718, drops by about 15% at 1000 °F from its ambient value (Stoloff, 1990). The spring constant, k_w, is proportional to this quantity and drops correspondingly to 6.8 x 10^4 lbf/in. Thus, at 1000 °F, F_w is further reduced to 210 lbf from the ambient temperature force of 248 lbf. The load on the spring washer is barely adequate to maintain the seal. However, by placing three washers in series, cupping each other, the force constant of the system can be increased threefold. With this design, h is still 0.005 in (0.013 cm), and F_w (maximum at temperature) becomes 630 lbf (2800 N) providing a large margin of error to preserve the seal.

In practice, the torque on the compression nut, T, is the quantity that is measured, not F_W. The force on the radius of the nut for V-thread screws, P, is

$$P = F_w \, [(l + 2\pi r_o f \sec(d)]/[2\pi r_o - l f \sec(d)] \tag{4}$$

and Pr_o = T (Castelli, 1996). Here, r_o is the nut radius = 0.343 in (0.87 cm), l is the pitch = 0.036 in (0.091 cm), d is the half angle of the V-thread =30°, and f is the coefficient of friction (sliding) = 0.42 (dry hard steel). This yields T= 0.173 (in) F_w.

Using Eqn. 4, the torque on the nut is calculated to be 207 in-lbf (24 N-m) when the washers are fully compressed to F_w =1200 lbf at ambient temperature. This is near the observed 175 in-lbf (20 N-m) where the "feel" on the wrench is that of significant stiffening or "bottoming out." This is adequate agreement considering the approximation in the coefficient of friction taken for dry hard steel instead of dry Inconel 625 which has a slight oxide coating. Without some extensive torque-tension testing, a more accurate value for this specific system is not available. At this point, the three washers are flat and adequate force is applied to the gold gasket to deform it into a conical seal. If the nut is turned beyond this point, torque increases rapidly with very little travel, and the force will crack the sapphire.

After approximately 20 thermal cycles, the windows often begin to leak. Testing after disassembly shows that the ambient-temperature torque on the windows has dropped below 100 in-lbf (12 N-m), caused by creep thinning of the gold gasket that allows the window to sink deeper in its seat. As the window moves, washer displacement, d, and F_W decrease. A leak occurs when creep allows sufficient travel that the washers can no longer balance the fluid pressure. At our typical operating conditions of 3625 psia (25 MPa) and 1000° F, the fluid in the cell exerts a force F_f = 177 lbf (785 N) from Eqn. 3. Setting F_W = 177 lbf (785 N) to exactly balance F_f implies a washer displacement d = 0.0009 in (0.0022 cm) in Eqn. 2 with $k_W = 2.0 \times 10^5$ lbf/in (3.4×10^7 N/m) for three washers. To get to this state, the washer deflection has to decrease 0.0022 in (0.006 cm) from d(initial at 1000 °F) = 0.0031 in (0.0079 cm) to d(final) = 0.0009 in (0.0019 cm). This will occur if the gold gasket thickness decreases from 0.010 in to 0.009 in. At this state, torque on the nut is calculated to be 25 in-lbf (2.8 N-m) at operating temperature, or 70 in-lbf (8.0 N-m) cold. In practice, we observe torques of 40-80 in-lbf (5–10 N-m) on leaking seals, with the gold gaskets, when removed from the cell, measuring 0.004–0.006 in (0.010–0.015 cm) in thickness. The fact that the gaskets are a little thinner than expected suggests that some thinning of the gold occurs during the initial deformation into the seat.

Stirred Optical Cell

Our stirred optical cell (Fig. 4) is a batch-type reactor capable of similar operating conditions as the flow cell, but providing a larger internal volume and larger windows. As its name implies, it is equipped with a mechanical stirring device.

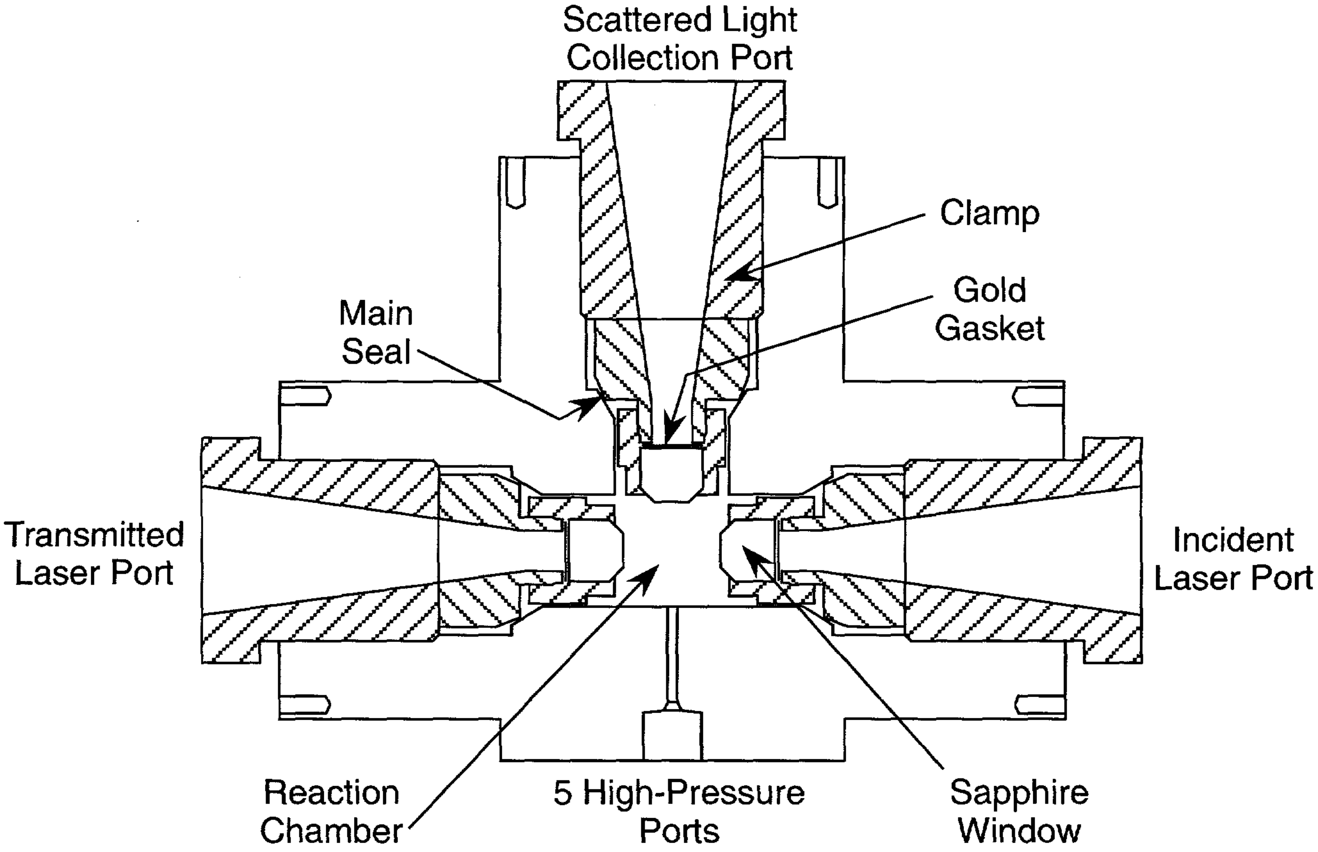

Figure 4. Cross-section schematic of the batch reactor without the stirrer showing the three window assemblies in the cell body.

This reactor uses fluid pressure to seal its 0.56 in (1.42 cm) diameter sapphire windows. As seen in Fig. 5, a window cap holds the window against a gold gasket. Torquing the cap to 75 ft-lbf (100 N-m) deforms the 0.010 in (0.025-cm) gasket sufficiently to provide an initial seal, and subsequent pressurization of the reactor improves the window seal. In addition, there is a gold ring placed between the window cap and the sapphire to evenly distribute stress on the window when it is tightened onto the assembly. The main seal holds the window assembly and is itself sealed by means of slightly mismatched tapers: the main seal is machined to 58° ± 1°, and the reactor body is machined to 61 °± 1°. The line of contact between these two components is a knife-edge, generating high contact pressures as the gland nut is torqued to 500 ft-lbf (650 N-m). The reactor body and main seal are both made of Inconel 718, but the vessel is hardened so that most deformation occurs on the main seal. Thus reconditioning is easily accomplished by retouching the main seal taper on a lathe. Differential thermal expansion is not a problem in this design since the contacting parts are made of the same material. We can routinely operate this cell up to 9000 psia (62.0 MPa) at 1000 °F (540 °C).

The sapphire windows were fabricated with the extraordinary axis in the plane of the window and aligned vertically in the high pressure cell such that the polarization of a probe laser used for Raman spectroscopy and the collected signal were along this axis. This is critical to preserve the polarization of the excitation and scattered signal over a range of pressures and temperatures. Note that many applications using sapphire windows typically call for the extraordinary axis to be located perpendicular to the faces within some small tolerance of several degrees, such that the polarization of the laser can be rotated freely and not emerge from the window elliptically polarized. In the case of our cell, however, the stresses on the window due to compression and elevated temperature cause significant dichroism to be generated in the single crystal windows when oriented this way. In this latter configuration, the stresses remove the uniaxial symmetry and introduce two planes of polarization, located at an arbitrary angle with respect to the vertical polarization of the excitation beam, destroying the planar polarization. By placing the unique crystallographic axis in the plane of the window face, and having its orientation coincide with that of the laser, this problem is eliminated. The stresses in the crystal are insufficient to overcome the significant difference in the index of refraction between the ordinary and extraordinary axes.

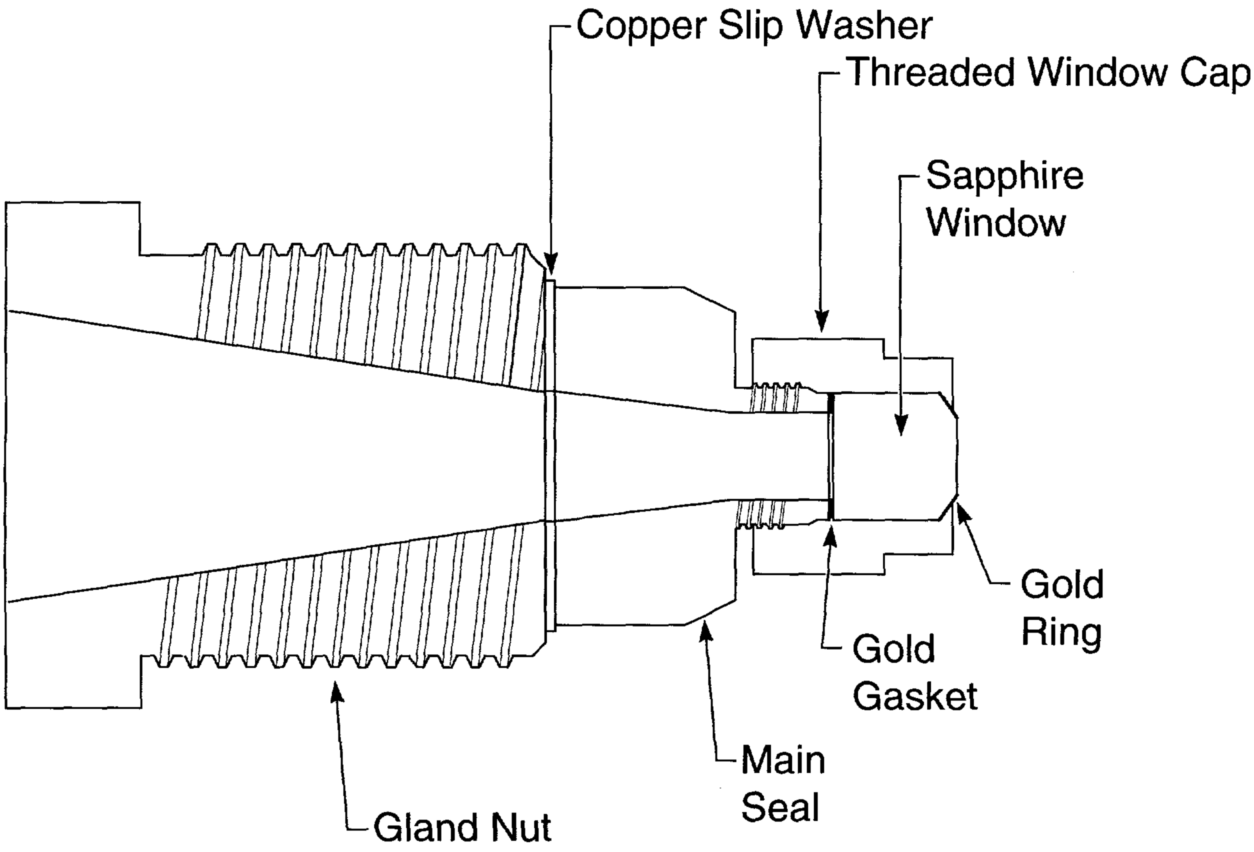

Figure 5. Detailed cross-section of the window assembly identifying the window seal at the gold gasket and the tapered main seal that is loaded by the gland nut.

This stirred optical cell is typically used for reaction kinetics experiments (Steeper et al., 1996) in which a reactant is rapidly injected into a high-density fluid and its reactivity is measured by Raman spectroscopy. Following injection, we have found that unaided mixing occurs on a time scale of several minutes. This is adequate for kinetics experiments with time scales of tens of minutes to hours. But for faster reactions, we require mechanical mixing.

Figure 6 is a schematic of the stirring system. Similar to other mechanically-actuated high-pressure feedthroughs (Costantino, 1991), it is based on a packed valve stem with dimensions similar to Autoclave Engineers, Inc. high-pressure valves. The shaft is driven by a variable speed electric motor and is operated at approximately 200 rpm for 5 seconds during injection in a typical experiment—sufficient time to thoroughly mix the reactor contents. The horseshoe-shaped paddle is designed so that when positioned vertically, it does not interfere with the input laser beam or the scattered light collection.

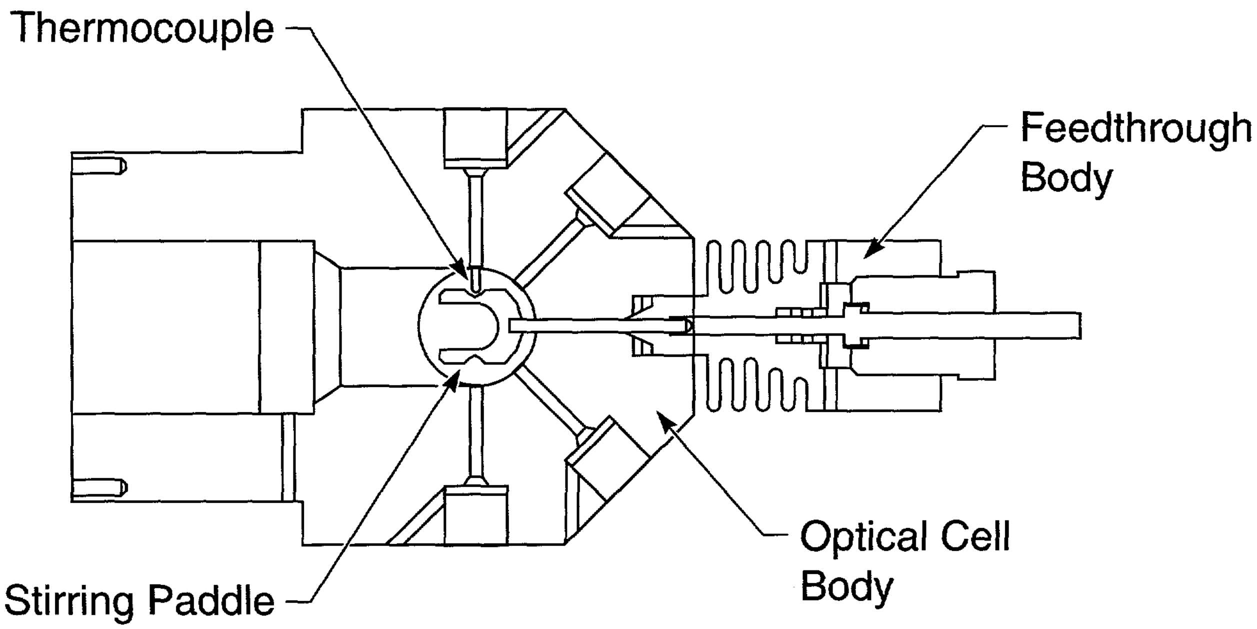

Figure 6. Cross-section of the stirred optical cell showing the horseshoe stirring mechanism installed through the middle high-pressure port.

Conclusions

The design principles for two high-pressure, high-temperature optical cells suitable for research in supercritical fluids are presented and illustrated by example. The smaller design is used in a supercritical water flow reactor. Its single seal depends on spring washers to balance system pressure. The design for larger windows is used in a supercritical water batch reactor. System pressure maintains the window seal, while a second, main seal relies on metal-to-metal, knife-edge contact. By adding a mechanical stirrer, we can use this reactor to optically measure kinetics rates for reactions with time scales as short as tens of seconds.

Acknowledgments

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References

Abdullah, A. H.; Sherman, W. F. *Journal of Physics E: Scientific Instruments* **1980**, 13, 1155-1159.

Bowers, Jr., W. J.; Bean, V. E.; Hurst, W. S. *Rev. Sci. Instrum.* **1995**, 66(2), 1128-1130.

Castelli,V. in *Mark's Standard Handbook for Mechanical Engineers* (F.A. Avallone, T. Baumeister, Eds.) McGraw-Hill, New York, 1996 p. 3-26.

Costantino, M. *Rev. Sci. Instrum.* **1991**, 62(6), 1668-1669.

Hanush, R. G.; Rice, S. F.; Hunter, T. B.; Aiken, J. D. "Operation and Performance of the Supercritical Fluids Reactor" Sandia National Laboratories Report No. SAND96-8203, **1995**.

Mankins, W.L.; Lamb, S.; in ASM International Metals Handbook 10th Ed., **1990**, Vol. 2. pp. 428-445.

Rice, S. F.; Hunter, T. B.; Rydén, Å. C.; Hanush, R. G. *Ind. Eng. Chem. Res.* **1996**, 35(7), 2161-2171.

Schilling, W.; Franck, E. U. *Ber. Bunsenges. Phys. Chem.* **1988**, 92, 631-636.

Steeper, R. R.; Rice, S. F.; Kennedy, I. M.; Aiken, J. D. *J. Phys. Chem.* **1996**, 100, 184-189.

Stoloff, N.S.; in ASM International Metals Handbook 10th Ed., **1990**, Vol. 1, pp. 950 - 977.

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