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Precise pressure control in hydrothermal experiments with cold-seal pressure vessels

S. Michael Sterner*
Bayerisches Geoinstitut, Universität Bayreuth, Postfach 10 12 51, 95440 Bayreuth, Germany

Abstract

A simple apparatus is described for precise static or dynamic pressure control in hydrothermal experiments with cold-seal vessels, and its performance is evaluated. The device consists of an auxiliary pressure-vessel furnace assembly, a pressure transducer, and a solid-state controller, configured to respond to deviations between the observed and the desired pressure by adjusting the temperature of the auxiliary station. Performance tests between 2 and 4 kbar revealed that pressure, as monitored by the transducer, could routinely be maintained to within ±0.3 bars of the desired value for durations of at least 16 d.

Introduction

Cold-seal type hydrothermal reaction vessels are used in a variety of geochemical, petrologic, and materials-research applications and allow convenient experimental access to pressures up to ≈7 kbar and temperatures as high as 800–1200 °C, depending on vessel design (Kerrick, 1987). In most cold-seal systems, temperature is monitored with a thermocouple (external or internal) and regulated by an external resistance furnace used in conjunction with a solid-state temperature controller. Pressure is set at the start of the experiment by adjusting the amount of fluid in the vessel and monitored using a bourdon-tube type mechanical gauge or a pressure transducer. Changes in pressure during the experiment that result from slow leaks, H_2 diffusion, or temperature variations in cold parts of the system (i.e., high pressure tubing, connectors, gauges, etc.) are compensated for by using a mechanical pump and isolation valves. Pressure fluctuations, in experiments of a few days' duration, resulting from ambient temperature instabilities in nominally well controlled environments are typically a few tens of bars but may approach 100 bars or more under less ideal circumstances or in the case of leaking or pressurizing with methane. Although deviations of this magnitude are of little consequence in many cold-seal applications, they can become very important in others (e.g., uncertainty in experimental pressure was identified as a principle source of error in density determinations of fluids using synthetic fluid inclusions: Sterner and Bodnar, 1991).

In this paper, a simple apparatus is described for precise pressure control in cold-seal experiments. The idea and the proposed design are elementary; the main impetus for this contribution is to document the precision with which pressure may be routinely controlled using such a device, so that its potential merits in specific applications can be estimated a priori. Apart from reducing the pressure uncertainty in hydrothermal experiments, the proposed apparatus also provides a convenient way to vary the experimental pressure independent of temperature, and vice versa, without constantly attending to the pump and isolation valves.

Pressure control apparatus

System description

A schematic representation of the pressure control apparatus assembled and tested in our laboratory is shown in Figure 1. The device is connected to a rapid-quench, cold-seal pressure vessel. The pressure control apparatus is the portion to the right of the secondary isolation valve (SIV) and consists of an auxiliary cold-seal pressure-vessel furnace assembly, a pressure transducer, and a solid-state controller. During operation, these three components make up a feedback loop, which continually monitors and adjusts the experimental pressure in a manner analogous to the control loop, which regulates the experimental temperature. The process variable (pressure) is measured with the transducer. The controller compares the process variable with a predetermined value stored in its memory (the set point). If the experimental pressure is below the set point, the controller responds by increasing the power to the auxiliary furnace, which, in turn, raises the temperature of the fluid in the auxiliary pressure vessel, causing the pressure to rise; if the pressure is too high, the controller reduces the power to the auxiliary furnace, thereby lowering the pressure.

The system contains two fail-safe devices. First, the controller is equipped with an alarm that is activated if the process variable exceeds a preselected value or if a break in the sensor or input circuit is detected. Second, the maximum temperature allowed for the auxiliary pressure vessel is regulated either by using an independent temperature-sensor alarm circuit or by limiting the max-

* Present address: Battelle, Pacific Northwest Laboratories, Richland, Washington 99352, U.S.A.

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imum output power to the auxiliary furnace (an option available on many controllers).

System performance and discussion

The principle advantages of the proposed apparatus are the long-term pressure stability it affords by filtering out the effects of slow fluctuations in room temperature and minor leaks and the greatly increased precision with which a given pressure condition can be reproduced between experiments. Also, the pressure system may be configured to produce a continuous (slow) change in pressure without manual intervention by using a programmable controller or by supplying the controller with an external set-point signal. The response time of the pressure-control loop is relatively slow; however, it is approximately the same as that of the temperature control loop because both are limited by the thermal hysteresis inherent in the pressure-vessel furnace assembly. Thus, the system responds poorly to rapid changes in pressure, i.e., it would contribute nothing to pressure stability during a rapid quench or severe leak. Additional details about the pressure-control apparatus are given in Figure 1, and results of both static (fixed pressure) and dynamic (variable pressure) tests are summarized below.

Three 16-d experiments were performed at 600 °C (primary pressure-vessel temperature) and 2, 3, and 4 kbar, respectively. In the 3-kbar experiment, two primary pressure vessels were simultaneously controlled—each at 600 °C. Additionally, four 12-d tests were conducted between 300 and 600 °C (primary temperature). During the latter experiments, the pressure was varied slowly from 2 to 3.5 kbar by changing the set point using the programmable option on the controller. In all experiments, the pressure, as measured by the transducer, was maintained within ±0.3 bars of the set point (generally within ±0.2 bars). Independent monitoring of fluctuations in set point through time revealed variations of $< \pm 0.02$ bars. Thus, the precision of the pressure-control apparatus is excellent.

The accuracy of the pressure control and measurement is limited by the calibration and stability of the transducer. Using the equipment available in our laboratory, it was not possible to perform sophisticated tests of the accuracy of the pressure determination. However, the stated reproducibility of the best pressure transducers currently available is approximately ±0.1%, or about ten times larger than the observed precision of the pressure controller. Provided the electronics in the solid-state controller do not interfere with the input signal from the pressure transducer (this was verified for the apparatus in our laboratory), the accuracy with which the pressure can be controlled should be approximately the same as that with which it can be measured (i.e., limited only by the accuracy and stability of the pressure transducer). In this context, it should be noted that certain pressure and temperature recording devices (i.e., strip-chart recorders, etc.) produce electrical interference that can disrupt the control circuit if they share a common sensor. This problem

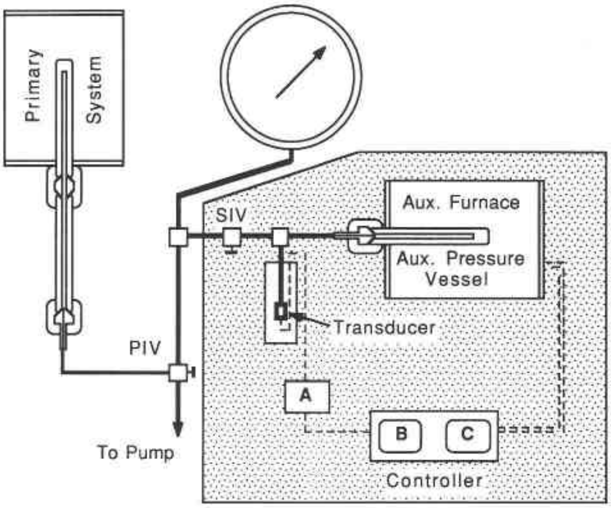

Fig. 1. Schematic illustration of the pressure-control apparatus (shaded region) and the cold-seal system on which it was tested. Total volume of pressurized fluid in system was ≈45 cm³; the inside furnace in the primary pressure vessel was ≈5.8 cm³; the inside furnace in the auxiliary pressure vessel was ≈7.3 cm³. Numbers in parentheses in the following description indicate approximate volumes (cm³) of pressurized fluid contained in each part of the assembly. The pressure-control apparatus: auxiliary pressure vessel (8.0), i.d. = 6.5 mm, o.d. = 38 mm, length = 24 cm; furnace, split-wound; thermocouple, K type; tubing (1.8), high-*P*; i.d. = 1.5 mm, o.d. = 6.5 mm, length = 102 cm; connector (0.1), 100 000 psi; secondary isolation valve (SIV) (0.1), 100 000 psi; pressure transducer (0.24), Wica Tronic model 891.01.2002; transducer power supply (A), Wica Tronic model 907.15.510; system controller (B), Eurotherm model 906S; furnace power supply (C), Eurotherm model 831. Dashed lines are electrical power leads. The cold-seal system: rapid-quench, cold-seal pressure vessel (17.9), i.d. = 6.5 mm, o.d. = 26 mm, length = 19.5 + 3 + 31.5 cm; furnace, concentrically wound, vertical; tubing (0.0), low-*P* (thin solid lines); i.d. = 0.15 mm, o.d. = 1.5 mm, length = 60 cm; tubing (1.1), high-*P* (thick solid lines); i.d. = 1.5 mm, o.d. = 6.5 mm, length = 60 cm; connector (0.1), 100 000 psi; primary isolation valve (PIV) (0.1), 100 000 psi; pressure gauge (15), Heise 16-in., 7000 bars. (The movable rod-and-magnet assembly used to adjust the sample position is not shown.)

can be eliminated by using a retransmitted process-variable signal (a retransmission board is an available option on most solid-state controllers). Also, pressure transducers, particularly the less expensive ones, are sensitive to ambient temperature fluctuations, hence, we thermally insulated the transducer in our experiments with a vacuum-insulated flask. Much greater stability could have been achieved by placing the transducer in a thermostated environment.

The temperature of the auxiliary pressure vessel was set at ≈260 °C at the start of the static pressure tests and varied $< \pm 20$ °C during the experiments. The performance of the pressure-control apparatus was found to degrade rapidly when the temperature of the auxiliary pressure vessel dropped below about 230 °C, although this was partly because the controller's tunable parameters had been optimized over a large range of (higher) temperatures. During the dynamic tests, the temperature of the auxiliary pressure vessel changed almost 600 °C (from ≈250 to ≈830 °C) to induce the 1.5-kbar increase in system pressure.

The control capacity of the apparatus depends on the total volume of fluid in each part of the system and the range of pressures that must be produced during the experiment. For static pressure control, at least two, and, in principle, several, cold-seal stations may be simultaneously regulated (at the same pressure) with a single device. For dynamic pressure experiments, the number of primary reaction vessels that can be simultaneously regulated is limited by the volume of the auxiliary vessel. If large pressure changes are desired, it may be possible to control only one station at a time. Differences between volumes of components in our system (see caption to Fig. 1) and those in other designs must, therefore, be taken into account before the results given here can be generalized to other applications. Although our auxiliary pressure vessel contained no filler rod (Kerrick, 1987), the total volume of pressure medium in it was small; the use of a larger-volume auxiliary vessel would facilitate a greater dynamic pressure range or require a smaller range of temperatures to produce the same pressure extremes.

H_2O was used as the pressure medium in all tests reported here. The relative incompressibility of H_2O at room temperature as compared with other commonly used media (i.e., Ar or gas mixtures) yielded the largest dynamic pressure range for a system of a given geometry. Larger auxiliary vessels may be required to achieve satisfactory results when using other pressure media.

In the absence of leaks, pressure fluctuations in conventional cold-seal systems occur as a result of temperature changes in the portions of the system that are at pressure but not under thermostatic control. The magnitude of the pressure variation caused by a given change in the ambient temperature depends on the compressibilities and the relative volumes of fluid at the experimental (V_{int}) and ambient (V_{ext}) temperatures. For example, at 3 kbar and an experimental temperature of 600 °C, an increase of 5 °C in the ambient temperature causes the pressure to rise about 20 bars if $V_{ext}/V_{int} = 1$, 32 bars if $V_{ext}/V_{int} = 2$, and 60 bars if $V_{ext}/V_{int} = 5$. The ambient temperature dependence increases at higher pressures and at lower experimental temperatures. The above calculations are approximate and assume thermostatic conditions along the entire length of the pressure vessel inside the furnace. In reality, instabilities in experimental temperature and variation of the thermal profile along the length of the vessel through time also contribute to the pressure uncertainty.

The sensitivity of the experimental pressure to changes in ambient temperature can be minimized by keeping the ratio of V_{ext}/V_{int} as small as possible. Unfortunately, minimizing V_{ext}/V_{int} is not always practical—as in the case of the rapid-quench design pressure vessel shown in Figure 1, where $V_{ext}/V_{int} \approx 2$ in the primary vessel alone. The additional volumes of gauges, transducers, pressure lines, and valves further increase the ratio. In a conventional cold-seal system (i.e., one without the large external reservoir), V_{ext}/V_{int} can be significantly reduced by using a small-volume pressure transducer instead of a mechanical gauge or by eliminating the pressure sensor entirely. (A 6-in., 7-kbar bourdon-tube gauge has an internal volume of ≈3.5 cm^3. Volumes of other pressure sensors are given in Figure 1. Although a temperature-compensated gauge displays the correct pressure, the presence of the gauge in the system still causes pressure fluctuations in response to ambient temperature changes.) On the other hand, filler rods, used by many investigators to occupy dead volumes and reduce thermal gradients in cold-seal vessels, significantly increase V_{ext}/V_{int} even when minimal external plumbing is used.

Finally, it should be noted that a controlled-pressure, cold-seal system like that shown in Figure 1 may be constructed using the components from two individual stations. Although the particular controller used here had the advantage of versatility (i.e., input and output ranges that can be scaled by the user, process-variable retransmission, and programmability), it was not fundamentally different from controllers used in many hydrothermal laboratories to regulate temperature. If the milliamp signal from a pressure transducer is converted to millivolts (like the input signal from a thermocouple) by adding a parallel resistor to the input circuit, a conventional temperature controller can also be used to regulate pressure.

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