

An internally heated, rapid-quench, high-pressure vessel

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ABSTRACT

A pressure vessel and furnace system were designed for rapid-quench operation while maintaining the advantages of sample size and hydrostatic loading inherent in an internally heated, Ar-medium vessel (IHPV). The rapid quench is achieved using the quench-wire technique common to atmospheric pressure quench furnaces; the sample capsules fall from their position in the furnace hot spot into room-temperature Ar gas at the bottom of the vessel chamber. The quench rate is several hundred degrees Celsius per second compared to a rate of about 3 °C/s in conventional IHPVs. The system operates at temperatures up to at least 1300 °C and pressures up to 1500 bars, conditions specifically chosen to study solubilities of H₂O, CO₂, and other volatiles in low-viscosity silicate melts that have shown severe quench effects in IHPVs having normal quench rates. Loading and unloading the pressure system is relatively simple and fast.

INTRODUCTION

Many phase equilibrium studies are hampered by the inability to quench the chemical and structural identity of one or more phases existing at the pressure-temperature conditions of the experiment. The problem is most prevalent in carbonate, sulfide, and low-viscosity silicate liquids, and in supercritical fluids. The most obvious quench effects in liquids are the formation of quench crystals or the overgrowth of quench rims on stable crystals. These effects can make it difficult or impossible to determine the chemical composition of the stable liquid. Quench effects in supercritical fluids may cause changes in their bulk composition by precipitation of solids or may cause changes in the abundance of species due to homogeneous reactions. The degree to which a high pressure-temperature assemblage is preserved depends on the quench rate of the experimental apparatus and the properties of the system under study. The quench rate varies widely among the apparatus types commonly used in experimental petrology (Holloway and Wood, 1988). Piston-cylinder and 1-atm quench furnaces have relatively high rates, whereas internally heated and cold-seal pressure vessels have much lower quench rates. The quench rate of cold-seal vessels was dramatically improved by the introduction of rapid-quench systems, first by Rudert et al. (1976), and with recent improvements by Ihinger (1991). Compared with cold-seal vessels, IHPVs offer advantages of higher temperature operation at a given pressure, and generally of larger sample size. However, the slow quench rate of IHPVs has made them unacceptable

for studies such as solubility of H₂O in basaltic liquids because the liquid often forms quench crystals. The formation of quench crystals may change the bulk H₂O content of the quench crystal + glass assemblage representing the stable liquid, and it certainly prevents the use of analytical techniques such as infrared spectroscopy, which rely on the presence of a glassy sample to determine quantitatively dissolved H₂O content. The purpose of this paper is to describe the design and operation of an IHPV that allows quench rates about 2 orders of magnitude greater than those obtainable with conventional designs.

Design objectives

In addition to the primary criterion that the system should obtain the greatest feasible quench rate, several other desired design features were identified: a maximum operating temperature greater than the liquidus of primary basaltic compositions; a stable, isothermal, hot zone longer than the length of the sample capsules; a maximum pressure high enough to achieve the solubility range coverage desired; and, finally, ease of operation.

Exploratory designs were tested in an existing IHPV with a 5-cm inside diameter and a 35-cm working length. A furnace consisting of two independently powered resistance elements had an inside diameter of 1.6 cm. The vessel is operated with its long axis vertical, so the furnace elements are positioned one above the other. The rapid quench modification is described in detail below. It is based on the quench-wire design used in 1-atm quench furnaces (Shepherd et al., 1909; Osborn and

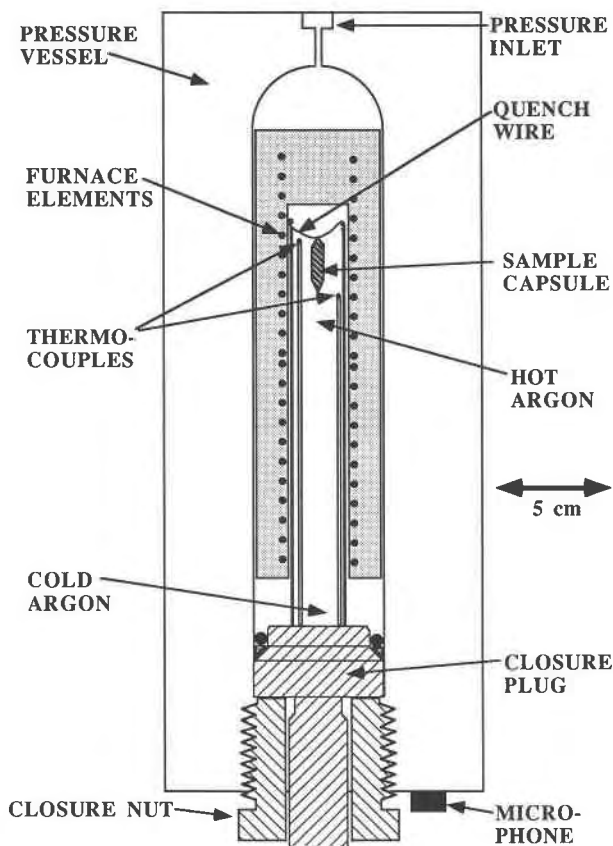


Fig. 1. Schematic cross section of the rapid quench vessel. The ceramic insulators in the furnace interior are not shown here but are shown in Figure 2.

Schairer, 1941), the only difference being the placement of the quench assembly inside the IHPV. The quench occurs when the sample drops from the hot spot of the furnace to the bottom of the vessel, where the Ar was determined to be at room temperature (20–27 °C) by a thermocouple placed at the point where the capsule comes to rest. In this design an open space exists between the sample and the bottom of the vessel to allow the sample to drop. Tests were made at a temperature of 1100 °C from pressures ranging from 500 bars to 5 kbar. It was found that at pressures of up to about 2 kbar the temperature gradient over a 4-cm length was within ± 15 °C and stable. At higher pressures, severe aperiodic temperature oscillations occurred and became larger as pressure increased. The oscillations could not be reduced by changes in the temperature controller settings, nor by changes in the proportion of power between the upper and lower furnace elements. These oscillations were eliminated when the open space below the samples was filled with a solid ceramic rod, and so we infer that they are the result of strong convection of Ar gas in the open column. The conclusion from the preliminary tests was that the rapid quench design would work at pressures below

2 kbar, but that the temperature oscillations precluded operation at higher pressures.

DESIGN

Vessel

An overall schematic of the vessel, furnace, and quench assembly is shown in Figure 1. Because of the upper pressure restriction caused by the temperature oscillations, a 2-kbar operating pressure was chosen. The diameter of the furnace used in the preliminary tests was satisfactory, but we chose a slightly larger inside diameter for the vessel to allow a small increase in the size of the hole below the sample capsules. The vessel (manufactured by the High Pressure Equipment Co.) is a single-end design with an inside diameter of 5.72 cm, a working length of 30 cm, and an outside diameter of 15 cm. It is made of AISI 4340 steel heat treated to 35 on the Rockwell C scale. The vessel was fitted for H₂O cooling by winding Cu tubing with an inside diameter of 0.96 cm on the outside of the vessel immediately after coating the vessel with a 3-mm layer of Al-filled epoxy cement. The vessel was permanently mounted in a vertical position, open end facing down, so that the open end is at a height of about 1.5 m above the floor. The pressure inlet to the vessel is through its closed end.

Closure head

The pressure seal on the closure head is a simple inverted Bridgeman type with a rubber O-ring backed by a stainless steel wedge ring (Holloway, 1971). The closure head contains two ports for furnace power capable of carrying currents of 25 A each and five low-power ports for thermocouples and the quench-wire electrode. All low-power ports consist of a wire onto which a tool steel cone is Ag soldered. The wires are Cu for the quench electrode lead, Pt compensated for one thermocouple lead, and PtRh₁₀ compensated for the other three thermocouple leads. The thermocouple leads and cones are electrically insulated from the head with heat-shrink thermoelastomer plastic tubing. There are three mounting holes for furnace support rods.

Furnace

The furnace is shown schematically in Figure 1. An outer stainless steel tube has an od of 5.7 cm, a length of 23 cm, and a wall thickness of 1.3 mm. The furnace has an id of 2.00 cm. Each of the two windings are about 9 cm in length. The samples are positioned about 1 cm below the boundary between the two windings.

Two winding materials are used, either an Ni alloy with a diameter of 1.02 mm and an approximate composition of Ni 76 wt%, Cr 16, Fe 8, Mn 0.5, Ti 0.35, Al 0.25 (Kanthal A-1), or a PtRh₃₀ alloy with a diameter of 0.5 mm. The Ni alloy works well at temperatures of up to 1200 °C, and the Pt alloy is used at higher temperatures.

The furnace ceramic used depends on the element type: for Ni alloy elements the ceramic is a hydraulic-setting

type of approximately CaSiO_3 composition (Saureisen no. 75), and in the Pt alloy furnaces a castable alumina-based ceramic (Ceramacast 510, Aremco Products) is used.

Thermocouples

Three Pt-PtRh₁₀ thermocouples are used. They are positioned at three different heights in the hot zone of the furnace (in early experiments at 1200 °C up to five sheathed, type K thermocouples were used to determine the optimum position for the samples). The three thermocouples share a common negative lead to minimize the number of leads required. Two-hole thermocouple ceramic insulators (99.9% Al_2O_3) are used to support and insulate the thermocouples electrically.

Quench assembly

The quench assembly is shown schematically in Figure 1, and details of the quench wire and capsule holder are shown in Figure 2. The assembly consists of a set of ceramic pieces with an outside diameter of 1.65 cm (Aremcolox 502-1400, Aremco Products), each containing a central 7.1-mm quenching hole and five 1.6-mm holes for the three thermocouples and two quench-wire electrodes. The quench electrodes are made of 0.7-mm Pt wire. One is grounded to the closure head, and the other connected to the Cu wire lead. The quench wire is isolated from the capsule clamp wire by a thin piece of two-hole thermocouple ceramic. Use of the separator minimizes accidental welding of one end of the quench wire to the capsule clamp wire (which is the most usual cause of a failed quench). The capsule clamp is fabricated from a piece of cast Pt rod and provides an easy mechanism for holding the capsule without damaging it.

OPERATION

Procedure

Setting up an experiment involves hanging the sample capsule on the quench wire, tying the quench wire to the electrodes, and attaching the furnace in place over the quench assembly. The entire furnace and closure-head assembly is then inserted into the vessel. The simple inverted Bridgeman (O-ring) seal allows the closure to be inserted into the vessel by hand.

The experiment is brought to a starting pressure of approximately 60% of the desired pressure before heating. Power is then applied and the temperature increased to the set point over a period of about 20 min. The experiment is terminated by connecting an 80000- μF capacitor charged to about 35 volts to the quench-wire electrodes. This explosively fuses the quench wire, allowing the capsules to fall to the bottom of the quench assembly. A microphone is attached to the bottom exterior of the vessel, and its amplified output allows audio confirmation that the capsule has fallen. The power to the furnace is then switched off, and the furnace allowed to cool to room temperature.

After bleeding the Ar gas to atmospheric pressure, the

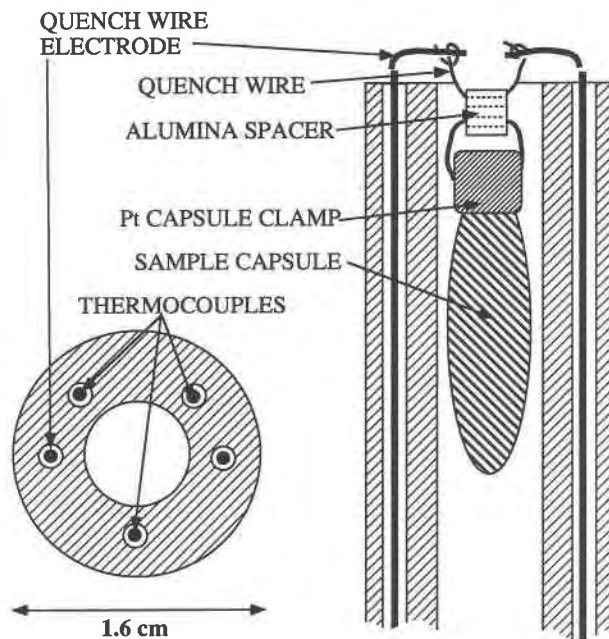


Fig. 2. Plan view and vertical cross section of the quench assembly.

closure nut is removed, and the closure-head and furnace assembly is removed by hand from the vessel. Because of the moderate pressures used, the closure seal components have long lifetimes, the rubber O-rings need replacing after 10–20 experiments, and the stainless steel wedge rings last for up to 100 experiments.

H control

For nominally H-free experiments such as those using fluids in the C-O system (Pawley and Holloway, 1991), pure Ar gas is used as the pressure medium. In samples with H as a component, f_{H_2} is controlled by using premixed H-Ar gas, following Joyce and Holloway (1991). We have noted that the vessel has a memory effect when switching from Ar containing relatively high H_2 to pure Ar; a significant amount of H is observed in the nominally pure Ar during an experiment, as evidenced by high H_2O contents in quenched basaltic glasses. The amount of H in subsequent pure Ar experiments is very low. This suggests that a significant amount of H dissolves in the components of the pressure system exposed to Ar, as noted by Joyce and Holloway (1991).

Furnace conditions

The optimal proportions of power to the windings are 50% upper and 50% lower. The power consumed at 1200 °C ranges from 400 watts at 200 bars to 500 watts at 1500 bars.

The temperature gradients vary among furnaces, ranging from 0 to 20 °C cm^{-1} over a 1-cm sample length. Temperature oscillations are on the order of ± 1 °C.

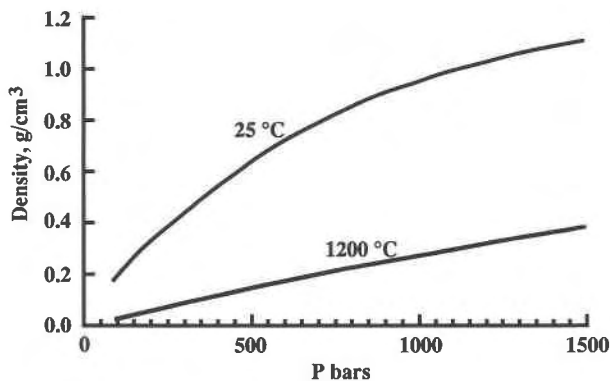


Fig. 3. Variation in the density of Ar as a function of pressure along the 25 and 1200 °C isotherms. Calculated using a Redlich-Kwong equation of state (Holloway, 1987) with a and b parameters of 9.54×10^6 bar cm^6 $\text{deg}^{1/2}$ and 21.6 cm^3 , respectively.

Quench rate

Use of this system results in an isobaric quench in which the capsule drops from a hot region of relatively low Ar density to a cold region of considerably higher Ar density (actually there is a small change in pressure observed when the capsule falls because of the displacement of cold Ar into hotter regions). Figure 3 shows Ar density at 25 and 1200 °C as a function of pressure.

The quench rate in this system is difficult to measure directly. We have observed that hydrous basaltic liquids, which did not quench to glasses in a conventional IHPV, do form excellent glasses in the rapid quench system (Dixon et al., 1991) demonstrating that the quench is faster in the latter system. Another approach is to calculate the quench rate using a conductive cooling model (see Carslaw and Jaeger, 1959, p. 199). We assume that the Ar convects the heat away from the cooling capsule and therefore maintains a constant temperature of about 25 °C at the outer contact of the capsule. We are most interested in the rate of cooling in the temperature interval between the experimental temperature (1200 °C) and the glass transition temperature for the sample. For a liquidus temperature of 1150 °C, the glass transition temperature is about 850–900 °C (Uhlmann and Onorato, 1979), but we have assumed a more conservative value of 700 °C. We can ignore the latent heat of crystallization because the melt is quenching to glass. Also we can neglect the effect of cooling the outer Pt capsule because the thermal diffusivity for Pt (0.25 cm/s) is much greater than

that for silicate melts (0.01 cm/s). With these values, the time needed for the center of a cylinder having a radius of 0.25 cm to reach the glass transition temperature is about 1 s, resulting in a quench rate of about 500 °C/s at the center of the capsule. Though the exact quench rate is a function of time and distance from the capsule wall, we are confident that we have achieved quench rates 2 orders of magnitude faster than those obtained in conventional internally heated pressure vessels.

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