A simple rapid-quench design for cold-seal pressure vessels

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Abstract

A simple rapid-quench design, utilizing conventional cold-seal pressure vessels, operates by flushing the capsule chamber with cold water injected through an axial capillary tube. Compared to a conventional air quench, improved quench rates are gained without the disadvantages associated with other rapid-quench methods (*e.g.* water-bath immersion or water-jacketed tilt mechanisms). The need for a rapid quench is illustrated by quench reactions in experiments with wollastonite-bearing equilibria in H_2O–CO_2 fluids. Upon air quenching, wollastonite reacts with CO_2 to form calcite and (presumably) silica in solution. Quenching experiments involving wollastonite and H_2O–CO_2 fluids indicate that back-reaction during cooling is minimized through use of the new rapid-quench design.

Introduction

Interpretation of hydrothermal experiments can be complicated by the precipitation of undesirable phases during quenching of conventional cold-seal pressure vessels. For example, calcite readily forms during compressed air quenches in experiments involving wollastonite equilibria in H_2O–CO_2 fluids (Kerrick and Ghent, 1980; Johannes, personal communication; Shmulovich, 1977; Ziegenbein and Johannes, 1974). Although rapid quenching of the pressure vessel through immersion into a water bath may alleviate this problem, repeated quenching by this method can shorten vessel life and lead to explosive failure. Use of water-jacketed rapid-quench vessels can be quite successful in reducing quench problems, provided precautions pointed out by Ludington (1978) and Rudert *et al.* (1976) are observed. The present paper describes a new rapid-quench design that utilizes a conventional cold-seal vessel (Tuttle, 1949) through which cool water is injected into the capsule chamber *via* an axial capillary tube; this procedure results in a rapid temperature drop in the immediate vicinity of the capsules. This new design is simple and requires little modification of a cold-seal hydrothermal laboratory.

Rapid-quench mechanism

Figure 1 is a schematic diagram illustrating the rapid-quench design used in this study. In our experiments, the pressure vessel was oriented horizontally to minimize temperature gradients (Boettcher and Kerrick, 1971). Temperatures ($\pm 2°C$) were measured with an internal, inconel-sheathed, chromel–alumel thermocouple which, along with capillary A (Fig. 1), extends through the hollow filler rod to the position of the capsules. Both the thermocouple and capillary A were silver-soldered to the nipple at the top of the T-junction. Valve A is used to isolate the pressure vessel from the main pressure line after final pressure adjustments are completed. Using water as a medium, pressures were generated with an air-driven hydraulic pump (Haskel # DSXHW-903). Pressures (± 20 bars) were monitored with a bourdon-tube gauge for each vessel, calibrated against a factory-calibrated standard gauge.

At the end of an experiment, pressure in the main line (Fig. 1) is equalized to that in the vessel. Valve A is then opened to connect the vessel to the main pressure line. The vessel is then removed from the furnace, placed in a stream of compressed air, and valve B is immediately opened, allowing the hot water in the vessel to exit through the T-junction, capillary B, and bleed line. Cool water, pumped in through capillary A as the hydraulic pump cycles to maintain constant pressure, flows over (and quenches) the capsules (see inset in Fig. 1). A large-volume water reservoir between each vessel and the main pressure line should help reduce momentary pressure drops which occur between each cycle of the hydraulic pump. When the vessel is cool, pumping is stopped
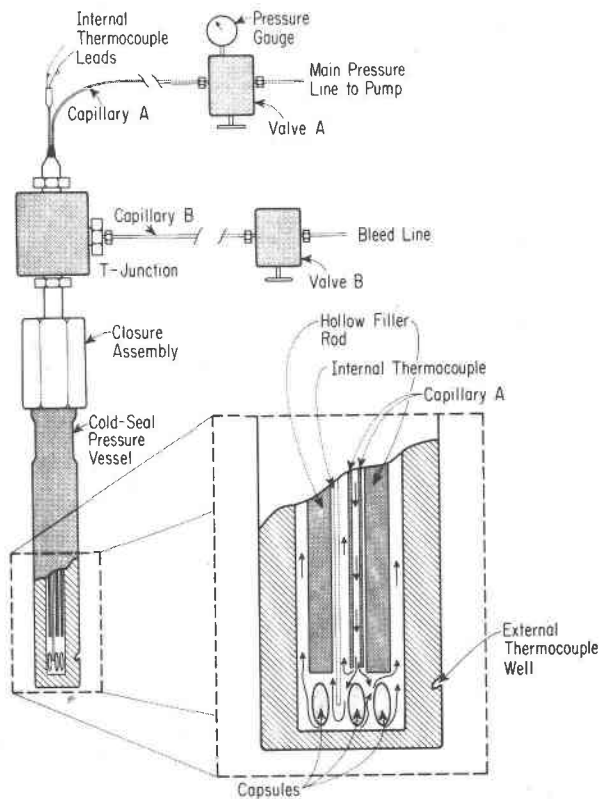
Fig. 1. Schematic diagram of the rapid-quench design. Enlarged inset shows details of hollow filler rod, internal thermocouple, and capillary A, illustrating flow of cool water (arrows) around the capsules.

and the pressure allowed to drop by closing valve A and letting the water flow out of the bleed line.

Experimental results

Quench rates

Quench rates from conventional compressed air quenches are compared to those utilizing the rapid-quench mechanism in Figure 2. The rapid-quench apparatus yields significantly larger temperature drops over the first 40 seconds of the quench. In fact, temperatures recorded with the rapid-quench mechanism averaged 150°C below those of the compressed air quench for the time span of 20–40 seconds. A temperature drop of 400° (from 600° to 200°C) occurs in about two thirds of the time with the rapid-quench design as it does with a compressed air quench. These results indicate that problems with quench reactions may be alleviated (or minimized) by utilizing the rapid-quench apparatus.

Quench reactions

The rapid-quench mechanism was used to reduce quench reactions in experiments dealing with wollastonite in H_2O–CO_2 fluids. As noted in the introduction, several authors have observed that wollastonite reacts with CO_2 during the quench to form calcite and SiO_2. X-ray analysis (Guinier camera) of some experimental charges where wollastonite reacted with CO_2 during the quench yielded patterns of wollastonite and calcite, but not quartz. This phenomenon, which was also observed in experiments by Shmulovich (1977), implies that quartz is not precipitating along with calcite; thus, silica remains in solution, and/or is present as an amorphous phase. SEM photographs of wollastonite from such experimental charges support this hypothesis. Abundant calcite rhombohedrons can be seen on the wollastonite grains; however, quartz is noticeably absent. One of the authors (D. M. Kerrick) has frequently encountered this phenomenon in thin sections of wollastonite-bearing metacarbonate rocks.

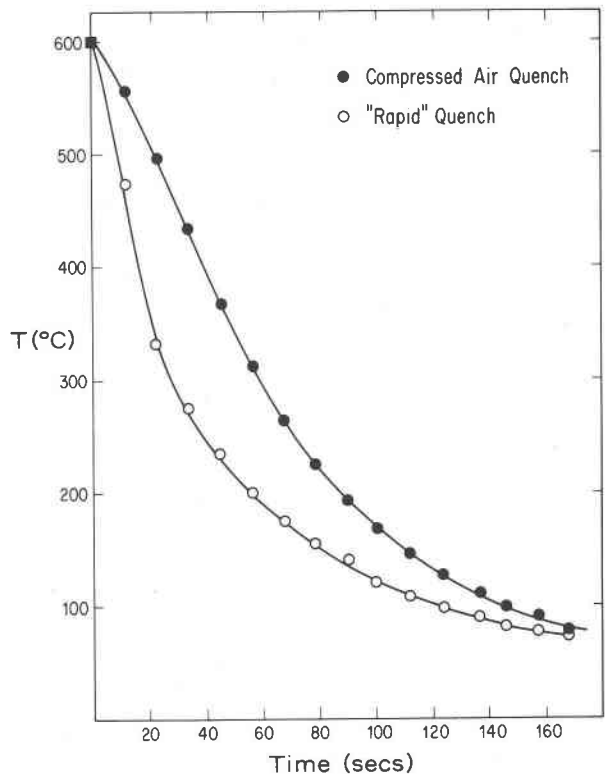Ag_{50}–Pd_{50} capsules were loaded with equal

Fig. 2. Temperature–time plot comparing conventional compressed-air quench to that using the rapid-quench design. Each symbol represents an average of 3 values. Initial temperature was 600°C at a total pressure of 2.0 kbar.
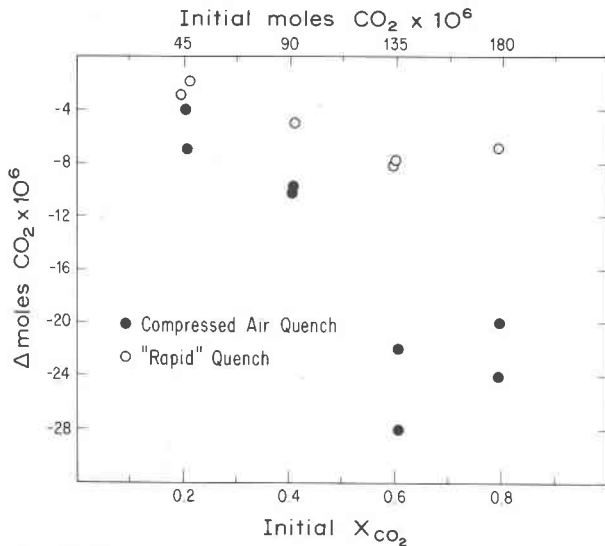
Fig. 3. Change in moles of CO_2 (final moles − initial moles) resulting from the quench reaction: wollastonite + $CO_2 \rightarrow$ calcite + SiO_2. Runs were quenched from the wollastonite + fluid field at 700°C and a total pressure of 1.0 kbar. A value of zero on the ordinate indicates no back-reaction.

yielded smaller CO_2 losses than the compressed air quench. This is especially evident at high initial X_{CO_2} values. For these CO_2-rich compositions, the quench path enters the calcite + quartz stability field at relatively high temperatures, where enhanced reaction kinetics cause greater losses of CO_2. Note, however, that for both quench methods the maximum loss of CO_2 occurs at initial $X_{CO_2} = 0.6$ rather than initial $X_{CO_2} = 0.8$. Apparently, quenching at initial $X_{CO_2} = 0.6$ represents the optimal combination of the rate-enhancing effects of H_2O and elevated temperature. Back-reaction is very limited at initial $X_{CO_2} = 0.2$ and 0.4 (see Fig. 3), which implies that even though the fluids are very water-rich, the temperatures at which the quench path penetrates the calcite + quartz field are too low for extensive back-reaction to occur. Thus, for this reaction, quench products are most likely to form in CO_2-rich fluids during the initial temperature drop of the quench, where the rapid-quench apparatus was shown to be most effective (see Fig. 2).

Discussion

Our rapid-quench device yields faster quench rates than conventional compressed air methods. Although quench rates with this device are not as rapid as water-immersion methods or water-jacketed tilt vessels, this new design does offer some advantages. It avoids the large temperature gradients which can be associated with some water-jacketed rapid-quench vessels (Ludington, 1978; Rudert et al., 1976). In addition, with this new design it is possible to carefully check sample temperatures through use of an internal thermocouple; the design of tilt-mechanism vessels precludes the use of internal thermocouples. Our rapid-quench design should provide a safe alternative to water-immersion methods under normal operating P-T conditions for cold-seal vessels, because compared to water immersion, the relatively small mass of injected water yields smaller overall short-term strain on the vessel. No failures have occurred in approximately two dozen runs with the new design at pressures to 2 kbar and temperatures to 700°C. Actual quench rates with other pressure media such as Ar or CO_2 have not been measured; however, improved quench rates are anticipated with the rapid-quench design compared to compressed air quenches with these pressure media.

amounts of −325 mesh wollastonite (for a chemical analysis of this specimen see Kerrick and Ghent, 1980) and silver oxalate + H_2O for the generation of various initial values of X_{CO_2} (Hunt and Kerrick, 1977; Slaughter et al., 1975). For each capsule, the ratio of wollastonite to fluid was approximately 8:2 (by weight). To eliminate any reaction between the wollastonite and CO_2 which may have occurred during the run-up, the capsules were first subjected to 9–14 day runs at 700°C and 1 kbar—conditions well within the wollastonite stability field (Greenwood, 1967). Some vessels were then quenched with a conventional compressed air stream, while others were cooled with the rapid-quench apparatus. The final composition of the fluid phase was determined by the weight-loss method of Johannes (1969). Initial and final amounts of CO_2 in the capsules should be identical if no quench reaction occurred. However, if wollastonite reacted with CO_2 during the quench, a net loss of CO_2 should be observed. Because pressure, X_{CO_2}, and surface area of wollastonite were kept constant in sets of experiments utilizing the two quenching techniques, the change in moles of CO_2 should provide a good comparison of the degree of back-reaction of the two different quench methods for each set of runs.

Figure 3 shows the results from the quenching experiments. At all initial X_{CO_2} values, some back-reaction occurred, evidenced by the net loss of CO_2 for all data points. However, the rapid-quench technique

As evidenced by experiments on the back-reaction of wollastonite during quenching, the new design does not eliminate all quench problems, but it does reduce them to a more acceptable level.

Acknowledgments

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