Temperature gradients in large cold-seal pressure vessels

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Abstract

Radial and longitudinal temperature gradients within cold-seal pressure vessels can contribute significantly to the total temperature uncertainty in any one experiment and it is important to calibrate such gradients before experiments are undertaken. We have measured temperature gradients in vertically mounted large cold-seal vessels at 1 atm and 1 kbar and in the temperature range 500–800°C. Radial gradients were measured with the vessel at various positions within the furnace by recording the temperature difference between a thermocouple in the internal bore of the vessel and one in a well in the top of the vessel. We find that when the vessel is at a certain position in the furnace, the temperatures read by these two thermocouples are equivalent to within 1°C. The contribution of radial gradients to temperature uncertainty can be thus be substantially minimized if experiments are undertaken with the vessel in this position. Longitudinal gradients of 2.8°C/cm at 500°C and 3°C/cm at 800°C were recorded at 1 kbar. These profiles are significantly steeper than those recorded at 1 atm. Not to calibrate temperature gradients at the experimental conditions or failure to calibrate vessels at all could lead to large temperature uncertainties.

KEYWORDS: cold-seal vessels, temperature gradients, calibration.

Introduction

COLD-SEAL VESSELS are used by experimental petrologists for purposes ranging from phase equilibrium studies in igneous and metamorphic systems through to studies of fluid phase chemistry. They have the advantage of being relatively inexpensive, simple to operate with a large sample volume and true hydrostatic pressure. In the majority of routine cold-seal experiments the temperature that is recorded is not that at the sample position but instead that recorded by a thermocouple placed in an external well positioned either in the top[†] or in the side of the vessel. A major disadvantage is therefore the inaccuracy in temperature measurement. This inaccuracy comes from two major sources. Firstly, the difference in temperature between the thermocouple tip and the sample (or parts of the sample). Secondly, there are temperature gradients along the length of the vessel (and thus capsule) which result mainly from conduction in the vessel and convection in the pressure transmitting fluid medium (Boettcher and Kerrick, 1971). As pointed out by Kerrick (1987), such gradients not only add to the total temperature uncertainty in any experiment but can lead to unwanted chemical fluxes within samples.

There have been few published studies of temperature calibration of cold-seal vessels, particularly of longitudinal gradients, and to the best of the authors' knowledge the work of Boettcher and Kerrick (1971) is the only detailed study dealing specifically with conventional cold-seal vessels.

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† Regardless of orientation we shall refer to the top of the vessel as the end where the sample is positioned and the internal bore of the vessel is closed. Likewise the top of the internal bore and bottom of the well bore is the closed end of the bore.

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Boettcher and Kerrick (1971) investigated radial gradients in vessels by placing one thermocouple in the bore of the vessel and another externally in a well in the side wall of the vessel with its tip in the same longitudinal position as the tip of the internal thermocouple. Their 20.3 cm long vessels were first immersed in the furnace to a maximum depth of 17 cm where readings for the internal and external thermocouples were taken. Further readings were taken at 6.35 mm intervals until the vessel was 5.08 cm from the maximum immersion depth. The experiments were conducted at 1 kbar and 300–400°C and 600–700°C with the vessel in three orientations:- (a) horizontal (b) vertical with the closure nut at the bottom and (c) vertical with the closure nut at the top. They found that for orientations (a) and (c), radial gradients were insignificant if a filler rod was used whilst for orientation (b) radial gradients were similar with or without a filler rod present and were of the order of a 10°C difference between the internal and well thermocouples. However, Boettcher and Kerrick (1971) did not measure longitudinal gradients within the bore of the vessels.

Rudert *et al.* (1976) and Charles and Vidale (1982) examined temperature gradients within rapid-quench cold-seal vessels. For comparative purposes both examined longitudinal gradients within horizontally mounted conventional cold-seal vessels at 2 kbar, although not in detail. Rudert *et al.* (1976) found that at temperatures of 500–750°C gradients were <10°C over 3 cm in 20.3 cm vessels but that temperature differences of up to 8°C existed between the internal thermocouple, located in the middle of the sample position, and the external thermocouple located in a well opposite the top of the sample. At 750°C, Charles and Vidale (1982) measured gradients of <10°C over 4 cm within the bore of 30.5 cm vessels. These results, together with those of Boettcher and Kerrick (1971), clearly show the need to carry out a thorough analysis of temperature profiles within the vessel. Such an analysis should aim to calibrate both radial and longitudinal temperature gradients. Here we present new data on the nature and magnitude of temperature gradients within large cold-seal vessels and discuss the application of these results to cold-seal pressure vessels in general.

Experiments

Equipment

All of the experiments were conducted in conventional-design, large cold-seal pressure vessels manufactured from René No. 41 material. The dimensions of the vessels are 40.64 cm long by 3.81 cm outside diameter with a 9.5 mm diameter bore. In some experiments stainless steel filler rods (6.3 mm O.D. by 3.2 mm I.D.) were used to fill the bore of the vessel except for a 1.7 cm space at the end that would normally be occupied by the sample capsule. The vessel was placed (with the closure nut at the bottom) in a vertically mounted furnace (30.5 cm by 30.5 cm O.D. by 4.5 cm I.D.) wound with Nichrome wire around a Mulite 671 ceramic tube with Al_2O_3 used as the furnace insulating material. The upper end of the furnace tube was closed by a plug of asbestos substitute and the gap between the top of the vessel and the plug tightly packed with silica wool.

Temperature was controlled by a Newtronic Micro 96 solid state controller to within ± 1°C of the setpoint. The $Pt/Rh_{13}Pt_{87}$ control thermocouple was located 15.25 cm from the top of the furnace adjacent to the furnace windings on the outside of the ceramic tube. Temperatures were measured with either ceramic-sheathed $Pt/Rh_{13}Pt_{87}$ (type R) thermocouples calibrated against the melting point of gold or, where stated, a steel-sheathed chromel/alumel (type K) thermocouple manufactured and calibrated by BICC Pyrotenax®. This latter thermocouple was checked against the boiling point of distilled water at 1 atm and recorded a temperature of 100.37°C. The relative precision of the $Pt/Rh_{13}Pt_{87}$ thermocouples was tested by placing each thermocouple in turn (3 in total) in the well thermocouple position when the vessel was in a set position in the furnace and recording the temperature. The temperature differences between the thermocouples was found to be less than 1°C over the temperature range investigated (500–800°C). The locations of the three thermocouples used for measurement during the calibration experiments are shown in Fig. 1*a*. Notice that the top of the bore of the vessel is not directly opposite the bottom of the thermocouple well. This is because experience shows that the pressure vessel would be seriously weakened if the well were to extend to within a wall thickness of the bore. Measurement of temperature was through a Solatron A200 digital voltmeter (DVM). The ambient temperature of the thermocouple lead/DVM junction was measured by a calibrated thermometer and the emf compensated for accordingly. Water was used as the pressure medium and pressure was recorded on a Budenburg Bourdon-tube gauge (type 316). All experiments at pressure were conducted at 1 kbar. The overall experimental set-up is shown in Fig. 1*b*.

Experimental procedures

Before taking the vessel to the pressure and temperature of the experiment it was carefully centered in the furnace such that the axis of the vessel coincided with that of the furnace. Once this had been done the vessel was first pressurized (if

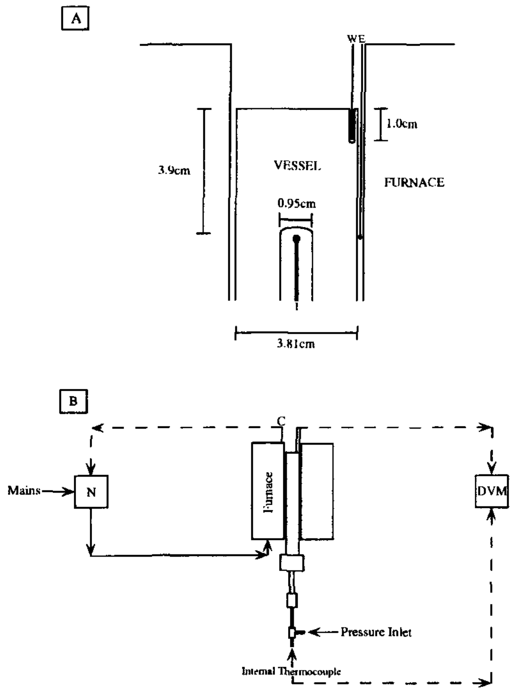

FIG. 1. (*a*) Scale diagram illustrating the positions of the three thermocouples at the start of each experiment. W = well, E = external and I = internal. (*b*) Overall experimental setup. C = control thermocouple, DVM = digital voltmeter and N = Newtronic controller.

necessary) and the furnace heated to the required setpoint.

The first set of experiments were designed to calibrate temperature differences between well and internal thermocouples with the vessel at various positions within the furnace. Experiments were conducted at 1 atm and 1 kbar (with and without filler rods) and at 500, 700 and 800°C as recorded by the control thermocouple. Temperature was measured at three localities within the vessel:- in the well, internally at the top of the bore and externally by a thermocouple placed between the vessel and the inner wall of the furnace with its tip in the same longitudinal position as that of the internal thermocouple. When experiments were conducted at pressure, a steel-sheathed chromel-alumel internal thermocouple was used in place of the ceramic-sheathed $Pt/Rh_{13}Pt_{87}$ at 1 atm. This was silver-soldered into a 'T' junction below the main closure nut assembly.

To begin with the vessel was immersed in the furnace such that the top of the vessel was 2.54 cm from the top of the furnace. After taking the measurements the furnace was moved such that the top of the vessel was now 3.81 cm from the top of the furnace. During the movement great care was taken to ensure the positions of all three thermocouples remained the same relative to the pressure vessel. This incremental movement was repeated until the vessel was 7.62 cm from the top of the furnace. After the furnace had been moved to a new position it was left for at least 90 minutes before the new measurements were taken. Temperature readings at each position were repeated by reversing the movement of the furnace until it was back at its original position with the top of the vessel 2.54 cm from the top of the furnace. In all cases the second set of readings were found to be within 1.5°C of the original readings. Much of this 1.5°C difference could be a result of small uncertainties (1–2 mm) in the repositioning of the furnace.

The second set of experiments measured longitudinal gradients along the bore of the cold-seal vessel at 1 atm (500, 700 and 800°C) and at 1 kbar (500 and 800°C, both with stainless steel filler rods inserted). All of these experiments were conducted with the vessel in its optimum position within the furnace, that is when the temperature read by an internal thermocouple at the top of the bore is the same (to within ± 1°C) as the temperature read by a well thermocouple (determined during the first series of experiments). This is the position that the vessel would be in during routine experiments and is also the same to within ± 1°C of the hotspot when the vessel is pressurized (see below). For the experiments at 1 atm an internal ceramic-sheathed $Pt/Rh_{13}Pt_{87}$ thermocouple was used, held in place by a cork placed in the bottom of the bore. To begin with the thermocouple was positioned at the top of the bore. As in the first series of experiments an external thermocouple was used and the temperature in the well was monitored throughout each experiment. Once the initial readings had been taken two of the three thermocouples (the internal and external) were moved down by 5 mm and further readings were taken. Readings were taken every 5 mm over a total distance of 8–9 cm. Each time the internal thermocouple was moved it was essential to ensure that it remained in an upright position with its tip located in the centre of the bore and not resting on the vessel wall.

Experiments at 1 kbar, 500 and 800°C, used a steel-sheathed chromel/alumel thermocouple (silver-soldered into position as described) to measure the temperature in the bore of the vessel. To check comparability with the 1 atm results the vessel was left unpressurized in the same configuration as used for the 1 atm measurements. The internal temperature at the top of the bore was, however, read with the chromel/alumel thermocouple rather than a Pt/$Rh_{13}Pt_{87}$ thermocouple and found to be within 0.5°C of the latter reading.

Once the vessel had been placed in the optimum position and pressurized to 1 kbar, readings were taken of the internal thermocouple at the top of the bore and of the external thermocouple. These two thermocouples were then moved and readings were taken every 1 cm over a total length of 5 cm. This distance covers the majority of capsule lengths used in cold-seal apparatus. To achieve this, experiments had to be depressurized after each pair of readings and the length of the chromel/alumel thermocouple shortened and re-soldered into the 'T' junction. The vessel and furnace remained in exactly the same position throughout this operation to ensure that thermal conditions were duplicated each time the vessel was repressurized.

Results

Radial gradients

The results of the experiments to calibrate temperature differences between the internal, external and well thermocouples with the vessel at different positions in the furnace are presented in Figs. 2 and 4. Figure 2 shows the results at 1 atm. It can be seen that the recorded internal temperature is highest and the thermal gradients within the internal bore are lowest when the top of the vessel is located 5.08 cm from the top of the furnace. We shall refer to this position as the hotspot.

The most striking and important feature of Fig. 2 is the temperature recorded by the well thermocouple. In all cases the well temperature is lower than the internal and external temperatures when the vessel is positioned 2.54 cm from the top of the furnace. However, as the distance between the top of the vessel and that of the furnace increases, the recorded well temperature becomes equivalent to and exceeds that recorded by the internal thermocouple and, in the case of experiments at 700 and 800°C, also that recorded by the external thermocouple. For example at 700°C (Fig. 2*b*) the well and internal thermocouples record the same temperature (to within 1°C) when the vessel is positioned 3.81 cm from the top of the furnace. This is what we shall term the optimum position. At 500°C this distance is 3.175 cm and at 800°C 4.128 cm. In Fig. 3 we show the vessel at three positions within the furnace and in each case we have sketched on possible isotherms, the positioning of which is based on temperature profiles of the furnace without the vessel and on the data presented in this paper. These diagrams do not take into account whether the bore is filled with air, water, ceramic or metal and also that a different mass of metal is

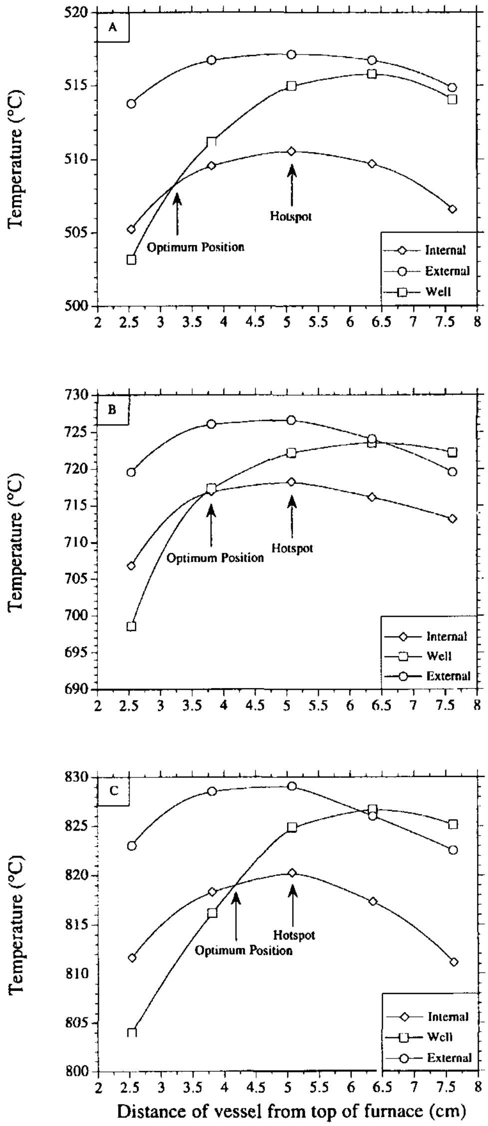

FIG. 2. Results of experiments at 1 atm and (*a*) 500°C, (*b*) 700°C and (*c*) 800°C to calibrate temperature differences between internal, well and external thermocouples. Graphs are shown as temperature, as read by each thermocouple, against distance between the top of the vessel and the top of the furnace. Both the hotspot and optimum position are indicated.

immersed in the furnace at each position and are thus only schematic. However, they are consistent with the thermal profiles that we observe. With reference to the data at 1 atm/500°C (Fig. 2*a*), Fig. 3*a* illustrates the position at which the external temperature > internal temperature > well temperature. This occurs when the vessel is 2.54 cm from the top of the furnace. At 3.175 cm the well temperature is equal to the internal temperature (optimum position) as shown in Fig. 3*b*. With increasing distance to 3.81 cm the temperature of the well becomes greater than that of the internal thermocouple (Fig. 3*c*). The hotspot at 1 atm/500°C is not coincident with the optimum position but occurs when the vessel is 5.08 cm from the top of the furnace as discussed above. In this case we should observe a small rise in temperature (<1°C) down the bore when the longitudinal profile is measured. Data presented below show that this is so. In most other cases the optimum position is very close to the hotspot (e.g. 1 kbar/700°C) and any rise in temperature would be difficult to detect given the size of the increments over which the longitudinal profile is measured.

The results for the experiments at 1 kbar are shown in Fig. 4. As with the 1 atm results, the hotspot in the vessel coincides with the top of the sample when the vessel is located 5.08 cm from the top of the furnace whether or not a filler rod is present. With no filler rod present the optimum position (well T = internal T) is 5.08 cm regardless of temperature (Fig. 4*a,c,e*). When a filler rod is present the optimum position is 5.4 cm at 500°C, 4.45 cm at 700°C and just under 4.45 cm at 800°C (Fig. 4*b,d,f*). The change in the optimum position from one set of experiments to another could result from whether the bore of the vessel is filled with air plus ceramic (1 atm), water (1 kbar, no filler rod present) or water plus metal (1 kbar, filler rod present). It is noticeable that there is rarely more than a 3°C difference between the corresponding well, internal and external thermocouples when the vessel is run with or without a filler rod at 1 kbar. For the equivalent control setting, temperatures recorded in the vessels at 1 kbar are generally higher than those at 1 atm being some 2–3°C higher in the well but up to 7°C higher in the bore where the top of the sample would be located.

To test the variation in thermal conditions between different furnace/vessel assemblies we ran an almost identical vessel/furnace pair (the only difference being that the outer diameter of the furnace is 28 cm rather than 30.5 cm) at 1 kbar/700°C with a filler rod in place and the thermocouples set up as previously described. Temperatures recorded were on average some 10°C higher for any given control setting which is probably a reflection of a small difference in the positioning of the control thermocouple between the two furnaces. However, we found that the temperature at the well position and the temperature at the top of the bore were equivalent to within 0.5°C when the top of the vessel was 4.45 cm from the top of the furnace, in excellent agreement with the results determined above for the original vessel/furnace pair (Fig. 4*d*).

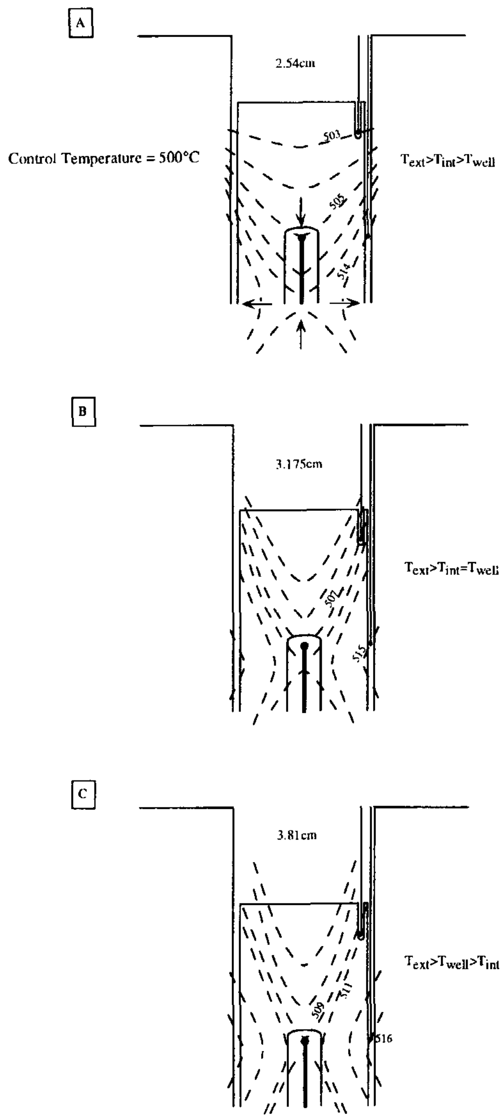

FIG. 3. Schematic isotherms at 1 atm/500°C with the vessel at three positions within the furnace, (*a*) 2.54 cm, (*b*) 3.175 cm and (*c*) 3.81 cm below the top. The temperature in the well is equivalent to that at the top of the internal bore of the vessel in (*b*). Arrows in (*a*) indicate direction of increasing temperature.

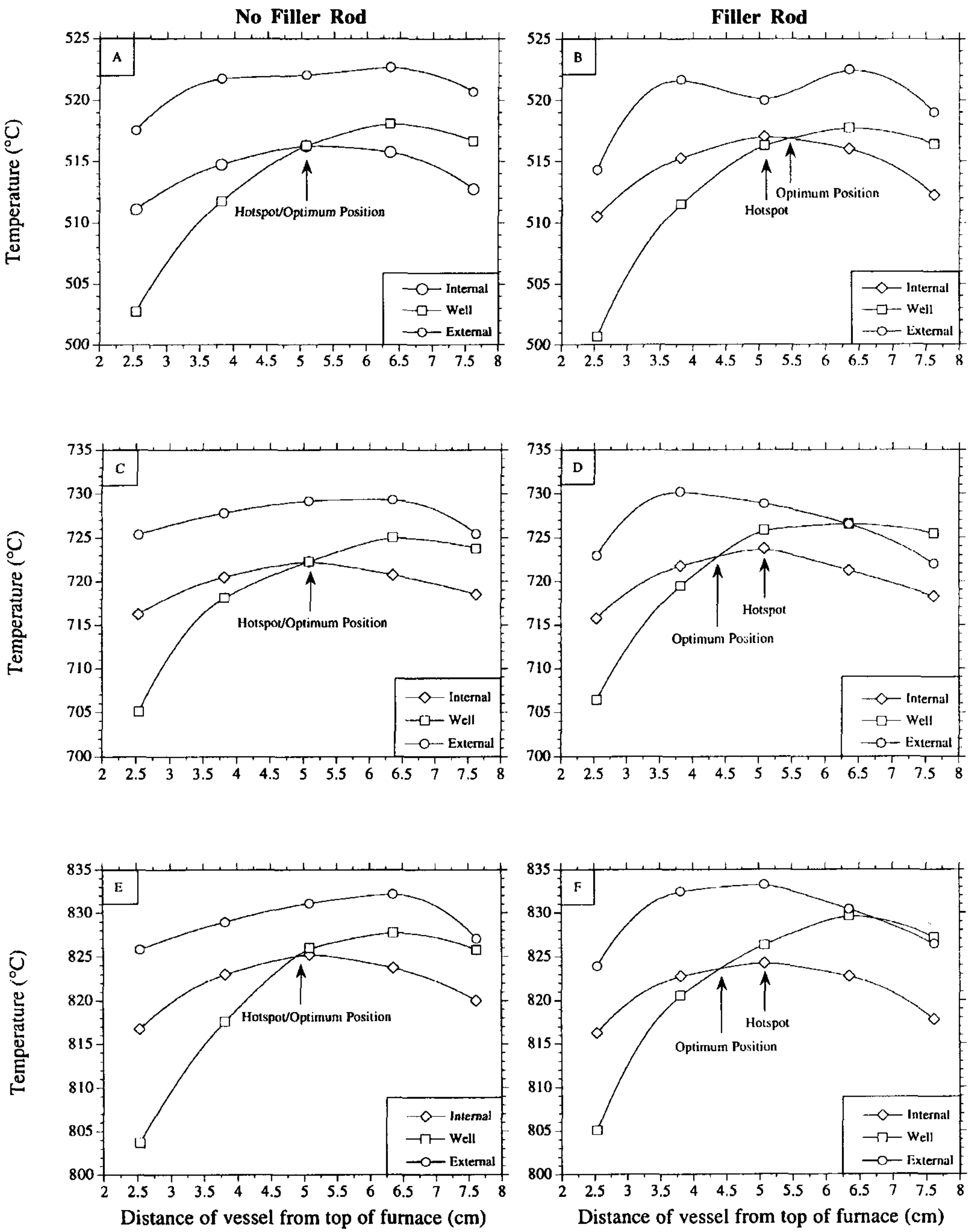

FIG. 4. Results of experiments at 1 kbar and (*a*) (*b*) 500°C, (*c*) (*d*) 700°C and (*e*) (*f*) 800°C to calibrate radial gradients. As for Fig. 2 graphs are shown as temperature, as read by each thermocouple, against distance between the top of the vessel and the top of the furnace. In (*a*), (*c*) and (*e*) a filler rod was present in the bore of the vessel. It can be seen that when a filler rod is absent from the bore, the position of the hotspot is coincident with the optimum position. When a filler rod is present, the temperatures of the hotspot and optimum position (well/top of sample) can be the same to within 1°C.

Longitudinal gradients

The results for the determination of longitudinal gradients at 1 atm are shown in Fig. 5. The internal profile begins at the top of the bore whilst the external profile begins at the top of the vessel. It can be seen that the internal gradient becomes steeper with increasing temperature. For example at 500°C (Fig. 5*a*) the temperature varies by little more than 1°C over the top 3.5 cm of the bore whilst at 800°C (Fig. 5*b*) over the equivalent distance the temperature falls from 818.8°C at the top of the bore to 813.42°C, a difference of 5.38°C. Figure 5 also shows that thermal gradients along the length of the vessel become larger with increasing distance away from the top of the bore. For example at 700°C the gradient is 0.5°C/cm at 1 cm from the top of the bore but increases to 3°C/cm at 5 cm. At all three temperatures, Fig. 5 shows that the internal and external temperature profiles become gradually closer as distance away from the top of the bore increases. This is a result of the fact that the isotherms within the furnace and vessel become progressively flatter and thus radial gradients become less towards the lower end of the vessel. Also shown in Fig. 5 is the position and temperature reading of the control thermocouple which is on the outside of the furnace ceramic. That the radial gradients do become less at this point is supported by readings from both the internal and external thermocouples which are in excellent agreement with the control thermocouple reading.

Results from longitudinal temperature gradient measurements at 1 kbar (filler rod present) are shown in Fig. 6. There is more scatter in the internal profiles compared with the external and 1 atm profiles which is most likely due to small inaccuracies in positioning of the pressure tubing each time the thermocouple was re-soldered. Over the calibrated distance (5 cm), the average temperature gradient is 2.8°C/cm at 500°C (Fig. 6*a*) whilst there is a slight increase to 3°C/cm at 800°C (Fig. 6*b*). Both Figs. 6*a* and 6*b* show that there is a slight increase in the thermal gradient as distance away from the top of the bore increases, although measurements at smaller increments would have to be taken to confirm this. This aside, our data show that at 500°C the gradient is 1.5°C over the first 1 cm increasing to 3°C/cm whilst at 800°C the gradient is 1°C over the first 1 cm increasing to 3.5°C over the remainder of the calibrated distance.

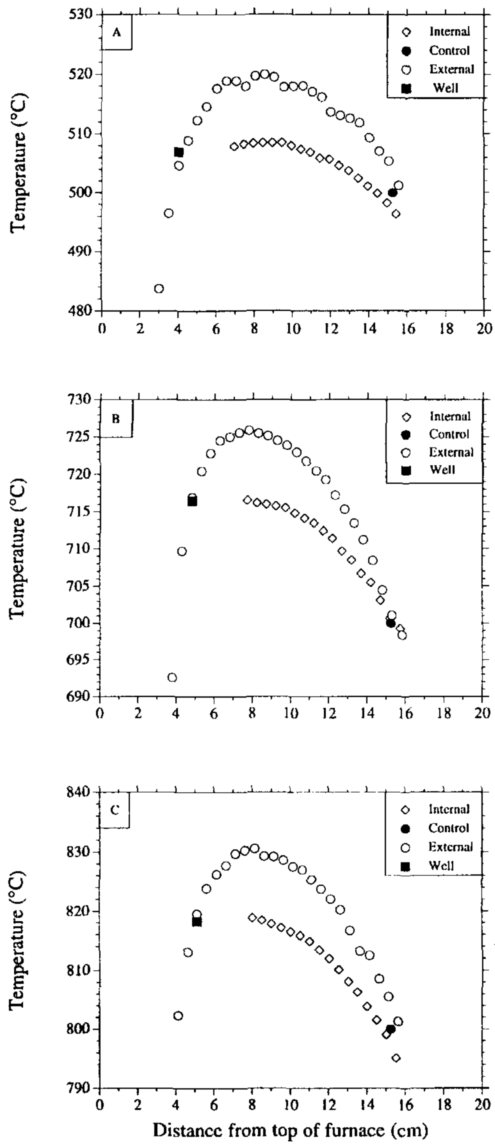

FIG. 5. Longitudinal profiles at 1 atm and (*a*) 500°C, (*b*) 700°C and (*c*) 800°C with the vessel at its optimum position in the furnace. Notice how the gradients become steeper away from the top of the bore and how the two profiles become closer as distance from the top of the furnace increases. The filled circle gives position and temperature of the control thermocouple.

Summary

The two largest contributions to temperature uncertainties in cold-seal vessels are radial and longitudinal gradients. Figures 2 and 4 demonstrate that radial gradients can be significant in vessels. Their contribution to temperature uncertainty can, however, be minimized if calibration is undertaken.

This enables two things to be achieved. Firstly, the hotspot can be located. Secondly, in vessels such as ours where temperature during normal runs is recorded by a well thermocouple and where any internal thermocouple can only be below the sample, one can calibrate temperature differences between the well and the top (or centre) of the sample position. We have shown that an optimum position can be located at which point the well temperature is equivalent to the temperature at the end of the internal bore. When the vessel is under pressure, this position is the same as the hotspot to within 1°C.

Temperature gradients along the length of the capsule also need to be calibrated regardless of whether temperature is recorded internally or externally. We have shown that these gradients are substantial and non-linear at 1 kbar (Fig. 6) and would be responsible for temperature differences of up to 15°C between the top and bottom of a 5 cm long capsule. It must be remembered that these

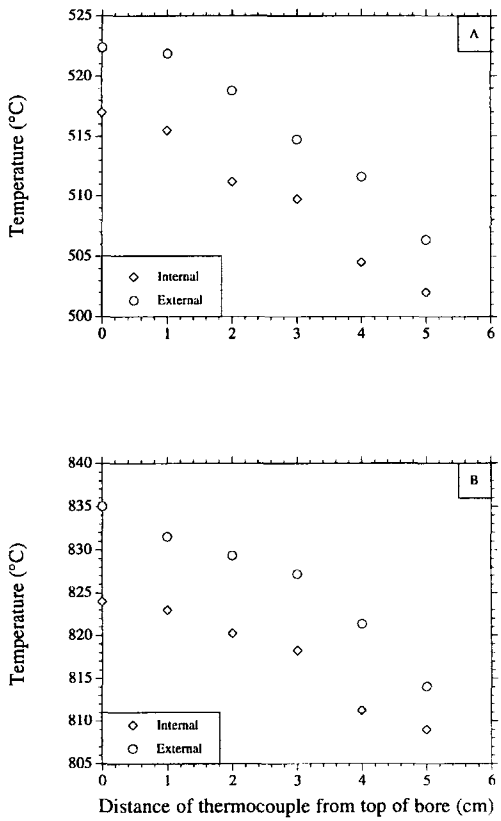

FIG. 6. Longitudinal profiles at I kbar and (*a*) 500°C and (*b*) 800°C with a filler rod present in the internal bore of the vessel. Notice that in both (*a*) and (*b*) the gradient is slightly less over the top 1 cm.

gradients were measured with the top of the sample position located in the hotspot position of the vessel (Fig. 4). Longitudinal temperature gradients could possibly be more severe if the vessel were located at some other position in the furnace. On this basis we would suggest that radial gradients are calibrated prior to longitudinal gradients. Our measured longitudinal gradients at 1 kbar of 2.8°C/cm (500°C) and 3°C/cm (800°C) are in close agreement with the studies of Charles and Vidale (1982) and Rudert *et al.* (1976) who recorded temperature gradients of 3.3°C/cm (500–750°C) and 2.5°C/cm (750°C) respectively. This is encouraging in light of the fact that vessels employed in these studies are substantially smaller than the one used in the present study. Moreover, the studies of Charles and Vidale (1982) and Rudert *et al.* (1976) calibrated vessels that were in a horizontal position in contrast to the vertically positioned vessel that we employed. One could conclude from this that longitudinal gradients better than 2.5–3°C/cm may not be achievable in conventional cold-seal vessels and are irrespective to some extent of size or positioning. The profiles that are shown in Fig. 6 may thus be applicable to other cold-seal apparatus.

The longitudinal profiles determined at 1 kbar (Fig. 6) are significantly steeper than those determined at 1 atm (Fig. 5) and warns against using a 1 atm calibrated profile to assess gradients at pressure. This leads us to one of the main conclusions of our work which had not been addressed by previous workers. Namely that both radial and longitudinal gradients must be calibrated over the range of pressures and temperatures at which one wishes to conduct experiments. Failure to do so could lead to substantial errors in temperature measurement.

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