

## Measurement of Gas Evolution from PUNB Bonded Sand as a Function of Temperature

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### Abstract

The gas evolved from thermal decomposition of the binder can greatly deteriorate the quality of sand castings. Binder gas models used in casting simulations require knowledge of the binder gas mass and molecular weight evolution, but available data are limited. In the present study, the mass and molecular weight of gas evolved from PUNB bonded sand are measured as a function of temperature. Thermogravimetric analysis is used to determine the changes in the binder mass with temperature. The binder is found to be fully pyrolyzed at temperatures above 710°C (1310°F), with its mass reduced by 82%. The binder decomposition does not appear to be a strong function of the heating rate. The evolved volume (and pressure) of the binder gas during heating and cooling is measured using a specially designed quartz manometer with a liquid metal as the working fluid. During heating at 2°C/min (3.6°F/min), the binder gas molecular weight is found to decrease in a complex manner from 375 g/mol at 115°C (239°F) to 33.3 g/mol at 898°C (1648°F). When the binder pyrolysis is complete above 710°C (1310°F), the binder gas is incondensable, but continues to decompose to lower molecular weight compounds until at least 1350°C (2462°F). If the binder is heated to a temperature not exceeding 510°C (950°F), the binder gas partially condenses during subsequent cooling; this condensation occurs below 165°C (329°F).

### 1. Introduction

Resin binders used to make sand molds and cores thermally decompose when subjected to the high temperature conditions in metal casting, and a significant amount of gas is produced when the binders degrade<sup>1</sup>. It is well understood that the evolved binder gas can profoundly influence the quality of metal castings<sup>2-4</sup>. Defects associated with binder gas generation from bonded sand molds and cores, with blowholes and pinholes being the most common<sup>5-9</sup>, result in large amounts of scrap and are of great concern to the casting industry.

In response to these issues, binder gas models have been incorporated into metal casting simulation software in order to better predict the occurrence of gas defects (for example, References 10-12). Crucial elements required in binder gas evolution models are the mass and molecular weight of the evolved gas as a function of temperature. Unfortunately, temperature resolved binder gas mass evolution and molecular weight data corresponding to the conditions experienced during sand casting processes are very limited. The objective of the present study is to measure the mass and molecular weight of the gas evolved during decomposition of phenolic urethane no-bake (PUNB) bonded sand as a function of temperature at conditions similar to those experienced during sand casting. The experimental results will provide improved input data for binder gas evolution models used in casting simulations.

Knowledge of the evolved binder gas composition facilitates the determination of the gas's molecular weight. Early studies by Bates and Scott<sup>13,14</sup>, Bates and Monroe<sup>15</sup>, and Scott *et al.*<sup>16</sup> involved pouring aluminum, gray iron, and steel into molds made using different binder systems

and periodically sampling the gas generated at the mold-metal interface. The gas samples were collected inside evacuated glass tubes and subsequently analyzed by gas chromatography (GC) to determine the volume concentrations (%*V/V*) of hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, and total hydrocarbons (measured as equivalent concentration of methane) in the binder gas. The measured average composition and mixture molecular weight of the gas evolved within two minutes after pouring metal into phenolic urethane cold-box (PUCB) and PUNB bonded sand molds are shown in Table 1. The reported volume concentrations are converted to mass fractions for the present analysis. The molecular weights calculated from the average gas compositions within the first two minutes after pour should approximately correspond to the pouring temperatures of the metal<sup>19</sup>. While the specific chemical formulations employed in PUCB and PUNB binder systems are different, these binder systems are based on the same urethane bonding chemistry<sup>17,18</sup>. This allows the composition and molecular weight of the gas evolved from PUCB and PUNB bonded sand to be reasonably compared.

The results in Table 1 show that the binder gas generated during pouring of the gray iron and steel castings was mostly comprised of carbon monoxide and carbon dioxide, had varying amounts of nitrogen and hydrocarbons, and low amounts of hydrogen and oxygen. The binder gas from the aluminum castings, poured at significantly lower temperatures than the gray iron and steel castings, was comprised almost entirely of oxygen and nitrogen. This indicates that the evolution of binder gas within the first two minutes after pouring the aluminum castings was insufficient to replace the air atmosphere originally in the molds. The hydrogen, carbon monoxide, carbon dioxide, and hydrocarbons evolve primarily at higher temperatures. It is also possible that the binder gas experienced some condensation before it escaped the mold and was collected, making the measured composition not entirely reflective of the actual binder gas composition. In addition, the binder gas samples had the opportunity to cool inside the collection tubes prior to injection of the samples into the gas chromatograph, which can also cause some binder gas to condense before it is analyzed. Regardless of these issues, the molecular weight data calculated from the data in References [13-16] are useful for comparison against the present molecular weight measurements.

\*TABLE 1\*

More recently, McKinley *et al.*<sup>20</sup> (with detailed information and analysis available in the work of Lytle<sup>21</sup>) performed flash pyrolysis of 1.5% PUCB bonded sand and used gas chromatography-mass spectroscopy (GC-MS) to analyze the evolved binder gas. Small samples of PUCB bonded sand were rapidly heated to 500°C (932°F), 700°C (1292°F), and 900°C (1652°F) under a helium atmosphere and held at these temperatures for various periods of time. The pyrolysis products were swept directly into the gas chromatograph, and gas species ranging from 10 g/mol to 425 g/mol were detected by the mass spectrometer. The mass fractions of the primary components emitted from the PUCB bonded sand during 20 seconds of pyrolysis at 700°C (1292°F) and 900°C (1652°F) and the mixture molecular weights calculated from the composition data are shown in Table 2.

The components in Table 2 comprise more than 99% of the measured gas species at each temperature, with the remaining gases being high molecular weight compounds. None of the components listed in Table 2 were detected during pyrolysis at 500°C (932°F), however the molecular weight of the gas mixture evolved at 500°C (932°F) was calculated to be 137 g/mol. It can be seen from Table 2 that, besides carbon monoxide, the major species evolved are

hydrocarbons. In addition, the binder gas composition experiences significant changes between 700°C (1292°F) and 900°C (1652°F). Reference 21 did not detect any oxygen or nitrogen in the binder gas. This further supports the conclusion that the nitrogen and oxygen measured in References 13-16 during all casting experiments were from the residual air in the mold. The significant hydrocarbon content at 700°C (1292°F) reported by Reference 21 also contradicts the results of References 13-16 for aluminum poured at 750°C (1382°F). Regardless of such measurement discrepancies, the detailed composition data from References 20 and 21 currently provide the only means to directly obtain reliable binder gas molecular weight data at various temperatures.

\*TABLE 2\*

Even though coupling GC with any one of the many types of gas detectors provides the means to analytically determine the binder gas composition and molecular weight, this technique is not well suited to generate the magnitude of temperature resolved molecular weight data required in binder gas models. The gas components evolved from bonded sand will freely mix together throughout the casting process, and Reference 20 acknowledges that the evolved binder gas components will interact with one another and may combine to form new compounds. This means that the gas species separation and thermal programming required for thorough GC analysis deviates from the conditions experienced during actual casting processes. Furthermore, binder gas condensation during the measurements must be prevented. In addition to these experimental problems, the gas composition analysis procedure is quite complex and the associated equipment costs are high. Therefore, determination of the binder gas molecular weight as a function of temperature from additional binder gas composition measurements is impractical.

An alternative method for determining the binder gas mixture molecular weight is to use the ideal gas law in conjunction with measurements of the evolved binder gas mass, volume, and pressure as a function of temperature. In this respect, it is important that the bonded sand sample and the gas are at a uniform temperature and that the heating rates are consistent among the various measurements. Thermogravimetric analysis (TGA) of bonded sand facilitates determination of the binder gas mass evolution as a function of temperature during controlled heating. Unfortunately, previous experimental techniques for measuring the volume and pressure of gas evolved from bonded sand (for example, References 15 and 22-25) are unsuitable for determination of the binder gas molecular weight as a function of temperature. Previous techniques do not ensure a sufficiently uniform temperature, do not fully prevent condensation of the binder gas, do not allow measurements of the gas volume, pressure and temperature to be performed on the same volume of evolved gas, and provide no means for controlling the heating rates of the bonded sand and binder gas during the experiments. Therefore, it is necessary to develop new techniques for measuring the volume, pressure, and temperature of gas evolved from bonded sand in order to determine the binder gas molecular weight as a function of temperature.

In the present study, the mass and molecular weight of the binder gas evolved during decomposition of PUNB bonded sand is measured under conditions similar to those experienced during casting. TGA is employed to measure the binder gas mass as a function of temperature at various heating rates. A specially designed quartz manometer, with a liquid metal as the working fluid, is used to measure the binder gas volume, pressure, and temperature during heating and cooling. These gas evolution measurements are combined with the ideal gas law to determine the

binder gas molecular weight as a function of temperature. The bonded sand is immersed in an inert atmosphere during the experiments to ensure that the binder pyrolyzes, which is reflective of the binder decomposition behavior experienced during casting. Unlike in previous studies, the evolved binder gas is contained and measured entirely within the “hot zone” of a furnace. This eliminates the potential for undesired binder gas condensation and issues related to non-localized measurement of the gas volume, pressure, and temperature. The present experimental techniques also allow for continuous measurement of the binder gas molecular weight variations with temperature.

## **2. Experimental Methods**

The following sub-sections describe the preparation of bonded sand specimens, the TGA experimental procedures, the design of the gas measurement apparatus, and the gas measurement procedures. Additional experimental details may be found elsewhere<sup>27</sup>.

### **2.1 PUNB Bonded Sand Preparation**

The PUNB bonded sand specimen composition and preparation procedure follow those employed by Thole and Beckermann<sup>26</sup>. Specimens of bonded sand were prepared from IC55 silica lake sand, black iron oxide (BIO), and a PUNB binder system. The values for the binder content (1.25% of total mass), binder ratio (60:40 ratio of Part 1 to Part 2), catalyst percentage (8% of binder mass), and additives (BIO, 3% of total mass) were selected based on feedback from seven steel foundries.

The sand and BIO components were measured using an Ohaus model PA4101 precision balance, and the binder components were measured using a Denver Instruments model S-403 precision balance. The specimens were prepared by first mixing the BIO into the sand with a KitchenAid<sup>®</sup> standing mixer to ensure uniform particulate distribution. Then the binder was added according to a procedure recommended by the binder manufacturer. Part 1 (Pep Set<sup>®</sup> X1000) and Part 3 (Pep Set<sup>®</sup> 3500) were combined in a paper cup and subsequently added to the particulate mixture. The batch was mixed for 45 seconds, and then vigorously tossed to bring the coated mixture from the bottom of the mixing bowl to the top. The batch was mixed for another 45 seconds and tossed again. After the second toss, Part 2 (Pep Set<sup>®</sup> X2000) was added to the batch and mixed for another 45 seconds, which was followed by a third and final toss. The batch was mixed for a final 45 seconds before dumping it into a box with rectangular patterns. The sand-binder mixture was rammed by hand into each pattern, while making sure the specimens were of uniform density, and allowed to set in the box before stripping. The specimens were stripped when the compacted mixture withstood 20 psi of compressive stress without visible deformation<sup>17</sup>. The pattern box was capable of making six bonded sand blocks, each with a 2.54 cm (1 in) square cross-section and a 22.88 cm (9 in) length. The specimens were immediately sealed in plastic bags to minimize evaporation of the solvents, and the specimens were allowed to cure for at least 24 hours before testing.

### **2.2 Thermogravimetric Analysis**

TGA was performed on PUNB bonded sand using a PerkinElmer model Pyris 1 thermogravimetric analyzer. The PUNB bonded sand blocks were cut down into smaller pieces, which were then shaped into small cylinders using a razor blade. The PUNB bonded sand

samples for TGA had a mass of approximately 55 mg, and the samples were about 0.45 cm (0.177 in) in diameter and 0.25 cm (0.0984 in) in height. The system was purged with argon gas at a flow rate of 25 cm<sup>3</sup>/min (1.526 in<sup>3</sup>/min), with flow rates of 15 cm<sup>3</sup>/min (0.915 in<sup>3</sup>/min) and 10 cm<sup>3</sup>/min (0.610 in<sup>3</sup>/min) to the balance and furnace sheath, respectively. The total flow rate was selected in order to minimize non-isothermality in the samples during testing.

The samples were heated from room temperature to 1000°C (1832°F) at rates of 2°C/min (3.6°F/min), 10°C/min (18°F/min), and 100°C/min (180°F/min). The heating rates for TGA were selected to reflect those experienced in molds and cores during casting processes. The high TGA heating rate of 100°C/min (180°F/min) simulated mold heating rates at a close distance from the mold-metal interface, and the 10°C/min (18°F/min) and 2°C/min (3.6°F/min) TGA heating rates simulated mold heating rates at distances further away from the mold-metal interface. Multiple tests were performed at each heating rate to verify repeatability of the experiments. The TGA machine was allowed to self-clean periodically between tests, and the sample pans were cleaned according to the recommendations of the manufacturer.

The fraction of original binder mass remaining,  $f$ , in a PUNB bonded sand sample as a function of temperature during heating is calculated from

$$f = 1 - \frac{m_s(T^0) - m_s(T)}{m_s^0 \chi / 100} \quad (1)$$

where  $m_s$  is the sample mass measured by the TGA machine at both the initial temperature  $T^0$  and varying temperature  $T$ ,  $m_s^0$  is the initial sample mass measured separately with an analytical balance, and  $\chi$  is the binder content of the bonded sand sample based on total weight percentage. The fraction of original binder mass remaining in bonded sand during heating was interpolated at intervals of 0.1°C (0.18°F) from the corresponding fractions obtained from the TGA measurements. This allowed the measurements of the binder gas mass evolution to be matched with the binder gas volume and pressure measurements (obtained from later gas evolution experiments) at discrete temperature points.

### 2.3 Gas Measurement Apparatus

A schematic of the gas measurement apparatus is shown in Figure 1. The primary component is the gas evolution device (GED), made by fusing quartz cylinders and discs together. Cylinder 1 was sealed at the top and bottom and had two quartz thermocouple wells attached to the top surface. One thermocouple well extended up from the top of cylinder 1, while the other extended 2 cm (0.787 in) from the top surface down into the interior of cylinder 1. Cylinder 1 had an internal diameter of 4 cm (1.575 in) and a height of 3 cm (1.181 in). Cylinder 2 was sealed at the bottom and had an internal diameter of 1.3 cm (0.512 in) and a height of 22 cm (8.661 in). Cylinders 1 and 2 were joined by a third quartz tube, creating a container with a “J-shaped” cavity that acted as a manometer.

\*FIGURE 1\*

A sample of interest was loaded into cylinder 1 of the GED, and the GED was filled with a near-eutectic alloy of gallium (75% by mass) and indium (25% by mass) to a specified initial

height in cylinder 2. Specific filling procedures will be described later. The metal alloy is liquid at room temperature and has low vapor pressures at high temperatures. A displacement boat, which was a quartz tube with the bottom end sealed, was inserted into cylinder 2 such that the boat rested on top of the liquid metal. The displacement boat diameter was 1.15 cm (0.453 in), which allowed for smooth vertical translation of the boat in cylinder 2. The boat's bottom surface was flat on the exterior and spherical on the interior.

The filled GED was placed on top of a square quartz plate, with 10 cm (3.937 in) sides and 0.3 cm (0.118 in) thickness, inside a Neytech model 85P radiative furnace capable of reaching 1100°C (2012°F). Three specially made ceramic-insulated Type K thermocouples were used to measure the furnace temperature (the bead touched the interior of a protective quartz sheath), the glass temperature at the top surface of cylinder 1 (the bead touched the bottom of the glass well), and the interior temperature of the liquid metal in cylinder 1 (the bead touched the bottom of the metal well). A displacement probe was threaded through a small hole in a stabilizer plate (attached to the furnace) and then lowered down to rest on the interior spherical surface of the displacement boat. The displacement probe was a thin quartz rod attached to a thin 2.5 cm (0.984 in) square quartz plate that was covered with black spray paint on the top surface. Argon was supplied to cylinder 2 at a rate of 200 cm<sup>3</sup>/min (12.205 in<sup>3</sup>/min) in order to prevent the liquid metal from oxidizing during the experiments.

A Micro-Epsilon model optoNCDT 1400 laser optical displacement sensor was mounted to a support rig above the furnace, powered by a Topward model 3306D DC power supply, and carefully calibrated to measure the vertical position of the displacement probe's square plate. A square steel tube was placed around the probe to reduce displacement measurement noise caused by disturbances from the surroundings. A fan forced air over the furnace to keep the laser sensor cool during tests, and the temperature near the laser sensor was monitored with a fourth Type K thermocouple.

The experimental data was collected using an IOtech model 3005 Personal DAQ system connected to a laptop via USB. DASyLab<sup>®</sup> software<sup>28</sup> was used to control the data acquisition system. Sampling was performed at a frequency of 10 Hz for all measurements, and this raw data was averaged and recorded at a frequency of 2 Hz.

In a typical experiment, the initial height of the probe was measured by the laser sensor for 5 minutes prior to the start of the test. The furnace was heated at a constant rate and the contents of the GED expanded. This caused the metal height in cylinder 2 to rise. The metal displacement moved the position of the displacement probe, and the probe's vertical translation was detected by the laser sensor. Thus, the total expansion of the GED's contents was measured as a function of temperature. Tests were monitored to ensure that the liquid metal did not overflow in cylinder 2. Cooling data were collected for some tests, and cooling was performed by turning the furnace off and allowing the GED to naturally cool to room temperature. After testing, the GED was removed from the furnace and the GED's contents were emptied. The liquid metal and GED were cleaned using a solution of low molarity hydrochloric acid, and any remaining particulate matter was removed from the liquid metal. The GED was then washed with acetone, dried, and heated in the furnace to volatilize any residual organic matter.

## 2.4 Metal-Only Expansion Tests

It was necessary to determine the expansion behavior of the liquid metal as a function of temperature. The GED was first purged with argon at a rate of 400 cm<sup>3</sup>/min (24.410 in<sup>3</sup>/min) for

10 minutes prior to filling. The argon flowed into cylinder 1 of the GED through a flexible plastic tube. The argon tube was then positioned in cylinder 2, and argon flowed into cylinder 2 throughout the remainder of the filling process. Cylinder 1 was entirely filled with liquid metal by evacuating cylinder 1 while simultaneously injecting the metal into the GED through a second plastic tube. Cylinder 2 was filled to the initial metal height  $h_2^0$  of 3.5 cm (1.378 in). This height was selected to ensure that the metal level in cylinder 2 was initially higher than the metal level in cylinder 1 (creating a slightly positive pressure in cylinder 1). The mass of the empty and filled GED was measured for all experiments using an Ohaus model EP613C precision balance. The metal mass was found by simply subtracting the metal-filled GED mass from the empty GED mass. The displacement boat was then lowered onto the metal surface in cylinder 2, and the filled GED was placed in the furnace. The thermocouples were set in their proper locations and the initial height of the displacement probe was measured by the laser sensor. The furnace was heated at various constant rates ranging from 2°C/min (3.6°F/min) to 15°C/min (27°F/min) while temperature and expansion measurements were obtained. Multiple tests were performed at each heating rate to ensure that the experiments were repeatable. The density of the liquid metal at room temperature (i.e., the initial temperature) was obtained by measuring the mass of metal that filled a calibrated volumetric flask. The metal density at room temperature was measured prior to filling the GED for all experiments.

The effective volumetric expansion coefficient of the liquid metal in the GED,  $\beta_m^{eff}$ , as a function of temperature was calculated from

$$\beta_m^{eff} = \frac{\frac{\pi}{4} D_2^2 \Delta h_2}{(T_m - T_m^0)} \left( \frac{\rho_m^0}{m_m} \right) \quad (2)$$

where  $D_2$  is the diameter of cylinder 2,  $\Delta h_2$  is the measured height change in cylinder 2,  $T_m$  is the measured metal temperature,  $T_m^0$  is the measured initial metal temperature,  $\rho_m^0$  is the density of the liquid metal at room temperature, and  $m_m$  is the mass of liquid metal in the GED.

Additional experiments were carried out to determine the true volumetric expansion coefficient of the liquid metal. A spherical borosilicate bulb was fused to a long and narrow borosilicate tube. The bulb was filled with liquid metal, placed in the furnace, and subjected to a step-heating program that simulated an “infinitely slow” heating rate. The true volumetric expansion coefficient was calculated using the measurements from the metal-only expansion in the bulb and Equation 2 (with  $D_2$  replaced by the bulb tube’s diameter and  $\Delta h_2$  replaced by the metal-only height change measured in the bulb tube).

## 2.5 Pure Gas Expansion Tests

Various volumes of argon and hydrogen gases were heated in the GED in order to observe the nature of the gas expansion in the GED and to determine the accuracy to which the molecular weight of a known gas could be measured. Aside from the insertion of a pure gas sample into the GED, the filling and setup procedure followed that of the metal-only tests. Once the GED was filled with metal, a specified volume of argon or hydrogen gas was injected into cylinder 1 of the apparatus through a flexible plastic tube. Liquid metal was simultaneously extracted from

cylinder 2 to maintain the 3.5 cm (1.378 in) initial height in cylinder 2. Argon gas flowed into cylinder 2 at a rate of 400 cm<sup>3</sup>/min (24.410 in<sup>3</sup>/min) during the injection of the gas sample. Once the GED was filled, the remainder of the setup was carried out as previously described. The furnace was heated at low rates of 2°C/min (3.6°F/min) and 3°C/min (5.4°F/min) while temperature and expansion measurements were obtained. These heating rates were chosen based on the results from the metal-only expansion tests and to ensure reasonable isothermality of the gas and the GED. Multiple tests were performed to confirm the repeatability of the experiments.

The gas temperature  $T$  and initial gas temperature  $T^0$  were not directly measured. Rather, these temperatures were assumed to be the same as the measured metal temperature and measured initial metal temperature, respectively. The reasoning behind this will be discussed later. The measured metal height change in cylinder 2 during heating of the gas samples was used to interpolate the corresponding height change at intervals of 0.1°C (0.18°F) over the measured temperature range. This was done to properly match the pure gas measurements with the metal expansion data, as well as to standardize the pure gas expansion measurements and subsequent calculations as a function of temperature.

The total gas volume,  $V_g$ , as a function of temperature was calculated from

$$V_g = \left( V_{fill}^0 - \frac{m_m}{\rho_m^0} \right) + \left( \frac{\pi D_2^2}{4} \Delta h_2 - \Delta V_m \right) \quad (3)$$

where  $V_{fill}^0$  is the volume contained by the filled GED (up to  $h_2^0$ ) at the initial temperature and  $\Delta V_m$  is the change in volume of the liquid metal. The first term on the right hand side of Equation 3 corresponds to the initial gas volume,  $V_g^0$  (which was verified against the supposed volume of gas injected into the GED), and the second term in Equation 3 corresponds to the change in gas volume,  $\Delta V_g$ , as a function of temperature. The volume change of the liquid metal in the GED corresponding to a given temperature change was determined using<sup>29</sup>

$$\Delta V_m = \beta_m^{eff} \left( \frac{m_m}{\rho_m^0} \right) (T - T^0) \quad (4)$$

As previously stated, the GED acted as a manometer, and the total gas pressure,  $P_g$ , as a function of temperature was calculated from<sup>30</sup>

$$P_g = \rho_m g \Delta H + P_{atm} + P_{probe} \quad (5)$$

where  $\rho_m$  is the density of the liquid metal at a given temperature,  $g$  is gravitational acceleration (9.81 m/s<sup>2</sup> or 32.2 ft/s<sup>2</sup>),  $\Delta H$  is the height difference between the metal surfaces in cylinders 1 and 2,  $P_{atm}$  is atmospheric pressure (101325 Pa), and  $P_{probe}$  is the pressure from the weight of the displacement probe and boat. The density of the liquid metal at a given temperature is given by



$$\rho_m = \frac{\rho_m^0}{1 + \beta_m^{eff}(T - T^0)} \quad (6)$$

The height difference between the metal surfaces in cylinder 1 and 2 was straightforwardly calculated from

$$\Delta H = (h_2^0 - h_1^0) + (\Delta h_2 + \Delta h_1) \quad (7)$$

where  $h_1^0$  is the initial metal height in cylinder 1, and  $\Delta h_1$  is the metal height change in cylinder 1. The metal height change in cylinder 1 of the GED was calculated from

$$\Delta h_1 = \frac{4 \Delta V_g}{\pi D_{1,eff}^2} \quad (8)$$

where  $D_{1,eff}$  is the effective internal diameter of cylinder 1.

The molecular weight of an ideal gas,  $M_g$ , being a single gas or a gas mixture, can be derived from the ideal gas law, i.e.,<sup>31</sup>

$$M_g = \frac{m_g \bar{R} T}{P_g V_g} \quad (9)$$

where  $m_g$  is the total gas mass and  $\bar{R}$  is the universal gas constant (8.314 J/mol/K). Manipulation of Equation 9 gives the ratio of the measured to known molecular weight (or simply the dimensionless molecular weight),  $\varphi$ , of a gas  $i$  as

$$\varphi = \frac{M_g}{M_i} = \left( \frac{P_g^0}{P_g} \right) \left( \frac{V_g^0}{V_g} \right) \left( \frac{T}{T^0} \right) \quad (10)$$

where  $M_i$  is the known molecular weight of the measured gas  $i$ ,  $P_g^0$  is the measured initial gas pressure found by inputting the initial measurement conditions into Equation 5. The accuracy to which the apparatus could measure the molecular weight of a known gas was evaluated through these dimensionless molecular weight measurements.

## 2.6 Binder Gas Evolution Tests

PUNB bonded sand samples for gas expansion measurement were prepared using the same methods as those used for TGA. The bonded sand samples for gas expansion measurement were shaped into small cylinders measuring about 0.8 cm (0.315 in) in diameter and 0.5 cm (0.197 in) in height, and the mass of the samples was approximately 0.2 g. The sample mass was measured with the same device used to measure the empty and filled GED. The small sample size helped minimize non-isothermality in the samples during testing, and multiple samples were used in

each experiment to achieve the desired total initial sample mass. The bonded sand samples had a porosity of about 33%<sup>26</sup>. Therefore, the bonded sand samples were placed in a plastic bag that was continuously flushed with argon gas and stored in the argon-filled bag for at least 24 hours prior to testing. This ensured that only argon gas occupied the empty space inside the bonded sand samples and that pyrolysis of the bonded sand could occur during the tests.

After purging the GED with argon as previously described, a small amount of metal was injected into cylinder 1 in order to create a flat surface of liquid metal at the bottom of cylinder 1. The argon injection tube was withdrawn from the GED, and samples were placed inside the GED such that the samples floated on top of the liquid metal. The argon and metal injection tubes were reinserted into cylinder 2, and the remaining filling and setup were carried out as described for the metal-only tests. The furnace was heated at a rate of 2°C/min (3.6°F/min) while temperature and expansion measurements were obtained. The heating rate was selected based on the results from the pure gas expansion tests (see below). Multiple experiments were performed to obtain the binder gas molecular weight for all temperatures of interest. The total initial sample mass ranged from about 0.4 to 9 g. In addition, measurements were collected as the furnace cooled during some of the tests.

A mixture of argon (from inside the bonded sand samples) and binder gas was present during heating of the PUNB bonded sand samples. The temperatures of the bonded sand samples, argon gas in the bonded sand samples, and evolved binder gas in the GED were not directly measured. These temperatures were assumed to be equivalent to the measured metal temperature. The validity of this assumption will be addressed later in the discussion.

By conservation of mass, the binder mass lost during thermal decomposition is equivalent to the binder gas mass evolved. The mass of gas evolved from the bonded sand samples,  $m_b$ , as a function of temperature is then given by

$$m_b = (1 - f) \left( m_s^0 \frac{\chi}{100} \right) \quad (11)$$

where  $m_s^0$  is the total initial PUNB bonded sand sample mass.

The measured total height change in cylinder 2 was interpolated such that the total gas volume and pressure could be determined at intervals of 0.1°C (0.18°F) over the measured temperature range. The total gas volume and pressure were found using the same methods as described for the pure gas volume and pressure calculations. Summation of the partial pressures of the argon and binder gases and manipulation of Equation 9 yields the binder gas molecular weight,  $M_b$ , as

$$M_b = \frac{m_b \bar{R}}{\left( \frac{P_g V_g}{T} - \frac{P_g^0 V_g^0}{T^0} \right)} \quad (12)$$

The interpolation of the binder gas mass evolution, volume, and pressure measurements at intervals of 0.1°C (0.18°F) allowed the data sets to be matched together when the experiments employed the same heating rate. This allowed Equation 11 to be directly inserted into Equation

12, and the binder gas molecular weight as a function of temperature was straightforwardly calculated.

### 3. Results and Discussion

#### 3.1 Thermogravimetric Analysis

Preliminary TGA experiments were performed to compare the decomposition behavior of PUNB bonded sand (55 mg) and pure IC55 silica sand (55 mg) for a heating rate of 100°C/min (180°F/min) with 25 cm<sup>3</sup>/min (1.526 in<sup>3</sup>/min) of argon gas flow. TGA of the pure sand was of interest to determine whether sand decomposition significantly contributes to gas evolution. Figure 2 shows the measured mass percentage remaining in the bonded sand and pure sand samples as a function of temperature. It can be seen that, as expected, the PUNB bonded sand loses far more mass than the pure sand during heating. The relatively minor mass loss in the pure sand is likely due to trace impurities being volatilized. In addition, Figure 2 shows that the bonded sand and pure sand curves show a small mass increase between about 20°C (68°F) and 115°C (239°F). This unexpected increase in the sample mass at such low temperatures necessitated additional investigation.

TGA was performed on 61 mg of broken quartz rods for a heating rate of 100°C/min (180°F/min) with 25 cm<sup>3</sup>/min (1.526 in<sup>3</sup>/min) of argon gas flow. The quartz rods were not expected to experience any mass change during heating, and the quartz rod sample mass was made to be similar to the mass of the bonded sand and pure sand samples. The measured mass percentage characteristic of the quartz rod samples during heating is superimposed on the bonded sand and pure sand curves in Figure 2. The increase in the measured quartz rod mass from 20°C (68°F) to 115°C (239°F) directly coincides with the increase in the measured bonded sand and pure sand sample masses. The quartz rod mass readings continued to show some variation up to a temperature of 1000°C (1832°F), and additional quartz rod tests at 100°C/min (180°F/min) showed that the variations were reproducible. Abnormal temperature dependent variations in quartz rod mass readings were also obtained at heating rates of 2°C/min (3.6°F/min) and 10°C/min (18°F/min). Subsequently, the quartz rod TGA measurements were used to account for the temperature dependent bias in the TGA machine's mass measurements and to correct the TGA mass measurements for PUNB bonded sand. Additional information regarding the TGA correction with the quartz rod measurements is presented elsewhere<sup>27</sup>.

\*FIGURE 2\*

Other preliminary TGA experiments revealed that increasing the PUNB bonded sand sample mass from 55 mg to 80 mg or 100 mg does not affect the results. Lowering the bonded sand sample mass below 55 mg was not desirable. This is because samples below 55 mg were more likely to have non-homogeneous distribution of the binder within the sand. Additional results for pure PUNB binder (without sand) decomposition and the effects of purge gas flow rate on the TGA measurements are documented elsewhere<sup>27</sup>.

The measured fractions of original binder mass remaining in 55 mg PUNB bonded sand samples heated at rates of 2°C/min (3.6°F/min), 10°C/min (18°F/min), and 100°C/min (180°F/min) with 25 cm<sup>3</sup>/min (1.526 in<sup>3</sup>/min) of argon gas flow are plotted as a function of

temperature in Figure 3. Because of the TGA mass measurement correction, the fractions remain very close to unity until binder decomposition begins at approximately 50°C (122°F). With increasing temperature, the fraction of original binder mass remaining decreases in a complex manner. The curves in Figure 3 are almost horizontal when the decomposition reaction is finished, indicating nearly complete removal of the bias in the TGA machine's mass measurements. The decomposition ceases at a temperature of about 710°C (1310°F) for a heating rate of 2°C/min (3.6°F/min) and at somewhat higher temperatures, approaching 800°C (1472°F), for heating rates of 10°C/min (18°F/min) and 100°C/min (180°F/min). It should be noted that applying the correction changes the fraction of original binder mass remaining by as much as 10% at the maximum decomposition temperature.

\*FIGURE 3\*

It can be seen from Figure 3 that good repeatability in the bonded sand decomposition is achieved at each heating rate. There are increasing delays (in terms of temperature) in the decomposition with increasing heating rate. The binder decomposition reactions can be expected to be time dependent in nature, and an increase in the sample heating rate may then shift the decomposition to higher temperatures. More likely, the delays are simply caused by greater non-isothermality of the bonded sand samples for higher heating rates. For high heating rates, the center of the bonded sand samples can be expected to be somewhat cooler than the surface. This implies that the lower heating rate results better reflect the “true” decomposition behavior at a given temperature. Overall, however, the decomposition behavior is fairly similar between heating rates and, to a first approximation, may be assumed to be independent of the heating rate within the range studied. It was later found that the heating rate of the GED needed to be low in order to ensure reasonable uniformity in temperature during the binder gas molecular weight measurements (see below). In light of this, only the 2°C/min (3.6°F/min) measurements of the fraction of original binder mass remaining were fit to a set of piecewise polynomials for use in the binder gas molecular weight calculations. Additional modifications were made such that the fitted fraction of original binder mass was set to be exactly equal to unity at or below 50°C (122°F) and to 0.1807 (the average binder mass fraction remaining at the conclusion of the decomposition) above 710°C (1310°F). The polynomial fit of the fraction of original binder mass remaining is superimposed on the corresponding measurements in Figure 3, and the equations of the polynomials are listed in Table 3.

\*TABLE 3\*

### 3.2 Metal-Only Expansion Tests

Figure 4 shows the measured metal-only expansion in the GED during heating at constant rates ranging from 2°C/min (3.6°F/min) to 15°C/min (27°F/min). The heating rate was always constant to within ±0.4°C/min (0.7°F/min). There is excellent repeatability in the height change measurements regardless of heating rate. It can be seen that the expansion behavior of the liquid metal is somewhat non-linear up until about 200°C (392°F). The non-linearity can be attributed to non-isothermality of the GED, as measured by the various thermocouples. The height measurement data in Figure 4 was used in Equation 2 to calculate an effective volumetric

expansion coefficient of the liquid metal  $\beta_m^{eff}$  as a function of temperature. This parameter describes the metal expansion behavior specific to the present setup.

\*FIGURE 4\*

The liquid metal volumetric expansion coefficient obtained from the separate metal-only expansion tests employing the borosilicate bulb was found to be constant with respect to temperature. This constant volumetric expansion coefficient of the liquid metal,  $\beta_m^{con}$ , is equal to  $1.12 \times 10^{-4} \text{ 1/}^\circ\text{C}$  ( $6.22 \times 10^{-5} \text{ 1/}^\circ\text{F}$ ). Using this value of  $\beta_m^{con}$ , the predicted metal height change in the GED is plotted alongside the measured metal height change in Figure 4. It can be seen that the measured and predicted height change curves are parallel above  $200^\circ\text{C}$  ( $392^\circ\text{F}$ ), implying that  $\beta_m^{con}$  is indeed the true metal expansion coefficient. However, the actual expansion behavior of the liquid metal, inclusive of any effects due to non-isothermality below  $200^\circ\text{C}$  ( $392^\circ\text{F}$ ), is directly described by  $\beta_m^{eff}$ . Subsequently,  $\beta_m^{eff}$  was interpolated at intervals of  $0.1^\circ\text{C}$  from the GED measurements for use in the pure gas expansion and binder gas evolution calculations. The average density of the liquid metal at room temperature was found to be  $6.297 \text{ g/cm}^3$ .

### 3.3 Pure Gas Expansion Tests

Figure 5 shows the ratio of the measured to known molecular weight of (a) pure argon gas and (b) pure hydrogen gas as a function of temperature during heating at low rates of  $2^\circ\text{C/min}$  ( $3.6^\circ\text{F/min}$ ) and  $3^\circ\text{C/min}$  ( $5.4^\circ\text{F/min}$ ). For both gases and most temperatures, the measured dimensionless molecular weights are within 5% of unity. This indicates that the present experimental setup allows for reasonably accurate gas molecular weight measurements over a large temperature range. The dramatic increase in the dimensionless molecular weight for hydrogen above  $560^\circ\text{C}$  ( $1040^\circ\text{F}$ ) is presumably due to dissolution of hydrogen into the liquid metal.

\*FIGURE 5\*

As previously noted, the true gas temperature was assumed to be equivalent to the measured metal temperature. Figure 5 shows that good agreement between the measured and true gas molecular weights is achieved when the gas temperature is approximated as the measured metal temperature. Additional calculations were performed assuming that the gas temperature was equivalent to the measured glass temperature, but the resulting molecular weights were very inaccurate. Therefore, equating the gas and metal temperatures was deemed acceptable.

Figure 5 shows that the dimensionless molecular weight measurements draw closer to the ideal value of unity with increasing temperature (aside from the hydrogen dissolution) and eventually become essentially constant. This indicates that, as the gas volume increases during heating, the sensitivity and accuracy of the molecular weight measurements increase. This is also reflected by the differences between the curves in Figure 5 (a). The argon molecular weight curves corresponding to lower initial volumes experience greater deviation from unity and are more erratic than the curves corresponding to higher initial volumes for all temperatures. Hence, there is low accuracy in the molecular weight measurements when the change in gas volume is low, and this is especially true at lower temperatures. Therefore, a gas measurement cut-off

criterion is imposed. The gas molecular weight measurements are considered reliable when the portion of height change in cylinder 2 from gas expansion  $\Delta h_2^g$  is greater than or equal to 0.8 cm (0.315 in). The gas cut-offs for the pure gas expansion tests are shown in Figure 5 on each of the dimensionless molecular weight curves. It can be seen that the molecular weight measurements to the right of the gas cut-off are to within better than 5% of the true gas molecular weight. These “trusted” dimensionless molecular weight measurements also have good repeatability.

Figure 5 (a-b) indicates that the greatest deviation of the dimensionless molecular weight from unity for either pure gas occurs between about 50°C (122°F) and 150°C (302°F). The GED was found to be the least isothermal within this temperature range. Non-isothermality in the GED increases the error from equating the gas temperature with the metal temperature, which subsequently increases the error in the molecular weight measurements. Figure 5 (a) shows that the error in the molecular weight measurements decreases with decreasing heating rate. The liquid metal acts as a large thermal mass, and lowering the heating rate reduces the temperature lag of the liquid metal compared to the other contents of the GED. It was concluded from these results that the binder gas tests were best performed at a low heating rate of 2°C/min (3.6°F/min), which would maximize the isothermality of the GED and minimize the error in the molecular weight measurements. Figure 5 (a-b) also shows that dimensionless molecular weight measurements for temperatures lower than 200°C (392°F) are closer to unity for the hydrogen tests compared to those for the argon tests. The initial volumes of hydrogen were somewhat greater than those for argon, which improved the accuracy of the hydrogen molecular weight measurements. In addition, the thermal conductivity of hydrogen is ten times greater than that of argon<sup>32</sup>. This caused the hydrogen to be more isothermal than the argon and further improved the accuracy in the hydrogen molecular weight measurements compared to argon. These findings further support the decisions to impose a gas measurement cut-off criterion and use a low heating rate of 2°C/min (3.6°F/min) for the binder gas evolution tests. Additional analysis of the GED isothermality and other experimental results for the expansion of pure gas in the GED may be found elsewhere<sup>27</sup>.

### 3.4 Binder Gas Evolution Tests

The measured height change as a function of temperature for all PUNB bonded sand tests performed using the GED are plotted in Figure 6. The heating rate was 2°C/min (3.6°F/min), and measurements during cooling (dashed lines) are shown when available. The different curves correspond to different initial bonded sand sample masses. Care must be taken when comparing them, since different initial sample masses result in different volumes of evolved gas. Figure 6 also shows the average metal-only height change for comparison. As expected, decomposition of the PUNB bonded sand generates a significant amount of binder gas and dramatically increases the measured height change. In general, the height change increases monotonically with temperature. At approximately 585°C (1085°F), however, the height change rapidly increases and then suddenly decreases with increasing temperature. This substantial peak in the binder gas volume is reproducible and will be discussed in greater detail later in the discussion. After the height change rapidly decreases, it levels out and then continues to increase monotonically with increasing temperature. The maximum achievable temperature was limited by the maximum allowable height change and the maximum temperature of the furnace. Larger initial sample masses were used to achieve greater height changes and, hence, more accurate molecular weight measurements at low temperatures. Good repeatability in the height change measurements for

similar sample masses can be observed. It can be seen that the height change during cooling decreases linearly for only the 0.637 g and 0.690 g tests. This indicates that the binder gas did not condense during the cooling portions of these tests. The binder gas behavior during cooling will be addressed in greater detail later.

\*FIGURE 6\*

Figure 7 shows the measured binder gas molecular weights for all PUNB bonded sand tests as a function of temperature. The testing conditions and curve coloring correspond to those of Figure 6, and only gas measurements meeting the gas cut-off criterion ( $\Delta h_2^g \geq 0.8$  cm (0.315 in)) are included. It can be seen that during heating, the binder gas molecular weight rapidly decreases from 375 g/mol at 115°C (239°F) to 99.8 g/mol at 200°C (392°F). Then, the molecular weight is approximately constant until 270°C (518°F), after which it decreases at a decreasing rate to 51.6 g/mol at 500°C (932°F). After decreasing slightly further above 500°C (932°F), the binder gas molecular weight steeply decreases from 47.7 g/mol at 550°C (1022°F) to 30.3 g/mol at 585°C (1085°F) and then steeply increases to 47.2 g/mol at 630°C (1166°F). This steep decrease and increase in the binder gas molecular weight measurements corresponds to the peak in the height change measurements mentioned in connection with Fig. 6. The molecular weight remains essentially constant from 630°C (1166°F) to 750°C (1382°F). Recall that no additional binder gas mass is generated at temperatures above 710°C (1310°F). Beyond 750°C (1382°F), the measured binder gas molecular weight gradually decreases to 33.3 g/mol at 898°C (1648°F), indicating that the binder gas components continue to react with each other after the solid binder decomposition is complete.

It can be seen from Figure 7 that the molecular weight measurements have excellent repeatability across the entire temperature range. It is also noteworthy how the molecular weight curves from different experiments agree at 300°C (572°F). The volume of gas evolved from the larger sample masses of bonded sand is large by 300°C (572°F), which ensures that the corresponding binder gas molecular weight measurements at this temperature are accurate. Figure 7 shows that the gas measurement cut-off (i.e., the point where the molecular weight measurements become reliable) when smaller amounts of bonded sand are employed corresponds to temperatures near 300°C (572°F). The good agreement between the binder gas molecular weight measurements at 300°C (572°F) for different amounts of bonded sand proves that the imposed gas measurement cut-off provides an effective means to differentiate between reliable and unreliable binder gas molecular weight measurements.

When the binder gas molecular weight was determined during the cooling portion of the tests, the binder gas mass was assumed to be constant and equal to the value at the test's maximum temperature. This assumption is valid only if the binder gas does not condense during cooling. The binder gas molecular weight cannot be calculated if condensation occurs, since the mass of the gas then decreases in an unknown manner. Figure 7 shows binder gas molecular weight measurements during cooling for those tests that clearly exhibited no binder gas condensation (dashed lines). It can be seen that the binder gas is composed of fixed gases for all tests where the GED was heated to temperatures above about 710°C (1310°F). Interestingly, this temperature corresponds to the one where the decomposition of the bonded sand samples ceases based on the TGA measurements.

\*FIGURE 7\*

The estimated error in the measurement of the binder gas molecular weight during heating was determined through a detailed root-sum-squares error analysis. The primary sources of error in the binder gas molecular weight measurements are shown in Table 4, with average values reported for parameters that are temperature-dependent ( $f$  and  $\beta_m^{eff}$ ). The significance of each primary error source on the molecular weight measurements is related to the total initial PUNB bonded sand sample mass and the measurement temperature. For example, when the bonded sand sample mass is large, more binder gas mass is evolved and the error in the fraction of original binder mass remaining has a greater impact on the molecular weight measurements. The average error in the present binder gas molecular weight measurements between 115°C (239°F) and 898°C (1648°F) is estimated to be 6%.

It was hypothesized that the dramatic inverse peak in the molecular weight measurements at 585°C (1085°F) was due to the effects of hydrogen dissolution into the liquid metal. Figure 5 (b) clearly shows that hydrogen dissolution does not cause any peak in the measured molecular weight. In addition, the composition data shown in Table 1 indicate that hydrogen evolution is insignificant at temperatures around 750°C (1382°F). This further supports the conclusion that the peak in the measured binder gas molecular weight is not due to hydrogen dissolution. Regardless of these facts, the possible issue of hydrogen dissolution and its potential effects on the measured binder gas molecular weight were investigated further. The rate of hydrogen dissolution into the liquid metal was determined from the pure hydrogen molecular weight measurements. As a worst case approximation, it was assumed that binder gas hydrogen dissolves into the liquid metal at the same rate as pure hydrogen. The volume of hydrogen corresponding to the mass of binder gas hydrogen that “hypothetically” dissolved during heating was added back into the binder gas molecular weight calculations. On a worst case basis, hydrogen dissolution changes the binder gas molecular weight measurements above 560°C (1040°F) by a maximum of only 4 g/mol. Since hydrogen is not expected to evolve within the temperature range of the present measurements, the above described hydrogen dissolution correction of the measured binder gas molecular weight was discarded. The details of correction for hydrogen dissolution are described elsewhere<sup>27</sup>.

It was also hypothesized that the inverse peak in the binder gas molecular weight measurements at 585°C (1085°F) was related to a volume change in the silica sand, caused by the increase in thermal expansion accompanying the sand’s  $\alpha$ - $\beta$  phase transformation at 573°C (1063°F)<sup>33</sup>. An additional experiment was performed to evaluate this hypothesis. The expansion of 1.018 g of pure silica sand, 3.8 cm<sup>3</sup> (0.232 in<sup>3</sup>) of argon, and the liquid metal in the GED was measured during heating at a rate of 2°C/min (3.6°F/min). The results show that no peak in the molecular weight measurements occurs when argon and sand are heated in the GED. Additional details are given elsewhere<sup>27</sup>.

It is also possible that the inverse peak in the measured binder gas molecular weight at 585°C (1085°F) is caused by a reaction between the binder gas and the sand. However, it is more likely that the peak simply reflects the actual binder gas evolution behavior. It can be seen from Figure 3 that the fraction of original binder mass remaining does not experience any unusual behavior at 585°C (1085°F). This implies that the inverse peak in the measured binder gas molecular weight may simply be due to a rapid formation of low molecular weight gaseous compounds followed by the formation of higher molecular weight compounds. Recall that the bonded sand samples in the GED were immersed in the evolved binder gas and that the binder gas was not purged during the tests. Therefore, it is possible that the simultaneous presence of binder gas and bonded sand



influences the manner in which additional gas is evolved from the bonded sand or the manner in which the previously evolved binder gas components react with one another during heating at temperatures near 585°C (1085°F).

The measured binder gas behavior during all tests, including both the heating and cooling portions, can also be compared in terms of the moles of binder gas per original binder mass,  $n_b$ . This quantity was calculated from

$$n_b = \frac{m_b/M_b}{m_s^0 \chi/100} = \frac{\left( \frac{P_g V_g}{T} - \frac{P_g^0 V_g^0}{T^0} \right)}{\bar{R} m_s^0 \chi/100} \quad (13)$$

The second equality in Equation (13) indicates that  $n_b$  does not depend on the mass of the binder gas,  $m_b$ , but can be directly calculated from the measured gas volumes, pressures, and temperatures. The moles of binder gas per original binder mass for all binder gas evolution tests are plotted as a function of temperature in Figure 8. Again, the testing conditions and curve coloring correspond to those of Figure 6, and only gas measurements meeting the gas cut-off criterion ( $\Delta h_2^g \geq 0.8$  cm (0.315 in)) are included. It can be seen that, as expected, all heating curves nicely coincide. A significant decrease in the evolved binder gas moles per original binder mass during cooling indicates condensation of the binder gas. As shown in Figure 8, the binder gas does not condense when heated to temperatures above about 710°C (1310°F). However, heating the PUNB bonded sand samples to temperatures not exceeding about 510°C (950°F) results in partial condensation of the binder gas during subsequent cooling. This condensation starts to occur at approximately 165°C (329°F) in all tests.

\*FIGURE 8\*

The present binder gas molecular weight measurements were fit to a set of piecewise polynomials. They were also extrapolated to higher temperatures based on the average molecular weights calculated using the binder gas composition data from References 13-16, and a final polynomial was fit to this extrapolation. The molecular weight polynomial curves and the binder gas molecular weights calculated from the data of References 13-16, 20, and 21 are plotted as a function of temperature in Figure 9. The equations for the binder gas molecular weight polynomials are listed in Table 5. Figure 9 shows that the decreasing behavior of the present molecular weight measurements between 710°C (1310°F) and 898°C (1648°F) is continued by the high temperature molecular weight data calculated from References 13-16. Following the extrapolated curve, it is expected that the binder gas molecular weight continues to decrease with increasing temperature from 898°C (1648°F) to 1350°C (2462°F). The molecular weight can be expected to remain approximately constant at 17.4 g/mol for temperatures above 1350°C (2462°F). In addition, the present measurements are consistent with the molecular weight data calculated from References 20 and 21, aside from the high molecular weight of 137 g/mol at 500°C (932°F) that appears to be an outlier.

\*FIGURE 9\*

\*TABLE 5\*

The measured variation in the binder gas molecular weight with temperature reflects the binder's thermal degradation mechanisms during heating. Giese *et al.*<sup>34</sup> used differential scanning calorimetry (DSC) to measure the energy released from pure PUNB binder samples (60:40 ratio of Part 1 to Part 2) during heating at a rate of 10°C/min (18°F/min). The various peaks in the DSC curve were associated with specific physical or chemical changes in the binder. Figure 9 shows a portion of the solid binder's thermal degradation mechanisms superimposed on the fit of the binder gas molecular weight measurements. The high molecular weights measured at temperatures below 200°C (392°F) are likely from vaporized solvents. The breaking of the binder's urethane bonds corresponds to the plateau in the gas molecular weight between 200°C (392°F) and 280°C (536°F). The breakdown of the binder to polymer aromatics coincides with the decrease in the binder gas molecular weight between 280°C (536°F) and 400°C (752°F). The binder's thermal degradation mechanisms above 400°C (752°F) are undetermined.

#### 4. Conclusions

The present measurements reveal the complex nature of the gas evolution from PUNB bonded sand during heating and cooling. The TGA experiments provide the detailed variation of the binder mass with increasing temperature. The binder is found to be fully pyrolyzed at temperatures above 710°C (1310°F). At that temperature, 82% (by mass) of the original binder has become gaseous. The measured binder mass decrease is not a strong function of the heating rate. The present GED measurements for a heating rate of 2°C/min (3.6°F/min) show that the molecular weight of the gas evolved from PUNB bonded sand decreases in a complex manner from 375 g/mol at 115°C (239°F) to 33.3 g/mol at 898°C (1648°F). When the binder is fully pyrolyzed, continued chemical reactions within the gas cause its molecular weight to decrease from 48 g/mol at 710°C (1310°F) to values as low as 17.4 g/mol at 1350°C (2462°F) and beyond. In this temperature range, the binder gas does not condense during subsequent cooling to room temperature. When the bonded sand is not heated to temperatures above about 510°C (950°F), the binder gas partially condenses during subsequent cooling. This condensation starts to occur at approximately 165°C (329°F). For easy use in casting simulations that include calculation of gas evolution in the mold and cores, the present data are fit to polynomials that describe the binder gas mass and molecular weight variations with temperature.

Since the experiments reveal that the binder gas mass evolution is not a strong function of the heating rate, it may be inferred that the present data can be used to describe the gas evolution behavior at any distance from the mold-metal interface. Nonetheless, additional measurements at very high heating rates, corresponding to locations very near the mold-metal interface, may be needed to verify this hypothesis. Furthermore, the present gas evolution measurements extend only up to about 900°C (1652°F), with the extrapolation to higher temperatures based purely on previous data. This extrapolation should be verified by additional measurements. From a fundamental point of view, it would be desirable to further investigate the exact cause of the inverse peak in the measured binder gas molecular weight near 585°C (1085°F). The nature of the binder gas condensation observed at low temperatures is also an item that requires additional research attention, since such condensation can affect the flow of gases in outer portions of the mold. While the present study focused on PUNB bonded sand, the measurement of gas evolution for different binder and sand systems would be highly valuable.

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Table 1: Time-averaged mass fraction and mixture molecular weight of gas components evolved from PUCB and PUNB bonded sand within two minutes after pouring during the experiments of Bates *et al.*<sup>13-15</sup> and Scott *et al.*<sup>16</sup>

Experiment Description		Component Mass Fraction						Mixture Molecular Weight [g/mol]
Binder System	Metal and Average Pouring Temperature	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CO	CO <sub>2</sub>	HC <sub>total</sub> *	
2% PUCB	Gray Iron at 1446°C	0.068	0.013	0.041	0.367	0.371	0.140	15
1.3% PUCB	Gray Iron at 1457°C	0.071	0.038	0.160	0.37	0.25	0.11	15
2% PUNB	Gray Iron at 1431°C	0.066	0.01	0.05	0.35	0.38	0.15	15
2% PUNB	Gray Iron at 1430°C	0.037	0.086	0.297	0.202	0.318	0.061	20
2% PUNB	Steel at 1620°C	0.050	0.066	0.244	0.404	0.215	0.020	18
2% PUNB	Aluminum at 750°C	0.0002	0.208	0.7288	0.0039	0.057	0.0018	29

\*Total hydrocarbons measured as equivalent to methane

Table 2: Primary chemical components identified by McKinley *et al.*<sup>20</sup> and Lytle<sup>21</sup> through GC-MS analysis during flash pyrolysis of 1.5% PUCB bonded sand.

Component	Chemical Formula	Mass Fraction at 700°C	Mass Fraction at 900°C
Methane	CH <sub>4</sub>	0.0881	0.0701
Carbon Monoxide	CO	0.2311	0.1243
Ethene	C <sub>2</sub> H <sub>4</sub>	0.0523	0.1008
Propene	C <sub>3</sub> H <sub>6</sub>	0.2053	0.3047
2-Propenenitrile	C <sub>3</sub> H <sub>3</sub> N	0.0000	0.0239
1,3-Butadiene	C <sub>4</sub> H <sub>6</sub>	0.0638	0.0921
1-Butene	C <sub>4</sub> H <sub>8</sub>	0.1816	0.1152
1,3-Pentadiene	C <sub>5</sub> H <sub>8</sub>	0.0590	0.0967
1-Pentene	C <sub>5</sub> H <sub>10</sub>	0.1118	0.0708
Mixture Molecular Weight [g/mol]:		36.3 at 700°C	38.00 at 900°C

Table 3: Piecewise polynomial fitted to the fraction of original binder mass remaining measured during TGA pyrolysis of PUNB bonded sand samples heated at a rate of 2°C/min with a total argon gas flow of 25 cm<sup>3</sup>/min.

Fraction of Original Binder Mass Remaining, $f$	Temperature, $T$ [°C]
1.000	$T \leq 50$
$2.067 \times 10^{-8} T^3 - 1.189 \times 10^{-5} T^2 + 5.036 \times 10^{-4} T + 1.002$	$50 < T \leq 200$
$-6.269 \times 10^{-8} T^3 + 5.148 \times 10^{-5} T^2 - 1.465 \times 10^{-2} T + 2.165$	$200 < T \leq 300$
$-1.711 \times 10^{-8} T^3 + 1.793 \times 10^{-5} T^2 - 6.747 \times 10^{-3} T + 1.583$	$300 < T \leq 580$
$-1.353 \times 10^{-8} T^3 + 3.876 \times 10^{-5} T^2 - 3.446 \times 10^{-2} T + 9.951$	$580 < T \leq 710$
0.1807	$T > 710$



Table 4: Primary sources of error in the binder gas molecular weight measurements.

Source of Error	$\pm$ Error
Fraction of original binder mass remaining, $f$ , during heating	0.012
Measured height change, $\Delta h_2$ [cm]	0.05
Liquid metal density at room temperature, $\rho_m^0$ [g/cm <sup>3</sup> ]	0.018
Effective volumetric expansion coefficient of liquid metal, $\beta_m^{eff}$ [1/°C]	0.00001
Total volume contained by the filled GED at room temperature, $V_{tot}^0$ [cm <sup>3</sup> ]	0.05

Table 5: Piecewise polynomial fitted to the binder gas molecular weight measurements obtained during heating of PUNB bonded sand samples at a rate of 2°C/min.

Binder Gas Molecular Weight, $M_b$ [g/mol]	Temperature, $T$ [°C]
$-8.638T + 1368$	$T \leq 132$
$-1.638 \times 10^{-4} T^3 + 9.988 \times 10^{-2} T^2 - 21.31T + 1677$	$132 < T \leq 200$
$-5.397 \times 10^{-5} T^3 + 4.001 \times 10^{-2} T^2 - 9.880T + 907.0$	$200 < T \leq 316$
$-6.447 \times 10^{-6} T^3 + 9.056 \times 10^{-3} T^2 - 4.253T + 720.0$	$316 < T \leq 551$
$-2.945 \times 10^{-5} T^3 + 3.230 \times 10^{-2} T^2 - 8.768T - 1.100$	$551 < T \leq 574$
$1.197 \times 10^{-4} T^3 - 0.1401T^2 + 41.04T + 3.500$	$574 < T \leq 595$
$-1.090 \times 10^{-5} T^3 + 1.367 \times 10^{-2} T^2 - 4.211T + 0.000$	$595 < T \leq 635$
$-2.680 \times 10^{-7} T^3 + 2.681 \times 10^{-4} T^2 + 1.269 \times 10^{-2} T - 0.1900$	$635 < T \leq 898$
$-7.139 \times 10^{-8} T^3 + 3.233 \times 10^{-4} T^2 - 0.4878T + 262.4$ *	$T > 898$

\*Extrapolated based on the molecular weights calculated from Bates *et al.*<sup>13-15</sup> and Scott *et al.*<sup>16</sup>

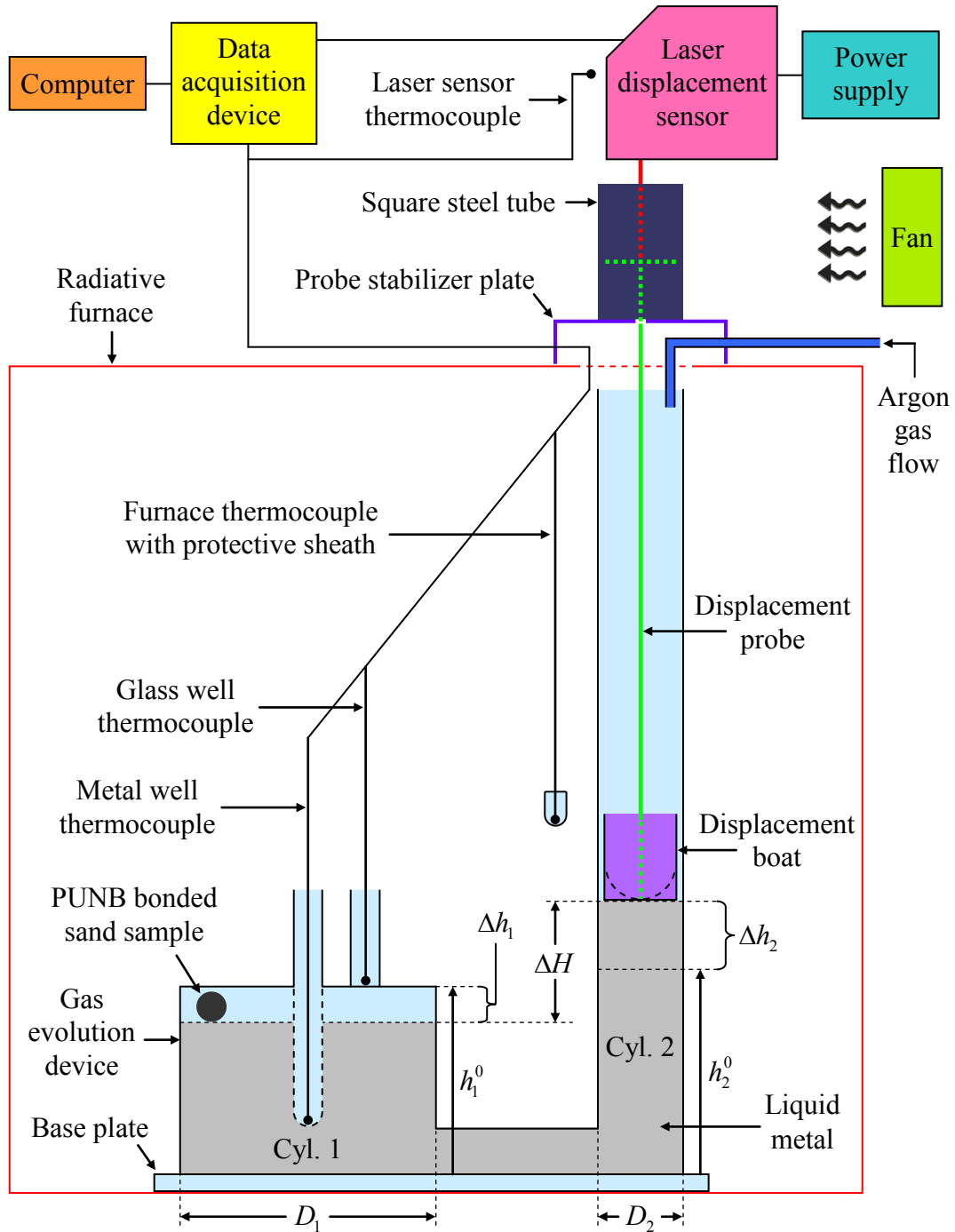


Figure 1: Schematic of gas measurement apparatus and important geometric quantities.

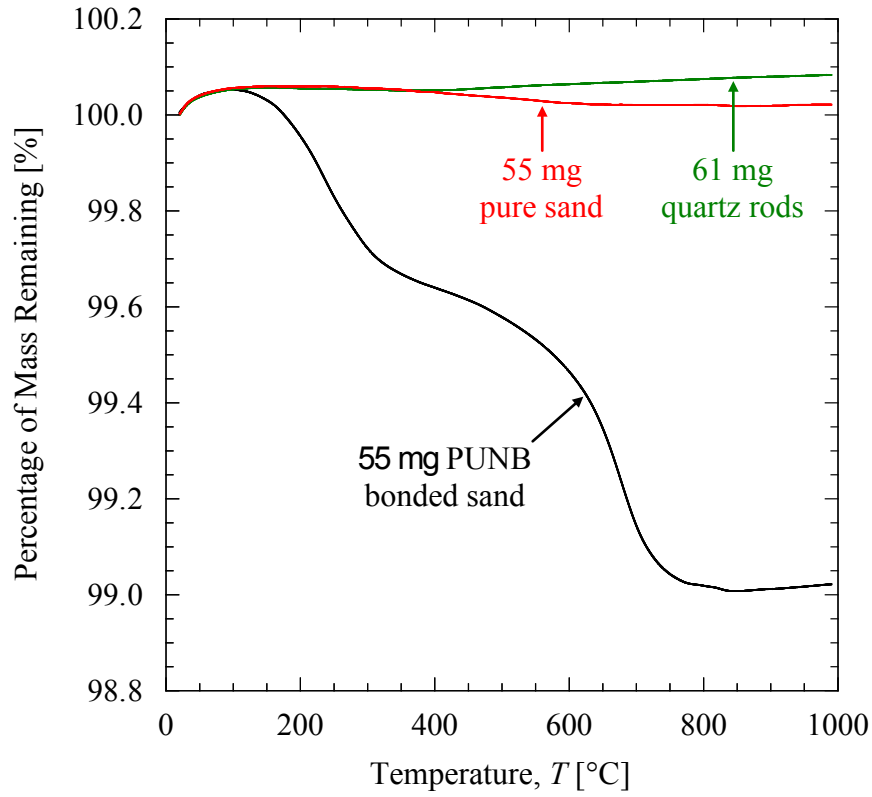


Figure 2: Measured percentage of mass remaining as a function of temperature typical of PUNB bonded sand samples, pure IC55 silica sand samples, and quartz rods heated at a rate of  $100^{\circ}\text{C}/\text{min}$  with a total argon gas flow of  $25\text{ cm}^3/\text{min}$ .

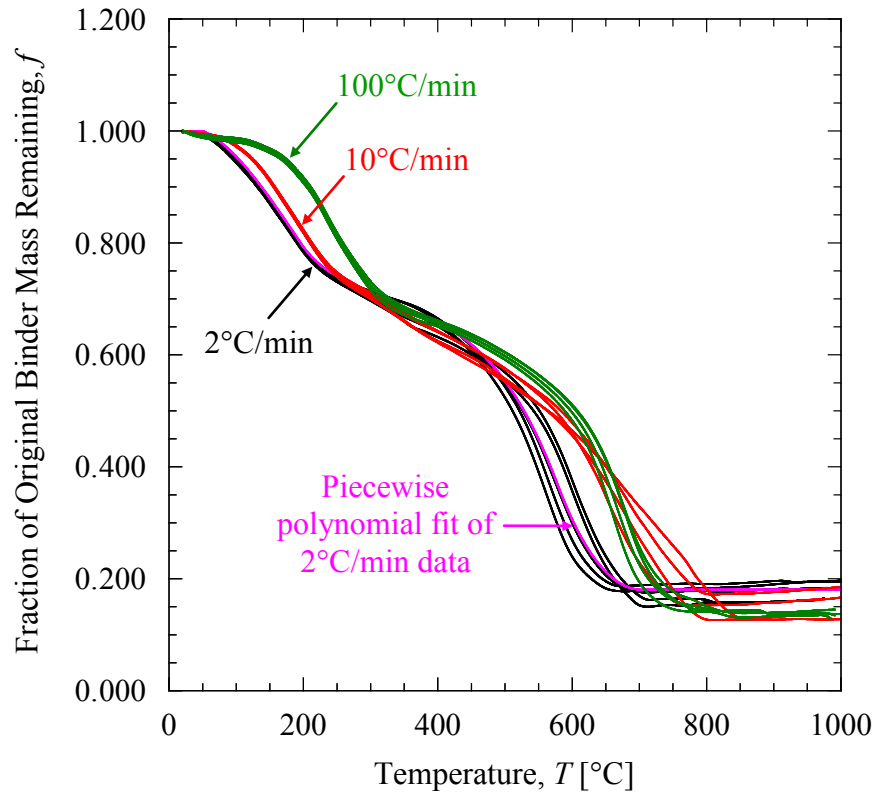


Figure 3: Measured fraction of original binder mass remaining as a function of temperature during heating of PUNB bonded sand samples at rates of 2°C/min, 10°C/min, and 100°C/min with a total argon gas flow of 25 cm<sup>3</sup>/min. The piecewise polynomial fitted to the measurements corresponding to the 2°C/min heating rate is also shown.

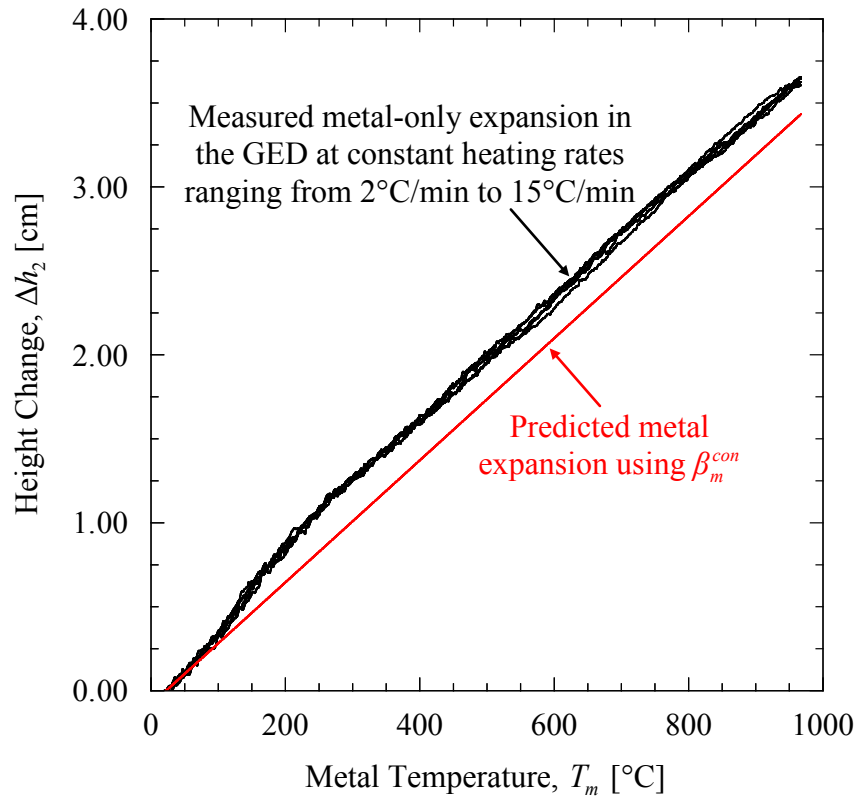
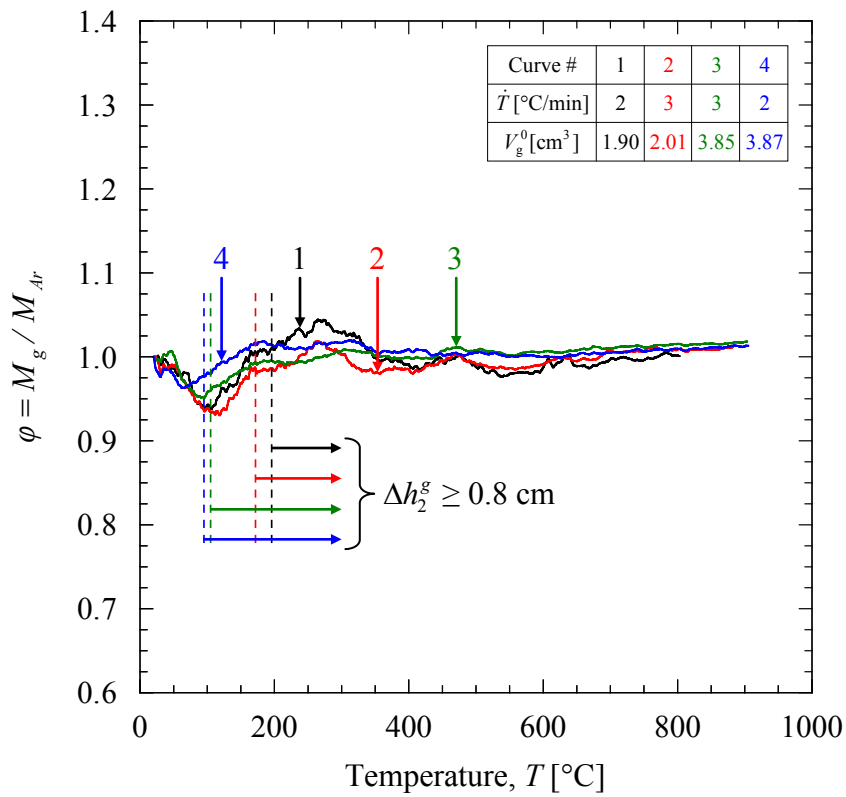
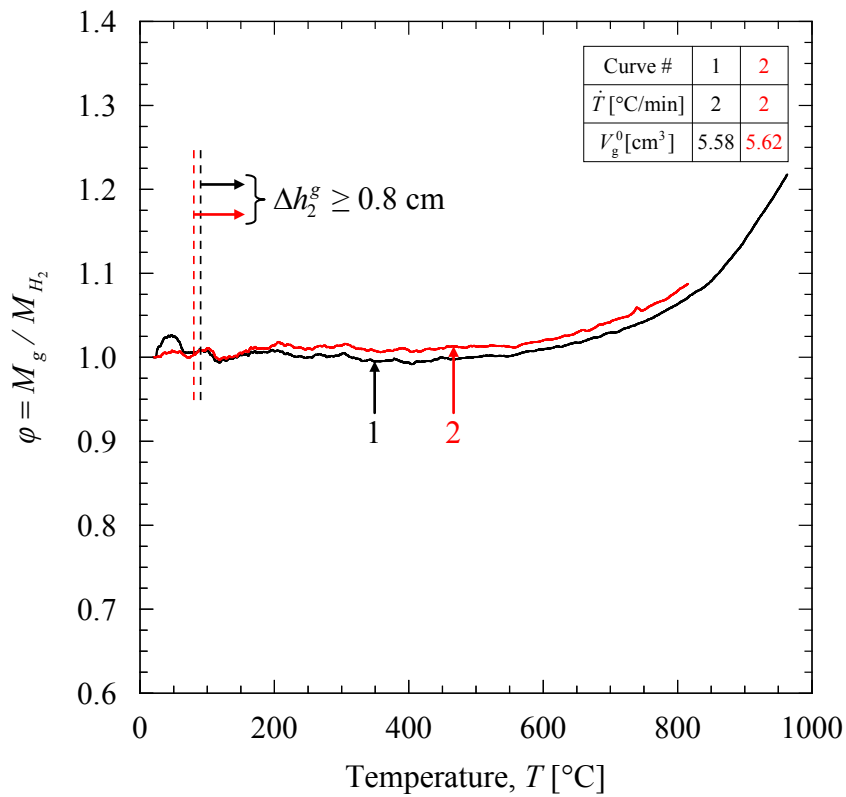


Figure 4: Comparison of measured and predicted metal-only height change as a function of temperature during heating. A constant volumetric expansion coefficient (obtained from separate experiments) was used to predict the metal expansion.



(a) Argon gas molecular weight results.



(b) Hydrogen gas molecular weight results. The dramatic increase in  $\phi$  above 560°C is presumably due to dissolution of the hydrogen gas into the liquid metal.

Figure 5: Ratio of measured to known molecular weight of (a) argon gas and (b) hydrogen gas as a function of temperature for low heating rates.

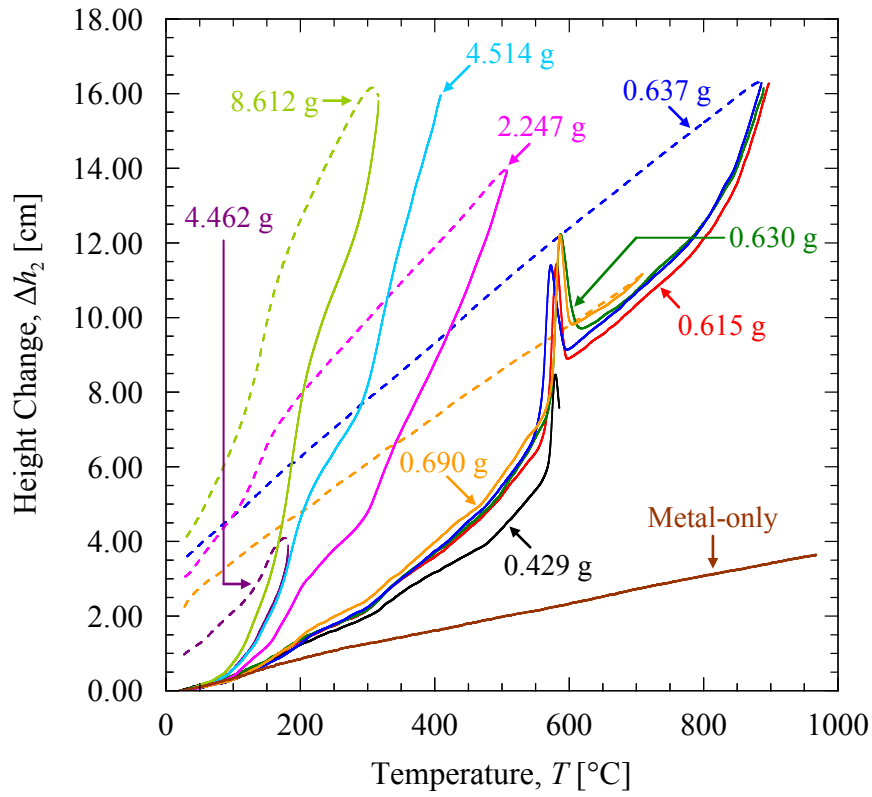


Figure 6: Measured height change as a function of temperature during heating and cooling of different PUNB bonded sand sample masses. Solid lines indicate heating at a rate of 2°C/min, and dashed lines indicate cooling after the furnace was turned off.



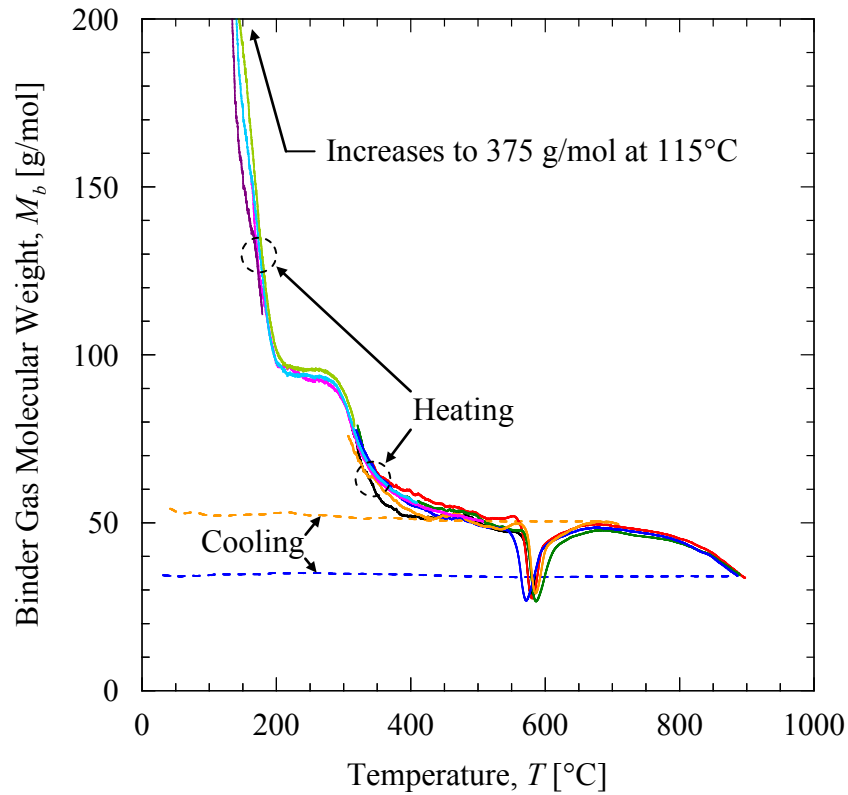


Figure 7: Binder gas molecular weight measurements as a function of temperature during heating and cooling of different PUNB bonded sand sample masses. The color scheme of the curves follows that of Figure 6. The heating rate was  $2^{\circ}\text{C}/\text{min}$ , and measurements during cooling are shown for tests that clearly exhibited no binder gas condensation.

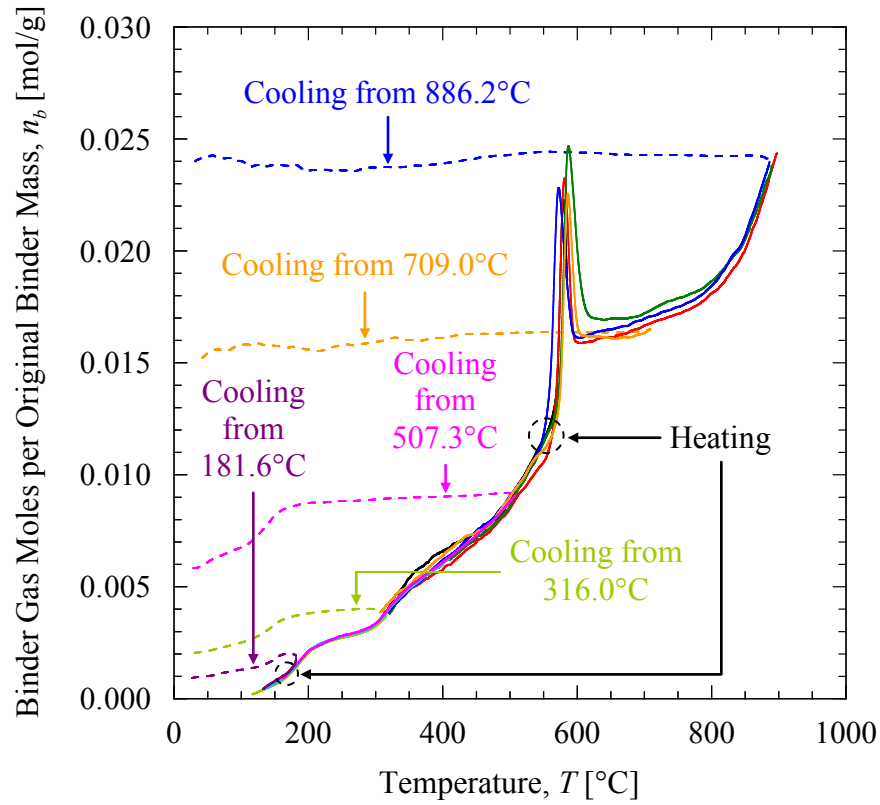


Figure 8: Measured binder gas moles generated per original binder mass as a function of temperature during heating and cooling of different PUNB bonded sand sample masses. The color scheme of the curves follows that of Figure 6. The heating rate was 2°C/min, and a significant decrease in  $n_b$  during cooling indicates condensation of the binder gas.

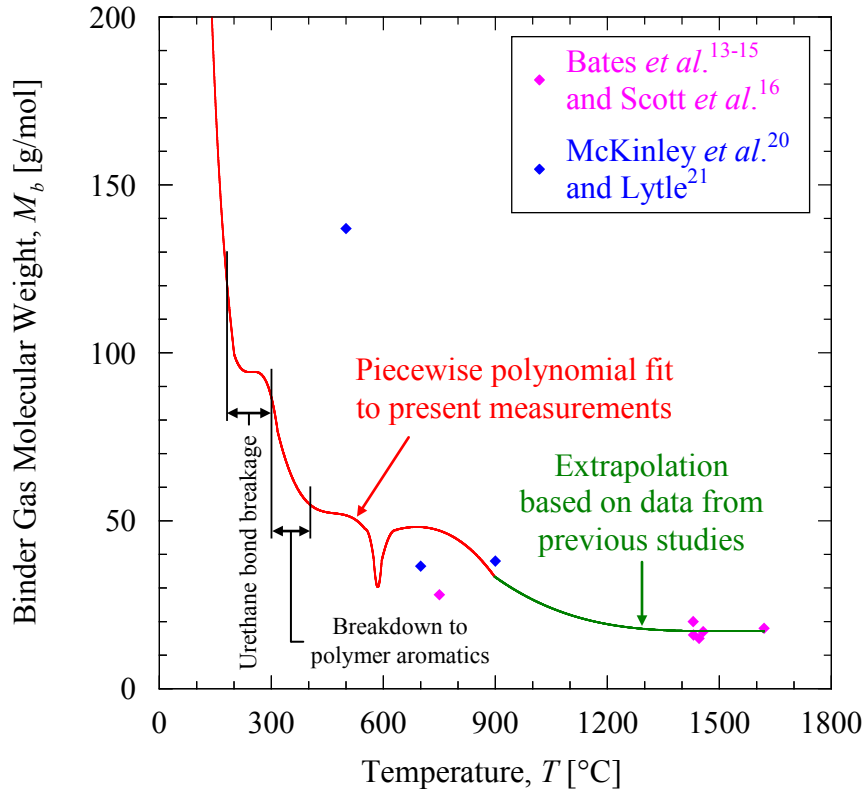


Figure 9: Piecewise polynomial fit of the binder gas molecular weight measurements as a function of temperature during heating at a rate of 2°C/min. The data fit is extrapolated based on the average molecular weights calculated from the data of Bates *et al.*<sup>13-15</sup> and Scott *et al.*<sup>16</sup> within 2 minutes after pouring. The fitted results are also compared with the binder gas molecular weights calculated from the data of McKinley *et al.*<sup>20</sup> and Lytle<sup>21</sup>. The partial thermal degradation mechanism for a 60:40 ratio pure PUNB binder sample heated at a rate of 10°C/min from Giese *et al.*<sup>34</sup> is superimposed on the data fit.