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Laboratory Studies of Hydrogen Gas Generation Using the Cobalt Chloride Catalyzed Sodium Borohydride-Water Reaction

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ADMINISTRATIVE INFORMATION

The work described in this report was performed by the Advanced Concepts & Applied Research Branch (Code 71730), the Applied Electromagnetics Branch (Code 52250), and the Ocean Engineering Branch (Code 56410), Space and Naval Warfare Systems Center Pacific (SSC Pacific), San Diego, CA.

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EXECUTIVE SUMMARY

OBJECTIVE

This report describes experiments to generate hydrogen gas using the cobalt chloride catalyzed sodium borohydride-water reaction. Space and Naval Warfare Systems Center Pacific (SSC Pacific) conducted experiments at ambient and cold temperatures as well as at pressure. The project team conducted these experiments to provide guidance in designing a reactor which could produce 330 standard cubic feet (SCF) of hydrogen gas and determine how to control the reaction to generate hydrogen gas to inflate lighter-than-air vehicles.

RESULTS

When using $CoCl_2$ as a catalyst, we discovered that distilled or deionized water should be used for the reaction to complete in a reasonable time. Much longer reaction times occurred when either tap water or seawater were used. We believe that the chloramine in tap water and dissolved organics in seawater form complexes with the catalyst impeding its ability to catalyze the reaction between $NaBH_4$ and H_2O. We discovered that the minimum ratio of $H_2O:NaBH_4$ that could be tolerated was 4.6:1. Lower $H_2O:NaBH_4$ ratios resulted in a very viscous sludge due to the precipitation of $NaBO_2$ hydrate crystals, foaming, and reaction temperatures approaching 90 °C. We used water running through Cu coils to remove heat from the reaction. The reaction rate could be controlled by either varying the flow rate of water through the Cu cooling coils or by keeping the flow rate constant and automatically turning the cooling on/off upon reaching a set temperature. Measurements using a forward looking infrared (FLIR) thermal camera showed that the temperature of the reacting solution was inhomogeneous and was hotter near the air/reagent interface. Consequently, placement of the monitoring/controlling thermocouple influences the control of the reaction. Experiments conducted under pressure showed that pressure suppresses foaming.

RECOMMENDATIONS

Experiment results show that we can control the reaction to generate hydrogen gas in a reasonable amount of time with little foaming. The temperature of the resultant gas was below 70 °C.

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1. INTRODUCTION

Lighter-than-air (LTA) vehicles support various payloads at altitudes ranging from a few hundred feet to several thousand feet. Depending upon the payload, these vehicles have many potential uses in surveillance, reconnaissance, force protection, border/port security, over-the-horizon (OTH) communication relays, incident awareness and assessment, and monitoring air quality and atmospheric conditions. The two primary lifting gases used in LTAs are hydrogen and helium [1].

Helium is not only used to fill LTAs, but also as an inert gas shield for arc welding, a protective gas in growing silicon and germanium crystals, and for titanium and zirconium production. It is also used as a cooling medium for nuclear reactors, a protective gas for semiconductor materials, and for cryogenic applications [2]. Helium is formed through the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th [3]. High helium reservoirs occur when high uranium and/or thorium exist in the basement rock, deep faulting, and strong seals. Helium is a trace component in natural gas, and extraction at more than a dozen sites around the world feeds a global demand of 170 million m^3 each year [4]. Roughly one-third of that helium comes from a geological stockpile in Amarillo, Texas—the U.S. Federal Helium Reserve. In 1996, U.S. lawmakers decided that the government should get out of the helium business, and ordered the sale of the stores to pay off the facility's accumulated debts of $1.3 billion. However, the U.S. Federal Helium Reserve is still under government control but its future is uncertain. Since manufacturing processes using helium have increased worldwide, the demand for helium has increased dramatically. Unfortunately, helium is a non-renewable source. As demand increases, supplies worldwide dwindle, driving prices up. Consequently, the use of hydrogen gas to inflate LTA vehicles is gaining greater acceptance; many countries (military and commercial) already use hydrogen for weather balloons.

Besides cost, hydrogen has other advantages over helium. Hydrogen has more lift than helium, so larger payloads are possible. It can be stored in a chemically dense form as a metal hydride (one just needs to mix with water and a catalyst to start generation). The later advantage is useful for missions that require long-term storage of hydrogen, as storing helium/hydrogen in tanks is impractical due to leakage, safety, and size concerns. Hydrogen is less flammable than gasoline.

In summary, the demand to use LTA vehicles for military and commercial applications is going to increase. Given the uncertainty in helium supplies, the use of hydrogen gas to inflate LTAs will also increase. To meet mission requirements for size, storage time, efficiency, and performance, we began to investigate the use of metal-hydride-generated hydrogen gas to inflate LTAs. Of the metal hydrides, we chose to explore the sodium borohydride chemistry. We chose this chemistry because of its energy density and stability of sodium borohydride in alkaline solution. We also made this decision because its byproduct (sodium metaborate) is relatively benign to the environment. In this technical report, we discuss a series of experiments used to determine conditions to generate hydrogen gas at a sufficient rate under controlled conditions. The ultimate goal is to develop a protocol the U.S. Navy can use to generate hydrogen gas for inflation of LTAs.

2. EXPERIMENTAL DETAILS

2.1 CHEMICALS

Sodium borohydride (GFS Chemicals), anhydrous cobalt (II) chloride (Sigma-Aldrich), and distilled water (Arrowhead) were used as received for these experiments.

2.2 EXPERIMENTAL APPARATI TO MEASURE HYDROGEN GAS GENERATION UNDER AMBIENT CONDITIONS

For water volumes of 50 mL, the reaction was carried out in a 250-mL tapered wall flask that had three necks with 24/40 ground glass joints and a fourth neck with a #7 Ace thread (Ace Glass part number 6963-34). The project team used a K-type thermocouple to make temperature measurements. This thermocouple was placed in a thin glass sleeve immersed in the reagents through the #7 Ace thread. We then placed a known amount of sodium borohydride inside the flask, followed by 49 mL of water. To initiate the reaction, a 1-mL sample containing a known amount of $CoCl_2$ was pipetted into the flask. A computer controlled data collection.

We used the reaction vessel shown in Figure 2.2-1a to generate 50 to 100 L of hydrogen gas. As the catalyzed reaction between water and $NaBH_4$ is exothermic, we used water flowing through the copper cooling coils to remove the heat generated during the reaction. Either a peristaltic pump or a bilge pump, with a check valve to keep the water flowing in one direction, was used to pump cooling water through the copper coils. The peristaltic pump made it possible to adjust the rate of water flow through the coils and study the effect of water flow rate on both the cooling and the reaction rate. The bilge pump enabled automatic control (using a computer) of the cooling. For automatic control of the cooling, we used a thermocouple inside the reaction vessel to monitor the temperature of the reaction. We then turned the cooling on and off when the reaction reached a given temperature set point. Figure 2.2-1b shows that additional K-type thermocouples monitored the inlet and outlet water temperatures of the copper cooling coils. An Omega FMA4000 Digital Mass Flow Meter was placed on the gas outlet to measure the flow rate of the generated hydrogen gas. A 50-µm filter was placed between the reaction vessel and the flow meter to prevent particulates and water vapor from entering the flow meter. A computer controlled data collection.

To conduct an experiment, we placed a known amount of $CoCl_2$ on the bottom of the graduated cylinder. Enough $NaBH_4$ to generate 50 to 100 L of hydrogen gas was then placed in the stainless steel basket. We used a 1-inch-diameter PVC rod in the center of the stainless steel basket to concentrate the reaction near the coils. This stainless steel basket was then placed within the Cu coils as shown in Figure 2.2-1a. A K-type thermocouple (Omega), Figure 2.2-1b, was placed inside the reaction vessel. This thermocouple was in contact with the reagents during the reaction and was used to monitor the reagents' temperature. The ratio of the water to $NaBH_4$ was 4.6 by mass. In some experiments, two K-type thermocouples were placed inside the reaction vessel at different heights. To initiate the reaction, we added water to the glass reaction vessel through one of the ground-glass joints.

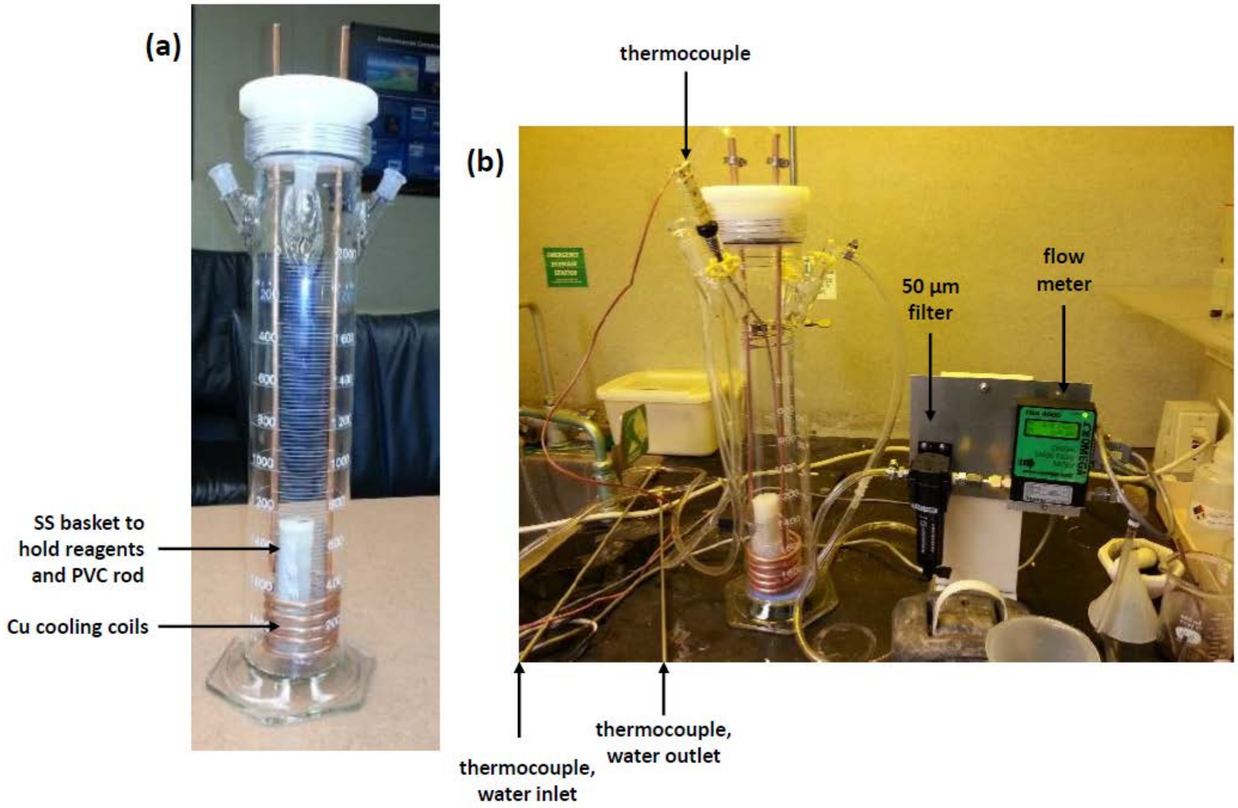


Figure 2.2-1. (a) Glass reaction vessel used to generate 50 to 100 L of hydrogen gas at ambient pressure where SS is stainless steel and PVC is polyvinylchloride, (b) reaction vessel and sensors used to monitor the hydrogen generation reaction.

2.3 EXPERIMENTAL APPARATUS TO MEASURE HYDROGEN GAS GENERATION UNDER PRESSURE

Figure 2.3-1a shows the glass reaction vessel used in the experiments. Cooling water flows through the copper coils. A dashed line in Figure 2.3-1a indicates the initial level of the reagents. We taped a plastic test tube on the water outlet. This plastic test tube houses a thermocouple that monitors the water temperature as it exits the cooling coils. A tape measure is epoxied outside the glass vessel. This tape measure measures the level of the reagents during the experiment. A glass sleeve housing four thermocouples at different heights is placed inside the glass reaction vessel, as shown in Figure 2.3-1a. Asterisks indicate the position of the thermocouples. The lowest thermocouple is in contact with the reagents. This thermocouple is also used to monitor/control the reaction. The thermocouple above the lowest one is initially at the reagent/air interface. The remaining two thermocouples are placed above the reagents in the air.

Once assembled, the glass reaction vessel was placed on a stand inside the reaction can, shown schematically in Figure 2.3-1b. Lead weights, shown in Figure 2.3-1a, hold the glass reaction vessel in place. The reaction can is a 316L stainless steel, 3-gallon capacity, portable, standard mouth ASME pressure tank (McMaster-Carr, part number. 6778K21). The pressure tank has a 185-psig maximum pressure rating at 37.8 °C and a maximum operating temperature of 149 °C. An adjustable 10- to 228-psig proportional pressure release valve (Swagelok, RL3) and a pressure gauge with a pressure transducer (Omega model PX835-300GI) are connected to the pressure tank. The pressure release valve is connected to the gas outlet and a hose that goes to the Omega FMA4000 Digital

Mass Flow Meter to measure the flow rate of the generated hydrogen gas. We placed a 50-µm filter between the reaction vessel and the flow meter to prevent particulates and water vapor from entering the flow meter. The pressure tank has pass-throughs for the thermocouples that are placed inside the glass reaction vessel and the plastic tube taped to the water outlet (see Figure 2.3-1b). This experimental set-up can be used to conduct testing under ambient conditions as well as under pressure. When pressure tests were done, the reaction can was pressurized using nitrogen gas. For safety, the pressure can also had a 200-psig burst disc and a manual emergency release valve on it, both of which are not shown in the schematic.

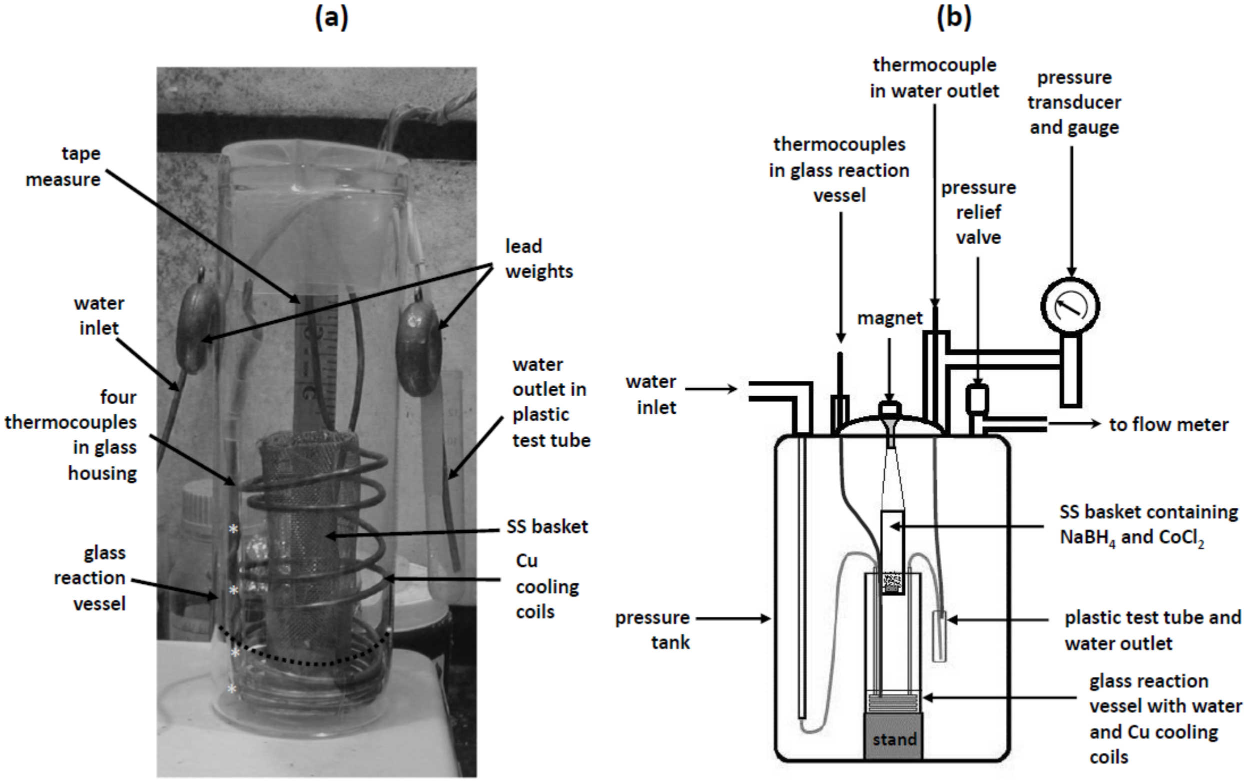


Figure 2.3-1. (a) Glass reaction vessel used in experiments conducted under pressure (the dashed line indicates the level of the reagents and the asterisks indicate the placement of the thermocouples - T_1, T_2, T_3, and T_4, from lowest to highest), (b) schematic of the pressure can (not shown is the manual release valve and the 200-psig burst disc).

As shown in Figure 2.3-1b, a tube inside the reaction can connects to the inlet of the copper coils of the glass reaction vessel. A hose on the water inlet connects this tube to a water can, which is not shown. The water can is another 316-L stainless steel, 3-gallon capacity, portable, standard mouth ASME pressure tank (McMaster-Carr part number. 6778K21). A pressure gauge and a water pump are attached to the water can. The water can houses the cooling water pumped through the copper coils. The water can is connected to a nitrogen tank throughout the experiment. It is maintained at a pressure that is ~ 20 psig greater than the reaction can pressure. The water pump has an on/off switch. When the temperature inside the glass reaction vessel reaches a given set point, the pump switches on and pumps water from the water can through the copper coils in the reaction vessel inside the reaction can. Because the water running through the coils dumps into the reaction can, the glass reaction vessel was placed on top of a stand. Besides enabling the project team to conduct experiments at different pressures, this set-up also allowed us to conduct experiments using either chilled or ambient temperature water for the cooling. A computer controlled experiments and data collection. In addition to temperature, pressure, and gas flow measurements, we used a GoPro® camera and a light-emitting diode (LED) light source inside the pressure can (not shown in the schematic) to record videos of the reactions.

To start the reaction, we placed a known amount of $CoCl_2$ inside a shallow polyethylene cup, which we then lowered into the stainless steel basket shown in Figure 2.3-1a. A known amount of $NaBH_4$ was then added to the stainless steel basket. We used a monofilament fishing line to tie the basket to a metal screw attracted to a magnet. A magnet on the outside of the pressure can (Figure 2.3-1b) holds the metal screw and the basket containing the reagents above 100 mL of water in the glass reaction vessel. Reaction starts when the magnet is pulled away, dropping the stainless steel basket with reagents into the water.

2.4 RAMAN SPECTROSCOPY

The project team used the Snowy Range Instruments Sierra Series™ Portable Raman system to obtain Raman spectra of the reaction products. The system's operational range is 200 to 3200 cm^{-1} and its resolution is 10 cm^{-1}). The system has a 785-nm diode laser that operates between 0.03 and 100 mW and a 3000-element, linear, cooled near-infrared (NIR)-enhanced charged coupled device (CCD) array.

3. EFFECT OF CATALYST AND WATER TYPE

The chemical reaction between $NaBH_4$ and H_2O is [5]:

$$NaBH_4 + (2+x)\, H_2O \rightarrow NaBO_2 \cdot xH_2O + 4\, H_2\uparrow, \qquad (1)$$

where x represents the excess hydration factor. In the absence of a catalyst, this reaction goes very slowly. Brown and Brown [6] examined many metal salts to catalyze this reaction. They showed that the reaction rate as a function of catalyst type was as follows:

$$RuCl_3,\ RhCl_3 > H_2PtCl_6 > CoCl_2 > NiCl_2,\ OsO_4 > IrCl_4 > FeCl_2 >> PdCl_2.$$

The researchers performed experiments using $RuCl_3$ and $CoCl_2$ to catalyze reaction (1). They conducted these experiments under nearly identical conditions, except less $RuCl_3$ was used. Figure 3-1 compares the results. While $RuCl_3$, $RhCl_3$, and H_2PtCl_6 outperform $CoCl_2$, these salts are comparatively expensive. Given the volume of hydrogen gas needed to inflate an aerostat, we chose $CoCl_2$ as the catalyst in these experiments. In the rest of this report, we calculate the percent catalyst relative to the mass of $NaBH_4$.

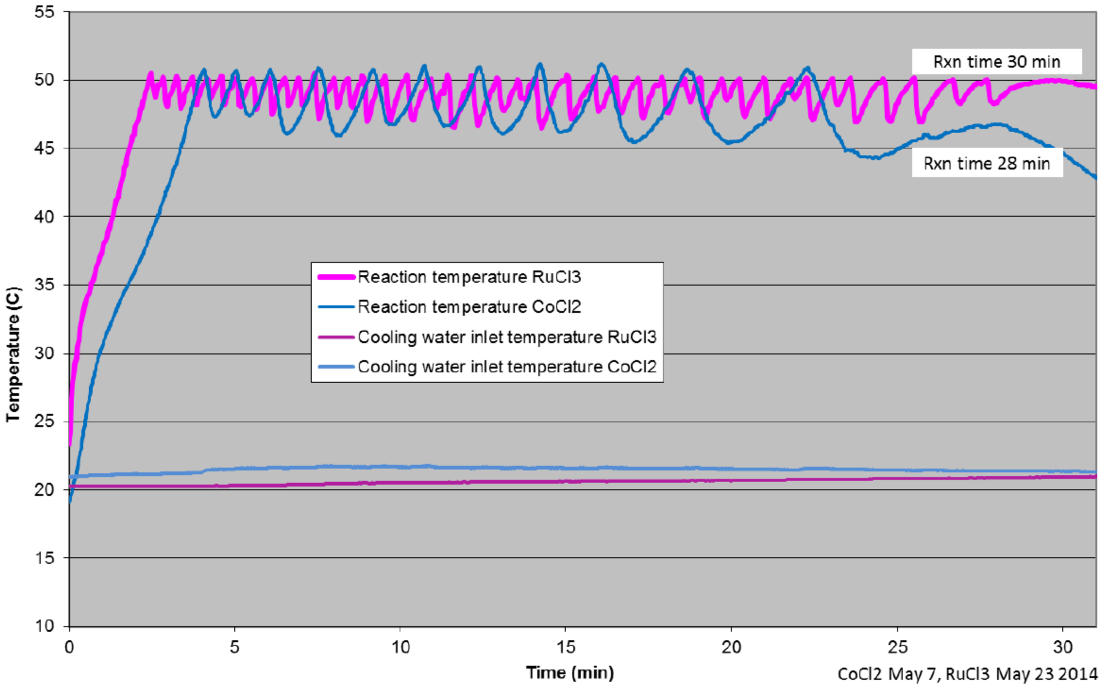


Figure 3-1. Comparison: 3.0% $CoCl_2$ vs. 0.84% $RuCl_3$ catalysts, where $H_2O:NaBH_4 = 4.61:1$, ambient temperature, 50 L, automatic cooling (on at 50 ºC, off at 50 ºC). Cooling water flow rates are 3.225 mL s^{-1} for $RuCl_3$ and 3.125 mL s^{-1} for $CoCl_2$. Both experiments were conducted in the reaction vessel in Figure 2.2-1a at atmospheric pressure. At ambient conditions, $RuCl_3$ exhibits a larger number of sawteeth with a smaller amplitude than $CoCl_2$, indicating tighter temperature control.

Depending on mission scenarios, using seawater may be more desirable than using distilled or deionized water. The advantage for maritime applications is that if seawater could be used, we would not need to carry water with us, which would reduce weight and simplify the design of a hydrogen gas generator. We conducted experiments using seawater and deionized water using the 250-mL tapered flask (see description above). The results are summarized in Figure 3-2. For deionized water, the temperature of the reaction ramped up to 52 ºC and the total reaction time was 5.6 min. For seawater, the temperature peaked at 30 ºC and the reaction time was > 30 min. We conducted an experiment using tap water. Figure 3-2 shows the temperature increasing to 42 ºC and the reaction time at 11.8 min. The results indicate that something in tap water and seawater poisons the catalyst. In the presence of $NaBH_4$ and H_2O, $CoCl_2$ reacts to form the catalyst, Co_2B [7]:

$$BH_4^- + 2\ Co^{2+} \rightarrow Co_2B + ½\ H_2 + 3\ H^+. \qquad (2)$$

Tap water contains 4-ppm chloramine [8] and seawater contains dissolved organics that have carboxyl, amine, and sulfhydryl groups present [9]. Both chloramine and the dissolved organics can form complexes with transition metals. We believe that formation of these complexes impedes the ability of Co_2B to catalyze the reaction between $NaBH_4$ and H_2O.

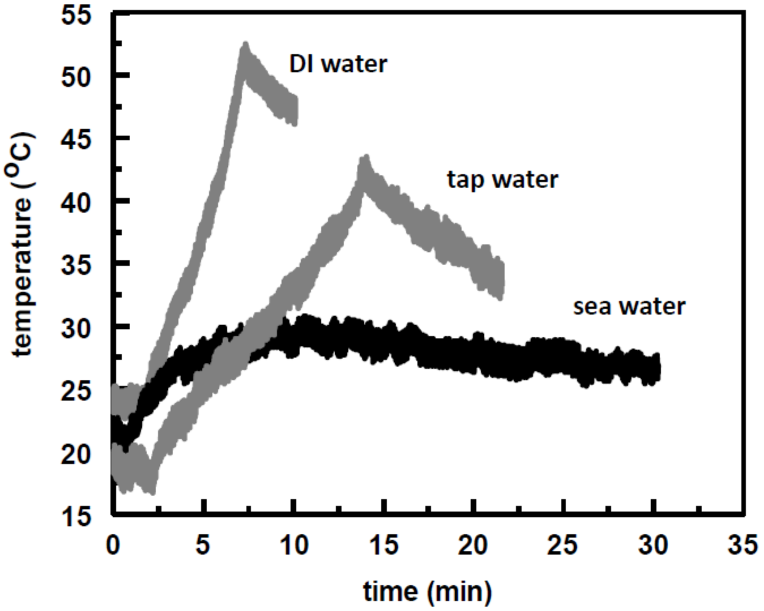


Figure 3-2. Plots of reaction temperature as a function of time when using deionized (DI) water, tap water, or seawater. Experimental conditions: 50-mL water, 7.5% $CoCl_2$, and H_2O:$NaBH_4$ ratio of 33.3:1.

The results summarized in Figure 3-2 indicate that seawater cannot be used with transition metal catalysts. Since we will have to carry our own water when using the $NaBH_4$/$CoCl_2$ chemistry, we want to minimize the amount of water needed. We then conducted experiments with deionized water to determine the minimum H_2O:$NaBH_4$ ratio that could be tolerated. An additional constraint was that the temperature of the reaction needs to be kept between 50 and 60 ºC to generate hydrogen gas at a reasonable and constant rate to inflate the aerostat, minimize the amount of water vapor entering the gas stream, and avoid damaging the balloon/aerostat (aerostats typically have an operational temperature range of -50 to 55 ºC [10]). The amount of water vapor entering the aerostat must be minimized. If water vapor gets inside the aerostat, it will condense to liquid water, which will increase the weight of the aerostat. In turn, this will reduce the lift capacity of the aerostat, affecting its performance. The temperature of the reaction depends on both the H_2O:$NaBH_4$ ratio and the percentage of $CoCl_2$ relative to $NaBH_4$. Experiments showed that the minimum ratio of water to sodium borohydride, by mass, that can be tolerated is 4.6. Anything lower results in a very viscous sludge due to the precipitation of $NaBO_2$ crystals. Increasing viscosity results in foaming and reaction temperatures approaching 90 ºC.

4. 50- TO 100-L HYDROGEN GENERATION EXPERIMENTS

Once we determined the minimum H_2O:$NaBH_4$ ratio, we conducted experiments using the apparatus shown in Figure 2.2-1. We conducted these experiments to optimize the amount of catalyst and the cooling. Besides generating hydrogen gas at a temperature below 60 ºC, we also wanted to generate at least 90% of the theoretical amount of the hydrogen gas with minimal foaming. Foam must be avoided because it introduces water and chemicals into the aerostat, which increases the weight and affects the lift capacity of the aerostat/LTA vehicle. In addition, the foam is alkaline, which could potentially cause chemical damage to the aerostat/LTA vehicle.

4.1 CONTINUOUS FLOW EXPERIMENTS USING AMBIENT TEMPERATURE WATER FOR COOLING

In one series of experiments, we allowed water to flow through the cooling coils continuously before and after the addition of the water to the glass reaction vessel. Regardless of the water flow rate and the amount of catalyst, a continuous flow of water though the Cu coils resulted in so much cooling that the reaction was essentially quenched. We then tried a protocol where we allowed the reaction to reach a set temperature before turning on the flow of the cooling water and leaving it on. Figure 4.1-1 summarizes the results of that experiment.

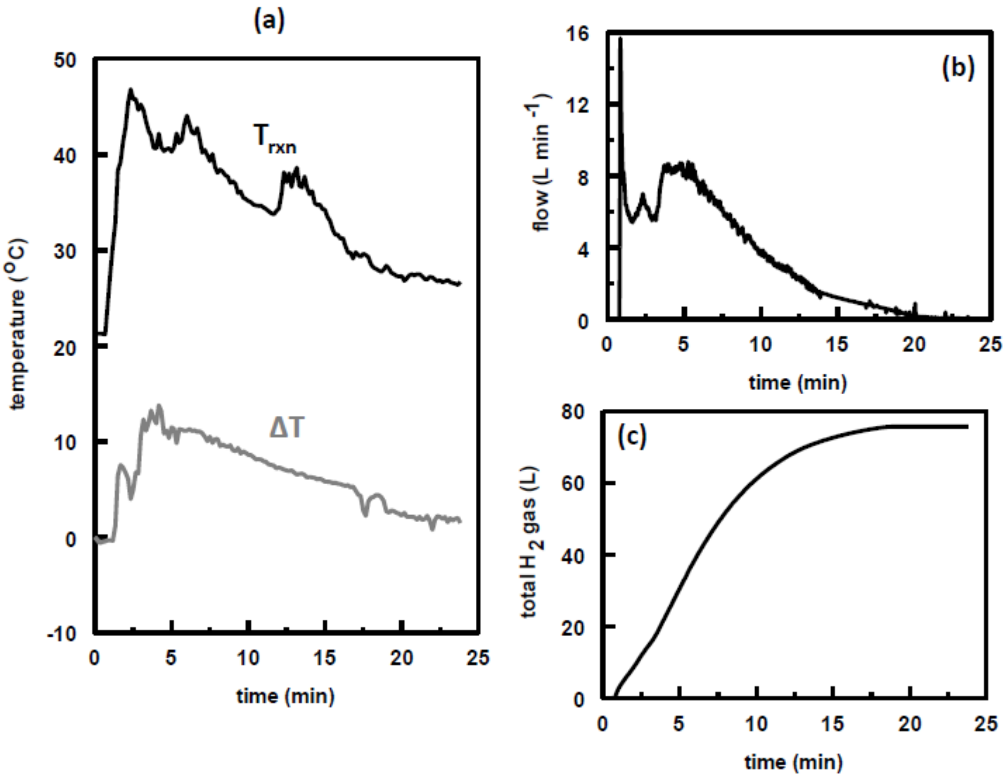


Figure 4.1-1. Results obtained when water flowed continuously through the cooling coils at a constant flow rate, where (a) is a plot of reaction temperature (T_{rxn}) and differential water outlet and inlet temperature (ΔT), (b) is a plot of the flow rate, and (c) is a plot of the total hydrogen gas, all as a function of reaction time. This 100-L experiment used a H_2O:$NaBH_4$ ratio of 4.6:1, 5% $CoCl_2$, and a cooling water flow rate of 3.2 mL s^{-1}. The cooling water was at ambient temperature and the peristaltic pump was used. The set temperature was 45 °C.

Addition of water to the $NaBH_4$ and $CoCl_2$ inside the glass reaction vessel causes a sharp spike in the flow rate, Figure 4.1-1b. This sharp spike, which peaked at 15.68 L min^{-1}, is due to the formation of the Co_2B catalyst, reaction (2). The temperature of the reaction increased rapidly, Figure 4.1-1a. When the temperature reached 45 ºC, we turned on the cooling and left it on throughout the rest of the reaction. No foaming was observed in this reaction. With continuous cooling, the temperature of the reaction decreases, Figure 4.1-1a. At the same time, we observed a decrease in the flow rate, Figure 4.1-1b, indicating that continuous cooling is quenching the reaction. As the water flowed continuously through the coils, the reaction rate slowed down and hydrogen gas generation ceased. Upon termination of the data acquisition, we observed that the reaction had not completed as indicated by the total hydrogen, Figure 4.1-1c, and bubbles of hydrogen gas continued to be released long after we stopped data acquisition. This test was supposed to be a 100-L test and the flow meter indicated that the test generated 75.6 L of hydrogen. To verify that the mass flow sensor was registering properly, we conducted tests generating 50 L of hydrogen gas using the water displacement apparatus shown in Figure 4.1-2. Occasionally, the mass flow meter registered 0.87 to 1.2 of the theoretical yield due to malfunction. However, the displacement cylinder verified that these reactions achieved ~ 98% completion. We conducted additional experiments with higher percentages of $CoCl_2$ and with lower cooling water rates. Under these conditions, the reactions achieved ~ 90% completion; however, foaming was considerable. Consequently, this method of cooling, while simple, did not meet all the criteria to control the reaction.

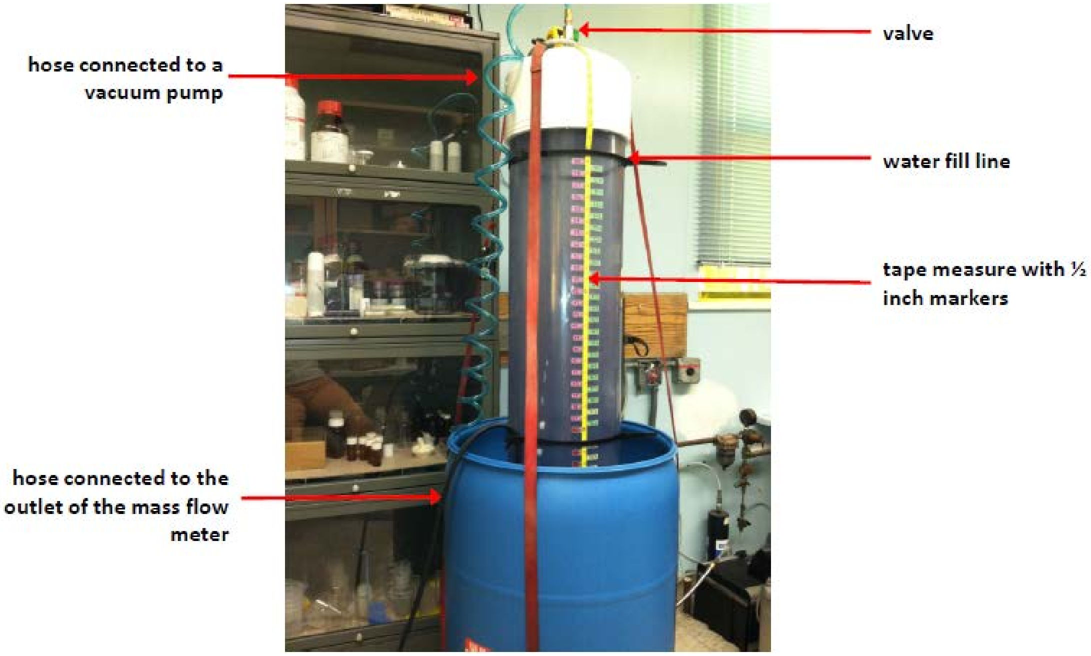


Figure 4.1-2. Apparatus used to determine the amount of hydrogen gas generated for a 50- to 60-L test. In these tests, the H_2O:$NaBH_4$ ratio was 4.6:1. To conduct the test, the project team used a vacuum to pull water into the clear PVC cylinder. Once filled with water to the water fill line, a valve was closed to keep the water at that level. The team laced a hose connected to the outlet of the reaction vessel inside the cylinder from the bottom. As hydrogen gas is generated, it bubbles inside the cylinder, displacing the water. At the end of the reaction, we measured the water level to determine the amount of water displaced, which is equivalent to the amount of hydrogen gas generated.

The peristaltic pump has a dial which can be used to vary the water flow rate through the coils. We conducted an experiment where we allowed the reaction to reach a set temperature before turning on the flow of the cooling water through the Cu coils and leaving it on. However, instead of keeping the flow rate constant, we varied it manually. The results are summarized in Figure 4.1-3. After the addition of water to the reagents, the sharp spike, due to the formation of the Co_2B catalyst, is observed in the flow rate, Figure 4.1-3b. This spike peaked at a flow rate of 10.01 L min^{-1}, which was less than what we observed in Figure 4.1-3b. This occurred because we used less $CoCl_2$ in this experiment. The reaction temperature increased rapidly, Figure 4.1-3a. After 4.7 min from when the water was added to the reagents, the reaction temperature reached 50 ºC, at which point we turned on the cooling water at a rate of 1 ml s^{-1}. The temperature and gas flow rate remained constant, Figures 4.1-3a and 4.1-3b, respectively. The reaction temperature began dropping below 50 ºC 18 min after we added the water to the reagents.. Then we reduced the water flow rate through the coils to 0.8 mL s^{-1}, which caused the reaction temperature and gas flow rate to increase. When the reaction temperature reached 52 °C, the water flow rate through the coils was increased to 2.3 mL s^{-1}. Despite this increased flow of cooling water through the Cu coils, the temperature continued to increase and reached a maximum of 60 °C, Figure 4.1-3a. The hydrogen gas flow rate also increased, and peaked at 6.54 L min^{-1}. The total generation of hydrogen gas was fairly linear, Figure 4.1-3c, and 91% of the expected gas was recorded.

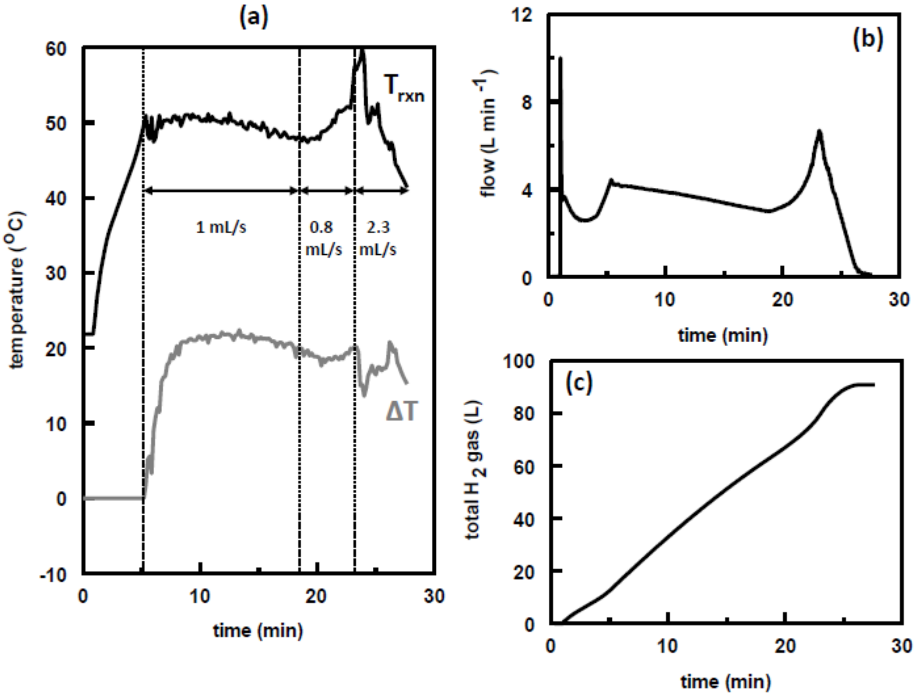


Figure 4.1-3. Results obtained when water was flowed continuously through the cooling coils at a varying flow rate, where (a) is a plot of reaction temperature (T_{rxn}) and differential water outlet and inlet temperature (ΔT), (b) is a plot of the flow rate, and (c) is a plot of total hydrogen gas, all as a function of reaction time. This 100-L experiment used a H_2O:$NaBH_4$ ratio of 4.6:1 and 3% $CoCl_2$. The cooling water was at an ambient temperature and the peristaltic pump was used. Water flow rates are indicated in mL s^{-1}. The set temperature was 50 °C.

4.2 COOLING USING AMBIENT TEMPERATURE WATER AND MANUALLY TOGGLING THE PUMP ON/OFF

We then began to conduct experiments where the flow of cooling water through the Cu coils was toggled on/off over a set temperature range. Figure 4.2-1 shows the results of a 100-L run using 4% $CoCl_2$ relative to the $NaBH_4$. A peristaltic pump was toggled on and off manually to keep the reaction temperature between 50 and 55 ºC. The reaction took 4.3 min to get to 55 ºC, when we started toggling the cooling on and off. Figure 4.2-1b shows that the gas flow rate followed the reaction temperature and spiked at a flow rate of 14.2 L min^{-1} (when the temperature peaked at 64.9 ºC). This reaction foamed badly. The plot of total gas as a function of time was not linear, indicating that the gas was not generated constantly.

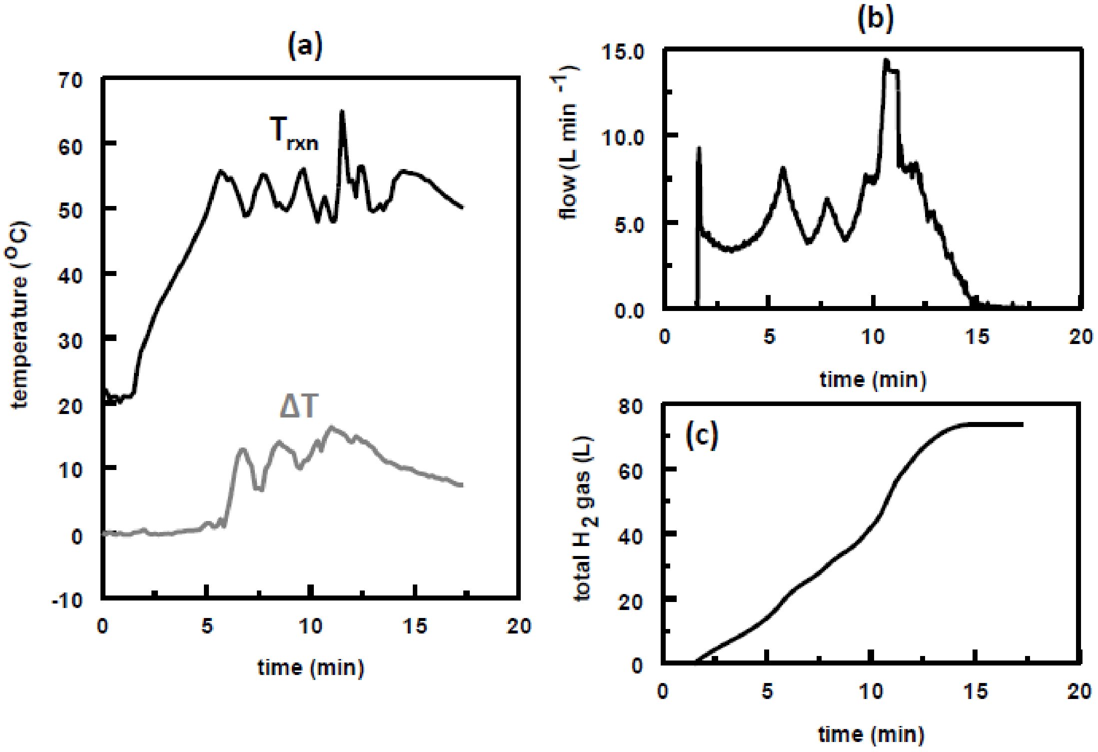


Figure 4.2-1. Results obtained manually toggling the water flow on/off to keep the reaction temperature between 50 and 55 °C, where (a) is a plot of reaction temperature (T_{rxn}) and the differential water outlet and inlet temperature (ΔT), (b) is the flow rate, and (c) total hydrogen gas all as a function of reaction time. This 100-L experiment used a H_2O:$NaBH_4$ ratio of 4.6:1 and 4% $CoCl_2$ relative to $NaBH_4$. The cooling water was at ambient temperature and the peristaltic pump was used. When on, the water flow rate was 3.2 mL s^{-1}.

The project team repeated this experiment using less $CoCl_2$ (2.5%) and manually toggled the cooling to keep the temperature between 55 and 60 °C. Figure 4.2-2 shows the results. Because we used less catalyst, the reaction took 9.6 min to reach 55 °C. Foaming was minimized and the plot of total gas as a function of time was more linear.

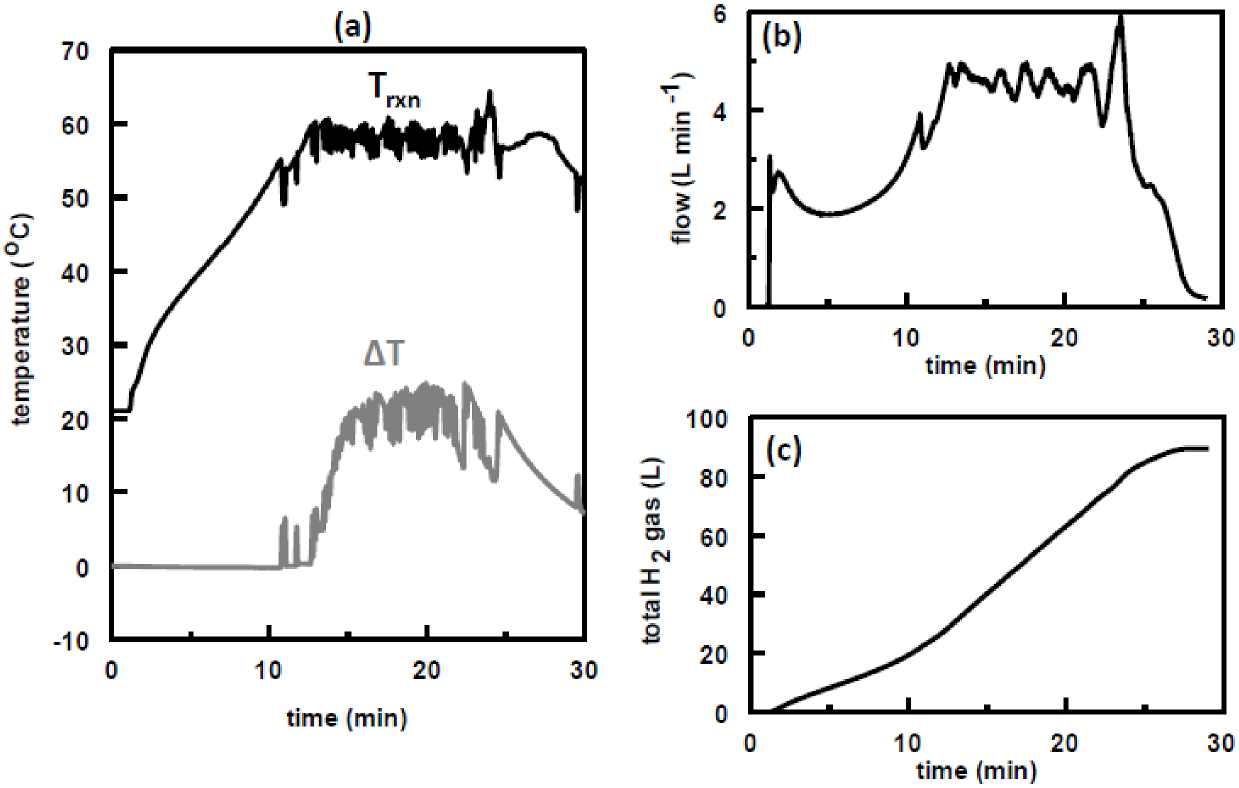


Figure 4.2-2. Results obtained manually toggling the water flow on/off to keep the reaction temperature between 55 and 60 °C, where (a) is a plot of reaction temperature (T_{rxn}) and differential water outlet and inlet temperature (ΔT), (b) is the flow rate, and (c) is total hydrogen gas, all as a function of reaction time. This 100-L experiment used a H_2O:$NaBH_4$ ratio of 4.6:1 and 2.5% $CoCl_2$ relative to $NaBH_4$..The cooling water was at ambient temperature and the peristaltic pump was used. When on, the water flow rate was 3.2 mL s^{-1}.

4.3 COOLING USING AMBIENT TEMPERATURE WATER AND AUTOMATICALLY SHUTTING THE PUMP ON/OFF

As was discussed above, we explored two methods to control the cooling water going through the coils, varying the water flow rate through the coils with continuous cooling and toggling on/off. To automate varying the water flow rate would require a flow meter and a valve to control flow rate, whereas toggling on/off requires a temperature sensor and an on/off switch. Given that temperature sensors, such as thermocouples, are compact and inexpensive and on/off switches are simpler than valves, we decided that toggling on/off would be easier to automate. We then began conducting experiments where the toggling on/off was automated. To accomplish this task, we used a bilge pump (in place of the peristaltic pump) and a computer to control toggling on/off for a given set temperature.

As shown in Figure 2.2-1a, the Cu cooling coils are below the 400-mL mark on the glass cylinder. While conducting the 100-L tests, we noticed that when the water was poured into the reaction vessel, the reagents were initially at the 500-mL mark, which is above the cooling coils. Therefore, cooling would not be homogeneous. We thought that this could be contributing to the foaming issues we observed. To ensure that the reagents were fully in contact with the cooling coils at the beginning of the reaction, we began tests that generated 50 to 60 L of hydrogen gas.

Figure 4.3-1 shows the results of an active cooling experiment using automatic control at a set temperature of 50 ºC and 3.25% $CoCl_2$. Figure 4.3-1a indicates that the reaction took ~ 5 min to reach the set temperature, at which time the computer turned on the bilge pump to flow water through the coils. The number of saw-teeth indicates the number of on/off cycles of the pump (22 cycles in this case). The temperature of the water outlet becomes 14 ºC hotter than the inlet, indicating that the coils are removing heat from the reaction. We observed that the foam level remained at or below the levels of the Cu coils. The rate of hydrogen gas generation was nearly constant, Figure 4.3-1b, and the total gas as a function of time was linear, Figure 4.3-1c. A similar reaction with 3% CoCl2 is shown in Figure 4.3-2. With slightly less catalyst, the flow rate (Figure 4.3-2b) decreases toward the end of the reaction.

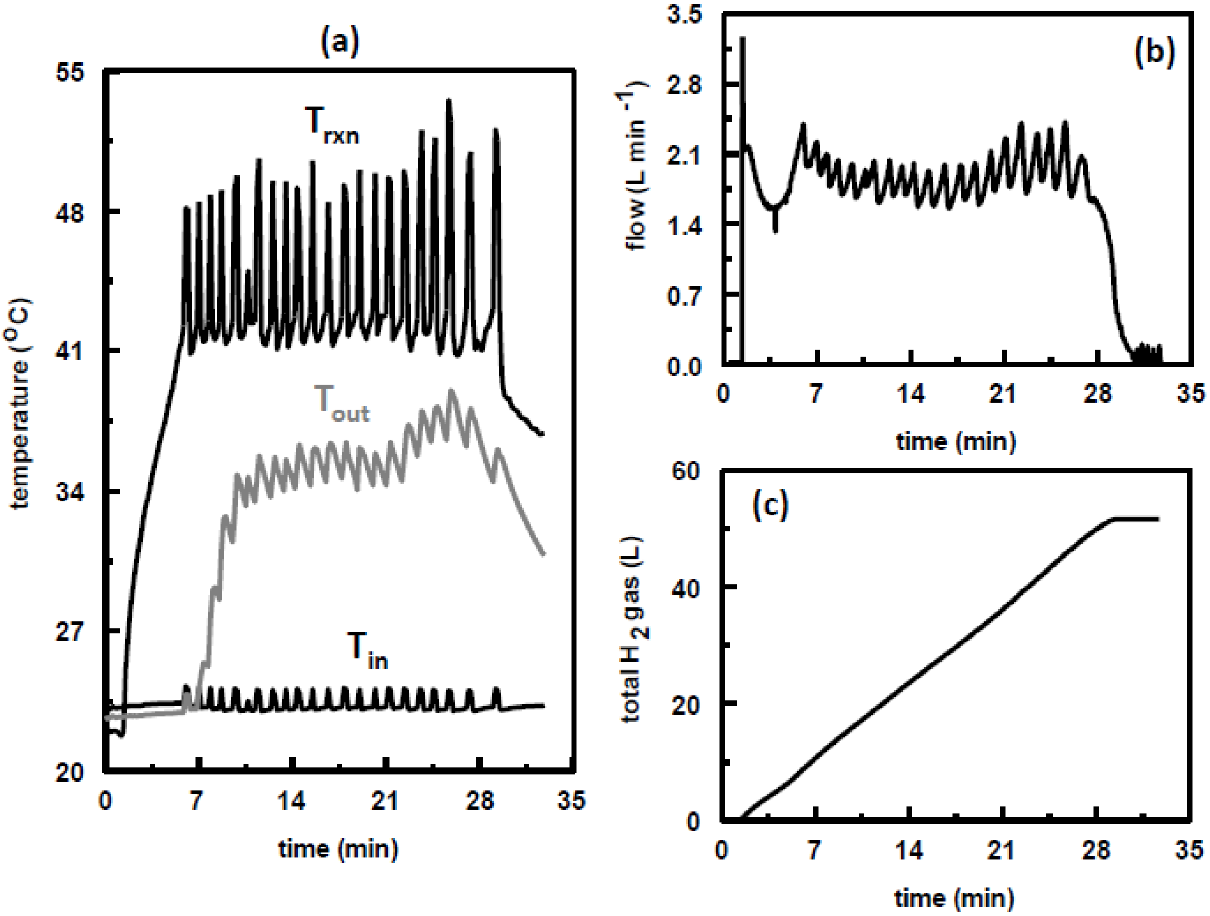


Figure 4.3-1. Results obtained for automatic control of cooling using water at ambient temperatures and a water flow rate of 2.5 mL s^{-1}, where (a) is a plot of reaction temperature (T_{rxn}) and water outlet (T_{out}) and inlet (T_{in}) temperatures , (b) is a plot of the flow rate, and (c) is a plot of total hydrogen gas, all as a function of reaction time. This was a 60-L experiment using a H_2O:$NaBH_4$ ratio of 4.6:1 and 3.25% $CoCl_2$. The set temperature was 50 ºC.

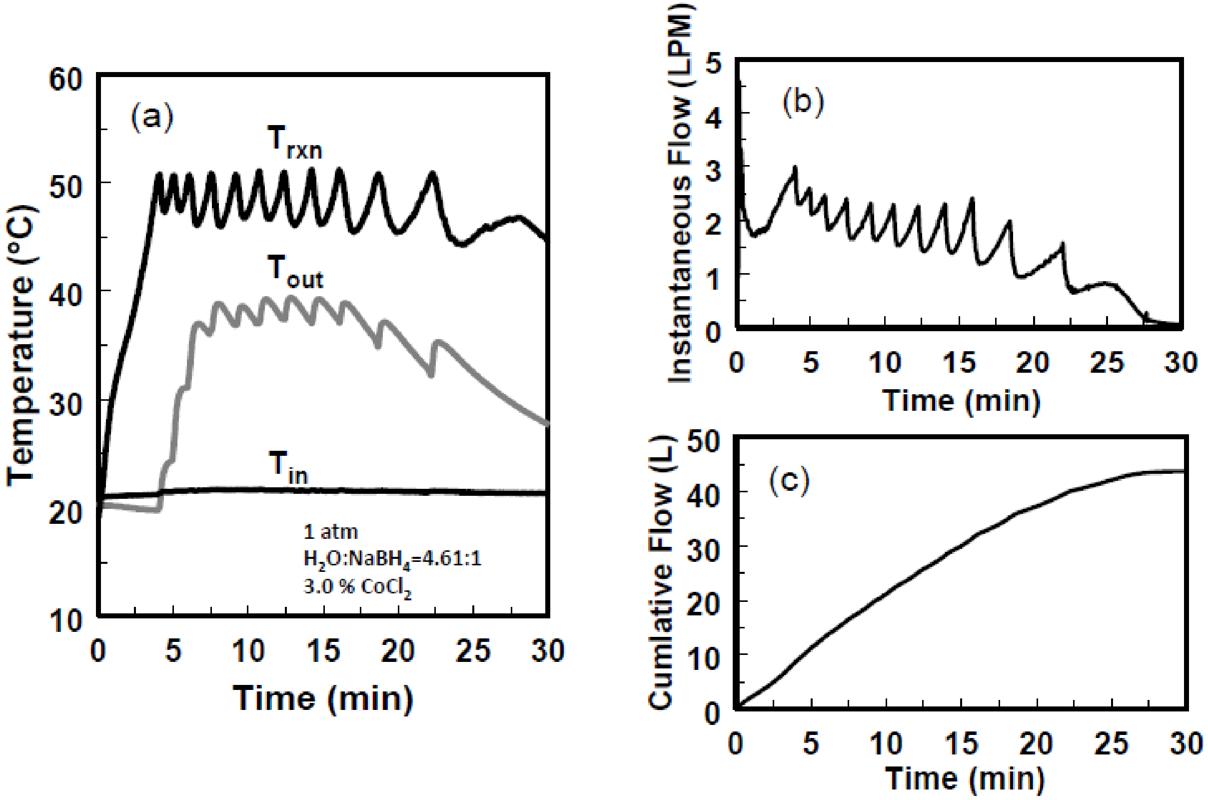
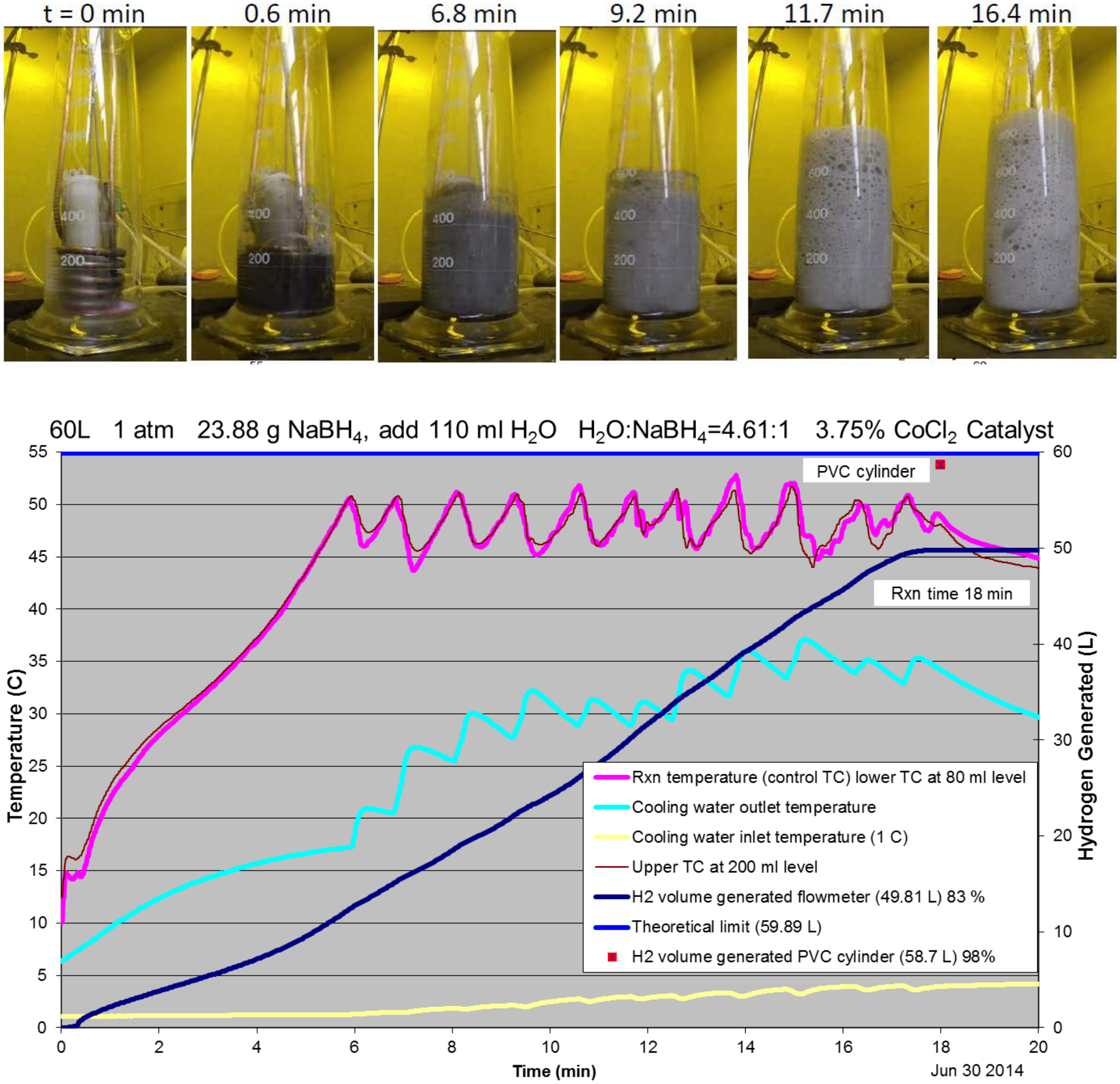


Figure 4.3-2. Results obtained for automatic control of cooling water at ambient temperatures and a water flow rate of 3.125 mL s^{-1}, where (a) is a plot of reaction temperature (T_{rxn}) and water outlet (T_{out}) and inlet (T_{in}) temperatures, (b) is a plot of flow rate, and (c) a plot of total hydrogen gas, all as a function of reaction time. This was a 50-L experiment with set temperature 50 °C.

4.4 COOLING USING CHILLED WATER AND THE EFFECT OF CONTROLLING THERMOCOUPLE PLACEMENT

Some LTA deployments will be in colder climates, so we conducted experiments using chilled cooling water. In these experiments, we immersed the bilge pump and hoses in an ice-water bath and chilled the glass reaction vessel by immersing it in an ice-water bath for ~ 1 hr. Prior to initiating the reaction, we took the glass reaction vessel out of the ice bath. The reaction was initiated by pouring chilled water into the reaction vessel.

Foaming was a greater problem when using chilled water for cooling. Figure 4.4-1 shows photographs taken of the reaction as a function of time. The photograph taken at 0 min shows that the cooling coils in the glass reaction vessel are at the 300-mL mark. The stainless steel basket containing the $NaBH_4$ and PVC rod are also shown. At 0.6 min, we had poured the water into the glass reaction vessel, starting the reaction. The mixture is black due to the formation of the Co_2B catalyst, and since it is at the 250-mL mark, the mixture is in contact with the Cu cooling coils. After 6.8 min, the mixture is gray due to the formation of $NaBO_2$ and the reaction is beginning to foam. Photographs taken at 11.7 and 16.4 min into the reaction show that the foam reached the 800-mL mark. Large gas bubbles are observed, indicating that the mixture is becoming more viscous. A chart of the reaction, Figure 4.4-1, shows that the temperatures of the control thermocouple at the 80-mL level and the upper thermocouple at the 200-mL level are nearly superimposed, indicating good mixing. As the viscosity increases, we observed white crystals come out of the solution, Figure 4.4-2a. We took Raman spectra of the white crystals. These spectra, shown in Figure 4.4-2b, indicate that the crystals are $NaB(OH)_4$ [11]. As shown by reaction (1), the solid by-product, $NaBO_2 \cdot xH_2O$, exists with varying degrees of hydration. To form $NaB(OH)_4$, each molecule of $NaBO_2$ will take out two molecules of H_2O. Removal of water will increase the viscosity, resulting in foaming.



Greater turbulence from foam provides better heat transfer to the coils. Upper and lower TCs read the same. Cooling rate: 3.23 ml/sec Auto-toggle cooling on at 50 C, off at 50 C

Figure 4.4-1. Photographs of a reaction that foamed badly (top). Times into the reaction are indicated. Temperature and flow data are show to the left. This was a 60-L hydrogen gas generation run. The $H_2O:NaBH_4$ ratio was 4.6:1, 3.75% $CoCl_2$ relative to $NaBH_4$, and a cooling water flow rate of 3.2 mL s^{-1}. The project team chilled the cooling water and used the bilge pump. The set temperature was 50 ºC and was controlled automatically. The controlling thermocouple was at the 50-mL mark of the glass reaction vessel. The set point temperature was under automatic control.

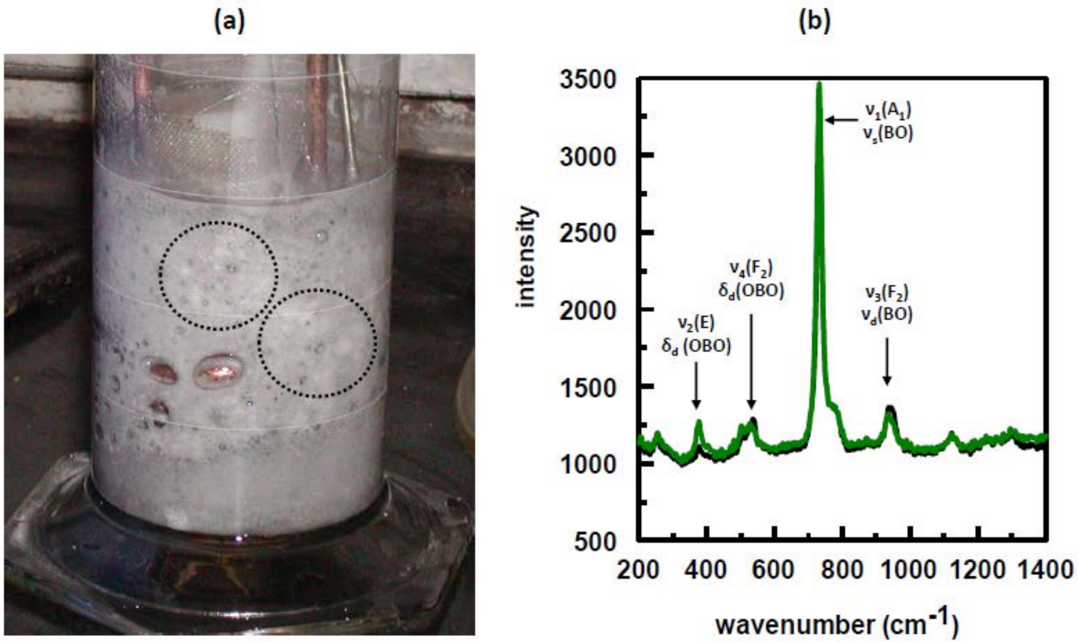


Figure 4.4-2. (a) Photograph of a reaction that foamed badly showing white crystals coming out of solution (circled), (b) Raman spectra obtained of the crystals that came out of solution. The molecule is tetrahedral. Peak assignments are shown.

A reaction was imaged using a forward looking infrared (FLIR) thermal camera. Images are shown in Figure 4.4-3. The images show that the reaction temperature is not homogeneous and that the temperature is hotter at the air/liquid interface.

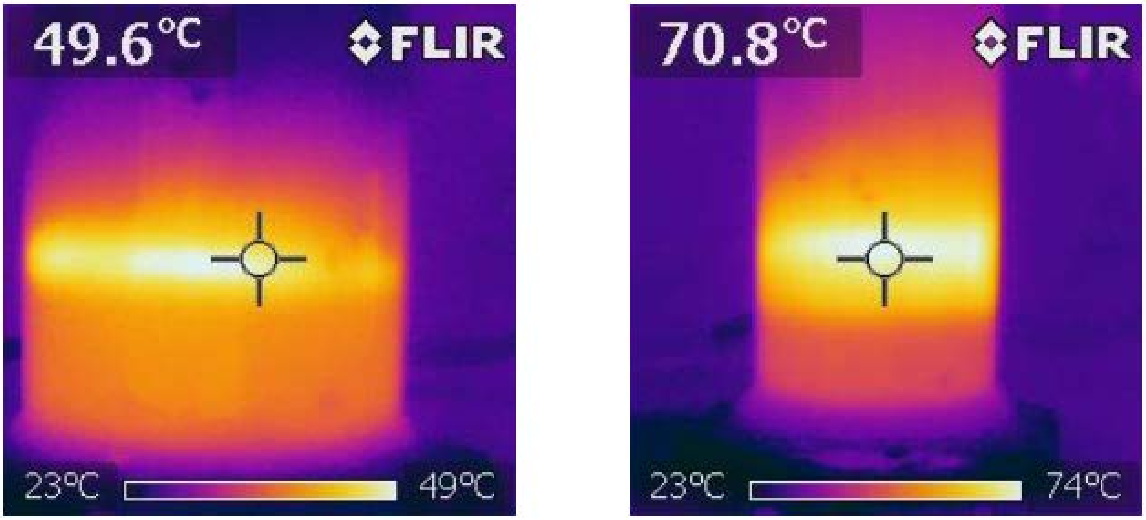


Figure 4.4-3. Infrared images obtained for a reaction that foamed badly. This sample was a 60-L hydrogen gas generation run. The H_2O:$NaBH_4$ ratio was 4.6:1, 0.83% $RuCl_3$ relative to $NaBH_4$, and a cooling water flow rate of 3.1 mL s^{-1}. The cooling water was chilled and the bilge pump was used. The set temperature was 50 ˚C and was under automatic control.

We then did 60-L experiments placing two thermocouples inside the reaction vessel at two different levels. The lower thermocouple was placed at the 50-mL mark and the upper at the 200-mL mark in the reagents (the liquid level started at the 250-mL level). In one experiment, we used the lower thermocouple to monitor/control the reaction. The results are summarized in Figure 4.4-4. The reaction took 9 min to reach the set temperature of 45 °C, at which point the computer turned on the bilge pump to flow chilled water through the coils. As shown in Figure 4.4-4a, the temperature of the lower thermocouple was maintained at 45 °C. The two thermocouples tracked one another until ~ 20 min into the reaction. At this point the temperature of the upper thermocouple began to increase. The temperatures registered by the upper thermocouple were temperatures 5 to 30 ˚C hotter than the lower thermocouple. At the maximum temperatures of the upper thermocouple, the foam reached the 500-mL mark. The flow rate, shown in Figure 4.4-4b, is fairly linear at ~ 1.4 L min^{-1}. However, ~ 20 min into the reaction, the flow rate increases and reaches its maximum at 5.7 L min^{-1}. The increase in flow rate coincided with the increase in temperature measured by the upper thermocouple. The total flow as a function of time, Figure 4.4-4c, is nonlinear.

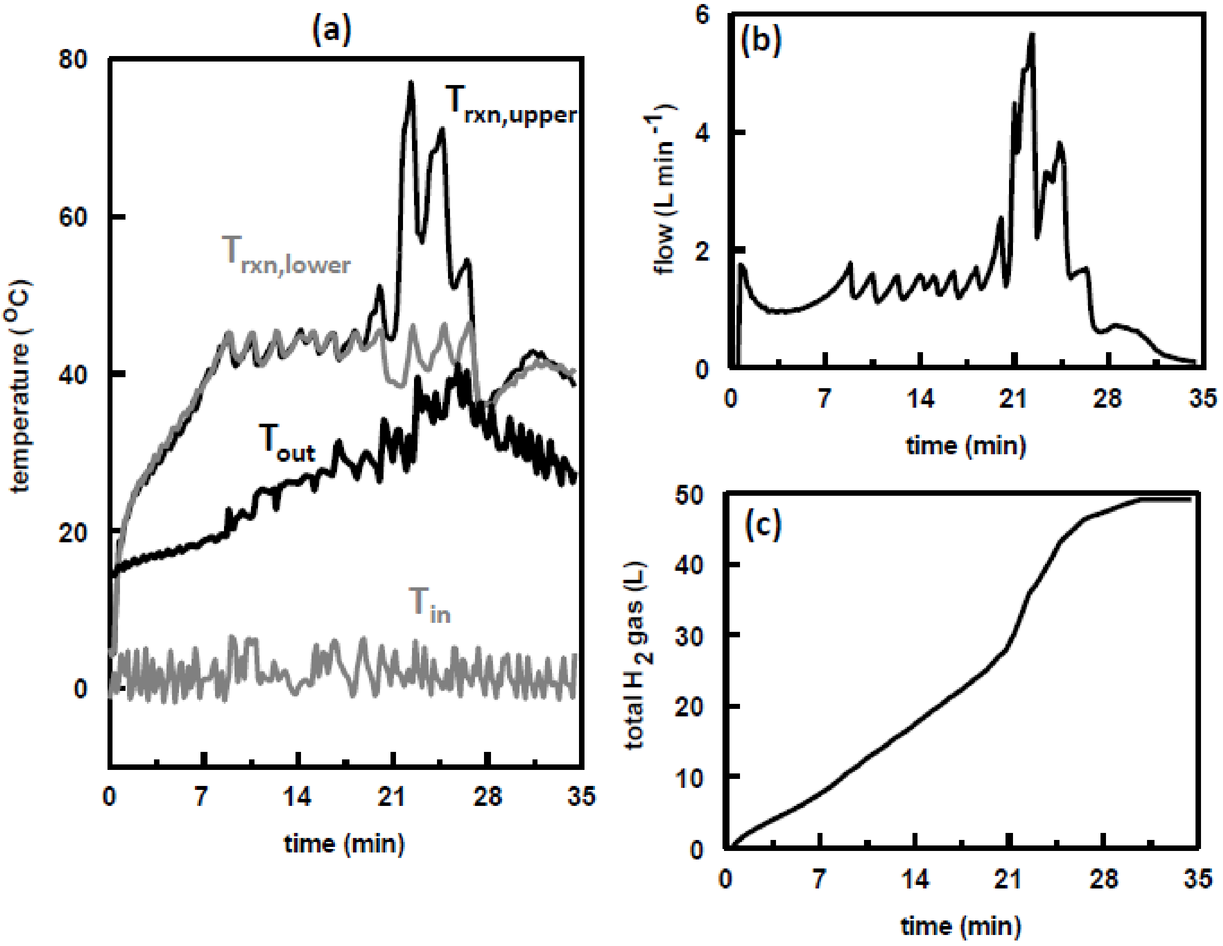


Figure 4.4-4. Results obtained for automatic control of cooling using chilled cooling water and a water flow rate of 3.0 mL s^{-1}, where (a) is a plot of reaction temperatures ($T_{rxn,upper}$ and $T_{rxn,lower}$) and water inlet (T_{in},) and outlet (T_{out}) temperatures, (b) is a plot of the flow rate, and (c) is plot of total hydrogen gas as a function of reaction time. This was a 60-L experiment using a H_2O:$NaBH_4$ ratio of 4.6:1 and 4.0% $CoCl_2$. The set temperature was 45 °C and the $T_{rxn,lower}$ thermocouple was used to monitor/control the reaction.

In the second experiment, we used the upper thermocouple to monitor/control the reaction. Other experimental conditions are similar to those used in the experiment using the lower thermocouple for control. The results are summarized in Figure 4.4-5. It took almost 20 min to get to the set temperature. The temperatures stayed at or below 45 °C, Figure 4.4-5a. The reaction took longer to complete. The flow rate was fairly constant, Figure 4.4-5b, and the total flow as a function of time, Figure 4.4-5c, was nearly linear. Foaming did reach the 400-mL mark.

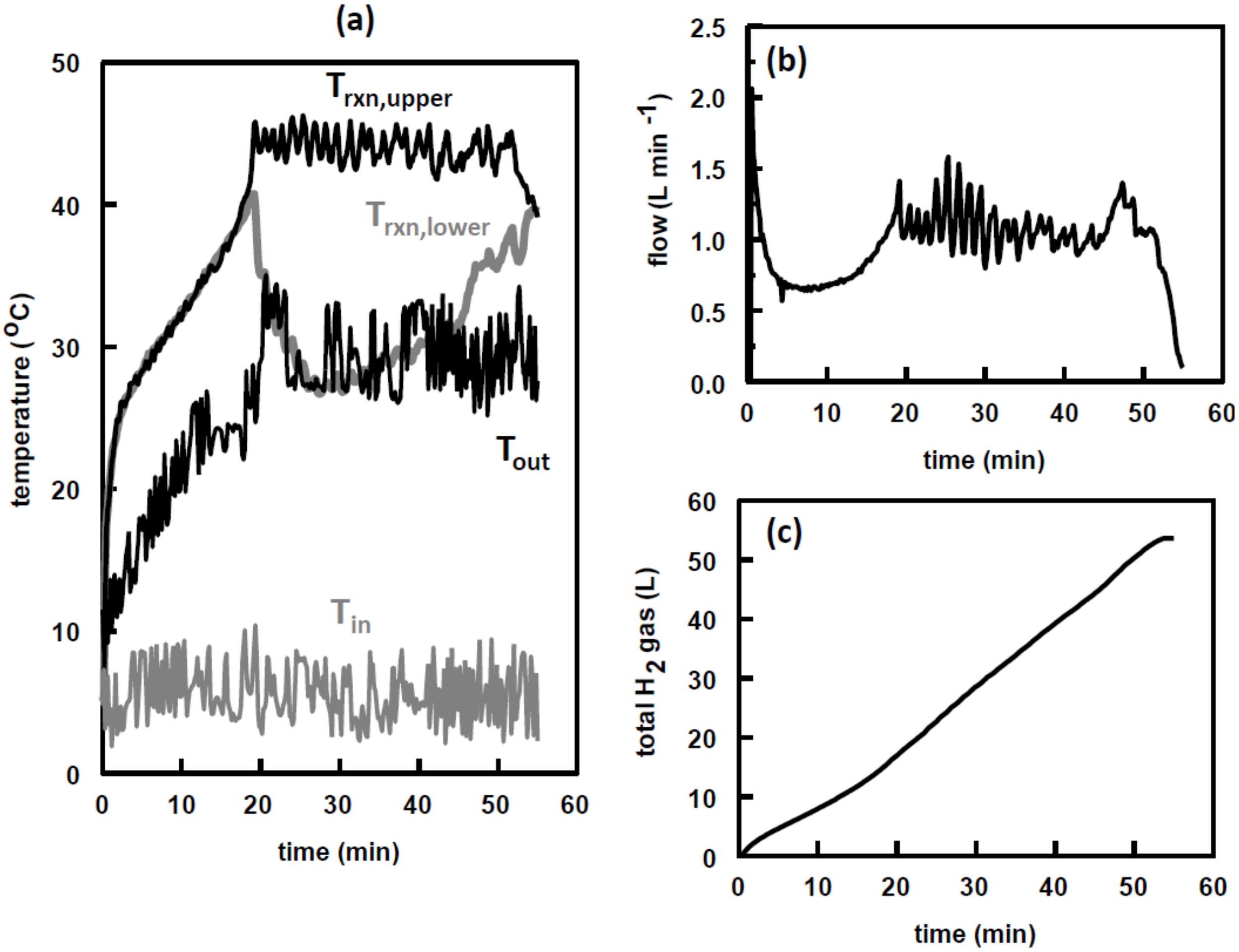


Figure 4.4-5. Results obtained for automatic control of cooling using chilled cooling water and a water flow rate of 3.2 mL s^{-1}, where (a) is a plot of reaction temperatures ($T_{rxn,upper}$ and $T_{rxn,lower}$) and water inlet (T_{in}) and outlet (T_{out}) temperatures, (b) is a plot of the flow rate, and (c) is a plot of total hydrogen gas, all as a function of reaction time. This was a 60-L experiment using a H_2O:$NaBH_4$ ratio of 4.6:1 and 4.0% $CoCl_2$. The set temperature was 45 °C and the $T_{rxn,upper}$ thermocouple was used to monitor/control the reaction.

5. HYDROGEN GENERATION EXPERIMENTS CONDUCTED UNDER PRESSURE

Foaming is a big issue in these experiments. Ways to alleviate it are to reduce the amount of $CoCl_2$, decrease the reaction set point, or increase the amount of water for the reaction. These actions would also create longer reaction times. Should weight be a constraining factor, increasing the amount of water may not be a viable option. Anti-foaming agents exist, but chemical methods of foam control may cause contamination problems as well as a reduction in mass transfer [12]. We then began to explore mechanical methods of foam control. Many oils foam when trapped gas is suddenly released under conditions of an abrupt drop in pressure [13]. Bilstein used pressure to prevent foaming in their off-road shock absorbers [14]. We then began to conduct tests under pressure to see if this would minimize the foaming. An added advantage of pressure is that it would reduce the amount of water vapor that will get into the gas stream. We used the apparatus shown in Figure 2.3-1 for these tests. In these experiments, we took five temperature measurements as a function of time. Four thermocouples were in the reaction vessel. Thermocouple T_1 was in contact with the reagents and was used to monitor/control the reaction. Thermocouple T_2 was placed at the air/liquid interface. Thermocouples T_3 and T_4 were placed above the reagents. A thermocouple was placed in a plastic test tube taped to the water outlet of the Cu coil to measure the temperature of outlet water, T_{out}. We used a GoPro® camera and a LED light source inside the pressure canister to obtain videos of the reactions.

5.1 EXPERIMENT CONDUCTED AT AMBIENT PRESSURE USING CHILLED COOLING WATER

To establish a baseline for comparison, we conducted an experiment at ambient pressure. In this experiment, the glass reaction vessel was placed on top of a stand so that it was not in contact with the cooling water exiting the Cu coils. The results are summarized in Figure 5.1-1 and in Figure 5.1-2. Figure 5.1-1a shows that it took 2.2 min for the reaction to get to temperature before the cooling was activated. The temperature of thermocouple, T_1, in the reagents stayed steady at 45 °C. For 6 min, thermocouples, T_2, T_3, and T_4, tracked thermocouple, T_1. After 6 min into the reaction, the temperatures of thermocouples, T_2, T_3, and T_4, increased, with T_2 peaking at 54 °C, T_3 at 62 °C, and T_4 at 65 °C. Figure 5.1-2 shows some images of the reaction taken at the times indicated. At point (a), the basket containing $CoCl_2$ and $NaBH_4$ has already dropped into the water. The water is dark, indicating the formation of Co_2B. At point (b), foaming begins to occur. After 5 min into the reaction, the entire field of view was engulfed in foam. From this time until 14 min into the reaction, all four thermocouples were immersed in foam, as represented by the photo at point (c). After 7 min into the reaction, the video shows large coalesced bubbles of hydrogen gas leaving the reaction mixture. An example of this is shown at point (d). These large bubbles indicate that the reaction mixture has become viscous.

Figure 5.1-1b shows the hydrogen gas flow rate as a function of time. The flow rate varies between 2 and 5 L min-1. The total flow rate as a function of time, Figure 5.1-1c, is nearly linear.

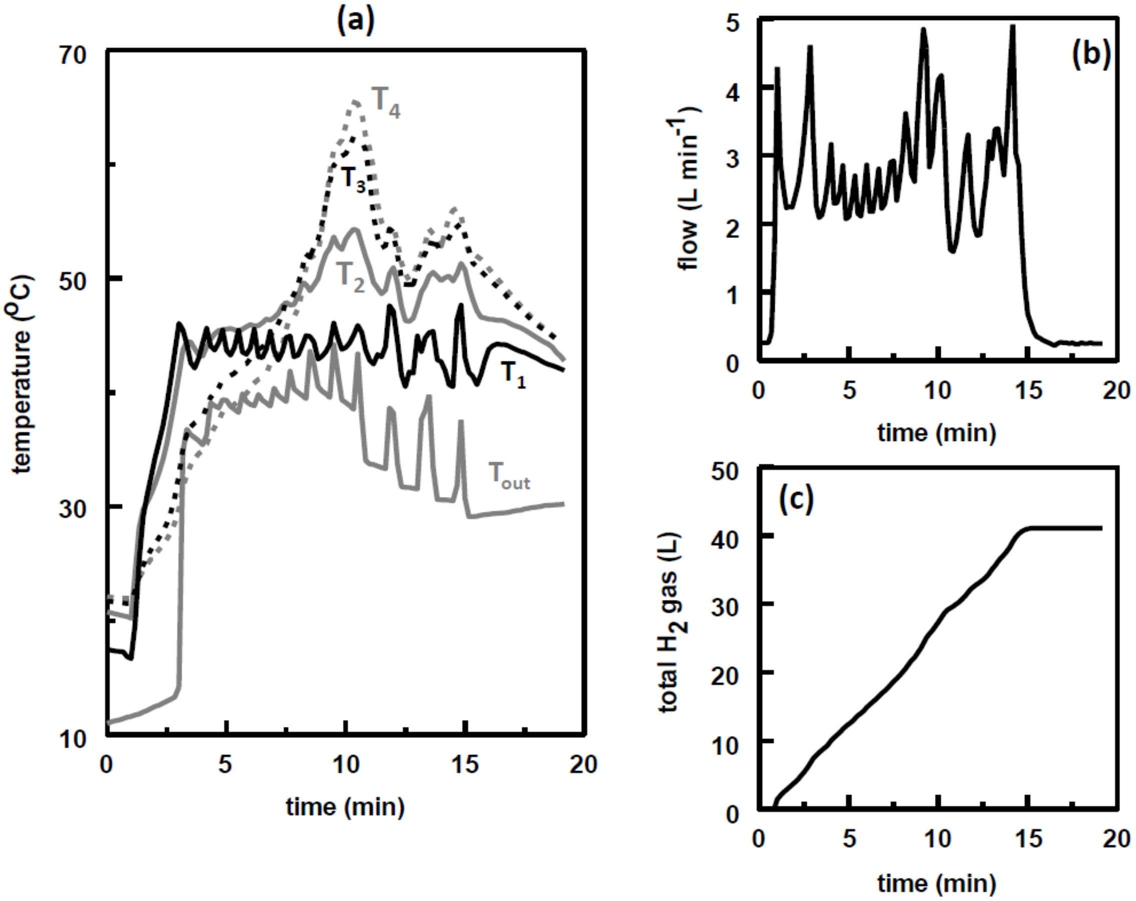


Figure 5.1-1. Results obtained for automatic control of cooling using chilled cooling water at 5.7 °C and a water flow rate of 4.6 mL s^{-1}, where (a) is a plot of reaction temperatures (T_1 through T_4) and water outlet temperature (T_{out}), (b) is a plot of the flow rate, and (c) is a plot of total hydrogen gas as a function of reaction time. This experiment was conducted in the pressure canister at an applied pressure of 0 psig, using a H_2O:$NaBH_4$ ratio of 4.6:1 and 3.0% $CoCl_2$. The set temperature was 45 ˚C and thermocouple T_1 was used to monitor/control the reaction.

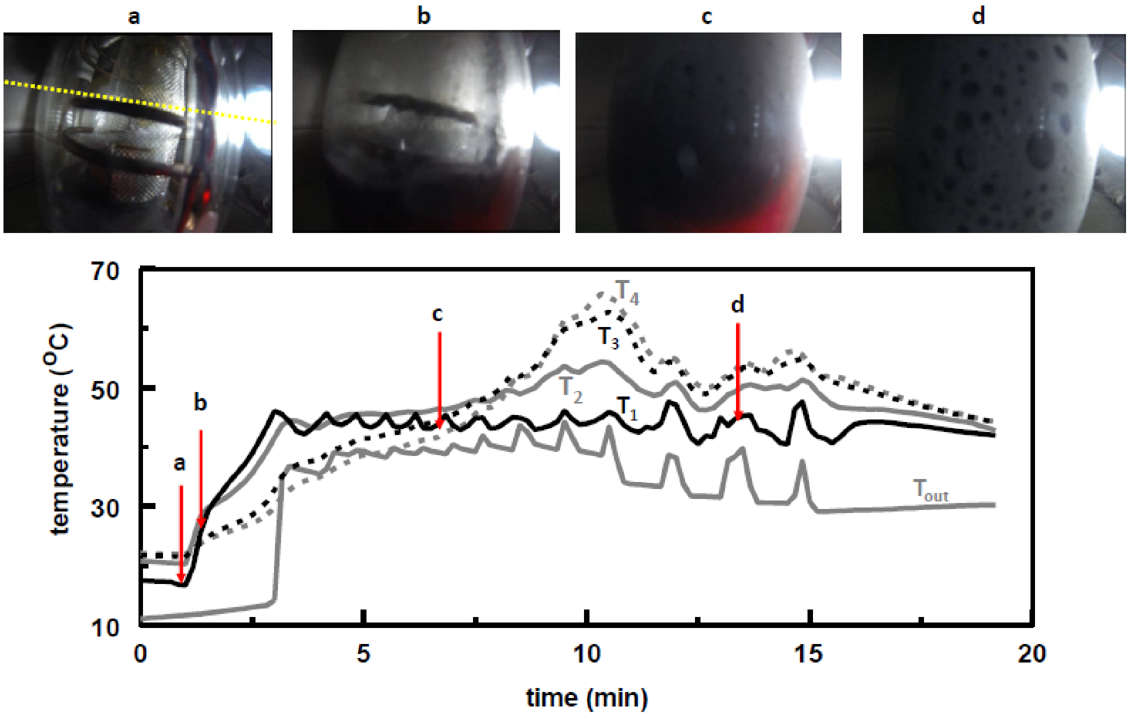


Figure 5.1-2. Images of the reaction at 0 psi showing foaming (yellow line in first image indicates the 2.4 in mark). Arrows in the temperature plots show when the images were taken. Thermocouples are indicated. This experiment was done in the pressure canister at an applied pressure of 0 psig using a H_2O:$NaBH_4$ ratio of 4.6:1 and 3.0% $CoCl_2$ relative to $NaBH_4$. The temperature of the chilled water was 5.7 °C. The set temperature was 45 °C and thermocouple T_1 was used to monitor/control the reaction.

5.2 EXPERIMENTS CONDUCTED UNDER PRESSURE USING AMBIENT TEMPERATURE WATER

In these experiments, the glass reaction vessel was not on a stand inside the reaction can, Figure 2.3-1b. Consequently, the glass reaction vessel would be in contact with the cooling water that exited the Cu coils. Experiments were conducted at applied pressures of 13 and 50 psig. Temperature and gas flow results for the 13- and 50-psig experiments are summarized in Figures 5.2-1 and 5.2-3, respectively.

Figure 5.2-1a shows the temperature data for the experiment conducted under a pressure of 13 psig. The set temperature was initially 45 °C. Thermocouple, T_1, was always in contact with the solution. T_1 took 1.1 min to reach the set temperature, at which time the cooling turned on. Even with active cooling, the temperature recorded by T_1 shot past the set point and peaked at 50 °C. The temperature of T_1 then came down and active cooling kept it at 45 °C. After 14 min into the reaction, the set temperature was changed to 50 °C. T_1 took 3.5 min to reach 50 °C. As shown in Figure 5.2-1a, the temperature of T_1 stayed steady at 50 °C and, after 24 min began to decrease due to completion of the reaction. The thermocouple placed near the reagent/air interface, T_2, showed higher temperatures than T_1 for the first 14 min, peaking at 55 ˚C. When the set temperature was changed to 50 C, T_2 tracked T_1 for 8 min, at which time the temperature recorded by T_2 dropped below that of T_1. This indicates that at 22.5 min into the reaction, T_2 is above the solution/air interface.

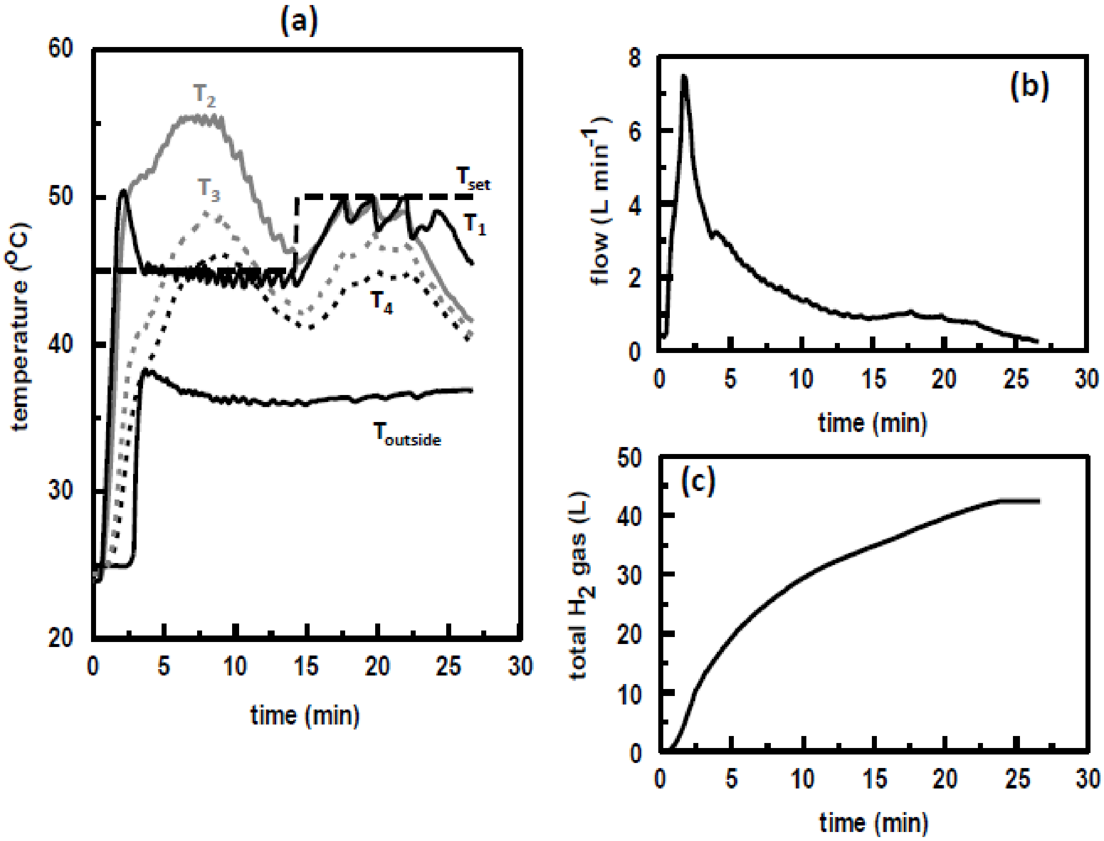


Figure 5.2-1. Results obtained for automatic control of cooling using ambient cooling water and a water flow rate of 4.6 mL s^{-1}, where (a) is a plot of reaction temperatures (T_1 through T_4,) and the temperature outside the glass reaction vessel ($T_{outside}$), (b) is a plot of the flow rate, and (c) is a plot of total hydrogen gas as a function of reaction time. This experiment was conducted in the pressure tank at an applied pressure of 13 psig using a H_2O:$NaBH_4$ ratio of 4.6:1 and 3.0% $CoCl_2$ relative to $NaBH_4$. The set temperatures are indicated, T_{set}, and thermocouple T_1 was used to monitor/control the reaction.

Figure 5.2-1b shows a plot of flow rate as a function of time. Most of the hydrogen gas generation occurred during the first 8 min of the reaction. The total flow rate, Figure 5.2-1c, is nonlinear. Using the video obtained from the Go-Pro® camera, we measured the foam level as a function of time. A plot of foam level as a function of time is shown in Figure 5.2-2. An initial spike to the foam exists at 1.7 due to the formation of the Co_2B catalyst. Compared to the images shown in Figure 5.1-2, the foam does not get to the 2.4-in mark, indicating that a pressure of 13 psig does suppress foaming.

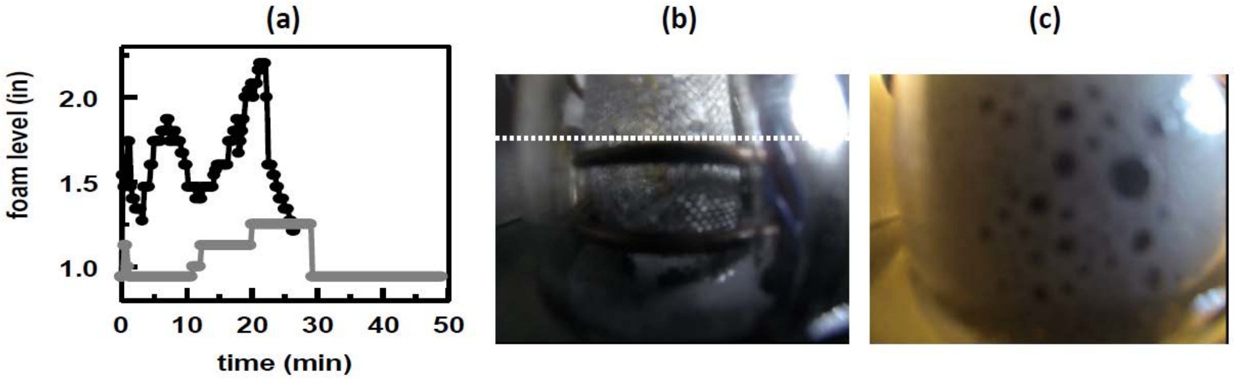


Figure 5.2-2. (a) Plot of foam level as a function of time for applied pressures of 13 and 50 psig. Temperature and flow data are shown in Figures 5.2-1 and 5.2-3. Images of the same reaction at applied pressures of (b) 50 psig (dashed white line is at the 2.4-in mark), and (c) 0 psig. In (c), the foam completely fills the field of view.

The temperature data for the experiment conducted under a pressure of 50 psig are summarized in Figure 5.2-3a. The set temperature was 45 °C. Thermocouple, T_1, was always in contact with the solution. T_1 took less than 1 min to reach the set temperature when the cooling was activated. Even with active cooling, the temperature recorded by T_1 shot past the set point and peaked at 61 °C. The temperature of T_1 then came down and active cooling kept it at 45 ^{O}C. This temperature spike was not observed in the experiment at an applied pressure of 0 psig, Figure 5.1-1a. The results in Figure 5.2-3a show that T_1 registered higher temperatures than the other thermocouples. Figure 5.2-3b shows a plot of flow rate as a function of time. Most of the hydrogen gas was produced during the first three minutes of the reaction. The total flow as a function of time, Figure 5.2-3c, is nonlinear. Figure 5.2-2a shows a plot of foam level as a function of time. This plot shows that a pressure of 50 psig suppresses the foaming better than a pressure of 13 psig. The suppression of foam by pressure is aptly demonstrated by the photographs shown in Figures 5.2-2b and 5.2-2c. Figure 5.2-2b shows an image taken of a reaction at 50 psig that had not gone to completion. No foaming is observed. When the pressure was released, Figure 5.2-2c, the foam filled the camera’s field of view.

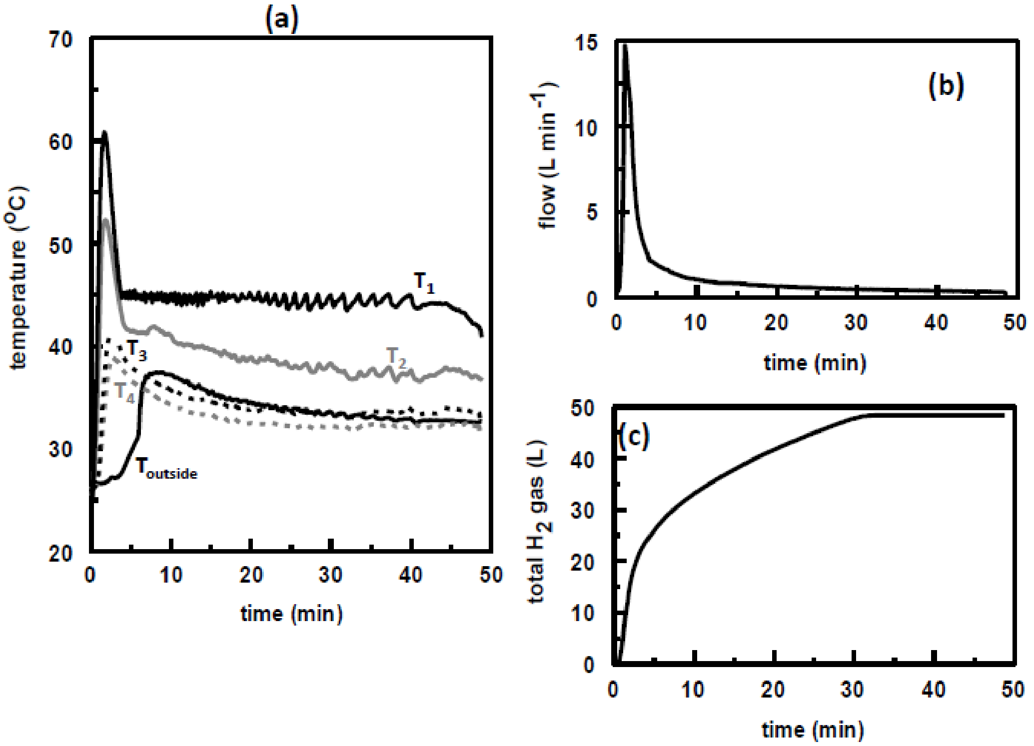


Figure 5.2-3. Results obtained for automatic control of cooling using ambient cooling water and a water flow rate of 4.6 mL s^{-1}, where (a) is a plot of reaction temperatures (T_1 through T_4,) and the temperature outside the glass reaction vessel ($T_{outside}$), (b) is a plot of the flow rate, and (c) is a plot of total hydrogen gas as a function of reaction time. This experiment was conducted in the pressure tank at an applied pressure of 50 psig using a H_2O:$NaBH_4$ ratio of 4.6:1 and 3.0% $CoCl_2$ relative to $NaBH_4$. The set temperatures war 45 ˚C and thermocouple T_1 was used to monitor/control the reaction.

5.3 EXPERIMENTS CONDUCTED UNDER PRESSURE USING CHILLED COOLING WATER

In these experiments, the glass reaction vessel was placed on a stand inside the reaction can, Figure 2.3-1b. We conducted the experiment summarized in Figure 5.1-1 under no applied pressure and used chilled water for cooling. This experiment was repeated using a pressure of 50 psig. Videos taken using the Go-Pro® camera inside the pressure can showed that foaming was suppressed. The results of this experiment are summarized in Figure 5.3-1. Figure 5.3-1a shows the temperature data. Like the experiment done under 0 psig pressure, it took ~ 2.3 min for the T_1 to reach the set temperature of 45 ˚C. However, unlike the 0 psig experiment, T_1 continued to increase and peaked at 64 ˚C. The temperature at the air/reagent interface peaked at 106 ˚C, and the temperatures in the air above the reagents peaked at 106 and 97 ˚C. The temperature of the water exiting the Cu cooling coils peaked at 73 ˚C, indicating that the coils were carrying away a great deal of heat. Figure 5.3-1b is a plot of flow rate as a function of time showing that most of the hydrogen gas is produced during the first 4 min of the reaction. Figure 5.3-1c shows plots of gas pressure and total hydrogen gas produced as a function of time. We observed a pressure spike that coincides with the flow rate. The total hydrogen gas generation was linear. At the end of the experiment, crystals were observed in the spent reagents. This indicated that, under pressure and using chilled cooling water, the $NaBO_2$ comes out of solution. When this happens, it takes out water. With less water, the reaction gets hotter and a thermal runaway occurs as shown by the temperature measurements, Figure 5.3-1a.

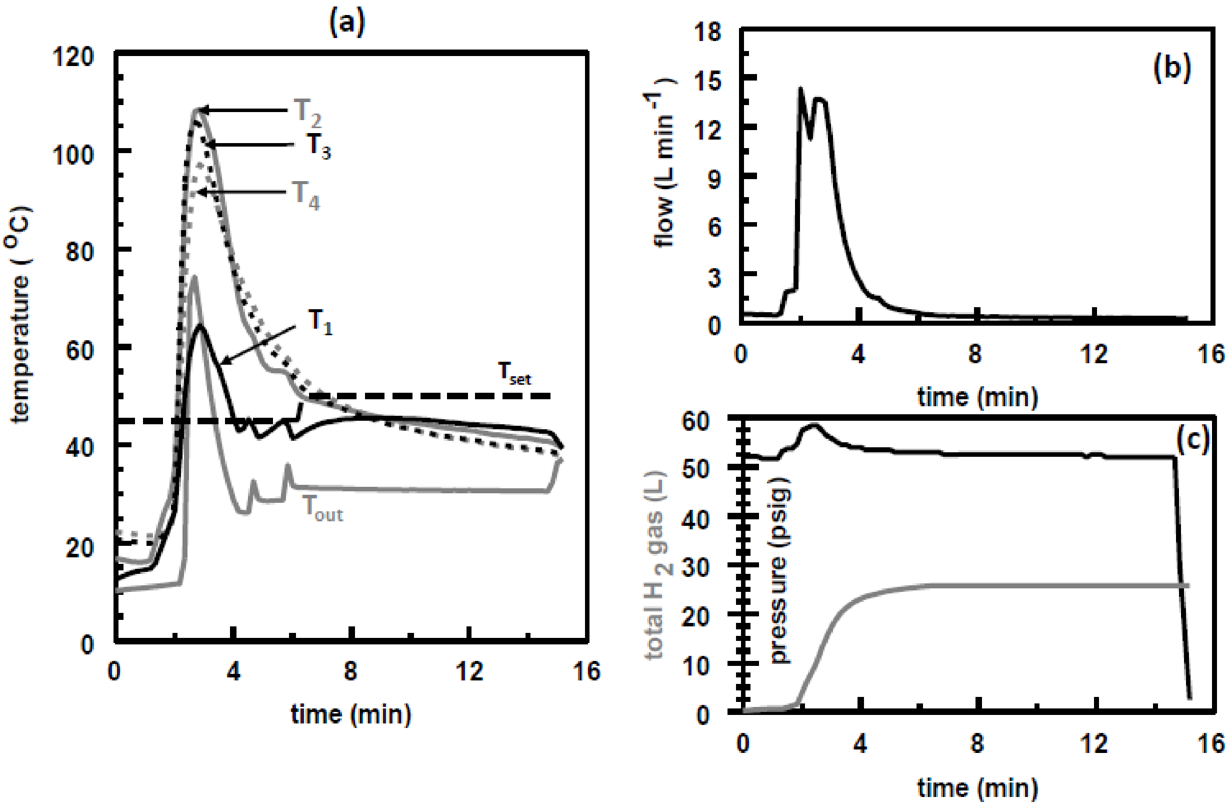


Figure 5.3-1. Results obtained for automatic control of cooling using chilled cooling water at 5.4 C and a water flow rate of 4.6 mL s^{-1}, where (a) is a plot of reaction temperatures (T_1 through T_4), set temperatures (T_{set}), and water outlet temperature (T_{out}), (b) is a plot of the flow rate, and (c) is a plot of the pressure, P, and total hydrogen gas, all as a function of reaction time. This experiment was conducted in the pressure canister at an applied pressure of 50 psig using a H_2O:$NaBH_4$ ratio of 4.6:1 and 3.0% $CoCl_2$. Thermocouple T_1 was used to monitor/control the reaction.

The experiment was then repeated using the same amount of $CoCl_2$ and a lower set temperature to see if this would prevent the thermal runaway. The results, summarized in Figure 5.3-2, showed that this did not prevent the thermal runaway. The experiment was repeated using 2% $CoCl_2$, instead of 3%, as well as using a lower set temperature. The results are summarized in Figure 5.3-3. Temperature measurements, Figure 5.3-3a, indicate that the reaction was controlled. The highest temperature reached was 67 ˚C, and this was at the air/reagent interface. The temperatures above the interface were lower. Figure 5.3-3b shows the flow rate as a function of time. No flow was recorded during the first 11 min because the pressure release valve was not functioning properly. However, Figure 5.3-3c shows a plot of gas pressure as a function of time. The gas pressure is increasing linearly during the first 11 min, indicating that the gas generation was fairly constant during this period. After 11 min, the pressure reached 54 psi and the release valve opened. When this happened, the flow rate, Figure 5.3-3b, was fairly constant and total hydrogen gas, Figure 5.3-3c, as a function of time, was linear.

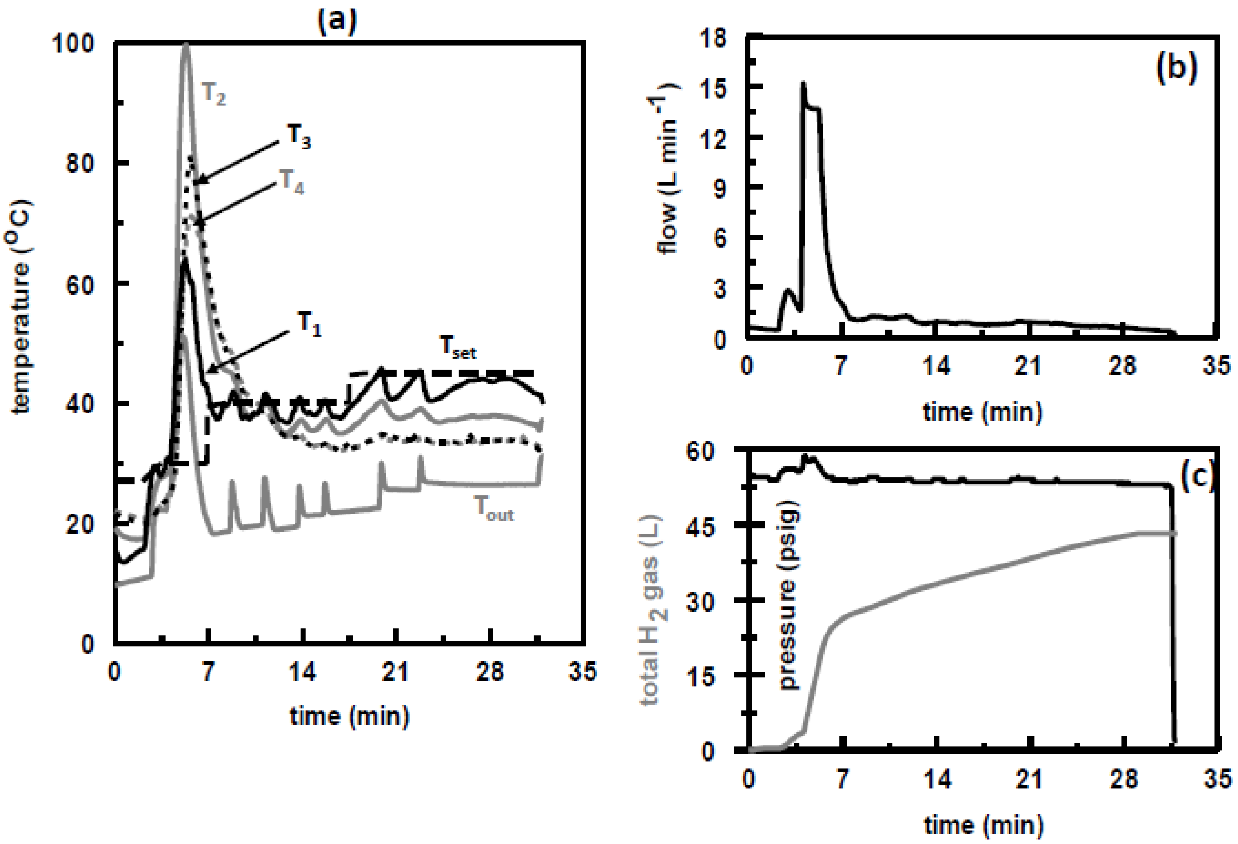


Figure 5.3-2. Results obtained for automatic control of cooling using chilled cooling water and a water flow rate of 4.6 mL s^{-1}, where (a) is a plot of reaction temperatures (T_1 through T_4), set temperatures (T_{set}) and water outlet temperature (T_{out}), (b) is a plot of the flow rate, and (c) is a plot of the pressure, P, and total hydrogen gas, all as a function of reaction time. This experiment was conducted in the pressure canister at an applied pressure of 50 psig, using a H_2O:$NaBH_4$ ratio of 4.6:1 and 3.0% $CoCl_2$ relative to $NaBH_4$. The temperature of the chilled water was 5.4 ˚C. Thermocouple T_1 was used to monitor/control the reaction.

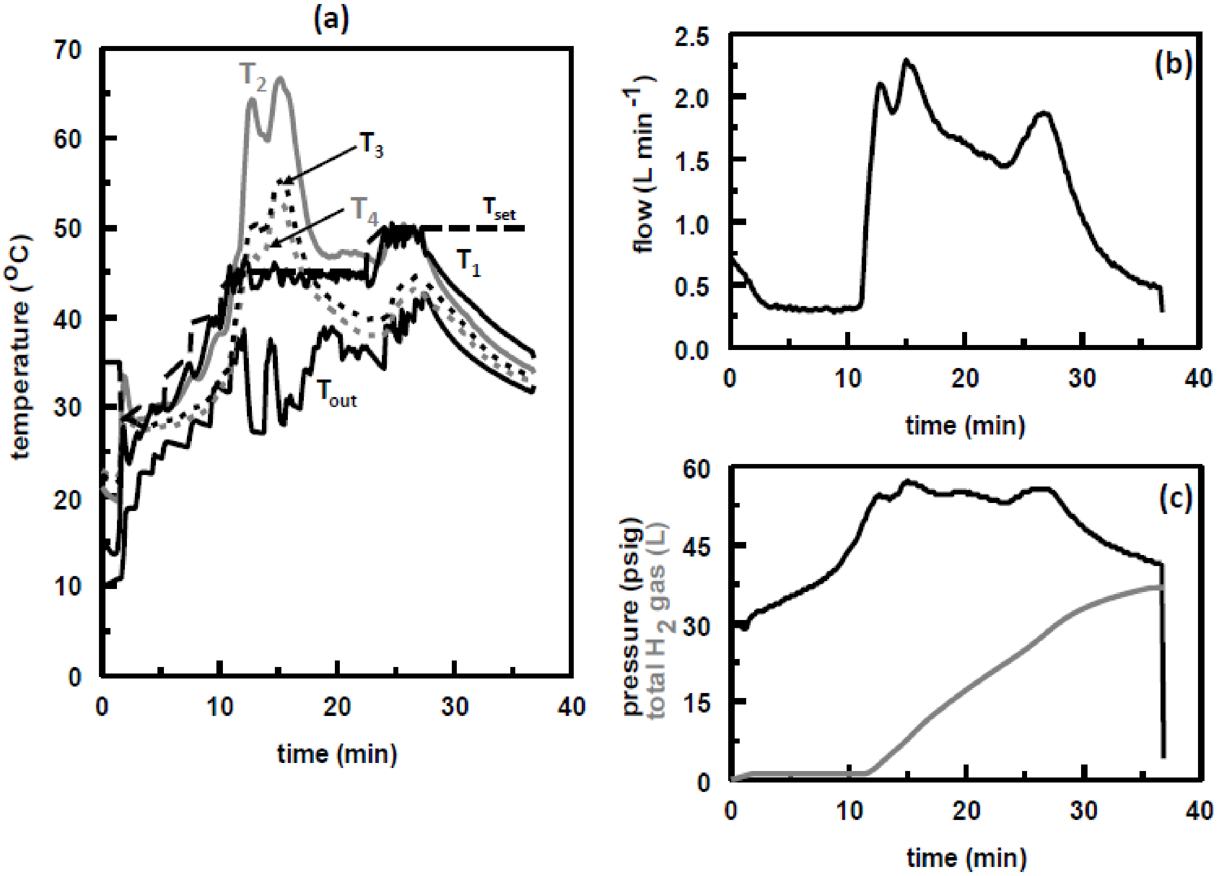


Figure 5.3-3. Results obtained for automatic control of cooling using chilled cooling water at 5.1 °C and a water flow rate of 4.6 mL s^{-1}, where (a) is a plot of reaction temperatures (T_1 through T_4,), set temperatures (T_{set}) and water outlet temperature (T_{out}), (b) is a plot of the flow rate, and (c) is a plot of the pressure, P, and total hydrogen gas, all as a function of reaction time. This experiment was conducted in the pressure canister at an applied pressure of 50 psig using a H_2O:$NaBH_4$ ratio of 4.6:1 and 2.0% $CoCl_2$. Thermocouple T_1 was used to monitor/control the reaction.

If the application allows it, another solution to the thermal runaway problem is to use more water compared with $NaBH_4$. This is summarized in Figure 5.3-4. Because of the extra water, one must increase the amount of $CoCl_2$ and use a higher set temperature.

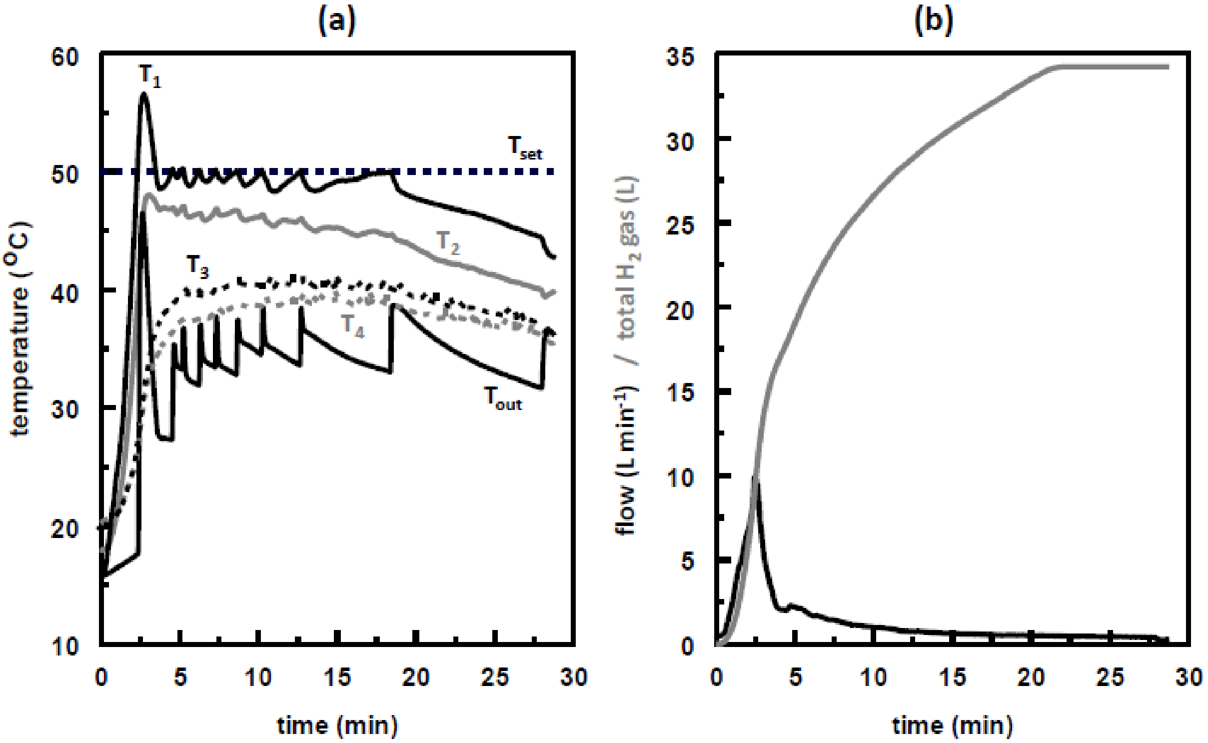


Figure 5.3-4. Results obtained for automatic control of cooling using chilled cooling water at 5.4 °C and a water flow rate of 4.6 mL s^{-1}, where (a) is a plot of reaction temperatures (T_1 through T_4), set temperatures (T_{set}) and water outlet temperature (T_{out}) and (b) is a plot of the flow rate and total hydrogen gas as a function of reaction time. The total hydrogen as a function of time is nonlinear and the flow indicated that most of the hydrogen production occurs during the first 5 min. This experiment was done in the pressure canister at an applied pressure of 50 psig using a H_2O:$NaBH_4$ ratio of 6.14:1 and 3.75% $CoCl_2$ relative to $NaBH_4$. Thermocouple $T_1$was used to monitor/control the reaction. Less $NaBH_4$ was used in this run compared to the run summarized in Figure 5.3-3.

6. CONCLUSIONS

SSC Pacific conducted experiments using the $CoCl_2$ catalyzed $NaBH_4$:H_2O system to generate hydrogen gas. For the reaction to complete in a reasonable time, either distilled or deionized water should be used. The minimum ratio of H_2O:$NaBH_4$ that could be tolerated was 4.6:1. We found that the reaction rate could be controlled by varying the flow rate of water through the Cu cooling coils, or by keeping the flow rate constant and automatically turning the cooling on/off upon reaching a set temperature. Measurements showed that the temperature of the reacting solution was inhomogeneous and hotter at the air/reagent interface. Consequently, placement of the monitoring/controlling thermocouple influences control of the reaction. Experiments conducted under pressure showed that pressure suppresses foaming. The lessons learned from these experiments provide guidance on how to control hydrogen gas generation to inflate LTA vehicles and we are implementing these findings in large-scale testing of hydrogen generation modules now underway.

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14. ABSTRACT

SSC Pacific conducted experiments using the CoCl2 catalyzed NaBH4:H2O system to generate hydrogen gas. For the reaction to complete in a reasonable time, either distilled or deionized water should be used. The minimum ratio of H2O:NaBH4 that could be tolerated was 4.6:1. We found that the reaction rate could be controlled by varying the flow rate of water through the Cu cooling coils, or by keeping the flow rate constant and automatically turning the cooling on/off upon reaching a set temperature. Measurements showed that the temperature of the reacting solution was inhomogeneous and hotter at the air/reagent interface. Consequently, placement of the monitoring/controlling thermocouple influences control of the reaction. Experiments conducted under pressure showed that pressure suppresses foaming. The lessons learned from these experiments provide guidance on how to control hydrogen gas generation to inflate lighter-than-air vehicles and we are implementing these findings in large-scale testing of hydrogen generation modules now underway.

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