Investigation of High-Temperature Metal-Water Reactions for Sustainable Hydrogen Production

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A thesis submitted to McGill University in partial fulfilment of the requirements of the Undergraduate Honours Program.

Abstract

An experimental method was developed to study metal-water reaction at high temperature and high pressure. This work includes the completion and testing of an experimental method and apparatus that allows for the separate preheating and fast mixing of metal powder and liquid water during a reaction. The metal powder and water are initially separated by a diaphragm. The reaction occurs when the increased vapor pressure of water causes the diaphragm to break. Diaphragms of different materials and thicknesses were tested. Experiments were conducted using aluminum and silicon as the metal powder in the reaction. The experimental method and apparatus were tested at reaction temperatures of 165 °C to 260 °C. The silicon powder did not show any indication of reaction with water in this temperature range. The aluminum powder consistently reacted with water in the same temperature range.

Abrégé

Un protocole expérimental a été développé afin d'étudier des réactions métal-eau à haute température et haute pression. Cette étude comprend la réalisation et la mise en pratique d'un protocole expérimental et d'un dispositif permettant le préchauffage séparé des poudres métalliques et de l'eau ainsi qu'un mélange rapide des deux phases pendant la réaction. La poudre métallique et l'eau étant initialement scindées par un diaphragme, la réaction intervient quand l'augmentation de la pression de vapeur d'eau entraîne la rupture de celui-ci. Plusieurs diaphragmes de matériaux et d'épaisseurs différentes ont été testés et des poudres d'aluminium et de silicium ont été utilisées comme réactifs. Le protocole expérimental inclut le test au sein du dispositif de la réaction à des températures comprises entre 165 °C et 260 °C. Aucun signe d'une réaction avec l'eau n'a été détecté pour la poudre de silicium dans la gamme de température précitée. *A contrario*, la poudre d'aluminium a réagi de façon notable dans cette même gamme de température.

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Acknowledgement

I would like to thank my supervisors, Professor Bergthorson and Professor Frost for the guidance, feedback, and the wonderful opportunity to work on this project. I wish to thank Dr. Goroshin as well for his help and advice. Thank you to my immediate supervisor, Keena Trowell, for introducing me to research and mentoring me throughout the past year and a half. I would also like to thank other members of Alternative Fuels Lab group for their help with this project. Lastly I want to thank my dad, who sparked my interest in science and engineering.

Chapter 1: Introduction

1.1 The Growing Need for an Alternative Energy Carrier

The combustion of fossil fuels releases pollutants and greenhouse gases (GHGs) that contribute to climate change [1]. Fossil fuel resources are also depleting and the cost is rising [1]. Since the dependence of fossil fuels for energy is proving to be increasingly unsustainable, there is a growing demand for an alternative energy carrier.

One promising fuel alternative is hydrogen, the most abundant element in the universe [2]. The main advantages of using hydrogen include that it is stable, nontoxic, nonradioactive, and can be produced via different methods. In addition, hydrogen can be used in internal combustion engine and fuel cell vehicles [3–6]. Hydrogen is also appealing because it contains higher energy per unit mass than any other fuel [3]. Furthermore, it is environmental friendly because the combustion product of hydrogen is water, which is harmless.

While using hydrogen as fuel has many advantages, there are fundamental challenges related to its production, storage, and transportation. Currently, 95% of hydrogen production in the U.S. is from methane reformation [7], an unsustainable practice that releases GHGs to the atmosphere. Furthermore, hydrogen storage and transportation need improvement [3], [8]. Leakages are a serious safety concern because hydrogen is highly flammable, and, owing to its small molecular size, it is difficult to adequately seal hydrogen containment systems [9], [10]. Hydrogen is also difficult to store and transport because of its low volumetric energy density. Current storage methods, such as storing it as a compressed gas or as a cryogenic liquid, do not meet the hydrogen-storage targets of the U.S. Department of Energy [11].

There is more hydrogen stored per unit volume in water than in liquefied hydrogen itself [11]. Therefore it might be more effective to extract the hydrogen from water using a chemical reaction when needed rather than developing methods to store hydrogen. One way to achieve this on-demand production of hydrogen from water is through metal-water reactions.

1.2 Metal-Water Reactions

Metals can react with water to produce heat and hydrogen gas. The hydrogen gas produced can be subsequently burned with oxygen to produce water and additional heat. Therefore using metals as energy carrier can generate hydrogen on demand while the metal-water reaction itself also produces heat that can be used in applications. Since the products of the metal-water reaction are hydrogen and metal oxide or hydroxide, no carbon dioxide is produced. After the reaction, the metal oxide can be reduced back to metal powder using an energy source. The metal-water reaction process is illustrated in Figure 1.

Metal-water reaction can be an effective way of storing and transporting renewable energy [12]. One major drawback of renewable energy is its reliability of supply because the energy is not always available where or when it is needed. Therefore using renewable energy to process metal powders, powders appropriate for use in metal-water reactions, becomes an effective way of storing and moving that energy.

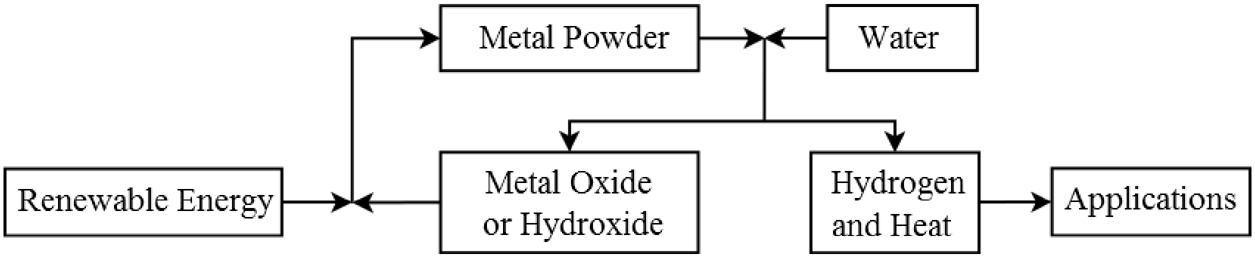


Figure 1: Metal as an energy carrier. The recycling of metal oxide or hydroxide stores the energy. Metal-water reactions release the energy.

Using of metals as energy carriers effectively eliminates the challenge of storing hydrogen on board. For instance in transportation application, metal can be stored on-board and could react with water to produce hydrogen. The hydrogen gas can be then used in internal combustion engines [13].

1.3 Aluminum-Water Reaction

Aluminum is one of the most suitable choices for metal-water reaction. It is relatively inexpensive, abundant in earth’s crust, energy dense, and can be easily stored and transported [14]. A wide range of applications of aluminum-water reaction has been proposed, including propulsion of underwater vehicles, generating hydrogen using waste aluminum sources, and on-board hydrogen-powered vehicles [15–17]. The reaction can take place through three different possible pathways, as shown in Equations 1–3 [17], [18]. Although all three reactions are thermodynamically favorable from room temperature to the melting point of aluminum, $Al(OH)_3$ is the most stable product from room temperature to 280 °C. From 280 °C to 480 °C, however, AlO(OH) becomes the most stable product. At temperatures above 480 °C, the reaction pathway that produces Al_2O_3 is favored. Each reaction produces a slightly different amount of heat, but they all generate the same amount of hydrogen with the same amount of aluminum.

$$2\mathrm{Al} + 3\mathrm{H_2O} \rightarrow \mathrm{Al_2O_3} + 3\mathrm{H_2} + 817\ \mathrm{kJ} \quad (1)$$

$$2\mathrm{Al} + 4\mathrm{H_2O} \rightarrow 2\mathrm{AlO(OH)} + 3\mathrm{H_2} + 846\ \mathrm{kJ} \quad (2)$$

$$2\mathrm{Al} + 6\mathrm{H_2O} \rightarrow 2\mathrm{Al(OH)_3} + 3\mathrm{H_2} + 871\ \mathrm{kJ} \quad (3)$$

When aluminum is exposed to air at temperatures lower than 400°C, a thin layer of aluminum oxide forms on its surface [19]. In aluminum-water reactions, this oxide layer acts as a barrier between water and aluminum, and thus it prevents the reaction from proceeding at ambient conditions. The reaction mechanism includes three stages [18–21]. The first stage is an induction period, during which the water hydrates through this oxide layer. Then, the induction stage is followed by a stage of fast reaction. The last stage involves slow reaction and termination of oxidation. To decrease induction time, the aluminum oxide layer must be removed or disrupted [17]. A variety of methods have been studied to achieve this, including activation of aluminum such as by using alkaline, oxide additive, or carbon materials [22].

1.4 Silicon-Water Reaction

Another promising choice for metal-water reaction is silicon. Silicon is abundant and has low reactivity with air at ambient conditions, making it safe and easy to transport [23]. About 75% of earth's crust contains silicon dioxide, or commonly known as quartz sand, which can be reduced to silicon. If the heat released from the silicon-water reaction and the subsequent combustion of the hydrogen produced are both considered, then the specific energy and energy density of silicon (32.6 kJ/g and 75.9 kJ/cm^3 respectively) are comparable to those of carbon (32.8 kJ/g and 74.2 kJ/cm^3 respectively) [23]. Currently, the production of silicon from quartz sand relies on the use of fossil fuels, although carbon-free methods have been proposed and verified on laboratory scale [24]. The silicon-water reaction is described by Equation 4 [23].

$$\mathrm{Si} + 2\mathrm{H_2O} \rightarrow \mathrm{SiO_2} + 2\mathrm{H_2} + 339\ \mathrm{kJ} \tag{4}$$

The reaction between silicon and water has been studied less extensively than aluminum-water reaction. Nonetheless, the idea of generating hydrogen using metal alloys containing silicon has long existed. In the 1920s, reaction between water and ferrosilicon, a combination of iron and silicon, was used to generate hydrogen gas to fill military and naval balloons [25].

Silicon has been widely studied and used in other industries as well. High purity silicon is used extensively in electronic devices and is the most common material for semiconductor in photovoltaic cells [26]. During the process of producing semiconductors, more than 40% of high-purity silicon is wasted in a slurry [27]. Thus silicon-water reactions have even been proposed as a method to generate hydrogen using silicon waste from the photovoltaic cells. Studies have been done to investigate the possibility of generating hydrogen using waste silicon by chemical reaction between the silicon and water using sodium hydroxide as a catalyst [27]. The results indicated that wasted silicon could be used to generate hydrogen through silicon-water reactions, which makes silicon-water reaction a practical method for hydrogen generation.

1.5 Reaction Temperature

The majority of previous studies on metal-water reactions have been conducted at ambient pressure and below 100°C [11]. These studies have often focused on maximizing hydrogen generation without taking advantage of the exothermic nature of the metal-water reactions [11].

To maximize the amount of energy extracted from the reaction, however, both hydrogen and heat released during the reaction should be maximized.

Significant thermal energy is often produced in metal-water reaction. For instance, the aluminum-water reaction described by Equation 1 produces 3 mol of hydrogen gas and 817 kJ of heat per every 2 mol of aluminum. Then the 3 mol of hydrogen gas reacts with oxygen, via combustion, to produce another 857 kJ of thermal energy, as demonstrated by Equation 5. Thus the aluminum-water reaction itself produces almost as much heat as the subsequent combustion of the produced hydrogen. Therefore taking advantage of the exothermic nature of the reaction can effectively double the amount of thermal energy created from the overall process. Similar calculation shows that the heat produced during silicon-water reaction is approximately 1/3 of the total thermal energy, and the other 2/3 of the energy is embodied in the hydrogen produced.

$$3\mathrm{H_2} + 1.5\mathrm{O_2} \rightarrow 3\mathrm{H_2O} + 857\ \mathrm{kJ} \tag{5}$$

Having a high reaction temperature allows the utilization of thermal energy from metal-water reaction by increasing the reaction rate. A higher reaction rate leads to a higher rate of heat evolution. Therefore the heat release is concentrated over a shorter period of time, which means it can be harnessed more effectively.

The reaction rate can be described by Equation 6, the Arrhenius equation, where k is the rate constant of reaction in units of s^{-1}, A is the pre-exponential factor in units of s^{-1}, E_a is the activation energy in units of $J\cdot mol^{-1}$, R is the universal gas constant in units of $J\cdot mol^{-1}\cdot K^{-1}$, and T is the temperature of reaction in units of K. The relationship between the rate constant of reaction and temperature is shown in Figure 2. According to Arrhenius equation, the rate constant of reaction increases exponentially as reaction temperature increases.

$$k = Ae^{-\frac{E_a}{RT}} \tag{6}$$

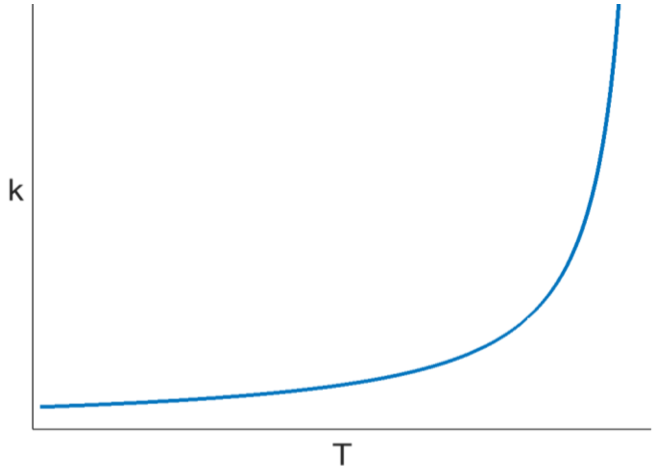


Figure 2: The Arrhenius equation plot shows the rate constant of reaction increasing exponentially with reaction temperature.

The increase of reaction rate with increasing reaction temperature has been observed experimentally for metal-water reactions. Yavor et al. explored metal-water reactions at temperatures between 80 °C and 200 °C using sixteen different commercially-available industrial metal powders, including aluminum and silicon [28]. It was found that all powders showed an increase in the reaction rate as temperature increased. In additional to higher reaction rate, the study found that the total hydrogen yield increased with temperature for all metal powders [28].

A higher reaction rate means that the reaction produces more heat and hydrogen in a shorter period of time. Therefore a high reaction rate leads to a higher rate of energy delivery and higher power density. Achieving high power density is especially important because applications that require high power density are currently dominated by the use of hydrocarbons [29].

Many studies have been increasing the reaction rate at low temperatures using methods such as using catalyst [30], [31] and decreasing particle size of the powder [30], [32]. While it can be convenient to produce hydrogen on demand at low temperatures, unintentional metal-water reactions can become a major safety concern. If the reactions can easily occur at close to room temperature, then there is a risk of unwanted sudden evolution of hydrogen when powders in storage are exposed to water. There has even been studies on suppressing hydrogen evolution such as using metal salts as inhibitors, to allow for more control over the hydrogen production [33]. Therefore another advantage of having the reaction at high temperatures is the reduced possibility of accidental reaction onsets.

Investigating metal-water reactions at high temperature also requires having a high pressure inside the reactor. The high pressure is necessary to keep water at liquid state, as seen from the vapor pressure curve of water in Figure 3. The vapor pressure of water increases exponentially as temperature increases. Therefore the apparatus needs to withstand both high temperature and high pressure.

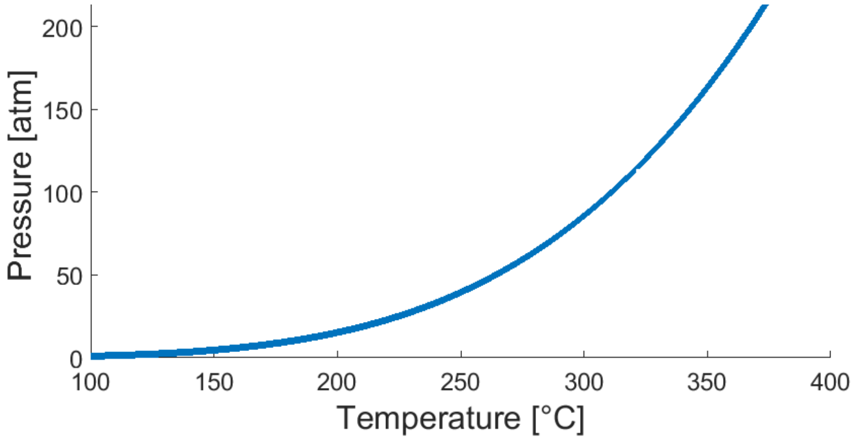


Figure 3: Vapor pressure of water increases exponentially as temperature increases.

1.6 Thesis Objective and Overview

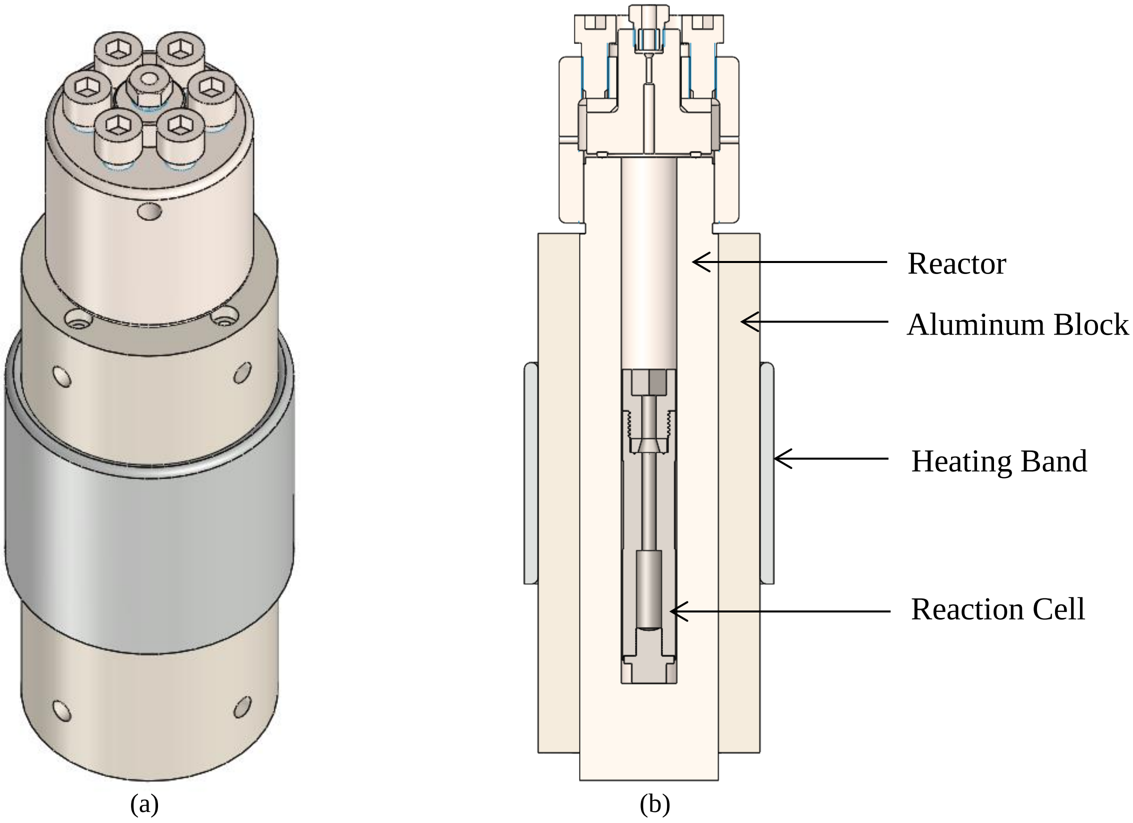
Previous studies on low-temperature metal-water reactions have found aluminum and silicon to be promising choices for metal-water reaction. High-temperature metal-water reaction allows for the utilization of heat released from the reaction, increases the rate of reaction, and decreases the chances of unwanted reaction onsets. Thus the objective of this thesis is to develop and test experimental method that allows for the separate preheating and fast mixing of reactants at desired temperatures to study metal-water reaction at high temperature and high pressure.

The motivation behind metal-water reaction has been introduced in Chapter 1. An overview of the current literature on aluminum- and silicon-water reactions has also been provided, which are the metal powders used in this work. Chapter 2 describes the new high-temperature high-pressure metal-water reactor. The development of the experimental method based on this apparatus is then discussed in Chapter 3. Chapter 4 presents and discusses the preliminary results obtained using the experimental method with silicon and aluminum powders. Lastly, Chapter 5 summarizes the development of the experimental method and discusses limitations and future work.

Chapter 2: Experimental Apparatus

2.1 High-Pressure Reactor

The apparatus used in this experiment is shown in Figure 4. Experiments are conducted in a reactor purchased off-the-shelf from High Pressure Equipment Company. The reactor body is made of stainless steel with an internal volume of 125 mL and a pressure rating of 82.74 MPa at 426.7 °C. Therefore the reactor also allows the opportunity to explore metal-water reaction using supercritical water, which is water at 22.06 MPa and 373.95 °C [34]. The reactor is housed in a fitted aluminum jacket that aids in both the heating and the cooling of the reactor during an experiment.



(a) (b)

Figure 4: (a) 3D and (b) cross-sectional views of the reactor assembly

During an experiment, metal powder is placed inside a reaction cell and sealed with a diaphragm. Then, the cell is placed in the reactor, and water is added into the reactor after the metal powder has been sealed inside the reaction cell. The water will not come into contact with the powder until the diaphragm breaks. Thus the diaphragm allows reactants to preheat separately. Separate preheating prevents any reaction from occurring until the desired temperature has been reached.

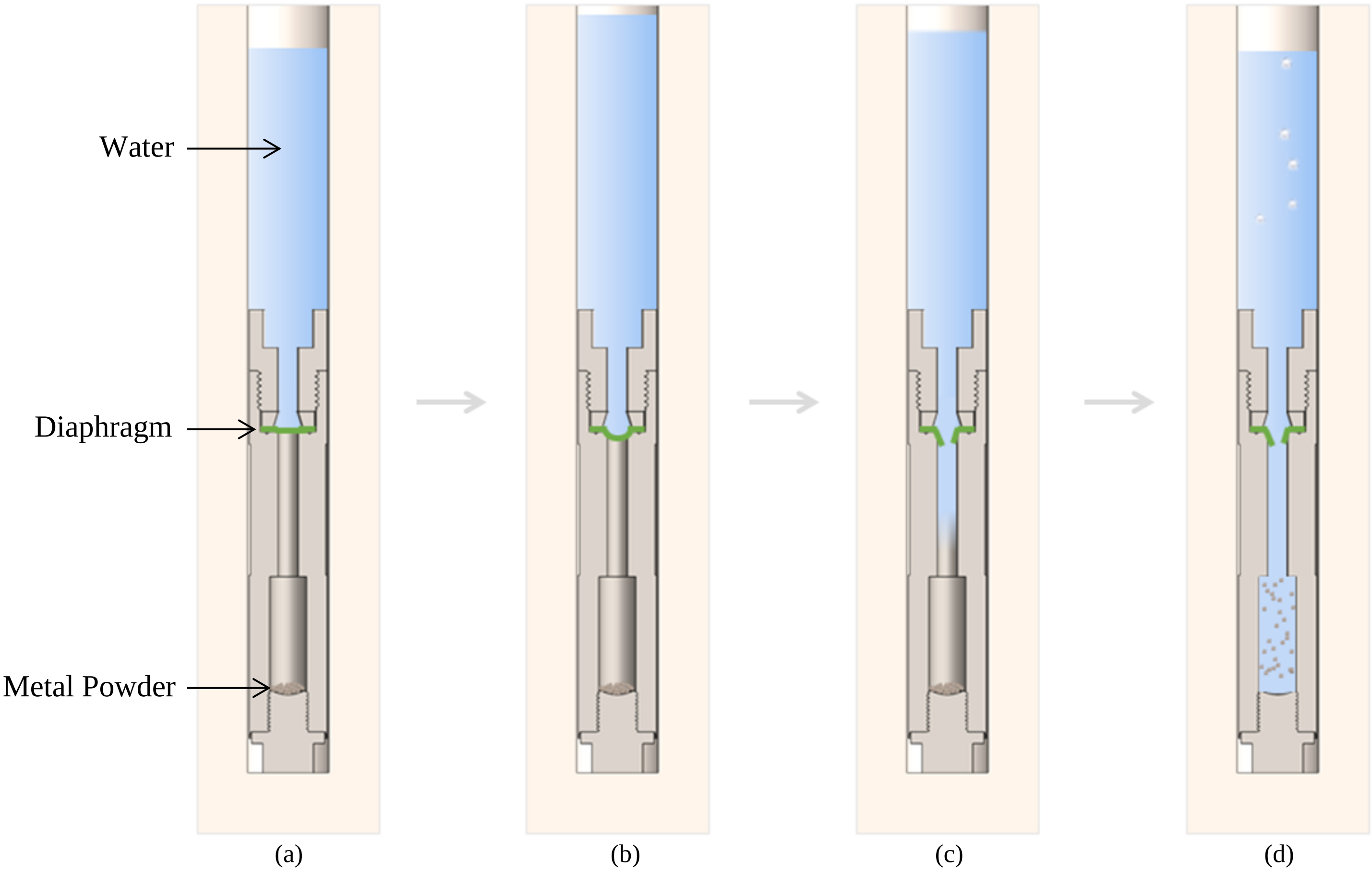


Figure 5: Illustration of the stages during an experiment. (a) The metal powder and water are initially separated by a diaphragm. (b) The pressure increases as the apparatus is heated, which causes the diaphragm to expand and (c) break. Then the water rushes into the reaction cell and mixes with metal powder. (d) If a reaction occurs, hydrogen gas is generated.

In Figure 5 (a) the reactants are prepared and separated by the diaphragm. Once the reactants are assembled and the reactor is sealed, the heating band is turned on. The temperature inside the reactor will increase steadily. The presence of the water vapor pressure, rising exponentially with temperature, above the diaphragm will cause the diaphragm to deform and break, as illustrated in (b) and (c). Once the diaphragm breaks, water will rush into the reaction cell and come in contact with the metal powder. Fast mixing of the water and powder is promoted by the pressure difference and the thin channel inside the reaction cell. As shown in (d), hydrogen gas will be produced if a reaction occurs.

2.2 Instrumentation

Figure 6 shows a schematic diagram of the apparatus with instrumentation. A K-type thermocouple extends into the reactor to measure the temperature inside. The thermocouple is purchased from Omega with the part number of KMQXL-062U-12. A pressure transmitter is connected to measure the pressure inside the system. The pressure transmitter is made by WIKA, and its model number is A-10. It is NIST certified and can measure from 0 psi to 5000 psi. The valve is closed during the experiment. After an experiment, the valve is opened to vent out any hydrogen gas produced.

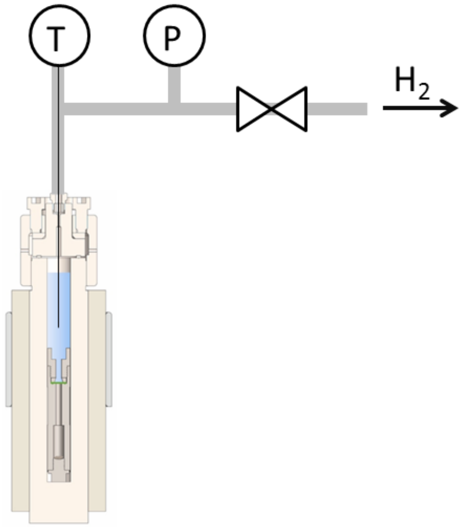


Figure 6: Schematic diagram of apparatus

The signals from the thermocouple and pressure transducer are monitored and recorded on an oscilloscope. Using an oscilloscope allows the signs of a reaction occurring to be monitored, which is indicated by a significant pressure increase due to hydrogen gas production. Figure 7 shows a photo of the complete experimental apparatus.

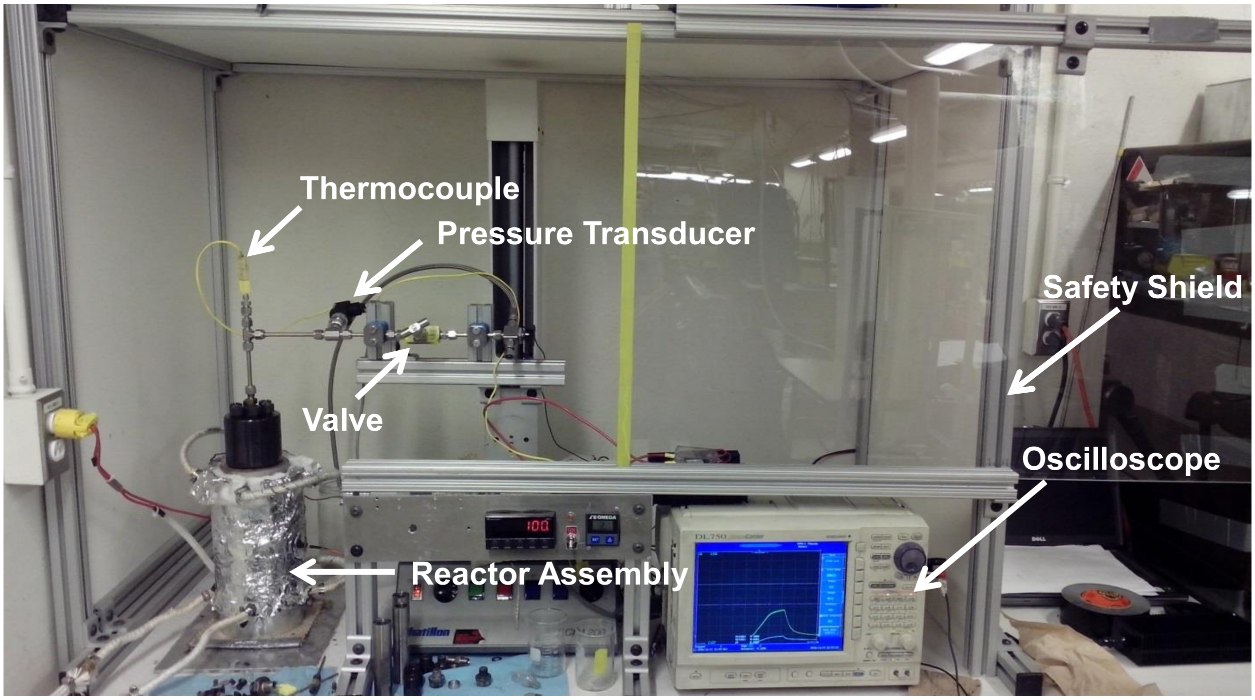


Figure 7: The complete experimental apparatus

2.3 Silicon and Aluminum Powders

The aluminum and silicon powders used in this experiment were produced by Valimet and Atlantic Equipment Engineers. Information about the powders is summarized in Table 1.

Table 1: Aluminum and silicon powders used in this work

Metal	Powder Name	Nominal Particle Size (μm)	Purity	Producer
Aluminum	H-2	6	> 99.7 %	Valimet
Silicon	Si-100	1–5	> 99%	Atlantic Equipment Engineers

In each experiment, 60 mL of reverse-osmosis water and approximately 0.25 g of either aluminum or silicon powder are used. Using Equations 1–3, it can be calculated that for 0.25 g of aluminum powder, 0.25 mL to 0.50 mL of water is required. Similarly, using the silicon-water reaction stoichiometry described by Equation 4, it can be determined that 0.32 mL of water is required for a complete reaction with 0.25 g of silicon powder. Thus, using 60 mL of water in each experiment ensures that the complete oxidation of the metal powder is possible.

Chapter 3: Development of Experimental Method

3.1 Water Vapor Pressure Reference

Before any metal-water reaction experiments are conducted, it is important to ensure that the apparatus is functioning properly. It is also necessary to confirm that thermocouples and pressure transducers are correctly calibrated. Thus trials were done by heating only water in the reactor.

Figure 8 shows the results from a trial with 90 mL of water. The data overlaps with the theoretical vapor pressure reference almost completely, except for the sudden increase in pressure after 320 °C. The pressure increase can be explained by the thermal expansion of water. The volume of water increases with temperature and becomes compressed when the entire internal volume is occupied.

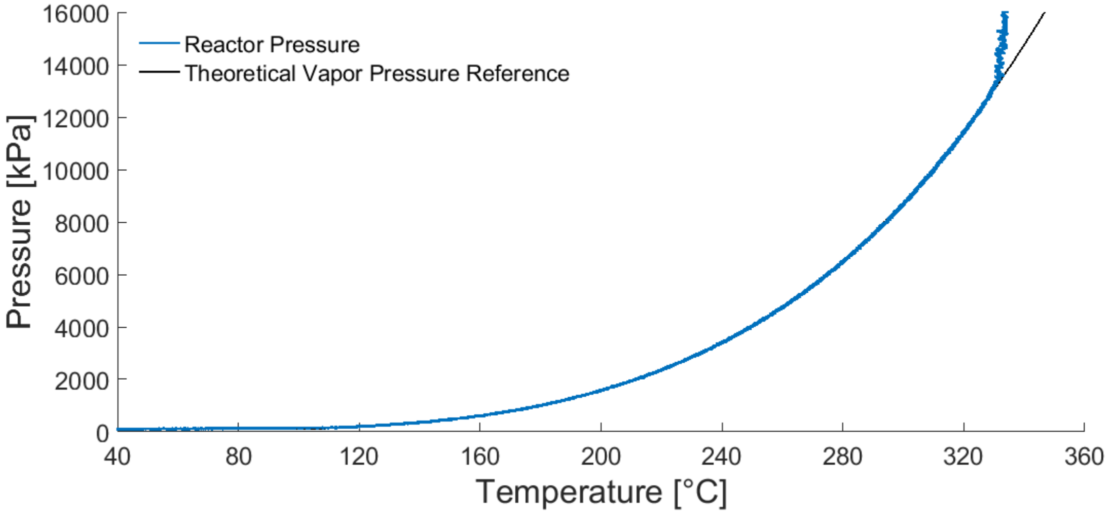


Figure 8: The pressure vs temperature plot of the heating of 90 mL of water.

The vapor pressure of water is calculated using the Antoine equation, as described by Equation 7.

$$P = 10^{A - \frac{B}{T + C}} \tag{7}$$

where P is the vapor pressure in units of mmHg, and T is the temperature in units of °C. For $1 \leq T \leq 99$, A is 8.07131, B is 1730.63, and C is 233.426. For $100 \leq T \leq 374$, A is 8.14019, B is 1810.94, and C is 244.485.

During an experiment with metal powder, the vapor pressure reference will be observed prior to the burst of the diaphragm. Once the diaphragm bursts and water mixes with metal powder, a reaction may or may not occur. If the metal powder does not react with water, the pressure inside the system will continue to follow the vapor pressure reference, as indicated in Figure 9. If reaction does take place, hydrogen gas will be produced. The sudden generation of hydrogen gas will cause an increase in pressure.

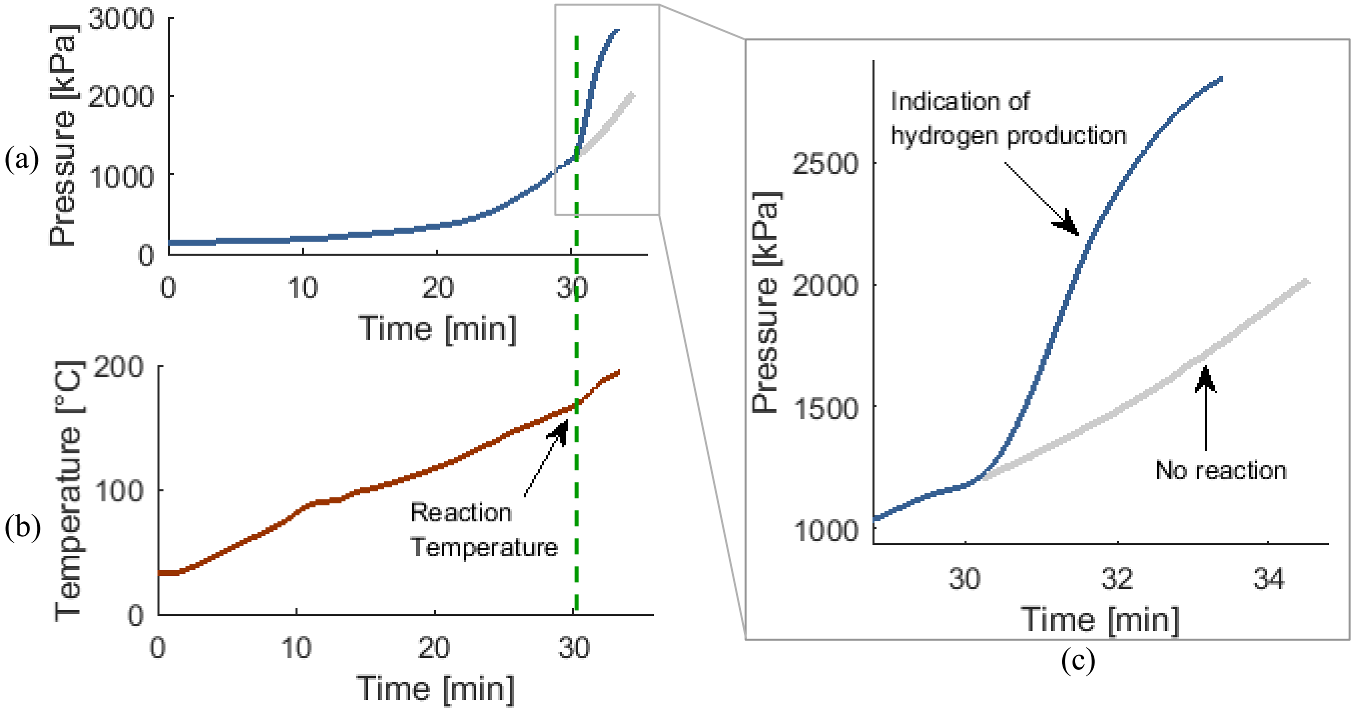


Figure 9: (a) Pressure and (b) temperature increase with time. (c) Pressure readings with and without a reaction occurring

The reaction temperature is the temperature at which the sudden rise in pressure is observed. In other words, the reaction temperature corresponds to the pressure at which the diaphragm breaks. Therefore to study the metal water reaction at a wide range of temperatures, a variety of diaphragms are needed.

3.2 Diaphragm Selection

The ideal diaphragm for this experiment must burst at a pressure that corresponds to a temperature within the range of interest, which is from 150 °C to 374ºC. It also needs to properly seal the reaction cell to prevent any leakage. To test diaphragms, the experiment is prepared as illustrated in Figure 5 (a) except without the metal powder. The burst of diaphragm causes a small disturbance on the pressure inside the system. The small disturbance in pressure corresponds to the burst temperature.

One of the first diaphragm materials tested is silicone rubber. Figure 10 shows two diaphragms made of silicone rubber. Both diaphragms are 1/16 inches thick and easy to seal. They burst consistently in the range of 165°C to185 °C. More diaphragms made from silicone rubber with higher tensile strength ratings were tested. These diaphragms, however, start melting when temperature reaches approximately 200 °C. To study metal-water reaction at even higher temperatures, the diaphragms need to be made of materials that can withstand higher temperatures. Therefore the possibility of making diaphragms from metal foils was explored.

(a) (b)

Figure 10: Silicone rubber diaphragms

It is more difficult to create a good seal using metal foils, but smearing the foil with anti-seize helps in creating good seal consistently. When using metal diaphragms, it is important to ensure that the metal diaphragm itself is not reacting with water to produce hydrogen. For instance, zinc is one of the diaphragms tested, as shown in Figure 11 (a). It bursts at temperatures between 227 °C and 260 °C when scored. The diaphragm, however, shows a small but noticeable amount of hydrogen production. Thus while it is can be used during the development of the experimental method, it will not be used during an actual experiment. The discoloration of the burst zinc diaphragm found after the experiment in Figure 11 (b) also suggests that chemical reaction has taken place.


(a) (b)

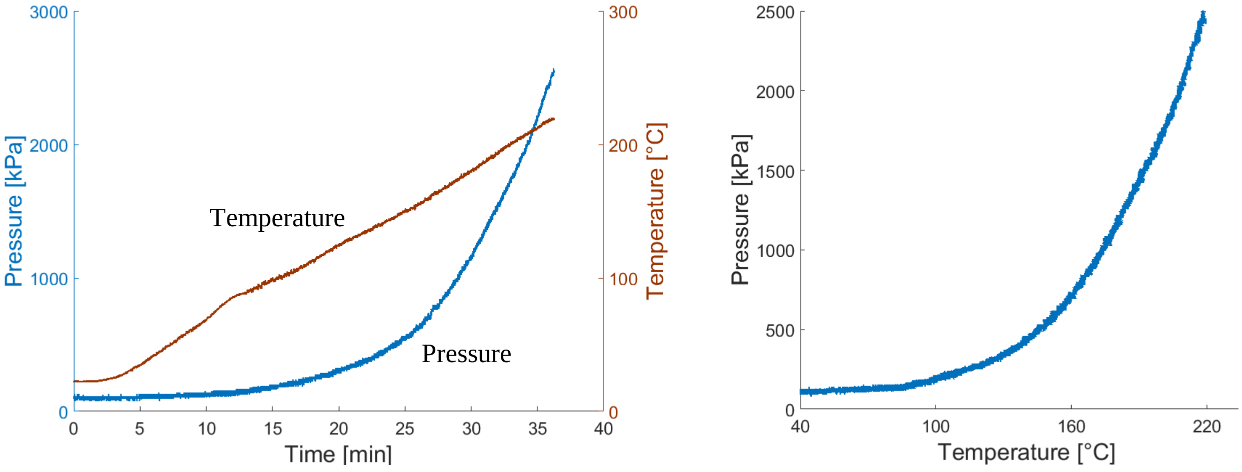
Figure 11: (a) Scored zinc diaphragm before an experiment, and (b) its appearance after an experiment. The diaphragm is scored and weakened so that it can burst at a lower pressure and temperature. Scoring the diaphragm allows a wider range of temperatures to be tested.

When choosing metal foils for diaphragms, results from previous metal-water reaction studies can be consulted [28]. The metal powders that yield the lowest amount of hydrogen, such as copper, would be more suitable for making diaphragms.

Chapter 4: Preliminary Results and Observation

4.1 Silicon-Water Experiments

Silicon powder shows no indication of reaction with water for the temperature ranges tested, which is between 165 °C and 260 °C. No signs of reaction are shown even when burst diaphragm and wet powder are observed after the experiment. Wet powder indicates good mixing between the water and the silicon powder. Since no reaction is observed, the results match with the vapor pressure reference curve, as shown in Figure 12. The plot resembles Figure 8, where no reactants are present in the reactor. Faulty experimental apparatus and method are ruled out as an explanation for the lack of reaction because, with the same apparatus, experiments performed using aluminum powder show consistent hydrogen production.



(a) (b)

Figure 12: An experiment using silicon powder

4.2 Aluminum-Water Experiments

Aluminum powder shows consistent reaction with water between 165 °C and 260 °C. The typical results are shown in Figure 13. As the reactor temperature increases, the pressure inside the system increases and overlaps with the vapor pressure reference. When the diaphragm bursts, which is at 174 °C in this trial, the pressure suddenly increases and is significantly higher than the vapor pressure reference. This particular trial used 0.2429 g of aluminum powder.

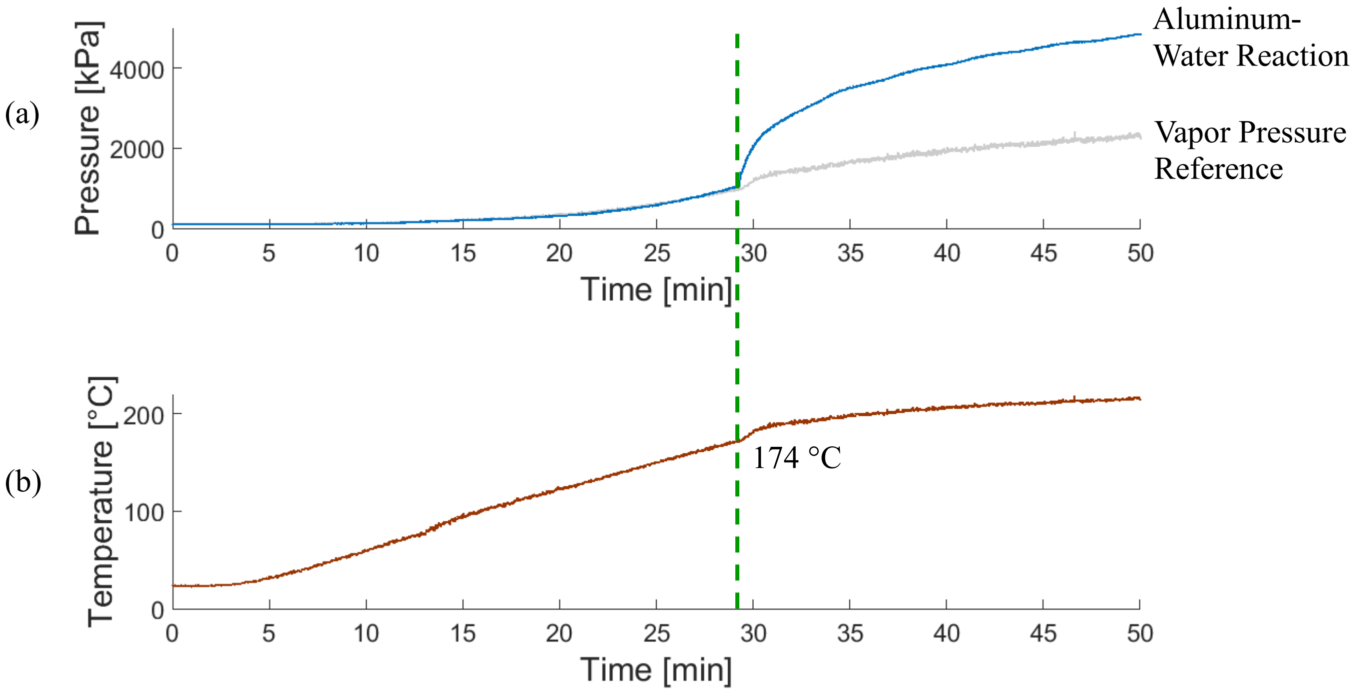


Figure 13: An experiment with aluminum powder using silicone rubber diaphragm

The data from Figure 13 can be plotted to show the relationship between pressure and temperature. Figure 14 shows the relationship between pressure and temperature for the trial in Figure 13 and a trial that used zinc diaphragm. The mass of aluminum powder used in this trial with zinc diaphragm is 0.2352 g. A typical reaction using the silicone rubber diaphragm shows a significantly smaller pressure increase compared to the trials done with the zinc diaphragm. The trial done with zinc diaphragm shows a small deviation from the vapor pressure reference before the sharp increase in pressure. The small deviation can be attributed to the hydrogen production from reaction between water and the zinc diaphragm.

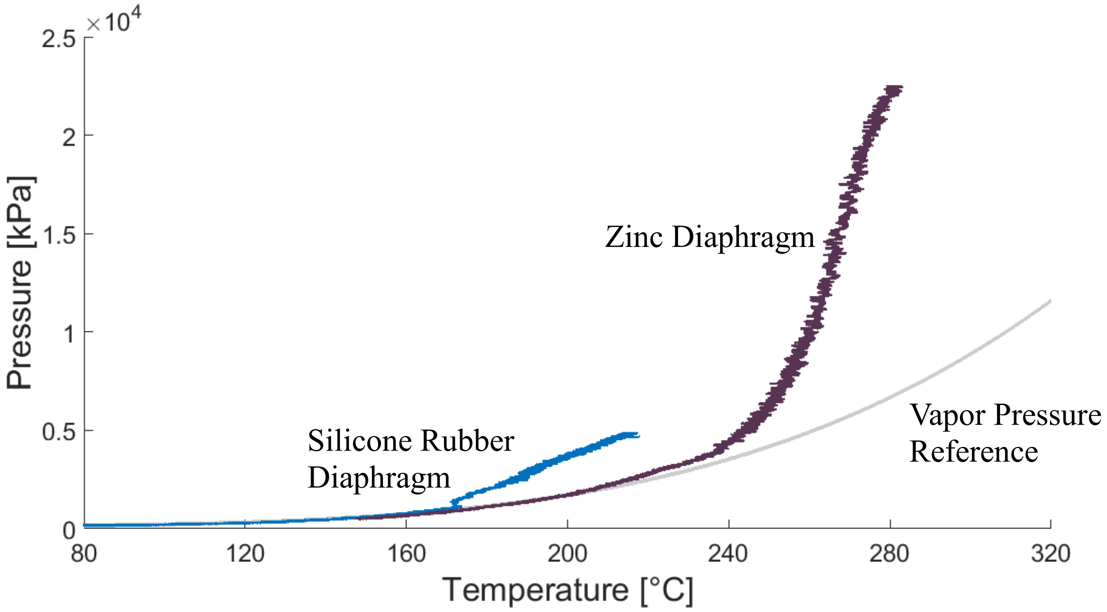


Figure 14: Experiments with aluminum powder using the silicone rubber and zinc diaphragms

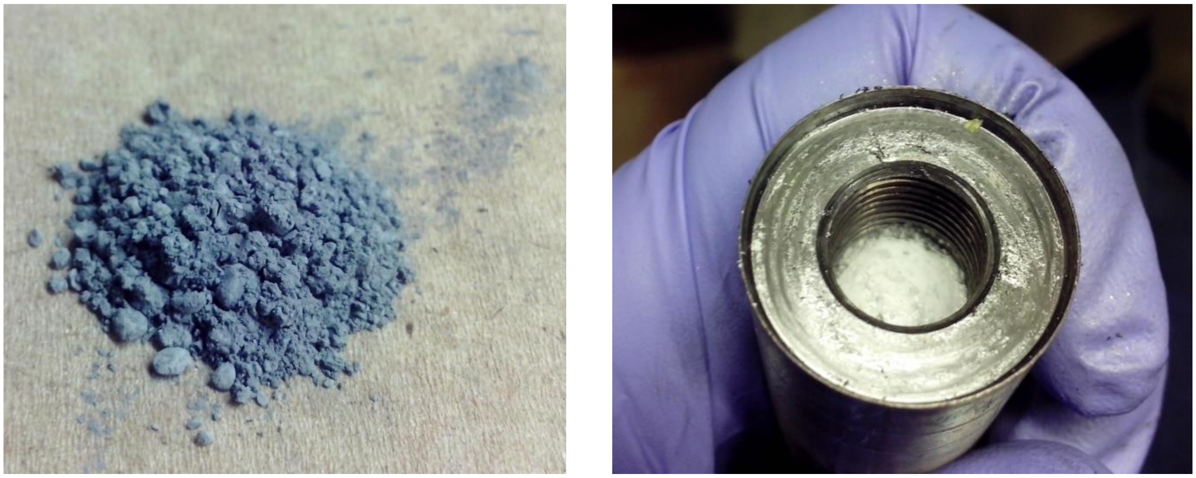
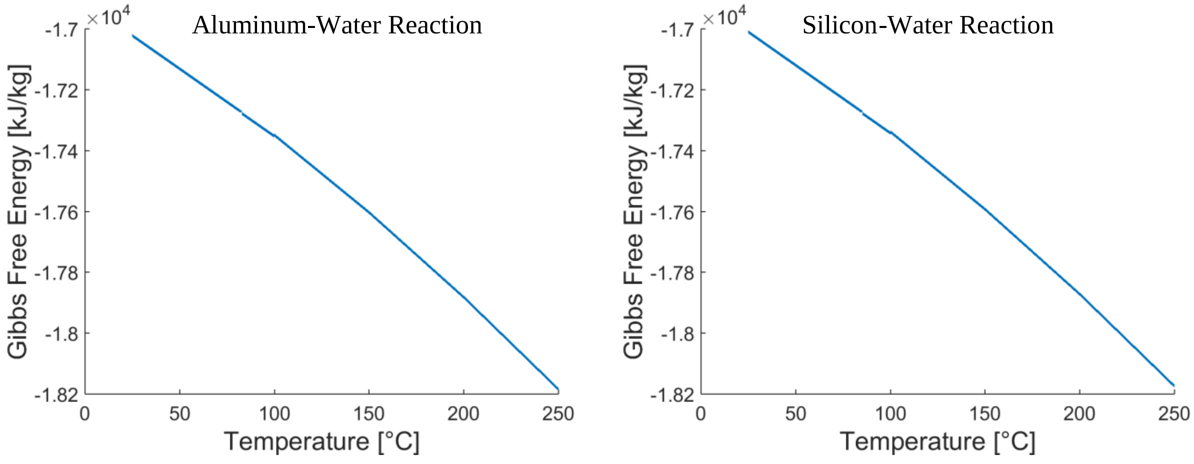

(a)
(b)

Figure 15: (a) A photo of the aluminum powder before reaction and (b) the observation of white substance in the reaction cell after an experiment using the zinc diaphragm

The potential solid products of aluminum-water reaction, $Al(OH)_3$, $AlO(OH)$, and Al_2O_3, are all white in appearance. After experiments using the zinc diaphragms, a white substance is consistently observed, as shown in Figure 15 (b). With the silicone diaphragms, small bits of white solids are often observed in the dark gray slurry of aluminum powder and water. Thus the observation of more solid products suggests a more complete reaction between aluminum and water. Reaction completeness is described by the experimental hydrogen yield divided by the maximum amount of hydrogen that can be produced. Although this qualitative observation supports the hypothesis that hydrogen yield will increase with reaction temperature, no quantification of the reaction products is made as part of this work.

4.3 Discussions

The preliminary results suggest that silicon powder does not react with water and that aluminum shows consistent reaction with water in the temperature range studied. It is also hypothesized that the aluminum-water reaction also yields more hydrogen at higher reaction temperature. The expectation of higher yield at higher reaction temperature is explained with Gibbs free energy of reaction, ΔG. Theoretically, a negative ΔG indicates that spontaneous reaction will occur at that particular temperature. ΔG is calculated for both aluminum- and silicon-water reaction from 25 °C to 250 °C using the NASA CEA code [35]. The numerical results are listed in Appendix A1 and plotted in Figure 16.



(a)

(b)

Figure 16: Gibbs free energy of reaction for (a) aluminum-water reaction and (b) silicon-water reaction from 25°C to 250°C.

For both powders, ΔG is found to be negative in this temperature region. ΔG also becomes more negative as temperature increases, which suggests that the reaction products are at a lower energy state. The trend of increasing ΔG in the negative direction correlates to the increasing hydrogen production from the aluminum-water as temperature increases.

The free energy of reaction also suggests that both reactions should proceed even at room temperature, which is not observed experimentally. Previous studies indicate that when the aluminum powder used in this work, H-2, is premixed with water and heated from room temperature, the reaction onset occurs at between 71 °C and 94 °C [36]. This can be explained by the oxide layer on the surface of the powder, as illustrated in Figure 17.

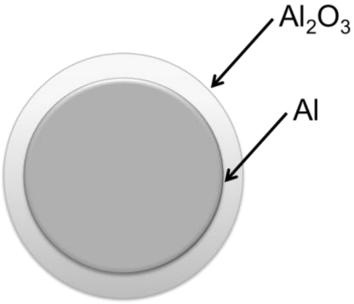


Figure 17: Aluminum particle covered by a layer of aluminum oxide

As mentioned in Section 1.3, a thin passivating layer of aluminum oxide is formed on the surface when aluminum is exposed to air at temperatures below 400 °C [19]. This oxide layer acts as a barrier between water and active aluminum thereby preventing reaction from occurring at room temperature. The reaction mechanism for silicon is still unknown.

Chapter 5: Final Conclusion and Summary

5.1 Summary and Conclusion

The high-temperature metal-water reaction experimental method and apparatus are completed and tested up to 260 °C. It is verified that different diaphragms burst in different temperature regions. Diaphragms made from silicone rubber burst consistently at the lower temperature region of 165 °C and 185 °C. Diaphragms made from metal foils are explored for higher temperature regions. In particular, scored zinc diaphragm bursts consistently at temperatures between 227 °C and 260 °C. It is also verified that metal foils, such as zinc, can potentially react with water to produce hydrogen and should be avoided during actual experiments.

Silicon and aluminum powders are used in the experiments. The silicon powder used does not show signs of reaction with water from 165 °C and 260 °C. The aluminum powder consistently react water in this temperature region.

5.2 Limitations and Recommendations for Future Work

To study metal-water reaction at even higher temperatures, more diaphragms must be tested. Scored zinc diaphragms burst in the temperature region of interest, and its own hydrogen production can be neglected during the development of the experimental method. Nevertheless, the zinc diaphragm should ideally be replaced by metal foils with no hydrogen production.

The hydrogen yield and reaction rate need to be determined and compared to results from existing literature. The hydrogen yield can be found using the final pressure inside the reactor after being cooled back to room temperature. The reaction rate can be calculated from the slope of the pressure increase at reaction onset.

It is recommended to continue investigating the aluminum-water reaction at temperatures of higher than 260 °C. More studies will need to be done on the silicon-water reaction mechanism to explain the observation of no reaction occurring at temperatures up to 260 °C. This experimental method and apparatus can also be used to study the suitability of other metal powders for their reaction with water to produce hydrogen.

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Appendix

A1: Gibbs Free Energy of Reaction

The Gibbs free energy of reaction, ΔG, is calculated using NASA CEA code [35]. Table 2 and Table 3 contain the results of the calculation. The initial system contains 60 g of water and 0.25 g of either aluminum or silicon.

Table 2: Gibbs free energy of reaction for aluminum-water reaction

Temperature (°C)	Gibbs Free Energy of Reaction (kJ/kg)
25	-17022.5
100	-17349.3
150	-17603.4
200	-17882.2
250	-18184.7

Table 3: Gibbs free energy of reaction for silicon-water reaction

Temperature (°C)	Gibbs Free Energy of Reaction (kJ/kg)
25	-17010.3
100	-17338.4
150	-17593.2
200	-17872
250	-18174.4