

# Hydrogen production via reaction of metals with supercritical water

Keena A. Trowell<sup>a,\*</sup>, Jocelyn Blanchet<sup>a</sup>, Sam Goroshin<sup>a</sup>,  
David L. Frost<sup>a</sup>, Jeffrey M. Bergthorson<sup>a</sup>

<sup>a</sup> Alternative Fuels Laboratory, Department of Mechanical Engineering, McGill University, Canada

## Abstract

Reactive metals have been identified as promising energy dense, sustainable energy carriers suitable for long-duration energy storage. The lack of such energy storage is a bottleneck in the transition towards an energy system compatible with arresting climate change. In this work, aluminum alloy plates, magnesium slugs, zinc slugs, and silicon, titanium, and zirconium powders are reacted with high-temperature liquid water and supercritical water (655 K, 230 bar) to produce hydrogen and heat. With the exception of titanium, which showed virtually no reactivity with water, it was found that, in all cases, reaction efficiency increased with temperature. Silicon and zirconium showed poor reactivity, while full hydrogen yield was observed in the supercritical regime for the aluminum alloys, magnesium and zinc. The magnesium slugs were the most reactive of the materials tested, reacting fully with liquid water at 525 K. A link between oxide solubility and reactivity with water is proposed.

---

\*Corresponding author: keena.trowell@mail.mcgill.ca

# 1 Background

Halting anthropogenic climate change will require a transition to non-hydrocarbon fuels. Hydrogen, offering a high specific energy, could replace the use of hydrocarbon fuels in many applications. However, challenges related to its production, storage and transportation have slowed the widespread adoption of this clean-burning fuel.<sup>1</sup> A solution to this problem may lie in the *in-situ*, on-demand production of hydrogen.<sup>2</sup> One pathway towards such a system is the use of metal-water reactions.

In metal-water reactions, the energy vector is the metal, rather than hydrogen itself. Metals have the qualities of an excellent energy carrier: energy dense, abundant, and recyclable.<sup>3</sup> The solid product of the reaction is benign and can be collected and recycled. Until the reaction occurs, the hydrogen is safely stored in water. In addition to hydrogen, metal-water reactions also produce heat. In some cases, the thermal energy accounts for more than half of the energy evolved in the reaction. High temperature reactions would allow for more of the energy of the fuel to be utilized.

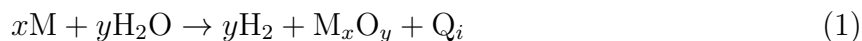
Much of the research in the field has focused on aluminum as the fuel in a metal-water system.<sup>4-8</sup> It is of interest to explore the potential hydrogen-production capacity of other light metals reacting with liquid water at high temperatures. Some studies have been conducted that consider metals such as Fe, Mg, Mn, Zn, and Zr as fuels for metal-water reactions,<sup>9,10</sup> but these studies have been limited to temperatures below 475 K. Expanding the range of metals that could be used in metal-water reactions would allow more flexibility in such systems, and allow users to make decisions based on practical matters such as availability, cost, energy cycle efficiency, and environmental impact(s) of metal processing.

It is also of interest to use salt water as an oxidizer. Marine transportation is an application where a metal-water fuelling strategy may be practicable. Relying on ocean water, and removing the need to carry water on-board, would improve power and energy density. Sea, or salt, water, would also allow for the use of metal-water reactions in regions where fresh-water is scarce.

In previous studies, fine powders were shown to produce hydrogen.<sup>9,11</sup> These studies suggested that there was a maximum penetration thickness, and therefore yield.<sup>11</sup> The implication was that, despite increased reaction temperatures, the maximum hydrogen yield could not be achieved with coarse powders. However, these studies were limited to temperatures of 475 K and below. It was subsequently shown that it was possible to fully oxidize coarse aluminum powders, ranging in size from 12 to 120  $\mu\text{m}$ , in liquid water if the temperature was sufficiently increased.<sup>12</sup> These studies demonstrated that 3mm aluminum slugs and soda cans could be fully oxidized in supercritical water (SCW).

This work expands on previous work<sup>12</sup> to include common aluminum alloys (alloys 5051 and 6062), magnesium slugs, zinc slugs, and silicon, titanium and zirconium powders. These metals were chosen because of promising, but limited, hydrogen production at lower temperatures.<sup>9</sup> The experiments from Trowell *et al.*<sup>12</sup> using aluminum slugs are also repeated, but with salt water as the oxidizer and held at constant temperature for 30 minutes.

When reacting with water, metals typically follow one of two reaction pathways to produce an oxide (Eq. 1), or a hydroxide (Eq. 2):



**Table 1:** Reaction pathways, thermodynamically predicted hydrogen yield, heat yield, experimental conditions, and specific surface area of materials used

Metal	Reaction Pathways	Hydrogen and heat yield		Time <sup>1</sup> [minutes]
		[mL <sub>H<sub>2</sub></sub> /g <sub>metal</sub> ](kJ <sub>chem</sub> /g <sub>metal</sub> ) <sup>2</sup>	[kJ <sub>therm</sub> /g <sub>metal</sub> ] <sup>3</sup>	
Aluminum	2Al+6H <sub>2</sub> O → 3H <sub>2</sub> +2Al(OH) <sub>3</sub> 2Al+4H <sub>2</sub> O → 3H <sub>2</sub> +2AlOOH 2Al+3H <sub>2</sub> O → 3H <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub>	1260 (13.4)	15	30 <sup>4</sup>
Aluminum alloys <sup>5</sup>	2Al+6H <sub>2</sub> O → 3H <sub>2</sub> +2Al(OH) <sub>3</sub> 2Al+4H <sub>2</sub> O → 3H <sub>2</sub> +2AlOOH 2Al+3H <sub>2</sub> O → 3H <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub>	1260 (13.4)	15	60
Magnesium	Mg+2H <sub>2</sub> O → H <sub>2</sub> +Mg(OH) <sub>2</sub> Mg+H <sub>2</sub> O → H <sub>2</sub> +MgO	933 (9.9)	13	30
Silicon	Si+4H <sub>2</sub> O → 2H <sub>2</sub> +Si(OH) <sub>4</sub> Si+2H <sub>2</sub> O → 2H <sub>2</sub> +SiO <sub>2</sub>	1616 (17.2)	12	120
Titanium	Ti+4H <sub>2</sub> O → 2H <sub>2</sub> +Ti(OH) <sub>4</sub> Ti+2H <sub>2</sub> O → 2H <sub>2</sub> +TiO <sub>2</sub>	948 (10.1)	7.8	60
Zinc	Zn+2H <sub>2</sub> O → H <sub>2</sub> +Zn(OH) <sub>2</sub> Zn+H <sub>2</sub> O → H <sub>2</sub> +ZnO	347 (3.7)	1	40
Zirconium	Zr+4H <sub>2</sub> O → 2H <sub>2</sub> +Zr(OH) <sub>4</sub> Zr+2H <sub>2</sub> O → 2H <sub>2</sub> +ZrO <sub>2</sub>	498 (5.3)	5.7	60

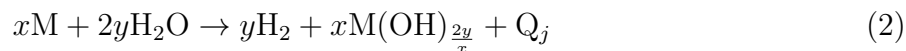
<sup>1</sup> Time at constant temperature.

<sup>2</sup> The value in brackets is the lower heating value of hydrogen, representing the potential heat generated if the hydrogen were to be combusted.

<sup>3</sup> Assumes oxide formation route.

<sup>4</sup> The data for the 2 mm aluminum plate is from Trowell *et al.*<sup>12</sup>

<sup>5</sup> The presence of alloying elements are neglected in the reaction pathways presented here.



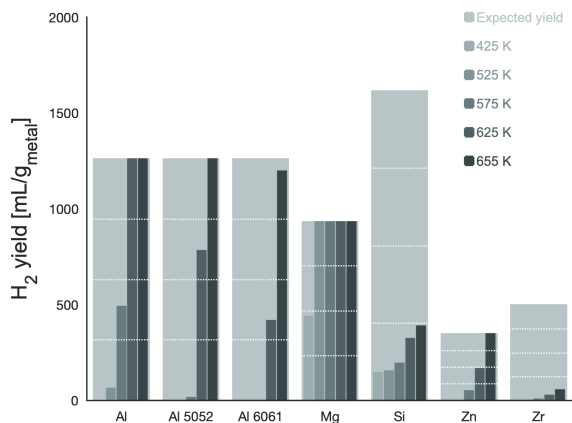
The theoretical specific hydrogen production of each reaction is independent of the solid product form (oxide *vs* hydroxide). The reaction pathways of the metals used in this study, as well as the specific predicted hydrogen and heat yields are shown in Table 1. The proportion of energy released as chemical energy ( $H_2$ ) and thermal energy,  $Q$ , varies between the metals. Values for  $Q_i$  and  $Q_j$  are on the same order,  $Q_i$  is provided in Table 1.

## 2 Methods

In this work, high-temperature and supercritical metal-water reactions were studied. The experiments were designed to ascertain the reaction efficiency of the metal samples. The experiments were conducted using a purpose-built high-temperature, high-pressure metal-water batch reactor apparatus detailed by Trowell *et al.*<sup>12</sup> The main component of the apparatus is a reactor designed to hold the pressures necessary to keep water in liquid phase from 373 K to the critical point of water. The reactor is housed in a mantle which has a series of channels machined into it. The mantle is wrapped by a 1250 W resistance heater to supply heat to the reactor during experiments. At the end of the experiment, cold water is passed through the channels to cool the reactor back to room temperature. Pressure and temperature inside the reactor are monitored by a pressure transducer and a dual-output K-type thermocouple, respectively. One output of the thermocouple is connected a temperature controller and the other output, as well as the pressure transducer, are connected to a Raspberry Pi data acquisition system.

The aluminum, magnesium, titanium and zinc used in this work were procured from Alfa Aesar. The 99.9% magnesium (metals basis) slugs measured approximately 4 mm in length, 3 mm in diameter. The zinc came in the form of a 99.99% zinc (metals basis) 3 mm-diameter rod. The rod was cut into pieces measuring approximately 4 mm in length. The titanium was a 99.9% (metals basis) 0–45  $\mu\text{m}$  powder. The pure aluminum plate and the 5052 alloy plate were approximately 2 mm thick. The 5052 alloy comprised of 97.25 wt% aluminum, 2.5 wt% magnesium and 0.25 wt% chromium. The typical composition of the 6061 alloy plate is 95.8–98.6% aluminum, 0.8–1.2% magnesium, 0.4–0.8% silicon, 0.04–0.35% chromium, 0.15–0.4% copper, and contains a maximum of 0.7% iron, 0.25% Zn, 0.15% manganese and 0.15% titanium. The 6061 alloy plate was approximately 0.81 mm thick. The silicon and zirconium powders used were procured from Altantic Equipment Engineers. The silicon powder was a 1–5  $\mu\text{m}$  powder with 99% purity. The zirconium powder was a 50-mesh (297 $\mu\text{m}$ ) powder with 99.5% purity.

For each experiment, approximately 1 g of the metal was placed in the reaction vessel along with a measured amount of water. The amount of water was calibrated to ensure the presence of liquid water at temperatures up to the critical point, and, at the critical point, the fluid would have the critical density of 322 g cm<sup>-3</sup>. The initial pressure,  $P_1$ , was recorded once the reactor was sealed. The sealed vessel was then heated to the temperature of the experiment, and then held at that temperature for a prescribed period a time. Once the time had elapsed, the reactor was cooled back down to room temperature and the final pressure,  $P_2$ , was recorded.



**Figure 1:** Hydrogen production for Al, Al alloys, Mg, Si, Zn and Zr. Mg is the most reactive, reacting completely at 525 K. The Al alloys and Zn show good reactivity which increases as temperature increases. Si and Zr show poor reactivity, even under supercritical conditions. The data for the pure aluminum plate, labeled *Al*, is from Trowell *et al*<sup>12</sup>.

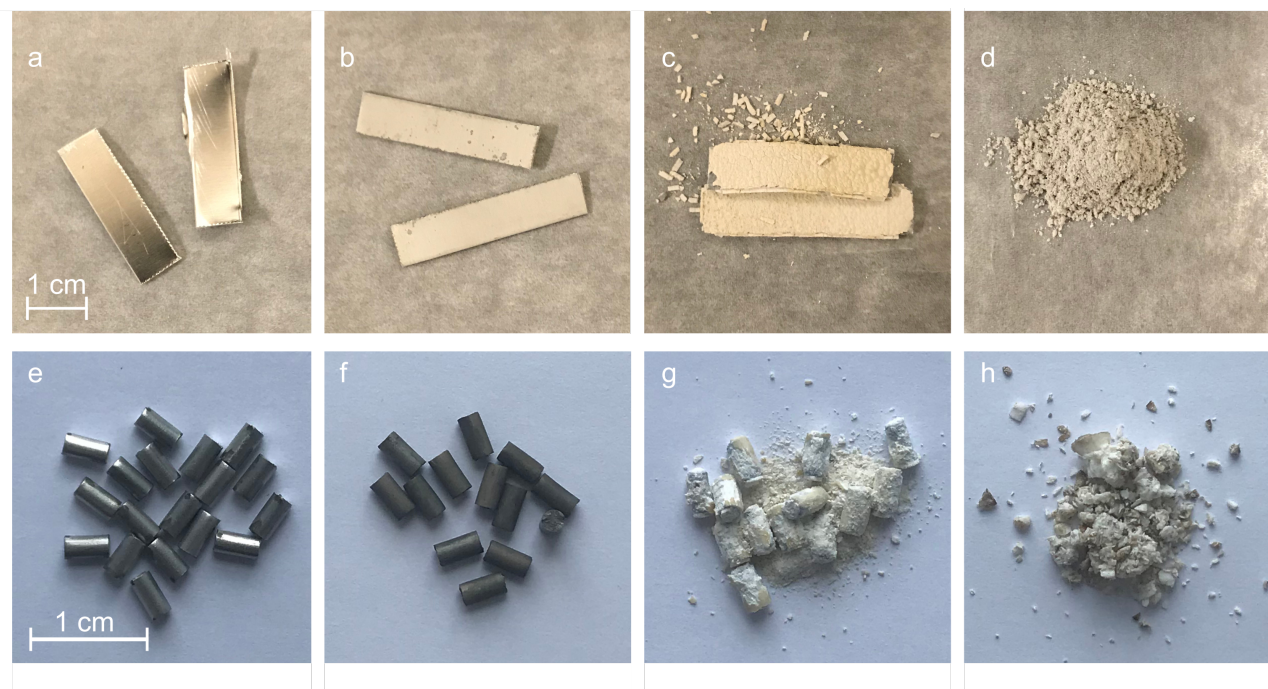
The efficiency of the reaction is calculated from the difference between  $P_1$  and  $P_2$ , using the ideal gas equation:

$$n_{\text{H}_2} = \frac{(P_2 - P_1)V}{RT} \quad (3)$$

where  $V$  is the free volume inside the apparatus [ml],  $R$  is the universal gas constant [83.14 ml·bar/mol·K] and  $T$  is temperature in Kelvin. Moles of hydrogen are then converted to mL of hydrogen at standard temperature and pressure. The expected yields for the metals used in these experiments are shown in Table 1. In this text, reaction efficiency is defined as the hydrogen yield, normalized to one gram of metal, and reported as a percentage of the theoretical maximum yield. It should be noted that the hydrogen yield reported includes hydrogen that may have evolved before the system reached constant temperature.

For each metal, experiments at five different temperatures were conducted: 425 K, 525 K, 575 K, 625 K, and 655 K. For each temperature, the pressure was the saturated vapour pressure and, for the supercritical experiments at 655 K the pressure was approximately 230 bar. In order to determine the time the reactants would be held at constant temperature, repeated experiments were conducted under supercritical conditions (655 K, 230 bar) for each metal. In the first case, the system would be held at constant temperature for 30 minutes before being cooled back down to room temperature. This was repeated, adding time increments of 10 minutes, until full yield was achieved, or 60 minutes had passed. This amount of time would then be used for each of the experiments at lower temperatures for that material. Magnesium, the most reactive of the three, was held at constant temperature for 30 minutes, the zinc slugs for 40 minutes, and the aluminum alloys and other metals, except silicon, for 60 minutes. Exceptionally, silicon was held at constant temperature for 120 minutes, based on its reported reactivity in earlier work in the field.<sup>9</sup>

The experiments using salt water follow the same procedure except rather than reverse osmosis water (referred to simply as water in this text), salt water with a concentration



**Figure 2:** Photographs of the 5052 alloy, magnesium slugs and reaction products. Top row: 5052 alloy (*a*) as received, (*b*) after experiment at 575 K, (*c*) after experiment at 625 K, (*d*) and after experiment with supercritical water. Bottom row: Mg slugs (*e*) as received, (*f*) after experiment at 375 K, (*g*) after experiment at 425 K, (*h*) and after experiment with supercritical water. The reaction products of the supercritical water experiments are a fine powder which is an indication of dissolution activity.

of 3.5% was prepared and used. The salt water experiments were done using 99.99% pure aluminum slugs from Alfa Aesar. The slugs were approximately 3 mm in length and diameter.

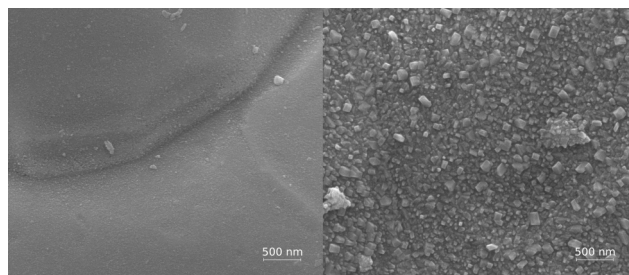
## 3 Results

### 3.1 Reaction with water

Figure 1 shows the hydrogen production for each of the metals used in these experiments, normalized to one gram of metal. The aluminum alloys produce very little hydrogen at temperatures below 575 K. As the temperature of reaction is increased, the yield increases and full hydrogen yield is achieved at the critical temperature. Neither alloy is as reactive as the pure aluminum plate which was held at constant temperature for 30 minutes. The zinc slugs are similar in that below a certain temperature threshold, in this case 525 K, no hydrogen is produced. Above this threshold, hydrogen production increases with temperature, with full yield being achieved above the critical temperature of 647 K.

The top row of Fig. 2 shows the reaction products of the 5052 aluminum alloy. When reacting with subcritical liquid water at 575 K, the reaction products adhere to the surface of the metal. As reaction temperature increases to 625 K, the products start to flake off. Under supercritical conditions, wherein full hydrogen yield is realized, the products are a fine powder that bears no resemblance to the initial morphology of the sample.

The magnesium proved to be the most reactive of the metals used in this work. Although



**Figure 3:** SEM images of the Ti powder at 30 000x magnification. *left* As-received *right* After exposure to supercritical water for 60 minutes. The surface of the particle transitions from an amorphous passivating layer to a more crystalline one and the colour changes from grey to a violet-blue. No hydrogen is produced.

in the form of 4 mm-long slugs, full hydrogen yield was realized after just 30 minutes in 525 K liquid water. Even at 425 K, the yield from these slugs was approximately 50%. By contrast, the zinc and the aluminum alloys, the next most reactive metals in these tests, did not produce any hydrogen at this temperature. Magnesium is known to be highly reactive with water,<sup>9</sup> however the reactivity of these coarse particles, at such temperatures, was surprising.

Silicon and zirconium showed relatively poor reactivity at all temperatures, including supercritical temperatures. At 425 K and 525 K the silicon powder produced approximately 12% of the expected hydrogen yield, the zirconium powder produced nearly no hydrogen at these temperatures. A steady increase in hydrogen production with temperature was observed. Nevertheless, the maximum hydrogen production observed was approximately 25% for silicon and 12% for zirconium.

The titanium powder did not produce any hydrogen in the experiments conducted. The samples turned from grey (as-received) to a blue-violet post reaction. The change in colour indicates an entrainment of oxygen in the oxide layer, but the lack of hydrogen production indicates that no oxidation, beyond the superficial, occurred. The SEM image shown in Figure 3 shows the changes to the surface of the particle. This is supported by X-ray diffraction analysis (XRD) which produced near identical profiles for the pre- and post-reaction samples.

### 3.2 Reaction with salt water

Figure 4 shows the results of experiments using 3 mm aluminum slugs reacted in water and in salt water. In both cases, hydrogen yield increases with experimental temperature, and complete conversion is observed for reactions taking place under supercritical conditions. Except for 625 K, the yields for both sets of experiments are comparable.

## 4 Discussion

### 4.1 Reactivity of magnesium

Of the metals tested in this work, magnesium was shown to be the most reactive, despite the magnesium material having the smallest surface to volume ratio. Magnesium, being an alkaline metal, is a strong reducing agent. In a metal-water reaction, the water is reduced

to hydrogen and oxygen. The electron structure of alkaline metals is conducive to oxidation because of the pair of easily ionized  $s$  electrons in the outermost orbital. In chemical reactions, the removal of the 2  $s$  electrons leaves a  $2^+$  ion which is readily stabilized by a solvent. Water, even at low temperatures, is an especially good solvent because of its high dielectric constant. The reactive properties of alkaline metals are a tempered version of the much more reactive alkali metals such as sodium and lithium. In both cases, the hydroxides formed do not have a strong passivating effect as evidenced by the fine powder shown in panels  $g$  and  $h$  of Fig. 2. The effect of this poor passivation, in the case of alkaline metals, is that high hydrogen yields are realized even at moderate temperatures. In the case of alkali metals, the reaction with water is quite vigorous.

## 4.2 Role of changing water properties

The sharp increase in reactivity of the aluminum alloys and the zinc slugs around 550 K can be explained by the changes to water properties at this temperature. Water in equilibrium is continuously forming  $\text{OH}^-$ ,  $\text{H}^+$  and  $\text{H}_3\text{O}^+$  ionic compounds as shown in Eqs. 4 and 5:



As temperature increases, the forward reactions are thermodynamically favoured, in accordance with Le Chatelier's principle, because both are endothermic reactions.

The ionic product,  $K_w$ , reaches a maximum at 573 K.<sup>13</sup> A high density of  $\text{H}^+$  and  $\text{OH}^-$  ions are the result of a high ionic product, and both contribute to an increase in reactivity. The  $\text{OH}^-$  ions are able to exploit any weakness or pores in the hydroxides on the surface of the metal.<sup>14,15</sup> The  $\text{H}^+$  protons form hydrogen gas.<sup>15</sup> The combined net effect is an acid–base catalyst that can self–neutralize.<sup>16</sup> Both acidity and alkalinity have been shown to increase rates of hydrolysis which, in turn, increases yields.<sup>16</sup>

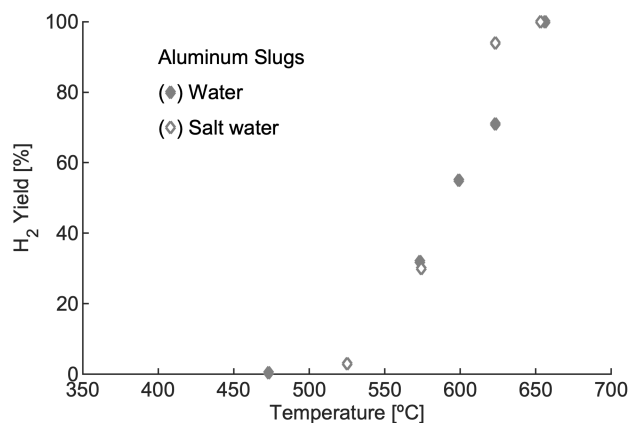
Supercritical water has the ability to dissolve non–polar species, a characteristic that has been employed in waste management.<sup>17</sup> The complete oxidation of the aluminum alloys and zinc slugs in the supercritical fluid may be attributed to this feature as well. As the metal oxidizes, it is unable to form a cohesive hydroxide layer, therefore new metal is exposed to the fluid and consequently corroded. This hypothesis is supported by the images of reaction products shown in Fig. 2. In all cases, the solid products of the supercritical experiments are a fine powder whereas the products of the experiments in subcritical water, which resulted in partial oxidation, still bear some of the geometry of the as–received material.

## 4.3 Role of oxidation state

All metals used in these experiments were thermodynamically favoured to react with water at the temperatures used in these experiments. With the exception of titanium, all the metals did react with the water, but silicon and zirconium showed poor reactivity. Even after two hours of exposure to supercritical water, the silicon yield was just 25% of the expected yield.

In water–oxidized reactions, the formation of sufficient  $\text{OH}^-$  ions is a requirement for the reaction to occur. Alkali and alkaline metals, which have ordinary oxidation states of





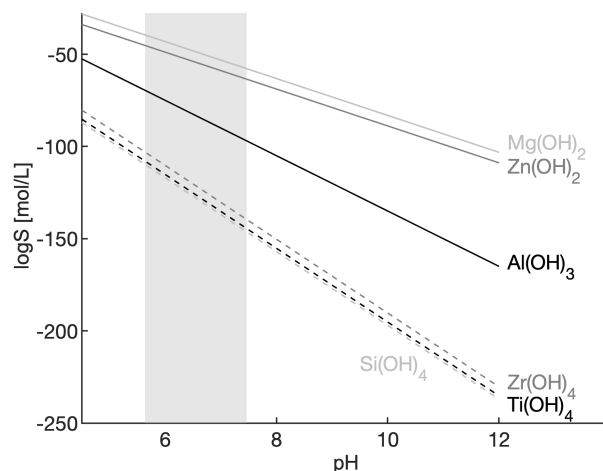
**Figure 4:** Hydrogen yield of pure aluminum slugs in water and salt water. The data for the experiments in water (filled diamond markers) are from Trowell *et al*<sup>12</sup>, the salt water data (open diamond markers) are from this work. Except for 625 K, yields are approximately the same, and full yield is realized in both cases in the supercritical case.

1<sup>+</sup> and 2<sup>+</sup> respectively, only require one or two OH<sup>-</sup> ions for the reaction. In comparison, silicon, titanium and zirconium have ordinary oxidation states of 4<sup>+</sup>, although silicon can have oxidation states 2<sup>+</sup>. Metals with higher oxidation states need a fluid which has a higher concentration of OH<sup>-</sup> ions. As discussed above, as temperature increases, the concentration of OH<sup>-</sup> ions increases and creates conditions more favourable to oxidation. For metals with an oxidation state of 3<sup>+</sup> or lower, the increase in OH<sup>-</sup> ions increases reaction efficiency. For metals with an oxidation state of 4<sup>+</sup>, the higher concentration of OH<sup>-</sup> ions is a pre-requisite to reaction. This is evidenced by the near-zero hydrogen production at temperatures below 575 K with the zirconium. Silicon, because of its access to oxidation state of 2<sup>+</sup>, can react with more efficiency at the lower temperatures (425–575 K), but there is also a jump in hydrogen yield above 575 K.

#### 4.4 Role of oxide properties and melting temperature

Titanium and zirconium are Group 4 metals which are known to be hard, refractory metals. Both metals have an ordinary oxidation of 4<sup>+</sup>, but only zirconium produced any hydrogen when exposed to the high-temperature subcritical liquid or the supercritical fluid. In the case of titanium, the strong electropositive property of the metals means that, after any exposure to an oxidizer, a dense oxide forms which protects the bulk metal beneath from corrosion and attack by acids or bases. The formation of TiO<sub>2</sub> is characterized by rapid absorption of oxygen, then a slower process until the oxide is saturated.<sup>18</sup> In these experiments, the change in colour from grey to blue-violet is an indication that Ti<sup>3+</sup> have formed,<sup>19</sup> allowing for a minute amount of further oxidation. This further oxidation is a thermally-controlled process, but a limited one. The formation of TiO<sub>2</sub> not only passivates, but, the interaction of the oxide and metal beneath also stabilizes the interface and prevents any oxidation beyond the film on the surface.<sup>20</sup> Subjecting titanium, once passivated, to an oxidizer will not result in the thickening of the oxide layer.

By contrast, the hydroxides that form in reaction of water with alkali and alkaline metals



**Figure 5:** Solubility of metal oxides and hydroxides as a function of pH, for reactions of the form  $M^{z+} + zOH^- \rightleftharpoons M(OH)_{z,aq}$ . The shaded region indicates the pH region of the experiments. Lower lines on the figure correspond to lower solubility. The reactive metals (Al, Mg, Zn) are shown to have higher solubilities than Si, Zr or Ti, which had poor solubility.

are soluble in water.<sup>21,22</sup> As the metals of the alkali group increase in atomic mass, the hydroxides they form increase in solubility in water which means that the formed hydroxides have no passivation effect.<sup>22</sup> Instead, metal is continuously exposed to the oxidizer until the metal is completely consumed. This is also the case with aluminum hydroxides: as temperature increases, aluminum hydroxides also decline in cohesiveness and ability to passivate, thereby allowing for increased reaction efficiency. Under supercritical conditions, as observed here and in previous work by Trowell *et al*,<sup>12</sup> aluminum will completely oxidize in supercritical water. The hydroxide that is left over is a fine powder regardless of the morphology or geometry of the initial sample, indicating that some form of dissolution and precipitation is taking place.

The metals used in these experiments can be roughly categorized as either readily reactive with water (Al, Mg, Zn), or not (Si, Ti, Zr). The first step in the oxidation of a metal by water is the hydration of its oxide layer to form a hydroxide.<sup>23</sup> A prerequisite for the formation of a hydroxide is the breaking of M–O bonds to form M–OH bonds, a process of oxide dissolution. Thus, it is possible that the readiness and degree to which a metal may be oxidized by water is fundamentally a function of the degree to which its oxide is soluble in water. With the exception of alkali metal oxides, most metal oxides are minimally soluble in water under ambient conditions. Solubility data for the metal oxides in the temperature range of this study is lacking in the literature, but it is still possible to make some inferences from ambient temperature data by using pH as a proxy for increasing temperature.

At ambient temperature, the dependence of solubility of oxides in water on pH is described by Eq. 6:<sup>24</sup>

$$\log S = -\log K_{\text{sol}} + npK_w - npH \quad (6)$$

where  $S$  is solubility [mol/L],  $K_{\text{sol}}$  is the thermodynamic solubility product,  $pK_w$  is the negative log of the ionic product,  $pH$  is the negative log of the concentration of  $H^+$  in the

fluid, and  $n$  is the number of hydroxyl groups in the hydroxide.

In pure water, the concentration of  $H^+$  and  $OH^-$  is the same, thus  $K_w = [H^+]^2$  and it can be written that  $pK_w = 2pH$ , simplifying Eq. 6 to:

$$\log S = -\log K_{sol} + npH \quad (7)$$

$K_{sol}$  is derived from the equilibrium constant,  $K_{eq}$ , for reactions of the form  $M^{n+} + nOH^- \rightleftharpoons M(OH)_{n,aq}$  through the following expression:<sup>25</sup>

$$\log K_{sol} = \log K_{eq} + n\log K_w \quad (8)$$

As temperature increases from room temperature, the pH value of pure water decreases, reaching a minimum at 573 K before increasing again. The  $npH$  term ranges from 11 (for a  $2^+$  metal at a low pH) to 28 (for a  $4^+$  metal at a high pH). The poorly reactive metals (Si, Ti, Zr) all have  $K_{sol}$  values on the order of 60 and the readily reactive metals have  $K_{sol}$  values on the order of 10–15 for Mg and Zn, and  $\approx 30$  for Al.<sup>25,26</sup> Substituting these values into Eq. 7, results in oxide solubility trends that correlate to the water reactivity behaviour observed in this study, shown in Fig. 5. This trend extends to metals not used in this work but which are known to be highly reactive with water (Li, Na, K), which have  $K_{sol}$  on the order of 2 to 5.<sup>25,26</sup> Further work is needed in order to understand the extent to which the ability to form hydroxides impacts metal–water oxidation.

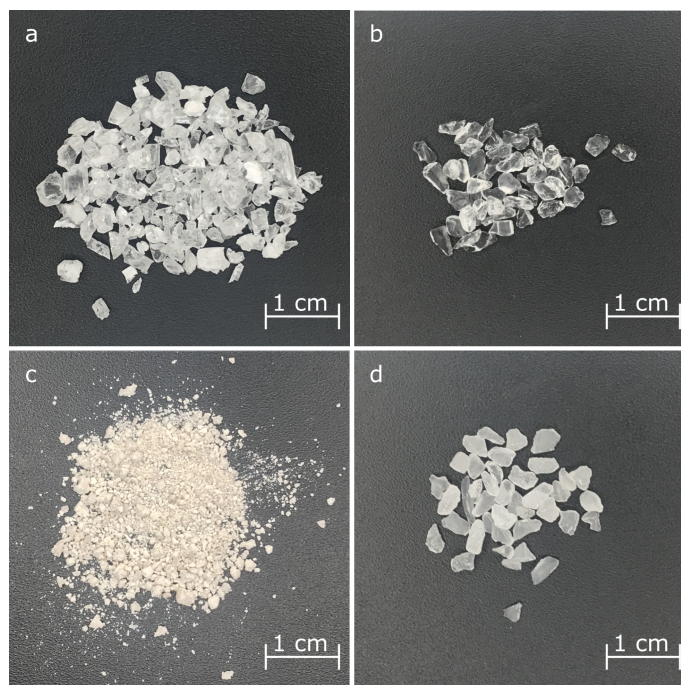
Photographs of MgO and SiO<sub>2</sub> before and after exposure to supercritical water for 30 minutes are shown in Fig. 6. The top row shows the samples before exposure, the bottom row shows the samples afterwards. The readily reactive magnesium has an oxide which clearly degrades in supercritical water while the oxide of the poorly reactive silicon exhibits superficial changes. These photographs provide further evidence that the protective properties of the oxide play an important role in the water oxidation of the metal.

The metals can also be roughly categorized as metals with low melting temperatures, *i.e.*, below approximately 1200 K (Al, Mg, Zn), as well as the alkali metals, and those with melting temperatures above 1200 K (Si, Ti, Zr). Melting temperature is directly related to the bond energy. Higher bond energy is a marker of stable compounds which are less prone to reaction. As with the hydroxide hypothesis outlined above, further work is needed.

## 4.5 Role of impurities

### 4.5.1 Alloying elements

At each temperature, the aluminum alloys produced less hydrogen than the pure aluminum sample, even though the pure aluminum sample was held at constant temperature for half the time. Aluminum alloyed with reactive metals have been shown to improve reaction rates under ambient conditions. Aluminum alloyed with 1–2.5 wt% lithium and made into a 9  $\mu$ m powder was shown to produce yields of up to 90% at ambient condition in just a few minutes.<sup>27</sup> The addition of varying amounts of gallium, indium, tin, and zinc has also been shown to improve reaction rates and yields.<sup>28</sup> These authors were relying on the introduction of dopants to improve yields and rates because, under ambient conditions, aluminum is very well passivated by a thin layer of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Another approach to increasing reaction rates and yields is to use liquid metal, which does not have a passivating layer. In one study,



**Figure 6:** Photographs of magnesium oxide and silicon oxide before and after exposure to supercritical water. (a) Magnesium oxide, as received, (b) Silicon oxide as received (c) Magnesium oxide after exposure to supercritical water for 30 minutes, (d) Silicon oxide after exposure to supercritical water for 30 minutes. The magnesium oxide shows evidence of dissolution and precipitation in the supercritical fluid while the silicon oxide shows minimal change.

a gallium-based aluminum alloy, which is liquid at room temperature, is shown to react efficiently at 315 K.<sup>29</sup>

The main dopant of aluminum 5052 is magnesium at 2.5 wt%, which, being more reactive than aluminum, would be expected to increase reactivity. However, the second alloying component is chromium, which is a common anti-corrosion doping element. With the exception of magnesium (0.8–1.2 wt%), the major doping elements in the 6061 alloy are metals that are known to be poorly- or non-reactive with water: silicon, chromium, copper, titanium and iron. The presence of these non-reactive species reduce the specific hydrogen yield of the metal and interfere with the reaction chemistry to render the alloys less reactive than the pure aluminum plate. Regardless, full hydrogen yield was achieved in each case under supercritical conditions, opening the door for the use of scrap aluminum as fuel in a metal-water fuelling strategy. Rates could be improved if the doping elements were highly reactive alkali metals, as was done by Elitzur *et al.*<sup>27</sup>

The reactivity of zirconium with water has been shown to be heavily influenced by alloying elements. Unalloyed zirconium is at real risk of reacting with steam at high temperatures ( $T > 1500$  K), conditions found in nuclear reactor cores.<sup>30,31</sup> To mitigate this risk, zirconium alloys such as Zircaloy-2 and Zircaloy-4 are used. The presence of nitrogen, carbon and aluminum in these alloys, even in minute amounts on the order of 0.1%, markedly increases their corrosion resistance.<sup>32</sup> The zirconium powder used in this study has an impurity of 0.5 wt%.; depending on the elements present, this level of impurity may have contributed to the low reactivity observed.

#### 4.5.2 Sodium chloride

Figure 4 shows that the presence of sodium chloride in the water, at most temperatures, does not have much of an effect on hydrogen yield. The dissolved ions in the water make it a weak electrolyte, which allows electrons to move more freely than in the pure water. The increased mobility of electrons in the water translates to faster electrochemical reaction between the aluminum and water, which may impact reaction rates but seems to have no impact on yield. These results indicate that sea water would be an appropriate oxidizer, from the viewpoint of the reaction, and could be used without any desalination efforts.

## 5 Conclusions

Metals are good candidates as energy carriers for renewable energy. Under normal conditions, the metals tested in this work are effectively inert to water oxidation. Their passivation layers contribute to the safety of storing such metals for long periods of time as well as reducing the risk of accidental or premature oxidation, both of which would negatively impact the efficiency and safety of the energy cycle. The most reactive of the powders was magnesium. If relying on magnesium as a fuel in a metal-water system, coarse particles (mm-scale and above) would be the safest choice. We have shown that it is possible to achieve full hydrogen yield from coarse samples of common aluminum alloys if the reaction is carried out using high-pressure and high-temperature water. In some cases, supercritical conditions were required in order to achieve complete oxidation. Such high-temperature, high-pressure metal-water reactions are an efficient method to convert the energy stored in metals to

heat and hydrogen for power applications. We also identified three metals that, although thermodynamically predicted to oxidize in water, do so poorly (silicon and zirconium), or not at all (titanium). In this work we identify several factors that contribute to the reactivity of metals in water including reaction temperature, oxidation state, oxide characteristics, and system impurities.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We acknowledge the support of the Natural Sciences and Engineering Research Council of Canada, the Fonds de recherche du Québec - Nature et technologies, McGill Sustainability Systems Initiative, Trottier Institute for Sustainability in Engineering and Design, and Vanier Canada Graduate Scholarships. We thank the members, past and present, of the Alternative Fuels Laboratory at McGill University, for their support and discussions which served to strengthen this work. We are grateful to D. Liu, and the Facility for Electron Microscopy Research for their help in obtaining the SEM images used in this work.

## References

- [1] U. Bossel, "Does a Hydrogen Economy Make Sense?," *Proceedings of the IEEE*, vol. 94, pp. 1826–1837, oct 2006.
- [2] J. M. Bergthorson, Y. Yavor, J. Palecka, W. Georges, M. Soo, J. Vickery, S. Goroshin, D. L. Frost, and A. J. Higgins, "Metal-water combustion for clean propulsion and power generation," *Applied Energy*, vol. 186, pp. 13–27, jan 2017.
- [3] J. M. Bergthorson, "Recyclable metal fuels for clean and compact zero-carbon power," *Progress in Energy and Combustion Science*, vol. 68, pp. 169–196, 2018.
- [4] M. Schoenitz, C.-M. Chen, and E. L. Dreizin, "Oxidation of Aluminum Particles in the Presence of Water," *The Journal of Physical Chemistry B*, vol. 113, no. 15, pp. 5136–5140, 2009.
- [5] A. B. Vorozhtsov, M. Lerner, N. Rodkevich, H. Nie, A. Abraham, M. Schoenitz, and E. L. Dreizin, "Oxidation of nano-sized aluminum powders," *Thermochimica Acta*, vol. 636, pp. 48–56, jul 2016.
- [6] E. I. Shkolnikov, A. Z. Zhuk, and M. S. Vlaskin, "Aluminum as energy carrier: Feasibility analysis and current technologies overview," *Renewable and Sustainable Energy Reviews*, vol. 15, no. 9, pp. 4611–4623, 2011.

- [7] S. Elitzur, V. Rosenband, and A. Gany, “Electric Energy Storage Using Aluminum and Water for Hydrogen Production On-Demand,” *International Journal of Applied Science and Technology*, vol. 5, no. 4, pp. 112–121, 2015.
- [8] F. Franzoni, M. Milani, L. Montorsi, and V. Golovitchev, “Combined hydrogen production and power generation from aluminum combustion with water: Analysis of the concept,” *International Journal of Hydrogen Energy*, vol. 35, pp. 1548–1559, feb 2010.
- [9] Y. Yavor, S. Goroshin, J. M. Bergthorson, and D. L. Frost, “Comparative reactivity of industrial metal powders with water for hydrogen production,” *International Journal of Hydrogen Energy*, vol. 40, no. 2, pp. 1026–1036, 2015.
- [10] S. Xu and J. Liu, “Metal-based direct hydrogen generation as unconventional high density energy,” *Frontiers in Energy*, vol. 13, pp. 27–53, mar 2019.
- [11] Y. Yavor, S. Goroshin, J. M. Bergthorson, D. L. Frost, R. Stowe, and S. Ringuette, “Enhanced hydrogen generation from aluminum–water reactions,” *International Journal of Hydrogen Energy*, vol. 38, no. 35, pp. 14992–15002, 2013.
- [12] K. A. Trowell, S. Goroshin, D. L. Frost, and J. M. Bergthorson, “The use of supercritical water for the catalyst-free oxidation of coarse aluminum for hydrogen production,” *Sustainable Energy & Fuels*, no. 4, pp. 5628–5635, 2020.
- [13] A. A. Galkin and V. V. Lunin, “Subcritical and supercritical water: a universal medium for chemical reactions,” *Russian Chemical Reviews*, vol. 74, no. 1, pp. 21–35, 2005.
- [14] W. Vedder and D. A. Vermilyea, “Aluminum + water reaction,” *Transactions of the Faraday society*, vol. 65, pp. 561–584, 1969.
- [15] B. C. Bunker, G. C. Nelson, K. R. Zavadil, J. C. Barbour, F. D. Wall, J. P. Sullivan, C. F. Windisch, M. H. Engelhardt, and D. R. Baer, “Hydration of passive oxide films on aluminum,” *The Journal of Physical Chemistry B*, vol. 106, no. 18, pp. 4705–4713, 2002.
- [16] D. K. Smith, D. K. Unruh, C.-C. Wu, and M. L. Pantoya, “Replacing the Al<sub>2</sub>O<sub>3</sub> Shell on Al Particles with an Oxidizing Salt, Aluminum Iodate Hexahydrate. Part I: Reactivity,” *The Journal of Physical Chemistry C*, vol. 121, pp. 23184–23191, oct 2017.
- [17] E. F. Gloyna, L. Li, and R. N. McBrayer, “Engineering aspects of supercritical water oxidation,” *Water Science and Technology*, vol. 30, no. 9, pp. 1–10, 1994.
- [18] L. I. Vergara, M. C. Passeggi, and J. Ferrón, “The role of passivation in titanium oxidation: thin film and temperature effects,” *Applied Surface Science*, vol. 187, pp. 199–206, feb 2002.
- [19] L. Kernazhitsky, V. Shymanovska, T. Gavrilko, V. Naumov, L. Fedorenko, and J. Baran, “Dark-blue titanium dioxide: Effect of phenothiazine on structural and optical properties of nanocrystalline anatase TiO<sub>2</sub>,” *Journal of Physics and Chemistry of Solids*, vol. 126, pp. 234–241, mar 2019.

- [20] S. M. Mendoza, L. I. Vergara, M. C. Passeggi, and J. Ferrón, “Metal–metal and metal–oxide interaction effects on thin film oxide formation: the Ti/TiO<sub>2</sub> and TiO<sub>2</sub>/Ti cases,” *Applied Surface Science*, vol. 211, pp. 236–243, apr 2003.
- [21] A. V. Skolunov, “Solubility of alkali metal chlorides and hydroxides in water,” *Khimicheskie Volokna*, pp. 26–29, 1993.
- [22] W.-P. Leung and Q. Wai-Yan Ip, “Alkali Metals: Inorganic Chemistry,” sep 2005.
- [23] M. Herrmann, “Corrosion of Ceramics in Aqueous Environments,” in *Encyclopedia of Materials: Technical Ceramics and Glasses* (M. B. T. E. o. M. T. C. Pomeroy and Glasses, eds.), pp. 921–931, Oxford: Elsevier, 2021.
- [24] F. Scholz and H. Kahlert, “The calculation of the solubility of metal hydroxides, oxide-hydroxides, and oxides, and their visualisation in logarithmic diagrams,” *ChemTexts*, vol. 1, no. 1, p. 7, 2015.
- [25] S. Koltry and L. Sucha, *Handbook of chemical equilibria in analytical chemistry*. New York, NY, United States: John Wiley & Sons, 1985.
- [26] W. Feitknecht and P. Schindler, “Solubility constants of metal oxides, metal hydroxides and metal hydroxide salts in aqueous solution,” *Pure and Applied Chemistry*, vol. 6, no. 2, pp. 125–206, 1963.
- [27] S. Elitzur, V. Rosenband, and A. Gany, “Study of hydrogen production and storage based on aluminum-water reaction,” *International Journal of Hydrogen Energy*, vol. 39, no. 12, pp. 6328–6334, 2014.
- [28] O. V. Kravchenko, K. N. Semenenko, B. M. Bulychev, and K. B. Kalmykov, “Activation of aluminum metal and its reaction with water,” *Journal of alloys and compounds*, vol. 397, no. 1, pp. 58–62, 2005.
- [29] S. Xu, X. Zhao, and J. Liu, “Liquid metal activated aluminum-water reaction for direct hydrogen generation at room temperature,” *Renewable and Sustainable Energy Reviews*, vol. 92, pp. 17–37, sep 2018.
- [30] P. Kuan, D. J. Hanson, and F. Odar, “Managing water addition to a degraded core,” tech. rep., US Nuclear Regulatory Commission, 1991.
- [31] A. C. Fraker and A. C. Fraker, “Corrosion of zircaloy spent fuel cladding in a repository,” tech. rep., National Institute of Standards and Technology, 1989.
- [32] C. L. Whitmarsh, “Review of Zircaloy-2 and Zircaloy-4 properties relevant to NS Savannah reactor design,” tech. rep., US Atomic Energy Commission, 1962.