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Solid hydrogen carriers as an Alternative Fuel and Impact Damper

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Synopsis

The search for cleaner and more sustainable fuels extends to the maritime sector, including the navy. Naval vessels have additional requirements regarding survivability and safety, as compared to commercial ships. A promising type of alternative fuels are the boron-based solid hydrogen carriers, specifically ammonia borane and sodium borohydride. These powders react with water to release hydrogen, resulting in a higher energy density. However, spills in and contact with water in confined areas should thus be avoided for safety reasons. The powders also react to heat, possibly releasing toxic and explosive substances. Ammonia borane starts reacting at 110 °C and sodium borohydride at 450 °C. The spent fuels exhibit significant advantages. They are thermally stable and, in the case of ammonia borane's spent fuel, even act as a flame retardant. These spent fuels may thus enhance the safety and survivability of the ship upon impact from a heat source. The significant differences between the fuels and their spent fuels require careful consideration of onboard storage locations and appropriate containment measures. Addressing these storage challenges will help pave the way for the safe and efficient adoption of solid hydrogen carriers, ultimately enhancing the environmental sustainability and survivability of naval vessels.

Keywords: Alternative fuel; Solid hydrogen carrier; Sodium borohydride; Ammonia borane; Hydrogen

1 Introduction

New, alternative maritime fuels are required to reduce or eliminate the use of fossil fuels in shipping. This need extends across all shipping industry sectors, including the Navy. However, Navy vessels comply with unique requirements compared to vessels within the general shipping industry. Increased safety and survivability is paramount for naval vessels. Alternative fuels like ammonia and hydrogen may not meet these safety standards. Ammonia is toxic, and hydrogen is extremely flammable. Other alternative fuels, such as methanol, require additional mitigating measures like cofferdams. However, solid hydrogen carriers seem to be a safe option despite requiring additional research (van Rheenen et al., 2023a).

These solid hydrogen carriers can store and release hydrogen when needed. Pure hydrogen gas is not present in large quantities, resulting in an increase in safety. Many substances are available to store hydrogen, ranging from metal hydrides to ice (van Rheenen et al., 2023b). The authors previously identified a set of three solid hydrogen carriers that show promising characteristics for use onboard ships: sodium borohydride, ammonia borane and potassium borohydride (van Rheenen et al., 2023b). These hydrogen carriers have relatively high energy densities, are generally considered safe, have medium to high technology readiness levels, and can be regenerated on shore to avoid unnecessary waste. Sodium borohydride, ammonia borane, and potassium borohydride are solids in the form of granulates or powders. As potassium borohydride has similar characteristics but lower energy density than sodium borohydride, it is not considered in this paper. However, the powder-like nature of these hydrogen carriers will give rise to new challenges. Additionally, to allow for on-shore regeneration, the spent fuels need to be stored somewhere onboard. It is currently believed these spent fuels may be stored in empty fuel tanks. Thus, bunkering, storage and distribution of the fuels and spent fuels onboard must change entirely, as powders behave differently from liquids and nowadays, nothing has to be taken back to shore. On the other hand, these powders may also give rise to new opportunities, enhancing the safety of ships as compared to current fuels.

Maritime safety is a broad topic, but the main focus of maritime safety is to protect human life at sea (e.g., SOLAS), the environment (e.g., MARPOL) and the integrity of the vessel itself and its cargo. These three pillars are all relevant when considering alternative fuels, each having its own specific connection. Crucially, the integrity of

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Authors' Biographies

Ir. Erin van Rheenen is a Ph.D. candidate at the TU Delft, Faculty of Mechanical Engineering in the Maritime Transport Technology Department. Originally a mechanical engineer and nuclear fusion physicist, she is currently working on the integration of hydrogen carriers on ships, within the SH2IPDRIVE project.

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the vessel itself will directly influence the other two pillars if the (alternative) fuel is released. This release may influence life on board as well as the environment. This is not a concern limited to naval ships; commercial vessels are equally vulnerable. Recent developments have seen a rise in attacks on civilian ships. Examples are MSC Sky II, which was hit by a missile on the 4th of March 2024. The missile caused a small fire (Bahtic, 2024). On the 6th of March, True Confidence was also hit by a missile. This missile set the ship ablaze, and 3 seafarers were killed (Bahtic, 2024). Next to deliberate attacks, commercial ships face a constant risk of collisions, both with other vessels and with natural objects like icebergs. Even though ships colliding with icebergs may feel as far away, the YONG XING 56 sank on March 1st 2023, after her hull was breached with ice, and the MS Explorer sank on 23rd November 2007 after striking an iceberg (Van den Bovenkamp, 2023; The Associated Press, 2007).

While solid hydrogen carriers themselves cannot prevent ships from sinking, their properties may offer potential safety advantages in the event of collisions. When stored within a ship's hull, these carriers may dampen the impact of a collision. The powdery nature of the hydrogen carrier could potentially solidify and even plug any resulting holes, reducing the release of the fuel through the hole. Additionally, some of these chemicals may have flame-retardant properties, potentially reducing large-scale fires. Finally, solid hydrogen carriers could minimize fuel loss compared to liquid alternatives. These characteristics suggest that solid hydrogen carriers may offer improved safety compared to conventional fuels like diesel or other liquid alternatives like methanol.

Thus, this research aims to investigate the consequences of storing solid hydrogen carriers as fuel in the ship's hull. Both impact with and without heat will be taken into account. The research will follow a conceptual approach based on chemistry and chemical reactions. This approach allows for the evaluation of alternative fuels for various ship types.

2 Method

An approach based on chemical reactions is proposed to investigate the possible usage of hydrogen carriers as impact dampeners. The influence of heat, water and a combination of heat and water on the hydrogen carriers is investigated. The likelihood of reaching relevant temperatures depends on possible environmental conditions and is not taken into account in this paper. However, the likely consequences of these impacts on hydrogen carriers are investigated. The mentioned hydrogen carriers are all circular in nature. Their empty fuel, called spent fuel, has to be stored on board and discharged and regenerated at a shore facility to enable renewable use. Thus, the ship will additionally carry the spent fuel of each of the carriers. This spent fuel depends on the reaction required to release the hydrogen. Both hydrogen carriers will release hydrogen through hydrolysis. For ammonia borane, the reaction is as follows:

$$NH_3BH_3 + 3H_2O \rightarrow 3H_2 + B(OH)_3 + NH_3 \tag{1}$$

The spent fuel will thus be $B(OH)_3$, which can possibly be stored in the same tanks as the original fuels. Thus, the spent fuel must also be investigated. For sodium borohydride, a similar reaction is regarded:

$$NaBH_4 + (2+x)H_2O \rightarrow 4H_2 + NaBO_2.xH_2O \tag{2}$$

In this case, the spent fuel thus consists of $NaBO_2.xH_2O$. The x here depends on the temperature at which the reaction occurs and the temperature at which the spent fuel is stored (Andrieux et al., 2012). To reduce weight, the x should be as small as possible. The resulting calculated weights of the spent fuel are given in table 1.

Table 1: Relation of x in equation 2 and weight of spent fuel

x	Weight of spent fuel [kg] per kg sodium borohydride
0	1.73
1	2.69
2	3.64

Thus, both the original fuel and the spent fuel will be investigated as to their chemical reaction to heat, water and a combination of heat and water. For this last scenario, the authors assume that the heat is a flash heat source, after which water will touch the products. What would happen without heat and water, with just a lack of confinement from the fuel tank, is not part of this research. Figure 1 shows the pathway of the chemical reaction paths that will be investigated in this study.

This research will focus on the chemical reactions, and the results of these reactions. Many of these chemical processes are step-wise processes. Some of these steps are exothermic and thus self-sustaining. This can potentially cause unwanted runaway reactions. Endothermic reactions, on the other hand, absorb energy and will stop once the initial energy source disappears. When considering products derived from these reactions, it's important to factor in their corrosive properties and typical applications. These substances may have undesired properties, such as high toxicity or flammability. Gasses are also less desirable than solids, as gasses can distribute themselves easily,

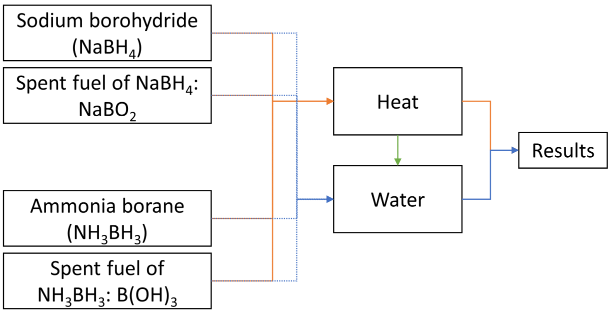

Figure 1: Overview of pathway to gain resulting chemical products for analysis in results

resulting in them coming to unwanted locations.

The substances formed will be evaluated based on their subsequent influence on the ship itself and the impact on the passengers and the environment. It is hard to quantify dangers exactly, especially as consequences depend greatly on the amount of substances produced and their location. However, a first overview of these dangers can be used to qualify whether they are large issues or can be overcome. Estimating these dangers is possible this way (van Rheenen et al., 2023a). The results can be used to determine the storage location of these hydrogen carriers based on whether they can or cannot be used as impact dampeners.

3 Results

This section discusses the reaction equations, the temperature at which they occur, whether they are endothermic or exothermic and the resulting products. Pure hydrogen is often a byproduct of the reactions and is discussed separately.

3.1 Ammonia borane

Ammonia borane reacts strongly with water and heat, releasing hydrogen and other substances during these processes.

3.1.1 Reaction with heat

Figure 2 shows the resulting reactions when ammonia borane is heated. This figure is a simplified version, as the actual reactions are more complicated, see for example Demirci (2020); Al-Kukhun et al. (2013). The figure omits many intermediate steps with the same outcome, involving different but short-lived products. These in-between products, often polymeric, usually decompose to the products as visible in figure 2. The only exception is polyiminoborane, which is thermodynamically stable and only releases hydrogen upon heating at higher (over 1000 °C) temperatures. Figure 2 shows multiple end products and several in-between products that are stable within rather large temperature windows.

Figure 2 shows a three-step process for the main pathway. The first step in this three-step process is an endothermic process, with a reaction energy of approximately 115 to 145 kJ/mol, producing aminoborane (Kumar et al., 2019). When aminoborane is heated to about 200 °C, it decomposes into hydrogen and polyiminoborane. This second step is an exothermic reaction, releasing approximately 21 kJ/mol (Demirci, 2020). It is thus self-sustaining, making aminoborane as an intermediate product less likely. The exact enthalpy of reaction, however, depends on the heating rate (Baumann et al., 2005), especially as aminoborane is only stable until about 115 °C, after which it slowly decomposes (Baumann et al., 2005). The result, iminoborane (BNH_2), is illusive and highly reactive (Baitalow et al., 2002). It quickly oligomerizes or polymerizes. Polyiminoborane is rather stable (Hu et al., 1978). However, it slowly releases hydrogen upon heating (Hu et al., 1978). When iminoborane oligomerizes, it is transformed into borazine.

Only at much higher temperatures, of around 1100 to 1400 °C, boron nitride is formed (Frueh et al., 2011). When borazine is heated, it also forms boron nitride. Boron nitride is a highly stable nitride, subliming at 2500 °C (Demirci, 2020; Patnaik, 2003).

During each of the steps, additional byproducts occur. Higher heating rates result in more volatile, unwanted byproducts like diborane and borazine (Baitalow et al., 2002; Karkamkar et al., 2007). During the first step, diborane and aminodiborane are produced. Diborane (B_2H_4) is produced at a ratio of 0.02 to 0.04 mol per mol of ammonia borane (Baitalow et al., 2002). Diborane, also known as borane, will readily oxidize (at temperatures lower than 54 °C) to B_2O_3 (boron trioxide) (House, 2020). Boron trioxide is a stable solid substance, vaporizing at 1500 °C (Patnaik, 2003). Boron trioxide is an ingredient in flame retardant (NCBI, 2024f), and is non-combustible.

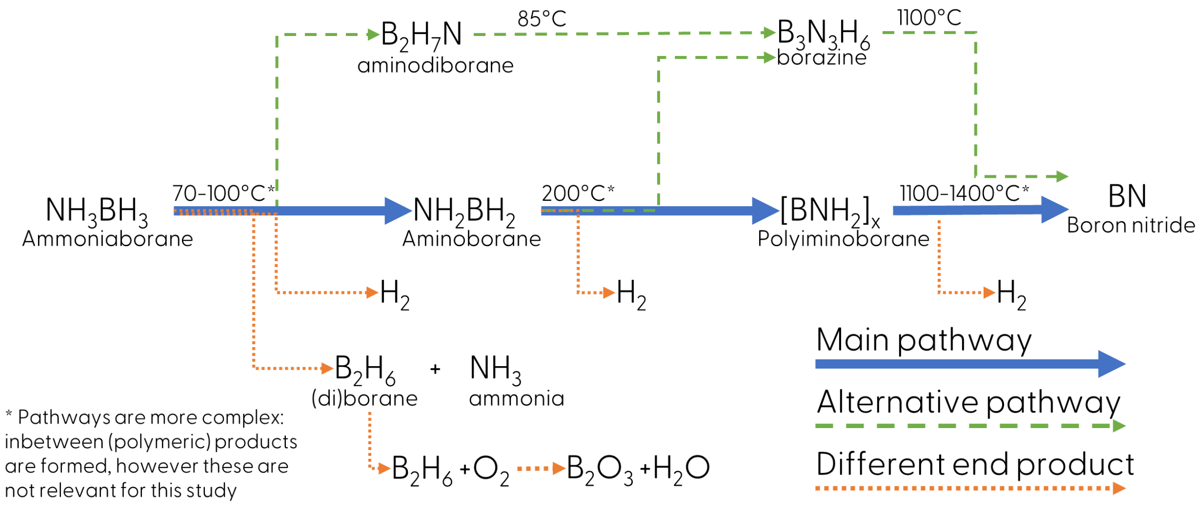

Figure 2: Reactions of ammonia borane in heat

Next to diborane, ammonia is produced. Ammonia is a toxic gas and is lighter than air. Ammonia has a flash point of 132 °C.
Next to diborane, aminodiborane can be produced simultaneously during the first step (Demirci et al., 2011; Al-Kukhun et al., 2013). Aminodiborane transforms later into borazine; this reaction happens at temperatures as low as 75 °C (Al-Kukhun et al., 2013). However, it takes time to produce amino diborane; the reaction is relatively slow (Al-Kukhun et al., 2013). Aminodiborane is generally hard to produce, resulting in very limited information available (Chen et al., 2010). It is reported as highly sensitive to air and moisture as it decomposes (Nair et al., 2023). However, it is likely to react with an in-between product of the main pathway, diammoniate of diborane, resulting in an alternative but slower path to produce borazine (Al-Kukhun et al., 2013).
Borazine is created during the second step as well. Approximately 0.03 to 0.06 moles of borazine per mol of ammonia borane are created during this process (Baitalow et al., 2002). Borazine is a dangerous liquid, which is highly flammable and causes severe damage to the eyes and skin (NCBI, 2024b). In water, it hydrolysis to ammonia, boric acid and hydrogen.

3.1.2 Reaction with water

Ammonia borane reacts with water in a process called hydrolysis. Equation 1 gives an overview of what happens during this process (Demirci, 2020). There are no known side reactions or alternative pathways (Demirci, 2020). However, the reaction rate is considered to be slow, as there are no catalysts or acids (Demirci, 2020; Li et al., 2022). Acids act as catalysts during hydrolysis; lower pH will result in faster reactions (Li et al., 2022). For higher pH, of about 10, no reaction was observed for 8 minutes, after which the experiment was stopped (Li et al., 2022). Additionally, the substance will self-stabilise if nothing is done about the pH value of the solution. Regardless of the concentration, the pH will become 8.7 to 9.1, close to seawater's pH (7.5 to 8.5) (Brockman et al., 2010; Chandra and Xu, 2006; Marion et al., 2011). At these pH values, the solution is reported to be stable for 80 days in an inert atmosphere (Chandra and Xu, 2006). Brockman et al. (2010) confirms this, testing ammonia borane in different amounts of water, resulting in very low (maximum of 10% of the overall hydrogen available in ammonia borane) hydrogen loss over several (at most 75) days. Unfortunately, the authors could not find data on what happens in a normal atmosphere. Thus, ammonia borane is estimated to react extremely slowly in seawater. Regarding the produced products, $B(OH)_3$, the original spent fuel, will be discussed in section 3.3 and hydrogen in section 3.2.2. Ammonia is the main product specific to the hydrolysis of ammonia borane in water. Ammonia is highly soluble in water and will react with water and form a solution according to the following equation (Demirci, 2020):

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \tag{3}$$

In this equation, ammonium (NH_4^+) and hydroxide (OH^-) combined are called ammonium hydroxide (Kass et al., 2021). The amount of ammonia dissolved in water depends on the amount of water and whether some of the ammonia can be lost in the gas phase (Demirci, 2020). It is unclear whether all ammonia is dissolved in seawater. Some sources believe that some ammonia will still be in the gas phase (Demirci, 2020), while others believe that all ammonia that contacts water will be dissolved (Kass et al., 2021). Thus, the assumption has to be made that

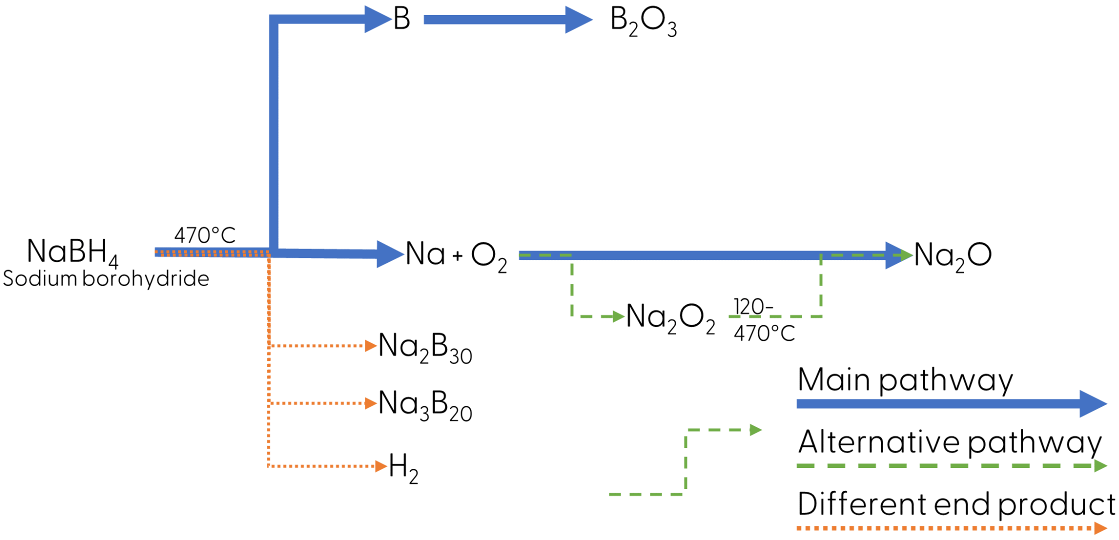

Figure 3: Reactions of sodium borohydride in heat

pure ammonia as a gas will be released, as well as ammonium hydroxide. Ammonium hydroxide is alkaline and corrosive. It will inhibit the reaction of ammonia borane with water and corrode materials nearby. It is also harmful to sealife (Kass et al., 2021).

3.1.3 Combined heat and water

Figure 2 shows several products resulting from heating ammonia borane. Ammonia itself was discussed in section 3.1.2. Borane/diborane has likely already changed into B_2O_3 (House, 2020), as visible in figure 2; however, if this does not happen, borane will react with water as follows:

$$B_2H_6 + H_2O \rightarrow 2B(OH)_3 + 6H_2 \tag{4}$$

In this equation, hydrogen and boric acid are produced. The reaction is strongly exothermic (Prosen et al., 1959). The authors refer to section 3.3.3 for the reaction of boric acid with water.

This leaves aminodiborane and borazine. As mentioned in section 3.1.1, aminodiborane decomposes in water (Nair et al., 2023). The authors cannot find the exact decomposition reaction. It will likely react similarly to borazine, forming hydrogen, ammonia and $B(OH)_3$ upon hydrolysis (Nagasawa, 1966; NCBI, 2024b; Nair et al., 2023). Generally, boron-nitrogen bonds are not stable in the presence of water (Nagasawa, 1966).

3.2 Sodium borohydride

Sodium borohydride is a salt and looks like a white powder. It can be thermolyzed and hydrolyzed to release hydrogen and will thus react with heat and water (Singh, 2021; Demirci et al., 2010).

3.2.1 Reaction with heat

Figure 3 gives an overview of the main and alternative pathways of thermal decomposition of sodium borohydride. Thermal decomposition starts at 470 °C and is in general as follows (Singh, 2021; Martelli et al., 2010; Kumar et al., 2017):

$$NaBH_4 \rightarrow B + Na + 2H_2 \tag{5}$$

All hydrogen is released at once when heated above 600 °C, although other sources estimate this to be 534 °C (Singh, 2021; Martelli et al., 2010). The process is exothermic and thus self-sustaining, releasing about 108 kJ/mol (Singh, 2021; Martelli et al., 2010; Kumar et al., 2017). The products formed are two solids (sodium and boron) as well as hydrogen.

Sodium is a well-known substance and is very volatile (Krolikowski, 1968; Lebel and Girault, 2018). Figure 3 shows the two main reaction pathways of sodium with oxygen, producing sodium oxide (Na_2O and sodium peroxide (Na_2O_2) (Krolikowski, 1968). This reaction occurs at temperatures at or below 105 °C and requires only 5% volumetric oxygen in the air (Krolikowski, 1968; Bulmer and Fire, 1972). The burning of sodium can reach temperatures of up to 3600 °C under ideal circumstances (Krolikowski, 1968).

Boron is a versatile material, and though it is generally categorized as interesting, there is still a lot unknown about

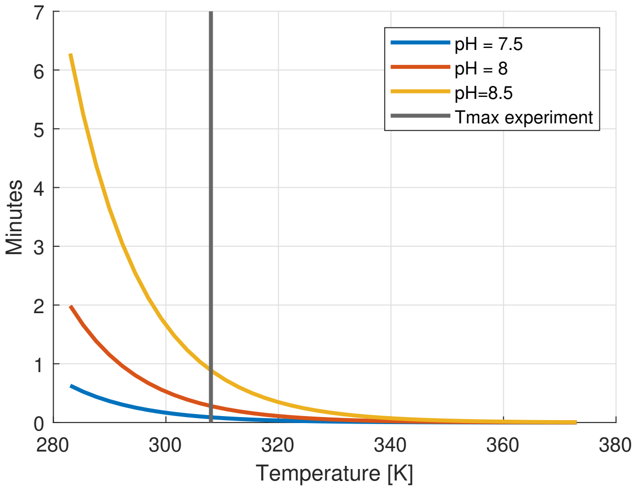

Figure 4: Release of half of the hydrogen from $NaBH_4$ during self-hydrolysis. Including the maximum temperature for which this equation, equation 6 has been validated, based on (Retnamma et al., 2011).

this material (van Setten et al., 2007). Boron generally does not react easily at room temperature and is not very volatile (van Setten et al., 2007). It is known, however, to burn readily and produce B_2O_3 (boron trioxide), which has been discussed previously in section 3.1.1 (House, 2020).
Next to these main products, also two combinations of boron and sodium are formed: Na_2B_{30} and Na_3B_{20}. Almost no data about Na_2B_{30} (Chang et al., 2021) is available and will thus not be discussed by the authors here. Na_3B_{20} is better studied. It is a pyrophoric substance if the particles are small, at larger particle size it is more stable (Albert, 1998; Albert and Hofmann, 1999). It is also possible that Na_3B_{20} only occurs at high temperatures (1050 °C) as it usually is synthesized at such high temperatures (Albert and Hofmann, 1999). It is thermodynamically stable, and likely only very small quantities are produced.

3.2.2 Reaction with water

The reaction of sodium borohydride with water is given in equation 2. No other pathways have been reported to the authors' knowledge. The reaction rate is strongly dependent on temperature and pH value. A higher pH value, indicating a more alkaline solution, will inhibit the reaction, while higher temperatures will result in a higher reaction rate (Sermiagin et al., 2022). A higher concentration will result in a faster reaction rate, too (Sermiagin et al., 2022). A temperature of 25 °C and pH of 7.4, lower than that of seawater, will result in approximately 67% of all hydrogen generated within 5 minutes and reaction rates of $2.05 \times 10^{-3}\ s^{-1}$ have been reported for pH values of around 8.5 (Sermiagin et al., 2022; Marion et al., 2011). Another source cites a half-life of $NaBH_4$ of about 36.8 seconds when dissolved in a solution with a pH of 8. The reaction rate has been captured empirically as follows (Retnamma et al., 2011; Hoeppner et al., 2008):

$$log(t_{1/2}) = pH - (0.034T - 1.92) \tag{6}$$

with $t_{1/2}$ in minutes and T, the temperature, in Kelvins. Figure 4 visualises the different half-life times. Considering typical seawater temperatures of up to 30 °C (or 303K) (Kennedy, 2014), the shortest half-lifes lie under a minute. These reactions can be considered fast.

3.2.3 Combined heat and water

Sodium, known to be highly reactive with water, is part of many of the products in figure 3 (Bulmer and Fire, 1972). However, if there is no air, the reaction may be non-explosive (Bulmer and Fire, 1972). Figure 5 gives an overview of the resulting reactions. The reactions are all exothermic. One of the alternative endproducts, H_2O_2, is known to cause thermal runaways, as it decomposes at low temperatures, lower than 100 °C (Wu and Qian, 2018). NaOH, the main reaction product, will dissolve in water, releasing heat (NCBI, 2024d). This reaction can possibly ignite other substances, such as hydrogen peroxide. It splits into Na^+ and OH^- and is a salt. When not strongly diluted, it is extremely corrosive (NCBI, 2024d).
Boron is unlikely to react, as it is relatively stable and also present in seawater, with concentrations ranging from 0.5 to 9.6 mg/L (Kochkodan et al., 2015). This is both natural as well as due to human causes.

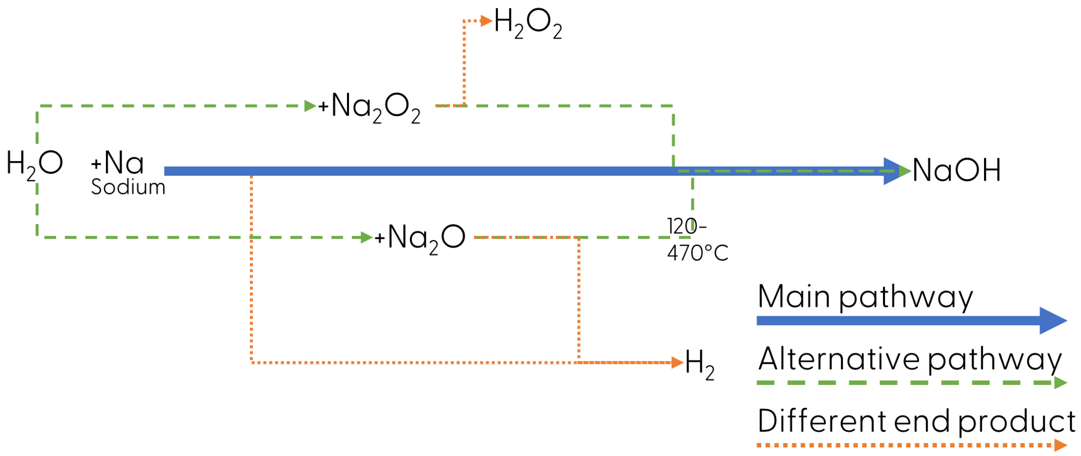

Figure 5: Reactions of products of sodium borohydride in heat, with water

3.3 *Spent fuel*

The spent fuel of sodium borohydride ($NaBO_2$) and that of ammonia borane ($B(OH)_3$ are very similar and composed of similar elements. Thus, they are considered both in this subsection. When dissolved in water, the spent fuel of sodium borohydride splits up in Na^+ and $B(OH)_4^-$, the latter which is also the spent fuel of ammonia borane.

Equations 1 and 2 give a high-over reaction overview. The exact composition of the spent fuel depends on temperature, whether and how the water is extracted and the pressure (Andrieux et al., 2012; Moussa et al., 2013).

3.3.1 *Heating of boric acid*

Boric acid, $B(OH)_3$, is a very weak acid and has been used as flame retardant (House, 2020; Sevim et al., 2006). Upon heating, boric acid releases its hydrogen and oxygen atoms in the form of water in a two-step reaction (Sevim et al., 2006; Kim and Hwang, 2021; Balci et al., 2012):

$$B(OH)_3 \leftrightarrow HBO_2 + H_2O \tag{7}$$

occurring at temperatures below 130 °C. The next step occurs at higher temperatures of around 200 °C, with a maximum of about 450 °C (Balci et al., 2012; Kim and Hwang, 2021). At temperatures higher than this, reactions will slow down. The second step is as follows:

$$2HBO_2 \rightarrow B_2O_3 + H_2O \tag{8}$$

It is possible that the second step already occurs before the first step is completed (Balci et al., 2012). The end result, B_2O_3, is called boron oxide. The first reaction, equation 7, is a slow reaction, taking up to 3 days for low temperatures (up to 100 °C) and 45 minutes for temperatures above 300 °C (Balci et al., 2012). The melting temperature of boron oxide depends on its structure. The exact structure of the end product of equation 8 is unclear, however the melting point will be around 450 to 500 °C (Sevim et al., 2006). Boron oxide is widely used, for example, in glass and ceramics, but it is also used as a fire retardant (Sevim et al., 2006). Boron oxide will evaporate at temperatures above 1025 °C (Lopatin et al., 2023).

3.3.2 *Heating of Sodium metaborate*

$NaBO_2$ is thermodynamically stable and does not react easily. It has a high melting and boiling point. The melting point lies at 966 °C and the boiling point at 1434 °C (NCBI, 2024c). On the contrary, it has also been stated to evaporate at temperatures above 800 °C (Lopatin et al., 2023).

3.3.3 *Reaction with water*

The reactions of water with the spent fuels are straightforward. These reactions also happen during the original dehydrogenation process, as both fuels are solved in water during the hydrolysis process. Sodium metaborate splits

Table 2: Resulting products of reactions of NH3BH3, NaBH4 and the spent fuels with heat, water and a combination of heat and water

	Heat	Water	Heat and water
Ammonia borane	NH_3(g), H_2(g), B_2H_6 (g), B_2H_7N (l), $B_3N_3H_6$ (l) T$<$1000 °C: $[BNH_2]_x$ T$>$1000 °C: BN	NH_4^+ (aq) + OH^- (aq) H_2 $B(OH)_3$ (aq) $\leftrightarrow$ $B(OH)_4^-$ (aq) + H^+ (aq)	H_2, NH_3, $B(OH)_3$
Sodium borohydride	Na (s), B (s), H_2 (g), Na_2O (s), Na_2B_30 (s), Na_3B_20 (s), B_2O_3 (s)	$NaBO_2$ (aq), H_2 (g)	H_2O_2 (l), NaOH (s/aq), H_2 (g)
Spent fuel	B_2O_3 (s) (NH_3BH_3) $NaBO_2$ (s) ($NaBH_4$)	$B(OH)_3$ (aq) $\leftrightarrow$ $B(OH)_4^-$(aq) + H^+(aq)	B_2O_3 +H_2O $\rightarrow$ $B(OH)_3$(aq) Na^+ (aq), $B(OH)_4^-$ (aq)

into two ions, sodium and metaborate (Atiyeh and Davis, 2007):

$$NaBO_2 \xrightarrow{\text{Water}} Na^+ + B(OH)_4^- \tag{9}$$

As sodium ions are common in seawater, they are not of interest in this study. Thus, the authors will focus on the metaborate-ion, $B(OH_4^-)$. This ion is unstable in water (House, 2020; Kochkodan et al., 2015; Kabay and Bryjak, 2015). It is the anion that is in balance with boric acid as follows:

$$B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+ \tag{10}$$

The pH of the water strongly influences this balance. The balance lies at $B(OH)_3$ for low pH and switches to the right for pH levels higher than about 8.5; the exact pH value where the balance shifts depends strongly on the temperature (Kochkodan et al., 2015; Kabay and Bryjak, 2015). At seawater with a pH of 8.3, the balance in equation 10 shifts to the left, and most of the substance is in the form of boric acid (Kabay and Bryjak, 2015).

In the case of having first a heating reaction and then a water reaction, boron oxide reacts with water exothermically to reform boric acid (Rasmussen et al., 2003).

3.4 Hydrogen

Risks of hydrogen in its pure form have been widely covered in the literature (for example, but not limited to (Mjaavatten and Bjerketvedt, 2005; Makarov et al., 2021; Gerboni and Salvador, 2009; Dagdougui et al., 2018; Patel et al., 2023). The main issue with hydrogen explosions is not the heat source but the power resulting from the pressure of the explosion (Makarov et al., 2021; Mjaavatten and Bjerketvedt, 2005). Even relatively small hydrogen explosions, where about 3.5 to 7kg of hydrogen exploded, had destructive influences on nearby buildings (Mjaavatten and Bjerketvedt, 2005). As most explosions occur due to over-pressure (Patel et al., 2023), however, it is hard to estimate whether a breach of a ship tank will result in hydrogen explosions.

4 Discussion

The previous section has given an overview of the possible reactions occurring when the solid hydrogen carriers come into contact with heat, water or a combination of heat and water. This will have implications on how and where these fuels can be stored and whether they can be used as impact dampeners.

Table 2 gives an overview of all resulting products from each of the possible reactions. These products are not produced proportionally; some of the products only occur in very small quantities, making them less relevant. As the exact amounts of the products are unclear, they will all be taken into account in this analysis.

4.1 Heating

Both fuels produce dangerous substances upon heating. However, the products and the respective temperatures differ strongly.

4.1.1 Ammonia borane

Ammonia borane reacts at lower temperatures, of up to 200 °C already. During these reactions, the toxic gasses ammonia and diborane and the flammable gas hydrogen are formed. Heating of ammonia borane thus forms a danger to both the ship and the people on board. As these substances are all gasses, they are more dangerous but also more safe. Their gas-like nature will result in a faster distribution and, thus, lower overall concentrations of each gas. This will make the gasses safer, as lower concentrations are less likely to be dangerous.

Hydrogen has a lower flammability limit of 4% and is easily ignited. Thus, the release of hydrogen may cause an explosion and, thus, a secondary heat source. These types of reactions may become self-sustaining, resulting in more release of hydrogen and other dangerous gasses. Diborane (B_2H_6) is also easily ignited, igniting in moist air at room temperature without external triggers (NCBI, 2024a). The flammability and easy ignition of both hydrogen and diborane may influence the ship's integrity, as these are likely to ignite. Additionally, the spontaneous ignition of diborane, despite very low concentrations, may cause the ignition of hydrogen. Hydrogen is likely to be present in larger concentrations and can influence the integrity of the ship.

Ammonia is not easily ignited, but is extremely toxic, and concentrations as low as 2500 ppm are considered lethal (NCBI, 2024e). Diborane is even more toxic. It has a strong smell and can be smelled at low concentrations, as low as 1.8 ppm (NCBI, 2024a). It is extremely toxic and can be deadly at concentrations as low as 0.46 ppm if inhaled over longer amounts of time. At 7.3 ppm, it has immediate effects (NCBI, 2024a). Another danger of diborane, as opposed to ammonia and hydrogen, is that it is heavier than air and thus will accumulate. Ammonia, on the other hand, is lighter than air and will disperse more easily. The toxicity of ammonia and diborane, especially the heavy weight and high toxicity of diborane, will strongly influence the safety of the people on board.

Finally, ammonia may influence sealife, but only if it touches water. If it comes into contact with water, it may have large consequences for local sea life (Kass et al., 2021). As it is lighter than air, this is not necessarily likely. Diborane forms no environmental hazard according to the GHS standards, but as it is so toxic to people, it is likely to also influence sea life, and of these three gasses most likely to enter the ocean.

Two other substances that are formed are aminodiborane and borazine, both liquids. Borazine is a flammable and corrosive liquid with a clear smell and no colour (NCBI, 2024b). The corrosiveness of borazine applies to the skin, as it causes skin burns and eye damage (NCBI, 2024b). Aminodiborane is an unstable liquid, decomposing at room temperature, likely towards borazine (Demirci, 2017; Al-Kukhun et al., 2013). Release of these two liquids will likely result in contact with the environment. Aminodiborane will slowly hydrolyse, completing hydrolysis in 2 months at room temperature (Demirci, 2017). It is unknown if aminodiborane is toxic to the environment. However, it is not likely to influence the ship's integrity. Borazine will strongly influence the safety of the people on board, as it is a liquid that should not come into contact with people. It is flammable and reacts violently with water, which may influence the ship's integrity if this substance comes into contact with water (NCBI, 2024b).

4.1.2 Sodium borohydride

The resulting products of heating sodium borohydride are dangerous. However, these products occur after heating at much higher temperatures (around 470 °C for sodium borohydride, versus 200 °C for ammonia borane). In the case of sodium borohydride, runaway reactions are more probable.

When heating sodium borohydride, the structural integrity of the ship is likely influenced. A major product, sodium, is a dangerous solid due to its flammability and corrosivity. It burns violently and may also cause explosions. These explosions, in turn, can set off more explosions from hydrogen. The corrosivity of sodium may influence the metal the ship is made of. The other three substances (boron, sodium oxide (Na_2O) and boron oxide (B_2O_3)) are not likely to influence the ship itself.

Boron, sodium oxide (Na_2O) and boron oxide (B_2O_3) may all influence the safety of people on board. Boron is an irritant and should not be swallowed. Boron oxide is a typical boron-based product and only has a health hazard. This health hazard is typical for boron-based compounds, such as boric acid and boron oxide: these may influence fertility or the unborn child (Chapin and Ku, 1994). It is thus unlikely to influence the people onboard strongly. Like sodium oxide, it does not harm the environment or the ship. Sodium oxide is also dangerous for the people onboard as it is corrosive to the skin and thus can cause eye damage. All of these substances should thus not be touched. As they are solids, they are not easily distributed, enhancing their safety.

Even though some reports that boron compounds may cause long-lasting harmful effects on aquatic life, there is no consistency on this (NCBI, 2024g). Whether any of the products resulting from heating sodium borohydride will harm the environment is not known.

4.2 Water

Both substances will react with water. The most positive side is that no alternative substances are produced, only the substances that are known and well-studied. However, these substances are not necessarily safe.

Hydrolysis of ammonia borane will result in ammonia, hydrogen and boric acid. Ammonia will harm local wildlife and, if not dissolved in seawater, may harm the lives of people onboard the ship and in the surrounding area. and the possibility of hydrogen explosions.

The spent fuel of ammonia borane, boric acid, may damage fertility or the unborn child, resulting in a health hazard (NCBI, 2024f). However, no other dangers have been stated for this substance. When touching the water, it will sink and dissolve completely (NCBI, 2024f).

Sodium borohydride will only produce the possibly explosive hydrogen. Again, hydrogen explosions may influence the integrity of the ship.

Table 3: Resulting dangerous products of reactions of ammonia borane and sodium borohydride and their relative spent fuel with heat, water and a combination of heat and water

	Heat	Water	Heat and Water
Ammonia borane	Dangerous gasses and liquids, which will influence the ship's integrity, life onboard and environment	Dangerous gasses, which may influence the ship's integrity, life onboard and environment	Dangerous gasses and liquids, which may influence the ship's integrity, life onboard and environment
Spent fuel: Boric acid	Flame retardant, will release water	May influence reproducibility of local wildlife	May influence reproducibility of local wildlife
Sodium borohydride	Dangerous gasses and solids which will influence the ship's integrity, and possibly life onboard and environment	Dangerous gasses, which may influence the ship's integrity	Dangerous gasses and solids which will influence the ship's integrity, and possibly life onboard and environment
Spent fuel: Sodium metaborate	Unlikely to react	May influence reproducibility of local wildlife	May influence reproducibility of local wildlife

The spent fuel, sodium metaborate, may be a danger to human reproducibility and, thus, also likely to wildlife reproducibility. However, the exact effects are unknown.

4.3 Combined heat and water

When heating ammonia borane, many different substances are produced. However, almost all of these substances react in a very similar way with water. The reactions are usually exothermic (Prosen et al., 1959; Nagasawa, 1966; Nair et al., 2023), and the resulting products are likely to be ammonia, hydrogen and boric acid. These products will likely influence all three pillars: the integrity of the ship, the safety of the people onboard and the environment and are extensively discussed in previous sections.

As the spent fuel of ammonia borane, boric acid, releases water upon heating, it changes into boron oxide. Boron oxide will absorb water exothermically. This reaction forms boric acid again. Thus, the reaction of boric acid upon first experiencing heat and then water is unlikely to result in different reactions as compared to experiencing water only.

The main products from sodium borohydride, when heated, are sodium, boron and hydrogen, as well as sodium oxide and sodium peroxide. Some of these products are volatile. Sodium reacts strongly with water, forming sodium hydroxide (NaOH). This reaction is highly exothermic and may influence the integrity of the ship. NaOH is readily dissolved in water but is extremely corrosive and can thus influence the integrity of the ship. Similarly, sodium peroxide reacts with water, forming hydrogen peroxide. Hydrogen peroxide can cause thermal runaways (Wu and Qian, 2018). Thus, heating sodium borohydride, followed by adding water, may result in various explosions, resulting in additional heat sources and thus a chain reaction. This chain reaction will likely influence the integrity of the ship.

Of these products, only hydrogen peroxide is dangerous to the people onboard and the environment. It can cause severe skin burns and eye damage and harm aquatic life (NCBI, 2024h).

As sodium metaborate is thermodynamically relatively stable, no different reactions are expected upon a combination of heating and water as compared to releasing sodium metaborate directly in water.

4.4 Overview

Table 3 gives an overview of all the hazards accompanied by heating, adding water or a combination of both. It is clear that both ammonia borane and sodium borohydride release dangerous substances. Heating is the most dangerous for ammonia borane, as a chain reaction is likely. Heating of sodium borohydride results in similarly dangerous products. However, as the products of sodium borohydride are only released at much higher temperatures (over 500 °C), overall sodium borohydride is more safe than ammonia borane upon heating. Both spent fuels are the most safe. Boric acid is more safe than sodium metaborate. Boric acid is a flame retardant and will release water, possibly extinguishing the fire, while sodium metaborate likely will not react.

When adding water, ammonia borane produces the least safe products. However, as the reaction rate of ammonia borane with water is extremely slow, especially compared to sodium borohydride, it is difficult to say which one is safer. Both have different hazards. Again, the spent fuels are safer than the original fuels.

Finally, when first adding heat and then adding water, sodium borohydride appears to be less safe. Heating sodium borohydride produces, amongst others, sodium, which reacts violently with water. Heating ammonia borane produces mainly dangerous gasses, of which only one (diborane) is heavier than air. Diborane is also produced in less high quantities. The same applies to the liquids produced, which are mainly byproducts. Thus, ammonia borane is the safer fuel in this case. As before, both spent fuels are safer and likely will not release dangerous substances.

5 Conclusion

While the zero-emission nature of alternative fuels is a major advantage, their benefits may extend even further. Especially solid hydrogen carriers, such as sodium borohydride and ammonia borane, may offer advantages unknown to liquid alternative fuels. This research investigated the consequences of storing solid hydrogen carriers of boron-based fuels in the ship's hull.

This research regarded three main safety pillars: integrity of the ship, safety of the life onboard and environmental impact. Regardless of the type of impact, ammonia borane will likely influence all three pillars. As it reacts already with low heat sources (around 100 °C), heat is to be avoided at all times. Adding water to the heated ammonia borane is unlikely to make it worse. The gasses and liquids released are flammable and toxic to human life. As ammonia borane is a boron chemical compound, it may influence the reproducibility of sea life. A possible storage location, if stored in the hull, would, therefore, be below the water line.

Sodium borohydride, on the other hand, reacts only at much higher temperatures, starting decomposition at 450 °C. However, the reaction products are extremely volatile. Amongst others, sodium is produced, which reacts violently upon touching water. This can thus influence the ship's integrity. However, none of the products of heating sodium borohydride are toxic. Thus, if sodium borohydride were to be stored in the hull, a possible storage location would be above the waterline. This will also limit the possible influence of sodium borohydride on the reproducibility of local sea life.

Unlike the original fuels, spent fuels from sodium borohydride and ammonia borane offer potential benefits regarding safety. The spent fuel of sodium borohydride is thermodynamically stable and unlikely to produce toxic or flammable gasses upon heating. The spent fuel from ammonia borane is a known flame retardant, releasing water when heated. These properties suggest that spent fuels are unlikely to form hazardous substances upon impact and may even mitigate the effects of heat.

Ultimately, considerations must be made on where to locate the fuels and their spent fuels onboard the ship based on safety and the handling of the powders. By carefully addressing these storage and distribution challenges, the full potential of these alternative fuels for a cleaner and safer maritime future can be unlocked.

6 Future work and recommendations

This fuel research as an indicator for impact dampeners is still subject to active academic discussion. This statement applies to all reaction products discussed here and their corresponding maritime influences, as this is part of ongoing research. To fully assess the feasibility and safety of the storage of these two solid hydrogen carriers onboard ships, further research is crucial. This research can include but is not limited to, the following key areas. First of all, experimental validation of containment loss is required. In this case, no external factors (such as heat or water) are necessary; the focus should lie on what happens during the loss of containment of the fuel. Experimental data on the reaction rates during relevant conditions is also desired. This will give information on whether the size and volume of the alternative fuels and, thus, the tanks are relevant. All these experiments can provide insights into, for example, whether a double hull (such as used with oil tankers) is advisable. The optimal storage location for both the fuel and spent fuels also requires investigation. While using empty fuel tanks to store the spent fuel is currently considered the most efficient approach, the distinct properties of each type may necessitate alternative storage configurations for enhanced safety and performance. Besides this, a comparison with current rules and regulations set by the IMO and classification societies based on the storage of fuels would result in additional insights into the storage of these alternative fuels. Possible mitigation measures required when using hydrogen carriers should also be researched, however this will depend on the scale of exposure and consequently the relative ship design. By addressing these areas, a robust framework for the safe and efficient adoption of alternative fuels in the maritime industry can be established, paving the way for a cleaner and more sustainable future for maritime transportation.

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