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## Solid Metal Fuels for Hydrogen Production for the Norwegian Heritage Fjords Maritime Sector

Bachelor's thesis in BIFOREN Supervisor: Prof. Steven Boles May 2023

echnology Bachelor's thesis

Norwegian University of Science and Technology Faculty of Engineering Department of Energy and Process Engineering



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FENT2900 - Bacheloroppgave Fornybar Energi

# Solid Metal Fuels for Hydrogen Production for the Norwegian Heritage Fjords Maritime Sector

Bachelor Thesis

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Norges teknisk-naturvitenskapelige universitet Institutt for energi- og prosessteknikk



og prosessteknikk

## **Bachelor** thesis

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## Preface

This is the bachelor thesis for the Bachelor in Renewable Energy under the Institute of Energy and Process Engineering at NTNU.

The supervisor of this thesis was Prof. Steven Boles. Thanks for the guidance and feedback during the thesis period.

Tanks to Albert Lau, CEO of EPRO Advanced Technologies for insight in the process of Si+.

## Summary

With a large amount of the maritime sector being responsible for 3% of global greenhouse gas emissions, environmentally friendly solutions for fueling must be looked upon. Using the electricity produced by fuel cells running on hydrogen gas is a solution for running ships and boats, with water vapor as the only substance emitted. Hydrogen gas can be produced, transported and stored in different ways which has their own pros and cons.

In the world heritage fjords in Norway there is a problem with pollution and zero emission maritime transport is required in the near future. To find the hydrogen production, transportation and storage method which is the most suitable for the maritime transport in these fjords, an analysis on emissions and costs must be done. The thesis will investigate if hydrogen production from solid metal fuels is feasible and can compete with current hydrogen production methods.

## List of Terms

Anode	The negative electrode in a fuel cell				
Austenitic stainless steel	Stainless steel containing added elements to improve certain characteristics				
Bar	Measurement of pressure				
Biochar	Remains after pyrolysis of biomass				
Boil-off	he loss of hydrogen in liquid hydrogen storage due to outside temperature				
Catalyst	Improves the speed of a chemical reaction				
Cathode	The positive electrode in a fuel cell				
Coal gasification	The production of syngas from mixing pulverized coal with steam or air				
Conversion enthalpy	he enthalpy required to convert a substance to another form				
Cryogenic	cience of the effects and production under low temperature $(<0)$				
Electrolyte	A specific ion transporting				
membrane	membrane				
Enthalpy	and the product of pressure and volume				
Exothermic	A process releasing energy				
Fossil fuels	Fuels made of decomposing plants and animals pressurized for millions of years				
Green cement	Type of cement that is carbon negative				
Hampson-Linde cycle	Liquefaction process for hydrogen				

	Organic compound				
Hydrocarbons	consisting of carbon				
	atoms and hydrogen atoms				
	Temperature interval				
Inversion	wheregas decreases				
temperature	in temperature when				
1	expanded				
T 11.	Process without a				
Isenthalpic	change isenthalpy				
Metal fume	Sickness caused				
fever	by inhaling $ZnO$				
	The actilibrium of				
N	I ne equilibrium of				
Normal nydrogen	para- and ortho-nydrogen				
	at RI				
onthe briter	Spins of both nuclei in				
ortno-nydrogen	the same direction				
nana hudnogon	Spins of the nuclei are				
para-nydrogen	in opposite direction				
	Magnetism created by				
paramagnetic	unpaired electrons in a				
	material				
	Substance helping with				
perlite	isolation in a COPV				
	Heating of organic material				
pyrolisis	without oxygen				
Shift-reactor	Component reducing				
	CO levels in a fuel cell				
a	Synthetic gas, mixture				
Syngas	of hydrogen- and				
	carbon-gas				
Thermolysis	Thermal decomposition				
	Trucks with cylindrical				
Tube-skids	storage vessels for				
	transporting compressed				
	hydrogen				
Water electrolysis	Production of $H_2$				
	by splitting water				
	hydrated aluminosilicates				
Zeolites	of the alkaline and				
	alkaline-earth metals				

## List of Abbreviations

atm	atmospheric pressure					
CAFS	Compressed Air Energy					
UALS	Storage					
CCS	Carbon Capture and					
005	Storage					
CEO	Chief Executive Officer					
CODV	Compressed Overwrapped					
001 V	Pressure Vessel					
$CO_2e$	CO2-equivalent					
EAT	EPRO Advance Technology					
GHG	Green House Gasses					
HE	Hydrogen Emrittlement					
kWh	kilo Watt hours					
kW	kilo Watt					
LCO	Li-ion Battery					
LH2	Liquid Hydrogen					
LNG	Liquid Natural Gas					
MW	Mega Watt					
MT	metric ton					
nbp	normal boiling point					
$Nm^3$	Normal cubic meter					
DEMEC	Proton Exchange Membrane					
	Fuel Cell					
PSFA	Perflourosulfonic Acid					
PV	Photovoltaics					
SMR	Steam Methane Reforming					
$tCO_2$	tons of $CO_2$					
TEU	Twenty-foot Equivalent Unit					
$tH_2$	tons of $H_2$					
TWh	Terra Watt hours					
UN	United Nations					
USD	United States Dollar					

## **Chemical Formulas**

43.0	
$AlO_4$	Aluminate
C	Carbon
CO	Carbon monoxide
$CO_2$	Carbon dioxide
$CH_4$	Methane
$e^-$	Electron
$H^+$	Hydrogen ion
$H_2$	Hydrogen
$H_2O$	Water
М	Metal
МО	Metal oxide
NaOH	Sodium hydroxide
$Na_2SiO_3$	Sodium silicate
$O_2$	Oxygen
Si	Silicon
Si+	Silicon +
$SiO_2$	Silicon oxide
$SiO_4$	Silicate
Zn	Zinc
ZnO	Zinc oxide

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## 1 Introduction

The world today uses more energy every year and as of 2021, the worlds total energy usage is 176 431 TWh [57]. The steep development in usage of energy shown in 1.1, will only lead to further global warning, unless a larger amount of the total energy produced comes from renewable energy sources. In 2021, around 12% of the world's total energy production came from renewable sources [57]. If the development of energy usage and sources remains with the trend shown in figure 1.1, it is hard to keep the earth a sustainable environment.



Figure 1.1: Global energy demand with sources [57]

Despite the Paris agreement actions to lower the goal of temperature only rising 1.5 °C within 2030, a report from UN Climate Changes from October 2020 shows that the earth temperature is increasing 2.5 °C in 2100 [10]. To stop the temperature from reaching 2.5 °C it is necessary to take action in the way energy is produced and used. There must be a shift in energy production from greenhouse gas emissive fossil fuels, to renewable energy sources. In order to make the transition from fossil fuels to renewable energy possible, there must be options for producing and storing energy in a renewable way. It is impossible to only choose one source of renewable energy as a solution to reducing global greenhouse emissions and temperature increasing. All the sources of renewable energy must work together to be able to produce enough energy to meet the world demand at the same time as shifting out fossil fuels.

One way to produce renewable energy is in the form of hydrogen. Hydrogen can be fed into a fuel cell, creating electricity. Hydrogen is one of the most abundant elements on earth, making it a renewable energy source. Another advantage is that the only emissions from energy production from hydrogen is water vapor. On the downside, hydrogen must be converted to its pure elemental form in order to be used in energy production, a form that is not available in nature. There are also challenges to storing hydrogen, but different types of technology are developed to make storing hydrogen more efficient. In this thesis, multiple methods of hydrogen storage are considered and discussed.

Hydrogen is a promising fuel when it comes to the maritime sector. The maritime sector stands for 90% of the global transport [17]. In 2018 1,056 million tons  $CO_2$  were emitted from marine transport, an increase in 9.3% since 2012 [21]. With marine transportation being the cause of 3% of global greenhouse gas (GHG) emissions distributed by 90,000 ships, the marine sector must change to more zero-emission ships [23].

In the case of the world heritage fjords in Norway, the Norwegian government have issued a requirement of zero emission of climate gasses from passenger ships as of 1st of January 2026[64]. To be able to achieve zero emission from passenger ships, new fuel technologies must be used to assure the protection of the climate in the fjords.

Mainly two technologies available for use in marine transportation: batteries and fuel cells. Batteries are heavy and have a power density so low that it is not suitable for long routes and large ships. Fuel cells on the other side can produce electricity on board the ship from stored hydrogen and is highly efficient.

This thesis will check if solid metal fuels used for hydrogen production is suited for a ship transporting 600 people through the world heritage fjords of Norway, compared to current production methods. In the case of this thesis fine silicon powder (Si+) and Zinc (Zn) as solid metal fuels and blue hydrogen stored in cryogenic tanks will be investigated.

## 1.1 Thesis goals

One goal of the project is to compare production, storage and transportation of silicon and zinc to the production, storage and transportation of hydrogen, to see which one is more beneficial for use in maritime transport in Norwegian world heritage fjords. The production of hydrogen from the reaction between water and silicon is similar to the reaction between water and zinc. These two technologies are also compared to see which technology is most suited for maritime transport.

## 1.2 Scenario

This thesis will carry out a scenario where different types of hydrogen technologies are used to fuel a cruise ship containing 640 people in the world heritage fjords of Norway. The scenario will contain how the hydrogen is produced, stored and transported to the consumer cite. Different production, storage and transportation methods will be carried out and compared to see which technology is most suited for maritime transport in the world heritage fjords of Norway in the given case. An environmental and economic analysis will also be included in the results.

## 1.3 Structure of the thesis

The first part of the thesis (chapter 2, 3, 4 and 5) consists of theoretical background for the rest of the thesis. Chapter 6 will include three scenario where the results are presented in chapter 7 and discussed in chapter 8 and followed by a conclusion in chapter 9. Chapter 10 discusses potential future work.

## 2 Hydrogen production

#### An overview

With hydrogen's strong electron affinity, hydrogen is always found combined with other elements, mainly in form of water and hydrocarbons. This means that in order to have pure hydrogen, work must be done to extract the hydrogen from different types of molecules. There are many ways of producing pure hydrogen.

Hydrogen can be produced from coal and natural gas where the hydrocarbons are reformed. 90% of hydrogen today is from using this method [8]. However, this method is mainly not for hydrogen to be used as energy storage or a fuel. It is used to streamline fossil fuels as it is the easiest way to obtain hydrogen. Being the easiest way to produce pure hydrogen, it is not environmentally friendly. A way to produce hydrogen from natural gas is shown in equation 2.1 where methane and water vapor are mixed to produce hydrogen gas. The by-product in this reaction is carbon dioxide  $(CO_2)$ , making this process a highly greenhouse gas distributor. Reforming coal has the same two products as reforming natural gas:  $H_2$  and  $CO_2$ .

$$CH_{4,(g)} + 2H_2O_{(g)} \to 4H_{2,(g)} + CO_{2,(g)}$$
(2.1)

To avoid carbon dioxide as a bi product, hydrogen can be produced by splitting water. One way is water electrolysis where electricity is used to split the water molecule as shown in equation 2.2 in an overall reaction. The products of this reaction are hydrogen gas and oxygen, making it an environmentally friendly process. The water electrolysis is a process that requires a lot of electricity, making it not as economically friendly as reforming hydrocarbons for hydrogen production. Different types of hydrogen are described later in the thesis.

$$H_2 O \to H_2 + \frac{1}{2} O_2 \tag{2.2}$$

In this thesis, a solid metal fuel is used to split water. Metal fuels have high energy density and can be used as fuels in the case of producing heat when burning, or in the case of reacting with water, hydrogen gas is also produced[46]. This is a reaction that happens spontaneously when water comes in touch with the metal, shown in a general form in equation 2.3. It is a process that doesn't require large amounts of energy to make the reaction happen, although multiple steps at detailed level requires energy, such separation of the products and turning the metals used to its pure form before the reaction can happen. Si+ and Zn is used as solid metal fuels in this thesis.

$$M + H_2 O \to H_2 + MO \tag{2.3}$$

#### 2.1 Different colors of hydrogen

#### 2.1.1 Brown hydrogen

Brown hydrogen is made from brown coal, also called lignite, which is the lowest rank of coal considering calorific value, ease of handle and storage stability[44]. The hydrogen is produced when brown coal goes through a process called coal gasification. The first step of the process is to mix pulverized coal and steam or air and heat it very hot to make syngas consisting

mostly of CO,  $CO_2$  and hydrogen. The syngas is cooled and cleaned to remove other gases and impurities. It is then sent to a shift rector where the CO is mixed with steam to make more  $CO_2$ and hydrogen. The hydrogen and  $CO_2$  is then separated, the hydrogen is cleaned and ready for use and the  $CO_2$  is dumped with no carbon capture[1].

Production of brown hydrogen produces 19  $tCO_2/tH_2$  into the atmosphere[66], making it the worst way of producing hydrogen emissions wise. Regarding this, it is still widely uses today because of its abundance and affordability, at a price as low as 90¢ up to 1.50\$ per kg[31].

## 2.1.2 Grey hydrogen

When hydrogen is produced from fossil fuels such as coal or natural gas, and the  $CO_2$  produced is not captured and stored, it is called grey hydrogen. To produce grey hydrogen there are two main methods, steam methane reforming (SMR) and coal gasification. In SMR methane reacts with water steam under high pressure and temperature with the presence of a catalyst, to make CO and  $H_2$ . The CO then goes through a water-gas shift reaction where it reacts with steam at high temperature and pressure, to make  $CO_2$  and more  $H_2$ [70].

These processes produce a lot of  $CO_2$ , and this  $CO_2$  is sent straight into the atmosphere. Hydrogen produced from natural gas release 10  $tCO_2/tH_2$ , which is still a large amount but almost half of what hydrogen from coal releases[66]. About 74% of all hydrogen produced in 2021 was grey hydrogen [37]. The price of gray hydrogen in 2022 was 2.00\$/kg[28], which makes it one of the cheaper options, but worse environmentally.

## 2.1.3 Blue hydrogen

When hydrogen is produced from methane reforming in combination with carbon capture and storage (CCS) it is called blue hydrogen[36]. The  $CO_2$  produced during the SMR is usually released into the atmosphere, but it can be captured and sent to storage sites that can be onor off-shore. It is possible to collect up to 90% of the  $CO_2$  produced, resulting in the carbon emission being reduced to  $3.2 \ kgCO_2 e$  per kg  $H_2$ [71]. This drastically reduces the emissions and environmental impacts of the hydrogen production[67].

Since most of the hydrogen produced today comes from brown and grey hydrogen, and we are going into a future where lowering emissions are important, blue hydrogen is a serious candidate for the solution. The cost of including CCS in an existing production chain is minor, where the price increases to around 3.00\$ per kg of  $H_2[25]$ . Since today's market is a decarbonized economy, blue hydrogen is the most viable and economical option in the near future.

## 2.1.4 Green hydrogen

Green hydrogen is hydrogen produced from renewable resources. The most common form of production is water electrolysis where a low to non-carbon emission energy source is used. The electricity and heat required usually comes from renewable sources such as solar, hydro and wind. Water electrolysis is when two electrodes are immersed in water and a direct current is passed through them. This splits the water molecules and hydrogen is generated at the cathode and oxygen is generated at the anode. The hydrogen gas is then extracted and can be used as fuel[3].

Only 0,1% of the hydrogen produced in the world comes from green hydrogen. It is projected that the production of green hydrogen will increase to 530 million tons by 2050. Since green

hydrogen is still quite expensive, at around 5.00-7.00\$/kg, the price needs to be reduced to be able to make the transition to green hydrogen affordable[3].

## 2.2 Challenges and opportunities

Hydrogen, unlike other fossil fuels, needs to be converted to its pure form from other types of substances like water or hydrocarbons. This is a energy demanding process, in other words it is a process resulting in expenses. Fossil fuels mainly have expenses for extracting the fuel, and then it is ready for the marked. For a fuel to be used in industry or in the daily lives of people, it must be cost efficient. To be competitive with other fuels, hydrogen's costs must be close in costs to other fossil fuels. This will require further research and innovate solutions. An important environmental aspect to consider is that hydrogen can be produced in a way that results in no  $CO_2$  emissions by splitting water using water electrolysis. It is a good solution to reduce the emission of GHG, but is an expensive process.

## 3 Hydrogen storage

Hydrogen is one of the most abundant elements in the universe, making it a renewable energy source. Combustion of hydrogen gas in a fuel cell results in only water vapor as a product. In this chapter of the thesis, the properties of hydrogen and methods for storing hydrogen is presented. The methods of hydrogen storage that will be looked upon is compressed- and liquefied-hydrogen. Transportation methods for hydrogen will also be presented.

Naturally hydrogen mostly comes in the form of water or hydrocarbons. The form of hydrogen used for energy storage or as a renewable fuel hydrogen in form of pure hydrogen gas, the  $H_2$  molecule. So, in order to use hydrogen for storage or fuels purposes, water or hydrocarbons need work applied to extract pure hydrogen gas. It means it is necessary to pay for the energy needed to make pure hydrogen gas compared to other existing fuels being free of charge since they already exist in the form used for fuel. Despite having expenses with production of pure hydrogen, hydrogen have good qualities and is very abundant, making it a renewable energy source. It is also environmentally friendly as water vapor is the only emission when used in a fuel cell.

In order to store energy, a high specific energy and volumetric energy density is preferable in an energy carrier. Hydrogen has a large specific energy making it suited for an energy carrier. As seen in table 3.1 the specific energy is higher than of other presented energy storage methods. The volumetric density is on the lower side, but unlike specific energy, different technologies for storing hydrogen can be applied to increase the volumetric energy density as seen in the case of compressed and liquefied hydrogen shown in figure 3.1.[80][8]

Technology	e/kWh kg-1	$\hat{e}$ /MWh m-3
Li-ion Battery (LCO)	0.19	0.56
Compressed Air Energy Storage (CAES)	0.14	0.012
Hydroelectric, pumped, 400 meter	0.0011	0.0011
Hydrogen, 1 bar	33	0.0027
Hydrogen, 700 bar	33	1.6
Hydrogen, liquid	33	2
Liquid natural gas (LNG)	15	6.1
Gasoline	13	9
Diesel	13	10
Jet-A fuel	13	10

Table 3.1: Specific- and volumetric energy for different types of energy carriers [8]



Figure 3.1: Specific and volumetric densities from table 3.1 [8]

#### 3.1 Compressed hydrogen

Hydrogen's volumetric density at 1 bar is quite low compared to other forms of energy storage media seen in table 3.1. To increase the density of hydrogen, the hydrogen gas can be compressed and stored in compressed hydrogen storage vessels with a pressure of around 700 bar depending on the type of storage vessel. Unfortunately, compressing hydrogen gas causes a decrease in the specific energy density [80]. This is because the thickness of the walls needs to become larger, the higher the pressure is inside the storage vessel.

The compressed hydrogen stored under pressures from 700-1 000 bar are stored in compressed overwrapped pressure vessels (COPV) [6] which reduces the damages caused by hydrogen embrittlement (HE) and can manage high pressures. Other types of pressure vessels are shown in figure 3.2. To maintain the compressed hydrogen at high pressures is a very energy demanding process and can be a possible danger in populated areas in case of an accident.



Figure 3.2: The four types of compressed hydrogen storage vessel [6]

The compression can be done with multiple steps of mechanical piston compressions. The reason for the series of compression and not one compression is that it the compression becomes almost isothermal and therefore more energy efficient. Due to the diffusivity of hydrogen, some changes may be done to the seals of the compression device. [80] [8]

#### 3.2 Liquid hydrogen

Hydrogen can be liquefied to be easier to transport and store when it comes to larger amounts of hydrogen. Liquid hydrogen has an increased volumetric energy compared to other forms of hydrogen, such as compressed hydrogen, (as shown in figure 3.1) which is an important factor when it comes to transporting energy. For the hydrogen to condensate, it needs to be cooled down to a temperature between 21.2 and 33 K which are the triple point and the critical point respectively as shown in figure 3.3. The liquid hydrogen is stored in cryogenic tanks with a temperature of 21.2 K at ambient temperature. [8] The hydrogen storage system must be an open system to prevent extreme pressure inside the cryogenic storage container because of the low critical temperature of 33 K. There are no liquid phase over this temperature. The expansion ratio for liquid hydrogen to hydrogen gas is 848 to 1. [80][41]



Figure 3.3: Phase diagram hydrogen [80]

Before hydrogen gas can be turned into liquid hydrogen, all hydrogen must be in para-form. The hydrogen molecule consists of two protons and two electrons. There are two forms of molecular hydrogen: para-hydrogen and ortho-hydrogen. The difference between the two has different spin orientation. Para-hydrogen has a spin of I=0 and ortho-hydrogen has a spin of I=1. This difference causes different physical properties, but the chemical properties remain the same. At room temperature and above the hydrogen is called normal hydrogen. The term normal hydrogen is defined as the equilibrium composition of 25% para-hydrogen and 75% ortho-hydrogen. When cooling hydrogen towards its normal boiling point (nbp) at 21.2 K the hydrogen converts from ortho-form to para-form. At the normal boiling point, just 0.2% of the hydrogen

is in ortho-form. The reaction that converts ortho-hydrogen to para-hydrogen is exothermic, meaning the reaction releases energy. The goal of the liquefaction process of hydrogen is to lower the temperature to 21.2 K and therefore the excess heat needs to be transported away from the system to prevent heating. The heat released in the conversion reaction is temperature dependent, where the conversion heat increases as the temperature of the hydrogen decreases. After reaching 77 K the conversion enthalpy becomes almost constant at 523 kJ/kg compared to the 270 kJ/kg at 300 K [80]. If all the hydrogen is not converted to para-form when placed in the cryogenic storage vessel, liquid hydrogen will be forced to evaporate. The reason is that the heat of evaporation is 451.9 kJ/kg, which is lower than the conversion enthalpy, causing the released conversion enthalpy to give enough energy for evaporation. [8] [50]

This evaporation is called boil-off. Boil-off is the heat leaks from the cryogenic storage tank to the outside environment and is due to its geometry and insulation. Transforming ortho-hydrogen to para-hydrogen is one factor that causes boil-off. If a catalyst is used, the conversion from para- to ortho-hydrogen would cause less boil-off. [75][50]

Even though the conversion from ortho-hydrogen to para-hydrogen happens spontaneously, a catalyst is often used to speed up the process. Materials that are highly surface-active and paramagnetic. For example, charcoal can absorb hydrogen before being cooled with liquid hydrogen before being desorbed in the liquid hydrogen mixture. [80]

Geometrically, the shape that causes the least boil off is a sphere. In a sphere, the force is evenly distributed on the walls as well as having the smallest surface to volume ratio which are proportional with the heat leakage losses. The problem is that the manufacturing cost is much higher than the cost of a cylindrical storage tank. Normally cylindrical vessels are used as they are cheaper and more convenient for truck transportation due to diameter restrictions on the road. The cylindrical vessel has around the same boil-off when increasing the vessel, while maintaining the diameter. [80][50]

The cryogenic storage vessel consists of three parts. The first part is the inner pressure vessel where the liquid hydrogen is stored. Often, austenitic stainless steel is used as a material in the inner pressure vessel. Since the liquid hydrogen is at a temperature of 21.2 K there must be a high level of insulation. For this, a wrapping with aluminum films in multiple layers or perlite is placed outside the inner pressure vessel. Around this insulation layer there is a protective jacket. The cryogenic storage vessel is shown in figure 3.4 [6]



Figure 3.4: Cryogenic storage vessel [6]

#### Liquefaction process

A process used to create liquid hydrogen is the Hampson-Linde cycle. An overview is shown in figure 3.5. It is a process where it is possible to liquefy gasses with a very low boiling point, like gasses found in the atmosphere. Firstly, the hydrogen gas gains external energy by being compressed, allowing it to flow in the upcoming cycle. The compressed gas is then introduced to cold surroundings before being cooled further via a heat exchanger where the coolant runs in the opposite direction of the compressed hydrogen gas. Because hydrogen warms up under expansion at temperatures over 202 K, the hydrogen gas needs to be cooled below this temperature before it undergoes expansion in the next step. This is because of the inversion temperature of hydrogen is 202 K [80]. The inversion temperature, also known as the Joule-Thompson effect, describes at which temperature the gas shifts from increasing temperature to decreasing temperature while undergoing expansion. By cooling hydrogen using liquid nitrogen at 78 K before starting the Hampson-Linde cycle, hydrogen is at a temperature lower than 202 K before entering the expansion valve in the next step. Here the compressed and cooled hydrogen gas undergoes an isenthalpic Joules-Thompson expansion and since it has a temperature lower than the inversion temperature at 202 K, the hydrogen gas is cooled further. A little amount of the cold expanded hydrogen gas is liquefied and the goal of creating liquid hydrogen is complete. The remaining amount of hydrogen that remains in gas form flows back to the heat exchanger on the opposite direction of before it is mixed with the hydrogen gas in the first step and repeats the cycle. [15][80][40]



Figure 3.5: Overview of Hampson-Linde cycle [72]

There is 40% loss in liquid hydrogen storage compared to 10% in compressed hydrogen. [6]

## 3.3 Transportation of hydrogen

When to hydrogen is produced, it needs to be transported to its end-use destination. In the market today, there are three main modes of transport; Ships, trucks and pipelines. Ships and trucks are the most established and used throughout the world today. A well designed and executed distribution system is important to make hydrogen a viable and affordable source of energy in the future[32]. The hydrogen market is growing in Europe and new technology is being developed to create a well functioning hydrogen supply chain in the future.

## 3.3.1 Cryogenic hydrogen trucks

The easiest way to transport hydrogen today is by road. To deliver liquid hydrogen, specially designed trucks with cryogenic tanks on the back are required. These tanks are usually double-walled, vacuum-insulated and made of stainless steel to minimize the boil-off during transport[4]. Usually, the trucks have a capacity of 3-4 tons of liquid hydrogen at a temperature of -253 °C, which is about ten times as much as equivalent compressed hydrogen trailers can carry each load[13]. The upside of this sort of transportation the affordability for medium to long distances and it has a lower carbon footprint compared to other options[16].

The downside is the high energy demand of the liquefaction of hydrogen. 15.2 kWh/kg is required to cool the gas down to -253 °C[80]. The tanker trucks have a potential boil-off about 0.5% per day, and during unloading at the delivery sight the boil-off is about 5%. If it is deemed affordable there are systems that can be installed at delivery sights that compresses and

recovers this boil-off when unloading[33]. Since some of the liquid hydrogen needs to remain in the distribution equipment to keep the liquid cold during unloading,  $\leq 90\%$  of the tanks volume is usable[16]. Linde-engineering uses these types of trucks to supply the worlds first hydrogen ferry, Hydra[47][63]. These trucks are 13.7 meters long and have a capacity of 4 000 kg[16].



Figure 3.6: A cryogenic hydrogen truck from Linde [69]

## 3.3.2 Cryogenic hydrogen carrier ships

Hydrogen can also be transported with hydrogen tankers by sea. These tankers where previously equipped with tube skids, or they could use a high-efficiency liquid storage container that are like the tanks used for road transportation. Newer technology has created specially designed ships that can carry large amounts of cryogenic hydrogen. These vessels bridges the gap between to consumer and producer of the hydrogen by being able to transport large amounts of energy dense hydrogen over vast distances [33].

The first of these liquid hydrogen carriers is called Suiso Frontier, and was built and finished by Kawasaki Heavy Industries in 2020. The ship is 116 meters long and weighs 8 000 tons. It has a capacity of about 88 tons of liquid hydrogen at a temperature of  $-253^{\circ}$ C. The tanks have a double-shell structure with overlapping inner and outer shell layers. There is a vacuum insulation between these layers, and they are supported by high strength glass-fiber-reinforced plastic. Technologies from the JAXA Tanegashima Space Center has been used to create ultrahigh thermal insulation performance, to prevent heat transfer from external sources[68]. It made its maiden voyage from Japan to Australia on 24 December 2021, and returned with its first load of hydrogen made from brown coal from Australia on 25 February 2022[35]. This carrier is power by a diesel-electric system, but Kawasaki has obtained approval of an even larger tanker which can carry up to 160 000  $m^3$  of liquid hydrogen. This vessel will be able to run on hydrogen and even boil-off gasses as fuel, which will greatly reduce  $CO_2$  emissions during transit[51].



Figure 3.7: Suiso Frontier, cryogenic hydrogen carrier ship[68]

C-Job Naval are planning on expanding this market to Europe. They have designed and are planning to build a liquid hydrogen tanker, called LH2 Europe, with a total capacity of 37 500  $m^3$ . It will carry green hydrogen from Scotland to Germany and they are hoping to have it operational by the end of 2027[52].

#### 3.3.3 Other modes of transportation

There are other modes of for transporting hydrogen that are used in the world today. One of these is are compressed hydrogen through pipelines. These pipelines can either be built on- or offshore where they can stretch for hundreds of kilometers. Existing natural gas pipelines can be used or modified to be able to transport gaseous hydrogen in them[56]. There is a plan to build a large pipeline network in Europe with a total of 840 projects from all parts of the value chain. Many of these projects are planing on being ready to use in the end of 2025[54]. There is also a large offshore hydrogen pipeline that will be built between Norway and Germany that is planned to be operational 2030[48].

Hydrogen can also be stored and transported in a pressurized form in pressure vessels. Pressurizing hydrogen results in higher volumetric density which are optimal for a energy storage technology. On the other side, the hydrogen loses some of its specific energy[80]. The compression is done by step wise isothermal compression until the  $H_2$  is reaches around 700 bar[8]. The compressed hydrogen at high pressures is stored in compressed overwrapped pressure vessels (COPV) [6] which reduced the damages caused by hydrogen embrittlement (HE). To maintain the compressed hydrogen at high temperatures is a very energy demanding process.

#### 3.4 Safety issues

Storing hydrogen and using it as a fuel comes with its safety risk. Hydrogen gas or liquid is ignitable and if not handled properly it can lead to serious damage to its surroundings. Hydrogen gas is a very small molecule making it easier to leak from its storage vessel compared to other fuels, but choosing materials as strong and high-quality steels can stop safety problems regarding HE. Hydrogen gas has faster leak time and sonic velocity than of natural gas or gasoline, but the energy density per unit is lower resulting in hydrogen being safer overall as of energy leaked for a given period of time. Leakage of hydrogen is not toxic to its surroundings since the result of combustion is water vapor. The small size of the hydrogen molecule makes it diffuse very easily, and with a high buoyancy, the spilled hydrogen gas is quickly diluted. In a large open space, the dilution is larger the farther away from the source, making the flammability of hydrogen local of the leak source. A fan can easily disperse the hydrogen gas as a safety measure. [41] [50]

Leakage becomes a big problem when the gas ignites and damages or ignites surrounding objects or people. The most important factor in hydrogen ignition is the lower flammability limit, and for hydrogen its lower than gasoline with a factor of 4, but a small amount higher than natural gas. The energy required for ignition however is very low at 0.02 mJ, but for the hydrogen to detonate in an open space a several factors reduces the likelihood for it to happen substantially. Some factors are the geometry of the surrounding environment in which the gas exists, the temperature and air to gas ratio. For a detonation to happen in a closed environment, the hydrogen gas concentration must be around 13% (the lower detonation fuel ratio being 13-18%) before the time of ignition. Hydrogen gas has the lowest explosive energy per unit compared to other fuels. The hydrogen flame's emissivity is low, meaning surrounding objects or people are hard to catch on fire or be damaged. In conclusion, hydrogen causes the least amount of damage if an explosion or ignition was to happen. The flame itself is almost invisible at normal daylight, making it hard to detect without adding chemicals that gives the flame color.[41] [50]

Liquid hydrogen leaks can cause cold burns and failure of pressure release valve in the cryogenic storing vessel could cause an explosion. Spills of cryogenic hydrogen fortunately has a very high evaporation rate because of its low nbp and will therefore dissipate faster.[41] [50]

#### 3.5 Challenges and opportunities

Hydrogen is not a easy element to store over a longer period of time. Hydrogen storage requires a large amount of energy to be stored in a way that makes it effective to transport. Normal hydrogen gas needs to be processed to have higher volumetric energy, like compress or liquefy it, so more quantities can be transported at a time. Hydrogen compression requires 2.21 kWh/kg theoretical work to isothermally compress hydrogen gas from atmospheric pressure (1 bar) to 800 bar. However, the process is not fully isothermal, and the actual required work is higher. Liquid hydrogen needs 15.2 kWh/kg of technical work to be converted to liquid. The large energy requirement to store the hydrogen is unlike other forms of fuels that can be easily stored in almost the same condition as it is when it is combusted. [80]

When storing hydrogen at high pressures some challenges appear. When the metal parts of the storage tanks come in contact with hydrogen a phenomenon called hydrogen embrittlement (HE) occurs. Hydrogen gets absorbed into metals because it is a small atom, causing the metals ductility to decrease. This is a problem regarding cracks in the metal. COPV can get its metal liners damaged, especially at higher pressures.[6]

To maintain the hydrogen in a storage effective form is also a energy requiring process. Compressed hydrogen needs to be kept at high pressures in the compressed hydrogen vessel, needing a constant flow of energy maintain the high pressure. Hydrogen stored at high pressures increases volumetric energy density, but also increases the amount of energy needed for pressurizing and the energy needed to keep it at the chosen pressure. Liquid hydrogen requires a lot of energy to maintain the cold temperature in the cryogenic storage vessel. In addition to maintaining the cold temperature, the nbp of 21.2 K at room temperature causes boil-off. The boil-off can result in 0.4% loss per day in a 50  $m^2$  cylindrical storage vessel [80], and around 5% when unloading the liquid hydrogen. Diesel, natural gas and other fossil fuels do not have this loss or the large requirement of constant energy usage when it comes to storage. [33]

Despite the large energy demand for pressurizing, liquefying and storing, hydrogen has a high

specific energy compared to other types of energy storage methods. Hydrogen has a specific energy of 33 kWh/kg, twice the amount of the fossil fuels listed in table 3.1. A high specific energy is crucial for energy storage, and with hydrogen being the most infinite element on earth, hydrogen can be applied in many scenarios if the storage efficiency is improved in the future.

## 4 Hydrogen as a fuel

#### 4.1 PEM fuel cells

A PEM fuel cell stands for Proton Exchange Membrane fuel cell, and it uses the reaction between pure hydrogen and oxygen to generate electricity. The PEMFC consists of two electrodes (anode and cathode) with an electrolyte membrane in the middle. These are combined in a fuel cell stack, as seen in figure 4.1, where the greater number of PEMFCs in a stack the greater the electric output[55].



Figure 4.1: Fuel cell stack[55]

In the PEMFC itself the anode and cathode is usually made out of platinum catalyst that is supported by porous carbon, and the electrolyte membrane is made out of perfluorosulfonic acid (PSFA). The electric generation consists of two reactions. Hydrogen gas  $(H_2)$  passes through the anode and the catalyst splits the gas into protons and electrons  $(H^+ \text{ and } e^-)$ , equation 4.1. The membrane only allows the hydrogen ions to pass through it, and the electrons must go around the membrane thus generating an electrical current, figure 4.2. Oxygen gas passes through the cathode and the oxygen, protons and electrons are combined to create water  $(H_2O)$ and excess heat [53][43], equation 4.2.

$$H_2 \to 2H^+ + 2e^-$$
 (4.1)

$$2H^+ + 2e^- + \frac{1}{2}O_2 \to H_2O \tag{4.2}$$



Figure 4.2: PEMFC[43]

## 4.2 Maritime use in Norway

Norwegian Havyard Group ASA are one of the companies that are operating with cruise ships in the Norwegian fjords. Their ships run on a combination of natural gas and batteries. When the heard that ships running on hydrocarbons would be banned from entering Norwegian heritage fjords in 2026, they wanted to prepare and make a solution for this scenario early. They are planning to modify the existing ships and implement LH2 tanks (liquid hydrogen) and fuel cells[27].

They signed a contract with PowerCell Sweden AB in 2019, to develop a 3,2 MW fuel cell system for maritime use. PowerCell Sweden managed to make the Marine System 200. It is the most compact and efficient PEMFC for maritime use on the market. It produces 200kW and when connected in parallel it can produce 3,2 MW or even 6MW[45]. This will be the largest fuel cell fitted on ship this large[27].

The 3.2 MW fuel cell system will be installed with a combination battery packs and storage tanks, where the size of the storage tank is 3.5 tons of LH2, see figure 4.3[22]. This will allow the ship to navigate Norwegian heritage fjords for up to 20 hours emission free[2]. The ship will sail from Bergen to Kirkenes and visit fjords along the way. They are hoping to get the ship retrofitted by the end of 2023 and getting it tested and approved for future use[27].



Figure 4.3: The technical layout of Havila Kystrutens ship [22]

## 4.3 Challenges and opportunities

A challenge of hydrogen as a fuel is the lack of infrastructure for hydrogen driven vehicles. The lack of fueling stations results in low sale of hydrogen vehicles and the low amount of hydrogen vehicles stops the investment in hydrogen fueling stations. This is a problem when the driving route varies for each individual vehicle. If the route of driving is set, a fueling station can be placed in a suitable spot. For marine transport for a set route, it is possible to build a fueling station with the right dimensions for the fuel usage. The hydrogen fueled to the vehicle is therefore no longer a big problem. However, distributing the hydrogen to the fueling station is a challenge. The transportation of hydrogen is as mentioned earlier, an energy demanding process with daily losses. If a hydrogen production facility is not nearby, hydrogen must be transported over large distances. A future solution can be pipelines of hydrogen from the production cite to the consumer cite.

The safety issue of hydrogen as a fuel is also a challenge. Hydrogen, being a highly flammable element can cause damage to personnel and components. Hydrogen does have a smaller emissivity compared to fossil fuels, but lacks smell and color making it a potential safety risk. The hydrogen flammability itself may not be a large safety concern, but it can heat up nearby components in a vehicle causing explosion.

## 5 Solid metals fuels in the hydrogen market

#### 5.1 Hydrogen from silicon

Silicon is the second most abundant element on earth, most often found in sand, making it almost impossible to use up the resource [60]. It has been known that bulk silicon can react with water to make hydrogen, but this reaction is very slow and inefficient compared to other solutions, like zinc or aluminum. Oxides would form on the surface of the bulk silicon and thus halting the reaction. Wanting to find a more efficient method of producing hydrogen without the risks of transporting the hydrogen itself, Paras N. Prasad and Mark T. Swihart from university at Buffalo started testing the idea of using silicon nanoparticles to produce the hydrogen gas more efficiently. Since the nanoparticles has such a high surface-area-to-volume ratio they thought it would speed up the reaction. They tested particles of the sizes 10 nm, 100 nm and 40  $\mu$ m and found that the 10 nm particle produced 1 mmol of hydrogen in five seconds, which is about six times quicker than the zinc and aluminum nanoparticles. They also tested the particles in a hydrogen fuel cell to check if the reaction produced any harm full products. The fuel cell ran for four minutes with no harm full bi products and no faults in the cell. However this was still deemed as not a good way of producing hydrogen in 2013 because the silicon nanoparticles were produced from silane gas, which when produced releases carbon dioxide and requires a lot of energy[34].

This is where EPRO Advance Technology (EAT) made the big leap in 2016, when they patented their own silicon called Si+. This silicon has an average pore size of 1-3 nm which makes the reaction speed very fast. This silicon can be produced in three different ways: Quartz + Met coke, Quartz + biochar or from recycled/scrap silicon[59].

The quartz + met coke combination makes their standard Si+. As seen in equation 5.1 they combine quartz  $(SiO_2)$  and metallurgical coal (C) in an electrical furnace at 1500-1750 °C to make silicon, and a byproduct in this process is carbon monoxide(CO)[62]. Since the metallurgical coal is mined in coal mines where  $CO_2$  is released and the process itself releases CO, it is carbon positive and worse than the other methods of producing Si+, regarding the environment. In the second process they use biochar, which is waste biomass that is converted into a solid material using pyrolysis. By using this method, the biomass will not burn or decay, and the  $CO_2$  is locked inside the solid material preventing it from being released. By using biochar instead of met coke they can make the process carbon neutral, since the carbon that was trapped when the biochar was made, is the released when the silicon is made. The power needed for these processes comes from renewable sources in the area. The third process is the best since they can use scrap or recycled silicon. They can crush used or broken solar panels and then extract the silicon that were in the cells of the panels. Some of the panels they use even come from Norway. They are also working on a new extraction method where they remove the entire silicon wafer itself from the solar panels without crushing them. This saves the a lot of effort and time, since they don't have to search and remove silicon fragments from a pile of other material [59].

$$SiO_2 + 2C \to Si + 2CO \tag{5.1}$$

To make hydrogen, silicon powder and water is only needed, as seen in equation 5.2. However, this reaction is fairly slow, therefore EAT came up with the idea to mix in NaOH with the water. This will not only make the reaction faster, but allow  $Na_2SiO_3$  to be created as a by product, equation 5.3. This by product can be used to make green cement and zeolites, which can be used in the commercial market[59].

$$Si + 2H_2O \to SiO_2 + 2H_2 \tag{5.2}$$

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$
 (5.3)

This process can happen on various scales, and figure 5.1 shows how the process can potentially work for a hydrogen powered vehicle. This model can generate up to 60 kg of hydrogen per day on-demand. Hydrogen is created in a hydrogen reactor at a pressure of 1-3 bar, and extracted to a compressor which compresses it to 450 bar. The compressed hydrogen is then moved to a buffering tank where it awaits to be pumped. When needed the hydrogen is pumped at a pressure of 350 bar into the vehicle[59].



Figure 5.1: Hydrogen generation to consumption

#### 5.1.1 Transportation of Si+

Si+ is the future of hydrogen storage. The hydrogen is not stored in the silicon, but it is stored in the water. This means that instead of shipping compressed liquid hydrogen in tanks on tanker ships that are designed for hydrogen, the silicon powder is shipped on container ships to where it is needed and then create on-demand hydrogen at that location. A normal liquid hydrogen tanker ship can transport 88.5 tons of hydrogen in one trip. A standard 20-foot shipping container can carry up to 20 tons of Si+ powder which equals 2.7 tons of hydrogen. this means that 33 containers can contain the same amount as the maximum load of a liquid hydrogen tanker ship. On average a standard container ship can carry up to 10 000 of these 20-foot containers, which makes the shipping of Si+ undeniably more efficient that shipping hydrogen in compressed liquid form, since 305 cryogenic tanker ships carry the same amount as one cargo ship. This comparison is visualized in figure 5.2[59]. Si+ also has an indefinite shelf life making the storing of the powder easy and energy efficient at the generation sight[59], compared to cryogenic liquid hydrogen which requires a lot of energy to be stored in liquid form



and some gets lost due to boil-off each day when stored.

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Figure 5.2: Comparison between Si+ and LH2 carrier ships with transportation of 27 000 tons of hydrogen

This will not only make the hydrogen a lot cheaper, but it is also safer notably safer to transport compared to compressed liquid hydrogen. The liquid hydrogen must be kept at low temperatures and high pressure. Any of the measures of keeping the hydrogen in this state can fail during the voyage, and since hydrogen as a very high combustibility the consequences can be fatal. There are a lot of safety measures put to use to prevent this, but compared to Si+ which is vacuum packed in a durable plastic bag, it is considerably more dangerous.

There were concerns that the silicon powder would react with condensation in the air, and then release hydrogen gas. This reaction will happen, but since there is no NaOH the reaction will not sustain. A passive oxide layer will be formed on the surface of the powder which will protect the rest of the powder in the bag from further reaction. Since the condition of the reaction is not optimal the hydrogen production will be very slow. In some instances the bag will be filled with nitrogen before the vacuum seal to prevent condensation[30].

Si+ is also safer than storing the hydrogen at the pump stations since the hydrogen from Si+ can be made on-demand and be stored for a short while in a buffering tank, instead of the hydrogen being stored at the station for a long time if it is liquid the entire journey. For instance, a hydrogen pump station exploded in Sandvika, Norway in 2019[18], which resulted in a lot of pumping stations closing in Norway and the scepticism increased within the population of the conversion to hydrogen. Si+ is the safer alternative and can bring a new renaissance within the hydrogen industry.

## 5.1.2 By-products

The bi-products from the hydrogen generation when using Si+ is sodium metasilicate  $(Na_2SiO_3)$ , as seen in equation 5.3. This substance can directly be used in the production of green cement and zeolites. Green cement is cement that is using carbon-negative processes of manufacturing. Green cement can reduce the  $CO_2$ -emissions during manufacturing by 80-90% compared to conventional cement[38]. To make green cement you need aluminosilicates such as metakaolin or fly ash, a user friendly alkaline reagent such as  $Na_2SiO_3$ , and water[29].

Zeolites are microporous crystalline aluminosilicates, and are usually composed of  $SiO_4$  or

 $AlO_4[5]$ . Zeolites have many purposes such as a drying agent in detergents and water and air purifiers. It is also sold and marketed as a supplement that can treat some cancer types, diarrhea, autism, herpes, hangovers, balance pH and remove heavy metals from the body. Currently there are no clinical trials that support these claims[73]. Zeolites are also commonly used as a catalysts in the petroleum industry, such as fluid catalytic cracking and hydrocracking[74]. Zeolites can even be used to clean up radioactive spillage and materials. After the tsunami hit the nuclear power plant in Fukushima, they dumped sandbags with zeolites into the sea to absorb radioactive cesium[42].

The reaction between the silicon powder and the water-nitrogen hydroxide mixture is exothermic, meaning heat is released when the reaction occurs. Per kg of  $H_2$  created, around 24 kWh of low grade heat is released. This heat can reach temperatures up to 70 °C, and can be used for anything from space heating, water heating and other purposes around the hydrogen generation station. In some cases this heat can even be transformed into electricity via thermo-electrics[30].

#### 5.2 Hydrogen from zinc

Another metal used to produce hydrogen with the splitting of water, is zinc. Zinc is fairly reactive and will combine with oxygen. For zinc to be able to produce hydrogen when mixed with hydrogen, it must be in its pure form. Zinc oxide can be reduced to zinc and oxygen under high temperatures in a heating chamber. A thermochemical cycle can be used to produce of hydrogen with the reoxidation of zinc. [7]

The first stage in this process is called the pyrometallurgy of zinc. The goal is to separate the oxygen atom from ZnO, resulting in pure zinc. Solid ZnO and carbon (for example coke) is heated to a temperature of around 1500 K using a solar reactor as the source of the heat. A surplus of carbon is also added to provide energy to the process. At this temperature ZnO is reduced to Zn, transferring the oxygen atom to the carbon, creating carbon monoxide, shown in equation 5.4. This is the solar carboreduction of zinc oxide. [7]

$$ZnO(s) + C(s) \to Zn(g) + CO(g)$$
(5.4)

The pure zinc is in gas form as the volatilization of zinc is finished at 1223 K [24]. The gas mixture of zinc and carbon monoxide created by the carboreduction is then cooled to a temperature of 1180 K and the zinc condensates and is separated from the carbon monoxide. Next, the pure liquid zinc is cooled even more to 700 K and reacts with water vapor, creating hydrogen gas and zinc oxide according to equation 5.5. The zinc oxide is now in solid form and the created hydrogen gas is sent off to be stored. The zinc oxide is transported back to the solar reactor and recycled, starting the process from step one. The carbon monoxide is oxidated with oxygen, creating carbon dioxide in equation 6.4, where some of it can be turned back to carbon and the rest becomes emissions.[7]

$$H_2O + Zn(l) \to ZnO(s) + H_2(g) \tag{5.5}$$

$$CO(g) + \frac{1}{2}O_2 \to CO_2(g) \tag{5.6}$$

#### 5.2.1 On cite production

The production of hydrogen from the solid metal fuel zinc, is presented in a cycle. This means that it is possible to produce the hydrogen on cite, recycling the main reactants in the cycle's steps. This limits the need for transportation of the energy carrier zinc. Hydrogen will therefore be produced at the hydrogen fueling cite. The only need for transportation is the first transportation of ZnO required to start the process, and the continuous additions of carbon.

The renewal aspect of using concentrated solar power to be able to reach the high temperatures needed for the process is used to make the thermochemical cycle more environmentally friendly. To make the process be as efficient as possible, there must be a good amount of solar energy available. In a lab experiment by A. Berman and M. Epstein [7] the kinetics of hydrogen production using the oxidation of zinc with water, 296 kg/h of zinc liquid is required to produce 100 Nm/h hydrogen. 100 Nm/h CO is also produced. The required amount of solar energy needed for this process is 542 kW. This experiment was carried out in the Weizmann Institute of Science at the Solar Researcher Facilities Unit in Israel[7]. The location of the experiment is in a place with good average solar irradiation compared to the cite of production in the case of this thesis, Norway. The average solar irradiation available for the selected moths January and July in Israel and Norway is presented in table 5.1. The lower irradiation in Norway is because of its located further away from equator than Israel, resulting in a larger angle of declination. The heating process happening in the solar reactor in Norway will therefore be less efficient than the same process happening in Israel. The process will take longer time, or another power-producing source can be applied to help with the energy demand of the process. Hydro power is highly available in the most regions of Norway, and may be an energy source that can help with the energy demand of the process.

	Israel	Norway
January $[kWh/m^2]$	2.98	0.1 - 0.35
July $[kWh/m^2]$	7.76	4-5.5

Table 5.1: Solar irradiation for selected months for Norway and Israel [20][26]

#### 5.2.2 By-products

The by-products of the main reaction in hydrogen production from zinc is zinc oxide and carbon dioxide. As mentioned, the zinc oxide is recycled in the solar reactor, meaning a constant flow of new metal is not needed to maintain the production of hydrogen gas. A correct amount of zinc oxide to begin with will therefore all that is needed for the hydrogen production process. Since solar power is used to provide energy for the heating process every time zinc is heated in the first step, the contribution of solar energy to the cycle can be up to 55%. [7]

Since carbon is used to reduce zinc oxide to zinc, it results in the production of carbon dioxide, a classic GHG, causing the process to not be carbon neutral. The recycling of the zinc on the other hand, makes it possible to avoid transportation emissions of zinc, although carbon needs to be continuously added for the process to keep producing hydrogen gas.

## 5.3 Safety issues

Transporting Si+ and Zn instead of pure hydrogen requires less complex technology. Si+ and Zn can be transported as metals inside containers. The containers do have to be secured and have a dry environment. The Si + and Zn powders themselves are not dangerous, but they can react when exposed to other factors.

Zinc is a flammable powder that produce poisonous gas when combusted in form of zinc oxide. The same poisonous gas will be generated when Zn reacts with water [77]. When Zn reacts with water or is combusted, ZnO gas will be produce which can cause metal fume fever if inhaled[79]. The transportation of ZnO in a powdered form at room temperature have no chance of igniting under normal storage conditions. Silicon powder is also a flammable powder and will react violently with water[61]. In the case of ignition of each of the metal powders, the container may explode. The powders therefore need to be transported in a closed, dry and controlled environment to prevent accidents.

## 6 Scenario

For the scenario, three types of energy storage methods are used: liquid hydrogen, Si+ powder and zinc powder. Each scenario will look at the mode of transport, distance, cost, emissions and logistics of transporting the given amount of hydrogen from each energy storage methods place of origin to the Port of Bergen as an end point.

The Port of Bergen is used as end point because this is where most of the tour cruise companies have their starting point and where the charter begins. This is then the most likely place they will fill up their tanks before voyage. There is most likely going to be built several fueling stations along the fjords and coast of Norway, but for these scenarios Bergen will be the destination the hydrogen is transported to.

The amount of hydrogen that will be delivered and compared in each scenario, is a full tank for Havila Kystrutens ship, which is 3.5 tons of liquid hydrogen. This parameter is chosen because Havila Kystrutens ships has about the same size and capacity as Hurtigrutas fleet, which are the two main companies that share the Bergen-Kirkenes route. Havila Kystrutens ships are 124 meters long and can fit 640 passengers[65]. Hurtigrutas ship MS Kong Harald, which travels the same route, is 122 meters long and has the capacity for 590 passengers[49]. Therefore when Hurtigruta inevitably converts to hydrogen, they will most likely use a similar system. When the values for each scenario is calculated or found, it is easy to compare each scenario and find out which is best. It is also easy to scale the values up or down if needed to look at similar scenario for future use.

Transport methods such as hydrogen pipeline, compressed hydrogen trucks and cryogenic hydrogen tankers will not be used as mode of transport in the scenarios.

The pipeline network in Europe is still extremely small and the technology is not mature enough to rely on this mode of transport. In the future as more pipeline is made and the infrastructure solidifies, it will be a relevant source of hydrogen.

Compressed hydrogen trailers have as mentioned a tenth of the capacity of a cryogenic hydrogen truck. Even though less energy is required to compress hydrogen instead of liquefying it, ten times more trips are needed to deliver the same amount of hydrogen. This makes compressed hydrogen highly inefficient to transport over medium to long distances. This is why this form of transport is not relevant as a scenario for this thesis.

Cryogenic hydrogen tankers are a relative new concept and they are mainly tested and used in Asia. Since the technology is so new and hydrogen is mainly transported over land in Europe, it is not a viable mode of transport yet in Europe. This technology will be more relevant in the future when companies like C-Job naval built and tested their concept of a cryogenic hydrogen tanker, and are able to establish a reliable supply chain.

The liquid hydrogen is assumed to be blue hydrogen produced in Germany and transported to the Bergen, Norway. The transportation route will go through Denmark and Sweden before arriving at its end point. Cryogenic hydrogen trucks will be used for, since the distance of transportation is not large and there is infrastructure good enough for the truck do drive the whole distance. The route is shown in figure 6.3

The second and third scenario will consist of Si+ powder and ZnO powder produced in Hong Kong and transported to the Port of Bergen by using standard shipping containers on a standard cargo ship.

#### 6.1 Scenario 1; Liquid Hydrogen

In this scenario a cryogenic tanker truck from Leipzig to the Port of Bergen. The trip will take 24 hours over a distance of 1 749 km, see figure 6.1. The tanker truck can transport 4 000 kg of liquid hydrogen in one trip. In a worst case scenario 90% of the tanks volume is usable due to liquid remaining in the system, 0.5% is lost in 24 hours due to boil-off and 5% is lost due to boil-off when unloading at the delivery sight. This means that the truck can deliver 3 380 kg of usable liquid hydrogen. This means that one truckload is not enough to fill up Havila Kystrutens LH2 tank, and two trips are needed to meet the requirements.



Figure 6.1: Shipping route from Linde's facility in Leipzig to the Port of Bergen[58]

The course of the trip will emit 1 310  $kgCO_2e$  per TEU (Standard 20-foot shipping container)[58]. Little to no information was found regarding emissions of a cryogenic tanker truck, the assumption is then made that the truck itself is the same as a standard cargo truck and the cryogenic tank is roughly the same size as two TEUs. This means that one trip will generate a total of 2 620  $kgCO_2e$ , and in total 5 240  $kgCO_2e$  is emitted to meet the requirements.

There is no data on the operation cost of Linde's cryogenic hydrogen trucks, but Hydrogenics produces a cryogenic tanker truck that has the same capacity as Linde's. Their most recent data is from 2017 where the operation cost is  $0.1 \, \text{kg}/100 \, \text{km}[14]$ . Assuming the two trucks are similar, this is the value that will be used for this scenario. One trip initially starts with 4 000 kg so that is the number that will be used to calculate the cost. Two trips are required, where each trip is 1 749 km and 4 000 kg is transported. This results in a total cost of:

$$0.1\$/kg/100km \cdot 4000kg \cdot \frac{3498km}{100} \approx 13992.00\$$$
(6.1)

If it is not the worst case scenario, and the usable volume of the is around 95%, the amount of usable liquid hydrogen that reaches the end point is 3 580 kg. Only one trip is then needed to reach the required amount of hydrogen to fill Havila Kystrutas tank. This will halve the worst case scenario cost and emission, reducing them to 6 996.00\$ and 2 620  $kgCO_2e$  respectively.

The cost of producing the blue hydrogen for a 3.5 ton tank will be 3.00\$ per kg of  $H_2$ , resulting in a total cost of 10 500.00\$.

3.2  $kgCO_2e$  are emitted for every kg of blue hydrogen produced, making the total amount emitted to produce 3.5 tons of blue hydrogen, 11 200  $kgCO_2e$ .

#### 6.2 Scenario 2; Si+

In scenario 1 the required amount of Si+ powder to fill a full tank of one of Havila Kystruten ships, which is 3.5 tons.

20 tons of Si+ is required to produce 2.7 tons of liquid hydrogen. This means that it requires 25.9 tons of Si+ to make 3.5 tons of liquid hydrogen. The inner dimensions of a standard shipping container(TEU), is 19 feet long, 7.9 feet high and 7.5 feet wide, see figure 6.2. EAT claims that they can fit 20 tons of Si+ powder in vacuum sealed bags inside one TEU. Since 25.9 tons of powder is required, two TEUs is needed to ship the required amount.



Figure 6.2: A standard 20 foot shipping container[11]

The Si+ is manufactured by EAT in Hong Kong, packed in vacuum sealed bags and two TEUs are packed with combined weight of 25.9 tons. The TEUs are loaded on to a cargo ship that will departure from the Port of Hong Kong and travel a distance of 19 377 km to arrive at Port of Bergen one month and ten days later, see figure 6.3.



Figure 6.3: Shipping route from Port of Hong Kong to Port of Bergen[58]

When the rout is plotted into routescanner.com[58], it says that the trip will generate total of 1165  $kgCO_2e$  per TEU. This will generate a total of 2 330  $kgCO_2e$  for the sea portion of the transport.

Table 6.1 shows the  $kgCO_2e$  per kg  $H_2$  for three different methods of producing  $H_2$  from cradle to gate[59]. The values are from EAT and does not include the transportation of Si+ from Hong Kong to Norway.

	Si+ from met coke	Si+ from recycled PV-modules	Si+ from scrap silicon
Emissions [kg $CO_2$ e per kg $H_2$ ]	+12.5	-22.5	-27.5

Table 6.1: Carbon footprint from different methods of producing Si+

The standard cost of transporting two TEUs is around 2 200.00\$[12].

There are no sources directly from EAT on the direct cost of Si+, but their CEO answered it in one interview from September 2022. He said that the price at that time was 20.00\$ per kg of hydrogen produced, and that he wanted to get it lowered to around 10.00\$ in the future. Not knowing what the price is now, it is assumed to be 20.00\$ per kg. This will make the total cost of 3.5 tons of hydrogen from Si+ to 70 000.00\$[81].

## 6.3 Scenario 3; Zn

There are many places zinc can originate from, such as Russia, Australia, USA and China[76]. For this scenario the zinc powder will come from China, more specifically the Fankou mine in Guangdong, which is the largest zinc mine in China. Hong Kong is in the same area as this mine, indicating that the zinc will be shipped from Hong Kong and follow the same rout as the Si+ powder. The transportation will use ZnO instead of Zn because of its cheaper price and less safety issues.

296 kg of zinc can make  $100Nm^3$  of  $H_2$ , which is the same as 9 kg of liquid hydrogen, see equation 6.3. 33 kg of zinc is then needed to make 1 kg of  $H_2$ . Compared to Si+ which requires 7.4 kg to make 1 kg of  $H_2$ , see equation 6.2. Roughly 4.5 times as much zinc is needed to make the same amount of hydrogen.

$$\frac{20000kgSi+}{2700kgH_2} \approx \frac{7.4kgSi+}{1kgH_2} \tag{6.2}$$

$$\frac{296kgzinc}{100Nm^3H_2} \approx \frac{296kgzinc}{9kgH_2} \approx \frac{33kgzinc}{1kgh_2}$$
(6.3)

To make 3.5 tons of liquid hydrogen, 115.5 tons of zinc is needed. Since there is no information on how much zinc that can be loaded in a TEU, the assumption is made that it is as much as Si+. Since one TEU fits 20 tons of zinc, a total of six TEUs are needed to transport the required amount of zinc. Accounting for 1 165  $kgCO_2e$  per TEU, a total of 6 990  $kgCO_2e$  is emitted by the trip.

It will cost around 6 500.00 to ship six TEUs[12].

From the process of producing 9 kg hydrogen from Zn, a by-product is the production of CO from the carboreduction of ZnO. 100 Nm<sup>3</sup> of CO is produced, and combustion of CO will result in  $CO_2$  emissions. 100 Nm converted to kg/h by multiplying with a factor of 1.229 [9], therefore 122.9 kg CO is produced per hour. To get  $CO_2e$  the weight of CO needs to be multiplied with a factor of 1.57 [19] and divided by 9 to get per kg of  $H_2$ , resulting in 21.44 kg  $CO_2e$  per kg  $H_2$  seen in equation 6.4.

$$\frac{122.9 \ kgCO}{9 \ kgH_2} \cdot 1.57 = \frac{21.44 \ kgCO_2}{1 \ kgH_2} \tag{6.4}$$

The price of ZnO in China today is 2009 USD/MT, which is 2.01 USD/kg. This makes the total cost of 3.5 tons of hydrogen from zinc to be 232 155.00 [78].

## 7 Result of scenario

Table 7.1 shows kg of  $CO_2e$  from the transportation of 3.5 tons of hydrogen in the form of liquid hydrogen, Si+, and Zn, from Hong Kong to Norway.

	Liquid hydrogen truck	Cargo ship (Si+)	Cargo ship (zinc)	
Emissions $[kgCO_2e]$	Worst case: 5 240	2 220	6 990	
	Optimal case: 2 620	2 330		

Table	7.1:	Transportation	emissions	in	the	form	ot	f COse	for	each	scenario
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The transportation costs for 3.5 tons of hydrogen in the form of liquid hydrogen, Si+, and Zn is shown in figure 7.2.

	Liquid hydrogen tuck	Cargo ship (Si+)	Cargo ship (zinc)
Costs (USD) [\$]	Worst case: 13 992.00 Optimal case: 6 996.00	2 200.00	6 500.00

Table	7.2:	Transportation	costs	for	each	scenario
		· · · · · · · · · · · · · · · · · · ·				

Table 7.3 shows the emission from the production of 3.5 tons of  $H_2$  using the hydrogen production methods for each scenario.

	Blue hydrogen	Si+	Zinc
Emissions $[kgCO_2e]$	11 200	Met coke: 43 750 Recycled: -78 750 Scrap: -96 250	75 040

Table 7.3: Production emissions of the presented hydrogen production methods

The production cost of 3.5 tons of hydrogen from each method presented in table 7.4.

	Blue hydrogen	Si+	Zinc
Costs (USD) $[\$]$	10 500.00	70  000.00	$232 \ 155.00$

Table 7.4: Hydrogen production costs for the presented hydrogen production methods

The total expenses and emissions are presented in table 7.5.

	Scenario 1	Scenario 2	Scenario 3
Emissions $[kgCO_2e]$	Worst case: 16 440 Optimal case: 13 820	Met coke: 46 080 Recycled PV: -76420 Scrap: -93 920	82 030
Costs (USD) $[\$]$	Worst case: 24 492.00 Optimal case: 17 496.00	72 220.00	238 655.00

Table 7.5: Total emissions and costs for each scenario

## 8 Discussion

## 8.1 Availability

Most of hydrogen today is made from non-renewable source such as coal or natural gas. Since this is a finite source, it will someday run out and a better alternative needs to become the new standard. Green hydrogen is a great alternative since it uses renewable energy to be made and it comes from abundant sources on earth. The green hydrogen comes most normally from electrolysis of water, which there are plenty of in the world. But since silicon is also abundant on earth, it would make a great alternative as a form of green hydrogen. Since Zinc is not as abundant as water and silicon, it would not be able to compete in this area. However, one downside of Si+ that after the powder is used to make hydrogen, the by-products cannot be used to make new Si+. Zinc however, can be recycled after use to make more powder, and the argument can be made that initially a lot of zinc needs to be extracted, but in the long run less zinc needs to make the same amount of hydrogen and availability might not be an issue.

Since silicon is the second most abundant element on earth, it is very obtainable. This makes it possible to make Si+ almost all over the world. If EAT manages to build a functioning production facility and a steady supply chain, and prove that it works, they may be able to expand their production making it more available to the world. This would lead to shorter transportation and a higher likelihood of this technology being used in the future.

Regarding recycling of silicon, the use of solar panels is only increasing in the world thus making a larger supply of used or broken panels that can go through the process of becoming Si+, and decreasing the need to use new sand to make Si+.

Since the process of making Si+ uses renewable energy and most of the energy produced in Norway comes from renewable sources, Norway would be a great place to build such a facility. Another reason to build a production sight in Norway is because Norway is already sending used solar panels to Hong Kong for recycling, so why not recycle them in Norway and cut out the middleman. This would lead to a much shorter distance between production and use in the ferry and cruise business sailing the Norwegian fjords.

Zn needs a solar reactor for the pyrometallurgy of ZnO because of the required high temperature. The solar conditions in Norway are not as good as the conditions in places closer to equator. The values for production of  $H_2$  from Zn used in this thesis are based on irradiation values from Israel. This means the actual production numbers found in scenario 3 will differ for a real case scenario. If the solar power produced from the solar reactor happens to not be enough, other sources of energy need to be looked upon. With Norway having 89% of its normal yearly energy production[39] come from hydro-power, there is a possibility to have the remaining amount of energy needed for the  $H_2$  production process from hydro-power.

## 8.2 Storage

Storing hydrogen cryogenically is not a suitable storage method for long term storage. It requires high amount of energy to keep the hydrogen in its cryogenic state, and the technology itself is costly. Due to boil-off in the tank, some hydrogen will also be lost over time. This results in hydrogen having to be delivered in a constant stream to the consumer cite, and not stored in large quantities over a longer period of time. This means that newer technology needs to be developed to make the storing of cryogenic hydrogen effective and affordable, or it will not be a viable method in the future. Storing Si+ and zinc is a lot easier and energy efficient to store than hydrogen in liquid form. Si+ and zinc can be stored in vacuum sealed bags in a dark storage container. These storage containers can be at the production sight without any need for energy or maintenance. They are also very space efficient since there are no gaps between them, and they can be stacked vertically. Si+ also has an indefinite shelf life, and can potentially be stored for many years without going bad or losing its efficiency. There is also no need for new infrastructure to store Si+, and all that is needed is space for containers and a source for purified water. There are also no safety measures that needs be made since the hydrogen is carried in the water and not in Si+.

The problem Si+ can face when being stored is condensation in the bags. This can cause some of the outer layer of the powder to react, but a lack of reactant will cause the reaction to halt. However, this can be prevented by infusing the bags with nitrogen during vacuum sealing, and the conditions inside the container being fairly dry.

Compared to cryogenic hydrogen storage zinc is somewhat superior and Si+ is highly superior in every way. It is safer to store, requires no energy to be stored, does not have an expiration date and takes up less space when stored. All these reasons make Si+ and zinc a great new alternative to store hydrogen at sight.

#### 8.3 Logistics

The traditional way of transporting hydrogen is not an effective way to transport large amounts of hydrogen over large medium to large distances. It can be quite efficient over smaller distances with smaller quantities, as seen in scenario 1 where in the worst case scenario two trips area needed to be able to fill up Havila Kystrutens tank. A constant stream of tanker trucks is also needed to making a supply chain between Germany and Norway, resulting in huge amounts of emissions from transport alone. The results from the different scenarios show that shipping Si+ releases the least amount of  $CO_2e$ . It shows that cryogenic transport emits over two times as much as Si+ when the worst conditions are applied, but even if the optimal conditions are applied it still emits more that Si+. Zinc will emit three times as much as Si+ since there is a lot more zinc required to produce the same amount of hydrogen. However, since zinc can be reused it would require fewer trips over time and might emit less than Si+ depending on the amount of times it is reused.

The thing that makes Si+ stand out is the share volume that can potentially be transported in one trip. If a standard cargo ship is fill up with 10 000 TEUs of Si+, a total of around 27 000 tons of potential hydrogen is transported in one trip. A cryogenic tanker truck would need to make 6750 trips to deliver the same amount, and 4.5 cargo ships of zinc would be needed for to deliver the same amount.

It will also be cheaper to ship Si+ rather than cryogenic hydrogen or zinc. With the worst conditions applied it would cost over six times as much to transport via a cryogenic tanker truck, and with the optimal conditions it would cost over 3 times as much. Since zinc requires three times the amount of TEUs to transport the same amount, it would also cost around three times as much.

Based on all these parameters, transporting Si+ via cargo ships seems to be far more superior than transporting cryogenic hydrogen via trucks and zinc via cargo ships.

#### 8.4 Economic

It is clear that the expenses of transporting liquid hydrogen on cryogenic storage trucks are greater than transporting Si+ and Zn in a container by cargo ship shown in table 7.2. Choosing solid metal fuels for transportation is a better choice despite having 11 times longer transportation route. However, the total production cost of  $H_2$  is much lower, both in the worst case and optimal case in scenario 1.

Despite the low transportation cost for Si + and Zn the production cost is far greater than producing blue hydrogen as presented in table 7.4. The transportation costs are much lower than the production costs, having little influence on the final expenses. As seen in table 7.5, the cost of scenario 1 is by far the best choice, even in the worst case.

The production costs of Zn is only based on the price of buying the ZnO powder. The cost of the  $H_2$  production process is unknown and in addition a certain amount of carbon is required for the process. With transportation and the purchase of Zn0 being a one-off case the profitability increases with each time the desired quantity of  $H_2$  is produced. Without taking the cost of C and production energy needed, the scenario 1 worst case must be done 9.7 times for Zn to be the same price and scenario 2, 3.3 times. These ratios will in reality be higher as there are more costs not considered in this thesis' analysis.

The blue hydrogen in scenario 1 is bought directly from a producer of hydrogen. Si+ and Zn on the other hand produces hydrogen on the fueling cite. To produce this  $H_2$  different components are required in each process causing additional expenses to scenario 2 and 3 compared to 1.

With the technologies of using Si+ and Zn for  $H_2$  production relatively new, the methods are therefore not very mature in the hydrogen market. The prices of the  $H_2$  produced using these methods are consequently expensive. Further research and testing can make it more cost efficient in the future.

## 8.5 Emissions

For each scenario the cruise ship will run on hydrogen resulting in only water vapor emission being produced. Nevertheless, it is important that the whole process from cradle to gate is as environmental friendly as possible.

Cryogenic storage trucks have a  $kgCO_2e$  of 2 620 in the case of only one truck being one truck and 5 240 if two is needed as seen in table 7.1. The production cost is presented in table 7.3 and is 11 200  $kgCO_2e$ .

EAT states that the production of Si+ is the first carbon negative cradle-to-gate hydrogen, using recycled PV modules and scrap silicon. Since its cradle to gate, the distribution and transportation of the Si+ is not included. The carbon negative process before the distribution will counter some of the  $CO_2$  emissions from the transportation of Si+ on a cargo ship from Hong Kong to Norway. From table 7.3 two production methods of Si+ results in carbon negative  $H_2$ . Since this thesis's scenario has transportation in addition to the production of Si+ and  $H_2$ , the shipping of the Si+ from Hong Kong to Norway influences the  $CO_2e$ . The shipping of the containers containing Si+ results in 2 330  $kgCO_2e$  found in table 7.1. This is a value of  $kgCO_2e$ that is competitive with that of transportation of cryogenic hydrogen with cryogenic trucks. For the total  $kgCO_2e$  of the cradle to gate process, the transportation to Norway makes little difference in total emission as seen in table 7.5. If the  $H_2$  from Si+ is produced by Recycled PV modules or scrap Si it is the only scenario resulting in a carbon negative footprint making it an optimal source for hydrogen production to preserve the world heritage fjords.

The emissions of Zn transportation are three times as high as Si+ presented in table 7.1, but it only must be done once as the thermochemical cycle of hydrogen production recycles the ZnOback to Zn in the solar reactor. This means that over time, the longer the hydrogen production continues, the more emissions is saved from transportation compared to liquid hydrogen and Si+ which needs to be continuously transported. The production emissions from using Zn is 75 040  $kgCO_{2}e$  as seen in table 7.3. Adding the  $kgCO_{2}e$  values from transportation the total  $kgCO_{2}e$ does not contribute much to the total emissions. The production emissions are 1.7 times higher than the production emissions of Si+ and 6.7 times higher than blue hydrogen production. Totally, the emissions from scenario 3 is by far the worst. With carbon being oxidized to COthe result is  $CO_2$  emissions. It is uncertain if the CO is recycled in its process cycle and how much, but in the wort case scenario the production of  $H_2$  from Zn causes scenario 3 to be the worst emitting scenario.

## 8.6 By-products

Hydrogen as a fuel is sought after in a sustainable environmental perspective because the only emission is water vapor. For each scenario, water vapor is the only product of the electricity producing process. However, in the hydrogen production processes there are different by-products created for the methods of  $H_2$  production used in each scenario. The utilization of the by-products is an important factor in the profitability and emission aspect of a process and prevents waste from being a part of the process. These are important factors which contributes to circular economy.

In the case of liquid hydrogen from blue hydrogen production,  $CO_2$  is a by-product. The  $CO_2$  is GHG, but the emissions are captured using CCS, reducing emissions by a large amount.

When producing  $H_2$  from the Si+ and water reaction,  $SiO_2$  is created as a product in addition to  $H_2$ .  $SiO_2$  is not usable by itself but by adding NaOH,  $Na_2SiO_3$  is produced, an important substance used in the production of green cement. Zeolites can also be produced using the  $SiO_2$ by-product.

The carboreduction of ZnO causes a relatively large amount of  $CO_2$ , which is not an attractive by-product in a environmental friendly perspective. Simultaneously as  $H_2$  is produced, the reacted Zn becomes the by-product ZnO. With the process of producing  $H_2$  from Zn being a thermochemical cycle, the ZnO is recycled and reused.

## 8.7 Safety

Different types of hydrogen storage methods comes with different safety issues. Liquid hydrogen storage is a more complex and dangerous type of storage method than transporting containers of metal which is the case for hydrogen produced from Si+ and Zn. Cryogenic hydrogen storage tanks have the possibility of exploding which will cause a lot of damage to the nearby surroundings. The operating storage temperature at 21.2 K requires a large amount of energy and a technologically complex system that can have faults.

Si+ on the other hand, is transported in its stable metal form in an environment that is easy to control and is itself not a danger. However, the environment of the metals must be dry and protected from potential ignition, as Si+ will react with water on contact and ignite.

The transportation of the ZnO come with few safety issues as it is a stable molecule requiring high temperatures to ignite. Inhalation of the powder can cause metal fume sickness.

## 9 Conclusion

If blue hydrogen is used, it will not be as available as green hydrogen, since blue hydrogen comes from non-renewable sources and green hydrogen comes from renewable energy and water. Since silicon is the second most abundant element on earth and it requires renewable energy to be produced, it becomes very easy to obtain an utilize around the world and in Norway. Zinc is not as common, but because it can be reused after production, not as much needs to be extracted to make the same amount of hydrogen. This makes liquid hydrogen, Si+ and zinc suitable options for hydrogen production in Norwegian maritime sector, in terms of availability.

 $LH_2$  cryogenic storage requires large amounts of energy to keep the low temperature. In addition, boil-off causes losses of  $LH_2$  over time. In other words, cryogenic hydrogen storage is not a suitable technology for hydrogen storage over time. Storage in form of solid metal fuels is on the contrary easy to store and only requiring a dark, dry and closed environment. No energy is needed for the storage only space for the storage containers to be placed, making solid metal fuels the best storage methods.

Si+ is logistically the best option out of the three scenarios. It is cheaper to transport than cryogenic hydrogen and zinc. It emits less  $CO_2$  than the other options when transporting the same amount of hydrogen. It is also better in terms of sheer amount of volume that can be transported, where 4.5 cargo ships of zinc and 6 750 trips with a cryogenic truck are needed to transport the same amount of hydrogen as Si+ can transport in one trip. All of these parameters indicates that Si+ is fare superior than the other options regarding logistics.

The cost of producing  $H_2$  from Si+ is so high it is not able to compete on the hydrogen market as the worst case scenario of blue hydrogen production results in 24 492 USD, being almost a third of the Scenario 2 cost. Overall, the introduction of Si+ as a production method for  $H_2$ is so expensive, the method is not financially possible with the technology it is operating with today. Zn hydrogen production has the advantage of being a recycling process. Even though scenario 3 would produced the desired amount of  $H_2$  after 10 cycles, the costs of the all the components needed for the production process, including a solar reactor, heating chamber and continuously added carbon, would be too high to be cost efficient. Therefore, liquid hydrogen would be the preferred choice from a economic perspective.

If the production of  $H_2$  from Si+ is from recycled PV modules or scrap, it is by far the most environmentally friendly scenario and outperform scenario 1 with blue hydrogen stored as a liquid. The worst emitting method is scenario 3, even though it recycles the ZnO produced in the  $H_2$  production. The Si+  $H_2$  production process is the only process that leaves no by-product to waste and being a carbon negative process

Safety wise, the solid metal fuels are considered the best option. Liquid hydrogen cryogenic tanks have a more complex system which needs to operate under specific conditions. The metal fuels only need to be stored in a dry, dark and closed environment. Production wise, the safety risks of the three scenarios are considered to be of the same risk.

To summarize, Si+ comes out as the most suitable option in every category, except economically. In the case of the world heritage fjords in Norway, the environmental aspect is the most weighted, making Si+ a great alternative to current solutions. The higher cost of Si+  $H_2$  production means that the costumers has to accept the higher price in favor for an effective and environmentally friendly source of fuel.

## 10 Future work

To further analyze the three chosen scenarios, a Life Cycle Assessments LCA on the cradle to grave on each scenarios to get more accurate measures of  $CO_2e$ . and other categories of emissions or damage, for example damage to human health. This would require closer cooperation between companies that produce hydrogen or the Si+ or Zn distributors.

An analysis of the solar irradiation on the hydrogen production cite can be carried out to prevent more accuracy of production values for the  $H_2$  production from Zn. With the irradiation not being the same on the production cite as the irradiation used in the calculation, it is a possibility to find out what a lower irradiation would do to the  $H_2$  production process.

For further work it would be interesting to see how hydrogen storage and transport technologies that becomes available in the future would affect the results of the scenarios. Examples on future storage technologies are pipeline connection from hydrogen production cite to the consumer cite and transportation of liquid hydrogen using cryogenic hydrogen carrier ships. Since more factors will be considered, this will produce a more accurate and well analyzed result for the possibilities of hydrogen as a fuel in the Norwegian maritime sector.

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