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# Towards Hydrogen-Fuelled Marine Vessels using Solid Hydrogen Carriers

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**ABSTRACT** Solid hydrogen carriers, such as sodium borohydride or potassium borohydride, are considered promising options to enable the use of hydrogen as a fuel for marine vessels, because of their favourable gravimetric and volumetric energy density compared to compressed or liquefied hydrogen. When using solid hydrogen carriers, in the form of granules or powder, as fuel for marine vessels, a 'spent fuel' forms which has to be stored on the vessel for the remainder of the voyage. The spent fuel has to be regenerated upon arrival at the destination port to achieve circularity. From an operational perspective, both the fuel and the spent fuel have to be stored for at least the duration of one vessel trip. To design the required storage and handling equipment to realize a circular bunkering process, the mechanical characteristics of both the fuel and the spent fuel e.g. particle size distribution, internal friction, cohesion, wall-friction, and flowability are required. However, little is known about these mechanical characteristics. Consequently, this paper aims to identify the relevant mechanical characteristics of solid hydrogen carriers in the context of bunkering marine vessels. Therefore, an extensive experimental plan using, amongst others, a ring shear tester and a ledge test is presented together with preliminary results of mechanical characteristics including time consolidation effects. The paper concludes with an outlook on the use of the results in DEM-supported design for storage and handling equipment, both onboard the vessel and in the port.

## 1 INTRODUCTION

Greenhouse gas emissions are responsible for global warming [1], and this could lead to significant and irreversible damage to the natural ecosystem and human society. Consequently, during the Paris Climate Conference in 2015 it was agreed that measures to limit global warming to a maximum of 2°C had to be taken [2]. As the maritime sector accounts for approximately 3% of the global emissions [3], which is projected to further increase in the near future [4], the International Maritime Organization (IMO) posed restrictions on the emissions of the maritime sector to pursue a decrease of emissions of 40% by 2030, and 70% by 2050, with respect to 2008 [5]. To realise this, marine vessels could switch to alternative fuels such as hydrogen [6, 7]. Traditionally, hydrogen is compressed and stored as a gas, liquefied, or cryocompressed (liquefied under high pressure). However, each of these methods has drawbacks such as high pressures, low volumetric density, high energy requirements, and thick (insulated) walls. To overcome these disadvantages, solid hydrogen carriers (SHCs) can be an alternative. Van Rheenen et al. [8] compared alternative hydrogen storage methods with these traditional methods using their gravimetric and volumetric energy densities (Table 1). They conclude that the solid hydrogen carriers sodium borohydride (NaBH<sub>4</sub>) and potassium borohydride (KBH<sub>4</sub>) could be used to store hydrogen more efficiently than traditional hydrogen storage. When using solid hydrogen carriers as fuel for marine vessels, the SHC reacts with water inside a reactor to produce hydrogen and a reaction product (spent fuel). The latter has to be stored for the remainder of the voyage and can be regenerated onshore through one of a number of possible energy-intensive processes which are currently under development [12]. Both the SHCs and their respective spent fuels are granular materials that can be classified as granulate or powder, depending on the size of their particles. Granular materials gain internal strength due to their particle-particle and particle-equipment interactions, which affects their behaviour, such as flow and handling characteristics. It is not possible to predict the behaviour of granular materials solely based on their physical and chemical properties, and therefore empirical data is required to determine their mechanical characteristics, such that equipment for the storage and handling can be designed. Unfortunately, while Lensing [13], Nievelt [14], and Düll et al. [15] investigated the use of NaBH<sub>4</sub> and KBH<sub>4</sub> as hydrogen carriers for marine vessels, they did not discuss their mechanical characteristics. Therefore, this paper aims to identify the required mechanical characteristics of SHCs such as NaBH<sub>4</sub> and KBH<sub>4</sub> and their respective spent fuels, to design equipment for handling and storage

using the Discrete Element Method (DEM). However, first an overview of the equipment required for bunkering solid hydrogen carriers is needed. Then, relevant mechanical characteristics can be discussed, and an experimental setup to determine these characteristics is presented as well. Finally, a conclusion is given, and how the empirically determined data can be used for modelling equipment with DEM is discussed.

**Table 1** Comparison Different Hydrogen Storage Methods

Storage Method	Ref	Volumetric Energy Density [MJ/L]	Gravimetric Energy Density [MJ/kg]
Compressed	[9]	4.9	6.8
Liquefied	[9]	6.4	9.0
Cryocompressed	[9]	4	6.5
NaBH <sub>4</sub>	[10]	27.3 <sup>1,2,3</sup>	25.6 <sup>1,2</sup>
KBH <sub>4</sub>	[11]	20.1 <sup>1,2,3</sup>	17.8 <sup>1,2</sup>

<sup>1</sup> Theoretical value. The practical energy density depends on the process used to extract hydrogen

<sup>2</sup> In case hydrolysis is used for dehydrogenation

<sup>3</sup> Depends on the particle size distribution

## 2 CIRCULAR PROCESS

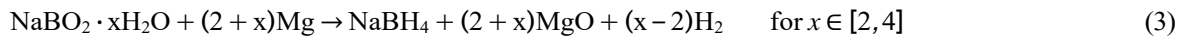
An overview of the circular bunkering process for NaBH<sub>4</sub> and KBH<sub>4</sub> is presented in Figure 1, based on the work of Düll et al. First the solid hydrogen carrier, which is referred to as the fuel, is stored in the port fuel storage, from where it can be transported to the fuel storage of the vessel when a vessel is moored along the quay. During vessel operation, the SHC has to be continuously mixed with water (fuel preparation), after which it can be fed to the reactor. Here, according to the hydrolysis reactions found in the work of Zhu et al [16] and Laversenne et al [17], an aqueous solution containing the SHC is converted into hydrogen (H<sub>2</sub>), and a reaction product, as shown in Equation 1:



While the hydrogen can be used to power the vessel, the reaction product (MBO<sub>2</sub>·xH<sub>2</sub>O) has to be stored in the vessel. This reaction product, also known as metaborate, is referred to as spent fuel and is separated by crystallisation from the unreacted fuel and water in the spent fuel treatment, where after it can be stored in the vessels spent fuel storage. When the vessel receives fuel, the spent fuel has to be transported to the port storage to be able to execute a new mission. At the port, the spent fuel can be regenerated into the fuel, schematically shown in Figure 1. According to Düll et al and Çakanyildirim and Gürü [18] this process can be described using Equation 2, if the crystalline water, present in the spent fuel hydrate, is removed by drying before regenerating (x = 0):



where MgH<sub>2</sub> and MgO denote magnesium hydride and magnesium oxide, respectively. However, drying the spent fuel can be energy intensive as temperatures up to 215°C or 250°C are required [17]. Therefore, according to the work of Ouyang et al [19, 20], the hydrated spent fuels of NaBH<sub>4</sub> can directly be used for regeneration together with magnesium (Mg) as expressed in Equation 3. To the best knowledge of the authors, the regeneration of hydrated spent fuels of KBH<sub>4</sub> is not described in literature, hence excluded from consideration.



The required process to bunker multiple vessels simultaneously is shown in Figure 2. The configuration and capacity of port storage facilities and handling equipment for both the fuel and the spent fuel depends on numerous factors, such as the amount of vessels N, the type of vessels, and the behaviour of the materials. As design of equipment for granular materials highly depends on the characteristics of the material, empirical data is required of both the fuel and spent fuel to gain insight in the different characteristics of granular materials and how they are affected by operational conditions such as temperature, humidity, and mechanical stresses. However, to be able to



It is important to note that the mechanical characteristics of granular materials are not constant, but depend on operational conditions such as humidity, stress, and temperature. For instance, in a humid environment, a bulk material absorbs moisture from the air, leading to capillary forces and increased cohesion. To effectively design the required equipment for the transportation and storage of solid hydrogen carriers, it is crucial to empirically determine their mechanical characteristics, and understand how operational conditions can affect these.

### 3.1 Relevant Mechanical Characteristics

To enable bunkering of both fuel and spent fuel, suitable equipment must be selected or designed. Therefore, it is essential to understand the different types of equipment needed for the bunkering process. As illustrated in Figure 2, two main types of equipment are required: storage equipment and handling equipment.

Storage equipment typically includes a silo, which is often equipped with a hopper for discharging the material when required [21]. During storage, the velocity of the bulk material is zero, while it is nonzero for handling applications. Handling equipment can be further classified into two categories: transport and transfer. Transport refers to the movement of a single stream of bulk material and often involves conveyors such as belt, pipe, screw, tube, or chain. Transfer, on the other hand, involves merging or splitting streams of bulk material, as shown in Figure 2. Although a transfer chute is typically used for transfer in the mining industry [22], transfer and transport are likely to be integrated for the application described in this paper.

According to Olanrewaju et al [23], the mechanical properties of the granular material being handled are critical when designing or selecting equipment. For example, when designing a silo and hopper, bulk characteristics such as bulk density, internal friction angle, and lateral stress ratio are important to determine the desired height and width of the silo. The inclination of the hopper walls is adjusted based on bulk density, internal friction, and flow function, as well as interface characteristics such as wall friction, to ensure smooth flow of material through the hopper. The angle of repose is essential for designing a belt conveyor [24], while transfer chutes are subject to wear due to friction between materials and the chute wall [22]. As there are numerous types of equipment, Table 2 provides an overview of typical storage and handling equipment, and examples of mechanical characteristics relevant for their design.

**Table 2** Example of Relevant Characteristics

Equipment	Ref	Relevant Mechanical Characteristics											
		Bulk Characteristics								Interface Characteristics			
		Bulk Density	Cohesion	Internal Friction	Flow Function	Angle of Repose	Roughness	Shape <sup>1</sup>	Size <sup>2</sup>	Wall Friction	Adhesion	Size <sup>3</sup>	Hardness
Silo	[21]	x		x						x	x		
Hopper	[21, 25]	x		x	x			x		x		x	
Transfer Shute	[22, 26]		x				x	x	x	x	x		
Belt Conveyor	[24, 27]	x				x							
Chain Conveyor	[28, 29]	x		x		x			x	x			x
Pipe Conveyor	[30, 31]	x		x		x	x						
Screw Conveyor	[32, 33]	x	x	x			x		x	x			
Pneumatic Conveyor	[34, 35]	x				x				x			

<sup>1</sup> Particle Shape Distribution

<sup>2</sup> Particle Size Distribution

<sup>3</sup> Characteristic Size

### 3.2 Relevant Operational Conditions

Mechanical characteristics of granular materials are not fixed but are affected by operational conditions such as moisture content, stress history, and temperature. According to Schulze [21], increased moisture content results in the formation of liquid bridges between particles, which increases cohesion through capillary forces. Furthermore, according to Rhodes [36] also adhesion increases with increasing moisture content. Stress history includes

handling, time consolidation, and packing, which all affect the mechanical characteristics. First, the handling of material could result in attrition and breakage of particles [37]. This affects the particle size and shape distributions, which in their turn could affect several other characteristics such as cohesion, internal friction, and wall friction. Second, time consolidation causes deformation inside the bulk material, leading to increased cohesion and adhesion. The specific packing of a material bed affects how particles are positioned with respect to each other, possibly affecting characteristics such as internal friction, bulk density, cohesion, and adhesion. Finally, the temperature can also play a role in affecting the bulk characteristics of granular materials. A change in temperature can cause the material to expand or contract, but could also change the moisture content, and both phenomena affect the bulk density and other characteristics. It follows that understanding the effects of these factors on the bulk characteristics of granular materials is essential for designing and selecting equipment for handling and processing these materials in various industrial applications.

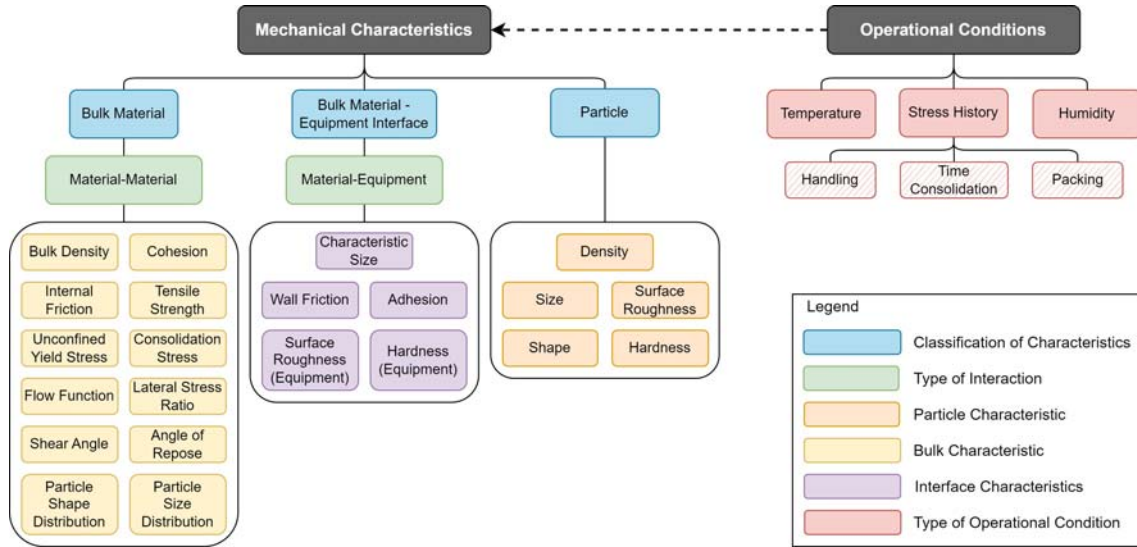
Consequently, the operational conditions described should be taken into account when the mechanical characteristics of solid hydrogen carriers are determined. Unfortunately, the stress history depends on the bunkering process, including both the storage time and the amount of material in the port's or vessel's storage equipment. As these are yet unknown, a range of possible storage times and different amounts of material will be taken into consideration instead. The moisture content and temperature of the hydrogen carrier stored at a port are dependent on the location of the vessel. If the storage conditions are assumed to be similar to the environment of the port, then in an environment with high temperature and humidity, the temperature and moisture content of the hydrogen carrier can be expected to increase compared to a colder and less humid environment. As the bunkering process is likely to be located at one or multiple of the 10 largest harbours around the world, the environments of these ports are taken into consideration. Table 3 summarizes the environments of these ports.

**Table 3** Operational Conditions of Top 10 Ports of Different Countries [38–41]

Port		Temperature [°C]			Humidity [% RH]		
City	Country	Min	Average	Max	Min	Average	Max
Shanghai	China	2	17	32	67	74	7481
Singapore	Singapore	25	28	32	78	80	83
Busan	South-Korea	1	15	29	56	69	87
Rotterdam	The Netherlands	2	11	22	73	78	85
Jebel Ali	Dubai	18	30	36	48	56	62
Port Klang	Malaysia	23	28	33	77	81	85
Antwerp	Belgium	2	12	23	71	78	86
Los Angeles	U.S.A	6	22	29	38	50	62
Hamburg	Germany	-1	10	23	73	80	88
Laem Chabang	Thailand	24	28	34	65	74	79

Using the relevant mechanical characteristics and effect of the operational conditions, Figure 3 is composed, which shows different mechanical characteristics of granular materials as well as the operational conditions that can affect them. Regarding the mechanical characteristics, a distinction is made between particle, bulk material, and interface characteristics. Furthermore, the difference in the interaction between particles and particles, and particles and equipment is taken into account. Lastly, since the exact relation between the operational conditions and the mechanical characteristics is not known, this is indicated with a dashed line. For more detailed information regarding the different characteristics shown, the reader is referred to Schulze [21].

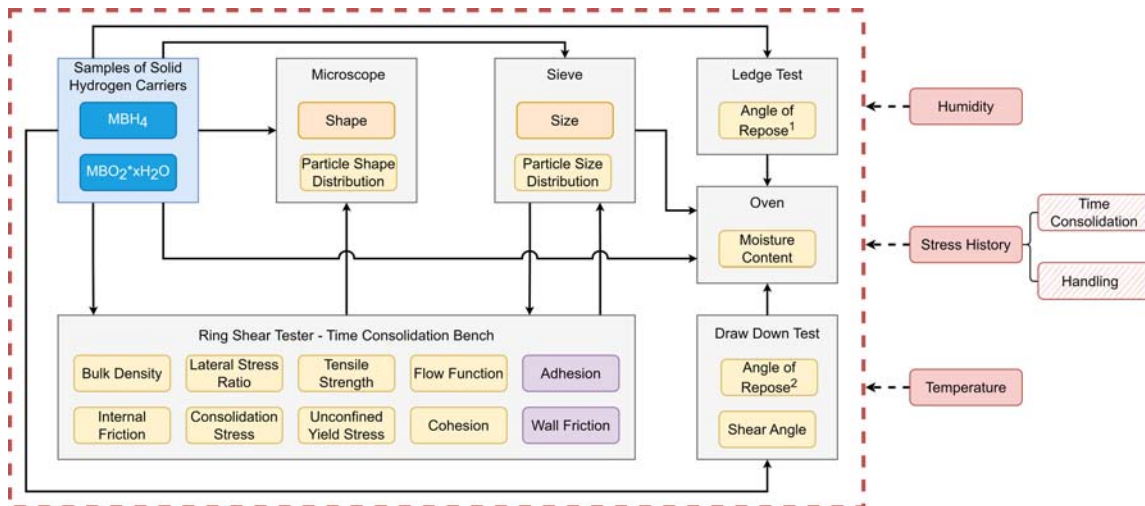




**Figure 3** Mechanical Characteristics and Operation Conditions

#### 4 EXPERIMENTAL PLAN

The experimental setup, presented in this section, aims to take into account relevant operational conditions while determining the relevant mechanical characteristics for the bunkering process of solid hydrogen carriers. Therefore, each experiment is to be conducted with samples of both the solid hydrogen carrier and its respective spent fuel, preferably both as powder and as granulate, while subject to different humidities, temperatures, and stresses, as shown in Figure 4.



**Figure 4** Schematic of Experimental Plan and considered Operational Conditions

##### 4.1 Ring Shear Tests

The Schulze Ring Shear Tester RST-01.pc will be used to conduct ring shear tests. A range of preshear stresses (as low and high as feasible) is used to be able to construct yield loci. To create a reference, tests are conducted with samples directly taken from a pure batch of solid hydrogen carrier. To simulate handling steps the same tests are conducted as for the reference, but now each with the same sample. Comparing is required to quantify the change in mechanical characteristics of the material. Furthermore, other operational conditions can be taken into account by preparing samples in a climate chamber (temperature and humidity), and by storing them under pressure

(time consolidation) before tests are conducted. The required time consolidation stresses are based on preliminary estimations using the work of Schulze, and a range of mechanical characteristics and different configurations for storage silos.

#### 4.2 Sieve Analysis

To determine the particle size distribution, samples of material need to be sieved. To establish a reference, samples directly taken from the batch will be sieved. Breakage or attrition (if any) can be detected by comparing the reference particle size distribution to the measurements obtained after sieving the samples tested with the ring shear tester. The sieve analysis will be conducted following the Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates: C136/C136M-19.

#### 4.3 Microscope Analysis

The particle shape distributions will be determined with a microscope. Both samples directly from the batch, as samples tested with the ring shear tester, will be analysed, as this could provide insight into possible changes in the particle shape distribution.

#### 4.4 Ledge Test and Draw Down Test

The ledge test and draw-down test are often performed as preparation for the calibration of materials models with the Discrete Element Method (DEM) [42, 43]. Both tests start with a rectangular box filled with material (fuel or spent fuel). For the ledge test, one side of the box is opened, such that a part of the material flows out. The slope of the material that remains in the box is referred to as the Angle of Repose and is noted with  $AoR^1$  in Figure 4. The box of material in the draw-down test (box 1) is placed on top of another box (box 2). Now, as a door in the bottom of box 1 is opened, the material flows into box 2. The slope of the material that remains in box 1 is also referred to as the Angle of Repose, and in Figure 4 denoted as  $AoR^2$ . The slope of the material in box 2 is called the shear angle. Both the AoRs as the shear angle depend mainly on the cohesiveness and internal friction of the material. Effects of time consolidation will also be taken into account, simply by placing a weight on top of the material bed for a certain amount of time before opening the hatch. It is also possible to investigate the effects of humidity and temperature, by preparing the sample or performing the ledge test in a climate chamber.

#### 4.5 Oven

First, samples of material as received from the manufacturer have to be checked for moisture content and will be assumed the reference value for the whole batch. According to Balbay et al [44], solid hydrogen carriers such as  $NaBH_4$  and  $KBH_4$  are hygroscopic, hence moisture uptake by the samples is expected. By measuring the moisture contents of tested samples, insight into the moisture uptake can be gained, but even more, it is required to verify that tests are comparable. Tests will be conducted following the procedure of the Standard Test Method for Total Evaporable Moisture Content of Aggregate by Drying: C556-19.

#### 4.6 Preliminary Results

Granular  $NaBH_4$  was purchased from CPH Chemicals, and after testing samples of the received batch in an oven it was concluded to be fully dry. Ring shear tests with samples of granular  $NaBH_4$  showed that the material is almost free-flowing, but time consolidation (128 hour at 10kPa) combined with increased moisture content ( $\approx 1\%$ ) affects the material in such a way that it can be classified as very cohesive or even non-flowing. However, a relatively low force was required to loosen the material after consolidation, after which it appeared to be free-flowing again. The moisture uptake was caused by the small gap between the ring shear cell and its lid. The humidity and temperature of the environment were approximately 40%RH and 20°C, respectively. Finally, a comparison between the reference particle size distribution (PSD) and the PSDs measured after ring shear tests were conducted showed no significant breakage or attrition, but more experiments are required to provide conclusive data.

### 5 CONCLUSIONS

Solid hydrogen carriers hold great promise as alternative fuels for the maritime industry, and a circular bunkering process has been proposed to effectively utilize these carriers and their respective spent fuels. However, the design



of storage and handling equipment for these carriers strongly depends on their mechanical characteristics, which are currently unknown. Therefore, an experimental plan has been proposed to determine the relevant mechanical characteristics of solid hydrogen carriers, as well as their spent fuels, under various operational conditions. Preliminary results from these experiments have demonstrated that an increase in moisture content in combination with a long period of storage can lead to a change in the behaviour of the material from free-flowing to non-flowing. These findings emphasize the importance of carefully considering the storage and handling conditions of solid hydrogen carriers to ensure their safe and efficient use in the maritime industry.

## 6 ACKNOWLEDGEMENTS

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## 7 NOMENCLATURE

H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
KBH <sub>4</sub>	Potassium borohydride
KBO <sub>2</sub> · xH <sub>2</sub> O	Potassium metaborate
MBH <sub>4</sub>	Metal borohydride
MBO <sub>2</sub> · xH <sub>2</sub> O	Metal metaborate
Mg	Magnesium
MgH <sub>2</sub>	Magnesium hydride
MgO	Magnesium oxide
NaBH <sub>4</sub>	Sodium borohydride
NaBO <sub>2</sub> · xH <sub>2</sub> O	Sodium metaborate
PSD	Particle Size/Shape Distribution
RH	Relative Humidity

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