Bjørn Romijn

Bulk material properties of $NaBH_4$

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By

Bjørn Romijn

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Supervisor:	Ir. M.C. van Benten Prof.dr.ir. D.L. Schott

Thesis committee:	Prof.dr.ir. D.L. Schott,	TU Delft committee Chair, 3mE
	Ir. M.C. van Benten	TU Delft, Supervisor
	Prof.dr.ir. J.T. Padding	TU Delft committee member, 3mE
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TU Delft

Preface

This report is the result of my graduation research project for my Master program "Multi-Machine Engineering", affiliated to the faculty of Mechanical, Maritime and Materials Engineering at Delft University of Technology, the Netherlands. The reported research is the graduation thesis, conducted during the period between December 2022 and December 2023.

Summary

This report provides a comprehensive analysis of the bulk mechanical properties of Sodium borohydride ($NaBH_4$) for its potential use as a material-based hydrogen storage solution. The focus is on investigating the changes in the mechanical properties under varying humidity conditions, which is crucial to understand how the material will behave during storage and handling.

The report commences with a literature review on what is known about the material properties of $NaBH_4$ and how these are influenced by temperature and humidity. This is followed by identifying the key factors that influence the material properties of similar materials when exposed to humidity.

Since humidity does not have a direct effect on material properties, but moisture content does, two experiments are performed to determine effect of humidity on moisture content in $NaBH_4$. During the experiments, two types of $NaBH_4$ are used, granules and powder, providing a comparative analysis on how or if they react differently.

The second set of experiments are designed to determine the mechanical properties with varying moisture content. This way, the link between humidity and bulk mechanical properties can be made.

The findings from these experiments are then concluded to form the basis for a deeper understanding of $NaBH_4$'s bulk mechanical properties and how they change when exposed to humidity. This knowledge is essential for effectively utilizing $NaBH_4$ granules or powder as a fuel source for marine vessels and other applications.

Summary (in Dutch)

Dit rapport biedt een uitgebreide analyse van de mechanische materiaaleigenschappen van bulk natriumboorhydride ($NaBH_4$) voor het potentiële gebruik ervan als energiedrager als chemisch gebonden waterstof. De nadruk van dit rapport ligt op het onderzoeken van de veranderingen in de mechanische eigenschappen onder variërende vochtigheidsomstandigheden, wat cruciaal is om te begrijpen hoe het materiaal zich zal gedragen tijdens opslag en behandeling.

Het rapport begint met een literatuuronderzoek naar wat er bekend is over de materiaaleigenschappen van $NaBH_4$ en hoe deze worden beïnvloed door temperatuur en vochtigheid. Dit wordt gevolgd door het identificeren van de belangrijkste factoren die de materiaaleigenschappen van vergelijkbare materialen beïnvloeden bij blootstelling aan vocht.

Omdat luchtvochtigheid geen direct effect heeft op de materiaaleigenschappen, maar het vochtgehalte van het materiaal wel, worden twee experimenten uitgevoerd om het effect van luchtvochtigheid op het vochtgehalte in $NaBH_4$ te bepalen. Tijdens de experimenten worden twee soorten $NaBH_4$ gebruikt: korrels en poeder, waardoor er vergeleken kan worden of en hoe deze verschillend reageren.

De tweede reeks experimenten is ontworpen om de mechanische materiaaleigenschappen bij variërende vochtgehaltes te bepalen. Op deze manier kan de link gelegd worden tussen vochtigheid en de mechanische materiaaleigenschappen.

De resultaten van deze experimenten worden vervolgens geconcludeerd om de mechanische materiaaleigenschappen van bulk $NaBH_4$, en hoe deze veranderen bij blootstelling aan luchtvochtigheid, beter te begrijpen. Deze kennis is essentieel voor het effectief inzetten van $NaBH_4$-korrels of -poeder als brandstofbron voor zeeschepen en andere toepassingen.

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Nomenclature

°C	– degrees Celsius
DVS	– dynamic vapor sorption
g	– gram
H_2	– hydrogen
H_2O	– water
kg	– kilogram
kPa	– kilo pascal
mg	– milligram
mm	– millimetre
MJ	– megajoule
$NaBH_4$	– sodium borohydride
$NaBO_2$	– sodium metaborate
Pa	– pascal
RH	– relative humidity
wt%	– weight percentage

1. Introduction

There is a transition occurring from fossil fuels to renewable fuel sources as the international community strives to limit the increase in the global average temperature to well below 2°C above pre-industrial levels, as agreed upon in the adoption of the Paris Agreement [1]. One way to inhibit the increase in global average temperature is by reducing global emissions of greenhouse gasses, which can be achieved by using renewable fuel sources. It is important to note that, according to the International Maritime Organization, the share of shipping greenhouse gas emissions in global anthropogenic emissions increased from 2.76% (977 million tonnes) in 2012 to 2.89% (1,056 million tonnes) in 2018. These emissions are projected to increase even further by 2050 [2]. To reduce the impact of shipping emissions on global average temperature, the amount of emissions created by the shipping industry has to be decreased, but since the global merchandise trade volumes has increased 20% between 2015-2022 and is expected to increase by another 1% in 2023 [3], it is necessary to find alternative and more renewable fuel sources for the maritime industry.

One possible renewable fuel source is hydrogen, as extracting energy from it, either through burning it or through hydrogen fuel cells, does not directly create any greenhouse gasses. Hydrogen in its pure, gaseous phase, H_2, is not abundant on earth, but it can be amply found bound to other elements in various sources, such as in water, H_2O. Pure water contains 11.2 wt% hydrogen, and seawater contains around 10.8 wt% hydrogen [4]. Hydrogen can be produced in a renewable way through several methods. One such method is electrolysis, which uses electricity from renewable sources such as wind or solar power to split water molecules into hydrogen and oxygen. Another method is photobiological processes, which use sunlight and microorganisms to produce hydrogen from water. Hydrogen gas has a very high gravimetric energy density of between 120-142 MJ/kg, however due to the low density of 0.090 kg/m3 under atmospheric pressure, it has a very low volumetric energy density. A low volumetric energy density means that a vast volume of storage space is required to store large quantities of energy, such as the energy required to power maritime vessels over long distances. The volumetric energy density of hydrogen can be increased by liquefaction or compression of the gas. However, liquified hydrogen has the downside of requiring constant refrigeration to keep boil-off losses low and compressed hydrogen keeps hydrogen stored at up to 700 bar and thus requires specialized high pressure storage solutions [5]. Furthermore, increasing the volumetric energy density by using these specialized storage solutions decreases the total gravimetric energy density of the total system (hydrogen + storage equipment) due to the added weight, as can be seen in *Figure 1*.

Instead of storing hydrogen in its pure form, either compressed or liquefied, hydrogen atoms can also be bound to carrier materials, realizing material-based hydrogen storage [6]. Advantages of this type of hydrogen storage is the significantly higher volumetric energy density and the absence of requiring high pressure storage solutions. Sodium borohydride, $NaBH_4$, is such a material-based hydrogen storage material, as can be seen in *Figure 1*. It is an inorganic salt which is mainly used as a bleaching chemical in the papermaking industry and as a reagent in organic synthesis in the chemical/medical industry [7].

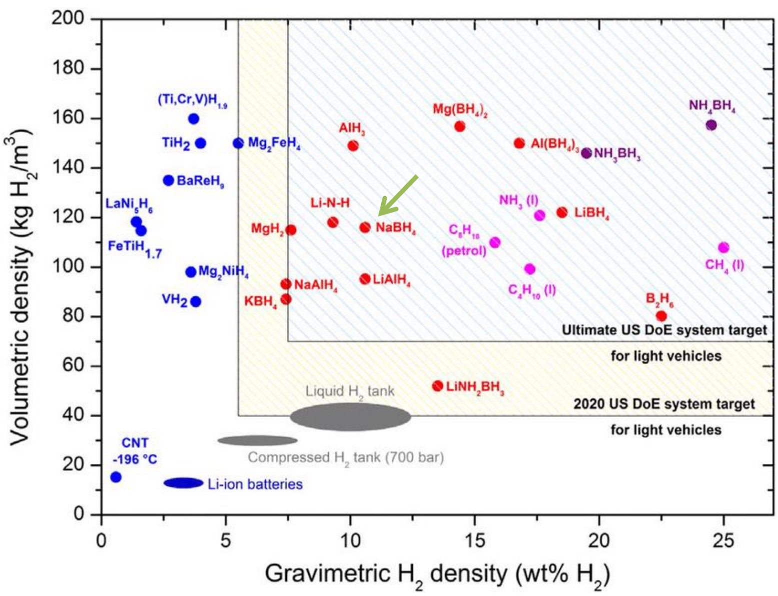

Figure 1.
Overview of various materials and their volumetric and gravimetric hydrogen density. The U.S. Department of Energy targets for hydrogen storage systems are also shown for comparison.
By K.T. Møller *[8]*

To use $NaBH_4$ as a viable fuel source the complete process cycle of storage, transportation, hydrolysis, and regeneration of the spent fuel must be thoroughly understood. While various information is known about the chemical and physical data of $NaBH_4$ [9], little to no information can be found on the bulk material properties of $NaBH_4$. Knowledge of these bulk material properties is required to design equipment for storage and handling to enable the use of $NaBH_4$ as fuel on maritime vessels.

1.1. Problem definition

As described, the bulk material properties of $NaBH_4$ have not been extensively studied, particularly with regards to its storage and handling at larger scales. Currently, $NaBH_4$ is primarily used in smaller quantities, and research has shown that the material tends to clump together, also called 'caking', in humid environments due to its hygroscopic nature [10]. While the effects of temperature and ambient humidity on small quantities of $NaBH_4$ have been investigated [11], there is a lack of research on the bulk material properties of $NaBH_4$ in bulk quantities under varying operational conditions, such as temperature, stress history, and humidity. To effectively utilize $NaBH_4$ as a fuel source for marine vessels, it is essential to understand its bulk material properties under varying operational conditions during storage and handling. Further research is necessary to achieve this understanding.

1.2. Aim of the research

The aim of this research is to determine the effects of ambient humidity on the bulk material properties of $NaBH_4$ during storage and handling. By presenting quantitative results, this research seeks to provide a better understanding of how ambient humidity influence the bulk material properties of $NaBH_4$.

1.3. Research questions

Using the problem definition, the following main research question is formulated:

What are the effects of ambient humidity on the bulk material properties of bulk $NaBH_4$ during storage and handling?

To be able to answer this question the following sub-questions have been formulated:

- What is the state of the art in the bulk material properties of bulk $NaBH_4$?
- What are the effects of ambient humidity on the moisture content of $NaBH_4$?
- What are the mechanical properties of bulk $NaBH_4$ under varying moisture content?
- In what ways do the bulk material properties of $NaBH_4$ powder and $NaBH_4$ granules differ when exposed to varying ambient humidity.

1.4. Outline

Chapter 2 begins with a comprehensive literature review to understand the current state of knowledge regarding the bulk material properties of bulk $NaBH_4$ and the effect that moisture has on it. This sets the groundwork for the experimental work that follows.

Chapter 3 provides clarity on the selection of experiments. The experiments are designed to explore how ambient humidity affect the moisture content of $NaBH_4$, as well as how moisture content affects the mechanical characteristics of $NaBH_4$. This chapter also details the procedures used in the experiments, explaining the design, variables used, and their role in understanding the mechanical properties of $NaBH_4$.

In Chapter 4 the results of the experiments regarding the effects of ambient humidity on the moisture content are visualized, and their key observations and results are documented. These results shed light on how ambient humidity influences the moisture content in $NaBH_4$. The observations made during these experiments are further utilized to discuss open versus closed storage environments, given that the rate of moisture content varies significantly when $NaBH_4$ is exposed to humidity in either environment.

Chapter 5 visualizes the results of experiments quantifying the influence of moisture content on bulk material properties. A comparative analysis is conducted between $NaBH_4$ powder and granules under diverse ambient humidity levels, with respect to their bulk material properties. This analysis aims to discern whether different forms of $NaBH_4$ exhibit distinct responses to changes humidity.

Finally, all findings are synthesized in Chapter 6 to answer the main research question: What are the effects of ambient humidity on the bulk material properties of bulk $NaBH_4$ during storage and handling? Through this approach, valuable insights into this area of research are expected to be provided.

2. State of the art

This chapter presents a review of the existing literature on the material properties of sodium borohydride ($NaBH_4$). It covers the hydrolysis reaction, mechanical properties, and the influence of operational conditions on the material properties of $NaBH_4$.

2.1. Hydrolysis reaction

In the current state of the art, the hydrolysis reactions of $NaBH_4$ hydrolysis are well understood [12]. It is known that $NaBH_4$, which contains 10.66 weight% hydrogen, can release hydrogen through the following hydrolysis reaction:

$$NaBH_4 + 2 \cdot H_2O \rightarrow NaBO_2 + 4 \cdot H_2 \quad (1)$$

However, in practical conditions, $NaBH_4$ requires an excess of water to dissolve and subsequently react [13], as shown in the following equation:

$$NaBH_4 + (2 + x) \cdot H_2O \rightarrow NaBO_2(x \cdot H_2O) + 4 \cdot H_2 \quad (2)$$

This reaction is particularly interesting because half of the hydrogen gas produced comes from the added water molecules, leading to a higher overall efficiency and effective volumetric energy density of $NaBH_4$ when the water is omitted. The by-product of this hydrolysis reaction is $\mathrm{NaBO_2(x \cdot H_2O)}$, which can be regenerated back to $NaBH_4$ through hydrogenation [14].

While these chemical properties are crucial, to fully understand the behaviour of materials like $NaBH_4$ in a variety of applications, such as its behaviour during storage and handling, a study on the bulk material properties is equally essential. Furthermore, particle size and operational conditions such as temperature, stress history, and humidity can influence these mechanical properties either directly or indirectly. This chapter aims to delve deeper into the current state of the art of the mechanical characteristics of $NaBH_4$.

2.2. Material properties of $NaBH_4$

While in recent years the use of $NaBH_4$ as a solid state hydrogen storage method is more researched [6, 15, 16], these works are more focused on the financial and chemical feasibility of using $NaBH_4$ as an energy carrier, rather than the behaviour of the material during storage and handling. Ghellab et al. [17] analysed the elastic, mechanical, and thermodynamical properties of $NaBH_4$ and $NaAlH_4$, such as the elastic constants, strain energies, bulk modulus, heat capacity, and thermal expansion coefficient. However, these properties describe the physical properties of the material itself, rather than the bulk material properties that describe the bulk behaviour of $NaBH_4$. Nagar et al. [18] use a discrete element method to model $NaBH_4$ powder and validate their model using a limited amount of physical tests. These tests include a wedge penetration test and a shear strength test to find the internal friction and cohesion of the material, but they do not give a complete picture on whether and how the bulk material properties would change under varying operational conditions, such as temperature, stress history, and humidity.

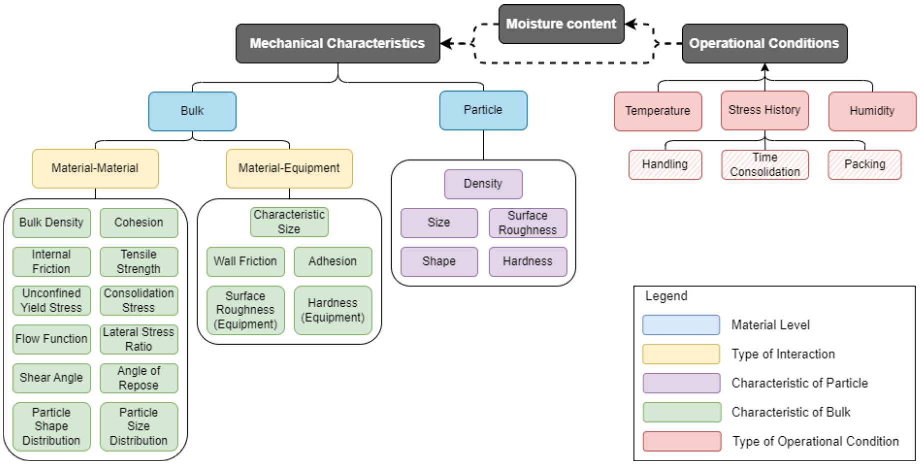

Figure 2.
Most relevant mechanical properties of a material for storage and handling.
Based on M.C. van Benten, *[19]*

Met opmerkingen [DS1]: Wat is er anders dan in Van Benten?

Met opmerkingen [BR2R1]: Marcel zijn afbeelding heeft heeft "Moisture content" er niet bij staan. Daar gaat een direct lijntje van Operational conditions naar Mechanical Characteristics. Gezien in deze paper moisture content een grote rol speelt moest ik die toevoegen.

The most relevant mechanical properties of a material in relation to its storage and handling, as described by M.C. van Benten [19], as well as the operational conditions that influence these mechanical properties can be seen in *Figure 2*.

The mechanical properties of a material are divided into the bulk material properties and individual particle properties. The particle properties describe the properties of the individual particles while the bulk material properties describe how those particles would behave in large numbers. The bulk material properties are further divided into material-material properties and material-equipment properties, where material-material properties describe the interaction of particles with each other, while material-equipment properties describe the interaction of particles with equipment. Characterizing these particle properties and bulk material properties is essential to be able to design functional storage and handling equipment for the material.

The operational conditions, such as temperature, stress history, and humidity, are external conditions that influence the mechanical properties either directly or indirectly. The stress history directly influences the mechanical properties by increasing the bulk density due to compression. The humidity and temperature have an indirect effect on the mechanical properties, as a change in temperature and/or humidity affects the moisture content of the material, which in turn increases the cohesion due to the formation of capillary forces between particles.

2.3. The effect of moisture and temperature on $NaBH_4$

Although $NaBH_4$ hydrolyses when it is mixed with an excess of water as shown in equation (2), it forms dihydrate crystals when it absorbs small amounts of water from the air, rather than reacting with the water, as researched by Filinchuk and Hagemann [20]. In a dihydrate crystal, $NaBH_4$ forms a 2D crystalline structure by forming hydrogen bonds between the hydrogen atoms of both $NaBH_4$ and H_2O molecules. However, if the temperature exceeds 40ºC, the crystal will decompose. The formation of dihydrate crystals might be a method that causes the material to cake together, thus changing the mechanical properties of the material. Other researchers also show the effect of humidity on the mechanical properties of $NaBH_4$. Minkina et al. [21] claims that "anhydrous $NaBH_4$ absorbs water in open air at room temperature and transforms into a wet foaming mass (hydrogen is liberated) and then into a vitreous mass" and Stepanov et al. [22] confirm this in their study by concluding that "$NaBH_4$ spontaneously undergoes simultaneous hydrolysis and hydration with water molecules absorbed from the surrounding air.", meaning that $NaBH_4$ is deliquescent at 22°C, 35% relative humidity (RH). Deliquescence is the process by which $NaBH_4$ absorbs moisture from the atmosphere until it dissolves in the absorbed water and starts a reaction. Murtomaa et al. [11] show that the moisture uptake rate of $NaBH_4$ increases when the temperature increases and when the RH increases. However, at 19% RH no uptake of moisture from the surrounding environment is observed, while at 31% RH moisture uptake is observed. Finally, Beaird et al. [10] establish a region of temperature and absolute humidity under which uptake of moisture is inhibited, as shown as the stable region in *Figure 3*, meaning that there is a region in the temperature-moisture domain in which anhydrous $NaBH_4$ would remain inert rather than forming dihydrate crystals or reacting with the available moisture in the air by deliquescence.

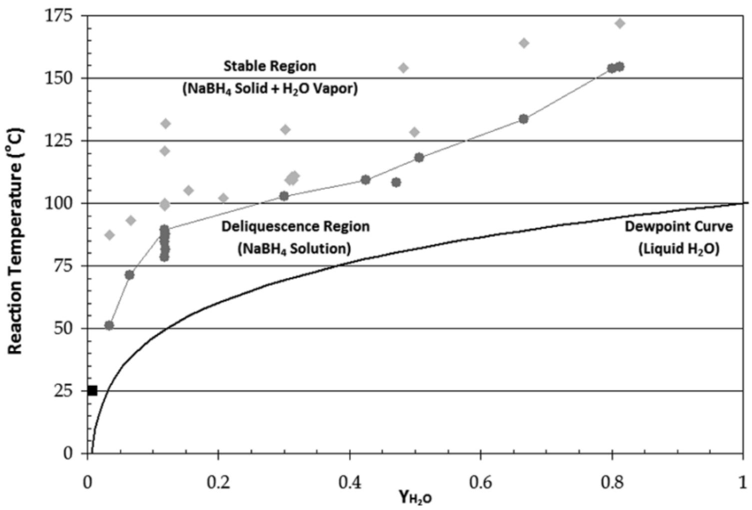

Figure 3.
$NaBH_4$ deliquescence phase diagram.
By Beaird et al. *[10]*

2.4. The effect of caking on similar materials

As caking has a significant impact on the mechanical properties of a material, and since caking occurs when $NaBH_4$ comes into contact with ambient humidity, it is important to understand what the key factors are that influence the mechanical properties during caking. Chen et al. [23] investigate the key factors that influence caking between two types of caking: amorphous caking, which is the caking of amorphous powders, and crystalline caking, which is the caking of crystalline powders, like $NaBH_4$. They provide key factors and potential factors which have the biggest influence on the two types of caking, and this is shown in *Figure 4*. They conclude that temperature and humidity are the key factors of caking processes. In addition, the subsidiary factors include particle size distribution, particle shape, stress, and consolidation time.

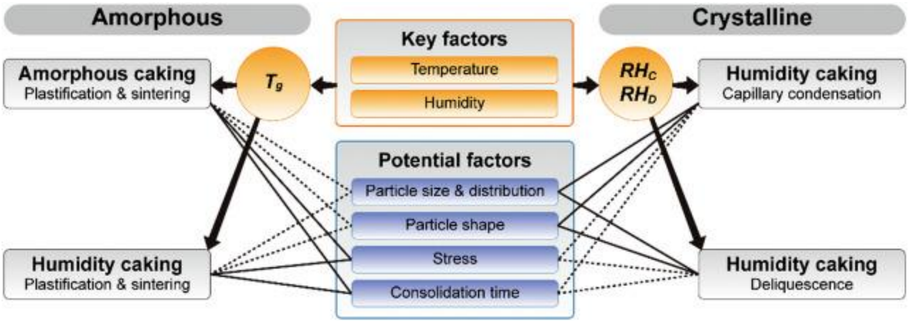

Figure 4.
Factors of amorphous and humidity caking. RH_C is the required relative humidity to achieve capillary condensation, and RH_D that of deliquescence. Factors connected by a solid line are considered to be relatively more important than the ones connected by dotted line.
By Chen et al. *[23]*

As $NaBH_4$ is a crystalline material which shows deliquescence, *Figure 4* shows that the key factors would be the temperature and humidity of the surrounding environment. As to the subsidiary factors, particle size, particle distribution, and stress have relatively more impact on the caking process of $NaBH_4$.

2.5. Conclusion

In conclusion, there is limited information available on the mechanical properties of $NaBH_4$. Currently only the physical properties of the material itself are known, such as the elastic, mechanical, and thermodynamical properties [6, 15, 16, 17], rather than the bulk material properties that describe the bulk behaviour of $NaBH_4$ either as a powder or granules. Only one paper known tests the internal friction and cohesion of $NaBH_4$ granules in order to simulate it using a discrete element method [18], but more testing is necessary to expand and validate the data.

Several papers report on the effect of moisture and temperature on $NaBH_4$, most notably that the material shows deliquescence and tends to begin to cake together when exposed to air somewhere between 19 - 31% RH [10, 11, 21, 22]. Caking significantly affects the mechanical properties of materials, so the key factors influencing caking in materials similar to $NaBH_4$ have been identified. Temperature and humidity are identified as the main factors, with particle size playing a secondary role [23]. The upcoming chapters delve deeper into the research on how ambient humidity affects the moisture content of $NaBH_4$ and how this subsequently influences the mechanical properties of $NaBH_4$.

3. Materials and methods

This chapter starts by providing some information on the source, storage, and particle size distribution of the $NaBH_4$ powder and granules used during this study. The following subchapter aims to provide clarity on the selection of experiments that are used answer the main research question and sub-questions. It also outlines the procedures followed in the experiments, the variables used, and the role of each experiment in understanding the mechanical properties of $NaBH_4$.

3.1. Materials

The sodium borohydride ($NaBH_4$) powder and granules used in the experiments were sourced from CPH Chemicals B.V. To prevent external conditions from impacting the material, they were stored in sealed polyethylene bags, which were further placed inside large, airtight iron drums. A size comparison of the powder and granules used in the experiments can be seen in *Figure 5*.

Figure 5.
(left) $NaBH_4$ powder, particle size 180-480 microns [24] and (right) granules, particle size 1.2 – 3.0 millimetres [25].

Both the powder and granules underwent a sieving process to validate particle size distribution. The cumulative frequency distribution resulting from this process for the granules and powder is depicted in *Figure 6*. The granules predominantly fell within the range of 1.2-3.0 mm, with over 90% of the material fitting this specification. Similarly, for the powder, over 90% of the material ranged between 180-480 microns.

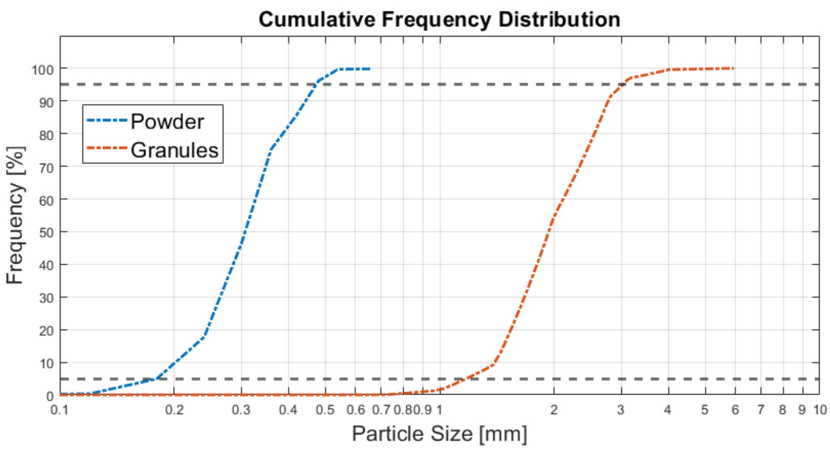

Figure 6. *Average cumulative frequency distribution of $NaBH_4$ granules and powder. The dashed horizontal grey lines represent the bracket which contains 90% of the cumulative frequency distribution.* Data provided by M.C. van Benten.

3.2. Experiments: which, why, and procedures

Although ambient humidity does not directly influence the bulk material properties of $NaBH_4$ powder and granules, it does indirectly affect them through its impact on moisture content. Therefore, understanding the effects of ambient humidity on the moisture content of a material are crucial to understand the bulk material properties of that material. Once the relationship between ambient humidity and moisture content is established, the effect of moisture content on the bulk material properties can then be measured to get an insight on how ambient humidity affects the bulk material properties of $NaBH_4$.

To determine the effects of ambient humidity on the moisture content of $NaBH_4$ powder and granules, two experiments are used: the Dynamic Vapor Sorption test and the Moisture Depth test. Subsequently the effects of moisture content on the bulk material properties of $NaBH_4$ are determined by performing two other experiments: The Ring Shear test and the Dry-Wet-Dry test.

The Dynamic Vapor Sorption test evaluates the moisture absorption rate of a material by monitoring the weight changes of a small sample (between 1 mg and 4 g) as it is exposed to progressively higher humidity levels at a fixed temperature. However, due to the small sample size used in this test, it does not provide a comprehensive picture of how bulk $NaBH_4$ powder and granules would respond to varying humidity. Therefore, a Moisture Depth test is also performed.

In a Moisture Depth test, multiple tubes containing different amounts of material are exposed to constant temperature and humidity levels. The weight of each sample is recorded at certain time intervals to determine the amount of moisture absorbed. The use of tubes with varying sample heights also enables the assessment of moisture penetration depth at different time intervals. The test is repeated using different combinations of humidity and temperature, such that variations in moisture content and penetration can be measured.

A Ring Shear test aims to identify the bulk material properties at varying moisture content levels by measuring the required shear load to failure of the material at several normal loads. These measurements are then used to determine the bulk material properties.

Finally, the Dry-Wet-Dry test is performed to ascertain whether a dry sample of $NaBH_4$ granules or powder maintains the same bulk material properties as material that has been dried after experiencing elevated moisture content levels. This test provides valuable insights into whether the material can be dried to regain its original mechanical properties if it becomes exposed to moisture during storage or handling.

The results gathered from all these tests, as summarized in *Table 1*, should offer a thorough understanding of how varying levels of humidity influence the bulk material properties of $NaBH_4$, in both its powder and granules form.

The following subchapters contain the test procedures of each proposed test.

Table 1. *Tests and test outputs.*

Test	Test output
Dynamic Vapor Sorption test	- Moisture sorption rate - Moisture desorption rate - Maximum total sorption * At varying humidity levels
Moisture Depth test	- Moisture penetration rate - Maximum total sorption * At high humidity level
Ring Shear test	- Consolidation stress - Unconfined yield strength - Flowability - Linearized yield locus - Internal friction at steady-state flow - Effective angle of internal friction - Cohesion
Dry-Wet-Dry test	- Moisture sorption - Moisture desorption - Change in material properties

3.2.1. Dynamic Vapor Sorption test procedure and settings

A Dynamic Vapor Sorption test (DVS) quantifies the rate of moisture uptake and loss of a material by directing Nitrogen gas at several specified relative humidity (RH) levels at constant temperature over a sample suspended from a weighing mechanism. The moisture sorption and desorption rate of the material is measured by weighing the sample during an extended period of time under varying humidity conditions.

-**Test procedure**-

Prior to initiating the test procedure, calibration of the DVS instrument to a known standard, such as 'ASTM E2551-20 – Standard Test Methods for Humidity Calibration (or Conformation) of Humidity Generators for Use with Thermogravimetric Analysers' [26], is performed in accordance with the specifications provided by the manufacturer. A dry sample, between 1 mg and 4 g, is then loaded into the sample pan of the DVS instrument, and its initial mass is recorded. Test parameters such as test temperature, range of RH to be tested, and rate of change of RH are configured in the DVS software provided by the manufacturer. The machine subsequently runs a baseline measurement at 0% RH to establish a starting point for the test. The RH is then adjusted to the first test point and maintained until equilibrium is achieved or a predetermined time has elapsed. During this period, the mass of the sample is recorded at regular intervals to determine moisture sorption. Upon reaching equilibrium or after a certain amount of time has passed, the RH is adjusted to the second test point and the process repeats until all test points have been examined. A schematic sketch of a DVS test can be seen in *Figure 7*.

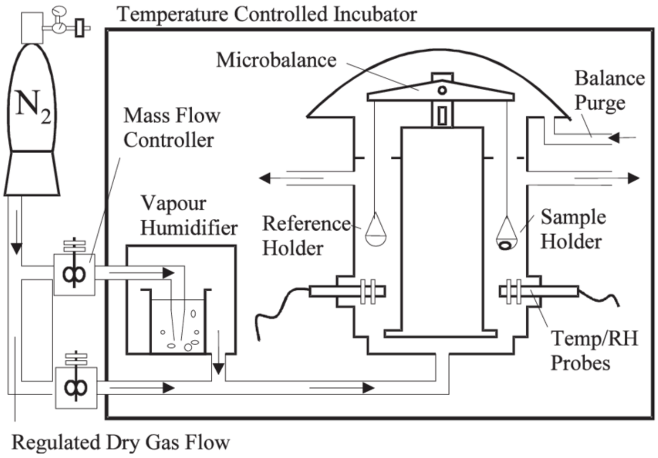

Figure 7.
Schematic sketch of a Dynamic Vapor Sorption test instrument.
By Janz et al. *[27]*

-**Test settings**-

The DVS machine used during the test is model *"IGAsorp HT"* by *Hidden Isochema Ltd.*, it can be seen in *Figure 8*. Typically, during a DVS test the RH is incrementally increased until it reaches a maximum, after which it is incrementally decreased back to 0% as this process measures the sorption and desorption isotherms of the sample separately. However, since $NaBH_4$ reacts when sufficient water is present, it was decided that after each increase in RH, the RH would first be maintained back at 0% until equilibrium was achieved or 90 minutes had passed. This approach ensures that $NaBH_4$ measurements are taken during desorption, rather than potentially measuring the desorption of the reacted material, $NaBO_2(x \cdot H_2O)$. The maximum time interval of 90 minutes was chosen by Delft Solids Solutions B.V. to limit the total test time. The maximum RH was set at 90%, which was the maximum of the machine, to gather data across the full available RH range. The RH steps were set at 5% to create a variety of data points while limiting the total test time. The test settings used during the DVS test can be seen in *Table 2*.

Table 2. *DVS test settings.*

Parameter	**Value**
Initial mass	61 mg
Test temperature	20 degrees Celsius (default)
Maximum RH	90% (max of device)
RH steps	5%
Maximum time interval	90 minutes
Test location / performed by	Delft Solids Solutions B.V.
DVS machine model	IGAsorp HT by Hidden Isochema Ltd.

Figure 8.
DVS machine used during test. Model IGAsorp HT, by Hidden Isochema Ltd.
Photo by Delft Solids Solutions B.V.

3.2.2. Moisture Depth test procedure and settings

A Moisture Depth test quantifies the rate of moisture uptake and the depth of moisture penetration within a sample. This is achieved by monitoring the weight of tubes, each filled with different quantities of material, over an extended period of exposure to a predetermined temperature and humidity level. The test necessitates a setting with a stable temperature and humidity, which could be provided by a climate-controlled room or an environmental chamber. It also requires the use of several test tubes, all having the same surface area for the hole. There is no documented international test standard regarding the test procedure, as the method test is recently created by Delft Solids Solutions B.V.

-**Test procedure**-

The test begins with the adjustment of a temperature and humidity-controlled environment to the required parameters. A series of test tubes of the same diameter and known weight are labelled and individually weighed. Each tube is filled with fresh, dry material, with varying quantities allocated to each tube, resulting in differing material heights. The material height and weight of each tube are documented. Subsequently, the test tubes are placed in the regulated environment, subjecting the material to the predetermined conditions. The weight of each tube, along with any increase, is measured and recorded at regular intervals. The test proceeds until a mass equilibrium is reached in the most filled tube or until a specified duration has elapsed.

-**Test settings**-

Throughout the course of the test, an environmental chamber accommodated six simultaneous tests. Each test comprised a set of six 3D printed tubes. To prevent material leakage, as the 3D printed tubes were not watertight, stickers were affixed to the bottom of each tube. Three sets of tubes were filled with powder, and three sets were filled with granules. This arrangement facilitated the concurrent testing of both granules and powder under identical test settings, thereby enhancing data reliability through multiple measurements of each material type. The test setup for the powder-filled tubes is depicted in *Figure 9*.

Figure 9.
Test setup of three simultaneous identical moisture depth tests of $NaBH_4$ powder.
Photo by Delft Solids Solutions B.V.

A consequence of utilizing 3D printed tubes, which lacked watertight properties at the base, was the visible presence of moisture on the sticker affixed to the bottom of each tube. This observation indicated that moisture had permeated to the base of the tube. By recording the time at which this occurred, it was possible to measure the duration required for moisture to traverse through the material.

However, upon moisture reaching the base of the tube, further weight measurements could not be conducted. The reason being that water would commence leaking, rendering any subsequent weight measurements invalid. Despite this, some tubes remained in the cabinet after moisture had permeated to their base. This allowed for visual observation of the effects resulting from extended exposure to moisture.

Tubes with holes of 50 mm diameter were created as these size tubes would have been able to be inserted into a rheometer to determine possible caking depth, however due to the lack of watertight properties this test could not be performed. The maximum tested weight, 80 grams, was also chosen with the rheometer test in mind and the other weights were chosen to gather data at regular weight intervals.

A RH of 60% and temperature of 40 degrees Celsius are chosen as these are the maximum settings the test cabinet could hold when regularly opened for measurements and thus these settings give the maximum / most extreme achievable real-world conditions.

The settings of the Moisture Depth tests can be seen in *Table 3*.

Table 3. *Test Parameters for Moisture Depth test*

Parameter	**Value**
Number of tubes per test	5
Weight of material in test tubes	10, 20, 40, 60, 80 grams
Tube hole diameter	50 mm
Temperature	40 degrees Celsius
RH	60%
Test duration	100 hours
Measurement times	Every hour for first day Then every following day at: 9:00 AM 1:00 PM 5:00 PM
Test location / performed by	Delft Solids Solutions B.V.

3.2.3. Ring Shear test procedure and settings

The Ring Shear test is a method used to determine various mechanical properties of a material, including consolidation stress, unconfined yield strength, the effective angle of internal friction, angle of internal friction at steady-state flow, and linearized yield locus. These properties are determined by measuring the shear load at which the material begins to flow under a specific compressive force after being pre-loaded and pre-sheared.

-**Test procedure**-

The complete test procedure is outlined in 'ASTM standard D-6773 – Standard Test Method for Bulk Solids Using Schulze Ring Shear Tester' [28]. The Ring Shear test begins with the filling of a ring shear cell with a loose, uncompacted specimen of the material to be tested. Care must be taken to remove any excess material from the cell without exerting downward pressure on the material. Subsequently, the cell is weighed, loaded onto a Ring Shear test device, and topped with a cell lid. The hanger, which will exert a downward pressure during testing, is then attached to the cross-beam after which the counterweight is also attached. Tie rods are employed to maintain the lid its stationary position and measure the applied shear force during the test. The test procedure itself comprises two steps:

- The initial step involves pre-loading the material by consolidating it inside a shear cell using a compressive force applied by the Ring Shear tester. The compressive pressure, selected in the control program of the Ring Shear tester, simulates varying depths of material in a large storage silo. A shear force is then applied by the machine by rotating the shear cell while keeping the lid stationary until the material yields / shears. The shear forces are measured to determine pre-shear loads and pressures. Following material yield, counter rotation of the shear cell removes the shear force, enabling execution of the second step of the test.
- In the second step of the Ring Shear test, the compressive force is decreased until a predetermined load pressure test-point is reached. The shear cell is then rotated again until the material inside fails and exhibits steady-state flow. The force required to shear the material is measured to determine the shear pressure and yield locus at this compressive force, as seen in *Figure 10*.

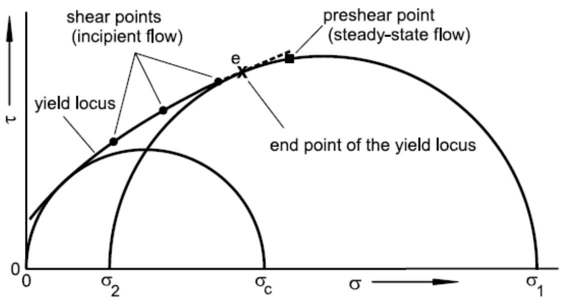

Figure 10.
Preshear point and shear points used to create yield locus and Mohr stress circles.
By Dietmar Schulze *[29]*

Repetition of these two steps continues until all test-points have been measured. Upon completion of the test, the compressive force is released, allowing for removal of the sample from the shear cell. The mechanical properties of the material are subsequently calculated using the pre-shear data points and measured yield locus points.

A setup for a filled ring shear test can be observed in *Figure 11*.

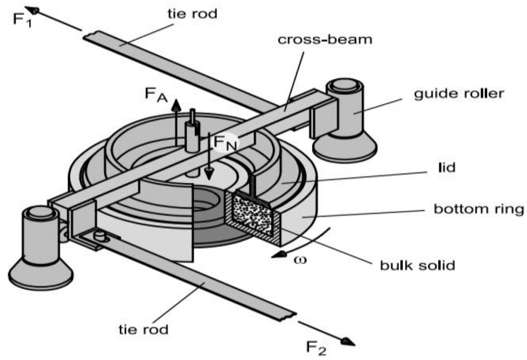

Figure 11.
Shear cell setup of a Schulze ring shear tester.
By Dietmar Schulze *[29]*

-**Material preparation**-

The Ring shear tester used during the test is model RST-01.pc by Dr. Dietmar Schulze GmbH, it can be seen in *Figure 12*. To prepare the material for the Ring Shear test, as material with elevated moisture content levels is used, 600 grams of dry granules and powder are placed in separate 12-litre buckets, along with an open container containing 15% of the mass of granules/powder in water. The schematic can be seen in *Figure 13*. 15 wt% water was chosen as this gave a consistent 7-9 wt% moisture content after 7 days during preliminary tests. The buckets are then sealed and left for 7 days at 30 degrees Celsius (ambient temperature) to allow the powder and granules to absorb moisture. After 7 days, the material is diluted and mixed with fresh material to achieve an exact moisture content of 6 wt%. Moisture contents of 4 wt% and 2 wt% are created by further diluting and mixing the moist material with fresh material, after the prior moisture content material is tested.

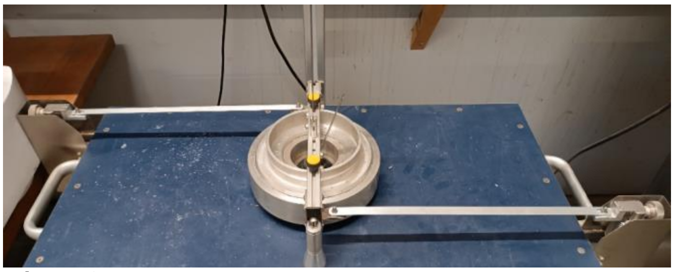

Figure 12.
Ring Shear tester used during tests. Model RST-01.pc by Dr. Dietmar Schulze GmbH.
Photo by M.C. van Benten

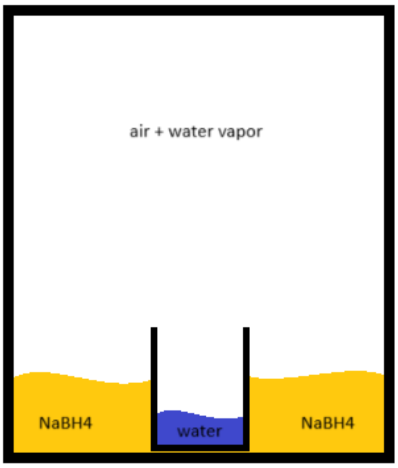

Figure 13.
Schematic overview of exposing $NaBH_4$ to humidity in enclosed environment.

-**Test settings**-

Both granules and powder were tested at normal stresses of 4, 8, and 16 kPa. For granules, moisture levels of 0, 2, 4, and 6 wt% were used, while the powder was tested at moisture levels of 2, 4, and 6 wt%. Only three tests were performed on the powder with 0 wt% moisture at a normal stress of 4 kPa due to inconsistent data and time constraints caused by stick-slip behaviour at greater normal stresses.

Each test is performed three times to evaluate the spread of the data. A total of 66 tests were conducted, the test matrix can be seen in *Table 4*. Each of the tests were performed using the shear data points seen in *Table 5*.

Table 4. *Test matrix for Ring Shear tester. *Data provided by M. C. van Benten.*

	Moisture levels	Preshear stresses	Repetitions
$NaBH_4$ granules	0*, 2, 4, 6 wt%	4, 8, 16 kPa	3
$NaBH_4$ powder	2, 4, 6 wt%	4, 8, 16 kPa	3
$NaBH_4$ powder	0* wt%	8 kPa	3

Table 5. *Normal stress measure points for each preshear stress used during testing (see Table 3).*

Preshear stress	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**	**Point 6**
4 kPa	400 Pa	600 Pa	800 Pa	1600 Pa	2400 Pa	3200 Pa
8 kPa	800 Pa	1200 Pa	1600 Pa	3200 Pa	4800 Pa	6400 Pa
16 kPa	1600 Pa	2400 Pa	3200 Pa	6400 Pa	9600 Pa	12 kPa

All Ring Shear tests were performed at the GranChaMlab (Granular Characterisation and Modelling lab) inside 3mE, TuDelft, by me, B. Romijn, and M.C. van Benten.

3.2.4. Dry-Wet-Dry test procedure and settings

In the absence of an international test standard to assess whether the mechanical properties of a material remain unchanged after exposure to moisture and subsequent drying, we devised the Dry-Wet-Dry test. This new and inhouse developed test procedure is designed to determine if the bulk material properties of $NaBH_4$ granules and powder remain unchanged after being exposed to moisture and then dried, compared to when it is dry. This is achieved by performing a Ring Shear test on dry $NaBH_4$ granules and powder, after which the powder and granules are exposed to moisture and subsequently dried to perform another Ring Shear test. This allows for a comparative analysis of any changes in the mechanical properties.

-**Test procedure**-

The test procedure involves conducting a Ring Shear test on dry material, the details of which are outlined in the preceding subchapter. The data collected from this test is then stored. Subsequently, the moisture content in the material is increased by placing it inside a sealed bucket that contains a separate container filled with water for an extended duration. Once the material has absorbed the desired amount of moisture, it undergoes another Ring Shear test to confirm changes in its mechanical properties. Following this, the material is dried using an oven until the rate of mass loss becomes negligible, indicating that all volatile components, such as water, have been eliminated. If feasible, the material is then subjected to another Ring Shear test to verify whether it has regained its original mechanical properties or if they have altered.

-**Test settings**-

The test is performed by using 470 grams of material, enough to perform a Ring Shear test at and have some material in reserve. The normal force of the Ring Shear tester was set at 8kPa, the test points can be seen in *Table 5*. After the Ring Shear test, the material is placed in a 12-liter bucket. A smaller open container, around half a litre in size and containing 15 wt% water compared to the initial mass of $NaBH_4$, is placed inside the bucket on the bottom, with the $NaBH_4$ being moved around the container, as seen in *Figure 13*. After a second ring shear test with the same normal stress of 8 kPa the material is put inside a metal tray to be placed in the oven. The oven is kept at 55 degrees Celsius and after 24 hours the sample is taken out. Further ring shear tests were impossible, as the material had completely clumped together into a brick.

The Dry-Wet-Dry tests were performed at the GranChaMlab (Granular Characterisation and Modelling lab) inside 3mE, TuDelft, by me, B. Romijn.

4. The effects of ambient humidity on the moisture content of $NaBH_4$

Considering the limited information available on the mechanical properties of $NaBH_4$, as outlined in Chapter 2, and the influence of moisture content on the mechanical properties, this chapter will focus on investigating the effects of ambient humidity on the moisture content of $NaBH_4$. To this end, three tests, which are outlined in Chapter 3, were conducted: a Dynamic Vapor Sorption test to determine the effects of varying levels of humidity on a small amount of powder and granules, a Moisture Depth test to determine the moisture penetration depth in $NaBH_4$ powder and granules at an elevated ambient humidity and temperature level, and a Dry-Wet-Dry test to investigate how much moisture the material would attract in a closed container with a separate open container of water inside and whether the $NaBH_4$ granules and powder would return to its original dry state when dried.

This chapter is divided into two subchapters. The first subchapter presents and discusses the results of the three conducted tests. The second subchapter explores the variance in moisture absorption between $NaBH_4$ powder and granules in open and closed storage containers. This is pertinent as the Dynamic Vapor Sorption and Moisture Depth tests mimic moisture sorption in open storage containers, while the Dry-Wet-Dry test replicates conditions in closed storage containers.

4.1. Test results

The following three subchapters provide a comprehensive presentation and discussion of the results from the Dynamic Vapor Sorption test, Moisture Depth test, and Dry-Wet-Dry test. Each subchapter begins with a thorough examination of the various observations made during the respective test. This is then followed by a summarization of the most significant observations and their relations.

4.1.1. Dynamic Vapor Sorption test

The first test is the Dynamic Vapor Sorption test, which aims to determine the effects of varying levels of humidity on a small amount of material.

Results

Several observations can be made from the data, firstly and most importantly that the rate of mass change (

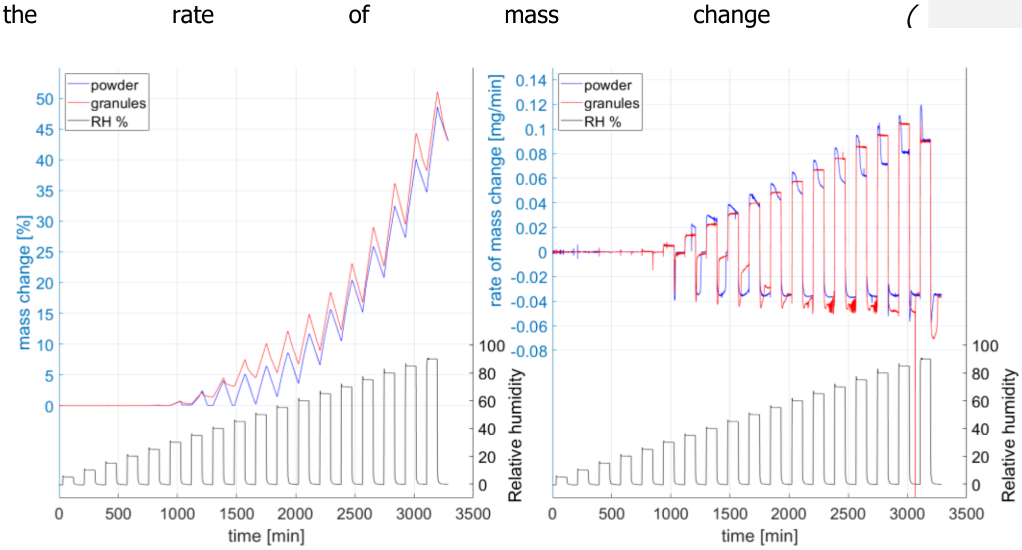

*Figure **14**, right)* during elevated RH levels out above 0 mg/min for both granules and powder which indicates that uptake rate of moisture does not decrease over time within the 90 minutes test window. Most other materials would show a continued decrease in moisture uptake rate up to 0mg/min during a Dynamic Vapor Sorption test as the moisture content in the material forms an equilibrium with the environment [30], but $NaBH_4$ granules and powder seems to keep attracting moisture when it is available.

The second observation is that both the granules and the powder start to increase in mass at 25% RH, which is not quite visible in

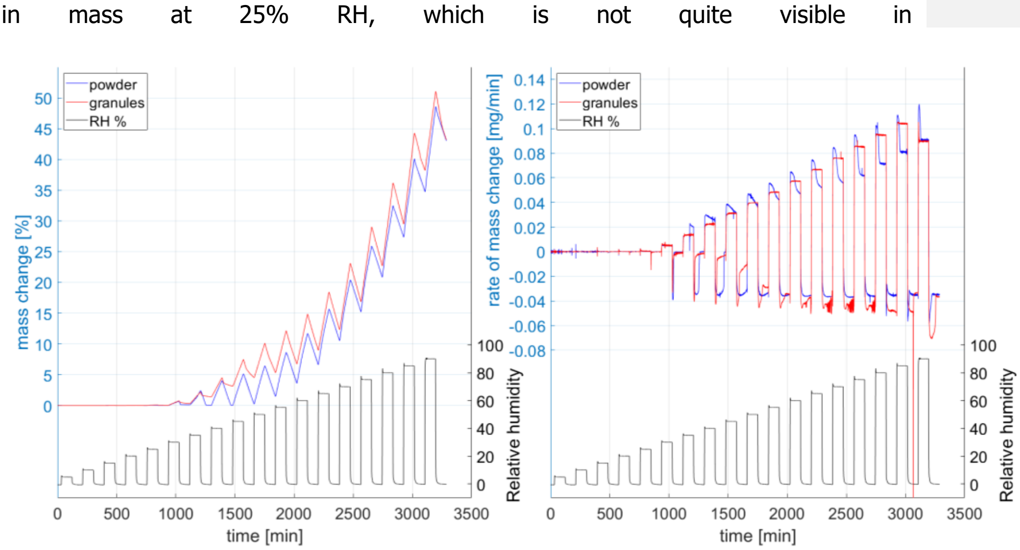

Figure ***14***. However, the data used to generate

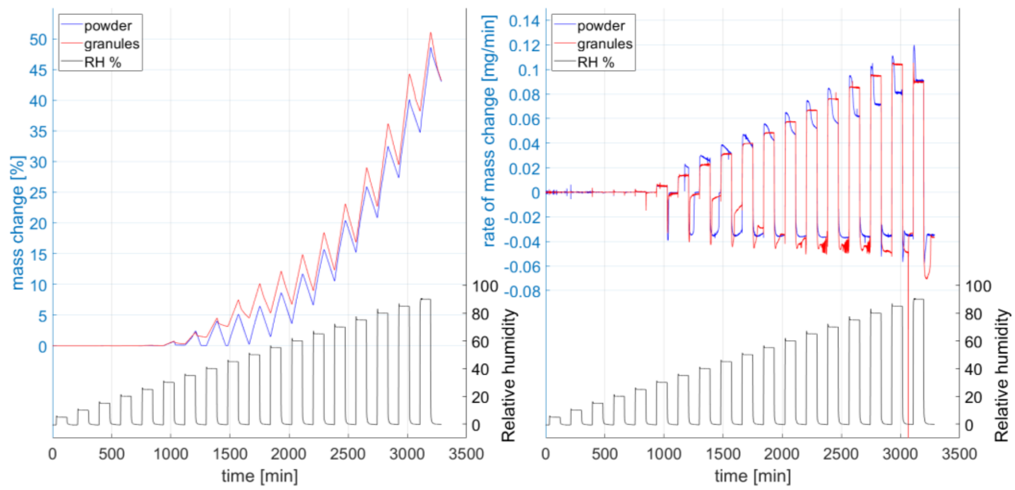

Figure ***14*** shows that the average rate of mass change for the powder at 25% RH is 1.5 µg/min, while the granules have an average rate of mass change of 4.5 µg/min. The rate of mass change becomes more noticeable at 30% RH and keeps increasing linearly from that point forward up to 0.1 mg/min at 90% RH.

Importantly, the material does not revert back to 0% mass change, back to a dry sample, when exposed to air with no humidity after exposure to elevated humidity. This leads to subsequent test cycles to not start with dry material, thus possibly skewing subsequent test results.

The powder seems to have a higher initial rate of mass change when the cycle changes back to high humidity, but this decreases over time to a level under that of the more stable uptake rate of granules. In the end granules have a slightly higher rate of mass change and overall mass change.

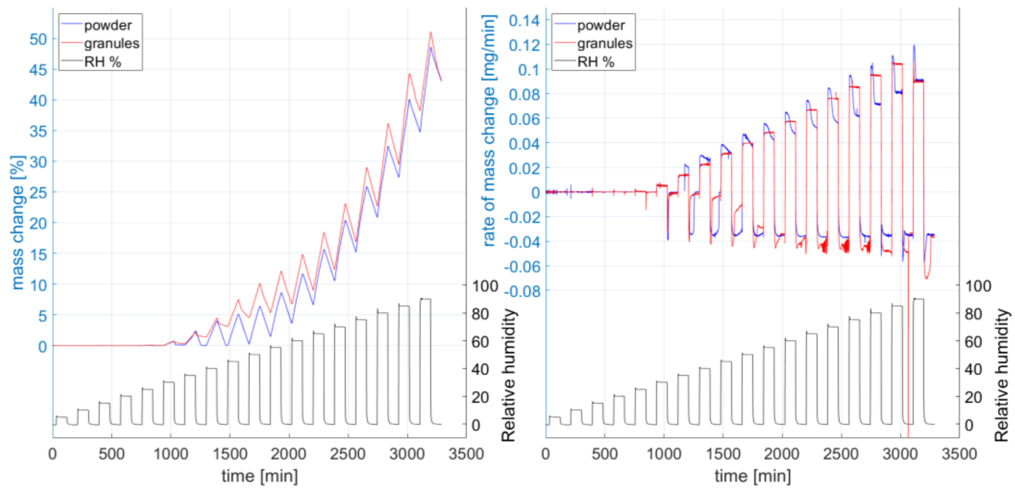

Figure 14.
(left) Mass change over time and (right) rate of mass change, in % of original sample weight, of $NaBH_4$ granules and powder when exposed to varying levels of ambient humidity. (The black lines in both show the relative

humidity during the test. From 5% - 90% RH in steps of 5%. Intervals of 90 minutes elevated RH, followed by 90 minutes of 0% RH.

Lastly, the rate of mass change during 0% RH quickly stabilizes for powder at negative 35 µg/min, showing that the discharge rate of moisture from $NaBH_4$ powder is not dependent on the amount of moisture present on the sample itself. $NaBH_4$ granules on the other hand have a lower discharge rate when the mass change is low, while increasing when the mass change increases. Eventually the rate of mass change seems to settle at minus 45 µg/min, which is higher than the powder, but still a lot less than then uptake rate during moisture exposure.

At 3065 minutes the rate of mass change for the granules seem to suddenly jump down to negative 0.29 mg/min during 0% RH, which exceeds the previously achieved stable negative 45 µg/min more than sixfold. This is believed to be an error or a disturbance during the experiment, as the subsequent rate of mass change for the granules does not seem to follow the same trajectory that the previous cycles seem to show. Further experiments would have to be run to validate the error.

Summary

In summary, the results of the tests indicate that the rate of mass change for both $NaBH_4$ granules and powder increases linearly as the ambient humidity increases, starting at 25% RH. The rate of mass change during exposure to humidity stabilizes at a positive value, depending on the RH, indicating that the material continues to absorb moisture indefinitely from its surroundings within the tested timeframe. When exposed to 0% RH after exposure to moisture, the release of moisture from both $NaBH_4$ powder and granules appears to plateau at negative 35 µg/min and negative 45 µg/min, respectively, regardless of the amount of previously gained moisture or previous humidity level. Lastly, the mass change of the material does not revert back to 0% after a test cycle of elevated humidity and no humidity. This could skew the results, especially when subsequent cycles start at elevated mass change, but further tests would have to be performed to validate how much, if any, this affects the results.

4.1.2. Moisture Depth test

The Moisture Depth Test is used to determine the moisture penetration depth in $NaBH_4$ powder and granules at an elevated ambient humidity and temperature level.

Results

The data on rate of mass change per hour gathered during the Moisture Depth test is presented in *Figure 15*. The results indicate that for both granules and powder, the rate of mass change is higher during the first few hours of the experiment compared to the remainder of the test. The rate of mass gain eventually stabilizes for both particle sizes, with the rate of mass change for powder being slightly higher initially at 0.5 g/h before stabilizing at a similar rate to that of granules at 0.4 g/h. The rate of mass change for both powder and granules is independent of the initial mass, likely due to the same surface area being exposed to the humid environment. The vertical lines in *Figure 15* indicate the average time at which the tubes with similar initial mass show moisture on the bottom. It shows that moisture travels faster through powder than through granules, as after 35 hours, only the tubes containing 80 grams of powder had not yet shown moisture on the bottom. In contrast, only the tubes with 10 and 20 gram of granules showed moisture on the bottom of the tube after 35 hours.

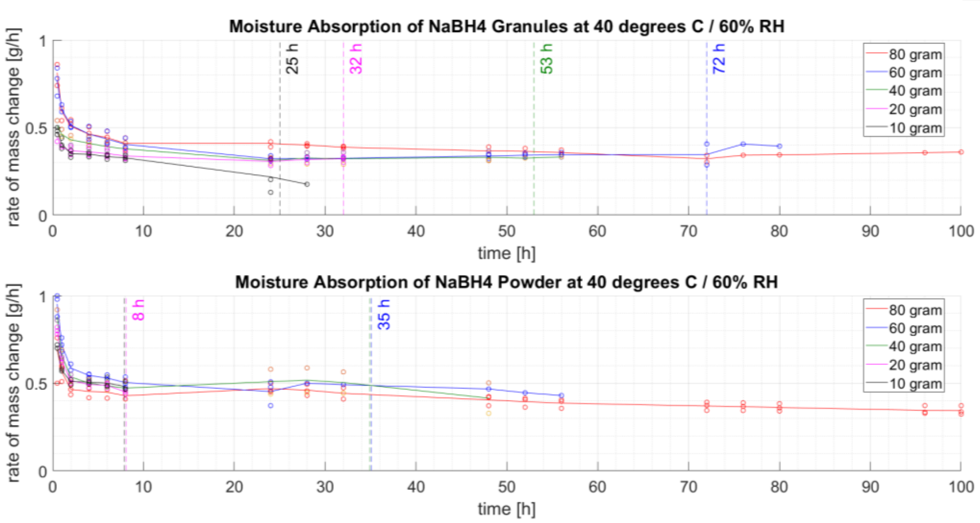

Figure 15.
The rate of mass change per hour of $NaBH_4$ granules (top) and powder (bottom) when exposed to 40 degrees Celsius, 60% relative humidity. The vertical lines (visual observations made by Delft Solids Solutions) show at which average timestep the tubes with similar mass show signs of moisture on the bottom.

Figure 16 shows the rate in mm/hour at which moisture travels through $NaBH_4$ powder and granules. It can be noted that granules exhibited a smaller rate at which moisture travelled through the material than powder as the powder had an average moisture depth penetration rate of 1.286 ± 0.409 mm/hour while the granules had an average moisture depth penetration rate of nearly half that, at 0.6827 ± 0.143 mm/hour. This is possibly due to the higher contact surface area of powder compared to granules, enabling the moisture to travel faster into the material by capillary motion. This could also explain the slightly higher rate of mass change of powder compared to granules which can be seen in *Figure 15*.

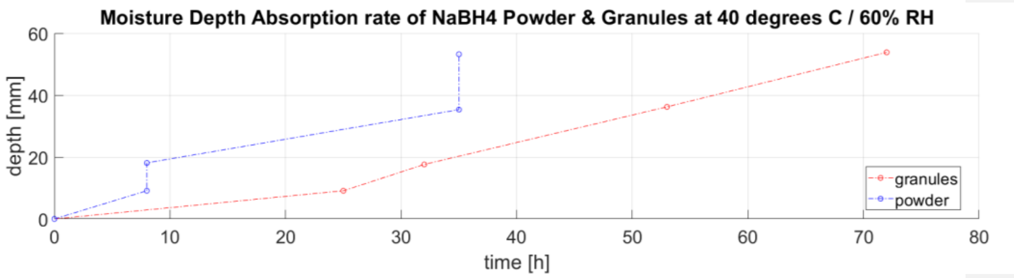

Figure 16.
The rate at which moisture travels through $NaBH_4$ powder and granules.

During the experiment, several noteworthy visual observations were made:

- Both the granules and the powder caked together and lost their ability to flow after just one hour. It is unknown if this was just the top layer of the material or if the caking occurred over the full depth of the tubes.
- Two hours into the experiment, the granules began to visually lose their shape and started to clump together due to the absorption of moisture and subsequent reaction of the material.
- By the end of the experiment, the granulated $NaBH_4$ had transformed into a shaved ice-like consistency from top to bottom, while the powder had formed a solid chunk and was completely submerged in water. Both can be seen in *Figure 17.* Interestingly, even while submerged, the chunk of powder continued to attract water with its mass increasing at 0.5 g/h, a similar rate as during earlier measurements, which can be seen in *Figure 15.*

Figure 17.
$NaBH_4$ powder (left) and granules (right) after running the Moisture Depth test.
Photo by Delft Solids Solutions B.V.

Summary

In summary, the Moisture Depth test aimed to determine the rate at which moisture travels through $NaBH_4$ granules and powder when exposed to humidity. The results showed that the rate of mass gain was initially higher for both granules and powder, before stabilizing at a similar rate. Additionally, both the granules and powder caked together and lost their ability to flow after just one hour of exposure to humidity. However, it is unknown if this caking occurred over the full depth of the tubes or just the top layer, further research will have to be done to verify if the material in deeper layers remains free flowing. Lastly, by the end of the experiment both granules and powder continued to attract moisture at a similar rate as earlier in the test at 0.5 g/h and 0,4 g/h, respectively.

4.1.3. Dry-Wet-Dry test

The Dry-Wet-Dry test is used to determine how much moisture the material would attract in a closed container with a separate open container of water inside and whether the $NaBH_4$ granules and powder would return to its original dry state when dried.

Results

The first test with $NaBH_4$ powder gained 5.16 wt% in moisture after 3 days in storage while the temperature inside the bucket remained between 26-30 degrees Celsius. The humidity inside the bucket rose to 30% RH and remained stable until the bucket was opened. When opened, nearly half of the initial water was still in the container and only the top layer of material appeared to have caked together, while the material under the caked layer flowed freely. The caked layer itself was easily broken up back into a powder by applying some force by hand. A change in bulk material properties was verified by the Ring Shear tester and the material was subsequently placed into the oven at 55-110 degrees Celsius for 24 hours. However, when the sample was taken out of the oven, it had become a solid brick, as seen in *Figure 18*, meaning that further Ring Shear tests were impossible.

Figure 18.
Dried $NaBH_4$ powder after exposure to 5 wt% moisture.

The test with powder being exposed to moisture in an enclosed environment was repeated three times, once for 1 day, once for 6 days, and once during preparation for the Ring Shear test for 7 days. The temperature in the bucket remained between 26-30 degrees Celsius in all tests and the humidity in the bucket rose to 30% RH in all tests. The 30% RH number corresponds to the RH at which $NaBH_4$ was observed to start attracting higher levels of moisture in the Dynamic Vapor Sorption test, which could indicate an equilibrium between moisture evaporation from the water container and moisture absorption by the $NaBH_4$. All tests resulted in the same caking behaviour as the 3-day test, where the top layer of the material would be firm and caked together, while deeper layers of the material would be free-flowing. It was also noted that the wt% moisture absorption during the 1-day test was 3.5 wt%, 6.5% during the 6-day test, and 7.0% during the 7-day test.

After drying, the powder formed solid bricks again, preventing any Ring Shear tests from being conducted on the dried material. The granules showed similar behaviour, but the test was only repeated once with 6 days in the bucket, gaining around 8 wt% moisture. The test with granules was only performed once, because the material also came out of the oven as a brick and subsequent tests were considered wasteful for the material.

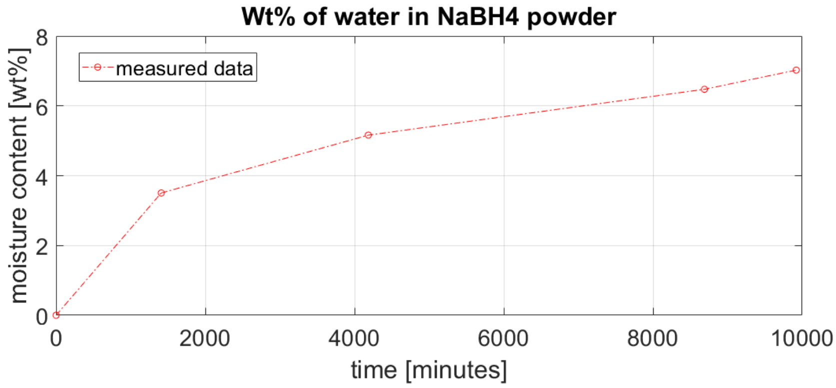

Figure 19.
Wt% of water absorbed by $NaBH_4$ powder in a closed container with an open water container inside.

Summary

In summary, three Dry-Wet-Dry tests were conducted with $NaBH_4$ powder and one test with granules. Both the powder and granules turned into hard bricks when dried, rendering them unusable for further Ring Shear tests. This suggests that $NaBH_4$ does not revert to its initial bulk material properties when dried after being exposed to moisture, likely due to a change in the physical structure of the powder and granules as observed during the Moisture Depth test. A noteworthy finding was that the interior of the closed bucket containing $NaBH_4$ powder or granules and an open container with 15 wt% water stabilized at 30% RH at 30 degrees Celsius. Furthermore, it was observed that not all the water inside the container migrated to the $NaBH_4$ during any of the tests, even during the longest test which lasted for 7 days. Additionally, the rate at which moisture was absorbed by $NaBH_4$ powder appeared to decrease over time, as can be seen in *Figure 19* and, in contrast to observations made during the Moisture Depth test and the Dynamic Vapor Sorption test. Further investigation is necessary to determine the saturation level of $NaBH_4$ at these temperatures and humidity levels, if one exists. Lastly, a layer of caking occurred in the closed container with the tests with granules and the test with powder. The material under the layer of caking remained free flowing, even during the 7-day test.

4.2. Open vs closed humidity environment

In the Dynamic Vapor Sorption and Moisture Depth tests, $NaBH_4$ is subjected to a continuously refreshed, humid environment, analogous to an open or externally ventilated storage container. The rate of moisture sorption remained consistent throughout these tests, even during the 100-hour Moisture Depth test, suggesting a continuous increase in moisture content, with moisture content weight percentages exceeding 50%. Post-test samples of $NaBH_4$ powder were fully submerged in water (*Figure 17, left*), yet continued to gain weight at a steady rate. Consequently, storing $NaBH_4$ in an environment with a constant supply of fresh, humid air is discouraged due to the propensity of the material to absorb excessive moisture, leading to clumping and reaction with available moisture.

The Dry-Wet-Dry and Ring Shear tests exposed the material to humidity within a closed environment containing a predetermined amount of water, simulating a sealed storage container with pre-existing humidity. These tests resulted in an internal RH stabilization at 30%, and a significantly lower rate of moisture sorption compared to the Dynamic Vapor Sorption and Moisture Depth tests. The rate of moisture sorption decreased over time (*Figure 19)*, with the moisture content weight percentage not exceeding 9% even after 7 days (168 hours). Most of the moisture content appeared to be concentrated in the top layer of material, resulting in a layer of caked material atop free-flowing material in the closed container. This contrasts with the material stored in open containers, which was uniformly affected by moisture. In summary, it is advisable to store $NaBH_4$ in a sealed environment to minimize exposure to humidity and prevent hydrolysis with moisture.

4.3. Conclusion

In conclusion, the results of the Dynamic Vapor Sorption test, Moisture Depth test and Dry-Wet-Dry test indicate that ambient humidity have a significant effect on the moisture content of $NaBH_4$.

The results of the Dynamic Vapor Sorption test indicate that the rate of mass change for small quantities of both $NaBH_4$ powder and granules (approximately 61 mg) increases linearly with increasing ambient humidity, beginning at 25% RH. The rate of mass change does not converge to zero, but instead stabilizes at a positive value. This indicates that the total moisture absorption continues to increase linearly, rather than reaching a steady value, which suggests that the material continues to absorb moisture from its surroundings within the tested timeframe of 90 minutes.

The Moisture Depth test extends this observation of a continuous elevated rate of mass change to larger quantities of $NaBH_4$ powder and granules and to a period of 100 hours, when the powder and granules are exposed to 40 degrees Celsius and 60% RH.

In contrast, during the Dry-Wet-Dry test $NaBH_4$ the rate of moisture absorption by the material decreases over time, while the humidity inside the container does not exceed 30%.

The comparison between the results of the Dynamic Vapor Sorption test and Moisture Depth test versus the Dry-Wet-Dry test suggests that storage in a ventilated container is not recommended due to excessive moisture absorption, while the use of enclosed containers may be a more viable solution. During the Dry-Wet-Dry test, it was observed that the material inside the container caked together. However, only the top layer of the material was affected, even after 6 days of exposure. In contrast, during the Moisture Depth test, the entire sample was affected by moisture after 100 hours of exposure. This could potentially be attributed to the higher humidity and temperature that was used during the Dynamic Vapor Sorption test. However, further research into storage in a ventilated container vs storage in an enclosed container in various temperatures and humidity levels is necessary to confirm this.

The method of exposing the material to moisture in an enclosed container is also used in the Ring Shear test in the next chapter, as this approach of exposure to humidity allows for a more controlled and accurate assessment of the effects of moisture content on the mechanical properties of $NaBH_4$.

5. The mechanical properties of $NaBH_4$ under varying moisture contents.

This chapter aims to investigate the mechanical properties of $NaBH_4$ under varying moisture contents. To achieve this, a Ring Shear test is performed on samples with different moisture content levels, as this test can be used to determine the mechanical properties of a material. The test procedure for the Ring Shear test can be found in Chapter 3.2.3. The test conducted in Chapter 4 demonstrate that the moisture content of $NaBH_4$ is significantly influenced by ambient humidity and when it is continuously exposed to high levels of humidity, $NaBH_4$ rapidly attracts moisture at a linear rate, resulting in undesirable changes such as changes to the shape of the particles and clumping of the particles. The method that involves subjecting the material to moisture within a sealed container, which is employed during the Dry-Wet-Dry test, is also used in the tests whose results are presented in this chapter. This is due to the fact that it offers a more predictable and less severe rate of moisture absorption. The data from the Ring Shear tests is used to determine the mechanical properties of the $NaBH_4$ powder and granules. This enables a more thorough understanding of how moisture content influences the mechanical properties of both powder and granular forms of $NaBH_4$ and highlights the distinctions in mechanical properties between these two forms.

5.1. Ring Shear test

Upon collection of the data generated by the Ring Shear test, an analysis can be performed on the 66 individual yield loci and their corresponding pre-shear points, which are shown in *Table 4*. The mechanical properties of $NaBH_4$ can be derived from the data by generating Mohr stress circle plots, as outlined in the book "Powder and Bulk Solids" by D. Schulze [29]. *Figure 20* illustrates such a standard Mohr stress circle and its derived properties.

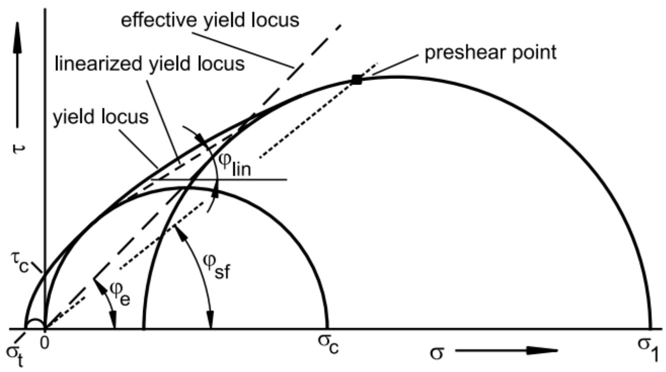

Figure 20.
Mohr stress circle and its derived properties: σ_1, the consolidation stress; σ_c, the unconfined yield strength; φ_{lin}, the slope angle of linearized yield locus; φ_{sf}, the angle of internal friction at steady-state flow; φ_e, the effective angle of internal friction; τ_c, the cohesion; and σ_t, the tensile strength.
By Dietmar Schulze *[29]*

Figure 21 depicts one such Mohr stress circle which is generated from the gathered data. After the creation of the Mohr stress circles all relevant mechanical properties can be extracted using the information found in *Figure 20*.

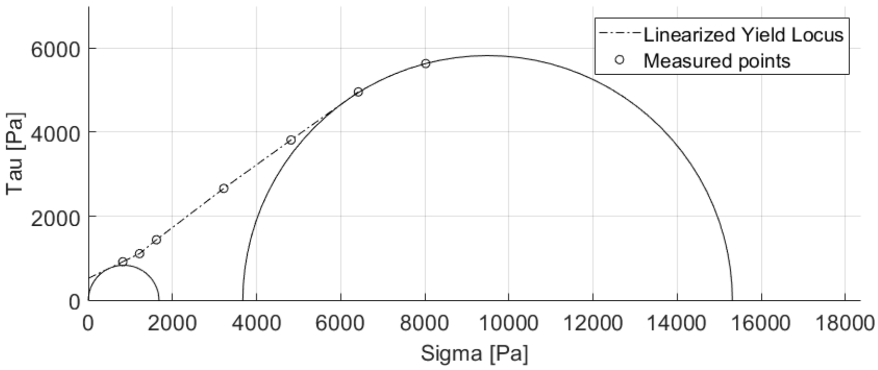

Figure 21.
Yield Locus and Mohr stress circles of $NaBH_4$ Powder at 8kPa preshear, 4 wt% moisture content.

Met opmerkingen [DS3]: Waarom lagere hellingshoek bij sigma is 0-1000

Met opmerkingen [BR4R3]: De data is linearized tussen tussen de meetpunten. De hellingshoek van de y-as naar het eerste meetpunt is gelijk aan de hellingshoek van het eerste meetpunt tot het tweede meetpunt. Vandaar dat de helling anders is van 0-1500.
Mijn matlab code kan ook de volledig linearized yield locus plotten en de desbetreffende Mohr cirkels, maar dan gaat er wel veel informatie in 1 plaatje staan dat alleen bedoeld is voor het visualiseren van een mohr cirkel van de werkelijke data.

5.1.1. Results

This subchapter presents and discusses the results of seven mechanical properties of $NaBH_4$ powder and granules. These properties include the consolidation stress, unconfined yield strength, flowability, slope angle of the linearized yield locus, angle of internal friction at steady-state flow, effective angle of internal friction, and cohesion. The focus is on visualizing these properties and examining the influence of moisture content on them.

Consolidation stress

The consolidation stress is the maximum normal stress that occurs on a plane where the shear stress is at its minimum. It is used together with the unconfined yield strength to describe the flow behaviour of bulk solids. Generally, the higher the consolidation stress gets, the better a bulk solid flow (given an equal unconfined yield strength).

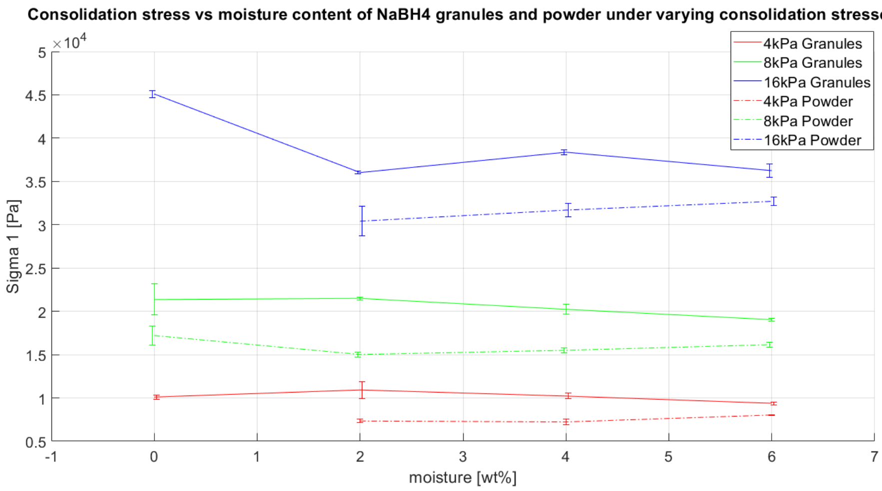

Figure 22.
Consolidation stress vs moisture content of $NaBH_4$ granules and powder under varying normal stresses

Figure 22 illustrates the relationship between moisture content and consolidation stress. It can be observed that, at each level of moisture content and normal stress, granules exhibit a higher consolidation stress than powder. This higher consolidation stress of granules is attributed to their higher shear strength at a similar normal stress, possibly due to the mechanical interlocking of larger particles within the granules. An increase in moisture content seems to have an effect of a decreasing consolidation stress on the bigger particles of the granules in contrast to an increase in consolidation stress on the smaller particles of the powder.

Unconfined yield strength

The unconfined yield strength is the maximum normal stress level that can be applied before bulk material in an unconfined state will fail in shear. Together with the consolidation stress it is used to determine the flowability of a bulk material, which will be discussed in the next subchapter.

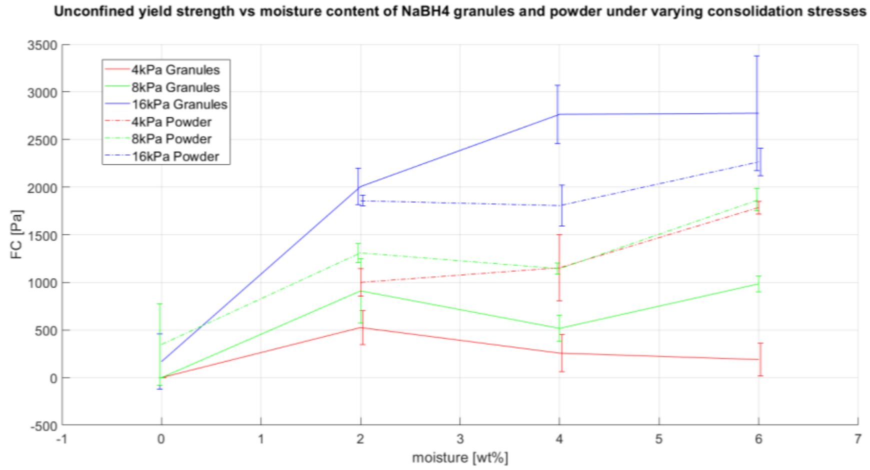

Figure 23.
Unconfined yield strength vs moisture content of $NaBH_4$ granules and powder under varying consolidation stresses.

Figure 23 presents the relationship between moisture content and unconfined yield strength. Both granules and powder exhibit a very low unconfined yield strength when no moisture is present, as observed during the handling of dry material as even after exposure to higher consolidation stresses, both materials without moisture content remain free-flowing when removed from the ring shear cell. At higher moisture content levels, the powder rapidly gains a substantial amount of unconfined yield strength, while the granules at 4 and 8 kPa consolidation stress are less affected by the moisture. This may be due to the larger surface area available for water to adhere to and interact with other particles in the powder, as opposed to the granules, which have larger particles and thus a smaller surface area. At 16 kPa, the granules suddenly gain a significant amount of unconfined yield strength, even surpassing that of the powder. It is uncertain whether this is due to mechanical interlocking at higher consolidation stresses or some interaction between the granules and moisture at higher pressures.

Flowability

Flowability is not an inherent material property, but it is the ratio between the consolidation stress and the unconfined yield strength, as can be seen in equation (3).

It represents a numerical value that indicates how well a material flows at specific consolidation stresses. The flow behaviour can be defined as follows:

- $ff_c < 1$ not flowing
- $1 < ff_c < 2$ very cohesive
- $2 < ff_c < 4$ cohesive
- $4 < ff_c < 10$ easy-flowing
- $10 < ff_c$ free-flowing

$$ff_c = \frac{major\ principal\ stress}{unconfined\ yield\ strength} \tag{3}$$

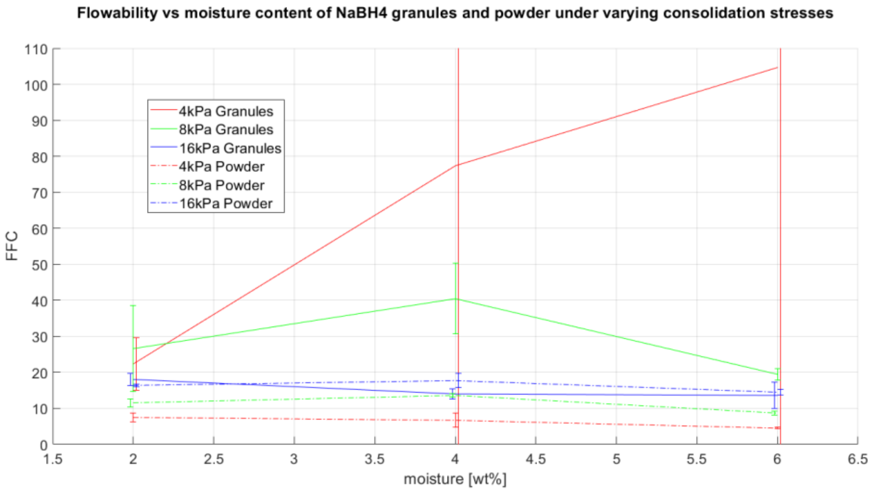

Figure 24.
Flowability vs moisture content of $NaBH_4$ granules and powder under varying normal stresses. The confidence intervals of 4kPa Granules exceed the graph due to high uncertainty.

As illustrated in *Figure 24*, all measured points remain within the free-flowing region, with two exceptions. The first exception is the entirety of powder at 4 kPa normal stress, which starts in the easy-flowing regime and transitions to the cohesive regime as moisture content increases. The second exception is the powder at 6 wt% moisture and 8 kPa consolidation stress, where the material changes from free-flowing to easy-flowing. In general, the flowability of powder seems to decrease with higher moisture content levels. Notably, the flowability of the powder increases with higher consolidation stresses, while that of the granules appears to decrease. However, the confidence interval of the granules data varies significantly, particularly at lower normal stresses and higher moisture content levels, making it difficult to verify a clear pattern from the available data.

Slope angle of the linearized yield locus

The following three figures are further flow properties that are mainly used for applications such as silo design. All three properties exhibit similar trends when the normal stress and moisture content of the material vary, due to their close interrelation.

The slope angle of internal friction, which is the angle that the yield locus makes with the σ-axis, varies along the yield locus. However, for many applications, it is sufficient to use a constant value for the internal friction. In such cases, the angle of internal friction is represented by the slope of the linearized yield locus, which is the angle of a straight-line tangent to both Mohr stress circles. *Figure 25* illustrates how the angle of the linearized yield locus changes with varying moisture content and consolidation stresses.

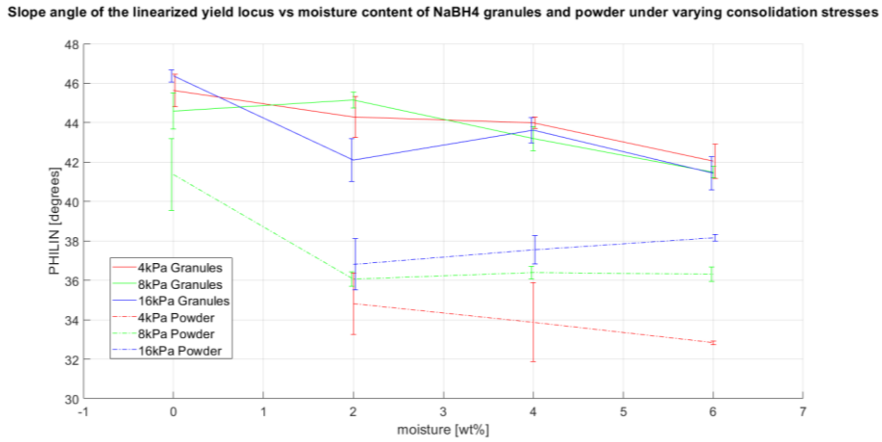

Figure 25.
Slope angle of the linearized yield locus vs moisture content of $NaBH_4$ granules and powder under varying consolidation stresses.

Angle of internal friction at steady-state flow

The angle of internal friction at steady-state flow represents the internal friction in the cutting plane parallel to the shearing velocity during steady-state flow. It is calculated from the ratio of the shear stress to the normal stress at the pre-shear point. *Figure 26* illustrates how the angle of internal friction at steady-state flow changes with varying moisture content and consolidation stresses.

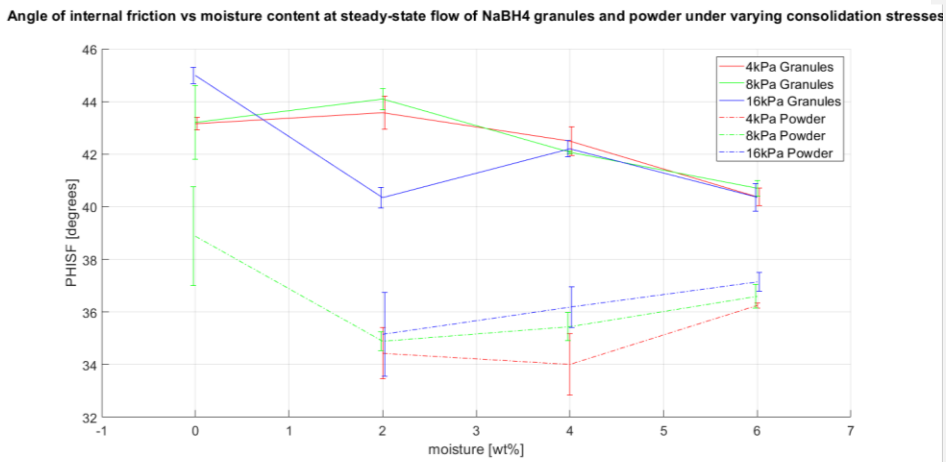

Figure 26.
Angle of internal friction at steady-state flow vs moisture content of $NaBH_4$ granules and powder under varying consolidation stresses.

Effective angle of internal friction

The effective angle of internal friction is the slope of the effective yield locus, which is represented by a straight line passing through the origin of the Mohr stress circle diagram and tangent to the larger Mohr circle. It characterizes the internal friction of the bulk solid and can also be considered as a measure of the internal friction at steady-state flow, similar to the previously measured variable. *Figure 27* illustrates how the effective angle of internal friction changes with varying moisture content and consolidation stresses.

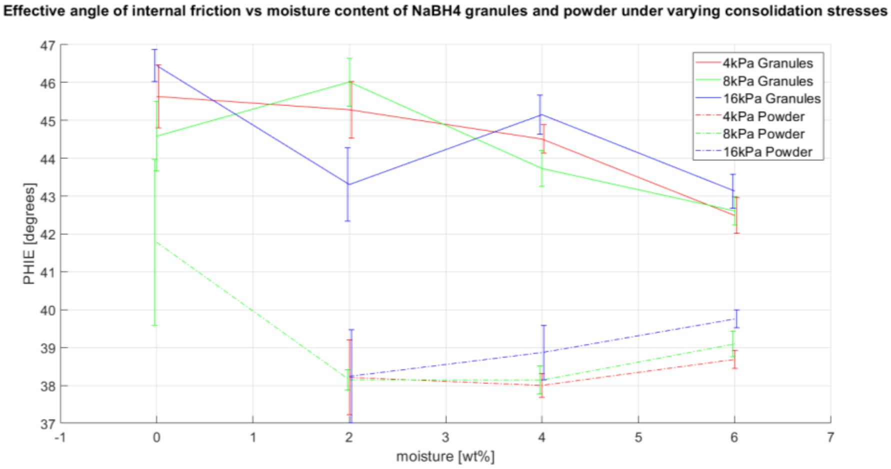

Figure 27.
Effective angle of internal friction vs moisture content of $NaBH_4$ granules and powder under varying consolidation stresses.

The linearized, steady-state, and effective angle of internal friction exhibit similar trends, as they are closely related to each other. Notably, the $NaBH_4$ powder consistently displays a lower angle compared to the granules. However, the difference in angle between the two decreases as moisture content increases since the angle of the powder appears to increase with higher moisture content while the angle of the granules decreases. A higher normal stress does not seem to significantly affect the angles, but generally results in a slightly higher angle. This implies that a silo subjected to higher consolidation stresses would require a slightly steeper funnel to facilitate smooth flow of the material. However, a wall friction test must be conducted to determine the appropriate dimensions and angles for the silo.

Cohesion

The last mechanical property that can be derived from the generated Mohr stress circle diagrams is the cohesion of the tested material. Cohesion is the value of the shear stress at the point where the yield locus intersects the τ-axis. It measures the resistance of the material to shear when no load is applied, indicating its cohesiveness. However, cohesion typically does not play a significant role in the handling of bulk solids and is not required for silo design.

Figure 28 illustrates how the cohesion of $NaBH_4$ powder and granules changes with varying moisture content and consolidation stresses.

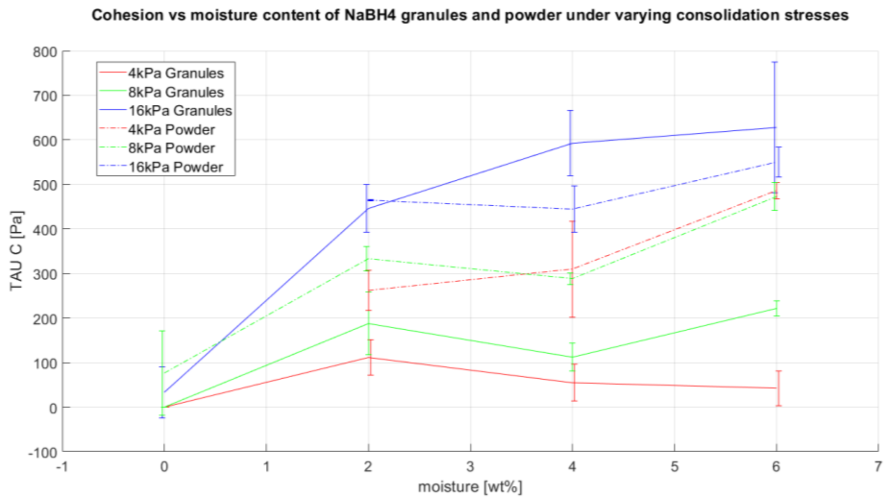

Figure 28.
Cohesion vs moisture content of $NaBH_4$ granules and powder under varying normal stresses.

5.1.2. Summary

In summary, a total of 66 Ring Shear tests were conducted to determine the effects of moisture content on the mechanical properties of $NaBH_4$ and to compare the results between $NaBH_4$ powder and granules. Seven different mechanical properties: consolidation stress, unconfined yield strength, flowability, slope angle of linearized yield locus, angle of internal friction at steady-state flow, effective angle of internal friction, and cohesion, were extracted from the data and analysed.

5.2. Conclusion

In conclusion, the Ring Shear tests have provided valuable insights into the mechanical properties of $NaBH_4$ powder and granules under varying moisture content and consolidation stress levels. The data presented in this chapter reveals that moisture has a different effect on powder than it does on granules.

Both materials exhibit similar unconfined yield strength, flowability, and cohesion at zero moisture content. However, they display very different behaviour at higher moisture content levels. The unconfined yield strength of granules changes little with increasing moisture content until the normal stress reaches 16 kPa at which point the unconfined yield strength rises sharply. In contrast, the unconfined yield strength of powder increases at low moisture content levels but does not change significantly with higher consolidation stresses. This is likely due to some interaction between powder and moisture at higher consolidation stresses.

Granules exhibit better flowability at all moisture content levels and consolidation stresses, but their results have a higher variance. Further research into the flowability of $NaBH_4$ granules at elevated moisture content levels is necessary to verify a clear pattern in the data.

Lastly, in terms of the effective angle of internal friction, $NaBH_4$ granules without moisture start at around 46 degrees and drop to 43 degrees at 6 wt% moisture content. In contrast, $NaBH_4$ powder rises from 38 degrees at 2 wt% moisture content to 40 degrees at 6 wt% moisture content.

6. Conclusions, limitations, and recommendations

In this final chapter the report is concluded by answering the main research question and sub-questions. This is followed by the limitations encountered during the experiments and recommendations for future research into the bulk material properties of $NaBH_4$.

Conclusions

The research aimed to provide an answer to the question of what the effects of ambient humidity on the bulk material properties of bulk $NaBH_4$ during storage and handling are. To be able to answer this question four sub-questions had been formulated, which can now be answered.

The first sub-question is: "What is the state of the art in the bulk material properties of bulk $NaBH_4$?". A literature review revealed that there is limited information available on the mechanical properties of $NaBH_4$, with only the physical properties of the material itself being well understood. Previous literature works do mention that $NaBH_4$ shows deliquescence, meaning it attracts moisture from the environment to the point of dissolving in the gathered liquid water, and that the material tends to cake together when exposed to the environment. Temperature and humidity were identified as the main factors influencing caking in materials similar to $NaBH_4$.

The second question is: "What are the effects of ambient humidity on the moisture content of $NaBH_4$?". Two experiments, a Dynamic Vapor Sorption test and a Moisture Depth test, were conducted to investigate the effects of ambient humidity on the moisture content of $NaBH_4$. The results indicated that ambient humidity has a major impact on the moisture content of $NaBH_4$. When exposed to an environment with 25% RH or above the material would start to attract ample amounts of moisture at a constant rate and subsequently clump together and react. However, when the material was exposed to humidity in an enclosed environment with a limited amount of available moisture in a separate container only the top layer of material would attract moisture and the rate of moisture absorption would slow down. Thus, the effects of ambient humidity on the moisture content of $NaBH_4$ depend greatly on the ambient relative humidity in the system and if the material is contained in an enclosed or ventilated system.

The third question is "What are the mechanical properties of bulk $NaBH_4$ under varying moisture content?". To answer this question a Ring Shear test and a Dry-Wet-Dry test were conducted. The Ring Shear test is conducted to determine the mechanical properties of $NaBH_4$ granules and powder, while the Dry-Wet-Dry test is used to determine whether the mechanical properties of dry $NaBH_4$ would differ from $NaBH_4$ that was first exposed to moisture and then dried again. As both experiments are performed with $NaBH_4$ granules and powder, the last sub-question, : "In what ways do the bulk material properties of $NaBH_4$ powder and $NaBH_4$ granules differ when exposed to varying ambient humidity?", is also answered. The results from the Ring Shear test showed that moisture has a different effect on $NaBH_4$ powder than it does on granules. Both materials exhibit similar unconfined yield strength, flowability, and cohesion at zero moisture content, but display very different behaviour at higher moisture content levels. Most notably, a higher moisture content level had substantial negative effects on the flowability of $NaBH_4$ powder, while it had less of an effect on the granules. Lastly, the Dry-Wet-Dry test has shown that both the powder and the granules do not revert back to their original mechanical properties, but rather form a solid mass when dried after exposure to moisture. This means that for the purpose of storage and handling the material is best not exposed to moisture and if it is exposed to moisture that it is best not dried in order to prevent the material from forming a solid mass.

In conclusion, the findings from the conducted experiments provide answers to the primary research question: "What are the effects of ambient humidity on the bulk material properties of bulk $NaBH_4$ during storage and handling?". Exposure of $NaBH_4$, in both powdered and granulated forms, to ambient humidity results in an increase in the moisture content of the material. This increase subsequently leads to a rise in cohesion and a reduction in flowability, with a more severe effect on powdered $NaBH_4$ compared to granulated $NaBH_4$.

Overall, this study has laid the foundation for further research into the bulk material properties of $NaBH_4$ in bulk quantities under varying levels of ambient humidity. This knowledge is essential for effectively utilizing $NaBH_4$ as a fuel source for marine vessels and other applications.

6.1. Limitations and recommendations

The experiments conducted in this report were designed to assess the mechanical properties of $NaBH_4$ under varying operational conditions. However, due to time and equipment constraints, it was not possible to run all experiments at multiple humidity and temperature configurations. As a result, only the most extreme achievable 'real world' configurations were considered for certain experiments, such as the Moisture Depth test, which took over a week to run. Other experiments, such as the Ring Shear test, were performed under conditions that reflected 'real world' conditions achieved in the laboratory, as measured during the Dry-Wet-Dry test. This report is therefore limited to the bulk material properties of $NaBH_4$ powder and granules under the specific operational conditions evaluated.

Further research is necessary to fully understand the behaviour of $NaBH_4$ under a wider range of conditions, such as a varying temperature, which can have a big impact on available moisture in the environment. Additional experiments could be conducted to investigate the effects of other operational conditions, such as temperature and stress history, on the bulk material properties of $NaBH_4$.

The main point that should be taken from this report is prolonged exposure to ambient humidity adversely affects the usability of $NaBH_4$ as a fuel source, as the material rapidly reaches moisture content levels that trigger hydrolysis and cause it to clump together, complicating storage and handling. The bulk material properties of powdered $NaBH_4$, especially the flowability, are more adversely affected by high moisture content levels. Therefore, granules are preferred for storage and handling, but to prevent $NaBH_4$ from attaining high moisture content levels altogether, it is recommended that the material be stored in a closed environment.

Acknowledgments

I would like to thank:

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Appendix A: Scientific Research Paper

Authors *B. Romijn, M.C. van Benten, Prof.dr.ir. D.L. Schott*

Bulk Material Properties of $NaBH_4$

B. Romijn, ir. M.C. van Benten, prof.dr.ir. D.L. Schott
Mechanical Engineering, TU Delft

***Abstract* - Sodium borohydride ($NaBH_4$) is a potential material-based hydrogen storage solution. However, a lack of information regarding its bulk material properties poses a challenge in designing storage and handling equipment. This report addresses this gap by conducting a series of tests to analyse the bulk material properties of $NaBH_4$ powder and granules, with a specific interest in how these properties change under varying humidity conditions.**

Since humidity does not have a direct effect on material properties, but moisture content does, the report first investigates the effect of humidity on moisture content in the material. The second set of experiments is then designed to determine the bulk material properties with varying moisture content, establishing a link between humidity and bulk material properties.

The findings reveal that prolonged exposure to ambient humidity negatively affects the cohesion and flowability of $NaBH_4$. This effect is more pronounced in powdered $NaBH_4$ compared to its granulated form. However, these adverse effects can be mitigated by storing the material in a closed environment. The study concludes by emphasizing the importance of a closed storage environment and the need for further research on $NaBH_4$'s behaviour under a wider range of conditions for its storage and handling.

I. INTRODUCTION

The international community is transitioning from fossil fuels to renewable fuel sources in an effort to limit the increase in the global average temperature to well below 2°C above pre-industrial levels, as agreed upon in the adoption of the Paris Agreement [1]. One way to inhibit the increase in global average temperature is by reducing global emissions of greenhouse gasses. However, the shipping industry has seen an increase in greenhouse gas emissions, from 2.76% (977 million tonnes) in 2012 to 2.89% (1,056 million tonnes) in 2018 and these emissions are projected to increase even further by 2050 [2]. For this reason, it is necessary to find alternative and more renewable fuel sources for the maritime industry.

Hydrogen is a potential renewable fuel source that does not directly create any greenhouse gases. Pure hydrogen gas (H_2) is not abundant on earth, but can be produced from various sources, such as water, through methods like electrolysis and photobiological processes. However, due to its low density, hydrogen has a very low volumetric energy density, requiring a large volume of storage space relative to conventional fuel sources. This can be somewhat mitigated by liquefaction or compression of the gas, but these methods have their own drawbacks [3].

An alternative is material-based hydrogen storage, which offers a higher volumetric energy density and does not require high pressure storage solutions. Sodium borohydride, $NaBH_4$, is an example of such a material-based hydrogen storage material. It is an inorganic salt which is currently mainly used in small quantities in the papermaking industry and as a reagent in organic synthesis in the chemical and medical industry [4]. However, $NaBH_4$ could also be used as a fuel source as it releases hydrogen gas when exposed to water through the following hydrolysis reaction:

$$NaBH_4 + 2 \cdot H_2O \rightarrow NaBO_2 + 4 \cdot H_2$$

In practical conditions, $NaBH_4$ requires an excess of water to dissolve and subsequently react [5], as shown in the following reaction:

$$NaBH_4 + (2 + x) \cdot H_2O \rightarrow NaBO_2(x \cdot H_2O) + 4 \cdot H_2$$

These reactions are particularly interesting as they show that half of the hydrogen gas produced comes from the added water molecules, leading to a higher overall efficiency and effective volumetric energy density of $NaBH_4$. As a hydrogen storage method $NaBH_4$ has a gravimetric energy density equal to that of refrigerated liquid H_2, but has a superior volumetric density, as can be seen in *Figure 1*, meaning that more hydrogen can be stored in an equal volume. After the release of hydrogen, the byproduct of the hydrolysis reaction, $NaBO_2(x \cdot H_2O)$ can be regenerated back to $NaBH_4$ through hydrogenation [6].

In recent years the use of $NaBH_4$ as a solid-state hydrogen storage method has been researched [7,8,9,10], but to use $NaBH_4$ as a viable fuel source the complete cycle

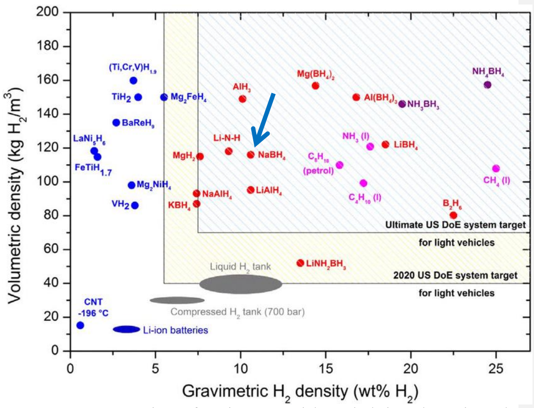

Fig. 1: *Overview of various materials and their volumetric and gravimetric hydrogen density. The U.S. Department of Energy targets for hydrogen storage systems are also shown for comparison.* [11]

Fig. 2: *$NaBH_4$ powder (left), particle size 180-480 microns [12] and granules (right), particle size 1.2-3.0 mm [13].*

of storage, handling, hydrolysis, and regeneration of spent fuel must be thoroughly understood, but in order to design the equipment for storage and handling of $NaBH_4$ the bulk material properties are first required.

Little is currently known about the bulk material properties of $NaBH_4$ and how they change when exposed to ambient humidity, so in this report the bulk material properties of $NaBH_4$ and the effects of ambient humidity on these properties are examined through experimentation.

II. MATERIALS AND METHODS

A. Materials

During the experiments two forms of $NaBH_4$ were utilized: granules and powder. Both samples were sourced from CPH Chemicals B.V. A size comparison of the powder and granules can be seen in *Figure 2* and the cumulative frequency distribution (CFD) of both materials is depicted in *Figure 3*. The CFD shows that the granules predominantly fell within the range of 1.2-3.0 mm, with over 90% of the material fitting this specification. For the powder over 90% of the material ranged between 180-480 microns, nearly 10x smaller compared to the size of the granules. To prevent external conditions from impacting the material, they were stored in sealed polyethylene bags which were subsequently placed inside airtight iron drums.

B. Methods

Although ambient humidity does not directly influence the bulk material properties of $NaBH_4$, it does indirectly affect them through its impact on moisture content. Therefore, understanding the effect of ambient humidity on the moisture content of a material is crucial to understand the bulk material properties of that material. Once the relationship between ambient humidity and moisture content is established, the effect of moisture content on the bulk material properties can then be measured to get an insight on how ambient humidity affects the bulk material properties of $NaBH_4$.

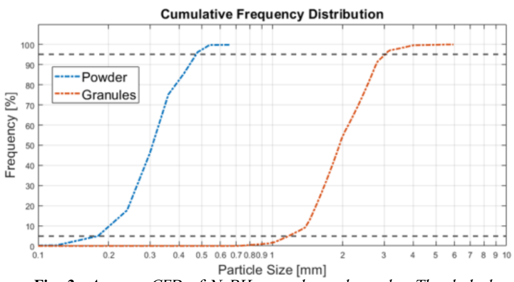

Fig. 3: *Average CFD of $NaBH_4$ granules and powder. The dashed horizontal grey lines represent the bracket which contains 90% of the CFD.* Data provided by M.C. van Benten.

To determine the effects of ambient humidity on the moisture content of $NaBH_4$ powder and granules, two experiments are used: the Dynamic Vapor Sorption test and the Moisture Depth test. Subsequently the effects of moisture content on the bulk material properties of $NaBH_4$ are determined by performing two other experiments: The Ring Shear test and the Dry-Wet-Dry test.

The results gathered from these tests, as summarized in *Table I*, offer a thorough understanding of how varying levels of humidity influence the bulk material properties of $NaBH_4$, in both its powder and granules form.

1) Dynamic Vapor Sorption test

The Dynamic Vapor Sorption (DVS) test evaluates the moisture absorption rate of a material by monitoring the weight changes of a small sample (between 1 mg and 4 g) as it is exposed to nitrogen gas at progressively higher humidity levels at a constant temperature.

-Test settings and procedure-

A dry sample of 61mg, either $NaBH_4$ granules or powder, is loaded into the sample pan of the DVS after which the test parameters are configured in the DVS software provided by the manufacturer. The machine subsequently runs a baseline measurement at 0% RH to establish a starting point for the test. The relative humidity (RH) is then adjusted to the first test point and maintained for 90 minutes. During this period, the mass of the sample is recorded to determine moisture sorption. After the time interval the RH is adjusted to 0% RH for 90 minutes to measure moisture desorption and the process then repeats until all test points have been examined. The test runs at 20 degrees Celsius with a maximum RH of 90% and steps of 5%. The DVS machine used during the test is model “IGAsorp HT” by Hidden Isochema Ltd and it is run by Delft Solids Solutions B.V.

2) Moisture Depth test

A Moisture Depth test quantifies the rate of moisture uptake and the depth of moisture penetration within a sample. This is achieved by monitoring the weight of tubes, each filled with different quantities of material, over an extended period of exposure to a predetermined temperature and humidity level.

Table I: *Tests and test outputs.*

Test	Test output
Dynamic Vapor Sorption test	- Moisture sorption rate - Moisture desorption rate - Maximum total sorption * At varying humidity levels
Moisture Depth test	- Moisture penetration rate - Maximum total sorption * At high humidity level
Ring Shear test	- Consolidation stress - Unconfined yield strength - Flowability - Linearized yield locus - Internal friction at steady-state flow - Effective angle of internal friction - Cohesion
Dry-Wet-Dry test	- Moisture sorption - Moisture desorption - Change in material properties

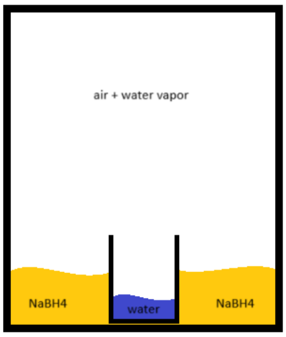

Fig. 4: *Schematic overview of exposing $NaBH_4$ to humidity in an enclosed environment.*

-Test settings and procedure-

Two series of tests, each containing 5 tubes of 50mm inner dimension, are filled with 10, 20, 40, 60, and 80 grams of $NaBH_4$ powder or granules, respectively. The tubes are labelled, material height measured, weighed, and then put inside a climate-controlled chamber at 40 degrees Celsius, 60% RH. The weight of the tubes is then measured again at every hour for the first day and then at 9 AM, 1 PM, and 5 PM every consecutive day for 4 more days. All tests were conducted by Delft Solids Solutions B.V.

3) Schulze Ring Shear test

The Ring Shear test (RST) aims to identify the bulk material properties at varying moisture content levels by measuring the required shear load to failure of the material at several normal loads. These measurements are then used to determine the bulk material properties.

-Test settings and procedure-

The procedure followed is the ASTM D6773-22 standard test method in conjunction with the manuals belonging to the RST machine, the RST-01.pc by Dr. Dietmar Schulze GmbH. The test matrix for the RST can be seen in *Table II.* When testing various moisture content levels, the material is exposed to humidity by placing 600 grams of dry material in a 12-litre bucket, along with an open container containing 15% of the mass of the material in water. A schematic overview can be seen in *Figure 4.* The bucket is sealed and left at roughly 30 degrees Celsius for 7 days for some of the water to evaporate and migrate to the material. After 7 days the bucket is opened after which the material is weighed, to determine the moisture content, and diluted to gain the required moisture content.

4) Dry-Wet-Dry test

This new and inhouse developed test procedure is designed to determine if the bulk material properties of $NaBH_4$ granules and powder remain unchanged after being exposed to moisture and then dried, compared to when it is dry. This is achieved by performing a RST on dry $NaBH_4$ granules and powder, after which the powder and granules are exposed to moisture, as mentioned in the RST test settings, and subsequently dried in an oven at 55-110 degrees Celsius after which another RST is performed. This allows for a comparative analysis of any changes in the mechanical properties.

III. RESULTS AND DISCUSSION

A. Humidity vs moisture content

Figure 5 shows the most important results of the DVS test: the rate of mass change, in % of the original sample weight, of a small sample of $NaBH_4$ granules and powder when exposed to varying levels of ambient humidity.

The first observation from the data is that both the granules and the powder start to gain a small amount of mass at an ambient humidity of 25%, at a rate of 4.5 µg/min and 1.5 µg/min, respectively. The rate of mass change becomes more noticeable at 30% RH and keeps increasing linearly from that point forward up to 0.1 mg/min at 90% RH. When the RH is increased, the powder seems to have a higher initial rate of mass change, but this decreases over time to a level under that of the more stable uptake rate of granules. In the end granules have a slightly higher rate of mass change and overall mass change.

An important part of the observation is that the rate of mass change does not converge to 0 mg/min, which is an indication deliquescent nature of $NaBH_4$, meaning it absorbs moisture from the atmosphere until it dissolves in the absorbed water and forms a solution, rather than forming an equilibrium between its moisture content and the ambient humidity. This is similar to an observation made by Stepanov et al [14] during their study of $NaBH_4$ hydrolysis and its behaviour at room temperature in which it is observed that "*$NaBH_4$ spontaneously undergoes simultaneous hydrolysis and hydration with water molecules absorbed from the surrounding air*".

The rate of desorption for the $NaBH_4$ powder and granules stabilized at minus 35 µg/min and minus 45 µg/min, respectively, showing that the discharge rate of moisture from the sample is not dependent on the amount of moisture present in the sample itself as the total moisture content of the samples kept rising from cycle to cycle.

Table II. Schulze *Ring Shear tester test matrix.*
**Data provided by M.C. van Benten.*

	Moisture levels	Preshear stresses	Repetitions
$NaBH_4$ granules	0*, 2, 4, 6 wt%	4, 8, 16 kPa	3
$NaBH_4$ powder	2, 4, 6 wt%	4, 8, 16 kPa	3
$NaBH_4$ powder	0* wt%	8 kPa	3

Preshear stress	*Point 1*	*Point 2*	*Point 3*	*Point 4*	*Point 5*	*Point 6*
4 kPa	*400 Pa*	*600 Pa*	*800 Pa*	*1600 Pa*	*2400 Pa*	*3200 Pa*
8 kPa	*800 Pa*	*1200 Pa*	*1600 Pa*	*3200 Pa*	*4800 Pa*	*6400 Pa*
16 kPa	*1600 Pa*	*2400 Pa*	*3200 Pa*	*6400 Pa*	*9600 Pa*	*12000 Pa*

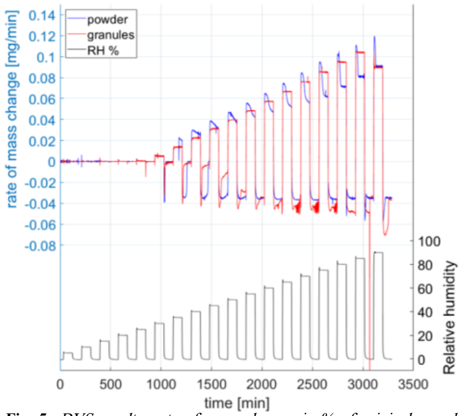

Fig. 5: *DVS results: rate of mass change, in % of original sample weight, of $NaBH_4$ granules and powder when exposed to varying levels of ambient humidity.*

The results of the Moisture Depth test, the rate at which moisture is absorbed by $NaBH_4$ granules and powder when exposed to 60% RH at 40 degrees Celsius for prolonged time, are shown in *Figure 6*.

The results show the rate of mass gain is initially higher for both granules and powder, before stabilizing at a similar rate with the rate for powder being slightly higher at 0.5 g/h compared to that of granules at 0.4 g/h. The higher rate for powder is possibly due to the higher contact surface area between particles of powder compared to granules, enabling the moisture to travel faster into the material by capillary motion. The eventual stable rate of mass change is independent of the initial mass, likely due to the same surface area being exposed to the humid environment.

Most importantly, just like during the DVS test, the rate of mass change does not converge to 0 even when exposed for 100 hours, indicating that the rate of moisture sorption is greatly dependent on the humidity level and not on the moisture content of the material.

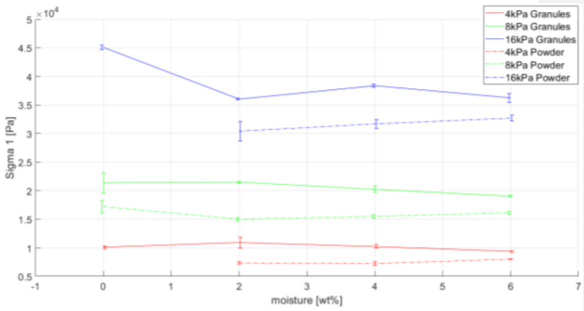

Fig. 7: *Consolidation stress vs moisture content of $NaBH_4$ granules and powder under varying normal stresses.*

B. Moisture content vs bulk material properties

After the effects of humidity vs moisture content are established, the effects of moisture content vs bulk material properties are measured using the RST. The most relevant results from the RST in regard to storage and handling of the material are as follows:

1) Consolidation stress

The consolidation stress is the maximum normal stress that occurs on a plane where the shear stress is at its minimum. It is used together with the unconfined yield strength to describe the flow behaviour of bulk solids. Generally, the higher the consolidation stress gets, the better a bulk solid flow (given an equal unconfined yield strength). *Figure 7* illustrates the relationship between moisture content and consolidation stress. It can be observed that, at each level of moisture content and normal stress, granules exhibit a higher consolidation stress than powder. This higher consolidation stress of granules is attributed to their higher shear strength at a similar normal stress, possibly due to the mechanical interlocking of larger particles within the granules. An increase in moisture content appears to have an effect of a decreasing consolidation stress on the bigger particles of the granules.

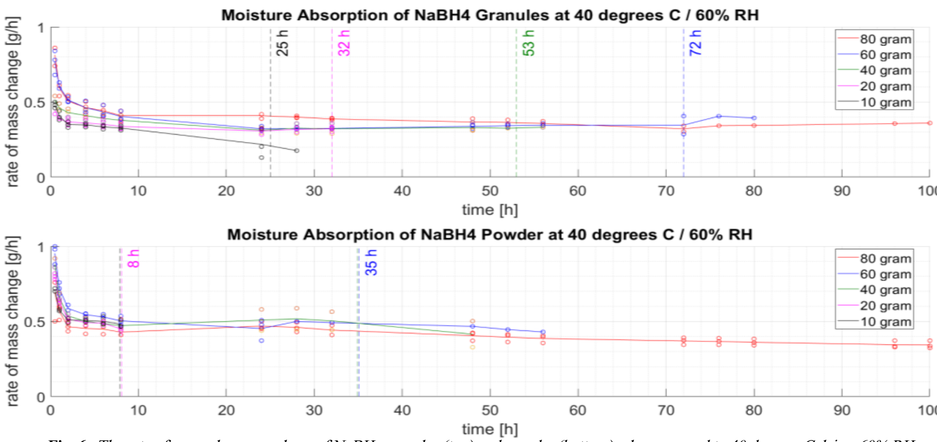

Fig. 6: *The rate of mass change per hour of $NaBH_4$ granules (top) and powder (bottom) when exposed to 40 degrees Celsius, 60% RH. The vertical lines indicate the average timestep at which moisture penetrated the bottom of the tube.*

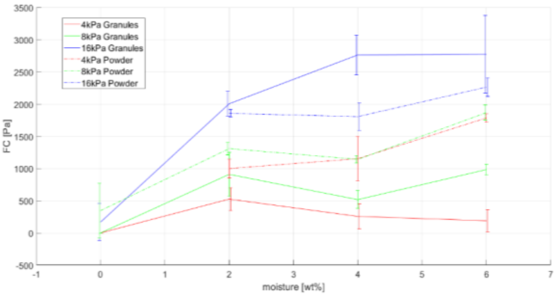

Fig. 8: *Unconfined yield strength vs moisture content of NaBH4 granules and powder under varying consolidation stresses.*

in contrast to an increase in consolidation stress on the smaller particles of the powder.

2) Unconfined yield strength

The unconfined yield strength is the maximum normal stress level that can be applied before bulk material in an unconfined state will fail in shear. *Figure 8* presents the relationship between moisture content and unconfined yield strength. Both granules and powder exhibit a very low unconfined yield strength when no moisture is present, as observed during the handling of dry material as even after exposure to higher consolidation stresses, both materials without moisture content remain free-flowing when removed from the ring shear cell. At higher moisture content levels, the powder rapidly gains a substantial amount of unconfined yield strength, while the granules at 4 and 8 kPa consolidation stress are less affected by the moisture. This may be due to the larger surface area available for water to adhere to and interact with other particles in the powder, as opposed to the granules, which have larger particles and thus a smaller surface area. At 16 kPa, the granules suddenly gain a significant amount of unconfined yield strength, even surpassing that of the powder. It is uncertain whether this is due to mechanical interlocking at higher consolidation stresses or some interaction between the granules and moisture at higher pressures.

3) Flowability

Flowability is not an inherent material property, but it is the ratio between the consolidation stress and the unconfined yield strength. It represents a numerical value that indicates how well a material flows at specific consolidation stresses. The flowability function and behaviour can be defined as follows:

$$ff_c = \frac{major\ principal\ stress}{unconfined\ yield\ strength}$$

- ffc < 1 — not flowing
- 1 < ffc < 2 — very cohesive
- 2 < ffc < 4 — cohesive
- 4 < ffc < 10 — easy-flowing
- 10 < ffc — free-flowing

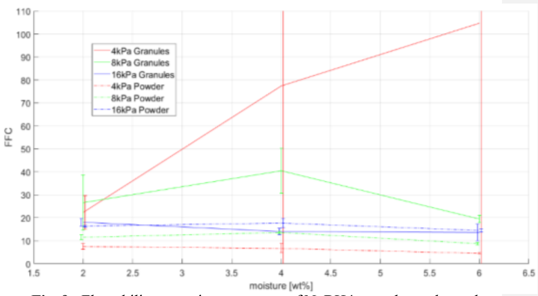

Fig. 9: *Flowability vs moisture content of NaBH4 granules and powder under varying normal stresses. The confidence intervals of 4kPa Granules exceed the graph due to high uncertainty.*

As illustrated in *Figure 9*, all measured points remain within the free-flowing region, with two exceptions. The first exception is the entirety of powder at 4 kPa normal stress, which starts in the easy-flowing regime and transitions to the cohesive regime as moisture content increases. The second exception is the powder at 6 wt% moisture and 8 kPa consolidation stress, where the material changes from free-flowing to easy-flowing. In general, the flowability of powder seems to decrease with higher moisture content levels. Notably, the flowability of the powder increases with higher consolidation stresses, while that of the granules appears to decrease. However, the confidence interval of the granules data varies significantly, particularly at lower normal stresses and higher moisture content levels, making it difficult to verify a clear pattern from the available data.

4) Effective angle of internal friction

The effective angle of internal friction characterizes the internal friction at steady-state flow. *Figure 10* illustrates how the effective angle of internal friction changes with varying moisture content and consolidation stresses. It can be seen that the NaBH4 powder consistently displays a lower angle compared to the granules. However, the difference in angle between the two decreases as moisture content increases since the angle of the powder appears to increase with higher moisture content while the angle of the granules decreases. A higher normal stress does not seem to significantly affect the angles, but generally results in a slightly higher angle. This implies that a silo subjected to higher consolidation stresses would require a slightly steeper funnel to facilitate smooth flow of the material. However, a wall friction test must be conducted to determine the appropriate dimensions and angles for the silo.

In summary, both materials exhibit similar unconfined yield strength and flowability at zero moisture content, but they display very different behaviour at higher moisture content levels. Most importantly, granules exhibit better flowability at all moisture content levels and consolidation stresses and they have a reducing angle of internal friction at higher moisture content levels, indicating they are easier to handle and store in bulk quantities.

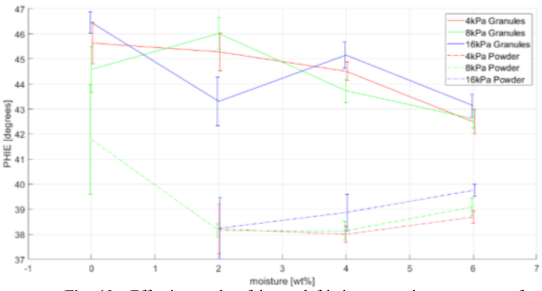

Fig. 10: *Effective angle of internal friction vs moisture content of NaBH4 granules and powder under varying consolidation stresses.*

Lastly, the Dry-Wet-Dry test is performed to determine whether the NaBH4 granules and powder would return to their original dry state when dried after exposure to an elevated moisture content, but also how much moisture the material would attract in a closed container with a separate open container of water inside. This method of storage simulates an enclosed container with a finite amount of moisture present, rather than an open container where moisture can be replenished from outside of the system. The amount of moisture content gained by $NaBH_4$ powder after 1, 3, 6, and 7 days of storage using this method can be seen in *Figure 11*. It was observed that not all the water inside the container migrated to the $NaBH_4$ during any of the tests, even during the longest test which lasted for 7 days. The cause might be that the RH inside the enclosed container quickly stabilized at around 30% RH, which greatly slowed the rate of moisture sorption by the $NaBH_4$. After 7 days the top layer of material was caked together while the material at around 1.7cm depth was still free flowing and did not seem to be affected by the moisture at all.

After a second RST to verify a change in bulk material properties compared to dry material, the powder was placed in an oven at 55-110 degrees Celsius to evaporate all moisture. The result of drying for both temperatures can be seen in *Figure 12*, a solid brick of $NaBH_4$. For both the powder and the granules the material would completely fuse together and form a solid mass, which made further tests using a RST impossible. The test with granules was only performed once, because the material also came out of the oven as a brick and subsequent tests were considered wasteful for the material.

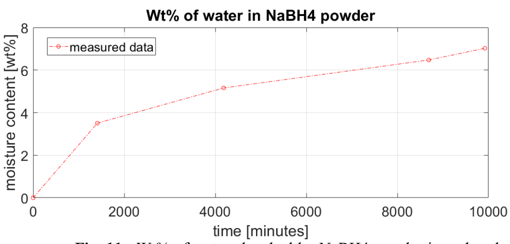

Fig. 11: *Wt% of water absorbed by NaBH4 powder in a closed container with an open water container inside.*

Fig. 12: *Dried NaBH4 powder after exposure to 5 wt% moisture.*

IV. CONCLUSIONS

Three experiments, the Dynamic Vapor Sorption test, Moisture Depth test, and the first half of the Dry-Wet-Dry test, were conducted to investigate the effects of ambient humidity on the moisture content of $NaBH_4$. The results indicated that ambient humidity, when above 25% RH, cause the material to attract moisture at a constant rate and subsequently clump together. However, when the material was exposed to ambient humidity in an enclosed environment, the RH inside the environment would quickly stabilize at 30% RH, inhibiting the rate of moisture sorption by $NaBH_4$ and thus causing lower moisture content levels. The DVS and Moisture Sorption test have also indicated that the rate of moisture sorption is greatly dependent on the humidity level and not on the moisture content of the material itself. Given these observations, it is greatly recommended to store the material in an enclosed environment or otherwise in an environment with a low RH.

A Ring shear test is conducted to determine the effects of varying moisture content on the bulk material properties of $NaBH_4$ granules and powder. The results indicate that moisture has a different effect on $NaBH_4$ powder than it does on granules. Both materials exhibit similar unconfined yield strength and flowability at zero moisture content but display very different behaviour at higher moisture content levels. The use of granules is preferred over powder as granules exhibit better flowability at all moisture content levels and consolidation stresses and they have a reducing angle of internal friction at higher moisture content levels, indicating they are easier to handle and store in bulk quantities.

Finally, the results from the Dry-Wet-Dry test indicate that drying the material after exposure is not recommended, as the material will form a solid mass.

The main point that should be taken from this report is prolonged exposure to ambient humidity adversely affects the usability of $NaBH_4$ as a fuel source, as the material rapidly reaches moisture content levels that trigger hydrolysis and cause it to clump together, complicating storage and handling. The mechanical material properties of powdered $NaBH_4$, especially the flowability, are more adversely affected by high moisture content levels. Therefore, granules are preferred for storage and handling, but to prevent $NaBH_4$ from attaining high moisture content levels altogether, it is recommended that the material be stored in a closed environment.

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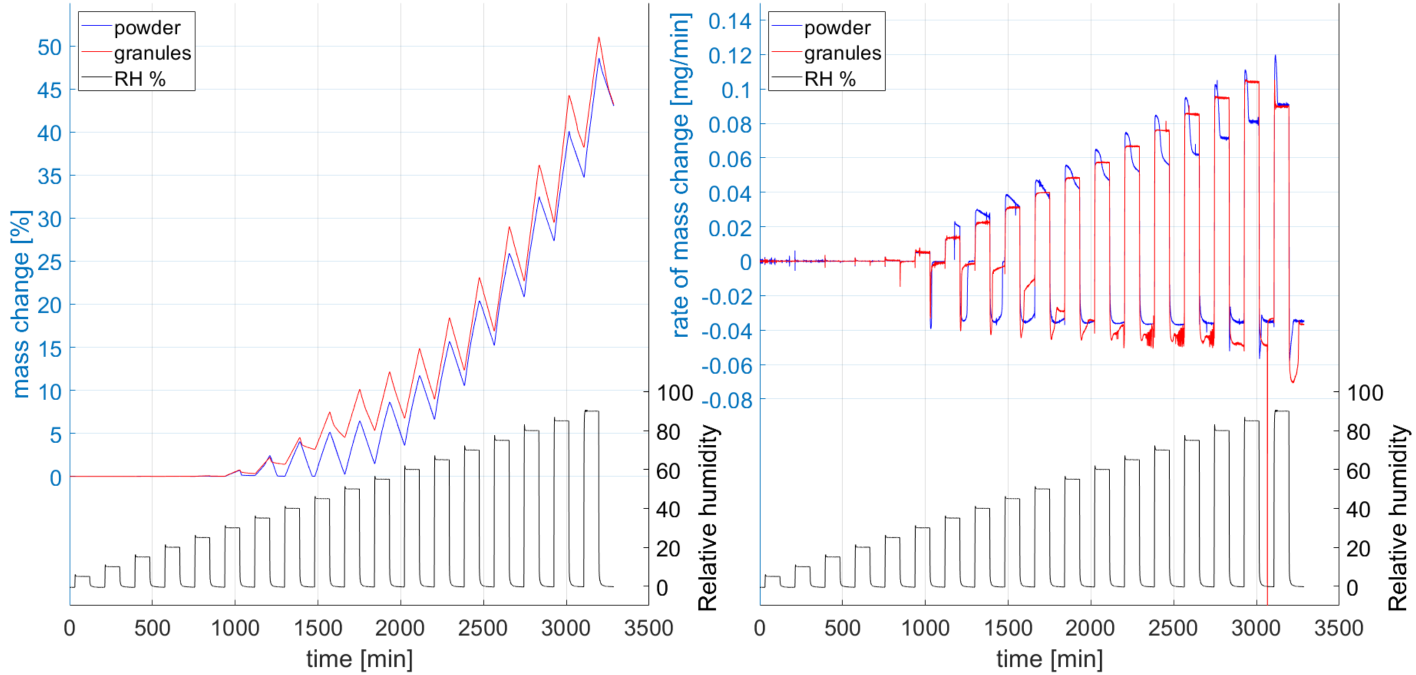
Appendix B: Data of experiments

Dynamic Vapor Sorption test

Since the Dynamic Vapor Sorption test resulted in huge amounts of data (roughly 400.000 lines of data), only the resulting image will be shown here.



Moisture Depth tests

SAMPLE CELL	MASSA (G)	HOOGTE (MM)
G1-3	80	75
G4-6	60	57
G7-9	40	38
G10-12	20	19
G13-15	10	10

Granules

		G1	G2	G3	G4	G5	G6	G7	G8	G9	G10	G11	G12	G13	G14	G15
	Leeg (g)	48.17	42.49	42.63	39.00	40.71	38.54	31.86	30.62	30.17	21.57	21.59	23.07	17.36	17.92	17.42
	Hoogte poeder (mm)	70.3	71.4	70.6	53.3	54.0	54.1	35.7	36.7	36.1	17.4	17.0	18.3	9.2	8.9	9.1
Dag	Tijd (h)															
Ma	0 (8:45)	128.21	122.53	122.65	99.10	100.71	98.86	71.51	70.89	70.12	41.66	41.70	43.24	27.77	28.18	27.38
	0.5 (9:15)	128.64	122.95	123.02	99.52	101.10	99.20	71.78	71.14	70.37	41.87	41.93	43.47	28.00	28.42	27.63
	1 (9:45)	128.84	123.14	123.19	99.73	101.30	99.45	72.00	71.34	70.56	42.04	42.09	43.63	28.15	28.62	27.78
	2 (10:45)	129.30	123.57	123.56	100.17	101.71	99.87	72.42	71.76	70.92	42.44	42.43	43.93	28.47	28.84	28.12
	4 (12:45)	130.22	124.40	124.32	101.13	102.50	100.59	73.31	72.49	71.64	43.23	43.07	44.63	29.17	29.51	28.82
	6 (14:45)	131.08	125.20	125.07	101.98	103.20	101.31	74.04	73.18	72.33	43.95	43.69	45.29	29.85	30.09	29.41
	8 (16:45)	131.74	125.83	125.64	102.62	103.78	101.96	74.80	73.83	72.97	44.59	44.27	45.84	30.50	30.67	30.00
Di	24 (8:45)	138.26	132.58	131.99	107.24	108.13	106.47	79.40	77.94	77.67	49.42	48.48	50.81	35.49	33.05	30.50
	28 (13:00)	139.34	133.96	133.69	108.44	109.63	107.77	80.73	79.06	80.12	50.84	50.07	52.41	25.38	27.07	32.32
	32 (16:45)	140.36	135.13	135.08	109.66	111.10	109.06	81.73	80.14	81.58	52.22	51.32	53.95			32.24

Woe	48 (8:50)	144.73	141.22	*	114.57	117.43	115.31	86.41	85.98	87.65	45.87	44.03	47.14			
	52 (12:55)	146.28	142.34		116.30	119.10	116.66	88.44	87.80	85.02						
	56 (16:35)	147.37	143.38		117.63	120.75	118.14	88.27	89.50							
Do	72 (8:45)	152.75	144.37		119.72	129.96	118.00		83.74							
	76 (12:50)	154.22	**		116.51	131.56										
	80 (16:50)	155.73				132.21										
Vr	96 (8:45)	162.42				123.53										
	100 (12:45)	164.20														

Powder

		P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15
	Leeg (g)	42.89	42.73	48.47	40.98	38.42	38.41	30.06	32.10	30.03	21.71	23.18	22.13	17.48	18.60	18.77
	Hoogte poeder (mm)	70.2	68.6	73.1	52.0	54.1	53.6	33.8	35.8	36.4	17.6	18.4	18.2	9.2	9.0	9.0
Dag	Tijd (h)															
Ma	0	122.95	122.68	129.06	100.91	98.08	98.54	69.56	71.95	69.70	41.55	43.85	42.54	27.40	28.58	28.79
	0.5	123.36	123.06	129.31	101.40	98.58	98.98	70.02	72.38	70.13	41.94	44.25	42.95	27.75	28.93	29.15
	1	123.55	123.27	129.57	101.63	98.84	99.22	70.25	72.58	70.35	42.17	44.47	43.18	27.97	29.15	29.37
	2	123.82	123.67	129.99	102.06	99.30	99.69	70.66	72.97	70.80	42.59	44.85	43.59	28.44	29.56	29.83
	4	124.62	124.57	130.94	103.12	100.28	100.67	71.66	73.84	71.72	43.56	45.75	44.55	29.47	30.56	30.82
	6	125.44	125.46	131.87	104.20	101.21	101.66	72.59	74.72	72.63	44.54	46.66	45.52	30.61	31.50	31.67
	8	126.23	126.17	132.59	105.20	102.07	102.36	73.68	75.48	73.39	45.04	47.45	46.27	31.48	32.33	32.52
Di	24	133.76	133.67	141.06	113.10	109.55	107.48	83.48	82.48	72.92	42.33	46.21	38.50	20.50	25.46	26.11

	28	135.01	135.48	142.90	114.92	104.97	103.17	86.02	84.47		45.66
	32	136.07	136.90	144.23	116.65			87.63	86.15		48.80
Woe	48	140.80	142.82	149.42	123.35			93.67	87.71		53.59
	52	141.85	143.84	150.63	124.10				83.88		
	56	142.94	144.92	151.81	125.02						
Do	72	147.77	149.60	157.28	124.93						
	76	149.12	150.63	158.58	122.71						
	80	150.28	151.41	159.76							
Vr	96	155.13	154.20	164.85							
	100	156.66	155.04	166.29							

Ring Shear test

material	pressure [kPa]	Moisture [%]	repeat	Sigma_c [Pa]	flowability	PHI_E [°]	PHI_lin [°]	PHI_sf [°]	Sigma_1 [Pa]	TAU_c [Pa]	Sigma_c_linearized [Pa]	flowability_linearized	PHI_E_linearized [°]	PHI_lin_linearized [°]	PHI_sf_linearized [°]	Sigma_1_linearized [Pa]	Tau_c_lin_linearized [Pa]
G	16	0	1	0	Inf	46.7	46.7	45.4	45915	0	503	90.4	46.9	46.7	45.4	45460	100
G	16	0	2	0	Inf	46.4	46.4	44.8	44544	0	0	Inf	46.3	46.3	44.8	44686	0
G	16	0	3	0	Inf	46.1	46.1	44.8	45069	0	0	Inf	46.1	46.1	44.8	45137	0
G	16	2	1	0	Inf	43.7	43.7	40.6	36211	0	1871	19.2	44.0	42.9	40.6	35902	408
G	16	2	2	174	208.6	42.5	42.4	40.1	36288	34	2140	16.9	42.6	41.3	40.1	36147	484
G	16	4	1	0	Inf	45.5	45.5	42.6	38840	0	2657	14.5	45.7	44.3	42.6	38573	560
G	16	4	2	0	Inf	44.5	44.5	42.1	38809	0	3111	12.4	44.7	43.0	42.1	38526	676
G	16	4	3	0	Inf	44.8	44.8	42.0	38250	0	2524	15.1	45.0	43.6	42.0	38027	541
G	16	6	1	0	Inf	43.0	43.0	40.3	36205	0	3065	11.7	43.3	41.4	40.3	35959	692
G	16	6	2	0	Inf	42.2	42.2	39.9	36144	0	3182	11.2	42.6	40.6	39.9	35654	731
G	16	6	3	248	149.9	43.5	43.3	40.9	37184	48	2079	17.9	43.5	42.3	40.9	37126	460
G	4	0	1	132	76.0	45.3	45.1	43.0	10070	28	0	Inf	45.6	45.6	43.0	9970	0
G	4	0	2	44	227.3	46.6	46.5	43.4	9942	9	0	Inf	46.5	46.5	43.4	9983	0
G	4	0	3	163	63.2	44.9	44.6	43.1	10330	35	0	Inf	44.8	44.8	43.1	10365	0
G	4	2	1	108	98.2	44.8	44.6	43.1	10614	21	568	18.5	44.9	43.8	43.1	10540	121
G	4	2	2	344	30.0	45.7	45.1	43.3	10334	75	332	30.7	46.1	45.5	43.3	10183	68
G	4	2	3	1402	8.9	44.5	42.0	44.3	12473	484	677	17.8	44.8	43.6	44.3	12051	145
G	4	4	1	0	Inf	44.3	44.3	41.9	9859	0	58	170.0	44.4	44.3	41.9	9836	12
G	4	4	2	374	27.6	44.3	43.6	42.5	10316	83	269	38.6	44.2	43.7	42.5	10369	57
G	4	4	3	533	19.6	44.9	43.8	43.0	10459	113	445	23.5	44.9	44.0	43.0	10448	94
G	4	6	1	0	Inf	42.8	42.8	40.6	9460	0	42	226.7	42.9	42.8	40.6	9437	9
G	4	6	2	46	209.8	42.5	42.4	40.6	9562	10	151	62.8	42.7	42.3	40.6	9505	33
G	4	6	3	0	Inf	42.0	42.0	40.0	9180	0	375	24.5	42.0	41.1	40.0	9210	85
G	8	0	1	0	Inf	43.8	43.8	41.7	19373	0	0	Inf	43.9	43.9	41.7	19304	0
G	8	0	2	0	Inf	45.5	45.5	44.4	22642	0	0	Inf	45.6	45.6	44.4	22467	0

G	8	0	3	0	Inf	44.5	44.5	43.5	21879	0	0	Inf	44.3	44.3	43.5	22319	0
G	8	2	1	138	153.7	45.5	45.3	43.6	21214	27	531	40.2	45.3	44.8	43.6	21348	110
G	8	2	2	0	Inf	46.2	46.2	44.3	21690	0	1195	18.1	46.2	45.0	44.3	21683	247
G	8	2	3	469	45.7	46.6	46.2	44.4	21398	89	1005	21.4	46.5	45.6	44.4	21471	205
G	8	4	1	0	Inf	43.5	43.5	42.1	20554	0	615	33.5	43.4	42.8	42.1	20630	135
G	8	4	2	0	Inf	43.6	43.6	42.0	20276	0	419	47.4	44.1	43.6	42.0	19845	90
G	8	6	1	0	Inf	41.9	41.9	40.4	19199	0	907	20.8	42.2	41.2	40.4	18878	206
G	8	6	2	0	Inf	42.6	42.6	40.8	19145	0	973	19.7	42.6	41.5	40.8	19138	219
G	8	6	3	0	Inf	42.9	42.9	41.0	19141	0	1073	17.8	43.0	41.7	41.0	19113	240
P	16	2	1	2155	13.6	37.3	35.5	34.0	29245	583	1817	16.1	37.4	35.9	34.0	29202	464
P	16	2	2	723	43.8	39.1	38.5	36.3	31661	160	1897	16.7	39.1	37.7	36.3	31614	465
P	16	4	1	1069	28.9	38.0	37.2	35.3	30909	254	1658	18.6	38.0	36.8	35.3	30838	415
P	16	4	2	967	33.5	39.4	38.8	36.8	32427	220	1705	19.0	39.4	38.2	36.8	32432	414
P	16	4	3	2401	13.3	39.1	37.4	36.4	31814	623	2053	15.5	39.1	37.6	36.4	31798	505
P	16	6	1	3469	9.6	40.0	37.6	37.5	33236	996	2426	13.7	40.0	38.3	37.5	33248	587
P	16	6	2	3149	10.3	39.6	37.3	37.0	32478	882	2215	14.7	39.6	38.0	37.0	32526	540
P	16	6	3	3110	10.4	39.7	37.4	36.9	32307	873	2151	15.0	39.7	38.1	36.9	32322	523
P	4	2	1	1121	6.5	38.4	34.5	34.4	7285	337	1016	7.1	38.5	35.1	34.4	7257	264
P	4	2	2	625	12.1	38.2	36.3	35.0	7569	151	820	9.2	38.5	35.9	35.0	7521	210
P	4	2	3	1351	5.2	36.8	31.8	33.1	7063	673	1168	6.1	36.8	32.5	33.1	7071	320
P	4	2	4	1233	6.1	38.8	34.7	35.2	7541	436	995	7.5	39.0	35.8	35.2	7501	255
P	4	4	1	1129	6.6	38.0	34.2	34.7	7475	363	951	7.8	38.1	35.0	34.7	7450	248
P	4	4	2	1235	6.0	38.1	33.9	34.7	7446	491	955	7.8	38.3	35.1	34.7	7419	248
P	4	4	3	1574	4.3	37.6	31.4	32.7	6829	439	1554	4.4	37.6	31.6	32.7	6822	435
P	4	6	1	1540	5.1	39.3	34.4	36.3	7889	978	1761	4.6	38.7	32.9	36.3	8050	478
P	4	6	2	1897	4.1	39.6	33.2	36.3	7851	672	1860	4.3	38.9	32.8	36.3	7998	507
P	4	6	3	1722	4.6	38.9	33.2	36.1	7929	741	1737	4.6	38.5	32.8	36.1	8035	474
P	8	0	1	462	36.6	42.2	41.6	38.8	16881	107	218	76.2	42.7	42.5	38.8	16641	48
P	8	0	2	224	83.3	43.0	42.8	40.8	18658	46	823	22.5	43.3	42.4	40.8	18476	182
P	8	0	3	0	Inf	39.4	39.4	37.0	16443	0	0	Inf	39.3	39.3	37.0	16505	0

P	8	2	1	855	18.0	38.1	36.8	35.3	15374	205	1195	12.8	38.2	36.4	35.3	15322	302
P	8	2	2	0	Inf	38.3	38.3	34.7	14843	0	1371	10.8	38.4	36.2	34.7	14803	348
P	8	2	3	942	15.9	37.8	36.3	34.6	14971	222	1363	11.0	37.8	35.7	34.6	14934	350
P	8	4	1	1148	13.8	38.2	36.5	35.8	15812	293	1185	13.3	38.4	36.6	35.8	15729	298
P	8	4	2	1681	9.1	37.8	35.1	35.1	15310	528	1101	13.9	37.9	36.2	35.1	15279	279
P	8	6	1	2563	6.2	39.3	35.2	36.3	15760	838	1979	8.0	39.0	36.0	36.3	15876	504
P	8	6	2	2431	6.6	38.8	35.0	36.4	16108	901	1742	9.2	38.8	36.2	36.4	16100	442
P	8	6	3	2435	6.8	39.4	35.8	37.1	16531	852	1883	8.8	39.5	36.7	37.1	16492	472