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RUHR-UNIVERSITÄT BOCHUM

MechEng
Mechanical Engineering



Vietnamese-German University

INVESTIGATION OF PH VALUES OF SILICIC ACID IN THE PRESENCE OF COMPRESSED CO₂

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Preface

This bachelor thesis entitled “Investigation of the pH-value of Silicic Acid in compressed CO₂” is the confidential information of the research at Fraunhofer Institute for Environmental, Safety and Energy Technology Umsicht, Oberhausen.

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Acknowledgement

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Finally, I would like to thank my co-workers at Fraunhofer for their assistance.



Abstract

Abstract

This thesis documents the design and construction of a high-pressure view cell designed to allow observation of the pH change of silicic acid under compressed CO₂. Additionally, this thesis also covers trial experiments using the high-pressure view cells. After the trials, the results are reviewed and discussed.

The idea of this thesis is that after observing the pH change of silicic acid, data can be retrieved to create H⁺ ions concentration-distance profile of the acid. This profile is then used in conjunction with the error function to determine the coefficient of diffusion of CO₂-silicic acid systems. Due to the complexity of such calculations, the calculations of the diffusion coefficient are omitted in this thesis. Based on the work done by this thesis, in the future others could replicate and go on further with the calculations.



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List of Symbols

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h	Thickness of each of the flanges	mm
ρ	Density of material 14462	kg/m^3
Π	Pi	
c	Specific heat capacity	$\text{J}/(\text{Kg}\cdot\text{K})$
m	Mass	Kg
ΔT	Temperature difference	Celsius
P	Power of the heating sticks	Watts
t	Time	Seconds
t_{\min}	Minimum wall thickness of the middle flange	mm
M	Combined mass of three flanges	kg
D_a	Outside diameter of cylindrical cell	mm
p	Design pressure	Bars
K	Design strength value at design temperature	N/mm^2
S	Safety factor at design temperature	
c_1	allowance for minus thickness tolerance	mm
c_2	wastage allowance	mm
v	weakening factor	
F_{SB}	minimum required bolt load	N
A_D	Area of the outer flange under pressure	mm^2
D	O-ring groove outer diameter	mm
d_k	minimum root diameter (minor diameter) of bolt	mm
n	number of bolts	
c	design allowance for rigidly connected bolts	mm
Z	auxiliary factor	
F_{SB}	Minimum required bolt load	N

List of Abbreviations

List of Abbreviations

Na_2SiO_3	Sodium Silicate / Waterglass
CO_2	Carbon Dioxide
H_2O	Water
H_2SiO_3	Silicic Acid
Na_2CO_3	sodium silicate / waterglass
$\text{Si}(\text{OH})_4$	Silicic Acid
$(\text{OH})_3\text{Si-O-Si}(\text{OH})_3$	Siloxane bridge
H_2CO_3	Carbonic Acid
H^+	Hydrogen Ion
CO_3^{-2}	Carbonate ion
H_2CO_3	Carbonic acid
Hind	Acidic form of liquid indicator
IndOH	Basic form of liquid indicator
Ind^-	Conjugate base of liquid indicator
Ind^+	Conjugate acid of liquid indicator



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1 Introduction

Silica Aerogel is an ultra-porous material, containing 90% air volumetrically. Additionally, Silica Aerogel has an impressively low density, with the lowest density of 0.003 grams/cm³ recorded. [1] Another attribute of aerogel which makes it desirable is its extremely low thermal conductivity. For the reasons mentioned, aerogel is an attractive material for thermal insulation uses.

The general Silica Aerogel production process comprises of three steps. First is the synthesis of the sol-gel, followed by an aging process and, lastly with the fluid extraction(drying) process. The sol-gel process uses a colloidal fluid as the starting material (also called precursor). This step is essentially a polymerization process in which siloxane bridges ($\equiv\text{Si-O-Si}\equiv$) are created. As a result of these bridges being formed, the precursor fluid is turned into a gel like substance. Sol-gel processes differ depending on the precursor. Although there is an array of precursors, the most prominent are TEOS, TMOS and waterglass (Na_2SiO_3).

The second step is quite similar among different precursors. During this step, the hydrogel is left in either room temperature or maintained at an elevated temperature. The purpose of this step is to allow additional siloxane bridges to form, enhancing the strength of the structure. Lastly, the drying process is done by extracting the fluid trapped in the pores of the structure of the hydrogel. The result could be aerogel or, xerogel. The type of gel produced in the end is contingent on the method of drying, whether it is ambient drying, supercritical drying or freeze drying.

At Fraunhofer, Aerogel is produced in a novel way, which uses compressed CO_2 to create Aerogel. Sodium silicate is dispersed into droplets which free fall from the top of a tower. While free falling, the sodium silicate solution droplets react with CO_2 which results in a drop in pH due to carbonic acid. With this method, the sol-gel method is completed nearly instantly.

Fraunhofer aims to find the most efficient parameters for the sol-gel process for Aerogel production. The method of producing hydrogel in Fraunhofer is quite unique. As a result, little to no literature is available to understand the sol-gel process further. The purpose of this project is to further understand the sol-gel process, which is the diffusion of CO_2 in the aerogel precursor. However, directly measuring the diffusion of CO_2 in a precursor solution is difficult. Fortunately, as CO_2 diffuses into water, it alters the pH of water. Therefore, one indirect way to observe the diffusion of CO_2 is to observe the pH change in the in a solution. An idea was proposed by professor Kilzer to build a high-pressure view that would house silicic acid and allow for observation of the pH change. A dispersed universal pH indicator is used to visualize the pH change. The concentration of H^+ ions at the surface can be determined based on the H^+ ions concentration-distance profile of the acid. Then, the coefficient of diffusion can be theoretically determined using the error function. However, due to the complexity of such project and the time constraint of the editing period of this thesis, this project only focuses on documenting the construction of a high-pressure view cell for visualizing the pH shift of silicic acid in compressed CO_2 , followed by carrying out a few experiments using said equipment. The topics of discussion will be as follows:

- Explaining the concept of determining pH using universal liquid pH indicators
- Determination of the theoretical approach and parameters of the experiments
- Construction of the high-pressure cell
- Testing the high-pressure cell
- Analysis of the results and evaluation of the high-pressure cell

2 State of the Art

2.1 Hydrogel definition

Hydrogel in general is a network of hydrophilic cross link polymer chains submerged in water. The water could be restricted by the network of cross links or freely moved within the network. These hydrogels could be differentiated based on its polymer network [2]. Silica hydrogel is a solid three-dimensional network formed from a solution of silica particles scattered in a liquid medium (sol). The solid network is formed when the liquid medium (such as silicic acid) creates siloxane bridges ($\equiv\text{Si-O-Si}\equiv$). The creation of siloxane bridges is called polymerization. This process of polymerization is termed the sol-gel process [1].

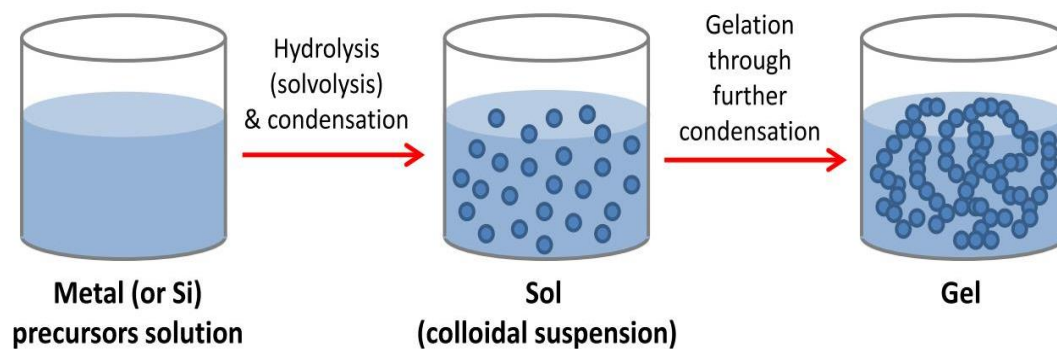
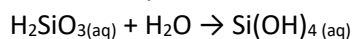


Figure 1: Sol-gel process of silica precursors [3]



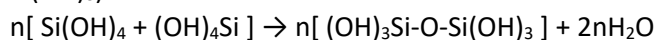
The gelation procedure of silicic acid could be described with the following chemical equations:

Silicic acid (H_2SiO_3) reacts with water to form acid sol ($\text{Si}(\text{OH})_4$) as can be seen in the following chemical equation:



Equation 1 [4]

The following chemical equation describes the silica sol ($\text{Si}(\text{OH})_4$) can form siloxane bridges ($(\text{OH})_3\text{Si-O-Si}(\text{OH})_3$):



Equation 2 [5]

The siloxane bridges condenses to form silica particles. These particles then form crosslink networks which create the structure of the resulting gel.

2.2 Diffusion of CO_2 in water

2.2.1 Definition of diffusion

As the gelation processes described above rely on diffusion of CO_2 in a solution, it is important to define what diffusion is. Diffusion is the movement of molecules from a higher concentration to a lower concentration. This movement can happen in gases, liquids, and solids. Additionally, diffusion can also occur between gases and liquids, such as the diffusion of CO_2 in water. The driving force of the diffusion of CO_2 in water is the difference in the partial pressure of CO_2 in the air and in the water. If the partial

pressure of CO₂ in air is greater than that of water, CO₂ molecules will diffuse and dissolve in water and vice versa [6].

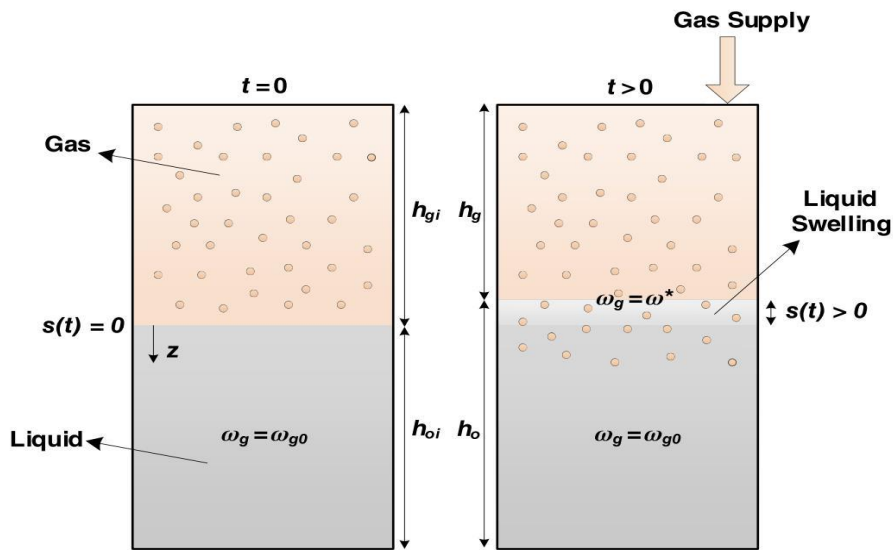


Figure 2: Illustration of diffusion of a gas into a liquid [7]

2.2.2 PH change

CO₂'s diffusion in water influences the water's pH value. The pH value of water differs depending on various factors such as temperature and pressure. Increasing the amount of CO₂ dissolved in water will reduce the pH value. More specifically, increasing pressure and decreasing temperature both serve to lower the pH of a solution. Under pressurized CO₂ conditions, pH values of water drops as low as 2.97 [8]. The drop in pH is due to the fact that when CO₂ is diffused in water, it reacts with water to form carbonic acid. The carbonic acid can then dissociate, releasing hydrogen ions, which lowers the pH of the water solution. The chemical equations which describe the aforementioned processes are as follows:

- Carbon dioxide reacts with water to form carbonic acid, as can be seen by chemical equation 3:

$$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$$

Equation 3 [9]

- The carbonic acid then dissociates, releasing 2 hydrogen ions as a result. This is demonstrated by equation 4:

$$\text{H}_2\text{CO}_3 \rightarrow 2\text{H}^+ + \text{CO}_3^{-2}$$

Equation 4 [9]

T/K	P/MPa	pH (Experimental)	pH (Model)
293.15	0.23	3.78	3.77
	0.74	3.53	3.52
	1.45	3.39	3.37
	2.15	3.32	3.29
	3.44	3.23	3.20
	5.07	3.18	3.13
323.15	0.23	3.88	3.86
	0.74	3.61	3.60
	1.45	3.48	3.46
	2.15	3.41	3.38
	3.44	3.32	3.28
	5.07	3.17	3.20
353.15	0.23	4.00	4.02
	0.74	3.70	3.73
	1.45	3.54	3.57
	2.15	3.46	3.49
	3.44	3.36	3.39
	5.07	3.28	3.31

Figure 3: Measured pH value of water under different Temperature and Pressure [10]

Figure 3 shows the pH of water at different temperatures and pressure. As can be seen in figure 3, increasing the pressure while maintaining the temperature results is a drop in pH. Increasing the pressure results in more diffusion of CO₂ into water. This results in more more hydrogen ions being released (as described by equations 3 and 4). The surge in the presence of hydrogen ions is what lowers the pH as pH measurements is essentially the measurement of the concentration of H⁺ ions present in a solution.

2.2.3 How pH values affect gelation

In theory, the condensation of silicic acid starts when the solution is supersaturated. Colloidal particles are generated, followed by the growth of these particles through polycondensation. Polymerization of silicic acid can be categorized into 3 stages, which is shown by figure 4. First is the formation of polysilicic acid from monosilicic acid and amorphous silica. Then, the formed polysilicic acid continues to grow by reacting with the monosilicic acid and solid silica. Last is the polymerization (or combination) between polysilicic acid chains. PH is a strong driver for the sol-gel condensation processes, as altering the PH would significantly result in a reduction or addition of gelation time. There are optimum PH values for each stage. These optimum PH values results in the least amount of time to fully polymerize the silicic acid solution[11].

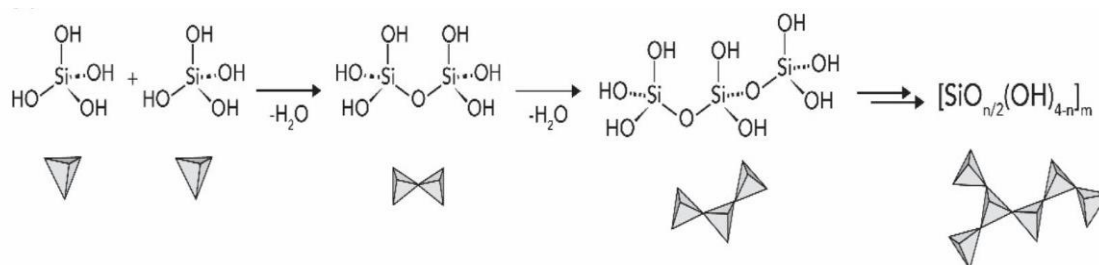


Figure 4: Condensation process of silicic acid [12]

pH value of the aqueous precursor solution has an immense impact on the rate of gelation. During a study of sodium silicate solution of 8% by weight, the ideal PH value for gelation is from 4-5. If pH values are above this, silica sols are negatively charged and repel each other. Below PH of 4, sols are positively charged, results in repulsion. In both scenario, the repulsion impedes gelation, leading to a substantial increase in gelation time[13].

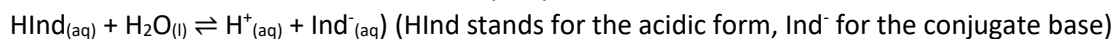
2.3 Methods for measuring the pH of silicic acid

Although pH probes are available at Fraunhofer, a large high-pressure cell would be required to fit the probes. This would lead to major material costs and installation difficulties. Furthermore, The widely available PH measurement probe measures pH at one minute point in the solution. This would mean that differences in PH between parts of a solution could not be measured. For example: During a study of the effects of pH of the sol-gel process on the structure of SnO₂ films, the entire solution of silica sol (or silica gel) was inspected as one instead of being inspected as constituent parts. Therefore, the usage of a pH probe is unreasonable [14]. Another common way of measuring pH values of water solutions is pH strips. However, pH strips could only be used once, making them undesirable for visualizing the change of pH values. Furthermore, pH strips, like pH probes, measure the acidity of the solution as a whole. For these reasons, universal liquid PH indicators are chosen. These liquid indicators are inexpensive and widely available. Most importantly, they can indicate differences in PH in a solution (by showing different colors).

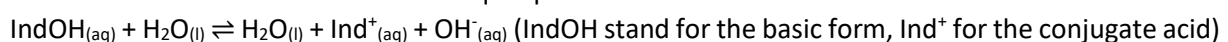
2.3.1 How liquid indicators work

Liquid pH indicators are chemical compounds (commonly weak acids are weak bases) which can visually indicate the pH of a solution when added in said solution. Typically, liquid indicators cause the color of a solution to change to different colors, depending on the pH of the solution. By inspecting the resulting color, the pH value can be determined. The chemical equations which describe the color changing process are:

- General reaction scheme of acidic liquid pH indicators:



- General reaction scheme of basic liquid pH indicators:



To further explain the general reaction scheme of liquid indicators, the acidic form(Hind) and the conjugate base form(Ind⁻) of the indicator have different colors. For the acidic indicator, depending on the amount of H⁺ Ions present in a solution, the equilibrium of the equation would shift towards more Hind or more Ind⁻. When the H⁺ Ions are abundantly present (in other words, the solution is very acidic), equilibrium will shift towards more Hind. This would turn the solution to turn into one color. When there are less H⁺ Ions (i.e., the solution is more basic), equilibrium would shift towards more Ind⁻, which would turn the solution a different color [15]. The reaction mechanism is similar for basic indicators.

2.3.2 Phenolphthalein

A typical example would be phenolphthalein. phenolphthalein shows a well-known color change from colorless in the acidic range and purple in the pH range of 8-9. The cause of this color change is due to the structural change of the molecule itself. When under pH of 8-9, the lactoid form Ph1 of phenolphthalein changes to Ph2 as the gamma-lactone ring is broken, which is shown by figure 5. This reaction is what gives the purple color of phenolphthalein. [16]

Construction of the high-pressure view cell

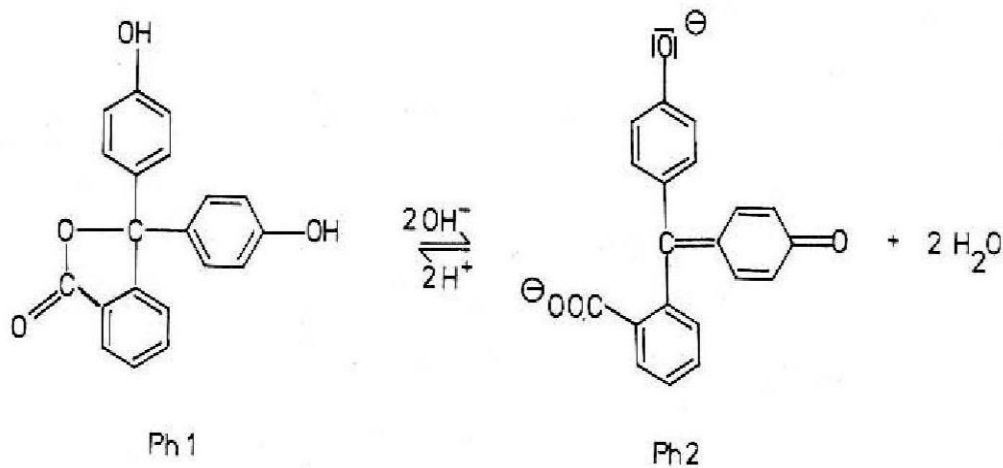


Figure 5: Structural change of Phenolphthalein from Ph 1 to Ph 2 [16]

2.3.3 Universal Liquid pH Indicator

As mentioned above, Phenolphthalein only visualizes the pH values of 8-9. As a result, phenolphthalein would be unable to visualize pH values of any other pH values. Like Phenolphthalein, several other common pH indicator such as Thymol blue, Methyl yellow, Methylene blue,.. share its limited range of pH value. Therefore, to wholly visualize a broader range of pH, universal indicators are required. Universal liquid pH indicators are a combination of well-known pH indicators. As a result, the universal pH indicators can visually illustrate a much broader range of pH values.

As explained in the previous chapter, when CO_2 diffuses into water, hydrogen ions are released. These hydrogen ions would shift the balance of the different forms of indicators, therefore changing the color due to the reaction mechanism of the indicator. If each region of a solution possesses a different pH value than the other, each region of the solution would display a different color than the other. The use of universal liquid indicators is relatively simple as there is only one solution covering a broad range of pH values instead of several solutions covering a narrow range of pH values. Furthermore, the results can be easily observed. However, it should be noted that more complicated measurements would give more exact data, even though the results could be harder to be interpreted. [17]

As universal liquid indicators possess a broad range, a simple set up (1 solution) and the results (color) could be easily analyzed, it is the perfect choice for the intention of this thesis, which is to visualize the pH change of silicic acid when being diffused by pressurized CO_2 .

3 Construction of the high-pressure view cell

To carry out pH measurement at elevated temperatures and pressures, a high-pressure cell must be used. However, since the requirement for the experiments of this thesis is quite unique, there are no available high-pressure cells at Fraunhofer that meet all the requirements. Therefore, an appropriate high-pressure cell must be constructed.

The objective of this thesis is to construct a high-pressure view cell and to carry out experiments concerning the measurement of pH of silicic acid. The ideas of the experiments are as follows. First, a container partially filled with a solution of silicic acid and universal liquid pH indicator. The container is then sealed before being pumped with compressed CO_2 and left to age for a certain amount of time. As the CO_2 diffuses into silicic acid, hydrogen ions are dissociated. This would alter the pH of the silicic acid and therefore cause a color change in regions of the acid where CO_2 has been diffused into. Assuming CO_2 -silicic acid system to be the same as CO_2 -water system, the more CO_2 is diffused into

Construction of the high-pressure view cell

the solution, the more acidic the solution gets. Different regions of the solution would display different colors depending on their acidity. By analyzing the colors, approximate pH values are obtained and the diffusion coefficient of CO₂ in silicic acid could theoretically be obtained. The experiment will be conducted at temperatures of 60, 80 and 100 degrees Celsius and pressures of 60, 80 and 100 bars.

3.1 Requirements list

The requirements of the middle flange must be determined before a sketch can be made. The general requirements are:

1. Visibility: Since the experiments involve taking pictures or videos of silicic acid to observe the color change, the silicic acid must always be visible during the experiments. This means that part of the high-pressure cell must be made of transparent material.
2. Temperature: Temperature sensors must be ideally placed to receive accurate reading of the temperature of silicic acid.
3. Pressure: The cell must be pressurized to a desired pressure, therefore a pressure sensor needs to be logically placed to attain accurate pressure readings.
4. Sealing: The cell must be completely sealed to prevent leakage of CO₂ or silicic acid. A method of sealing must be determined.
5. Heating: The cell must be heated to a desired temperature. Therefore, a method to evenly heat the entire cell is required.
6. Material: The high-pressure cell must be able to withstand the corrosive nature of silicic acid. As the experiments will be conducted at elevated temperature (60 degrees and above), the high-pressure cell must be able to raised to and maintained at the desired temperature. As the experiments also consist of introducing pressurized CO₂ (up to 100 bars), the high-pressure cell must be able to withstand forces resulting from the pressure.
7. Dimension: The high-pressure cell must be compact and relatively lightweight to be economically reasonable and easily manufactured and assembled.
8. Repeatability: As the experiments involve photography and videography, lighting conditions are crucial to repeatability. A method must be constructed to ensure every experiment is conducted under the exact same illumination condition to obtain comparable data.

3.2 Overall dimensions of the middle flange and the channel

Fortunately, a cylindrical pressure cell which meets all the requirements for the thesis is available at RUB. It is comprised of 2 cylindrical flanges made of stainless steel (outer diameter 100mm, 30mm thick, material 14462, sapphire windows (25mm) for visibility) and a 1mm thick aluminum sheet in between. This is shown in figure 6. These flanges are custom made and the stock pieces are widely available at RUB. However, a slight modification of the 2 outer flanges and a replacement of the aluminum sheet must be made.

Construction of the high-pressure view cell

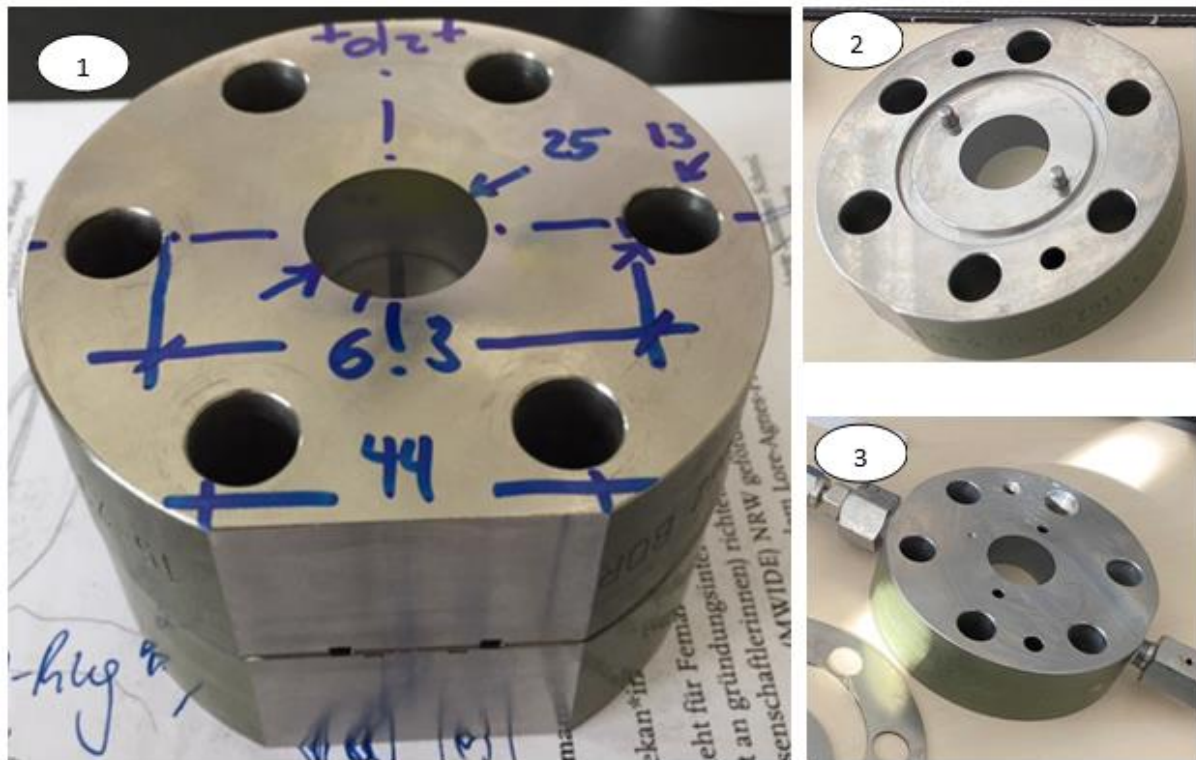


Figure 6: Cell outside surface (1) and inside surfaces (2) and (3)

To insert and observe the silicic acid, a middle flange must be made to contain the silicic acid. The 2 outer flanges would press against each side of the middle flange. The sapphire glass window present on each outer flange allows for visibility inside the channel. Figure 9 shows the concept design.

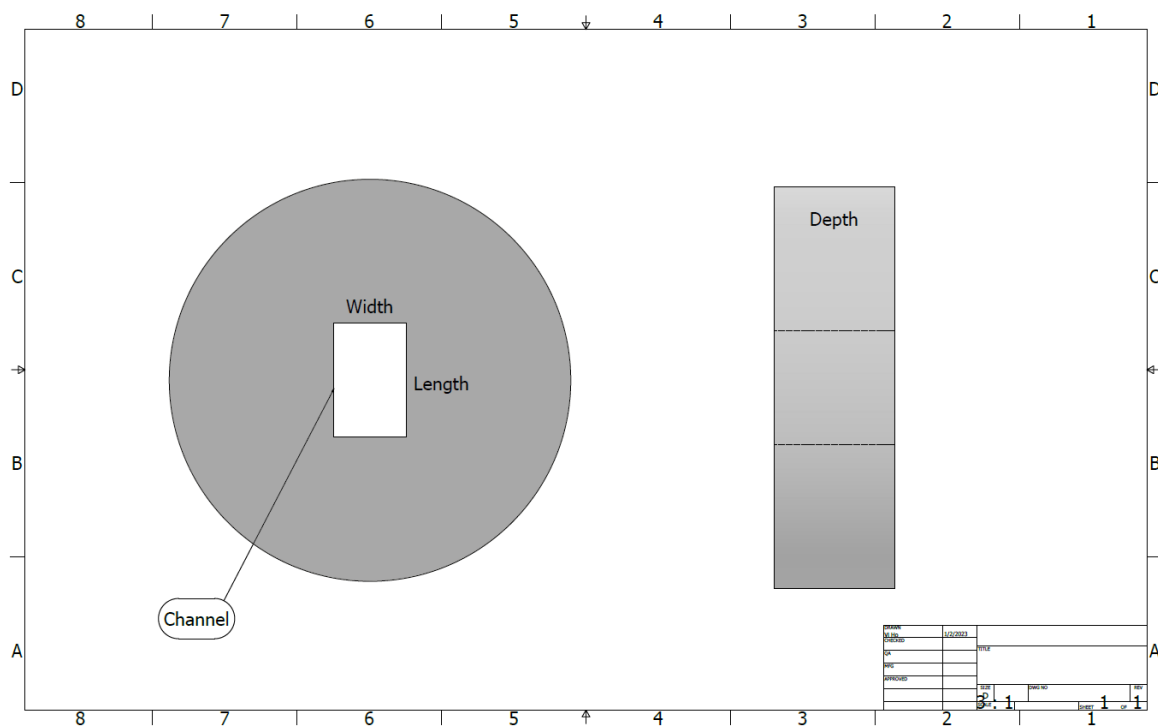


Figure 7: Concept design of the middle flange

However, there are some restrictions when it comes to the dimensions of the channel. On one hand, the width and depth of the channel must not be too wide to avoid Rayleigh-Taylor instability and

Construction of the high-pressure view cell

instability due to temperature gradients. Rayleigh-Taylor instability is the mixing of fluids of different densities as an effect of earth's gravity. When a denser fluid lies atop of a lighter fluid, due to gravity a parcel of the heavier fluid moves downward as an equal volume of the lighter fluid moves upwards, resulting in mixing. As CO₂ diffuses in water, given that the temperature remains the same, the density increases [18]. This results in the top layer of the solution having a higher density than the layer below. Therefore Rayleigh-Taylor instability could occur. As for instability due to temperature gradients, before temperature equilibrium, parts of the solution that are closer to the heating element would have a higher temperature than parts that are further away. This would also create differences in density and promote internal mixing. These mixing would affect the premises of this thesis as mixing is not strictly one-dimensional diffusion. Fortunately, for a given geometry (such as the geometry of the channel), there is a critical dimension (such as width, length, depth) such that similar geometries with dimensions not exceeding the critical dimensions will not observe Rayleigh-Taylor instability or instabilities due to temperature differences.

On the other hand, if the width of the channel is too small, surface tension would create a curved liquid surface affecting the diffusion of CO₂. Furthermore, if the channel's depth is not sufficiently large, the solution would appear nearly transparent, making any color detection impossible. Based on self-conducted experiments, channel thickness of at least 10mm is required to reliably detect the color of the solution. However, due to the time-consuming nature of manufacturing such a metal flange, a thickness of 30mm (which is the thickness of the stock pieces) is chosen. As for the channel width, due to the uniqueness of the geometry of the channel, data is unavailable concerning the calculation of the Rayleigh-Taylor instability and the instability caused by temperature gradients. As a result, the critical dimensions to avoid mixing due to differences in density could not be calculated. Therefore, a thickness of 3mm is chosen as an estimation of Professor Kilzer. The length of the channel is chosen to be 20mm. The diameter and material of the middle flange are identical to the stock pieces (which are 100mm and material 14462).

3.3 Specific design of the middle flange and accessories

Based on the requirements list and the determined dimensions in, a morphological box can be made.

Table 1 Morphological table of dimension and accessories

Morphological Table		
	Requirements	Solution
1	Visibility	Sapphire glass
2	Temperature sensor placement	Placed inside the middle flange
3	Temperature sensor	Thermocouple (TC Direct, Type K, 405-023, 3 mm diameter x 100mm length)
4	Pressure sensor placement	Placed inside piping system
5	Pressure sensor	WIKA (model A10, range 0-160 bars)
6	Heating method	Heating sticks (Niggeloh, 6.22mm diameter x 90mm length)
7	PID controller	Jumo (Quantrol LC100)
8	Sealing	O-rings (NBR, 52x3mm)
9	Alignment	Dowel pins (4x14mm, m6, DIN 6325)
10	Material	14462
11	Dimensions	100m diameter, 30mm thickness, 20x3x30mm channel
12	Tightening elements	M12 bolts (DIN912, A4 – 80), M12 nuts (DIN934, A2 – 80)
13	Repeatability (lighting conditions)	Blackbox with interior lighting (520x520x520mm, Proxistar studiolerate light tent)

Construction of the high-pressure view cell

Further explanation of the solution is given as follows:

As the objective of heating is to elevate the temperature of the acid and maintain that temperature, the temperature sensor should be placed as close to the acid as possible (which is inside the middle flange). There would be 2 temperature sensors, one to measure the exact temperature of the acid, the other to measure the temperature of the flange itself (for temperature regulation of the heating sticks). There are several heating methods such as submerging the cell in heated water, using heating oils and using heating sticks. Although submerging the entire cell in heated water would ensure that the set-up is evenly heated, implementing such a system that can contain the high-pressure cell underwater while maintaining visibility inside the high-pressure cell is unnecessarily complicated and time consuming. A heating system using oil would also be unnecessarily complicated and time-consuming. Although heating sticks would not ensure temperature homogeneity across the equipment, it is cost effective and easy to design and install. The pressure sensor would be placed in the piping system instead of inside the flanges. This is done to ensure accurate readings and to provide space in the flanges for other accessories. The material and dimensions of the middle flange is chosen to be the exact same as the stock pieces to avoid manufacturing complications and to optimizing the manufacturing time. M12 bolts (DIN912, A4 – 80), nuts (DIN934, A2 – 80), heating sticks (Niggeloh, 6.22mm diameter x 90mm length), O-rings (NBR, 52x3mm) are chosen as the provided outer flanges already have 6 drilled holes for M12 bolts, 2 drilled holes for 6.22mm diameter heating sticks and an O-ring groove for 52x3mm O-rings (Although there was already an O-ring groove present in one of the outer flanges, no O-rings were provided. The suitable O-ring dimension was determined using C. otto Gehrckens O-ring calculator [19]). The chosen heating stick has a power of 50 watts. To ensure that this is a reasonable choice, an estimation of the heating time has been calculated:

The set up comprises of 3 roughly identical cylindrical metal pieces of material 14462. Assume the flanges to be completely solid. The total mass of the setup is can be calculated using equation 5:

$$M = 3 \times \left(\frac{D}{2}\right)^2 \times \pi \times h \times \rho$$

Equation 5

Where h is the thickness of each of the flange (30mm) and ρ is the density of the flanges (7805 kg/m³)

$$M = 3 \times \left(\frac{0,1}{2}\right)^2 \times \pi \times 0.03 \times 7805$$

$$M = 5.52 \text{ (kg)}$$

As 2 heating sticks are used, the total power is 100 watts. Assuming the heat loss is negligible. The amount of time needed to raise the temperature of the equipment from room temperature (20 degrees Celsius) to 100 degrees Celsius is:

$$P \times t = m \times c \times \Delta T$$

Equation 6

Where P is the combined power of the heating sticks, t is the time needed to raise the temperatures of the flanges, m is the total mass of the flanges, c is the specific heat capacity and ΔT is the units of temperature to be raised. Continuing with equation 6:

$$100 \times t = 5.52 \times 450 \times (100-20)$$

$$t = 1806 \text{ (seconds)} = 30.1 \text{ (minutes)}$$

A maximum waiting time of 30 minutes for the equipment to preheat is reasonable.

Construction of the high-pressure view cell

Dowel pins (4x14mm, m6, DIN 6325) were chosen to properly align three flanges together. For repeatability, a black box (520x520x520mm, Proxistar studiogerate light tent) is chosen to encapsulate the flanges. This would provide each iteration of the experiments with identical lighting conditions. The temperature sensor (TC Direct, Type K, 405-023, 3 mm diameter x 100mm length), pressure sensor (model A10, range 0-160 bars, WIKA) and the PID controller (Jumo quantrol LC100), are chosen because they are widely available to Fraunhofer and reliable as every other high-pressure cell at Fraunhofer are equipped with them.

In addition to the accessories, fine scratches, each 0.5mm apart, are made on the edge of the channel. This is done to help track the position of the color change.

3.4 Implementation of accessories into the design of the middle flange

3.4.1 Bolt holes and heating sticks holes

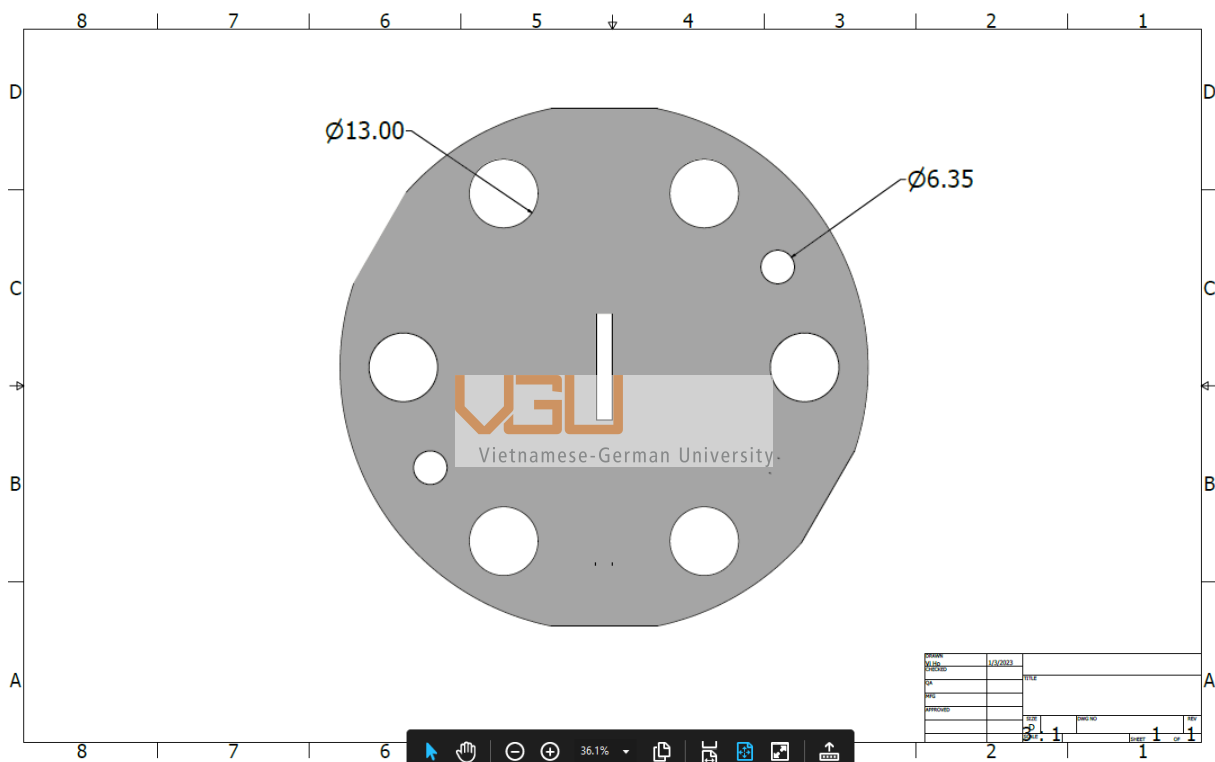


Figure 8: Drawing for concept design of bolt holes and heating stick holes

Like the provided outer flanges (figure 6), figure 8 shows the design for the middle flange, which has 6 bolt holes (13mm diameter) and two holes for heating sticks (6.35mm diameter).

3.4.2 Dowel pins, Thermocouple holes, O-ring grooves, input and output channels

As can be seen in figure 6, one of the outer flanges (picture 2) has dowel pins while the other has holes for dowel pins. Therefore, the middle flange must have holes on one side and dowel pins on the other side.

One of the thermocouples must make contact with the acid inside the channel to receive a reading of the temperature of the acid. The other will be used to regulate the heating sticks to preheat the high-pressure cell, therefore it must be in contact with the metal. The purpose of preheating the flanges is to bring the temperature of the acid to a desired temperature. Therefore, the point of measurement for the second thermocouple must be in close proximity to the channel, where silicic acid makes contact with the flanges.

Construction of the high-pressure view cell

The input of silicic acid and CO₂ should be done in two separate pipelines so that the equipment can be easily operated and maintained. There would be 2 through holes drilled, one on top of the channel and one below the channel. The through hole below will be used to input the silicic acid while the upper hole will be used to input CO₂. The silicic acid will partially fill the channel, leaving a small gap on top for the CO₂ to infiltrate.

As can be seen in figure 6, one of the flanges already possesses an O-ring groove. Therefore, only one side of the middle flange will require an O-ring to prevent any leakage from the channel.

When the experiment is conducted, the channel will be pressurized with compressed CO₂. Therefore, it is imperative that any through holes to the channel be completely sealed. There are three through holes to the channel in total, they are the silicic acid input hole, the CO₂ input hole, and the hole for the thermocouple to measure the temperature of the silicic acid. The hole for the CO₂ input will be sealed using Buttech 3/8" screw thread as the CO₂ piping system at Fraunhofer also uses Buttech 3/8". The other holes will also utilize the exact same kind of screw thread for simplicity's sake.

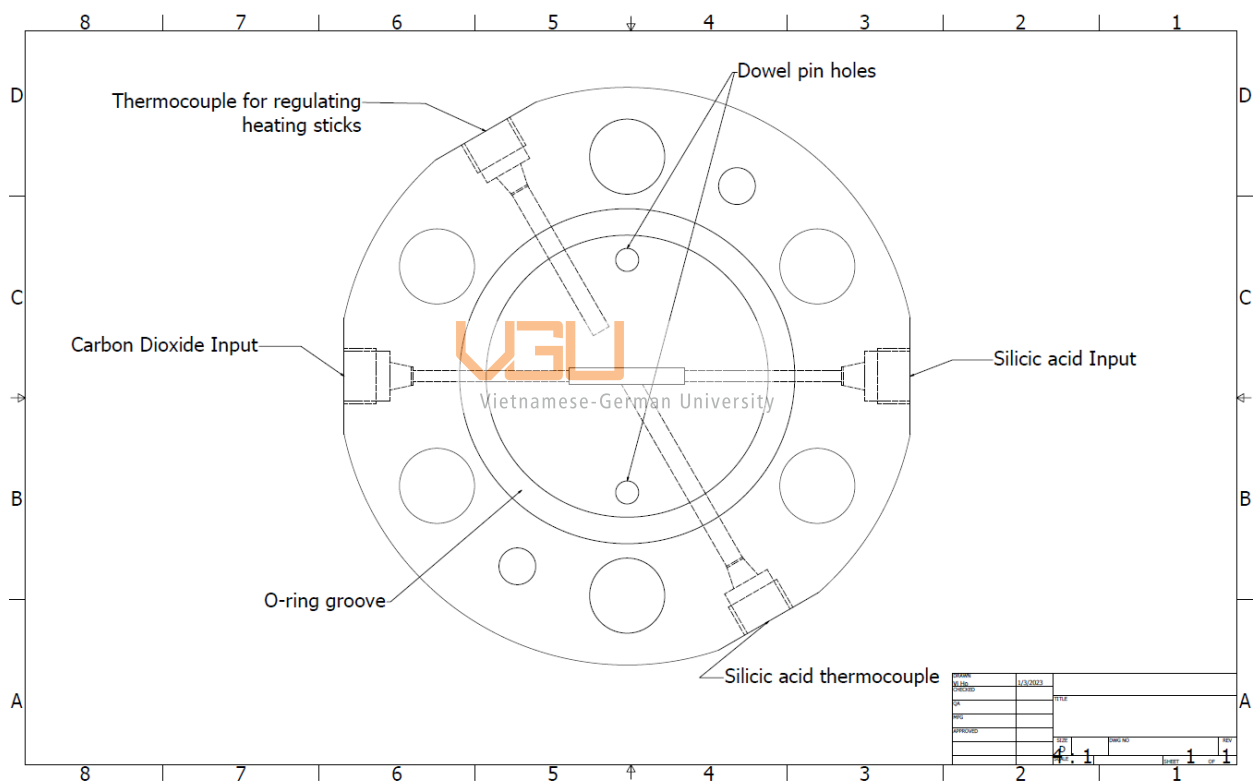


Figure 9: Drawing for concept design of thermocouple holes, dowel pin holes, O-ring groove, Silicic acid input and CO₂ input

It should be noted that in this drawing, the cell is oriented differently than how it would be when installed. When installed, the path for silicic acid input and CO₂ input would be perpendicular to the ground.

3.4.3 Official drawings of the middle flange

The official drawings with specified dimension of the middle flange are as follows:

Construction of the high-pressure view cell

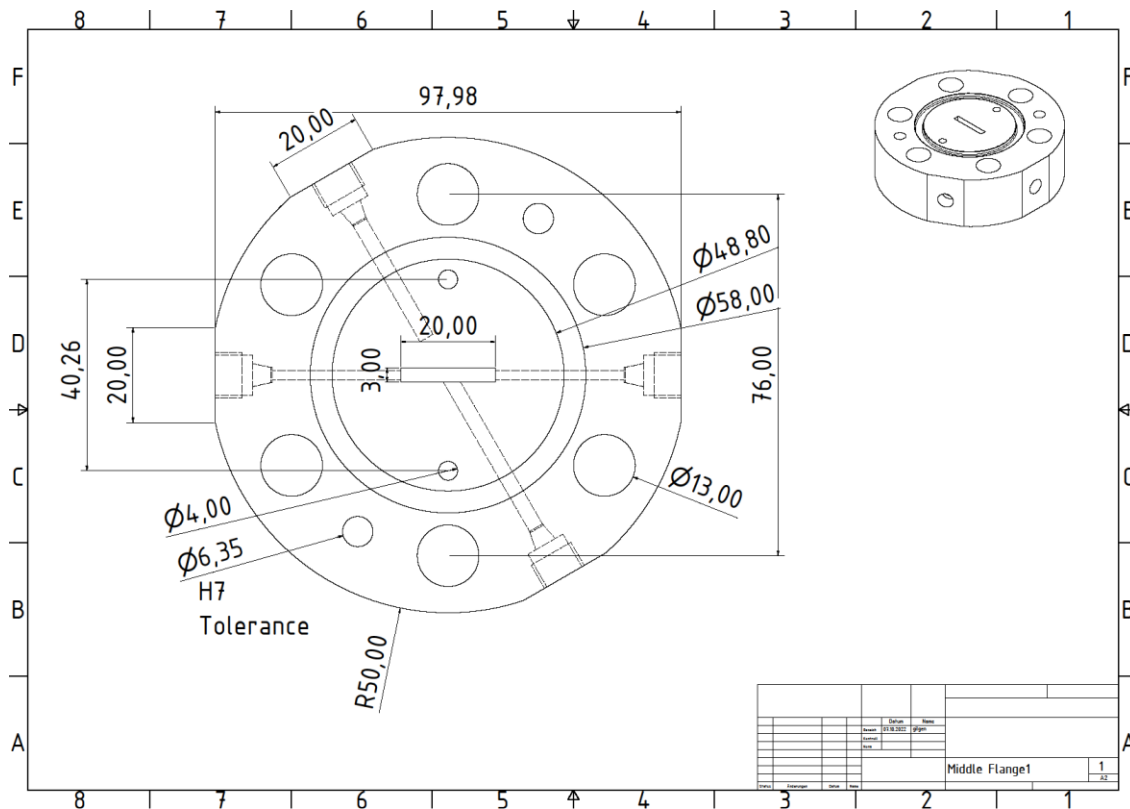


Figure 10: Front view of middle flange with the overall dimensions and the dimensions of bolt holes, heating stick holes, dowel pin holes, O-ring groove and the channel

As can be seen from figure 10, the H7 tolerance is chosen for the dowel pin holes (4mm diameter) (the tolerance does not apply to the 6.35mm diameter hole for the heating sticks). For cleaning purposes, it is desirable that the dowel pins can be removed if wanted. At the same time, the dowel pins should be firmly in place. As the dowel pin is made with a tolerance of m6, a tolerance of H7 for the hole satisfies these requirements [20].

Construction of the high-pressure view cell

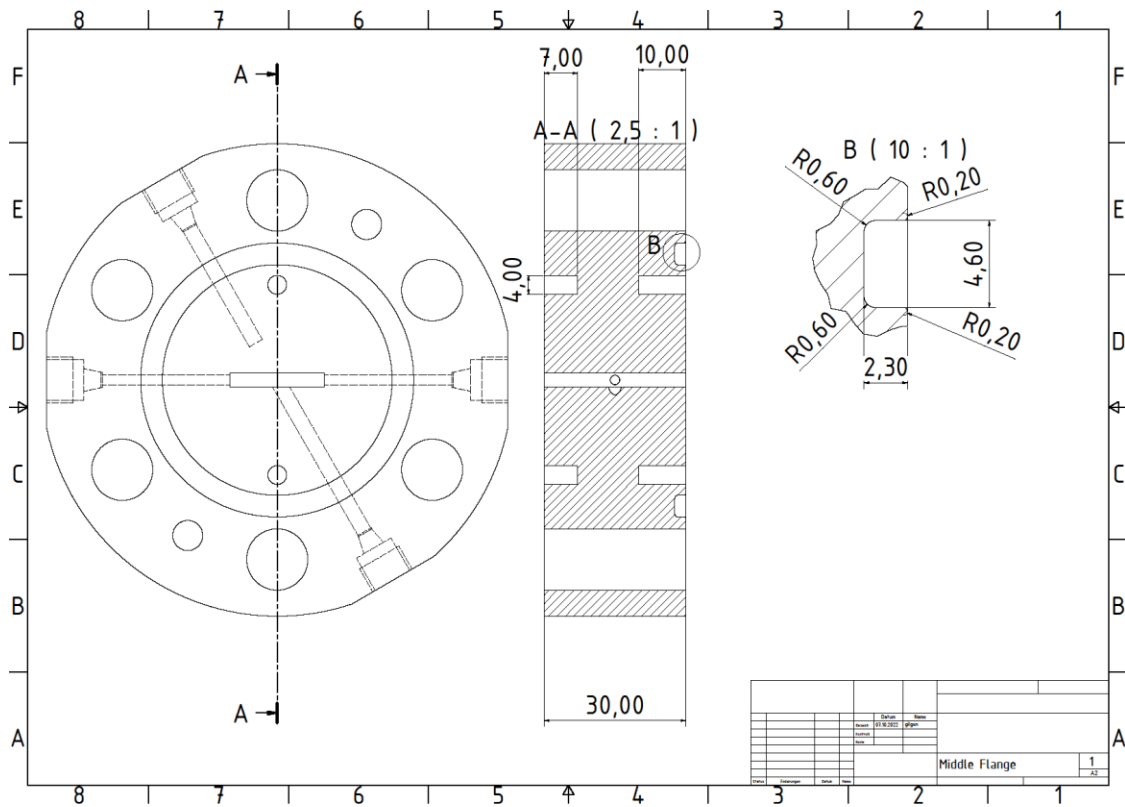


Figure 11: Side view of middle flange with the dimensions of dowel pin holes and the enlarged detailed drawing of the O-ring groove (section B)

The dimensions of the O-ring groove are taken from the dimensions of the already present O-ring groove in one of the outer flanges. In figure 11, the holes for dowel pins on each side of the flange have different depths. On one side, there are 7mm holes to adapt the dowel pins that come with one of the outer flanges. The other side has deeper dowel pin holes of 10mm to compensate for the shallowness of the dowel pin holes in the other outer flange piece.

Construction of the high-pressure view cell

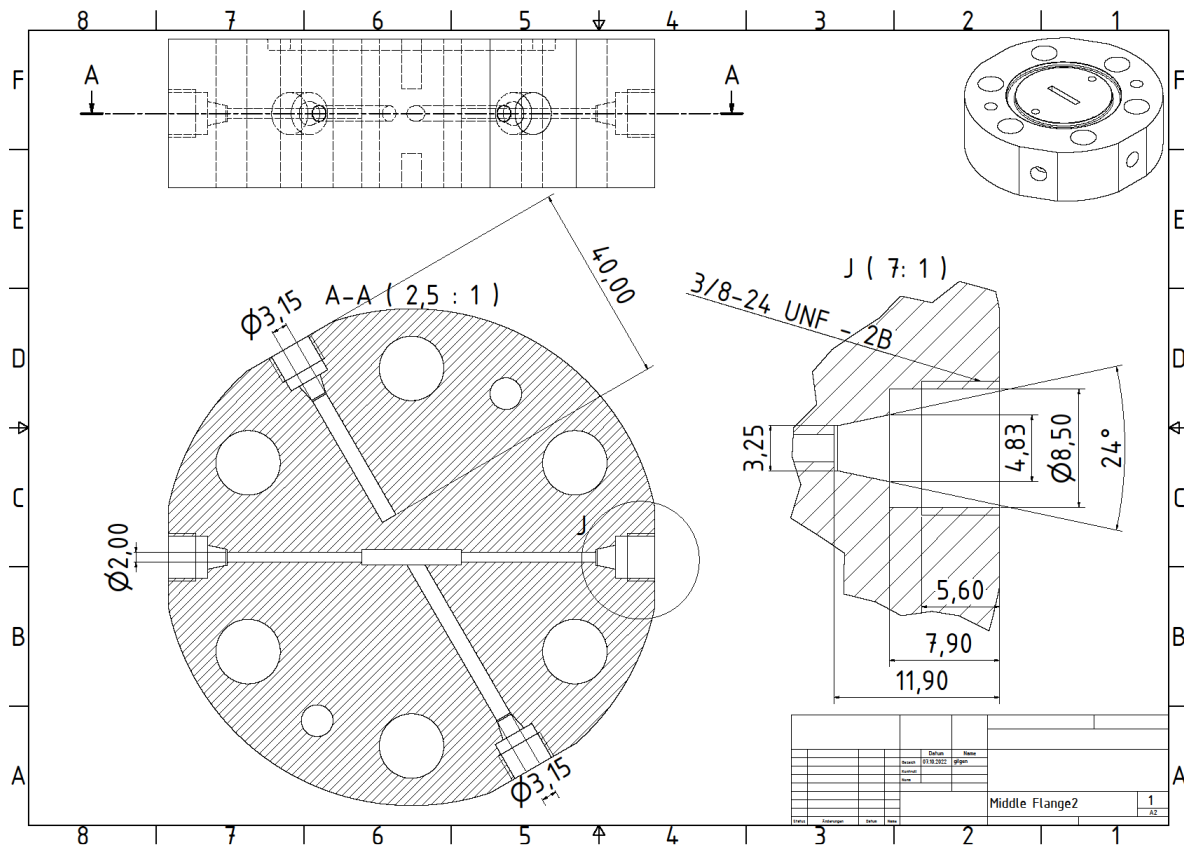


Figure 12: Half section view of middle flange with enlarged drawing of adapted hole for 3/8" Butech screw head

As can be seen from figure 12, the edge of the flange is flattened instead of round where the holes are. This is done to aid the workshop at RUB with the construction of the adapted holes, as it is easier to create threaded holes on flat surfaces compared to curved ones. The dimensions for the Butech screw heads are taken from the Butech catalog [21]. The holes for the thermocouples are made 0.15mm wider than the diameter of the thermocouples for ease of insertion. As the thermocouples only measure temperature at the tip, there is no need to design tightly fitted holes. The thermocouple is functional if the tip is in contact with the subject to be measured. The input hole for silicic acid is made as narrow as possible so that the hole could be cleaned by blowing compressed air through. The same geometry is used to create the input hole for carbon dioxide. This is done so that the hole for carbon dioxide and silicic acid can be used interchangeably.

3.5 Calculation for minimum wall thickness confirmation, minimum bolt size confirmation and determination of tightening torque

Since the high-pressure cell is subjected to pressures of up to 100 bars, it is essential to ensure that the contraption will be able to hold the force. Minimum wall thickness will be calculated to decide whether the design meets the minimum thickness to withstand the pressure or not. The calculations made in this chapter are completed with the assistance of Mr. Joachim Hillers, an employee at Fraunhofer.

3.5.1 Minimum wall thickness calculation

According to AD Merkblatt 2000 [22], section B0 and B1, the minimum wall thickness for a vessel made of material 14462 subjected under 100 bars of pressure is:

Construction of the high-pressure view cell

$$t_{\min} = \frac{D_a \times p}{2 \times \frac{k}{s} \times v + p} + c_1 + c_2$$

Equation 7

Where D_a is the diameter of the middle flange (which is 100mm), p is the maximum pressure that the flange will be subjected to (100 bars), S is the safety factor (1.5), c_1 is the allowance for minus thickness tolerance (0), c_2 is the wastage allowance (0), v is the weakening factor (1) and K is the design strength value of material 14462 (540N/mm² at 20 degrees Celsius and 210N/mm² at 100 degrees Celsius).

Plugging the variables in equation 7, the minimum wall thickness is:

$$t_{\min, 540} = 1.33\text{mm} \quad \text{or} \quad t_{\min, 210} = 3.45\text{mm}$$

According to the calculation, the middle flange must exceed 3.45 mm in wall thickness. However, the thinnest part of the middle flange (the walls separating the O-ring groove and the bolt holes) is only 2.5mm thick, which is smaller than the minimum thickness. Although one of the outer flanges had the exact same flaw, they were successfully used under conditions of much higher than 100 bars. After taking these facts into account and consulting the RUB workshop, it was decided that no redesign is necessary.

3.5.2 Minimum bolt size calculation and determination of tightening torque

When pressurized, CO₂ will push against the outer flanges. This would result in a force pushing both outer flanges away from the middle flange. The minimum required bolt load is therefore equal to the exerted force. The required bolt force, as described by equation 8, is:

$$F_{SB} = P \times A_D$$



Equation 8

Where F_{SB} is the minimum required bolt load, P is the maximum operating pressure (100 bars) and A_D is the area of the flanges under pressure. The area under pressure can be calculated using equation 9:

$$A_D = \frac{D^2}{4} \times \pi \times 2$$

Equation 9

Where D is the outer diameter of the O-ring groove. Continuing with equation 9:

$$A_D = \frac{58^2}{4} \times \pi \times 2 = 5284 \text{ (mm}^2\text{)} \text{ (D is the outer diameter of the O-ring groove)}$$

Continuing with equation 8, the required bolt load is then:

$$F_{SB} = 10 \times 5284 = 52840 \text{ (N)}$$

As there are 6 bolts, the required load for each bolt is:

$$F_{SB1} = \frac{52840}{6} = 8806 \text{ (N)}$$

Equation 10

The equation to calculate the minimum root diameter of each bolt (equation 11) according to AD Merkblatt 2000 [22], section B7 is:

Testing the high-pressure cell

$$d_k = Z \times \sqrt{\frac{F_{SB}}{k \times n}} + c$$

Equation 11

According to section B7, c (the design allowance) is equal to 3(mm), Z (the auxiliary factor) is equal to 1.75 and the design strength value (k) for M12 bolts is 1200N/mm². Therefore, the minimum root diameter is:

$$d_k = 1,75 \times \sqrt{\frac{8806}{1200}} + 3 = 7.74$$

The required root diameter for the tightening bolt is less than the root diameter of M12 bolts. Therefore, M12 bolts are sufficient. Based on the information provided by Mr. Joachim Hillers, the required torque for M12 bolts of strength class 80 is 75Nm.

VA Schrauben A2/A4 Anziehdrehmoment in Nm				
A2-50 und A4-50: Werte gelten ohne Längenbegrenzung A2-70 und A4-70 sowie A2-80 und A4-80: Werte gelten nur für Schraubenlängen bis zum achtfachen Gewindedurchmesser				
Gewinde	Steigung	Festigkeitsklasse		
		50	70	80
M5	0,8	1,7	3,5	4,7
M6	1,0	3	6	8
M8	1,25	7,1	18	22
M10	1,5	14	32	43
M12	1,75	24	58	75
M16	2,0	58	135	180
M20	2,5	114	280	370

Figure 13: Torque table for different sized and different strength class bolts

After the calculations, it is clear that the middle flange will be able to withstand the highest pressure setting of the experiment (100 bars).

4 Testing the high-pressure cell

4.1 Setting the parameters of the experiments

For each iteration of the experiment, a sample size of 1.7ml is chosen. As the camera is positioned as close to the cell as possible to maximize the definition of the color of silicic acid, the amount of acid used should be as little as possible as the more silicic acid used, its profile in a picture frame becomes larger and the effects of lens distortion is amplified. At the same time, there should be an adequate amount of silicic acid so that the fluid level is high enough to make contact with the thermocouple. The amount of 1.7ml is chosen to satisfy both requirements. After set of trials were done using the high-pressure cell at Fraunhofer, it was found that after 20 minutes, the change of pH slows down dramatically. Therefore, carry out as many trials as possible while getting the most out of each trial, a duration of 20 minutes is chosen. If the lighting setting of the camera is too bright (i.e., shutter speed too slow and ISO too high), colors are harder to tell apart. Lower lighting settings are more favorable in terms of color detection and color distinction. If the lighting setting of the camera is too low, the 0.5mm scratches become undetectable, making dividing the channel into equal layers impossible. Brighter settings are more favorable when it comes to the visibility of the scratches. After

Testing the high-pressure cell

experimentation with several settings, 1/60 shutter speed, f5.6 and ISO 80 is found to be the best middle ground.

Aerogel is produced at Fraunhofer at 60 degrees Celsius and 100 bars. As the ultimate purpose of studying the pH change is to determine the optimum temperature and pressure setting for Aerogel production, this thesis aimed to conduct experiments at 40, 60, 80 and 100 degrees Celsius. However, after several trials, it was discovered that experiments at 80 and 100 degrees were not possible. Silicic acid would gel nearly instantaneously after coming in contact with the channel when the cell is preheated to 80 or 100 degrees (As can be seen in figure14). Not only that, coming in contact with the view cell at such temperature completely altered the pH of the solution of basic (approximately 10.5) to neutral (approximately 7) without the presence of CO₂.

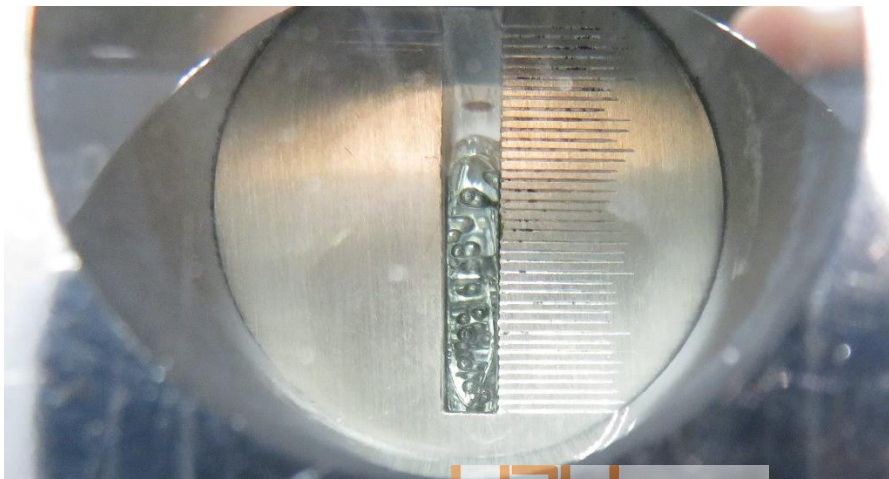


Figure 14: Silicic acid solution moments after being inserted in 100 degrees Celsius preheated cell

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As a result, experiments could only be conducted at 40 and 60 degrees Celsius. At each temperature, a pressure of 60, 80 and 100 bars is tested. Each setting is replicated three times for reliability purposes. This results in 18 experiments in total for the 7% solid content silicic acid solution. Due to the time constraints, silicic acid with different solid content could not be tested.

4.2 Silicic acid preparation

To have silicic acid as a precursor, it must first be synthesized using water glass. The synthesis system can be shown by figure:

Testing the high-pressure cell

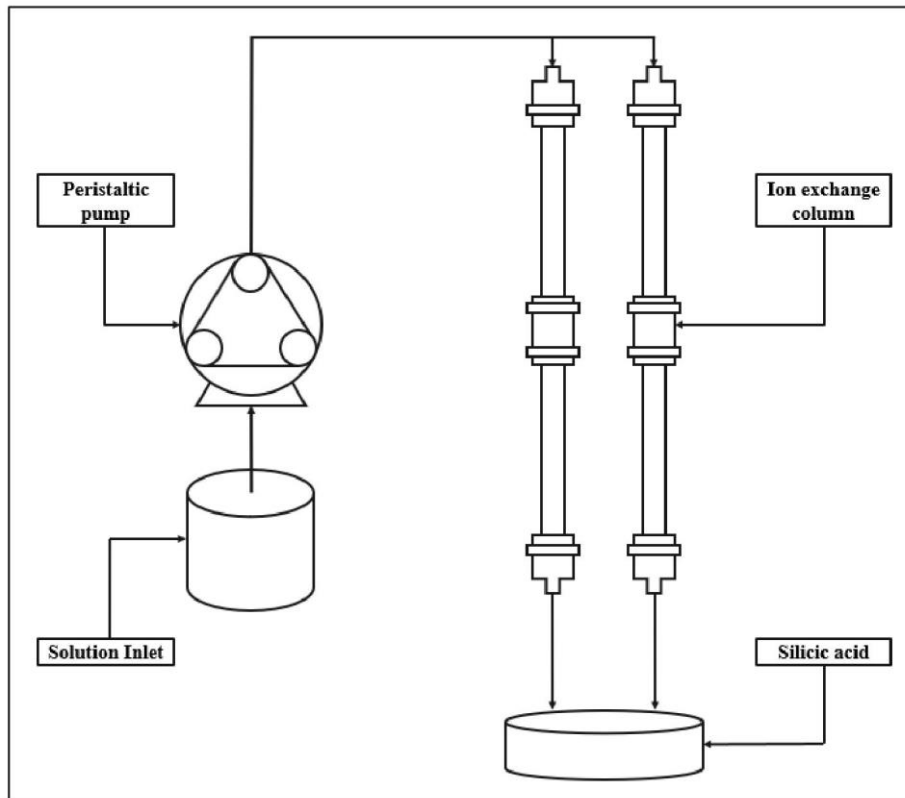
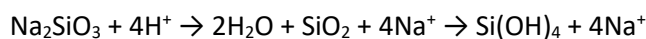


Figure 15: Silicic acid synthesis equipment [23]

The ion exchange column is filled with resin (Amberlite IR120, CAS no.78922-04-0, ACROS ORGANICS). The process of producing silicic acid at Fraunhofer requires several steps of pumping different solutions such as distilled water, sodium hydroxide (synthesized from sodium hydroxide beads (CAS No.1310-73-2, Roth) and hydrochloric acid (CAS No.7647-01-0, VWR Chemicals) to prime the resin inside the columns. At the start of the process water is pumped through the columns until the solution flowing out has a neutral pH. Then sodium silicate is fed through the columns. The resulting solution is silicic acid. After the collection of silicic acid, sodium hydroxide, water and hydrochloric acid is pumped through the columns to condition the resins for the next use. The chemical equations which describe the formation of silicic acid inside the columns are as follows:



Equation 12

The solid content of the produced silicic acid is then determined by leaving approximately 1 gram of silicic acid in a heating oven (Heraeus UT6102) at 120 degrees Celsius overnight. After drying, the remaining solid content is weighted using a scale (WAS 220/C/2, Radwag) to determine the solid content of the produced acid. The acid is then diluted to 7% solid content. The silicic acid is then sealed and refrigerated at 4 degrees Celsius.

4.3 Experimental procedure

4.3.1 Sample preparation

According to previous experiments, silicic acid starts to gel when its pH value reaches neutral (pH 7). For silicic acid to gel in the presence of compressed CO₂ (i.e., pH of silicic acid to drop to neutral in the presence of CO₂), it must first be brought to basic pH values. To prepare a silicic acid batch for experiments with the Henske cell, 50 grams of 7% silicic acid is mixed with 1.9 grams of ammonia

Testing the high-pressure cell

(EMSURE, CAS no.1336-21-6) while the rest stays refrigerated for the coming trials. This raises the pH value of the solution from approximately 1.5 to approximately 10.5. Twenty drops (2 drops per 5 grams) of universal liquid indicator (UNISOL 410, UN-Nr.3316) is dispersed in the batch using a 1ml syringe (ISO 7886, type LDS, BBRAUN). This would turn the solution purple. The universal indicator (UNISOL 410, UN-Nr.3316) is chosen because it has the most precise pH range and the colors between different pH values are the most distinctive out of the available universal indicators on the market. The contents of this universal indicator is unretrievable as it is confidential to the manufacturer. As silicic acid is known to be unstable and easily gelled under the influence of temperature, the batch is then sealed and stored at 4 degrees Celsius inside the refrigerator at Fraunhofer. A batch only lasts for one day, each day a new batch is prepared.

4.3.2 *Setting up and setting the parameters of the experiments*

The entire assembly (comprising of the 2 outer flanges, the middle flange and the camera) is fitted inside the Proxistar light tent. A consumer grade camera (PowerShot SX730 HS, Cannon) is used to record the diffusion process inside the view cell. The light tent is lined with the Proxistar white backdrop. A metal frame is constructed to secure the relative position of the view cell to the camera. This would ensure that the video recording condition is consistent throughout the trials and the results of different trials are comparable.

4.3.3 *Conducting the experiment*

First the high-pressure cell is fastened with 6 M12 bolts before being preheated to a desired temperature. The 1.7ml sample of silicic acid solution is extracted from the batch using a 2ml syringe (ISO 7886, BBRAUN). The entirety of the sample is then fed into the channel of the middle flange. The solution reached the desired temperature seconds after being inserted due to the miniscule amount used in each trial. The cell is then pressurized with compressed CO₂ to a desired pressure, which may take a few seconds. After reaching the wanted pressure, the process is video recorded for 20 minutes. The camera is set at 1/60 shutter speed, F5.6 Aperture and 80 ISO.

After each trial, the set-up is de-pressurized. The flanges are dismantled from the frame and cleaned. Each flange is washed with water and dishwash soap before being blow dried with compressed air. The surfaces of the sapphire windows are carefully wiped.

4.4 Data analysis

DaVinci Resolve is used to create a screenshot of the video at the 20-minute mark. The image is then cropped, leaving only the part of the picture with the channel behind. Afterwards, the image is fed into a MATLAB program to extract the RHB color values of each pixel (which are the red, green, and blue values of the picture). This RGB value is then converted to an HSV value. From the HSV values, the hue value is used to correlate the between the color and the pH value of the solution. This is due to the hue value's insensitivity to the illumination conditions and concentration. Furthermore, the relationship between the hue value and its corresponding color is quite stable [24]. Due to the stable nature of the hue value and the simplicity of the setup, an inexpensive consumer camera can be utilized.

To analyze the colors, we need to find out which hue value correlates to which pH value. Ideally, by adding precise amounts of ammonia to silicic acid, we could create solutions with precise pH values (pH 4, 5, 6, 7, ...). This solution is then mixed with universal indicator and inserted in the channel to replicate the same lighting conditions as the actual experiments. Under the same lighting conditions and camera settings as the actual experiments, pictures can be taken, and hue values can be extracted from the pictures. The correlation between the hue values and pH values can then be made. However,

Results and discussion

silicic acid is quite unstable and would gel nearly immediately after a pH of 5, 6, 7 or 8 is reached. This makes inserting the solution into the channel impossible. Therefore, to correlate the hue value to the pH value, seven clear buffer solutions (CAS No.1310-77-0) were used. The pH values of the seven buffer solutions are 4, 5, 6, 7, 8, 9, 10 respectively. First, 50 grams of each buffer solution is mixed with the same universal liquid pH indicator at room temperature. Then, each buffer solution is inserted in the high-pressure cell (which is kept at room temperature) while being recorded by the cannon camera at the exact same setting (1/60 shutter speed, F5.6 Aperture and 80 ISO). DaVinci Resolve is used to create cropped screenshots of each buffer solution. Since the pH of each buffer solution is quite homogenous, each buffer solution only displays one color. The cropped images are fed through the MATLAB program to extract the hue value of the color. From this, we can assign a hue value to a pH value (from 4 to 10). Therefore, by analyzing the hue values of the images of silicic acid, we can determine the pH values present in the acid. However, it must be noted that universal liquid indicators are not precise, therefore no interpolation can be made from the hue values and the pH values. During the analysis of the images of silicic acid, recorded hue value is presumed to correlate the pH of the closet median hue value to it. For example: a recorded hue value of 50 is presumed to correlate to a pH value of 5. This is because the hue value of 50 is closest to the median hue value of pH 5 (which is 34.16). The cropped image is divided into multiple rows of 0.5mm thick. The average hue value of each row will be obtained and as a result, the average pH value of each row can be determined.

Table 2: Relation between pH values and hue values for reference

pH value of buffer solution	Median hue value	Hue value range recorded
5	34.16	30.67 - 47.65
6	82.33	75.35 - 89.3
7	119.53	104.57 - 134.48
8	156.67	150 - 163.33
9	164.52	159.38 - 169.66
10	202.5	195 - 210
4	335	320 - 350

After mixing universal pH indicator with silicic acid, the pH value of silicic acid can be determined by taking the hue value of said acid solution and cross referencing it with the values in Table 2. A visual representation of the colors of the buffer solution after being mixed with universal liquid indicator is shown in figure 16.



Figure 16: Recorded color profile of buffer solution mixed with universal indicator from pH 4, 5, 6, 7, 8, 9, 10 (left to right)

5 Results and discussion

Although there are successful results, the unstable nature of silicic acid has made it impossible to generate reliable results. This is an example of a successful trial using 3 days old silicic acid:

Results and discussion

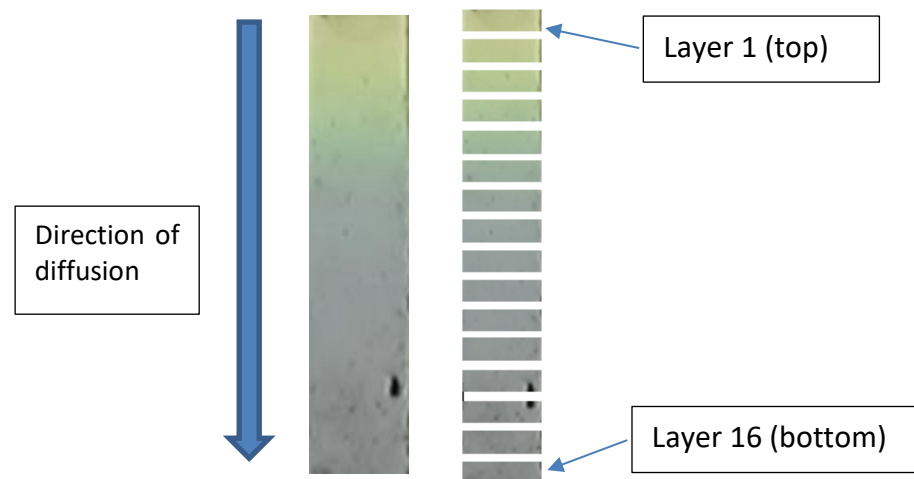


Figure 17: Gelled silicic acid solution at 40 degrees Celsius and 60 bars, after 20 minutes, trial 2

Due to the lighting condition, the surface of silicic acid gel was overcast with shadow that could not be eliminated. As a result, the surface appears black, and no colors can be detected. For this reason, the surface of the silicic acid is cropped out of the image (figure 17). This image (figure 17) is fed through the MATLAB program to retrieve hue values of each pixel. Utilizing the scratch marks next to the channel, the gel was divided into 16 rows (or layers), each 5mm thick. The average hue value of all the pixels of each layer was calculated, and the pH value of each layer was determined. It should be noted that the image is only used for extracting hue values. The segmentation into 16 layers is done entirely using excel. First, using the 0.5mm scratch marks, we can determine the height of the silicic acid in the channel and therefore determine how many 0.5mm thick layers there are. Then, the image is fed into MATLAB to retrieve the hue values of each pixel in the picture. The hue values are then divided into groups (with each group representing a 0.5mm thick layer) using Excel. The average hue value of each group is calculated and the pH value of each group (or each 0.5mm thick layer) is determined. The visual segmented image in figure 17 is only for the purposes of demonstrating how the process works.

Table 3: Hue values and pH values of experiment conducted at 40 degrees Celsius, 60 bars, trial 2

Layer	Average hue value	Correlating pH value
1	65.88	6
2	72.15	6
3	80.79	6
4	90.12	6
5	107.63	7
6	120.12	7
7	141.66	8
8	154.88	8
9	159.01	8
10	161.39	9
11	155.45	8
12	148.56	8
13	146.02	8
14	140.88	8
15	142.22	8
16	143.46	8

It is expected the pH values would decrease as we descend to lower layers. This is because CO₂ diffuses from the top down, making it more abundant in upper layers. As can be seen from table 3, layer 10 has

Results and discussion

a pH of 9, higher than layers adjacent to it (which have pH values of 8). This is because the hue values for pH of 8 and 9 are only 8 units apart, making the distinction between a pH of 8 and a pH of 9 troublesome.

Out of 21 recorded trials, only 4 produced analyzable results. Through the 4 successful attempts, it was seen that pH values decreased with an increased of temperature setting. The problem was the unpredictability of silicic acid. How long silicic acid has been refrigerated has an immense effect of the pH value and the gelation behavior. The experiment only works if silicic acid gel upon contact with CO₂. Silicic acid of 1 day old or less has difficulty gelling upon contact with CO₂. This results in the distortion of the body of silicic acid inside the channel after being pressurized. As a result, one dimensional diffusion could not be guaranteed and rendering the results of the trial unusable to determine the diffusion coefficient. If silicic acid has been refrigerated for too long, gelation can happen too quickly, leading to the difficulty of inserting the silicic acid in the channel. Moreover, old silicic acid gels and changes its pH at the presence of elevated temperature, even before being introduced with CO₂.

In general, a trend was observed. If the batch is made from silicic acid that is too fresh (1 day old or less), the sample inside the channel would not gel and silicic acid is forced into the crevices between the flanges when pressure is introduced (in other words, the sample would not gel quickly enough). This results in a distorted surface of the silicic acid. The distorted surface would affect the diffusion behavior of CO₂, making diffusion not strictly one-dimensional. As a result, this would affect the pH values of the silicic acid inside the channel.

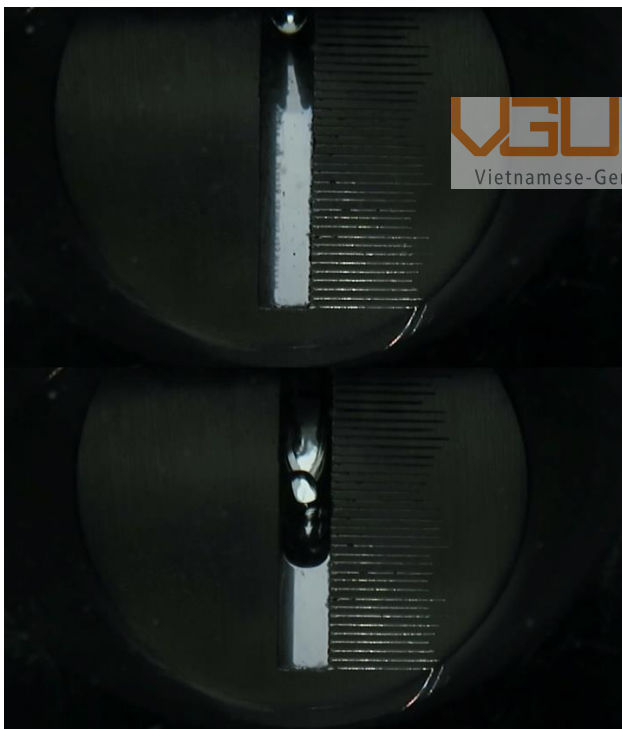


Figure 18: High pressure cell before (upper image) and after (lower image) being pressurized

Figure 18 demonstrates what would happen if a sample of silicic acid that is too fresh is used.

The experiment only works when the sample is prepared from a two to three days old silicic acid. It should be noted that the daily batch of silicic acid solution deteriorates much faster than the pure solution. Depending on the age of silicic acid the batch is made from, the batch could stay liquid for the entire day or gel within minutes of being prepared. When the batch is made from silicic acid of 2-3 days old, the batch can only remain liquid for up to two hours before gelling on its own, even if it is

Results and discussion

stored in a refrigerated condition. Right after the batch is made, silicic acid solution has trouble gelling, like batches made from 1-day old silicic acid. However, between the time of the creation of the batch and the two-hour mark, there is a small window where the silicic acid solution is perfect for the experiment. The solution stays liquid long enough to infiltrate all the cavities of the channel without leaving any air bubbles and gels quick enough for the body of silicic acid in the channel to retain its shape after being pressurized with CO₂. After 20 minutes, the pH change caused the diffusion of CO₂ can be seen as the top layers display neutral to acidic pH while the bottom layers display basic pH values. All four successful trials used samples from batches in this condition. The problem is that the window of time where silicic acid solution from the batch behaves in this manner could not be determined. Therefore, it was not possible to carry out replicable experiments.

If the daily batch is made from silicic acid that is 4 days old or more, the sample would gel as a result of elevated temperature (or in other words, the sample would gel too quickly). This would provide difficulty in filling the channel with silicic acid solution. As can be seen in 9, the thermocouple hole is a through hole. Silicic acid solution needs to infiltrate the hole to fill the channel. When the acid is too old, it gels and shapes its form before an adequate amount of silicic acid can enter the through hole. As a result, when the part of the acid adjacent to the hole enters it, the surrounding acid is too rigid to reshape. This results in an air gap in the middle of the body of the solution. This affects visibility and distorts the diffusion path of CO₂, making the diffusion not purely one dimensional. This effect can be seen in figure 19. In figure 19, the air bubble created is due to part of the silicic acid infiltrating the thermocouple hole and the surrounding acid being too rigid to reshape.

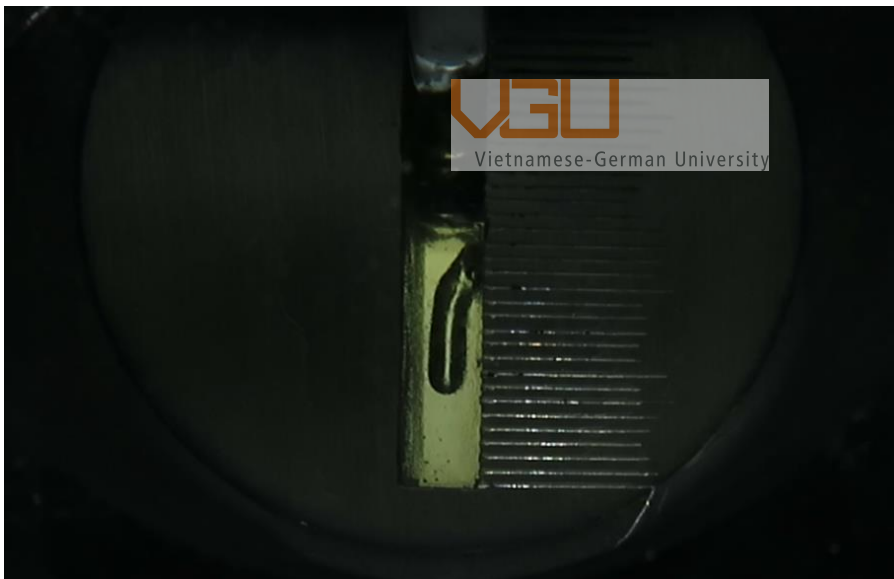


Figure 19: Silicic acid solution at 60 degrees Celsius, 80 bars after 20 minutes, trial 1

One more problem with silicic acid being too old is the pH change. Any sample made from silicic acid of 4 days old or more will wholly turn neutral, instead of turning more acidic near the surface and more basic near the bottom. In other words, under the same temperature and pressure conditions, silicic acid can display different pH values depending solely on its age. This renders the results inconsistent and invaluable.

Drawbacks and limitations

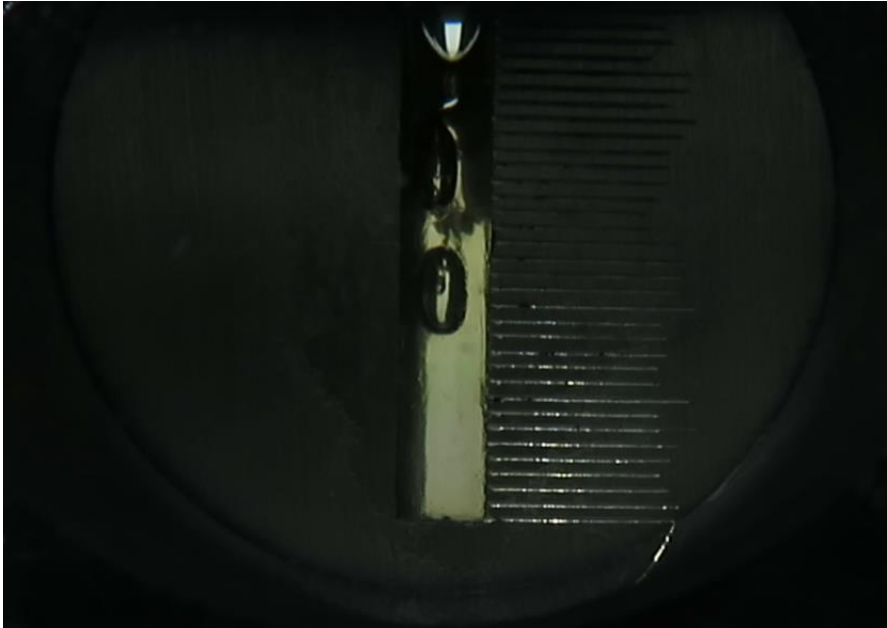


Figure 20: Silicic acid solution at 40 degrees Celsius, 100 bars after 29 minutes, trial 3

As can be seen in figures 19 and 20, the entire solution has a neutral pH from top to bottom. This is a result of using silicic acid that is too old.

6 Drawbacks and limitations

One of the uncertainties of the experiments is whether the universal liquid indicator works consistently under pressure or not. There is a possibility that for the same pH value, the liquid indicator would display different colors at different pressures. As the experiments correlated the hue values and the pH values were conducted at ambient pressure. It is uncertain that the correlation holds true for solutions under elevated pressures. Due to the time constraints, the consistency of universal liquid pH indicator could not be tested. However, this thesis can propose a testing concept for those who wish to replicate the construction of this thesis. First, cross-reference data between hue values and pH values is prepared at ambient pressure, like what was done in section 4.4. Then, a mixture of liquid indicator and a solution of predefined pH (such as distilled water) can be prepared. Using a capable pump, the high-pressure view cell can be pressurized to a desired pressure using said solution. The pressurization process can be video recorded with a consumer grade camera. Although a change in pressure results in a change in temperature and these changes will alter the pH of water. Fortunately, literature containing data of pH of distilled water at different temperatures and pressure is widely available. Afterwards, hue values from the recorded footage can be analyzed using the cross-reference data between hue values and pH values so that we can determine whether the solution display colors appropriate to the expected pH value or not.

Another uncertainty regarding the theoretical approach of this thesis is whether mixing due to Rayleigh-Taylor instability occurs or not. Unfortunately, this could not be theoretically determined because of the lack of data and the unavailability of formularies for the exact geometry of the channel inside the middle flange. The instability could be determined experimentally using PIV particles that have the same density as silicic acid. The same experimental procedure as section 4.4 can be carried out using a solution of silicic acid mixed with PIV particles. By examining the movement of the PIV particles during and after pressurization, it can be determined whether mixing due to differences in densities occur.

Conclusion and Outlook

A setback this thesis encountered is that buffer solutions are used instead of silicic acid to correlate the pH values to the hue values. As stated in section 4.4, the hue values that correlate to pH values of 5, 6, 7, 8 of silicic acid cannot be definitively determined under the lighting condition of the experiments. It cannot be certain that for the pH values of 5, 6, 7, 8, the silicic acid would display the exact same hue value as the buffer solutions of the respective pH values. However, the pH value of 10 can be tested and was tested. Silicic acid with a pH of 10.38 and a buffer solution with a pH of 10 were compared. Since the pH range of the universal indicator is 4-10, solutions with pH values greater than 10 will display the same color. It was found that the mean hue value for the silicic acid and buffer solution differed by 2 units. Given that hue values range from 0-360, a difference of 2 units is 0.56% of the range. It is then reasonable to conclude that for pH values of 10 and higher, the buffer solution and silicic acid display the same hue value. For the purpose of this thesis, it is reasonable to assume that for the rest of the pH values, silicic acid displays the same color as the buffer solutions.

7 Conclusion and Outlook

The method for correlating hue values to pH values and the determination of pH values from hue values based on the correlation were successful. However, the majority of the experiments were unsuccessful as several problems were encountered due to the instability nature of silicic acid. One of the issues was that fresh silicic acid would not gel fast enough which lead to the distortion of the surface, affecting the diffusion path of CO₂. Another problem is that samples made from silicic acid of different ages would display different pH values even under the same temperature and pressure conditions. This inconsistency renders all of the results unreliable. In order to successfully carry out the experiments with reliable and consistent results, a substance with the appropriate gelation speed must be used. Due to the time constraints placed upon the editing period of this thesis, only silicic acid with 7% solid content has been tested. According to previous experiments conducted at Fraunhofer, silicic acid with higher solid content gels more quickly under the presence of CO₂. Perhaps in the future these experiments could be repeated using silicic acid of higher solid contents than 7% to determine whether reliable results could be obtained or not. Another possible solution to this problem is to re-design the middle flange. Instead of using a 52mm diameter O-ring, a smaller rectangular O-ring with dimensions proportional to the height and width of the channel can be used. The O-ring shall be as small as possible to minimize the volume of crevices that silicic acid can escape into while meeting the minimum required wall thickness. This would make the drop of the acid level inside the channel less severe, and the distortion of the surface can be lessened. If the redesign is adequate, fresh silicic acid could be used for every trial, which will make the results more consistent.

The data analysis process which includes cropping the images, segmentation of the silicic acid into different layers and calculating the average pH value of each layer is manually done by DaVinci Resolve and Excel, respectively. This is very time consuming, especially segmentation of layers and calculating their respective pH values. To utilize these processes, in the future a MATLAB program may be constructed to automatically handle these tasks.

The next step of this work is to search for a more suitable substance or to redesign the O-ring groove. If results can be successfully and consistently produced, further calculations can be made. A concentration-distance profile can be made. Using the profile, the concentration at the surface can be calculated and used in conjunction with the error function to calculate the diffusion coefficient of CO₂-silicic acid at different temperatures and pressures.

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Appendix

Appendix

Results of 3 other successful experiments. Each of the trials have a different number of layers due to different amounts of silicic acid leaked when pressure was applied. This is due to the acid having slightly different gelation speed.

Experiment conducted at 40 degrees Celsius, 60 bars, trial 3



Layer	Average hue value	pH value
1	63.95	6
2	67.65	6
3	75.58	6
4	81.41	6
5	92.24	6
6	97.80	6
7	104.05	7
8	110.60	7
9	115.15	7
10	123.51	7
11	136.05	7
12	138.51	8
13	140.62	8
14	153.35	8

Experiment conducted at 60 degrees Celsius, 60 bars, trial 1



Appendix

Layer	Average hue value	pH value
1	73.24	6
2	73.37	6
3	76.05	6
4	81.12	6
5	86.70	6
6	92.74	6
7	97.25	6
8	100.70	6
9	106.29	7
10	109.13	7
11	113.87	7
12	119.36	7
13	116.11	7
14	121.46	7
15	115.98	7
16	118.24	7

Experiment conducted at 60 degrees Celsius, 60 bars, trial 2



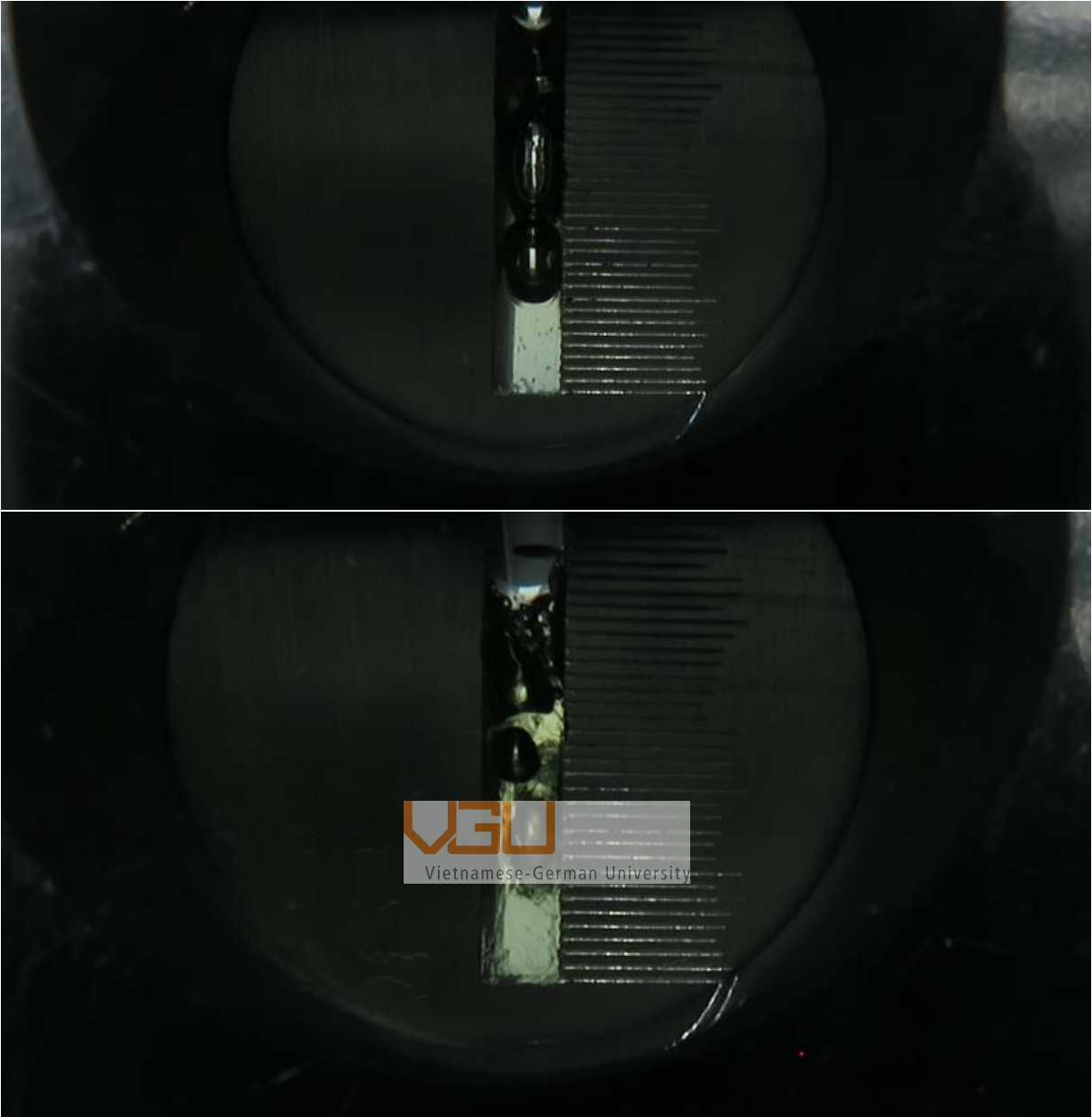
Layer	Average hue value	pH value
1	81.05	6
2	82.53	6
3	86.33	6
4	92.49	6
5	101.16	7
6	109.56	7
7	118.39	7
8	123.05	7
9	126.98	7
10	127.84	7
11	127.99	7
12	124.30	7
13	127.65	7

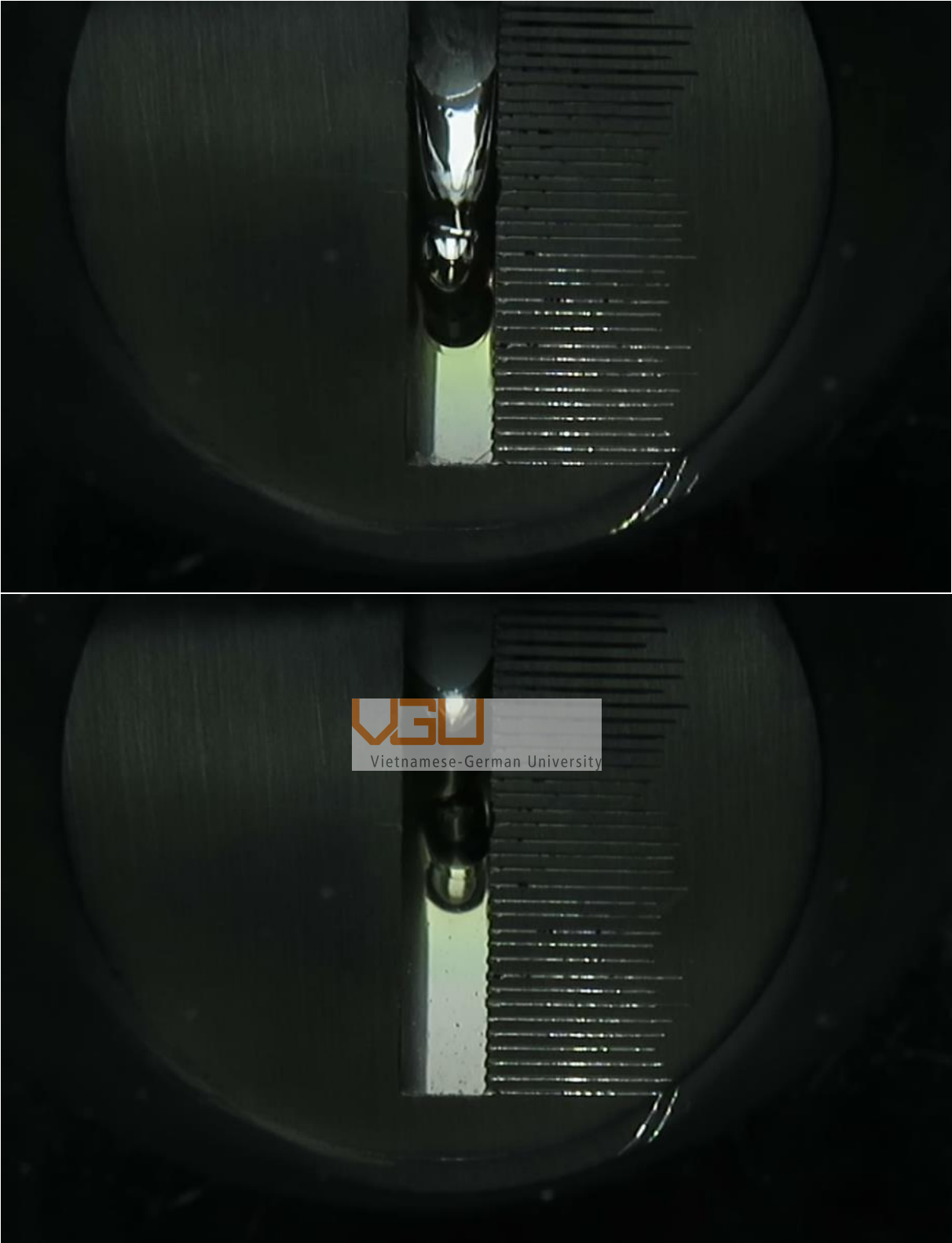
Appendix

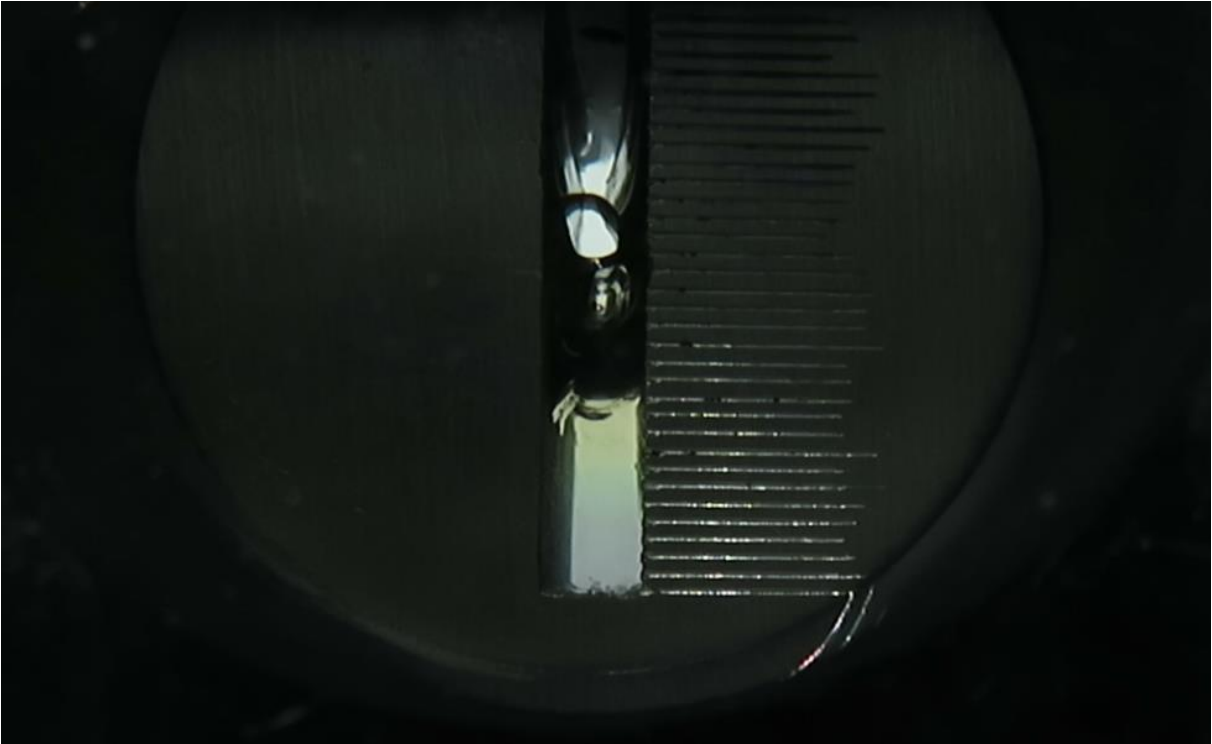
14	126.61	7
15	126.98	7
16	122.98	7
17	123.54	7
18	123.28	7

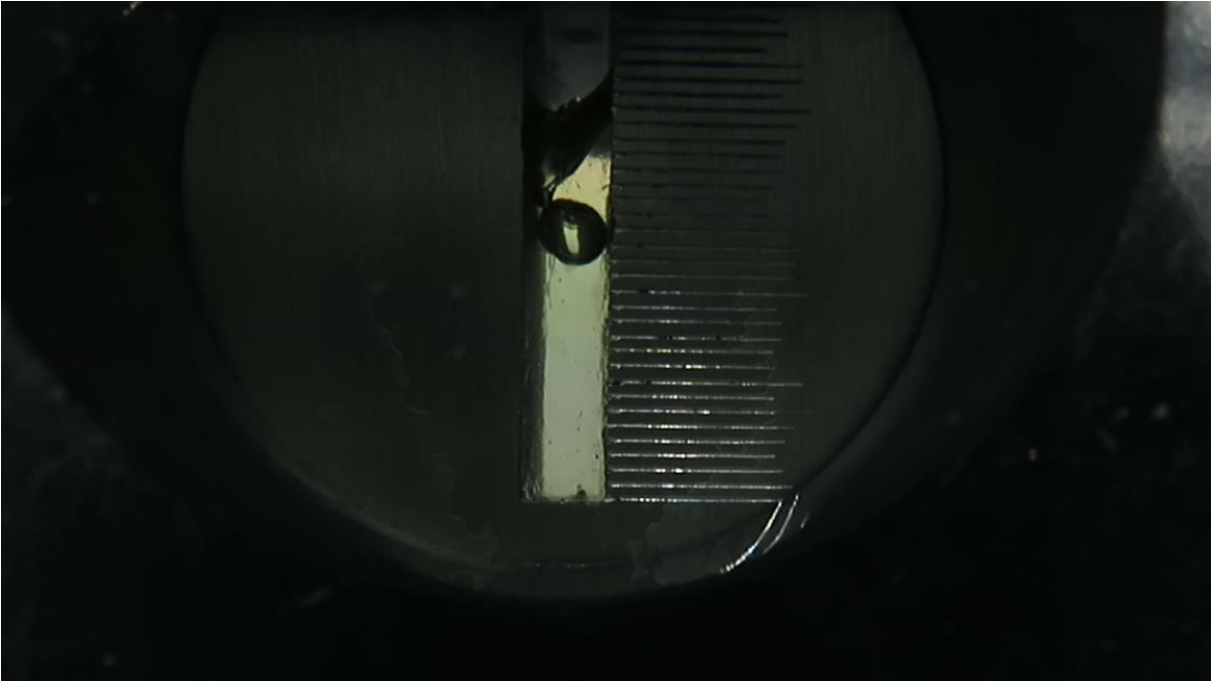
Collages of failed attempts

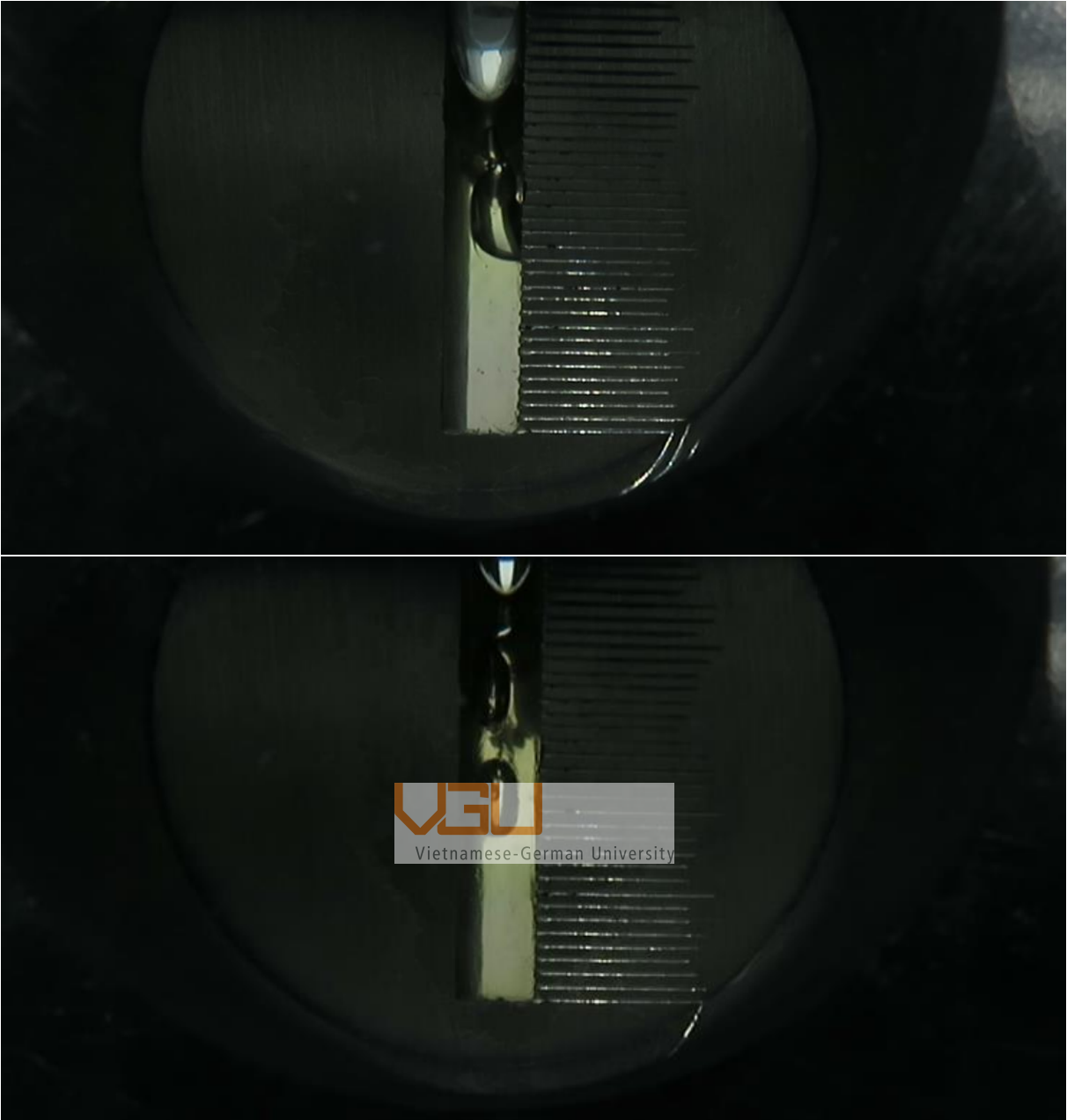














Declaration

Declaration

I hereby declare that the information reported in the current paper is the result of my own work, except where due to references are made. This thesis has not been expected for any degrees and is not concurrently submitted to any supervisors for any other degrees.

Place, Date and Signature

