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# Development of prototype versatile permeation cells for hydrogen diffusion measurements in ferritic steels

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# Abstract

This thesis provides three different design solutions for hydrogen permeation cells based on Devanathan and Stachurski method for hydrogen charging.

The first part of the thesis is built as a background analysis for the development processes. The focus lies on how the experiment functions and its critical parts, and how others have solved it. Available systems have been analyzed and studied, and more are presented from the literature. A user is followed to further inspect the needs of the experiment both in terms of simplicity and function. This information is gathered, and it is created a table of what the system must and should contain.

For the industrial system, the development is built up by first suggesting concepts for the crucial parts in the system. The crucial parts are considered as the parts not being bought by another producer. Several solutions are presented to each of the parts, before two different concepts are presented. These concepts are the tube and the box. The individual parts are discussed in terms of how they would perform under the given conditions. After this a final design is suggested and presented as CAD-models. One critical part of the industrial cell is the effectiveness of the heating with regards to heat loss. Calculations are performed that show that the fluid inside the cells should be able to be heated to the desired temperature in less than one hour, while cooling will take longer time than wanted.

The laboratory system will use water for heating. Two concepts are suggested. This can be done by either a double walled cylinder made of glass, or by using tubes. For the double walled cylinder two different CAD-models are presented: One that focuses on using a sample holder, the other that focuses on pressure to seal the electrolyte from the outside. Calculations of flow through the double walled cells are done, and it is suggested that a positive displacement pump with a capacity of 5.4 l/min is used to make sure the water is able to heat the whole cell. For the checking the stresses in the cells, a FEA is done, to make sure that the glass will not break. The force is reliant on the pressure needed to compress the O-rings for sealing. An approximation with a force of a 1000N on the edge of the cylinder gives stresses that are at the most 37.8 MPa. This will not break the glass and will compress an O-ring. To find out if the O-ring seals it must be calculated non-linearly, but it is easier to test.

The Nano-indenter system has different problems than the other systems. The cells are vertical and bubbles will attach easier to the surface of the sample. Testing is done to determine which method that can be utilized to remove the bubbles. After testing a system using flow as the bubble removal is suggested. The development progresses in iterations by continuously improving problems that can occur during the experiment until a final suggestion is made. It is emphasized that this model should be function tested under better conditions.

# Sammendrag

Denne masteroppgaven gir tre ulike designforslag for hydrogen diffusjonstester, basert på Devanathan og Stachurski metoden for hydrogenladning.

Den første delen av oppgaven er bygd som en bakgrunnsanalyse til utviklingsprosessen. Fokuset ligger på hvordan eksperimentet fungerer og dets kritiske deler, og hvordan andre har løst dette. Tilgjengelige systemer har blitt studert, og flere eksperimenter fra litteraturen blir presentert. En bruker følges for å gjøre en grundigere analyse av behovene til eksperimentet, både med tanke på enkelhet og funksjon. Denne informasjonen blir samlet, og det blir laget en tabell over hva et system må og bør inneholde.

For det industrielle systemet er utviklingen bygget opp av først å foreslå konsepter for de viktige delene i systemet. De viktige delene er deler som ikke blir kjøpt av en annen produsent. Flere løsninger blir presentert til hver del, før det presenteres to ulike konsepter. Disse konseptene er tuben og boksen. De individuelle delene blir så diskutert med tanke på hvordan de vil fungere i de gitte systemene. Deretter blir en endelig løsning presentert ved hjelp av CAD-modeller. En viktig del av den industrielle cellen er hvordan varmesystemet vil fungere når det er varmetap. Beregninger blir utført og viser at væsken inne i cellene kan bli varmet til den ønskede temperaturen på under en time, men at avkjølingen tar lenger tid enn ønsket.

Laboratoriesystemet skal bruke vann til å varme opp cellene. To konsepter blir foreslått. Dette kan enten bli gjort ved å lage cellene med doble vegger, eller ved å ha vannrør rundt cellene. For cellene med de doble veggene er det to mulige løsninger. En som fungerer ved å bruke en prøveholder, og en som blir satt under press for å hindre lekkasjer. Beregninger av strømningen gjennom veggene blir gjort, og det blir foreslått at en pumpe med en kapasitet på 5,4l/min blir brukt for å sørge for at vannet vil varme opp hele cellen. For cellene som skal settes i press blir det gjort en FEA. Kraften som til slutt skal brukes i disse beregningene, blir satt opp mot trykket o-ringene krever for å forsegle cellene. Et overslag på 1000N kraft på kantene av cellene blir analysert til å gi 37.8 MPa spenning på det meste. Dette skal ikke være nok til å knuse glasset og vil komprimere en o-ring. For å finne ut om o-ringen forsegler må man gjøre en ikke-lineær analyse, men det er enklere å teste.

Systemet til nano-indenteren har andre problemer enn de tidligere systemene. Cellene er vertikale og bobler vil enklere feste seg til overflaten av prøven. Testing blir gjort for å finne en metode som kan brukes til å fjerne boblene. Etter testing blir en celle som baserer seg på massestrømmer foreslått. Utviklingen fortsetter med iterasjoner for å kontinuerlig utbedre problemer som kan oppstå under eksperimentet inntil en endelig løsning blir gitt. Det understrekes at dette systemet bør funksjonstestes under bedre forhold.

# Preface

The background for this thesis is to improve the function of hydrogen permeation tests by improving the design of the systems. Hydrogen permeation experiments are complicated and require vigilant supervision from the user. New cells and setups are needed to make the experiments easier. These systems should be versatile, operator independent and exclude the human error.

The thesis started out with the problem text in the appendix. This was a cooperation task with Bendik Wendt Simonsen. Later in the project, we found it more appropriate to split the thesis in two and deliver separately. Bendik was focusing on the software and analysis, I was focusing on the product development and hardware. After agreeing with our supervisor we did not add the new problem text to the assignment.

Being a mechanical engineering student at the institute for engineering design and materials on NTNU, this assignment is a good mix of knowledge from almost every subject during my period of study. With product development as the red thread, it is interesting to apply that into material science. This is a new type of products that I have never been acquainted with, and a long period of time was used to just understand the task at hand. Knowledge of how diffusion worked, was measured and some basic electrochemistry was needed to be obtained before I could start my work. Spanning over this large amount of the curriculum from previous years needed to be refreshed before I could start the main task.

I would like to thank Afrooz Barnoush, who was the main supervisor for the thesis for guidance. I also would like to thank Martin Steinert and Troll-Labs who assisted in kicking off the thesis as a product development project, PhD student Tarlan Hajilou assisted with the design of the Nano-indenter cell, and fellow master students Bendik Wendt Simonsen and Malin Berglund Hope helped with discussions, lab experiments and feedback during the thesis.

Since this thesis spans across a lot of subjects and three different main designs, the task is large. The thesis is primarily a product development thesis, with supplements as thermodynamics, fluid dynamics, mechanics and materials science. These supplements will not be done in detail for every solution and step in the process. Calculations will be conservative and mostly focus as a guide for the development process. This means assumptions and simplifications were needed to be made. With no focus on literature study and theory chapters, theory and references are supplemented during the text when needed.

## Table of contents

Abstract ..... i

Sammendrag ..... ii

Preface ..... iii

1 Introduction ..... 1

2 Pre-study ..... 3

- 2.1 Vision and mission for the development ..... 3
- 2.2 Existing solutions ..... 3
  - 2.2.1 Principle design ..... 3
- 2.3 User experience ..... 8
  - 2.3.1 Needs ..... 10
  - 2.3.2 Possibilities and restrictions ..... 14

3 Concept studies for system parts ..... 15

- 3.1 Concepts for the individual parts ..... 15
  - 3.1.1 Cell design ..... 15
  - 3.1.2 Sample holder ..... 16
  - 3.1.3 Method of heating ..... 18
  - 3.1.4 Venting system ..... 18
  - 3.1.5 Faraday cage ..... 20
- 3.2 Concept suggestions ..... 20
  - 3.2.1 Box solution ..... 20
  - 3.2.2 The tube ..... 21
- 3.3 Discussing the solutions ..... 22
  - 3.3.1 Assessment of the box solution ..... 22
  - 3.3.2 Assessment of tube solution ..... 23
- 3.4 Laboratory system ..... 24
  - 3.4.1 Problems with the water bath ..... 24
  - 3.4.2 Suggestion 1: The double walled cell ..... 25
  - 3.4.3 Suggestion 2 Rig with tubes ..... 26
  - 3.4.4 Pumps ..... 27
- 3.5 Nano-indenter cell ..... 27
  - 3.5.1 Methods for removing bubbles ..... 27
  - 3.5.2 Testing of system for the Nano-indenter ..... 28

4 Final designs ..... 33

- 4.1 Industrial system design ..... 33

4.1.2 Main principle ........ 40

4.1.3 Material selection ........ 44

4.1.4 Calculations of heat transfer ........ 46

4.2 The laboratory system ........ 50

4.2.1 The design of double walls ........ 50

4.2.2 Second design of double walls ........ 53

4.2.3 Laboratory cell flow calculations ........ 55

4.3 Nano-indenter cell ........ 57

4.3.1 The design of the flow system ........ 57

4.3.2 Flow in the Nano-indenter cell ........ 63

5 Conclusion ........ 67

6 Referanseliste ........ 69

Appendix A: Problem Text ........ 71

Appendix B: Risk assessment ........ 73

Appendix C: Matlab code ........ 81

Appendix D: Drawings from Siemens NX ........ 83

# 1 Introduction

Hydrogen embrittlement is a risk to high strength steels. Hydrogen severely reduces the ductility of the steel and the strengths of embrittled steel can no longer be trusted. This can lead to strengths lower than the designer anticipated, and then get brittle fracture. The hydrogen can come from different sources, for instance cathodic reactions or $H_2S$.

The rate the hydrogen is diffusing through the material is a key component when understanding this phenomenon. This permeability can be high or low, depending on the microstructures in the material. Feritic steels have a microstructure that is susceptible to hydrogen embrittlement. Often the more ductile a material is, the more resilient it will be against hydrogen embrittlement.

Hydrogen embrittlement is a challenge in several industries. For the oil and gas industry the challenge is often at the subsea equipment. This equipment often needs cathodic protection to protect it from corrosion and $H_2S$ can be in the pipeline flow. For the aerospace industry the same problems can occur from electrolytic plates or metal finishes.

Hydrogen embrittlement is not very well understood. This thesis focuses on making hydrogen experiment tests more available, making the test easier for the operator. This way knowledge of the driving mechanisms of hydrogen can be better understood. The systems developed in this thesis cannot be used for every kind of problem a researcher wants to test, but it can be used to gain more basic knowledge.

In chapter 2 earlier experiments and systems will be studied to gain an understanding of the key components in the setup. From a product developer's point of view, it will focus on what improvements must be made to make the systems easier for the operator.

In chapter 3 concept suggestions for an industrial model will be made, with the key parts in focus. What is practical to use at a given problem or in a setup is a key to this chapter.

Chapter 4 will present the final design suggestions for three different problems, one for the industry, one for a laboratory, and one for use in the Nano-indenter. Calculations and considerations will build up the different designs feasibility.

# 2 Pre-study

## 2.1 Vision and mission for the development

When understanding the problem, a target goal or ultimate goal may be defined as a vision and a mission for the development. The problem is to design systems that can measure hydrogen diffusion rates in feritic steels, which can also be seen as a target. This is also a rather definite target of the product that this thesis will result in. The main vision of the project should be grandeur and not put limitations on the development, it is basically a slogan. The vision of this project should be to completely understand hydrogen diffusion. This is not achievable for this master thesis, but it takes a small step in the correct direction. The mission of this project is to make hydrogen diffusion experiments more accessible and simple for the user. During the design phase the mission objective should be considered at every evaluation, such that it will always be prioritized.

## 2.2 Existing solutions

Although it can be a little controversial to look at existing systems for product development, it can be useful as well to gain an understanding of the assignment. This chapter will look closer at the existing designs to understand which components that is required for making a functioning machine. This will give the basis for creating a user experience which will give an understanding of which parts and components of the process that are essential for the operation of the machine.

### 2.2.1 Principle design

The experiment is based on the Devanathan and Stahurski method for measuring hydrogen diffusion. The principle design of the experiment is the same in all cases. There is a need for two cells, connections for two potentiostats and one sample with electrical contact. However, these components are not needed to look the same or be the same in every design as long as they are connected with the same functions as in the basic principle. For instance, the cells can have almost any desired functional form as long as they are connected on each side of a sample.

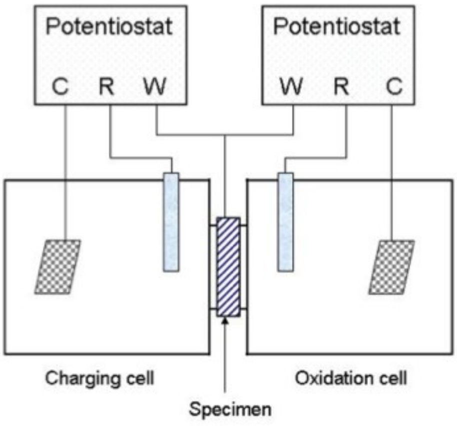

Figure 2.1 Principle design of the Devanathan and Stahurski method[1]

The experiment is conducted by applying a galvanostatic current or a potential in the charging cell, making the cell cathodic. This produces hydrogen ions ($H^+$) from the electrolyte. According to diffusion laws the hydrogen will diffuse and spread around in the contained area. An open hole at one end of the container is covered by the test sample. If this sample allows hydrogen permeation, the hydrogen ions will diffuse through the sample and into the other container. This container is made anodic by only applying a voltage (polarized). This will force the hydrogen to oxidize and the current needed in this process is measured. The currents will be larger after more hydrogen has diffused through the sample. By these measurements it is determined how much of the hydrogen is let through the sample. At one point in time, the measured current will stabilize and the steady state diffusion is achieved. The data from the measurements can be used to determine the permeation data for the material[2].

The industrial standard practice[3] says it needs to be one oxidation cell and one charging cell that are separated. Using a palladium coating on the oxidation side of the sample improves the reliability of the measurements, since the hydrogen will oxidize faster on the surface of the palladium than on pure iron[4]. This is debated, and might not be needed in all setups.

Air gaps and oxides may affect the measured currents. The standard says that only non-metallic materials which are inert to the test environment should be used for cell construction. This must also apply at higher temperatures.

Placement of the reference electrode should be as close to the specimen as possible, to ensure minimal potential drop. A Luggin capillary may be used for this purpose under the right conditions.

#### *2.2.1.1 Equipment for measuring hydrogen diffusion at different temperatures, hydrostatic pressures and mechanical stresses*

This design[1] was created for Anna Smirnova's PhD project by her and Cormet Testing Systems. In this setup, parts that are in contact with the electrolyte are made of Titanium Grade 2(UNS R50400). This allows for using several different electrolytes, and titanium is not susceptible to hydrogen diffusion. Non-wetted components are made of AISI316 steel (UNS S31600). The volumes of the autoclaves are 0.5 l, and they are bolted together when in use. The autoclaves have an opening of 35x35mm for exposure to a specimen. Temperature control is done by a heating bath around the autoclaves. It has safety valves for protection against overpressure and allows bubbling of the electrolyte in use. The autoclaves are constructed with magnetic stirrers to agitate the electrolyte. The apparatus can apply constant loading, fatigue loading and slow strain. It was also designed to allow for high pressure testing.

The author lists 4 parameters that are important in construction:

1) Two compartment cells consisting of a separate charging and oxidation cell
2) Each cell should have its own reference and counter electrode
3) The ratio of volume of solution(in mm) to metal area(in square cm) in the oxidation chamber should be greater than 20:1

4) Construction of the cells should allow inert gas purging through the electrolytes in order to remove oxygen.

The materials were selected on basis of corrosion rates, since the main electrolyte in the testing was sea water.

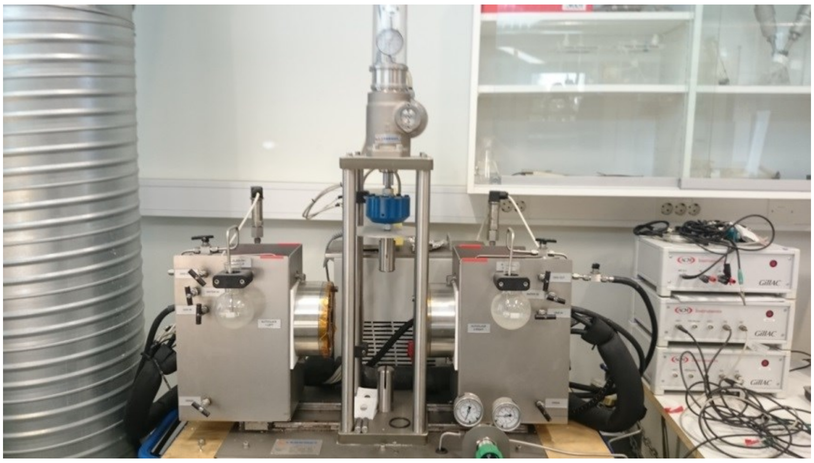

**Figure 2.2 Apparatus in Corrosion lab**

This is high-end testing equipment. It allows for several advanced tests, but needs a lot of knowledge to operate.

#### 2.2.1.2 Basic hydrogen measurement test

This apparatus has an easier set up. It has the same base design, with two separated compartments for oxidation and charging. The cells are made of glass and have a volume of 120ml each. They are attached together with POM-parts. The heating is done with an external water bath. The reference electrode measures the electronic potential with a capillary. The setup is exposed to a lot of electrical noise, and has a faraday cage around it.

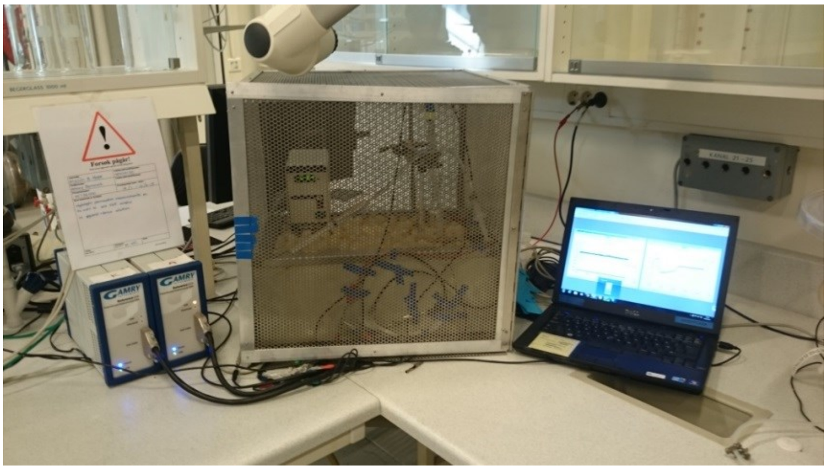

**Figure 2.3 Apparatus in corrosion lab**

The cell design is a cylinder with connectors to a counter electrode and a reference electrode.

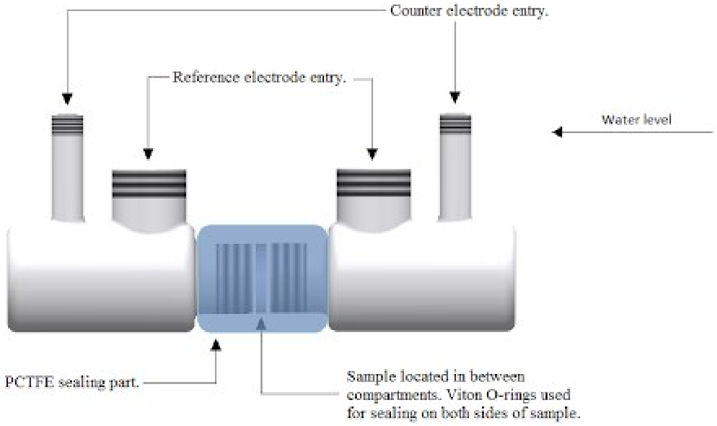

Figure 2.4 Picture of the assembled cells with sample holder[5]

The core of this design is simple. The problem arises when you need external components for heating and avoidance of electrical noise. The connections for the potentiostats are not as good, as it requires wires connected from the outside of the Faraday cage through a small opening in the door. This reduces the shielding of the Faraday cage and can give electrical noise.

#### *2.2.1.3 Other experiments from literature*

This chapter describes different experiments from literature. This has not been a hands-on review, so a lot of information has been lost in the transition. Unless stated in the articles it has been hard to figure out the material, sizes and even final design of the different systems.

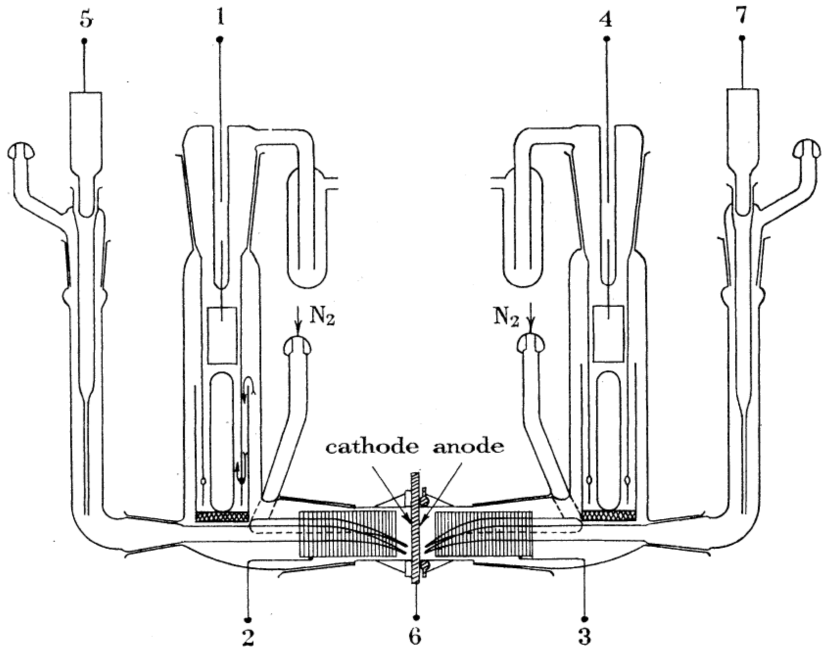

Figure 2.5 Proposed setup from Devanathan and Stachurski[6]

Figure 2.5 describes Devanathan and Stachurski's own setup of their proposed electrical circuit. The description of the setup are[7]:

1. Pt-counter electrode in the cathodic side
2. Cathodic cell
3. Anodic cell
4. Pt-counter electrode in anodic cell
5. Reference electrode cathodic side
6. Sample membrane
7. Reference electrode anodic side

An experiment performed by Xia and Lang used two seemingly identical glass cells with several connections for electrodes and deaeration of oxygen. The sample was rectangular and fixed by pressure plates between the cells[8].

Another experiment also used the double cell. It was found necessary to only use one reference electrode. The setup was small with specimens of 15mm diameter[9].

A modification of the Devanathan and Stachurski method was used to compare hydrogen diffusion in three different microstructures[10]. It was used glass cells, polycarbonate or polyvinyl junction caps to hold the sample and Viton O-rings for sealing. The fluid in the cathodic chamber was continuously changed and the new fluid added was directly by the cathodic surface of the sample. This allowed the electrolyte in the cathodic cell to be purified during the experiment in another reservoir. Deaeration did not happen in the anodic cell. This reservoir was heat regulated to ensure the temperature was consistent during the experiment. Reference electrodes were placed close to the sample through capillaries and platinum counter electrodes were used.

Diameters of test samples vary a lot. Some tests use large samples[11], others quite small[9]. The ranges have been between an exposed surface area of $1.7cm^2$ to $19.6cm^2$, and thicknesses for 0.5 mm to over 10 mm, often being rectangular.

Tests for permeation without using electrochemical charging are also common. A device was built to test the influences of temperature and pressure on permeation tests. The input side was built out of metal and was filled with a solution of NaOH and NaCl. This was deaerated with $N_2$ gas for some time before the $H_2S$ gas was bubbled through. The detection side was built of an insulator attached with a sealing to contain 2MPa of pressure to the input device. The design allows testing at 250°C[12, 13]. From Figure 2.6 it seems that design for the detection side has three connections for the different type of electrodes.

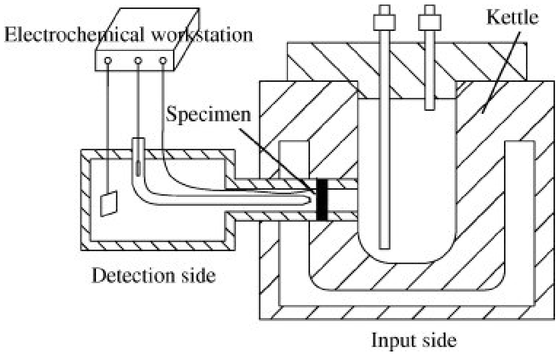

**Figure 2.6 Sketch of permeation device using H2S for permeation[12]**

An adaptation of the Devanathan and Stachurski method was used for another $H_2S$ experiment. This had a charging cell consisting of bubblers for deaeration, a reference electrode with a lugging capillary and a platinum electrode. The platinum electrode was mainly used for polarization when it was required. The detection cell had gas inlets and gas exhausts, a reference electrode and a counter electrode. The main material in the charging cell was PTFE, while in the detection cell it was PTFE or Perspex. The specimens mounted was square with an exposed area of 4.83cm$^2$ [14]. Figure 2.7 shows the setup.

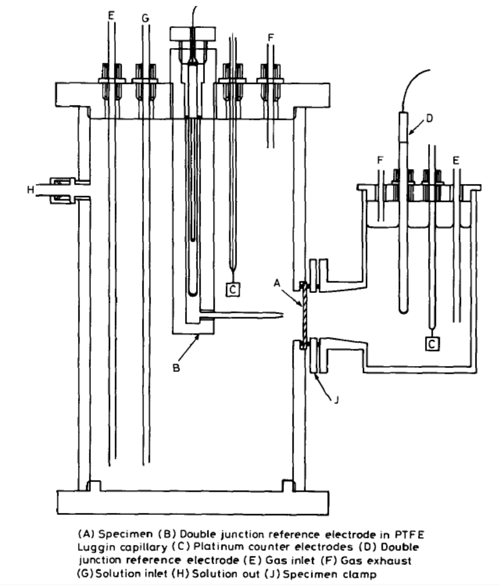

**Figure 2.7 Sketch of permeation cell from [14]**

## 2.3 User experience

At NTNU's corrosion lab two of these experiments are available. Only the experiment in chapter 2.2.1.2 is in use during the writing of this master thesis. This is also the experiment that is easier to base a user experience analysis on. Since it is also the simpler of the two, it is more likely that the prototype would look more like this. The user experience is presented as a walkthrough of the different steps in the setup procedure, identifying pain points that should be fixed. It will also present the different problems that can occur while running the experiment.

The experiment starts with the specimen. This needs to have the correct radius so it can fit into its holder. If it varies too much the sealing might leak and the experiment would be compromised. The sample also needs to have polished and clean faces. If there is any residue or irregularities on the sample, the results would not be correct. The size requirements are described in the standard as minimal ratio of 10:1 radius to thickness, and no more than 5% deviation in thickness[3]. This is not directly a relevant for the development of the prototype, but it gives an indication of an important factor that can be easy to forget.

The operation of putting the sample into its holder was the one that caused most of the pain in this setup. The design for the sample holder is good with regards to sealing, but the sample needs to be pushed into place. The space for the sample is narrow and requires the sample to be perfectly cut. Pushing and touching the sample can compromise its surface as mentioned earlier. When the holder is narrow, a lot of fine adjustments need to be made to make the sample straight, and this takes a lot of time and if not done correctly, there might be flow from one cell to the other.

When the sample is in place the cells need to be attached to the holder. The ends of the cells are threaded so it is an easy process. The only problem that can occur is that it needs to be tight enough to prevent leakage. This means enough threading must be available on each part.

The next step is to fill the cells with electrolyte. This can easily be done through the connections for the electrodes. In this case it is the opening for the reference electrode that is being used. The only problem that has arisen with the electrolyte filling is the amount needed. When the temperature is increased the electrolyte expands. This can lead to some electrolyte coming out of the cells, but it does not affect the tests, but can make a mess.

Now the electrodes are to be connected. The counter electrode is just a small platinum thread and it is attached to a screw cap. The attachment is threaded and the cap is screwed on. The reference electrode is a bit harder. A capillary is attached to the same type of cap. The size of the capillary versus the size of the cell is important, as it needs to be as close to the sample as possible. In the current design this is not a problem. The problem with the capillaries is to fill them with an electrolyte. They are narrow, and by using the designated electrolyte with relatively high viscosity, it can create small air bubbles in the capillaries. If these bubbles are not removed there will be no electrical contact with the reference electrode, there is no flow of ions and the test would not work. The bubbles must be removed by slightly tapping the capillaries until they are loosened. This is a small pain point, since it gets better with experience. When this is done the cap is screwed on.

In this setup the electric connection for the reference electrode goes up through a tube to a holder for the electrode. This container also has electrolyte in them. In the holder the reference electrode is placed. This makes the setup tall and unstable and it requires a rack to stand in the water bath. The size is not a pain point for doing the test. It is not hard, but for the design of a new cell it is certainly something to be changed.

Connection to the work electrode is hard. When the sample is put into place it needs to touch a small screw so it can have electric connection to the outside. From the outside small electrodes are attached to the screw.

When all wires are attached from the potentiostats to the electrodes, the assembled cells are placed in a water bath. The water bath is used to maintain a stable temperature during the testing. This works without any problems and it is easy to use. However it does have some pain points. Using a water bath at higher temperatures requires refilling of the water often. If the water level drops too low and don't cover the whole cell, the temperature might not be uniform in the cell. This means the test cannot go unattended for its duration. The water bath may also cause electrical disturbances because of the pump that is used.

A Faraday cage is then used to minimize electrical noise from the outside. This was shown to be needed when the earliest test gave so much noise it disturbed the experiment to a high degree.

### 2.3.1 Needs

The problem that is set to solve is interpreted to make the experiment as accessible and functional as possible for any interested party. This means that the design concepts should focus on simplicity and intuitiveness. It should be easy to use for non-researcher personnel, who have little to no knowledge of hydrogen diffusion testing and its components.

When following a user during the setup stage, we found different pain points during the process. Pain points are the problems and difficulties that arise during a period of time. When following a user both their experienced needs and the observed needs are focused upon[15, 16]. It gives knowledge on what needs are important for a new experiment. It is the pain points that cause the most pain that need to be fixed. They have all different potential of improvements and different risks. That means that some problems are easier to solve than others.

The objective of the machine is clear, and the testing is done by an industrial standard. There are some things that cannot be changed. This includes for instance nature laws like electrical conductivity. Much of this knowledge is based on experience and should be discussed with experienced users.

Saving cost and time is essential in experimental work as long as it isn't a trade-off with result quality. This experiment, especially at low temperatures, can last for days for only a single test. This means that the setup of the experiment is not as time consuming compared to the test itself. However, when the experiment is set up it is in need of man-hours. Making a simple setup will conserve cost on this regard.

This information leads us to a user demand specification. It is basically what the machine must do, and what it should do. For a useful machine, all of the "must" criteria are fulfilled. For a machine with even greater functionality, all the "should" criteria are implemented. The table below is used as the governing criteria when developing concepts.

**Table 2.1 User specifications table tells what must be and what should be in the final design**

| ***User specifications*** | | |
|---|---|---|
| | **Must** | **Should** |
| **Machine** | | |
| Robust | X | |
| Small in size | X | |
| No electrical noise | X | |
| See through | | X |
| **Cell and sample holder** | | |
| Change specimen | X | |
| Change electrolyte | X | |
| Connect 2 electrodes to each cell | X | |
| Connect electrode to specimen | X | |
| Sealed for electrolyte and oxygen | X | |
| Be able to change specimen radius | | X |
| Change specimen thickness | | X |
| Room for capillary | | X |
| **Temperature control** | | |
| Keep a steady temperature | X | |
| Be able to change temperature | X | |
| Warmer temperature than ambient | X | |
| Colder temperature than ambient | | X |
| **Venting** | | |
| Venting of H2 gas | X | |
| Automatic venting of H2 gas | | X |
| **Maintenance** | | |
| Easy to clean | X | |
| Able to remove cell | | X |
| Changeable parts | | X |

#### 2.3.1.1 Machine

As previously stated, the machine should be robust. If it is fragile the machine will break. Although there is no movement and small forces acting on the system, it needs to not feel fragile. Using small wall thickness and weak materials will make it break. To be easy to use, there should not be any need for external equipment and unnecessary carefulness. Basically, you should not be afraid to touch it.

Having it small in size is another requirement. This is a simple setup and it is unnecessary to make it too big. A smaller setup requires less laboratory space and then the experiment might be used more often.

Electrical noise ruins the experiment. Since the experiment measures electrons oxidizing in a cell, only a small amount of current is measured, usually milli- or microampere. Since the charge of an electron is so small, outside noise can easily corrupt the experiment and render it useless. This is why shielding from outside electrical noise must be done.

The ability to see through is not a must. It can however be useful to an extent. The ability to see through lets you know if the charge is right, since bubbles are produced when it is too high. The electrolyte boiling from heating can also be seen. Making it see through will be a manually operated control system. You can check if the electrolyte is compromised with corrosion and changes color, if there are hydrogen bubbles on the sample piece, and if there are any leakage in the system. The leakage is controlled when you can see the liquid level drop. The level of electrolyte is also important to be able to see that the sample is fully covered when starting up. Thermal expansion of the electrolyte may have an impact on the degree of filling, and filling schemes should be given at different temperatures. The possibility to see through the system should be applied, at least for the cells.

#### 2.3.1.2 Cell and sample holder

Many of these requirements are obvious. If you want to test different samples, the samples have to be interchangeable. The same applies for the electrolyte. If the electrolyte is compromised, it will need to be changed. This needs to be easy to do.

The experiment requires two electrodes to be attached to the cell, a counter electrode and a reference electrode. It also requires that there is electrical contact with the sample for connection for the work electrode.

The system should have no leakage and be sealed for air to come inside. A leakage may lower the electrolyte levels to a point where the sample is not covered. Then the experiment would be ruined. The air can compromise the electrolyte, but also the sample. Although not the most likely scenario,

The ability to change the radius of the sample could prove useful. It can accept less accurate machining of the sample and in turn takes less time. A scenario where a piece is cut, then grinded and polished and then the user figures out that the sample does not fit and needs to go through the same process again, is time consuming. So it is a must to have a tolerance for not perfect radius, but a user might also want to test a sample with a greater surface area. While a greater surface area is not an important factor in the diffusion constant's calculation, but is a way to ensure that the supply of hydrogen ions on the surface is always good enough to get the correct diffusion coefficients. In other words, it is the thickness that shall be the delay in the measurements, not area. Thickness is the factor that influences the diffusion coefficient, and it is crucial for how much time the diffusion needs to reach the steady state.

It should also have room for a capillary. This capillary is connected to the reference electrode. The closer the capillary can come to the sample the better, since it can measure the potential between the electrolyte and the sample better. When this is measured it is possible to see what the reactions in the experiment contribute with in the measurements.

#### 2.3.1.3 Temperature control

It is crucial for the system to maintain a stable temperature. The diffusion coefficient relies on temperature[17]. There should be no more than +/-0.5°C difference at any time during the testing. If the temperature changes more, the results will be affected. This is a non-negotiable trait of the system.

By changing the temperature you will get different diffusion coefficients. This can help to estimate trapping and the general diffusion properties in the material. Since this often is the user's goal, the system needs to be able to test it at different temperatures. Especially warmer testing is needed. Testing at cooler temperatures than the ambient would be good to comparability and see the effect over a wider range of temperatures. Subsea equipment at the sea bottom would often have an ambient temperature of 4°C. To be able to test the material performance under these conditions, such a system could be implemented in the final solution.

#### 2.3.1.4 Venting

Since hydrogen gas may be produced during the experiment, the system should have venting. Hydrogen is explosive, and if ignited the equipment might be damaged. This needs to be vented out of the system. Since the experiment may take days, it is an advantage if this is done automatically. If done manually, the risk is that a lot of hydrogen will escape into the air at the same time and may explode later. By having a low pressure release this will not happen, especially if the system is placed under a ventilator.

#### 2.3.1.5 Maintenance

Easy to clean and maintain is important. If residue is left in the cell after use, it could affect the next test. This sets a limit to the minimization of the system, since small equipment is harder to maintain.

If the system lets you remove the cell, it could be changed with another ready one when the test is finished. This might save some time for the testing. Also it will be easier to clean everything. Having interchangeable parts makes the system user friendly. If something stop working it should be possible to have a spare part to change with the broken one. Then the testing can continue and there is no need for rescheduling while waiting for reparations or a new order.

### 2.3.2 Possibilities and restrictions

The cells are the main component in the machine. To make it as small as possible, the cells need to be as small as possible. As mentioned earlier, there is a volume to size ratio that is the absolute minimum for volume. There is also a rule of thumb on the distance between the counter electrode and the work electrode which should be no less than the diameter of the sample. This is to make sure the reactions are completed. The radius of the cell should also be greater than the radius of the sample. This may not be possible for the cell mouth, but for the inner chamber it is important. It contributes to give the reactions from the counter electrode enough area to work on. Another problem is when heating the electrolyte it can have a thermal expansion. This gives a minimal size for the cells. Designing at the minimum makes it harder to use, so it might have to be larger. This needs to be tested before final manufacturing.

There are a lot of advantages by making the cells as small as possible within the restrictions. This is primarily related to heating, since it would have less mass to heat up, less energy is need to be applied.

# 3 Concept studies for system parts

## 3.1 Concepts for the individual parts

In how many ways can the problems be solved? The user specifications listed in chapter 2.3.1 need to be addressed with solutions. In this chapter, the isolated parts of the experiment will be presented with different solutions. This will let us generate several concepts for solving the main problem. The user specifications will govern the main process.

### 3.1.1 Cell design

The cell design is related to form and connection for reference electrodes. The industrial standard suggests the use of a Luggin capillary for small scale cells. Since this is one of our aims, we should try to make sure the cells have enough space for this. This excludes a couple of forms like a long narrow cylinder. The first suggestions would be based on the possible forms.

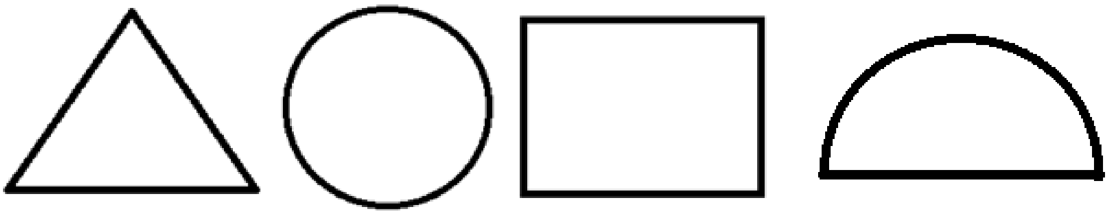

**Figure 3.1 The different shapes considered**

These forms can be almost anything, and it might be considered random to present. However, each form has its own characteristic traits and should be considered according to the needs.

The *triangle form* is stable when put on a table. This makes the larger design of the total machine simpler, since it does not need additional support. It is also relatively small in volume so a lot of space can be conserved. The down side is that the corners are tight, and cleaning might be hard. It is also hard to produce an efficient venting system for hydrogen since it needs to be drilled through at the highest point.

The *cylindrical form* is easy to maintain and clean since there are no sharp edges. It is easy to produce and gives much space for a capillary. It is unstable and requires support to be standing up. This will complicate the main design. Manufacturing connections for electrodes might be hard and time consuming.

*The rectangular/quadratic form* is stable. It has a good volume and space inside for a capillary, and is easy to manufacture. Attachments for venting and electrodes can easily be manufactured. The problem is the cleaning and maintenance. The edges may be hard to get clean and it requires more electrolyte to fill up.

The *Half cylindrical form* is stable, and has less volume than others. It has to have a large radius to fit a capillary, but else it has the same drawbacks and functionality of the cylindrical form.

### 3.1.2 Sample holder

The sample holder brought the most pain in the existing setup. This needs to be addressed. From the user demand we can see that the parameters to consider are:

1) Able to change specimen
2) Electrical contact to specimen
3) Sealed for electrolyte and oxygen
4) Sealed between compartments
5) Have possibility for different thickness of specimen
6) Should have the possibility to change radius of specimen

These must be governing for all solutions. The solutions will be diverging into several different possibilities, and all might not be functional for a final prototype. The value of not having a submerged cell must be taken into consideration when finally choosing a part.

The n*ut* solution is the one that is already used in a project at NTNU described in chapter 2.2.1.2. It consists of three parts. One PTCFE-part holds the sample and is screwed on one cell, a POM-part that is screwed on to the other cell and a POM-nut for connecting them. The PTCFE-part is threaded on the inside, while the POM-part is threaded on both sides. The POM-nut is placed over the PTCFE-part and screwed onto the POM-part, connecting the parts and cells together. Sealing is done by the cells pressure on an O-ring that lies against the sample. Electrical contact is secured through screw through the PTCFE-part[5].

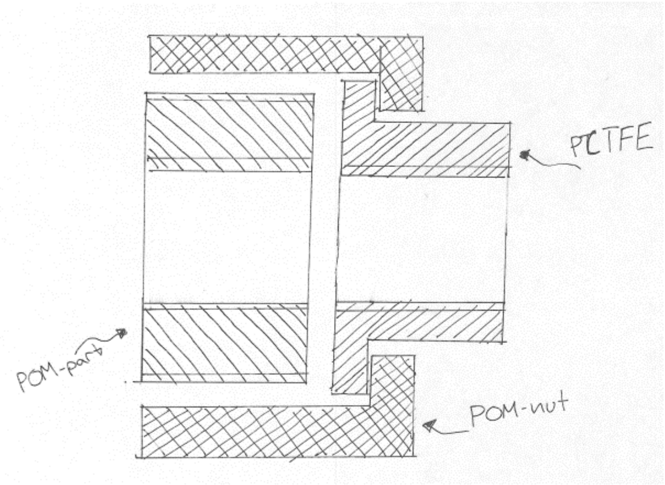

**Figure 3.2 The nut solution drawn in cross-section**

The *split chamber solution* is based on the original solution from the user experience. The difference is that the innermost part is split in half along the axial direction. Since this makes two parts of the screw, a slot can be inserted on the inside. In this slot the sample can be put.

This allows for different thickness of the sample, depending on sealing from the rings placed around it. The two parts of the screw are then put together and a nut is screwed on the outside. The electrical contact is still done by a steel screw. This will not have a large degree of radius freedom, but production flaws are fixed.

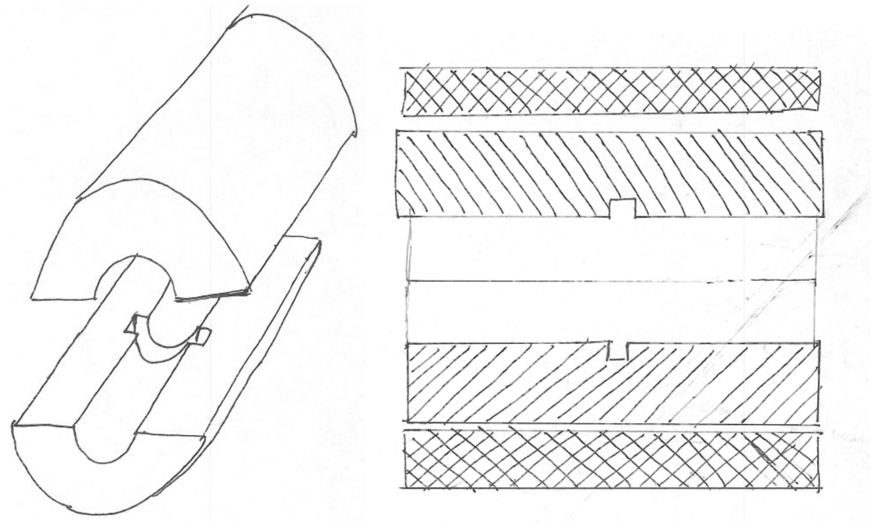

Figure 3.3 Drawings of the split chamber solution

The *disk solution* is a solution where a disk is put between the cells. The disk has a hole in the middle which exposes an area of the sample. The sample is put in from on top of the disk with O-rings on each side for sealing. This allows for thickness variation and radius variations if you have several disks. The cells are attached through threading or force fit. Electrical contact will be ensured through the top of the disk and out the open hole.

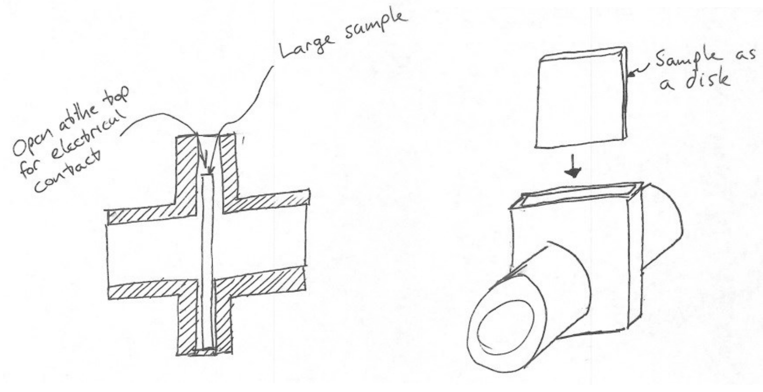

Figure 3.4 Drawings of the disk solution

The *clamp* solution is to put the sample between two different compartments before applying pressure. This can be utilized if the cells are not submerged, and not affected by corrosion. The compartments must have a sealing material at its end or use O-rings. It would be easier if the sealing was already attached to the cells. A clamp pushes the cells together against the sample and seals it. This requires a sturdy cell that won't break or buckle. The electrical contact is easy by attaching electrical wires to the sample. It gives the largest freedom in thickness and radius, when radius is only dependent on the cell mouth.

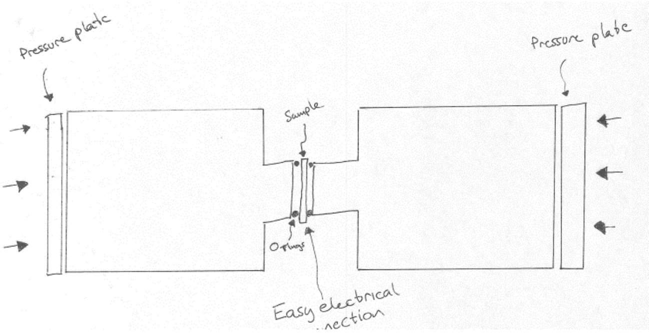

**Figure 3.5 Principle sketch of the clamp solution**

### 3.1.3 Method of heating

For the heating there are a couple of options available. The important factor to think about in the heating is that it needs to keep a stable temperature, with max deviation 0.5 degrees Celsius for several days. The next presented methods for heating can be of interest, but it will depend on final concept.

*Peltier elements* are small heating elements that can both heat and cool depending on the electrical current that is applied. The downside for this system is that they cannot be enclosed since they have one cool and one hot side. Another problem with Peltier elements is that they are mainly used for cooling. This is because the cold side transports heat over to the hot side. This means it needs external heating to be able to transport the necessary heat to the hot side. Then a more complex system with heat sinks needs to be applied.

*Water bath* is a solution where the cells would be put in water which is heated. On the plus side this is quite stable as long as the heating element is good, but it requires space and at high temperatures the water might evaporate. The temperature will be equally distributed through the bath when it is pumped around.

*Heating pipes* is much of the same as a water bath. A fluid is pumped through pipes running around the cells. It requires a pump, but needs less space around the cell than the water bath. With good circulation the temperature is also maintained stable.

*Traditional heating elements* could be used in an enclosed area. If it is mounted in air, it may not have the same temperature stability as a water bath, but the water is not needed. The heating elements are also rather small, and can be mounted inside an enclosed area.

### 3.1.4 Venting system

The venting system is crucial to let out any hydrogen gas that could have been produced. This may happen if the electric current is set too high. If the hydrogen gas should ignite, it could create a lot of disturbances and some damage to the cell. Venting is therefore crucial for a good concept. The pressure in the cells is low so the system needs to be sensitive to small pressure changes. Another demand is that the system does not allow air to run the other way.

*Safety valves or relief valves* can be used. They can be either electronic or mechanical. This is a good solution, but requires maintenance and very fine machinery to release the pressure. The pressure build up can't be too large. The *mechanical valve* has a closing mechanism attached to a spring. The pressure is released when it is larger than the pressure from the spring. The problem with this solution is that the strength of the spring is usually quite large. The *electric valve* can be set to a certain pressure. This means it can open at any the given time, but this complexes the build of the machine. Both of these solutions will do be able to do the job required.

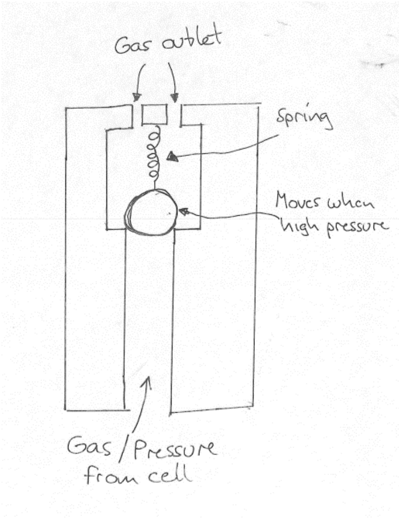

**Figure 3.6 Function of a mechanical relief valve**

A *bubbler* is another viable option. This is a cheap option that in its simplest setup requires a u-tube and water. The water will keep outside air from flowing in, and still release the created gas. The problem is that the water level needs to be correct for release on an exact pressure. The pressure for liquid movement needs to be calculated before use. This solution is low maintenance and has no moving parts, but requires the user to fill it with water and connect them each time.

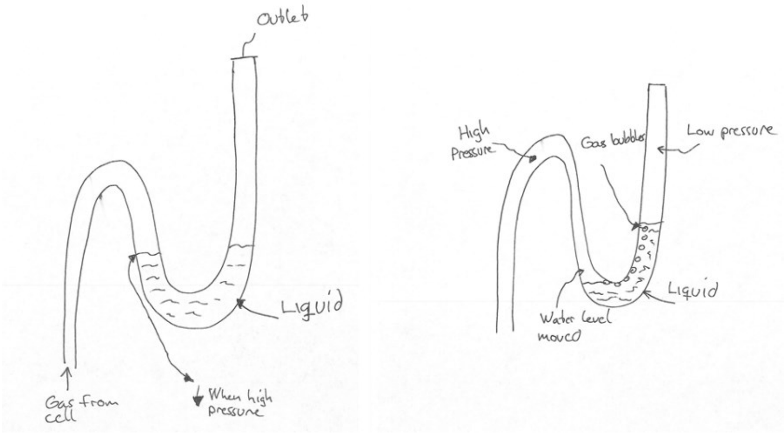

**Figure 3.7 Function of a bubbler**

### 3.1.5 Faraday cage

When working with small electrical currents, signals creating interfering noise should be filtered out. Noise is unwanted disturbances that obscures or interferes with a desired signal[18]. Noise can be created from digital circuits, electromagnetic radiation from other subsystems, penetrations from objects into the electrode area and ground loops[19]. Effects from electromagnetic radiation and ground loops can be reduced with a faraday cage.

A faraday cage is simply a uniform conductive box of a restricted area. The electrical currents will go around and along the surface, but not through. That means that electrical currents from the outside, will not affect what's happening on the inside and vice versa.

The electromagnetic radiation can come from several different sources like visible light, especially fluorescent, and other electronic waves. In a lab area, this can create much disturbance for the equipment. The faraday cage is a simple construction. It should be built of a high conductive material, since this will give the best attenuation against EM waves. A faraday cage absorbs and reflects the EM waves. Many faraday cages have gaps or holes in them. These must be half the size of the wavelength of the EM waves, or they will not provide shielding from it[20]. The full design should include a faraday cage to prevent the noise that can be built up. The wavelength of an electromagnetic wave can be calculated as

$$y = \frac{c}{f} \tag{3.1}$$

Where y is wavelength in m, c is the speed of light and f is the frequency in Hz [21].

## 3.2 Concept suggestions

In this chapter, some final suggestions on how to build the machine will be presented, consisting of the different part suggestions in chapter 3.1. They will be discussed using the user specification table and how it will perform based on these requirements. Also the main mission of the task will be taken into account. The goal is be able to choose an end design for actual testing.

The design suggestions will be based on different concepts for the end design. They can contain some of the same parts, but will be principally different in the setup.

### 3.2.1 Box solution

The box solution consists of making a larger insulated box to contain the cell. The cell itself will be put into the box. This means the cell should be stable and probably have a flat bottom. All of the suggestions for connecting the cells with the sample can be used, but the clamp solution could be utilized in a greater manner. Springs and pressure plates can be built into the box, and will then make a slot for placing the cell in.

Since a larger volume needs to be heated, the heating systems should be either traditional or using a water tube system. Using a traditional system, several heaters may need to be applied to be sure that the temperature is equal in the whole area. Temperature measurements can be done outside and inside the cells for the best comparison results. With a water tube system the same applies, but only the cell needs to be heated. It could be harder to get a uniform temperature over the whole cell since it will be put down into a slot with no top cover. The whole box might also be tubed, but this requires more piping and a bigger pump.

The faraday cage could be in the walls of the cage, effectively making a barrier from outside noise. Noise can however be created by the heating system, pumps, or other equipment in motion or with electricity in the box. A faraday cage around a solution using clamps could make the cage larger, but with the other solutions for attachment the shielding can be on around the cells, and the heating outside, creating less noise.

The venting needs to be directed out of the box. This requires a tube that runs through to the top of the box. This will create less space in the cage. All systems can be used, however, electronic might be favored if the pressure sensor can be read. This will give the easiest way to know the valve is functioning.

Electrical connection could be wired through the walls of the box for simple connection for potentiostats. This will not let a lot of wires lying around, and increase the user friendliness of the experiment.

One interesting application for this box is the availability for using a series of cells. An insulated box itself is not a big breakthrough, but creating one with connection for potentiostats and correct heating may have its applications since it leads to higher user friendliness. The most time consuming part of the experiment is the testing itself. Up to three tests on the same temperature is often required on the same sample type. With a series these can be done at the same time. This will cut the time consumption to a third of what a single cell needs, and could ensure equal environmental conditions for all tests. For this a more intricate heating system is required and it needs more work.

### 3.2.2 The tube

The tube solution is based on making a faraday cage as the outer layer of the system. The solution looks like the only the cell itself. The heating could be done by Peltier elements attached on the outside of the cell. This will heat the whole device and be able to cool it as well. There are also other solutions that can be used, as long as they can direct the heat towards the cell. Also a water tube system would work, or sinking the device into a water bath. This will lead to the machine being larger in size.

The connection to the sample needs to be the nut, the split chamber or the disk solution. All of them can be utilized without any problems.

Since the faraday cage is in the compartment walls, there will be a lot of penetrations through. This will lead to less shielding if the wires are not shielded themselves.

Since this concept focuses on being compact, there will in the basic design be no easy connection for the potentiostat. This will lead to a lot of wires lying around. To prevent this, a base could be designed. This will however only be done if needed.

The form itself should have a flat bottom. Both quadratic/rectangular and triangle forms may be used. The best heat effect would probably come from a triangle form, since there is a smaller volume to heat. Straight edges will also make it easier to build a faraday cage to fit.

All the venting systems can be used for this solution. The hydrogen gas will only be let out into the air around the device.

## 3.3 Discussing the solutions

### 3.3.1 Assessment of the box solution

With regards to the user specifications presented in chapter 2.3.1, the following assessments are made from the design.

The machine category, the robustness is the most governed attribute for this solution. Since the cell itself is protected by an outside wall. This will however give a worse grade on the size focus. This solution will be larger, but with a good design for the cells, the total volume won't be discouraging. The shielding of outside electrical noise can be very good and easy to make, since it can be fitted into the box design. It would be able to make it a see through by making a glass window in the box, and the cells can also be made of glass. Using conductive glass on the shielding can make it possible to see through the faraday cage too.

The cells will manage all the "must" criteria for them. All the different solutions will be able to change specimen thickness. The clamp and the disk solution might have the possibility to change the radius. However, this might not be needed since the mouth of the compartments will be governing. All forms will have room for a capillary if the larger size is needed. The attachment for the capillary needs to have a rotating degree of freedom so it will not crash into the walls when attached.

The temperature control will be good, since the box creates an environment for the testing. Using ordinary heating elements is probably the best, as long as they can be fine-tuned for steady temperature. The problem with traditional heating elements is that they cannot refrigerate the environment. For this a cooler must be used. The box allows for placement of this. Since the temperature in the environment is directly related to the temperature in the cells, measurements of the temperature will be easier to obtain without interfering with the electrode measurements.

The venting system will be a problem. If the box isn't sealed, the temperature will not be steady. Therefore a tube has to run from the valve to the outside of the box. The tube needs to be pointed upwards so no hydrogen will be trapped in a bend. This can be hard to find a good connection for, but can be led into the walls.

The maintenance can be easy if constructed correctly. With few moving parts most of the spaces can be cleaned. The compartments for the electrolyte are also easy to clean, as long as there is a possibility to exchange the fluids. The cell itself can be removed for easier inspections.

This is a viable option to use for the main concept. It will manage to do some of the work needed. This may not be seen as a new device, but more of a way to simplify todays use. Based on the initial criteria for the machine, being small and robust, the size might be affected. This depends on the size of the cell. The heating elements should not need to be too large, and not the thickest insulation is needed. It will be bigger than other solutions, but might be the better one.

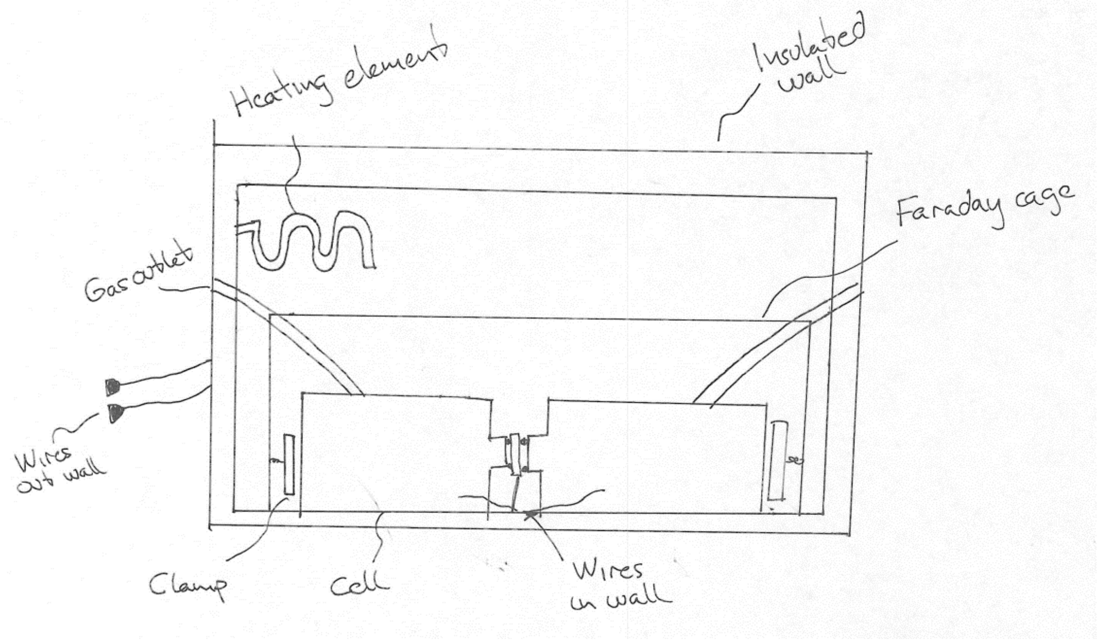

Figure 3.8 Principle sketch of a box solution

### 3.3.2 Assessment of tube solution

The tube solution will be small, since everything is attached directly to the cell. It will however not be as robust unless a second layer of shielding is applied. This will not work great with Peltier elements, since it needs to have good heat transfer on the cold side. They could be attached on the outside, but will not provide enough heat to be used alone. Another system should be used for the high heat transfer. Temperature control will be harder than in the box solution. The heat needs to be directed toward the cell. The cells will have heat loss, and there may be a need to insulate the walls to be able to keep a steady temperature. Otherwise it will need effective and exact monitoring of the temperatures in the cell. Water solutions is also a problem, since they usually requires a pumping system. This will complicate the system, and make the size too large with regards to the goal.

The sample holder can use any of the presented solutions, except for the clamp solution. The electrical contact to the sample itself will be a little tricky since a faraday cage will be tightly attached to the whole cell. The tight faraday cage will make it harder to free just the cells, without dismantling the whole setup. The other criteria should be functioning as they should.

Venting systems will create a hole in the shielding and be detrimental to the total shielding. Making the holes small and conductive could be an option to prevent this.

Maintenance could be hard. The whole system may have to be disassembled to access a part. The final design should emphasize on simple attachments for fast assembly and let it be easy to clean and change parts.

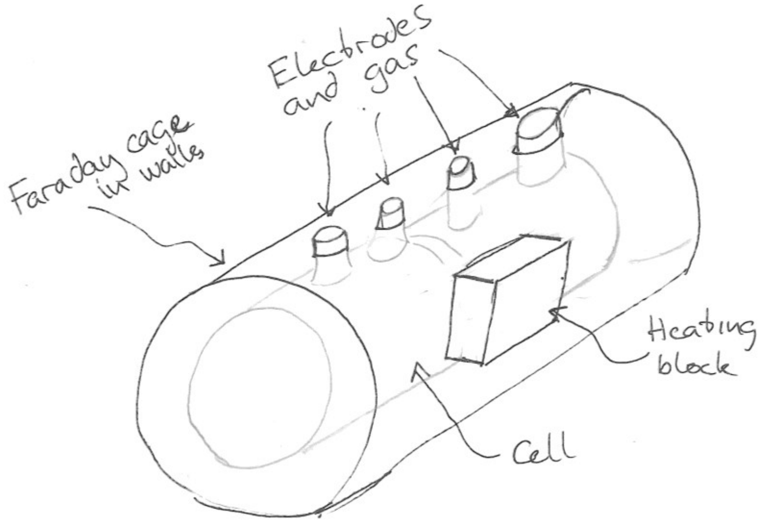

Figure 3.9 Principle drawing of the tube

## 3.4 Laboratory system

These are concepts for another type of problem. In this problem the user wants to have glass cells and use water for heating. This based upon improving the experiments in chapter 2.2.1.2.

The problems will be explored and two different concepts will be given.

### 3.4.1 Problems with the water bath

Earlier a water bath has been used for the experiments. The first problem is that it is large, the second problem is that the pump makes electrical noise. The Faraday cage is placed outside this type of heater. The faraday cage can be placed in the water, but it may have some drawbacks. A silver cage might be used, but the cost of this will be high. Copper is an alternative, but also has a high price. Aluminum will not corrode, but create aluminum oxides, which work as an electric insulator, and thus the cage will lose its functionality.

The pump also makes a lot of movement that can be translated to noise in the water, which might affect the measurements. Another worst case scenario is that the cell is knocked over and the electrolyte will not cover the entire sample and thus give the wrong readings. Glass might also break.

Using a water bath on high temperatures can also be disadvantageous. As long as the water is not pressurized we will see evaporation of the water. This means it needs to be filled up during these tests. This can lead to temperature variations that will affect the tests. It will also require constant monitoring of water levels.

The water bath is not all bad, it will create a constant environment for the cells, and then prevent significant heat loss in the cells. This will allow the right conditions at all time for reliable testing.

### 3.4.2 Suggestion 1: The double walled cell

Making a more compact water system still requires a pump and tubes. These chapters will focus on what happens around the cell.

The double walled cell is a possibility. Creating an outer layer on the cell to let heated water flow through is an opportunity that is exciting. Since the whole compartment filled with the electrolyte will be covered with water, the electrolyte will not have a heat loss itself. This will resemble the traits of the water bath in a much smaller scale. Using a flow of heated water it will ensure that the temperature is kept the same around the cell at all times. The flow will also help affect the time of heating, since more energy is brought into the system at all times.

Some problems may occur with this system. From a design aspect the flow between the cells can be difficult. There needs to be enough room at each end to allow for tubes from one cell to the other. Replaceable tubes that can be put on and off needs to be used to be able to disassemble the cells and put a new sample piece in. Connecting the cells to each other might prove ineffective. The cells should have separate flows by using a second pump or a y-connector on the tubes to connect one flow to each cell. This might be the cheaper and simpler option.

The connections for the flow should be at the top on one side, and at the bottom on the other. This is to reduce flow problems and improve the distribution of heat. With a top-top connection, the chamber will fill up, but you risk having different temperatures in the water since most of the flow of fresh hot water will be at the top. A bottom-bottom connection could be used, but may have some of the same problems.

Thermal problems will be an issue, and temperatures will need to be measured throughout the flow. The total amount of tubing should be low and insulated to prevent heat loss. Using separate flow for the cells would also make sure that the temperatures in each cell would be more as the same, since no heat from a flow will be lost at the other cell.

Even if it is desired for see-through abilities, the outer layer might not need to be made of glass. A flow can be hard to see through, even if the flow rate is slow. Then glass is not needed, since nothing is visible in the cells. It will only be at the start of the test that we are able to see through it, and this can be solved if the inner cell can be dismantled. Making the outer layer of glass may also be hard to manufacture compared to a plastic box for the outer layer. The necessary connections between the cell and the outer layer will be more solid than in a glass-glass solution. Repairing damage parts will also be easier. Manufacturing a double walled cell out of glass is not a problem, but cannot be made from the existing cell. A new cell needs to be produced.

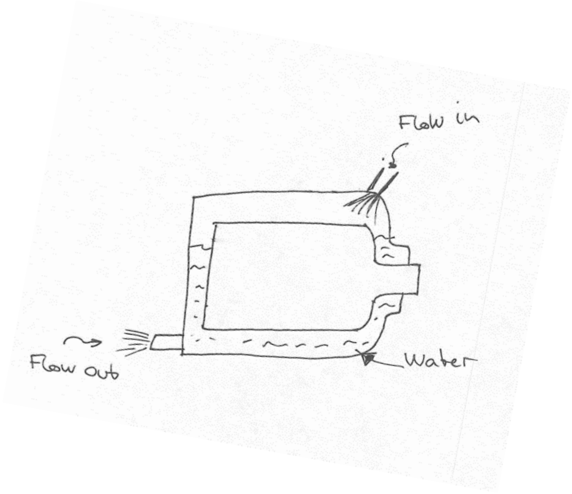

**Figure 3.10 Principle sketch of the double-walled cell**

### 3.4.3 Suggestion 2 Rig with tubes

This suggestion consists of making a rig for the cells that has replaceable tubes attached to it. It will use several tubes connected to the main tube through a splitter. The rig can be the length of the cell and be able to put the cell between the tubes. Using replaceable, elastic tubes the tubes can be “forced” onto the cell to cover the most area as possible. The advantage with this system is that it will be easy to produce and maintain. The flow will not be a problem, since it is only flow through pipes of different diameters. This is more of an external heating system than a modification to the cell. The problem is that more heat loss is to be expected from the cells. Even the flow of heat into the system can be hard to control. This requires temperature measurements inside the cell.

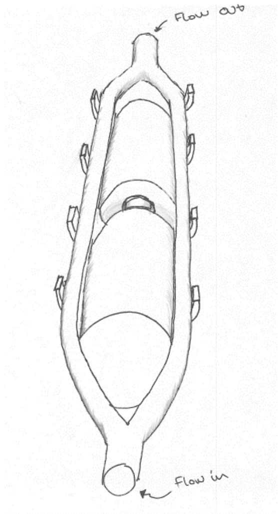

**Figure 3.11 Principle sketch of the tube solution**

### 3.4.4 Pumps

A pump is needed in such a system. There are basically two types of different pumps, positive displacement pumps and dynamic pumps. The positive displacement pump fills a chamber with a fluid and then forces it out to create pressure. These pumps are best used where high pressure is needed and for applications with exact amounts of liquid needs to be pumped. Dynamic pumps can again be divided into several categories, both rotary and non-rotary. A centrifugal pump is a type of rotary pump. Fluid enters into the middle of the rotary blades and as it moves outwards due to centrifugal forces the velocity decreases as it hits the wall which in turn increases the pressure. Axial pumps work as a propeller and create a high pressure on one side of the rotary blades [22]. The dynamic pumps usually need a Net Positive Suction Head (NPSH) to work,

The pump in this system does not need to have to utilize high pressure or very viscous fluids, so a dynamic pump is tempting to use. The problem is that there will be almost no net pressure to use, and therefore a positive displacement pump is needed.

This system will have low mass flows and low pressure throughout. The only important parameter is that heated water is moved through the system. This means that only a small, simple pump needs to be used. The requirement is that the pump can handle the temperature of the water. The temperatures might be up to 90°C, and it requires the correct material for the use. Max operating temperature is usually given by the retailer.

## 3.5 Nano-indenter cell

The third problem in this master thesis is a design for a Nano-indenter cell. It is a different problem since the cell needs to be vertical and has a maximum size to operate. The bubbles created in the electrolyte attaches to the sample and insulate it hindering diffusion and surface reactions. This chapter will focus on ways to remove the bubbles effectively.

### 3.5.1 Methods for removing bubbles

#### *3.5.1.1 Suction*

A suction tube is placed close to the sample from the side. The end of the tube needs to be as close to the sample as possible. When gas is created in the cell the suction tube will create a force on the bubbles, either by sucking them in before they reach the sample or create a force on the ones attached to the surface. Another tube is used to fill up the remaining space with new electrolyte, since it is unrealistic to think that only gas will be removed and not electrolyte. The negative pressure can either be created by using a positive displacement pump, or manually using syringes.

#### *3.5.1.2 Flow*

Instead of creating a negative pressure, a flow of new electrolyte can be used on to push the bubbles away. By directing the force from one side, a collector can be used on the other side to let the bubbles be trapped on the outside of the sample. There need to be an outlet for the extra fluid added. This can be done with a basic pump in a closed system or manually. The flow must be directed at the sample to try to spread the bubbles. Some of the bubbles will probably not be removed, especially those that are on the edge of the O-ring on the same side as the flow tube. The bad part is that it is not clear how a flow through the cell will affect the measurements

#### 3.5.1.3 Hole in sample

This is the most radical of the suggestions. The standard says that the area of measurement on the anodic side can be smaller than that of the cathodic side. That means a hole can be created on the sample surface. This will allow air and gas to flow through it, also making the cell easier to fill. Using a suction tube in this hole can prove efficient. The rest of the cell will have the same setup as the other suction suggestion with an inlet for new electrolyte.

#### 3.5.1.4 Brushing

Brushing is also a radical solution. This might harm the microstructure[23], but testing shows that this is the only way to really remove the bubbles.

#### 3.5.1.5 Chemical substance

This is just a concept, and needs several tests to know if it will work or not, but using a recombination poison solved in the electrolyte that reacts with H2 molecules is probably the ideal solution as long as it does not affect the experiment. Of course this would need a lot of testing and comparisons with electrolytes without the substance as well.

### 3.5.2 Testing of system for the Nano-indenter

The testing for the Nano-indenter was done with regards to suction and to flow. This was rapid testing of the mechanical functions. The equipment was not specially designed for this operation, and certain errors would occur.

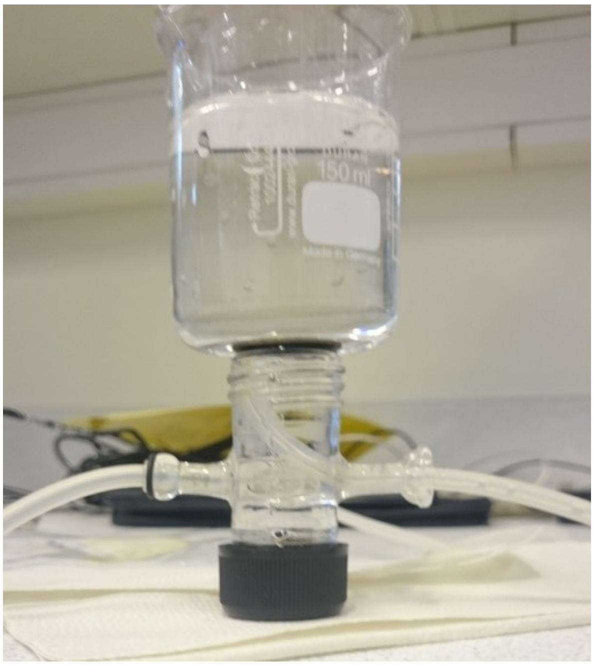

**Figure 3.12 First setup for testing**

**Figure 3.13 View of the tubes performing the suction in the first setup**

The first test setup was a glassware open cylinder with three different ports for other attachments. The bottom opening was closed with a lid, and placed with this end down. In two of the ports tubes were inserted and connected to two different syringes, one filled with electrolyte and one empty. The end of the tube connected to the empty syringe was placed as close as possible to the open end of the cylinder. The third port was sealed, with the possibility of having a counter electrode for inducing hydrogen bubbles in the cylinder. The cylinder was filled with electrolyte and a rubber seal was placed between the glassware and the sample. A weight was put on top of the sample to seal the system.

The first tests were done without hydrogen bubbles, as to see how this system would work. The empty syringe was used to suck air out of the system by creating a vacuum. The suction itself worked, but outside air was sucked into the container from the ports. This only happened from the different ports, but not from the top. After this discovery the test setup was rejected for testing with suction of the hydrogen bubbles, since we would suck out more air than hydrogen bubbles.

When flow testing started, it did not work properly. The weight on top of the sample was not enough to keep it from leaking when influenced by a flow that increased the pressure. The test set up was rejected from this as well.

This might have seemed like a waste of time with the testing, but it proved a useful tip for designing the cell: Having entrances to the cell compartment at a lower point than the end of the suction tube will cause air to slip in. Of course the ports might have been sealed better, but this could prove difficult when having several ports.

The next setup used the equipment for the earlier presented experiment in chapter 2.2.1.2. The cell was now horizontal for the testing. One cell was filled with electrolyte, and first both the capillary and the counter-electrode was attached.

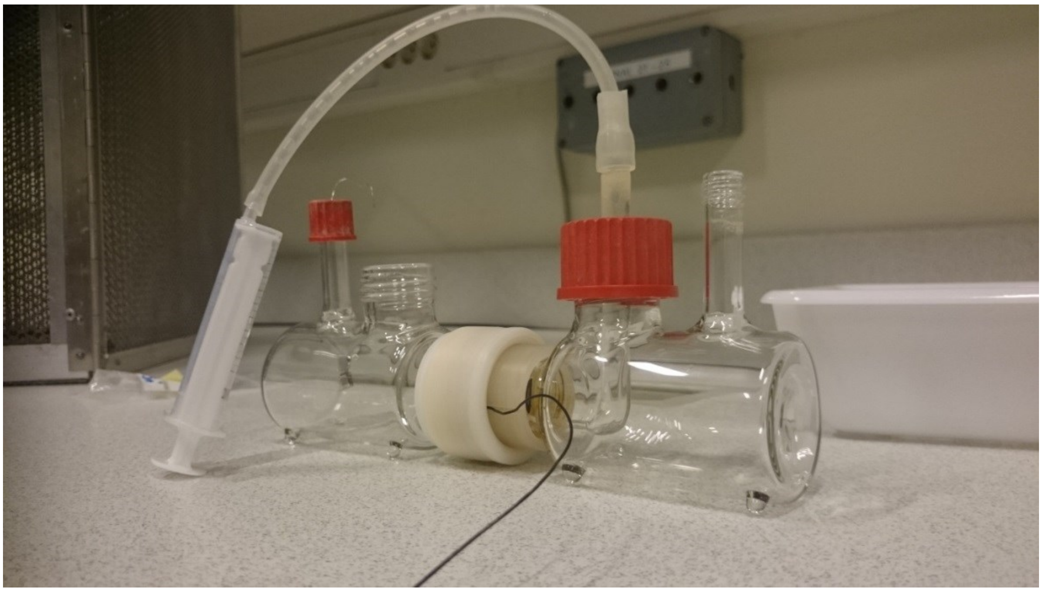

**Figure 3.14 Second setup for the tests**

Before charging with hydrogen, it was tried to suck air and electrolyte through the capillary. This would not work, as the ends were tightly sealed with aluminiumoxide. The hope after the first test was that it would have been able to let gas slip through, and not liquids. This would have proven as a much more stable system for testing.

When the capillary did not work, it was removed and the tube from the syringe was placed inside and directed towards the surface of the sample. When trying the suction now, no air was drawn into the syringe. This supports the former theory from the other test.

Then the cell was charged with hydrogen. For fast paced testing, we used a current of 1 mA/cm$^2$. The hydrogen bubbles were quickly attaching to the counter electrode and the sample. When the layer of bubbles was visible the hydrogen was tried extracted.

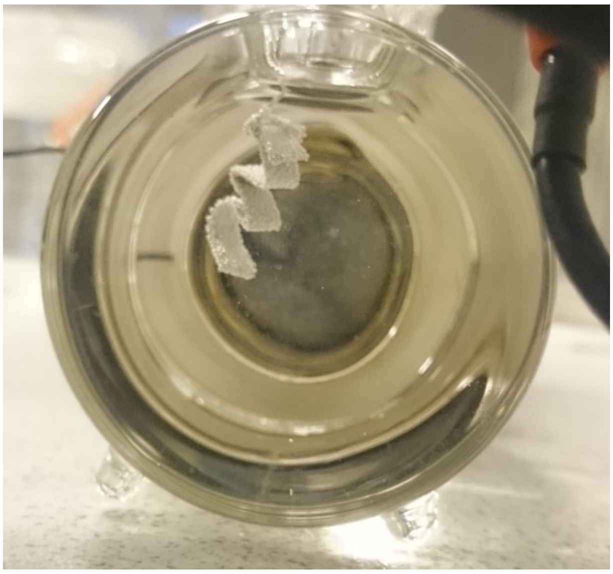

**Figure 3.15 Bubbles have formed on the counter-electrode and some on the sample**

**Figure 3.16 The bubble in the syringe was extracted from the sample**

It was possible to clearly see this bubble running through the tube, and it proves that we managed to suck some kind of gas from the sample surface, most likely hydrogen. When inspecting the surface of the sample through the glass, we could clearly see that some of the hydrogen was removed.

**Figure 3.17 Some hydrogen have been removed from the sample piece**

The problem was that this was very local to the area around the end of the tube. Several tests were done when more hydrogen had attached to the sample. They all showed the same effect.

A flow was also tested. The effects were tried on the counter electrode. It managed to push some of the bubbles away, but not all of them. This can have several reasons, but one of the most difficult things to do was direct a flow at the correct spot. Testing on the samples was tried, but the electrolyte became so filled with small bubbles that it was hard to see what bubbles actually were attached to the sample surface.

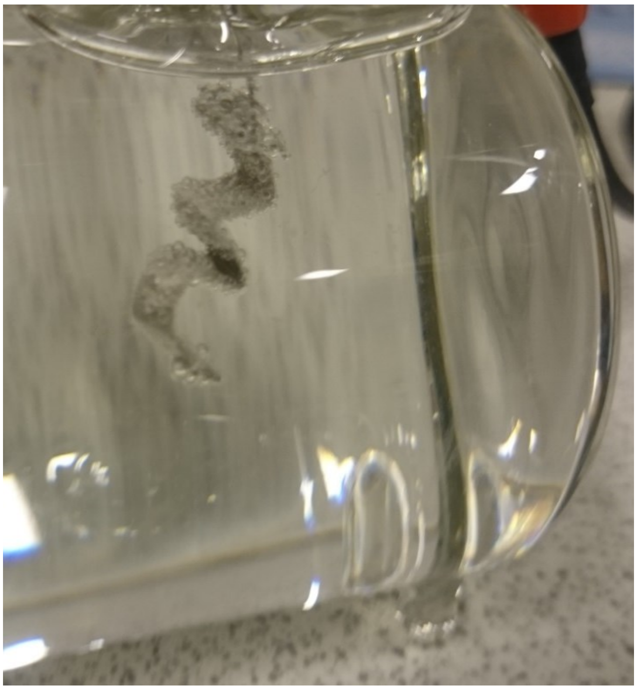

**Figure 3.18 Counter-electrode after trying to use flow to remove bubbles**

The problems with these tests were the lack of suitable equipment. Having specially designed equipment would make conclusions easier, as the results would be more determined. The tube touched the sample several times, and might have been the reason for some of the bubble removal.

The conclusions from the testing would be that both of the solutions work. Suction is better on a thick layer of bubbles, but has some drawbacks from the need of a completely sealed system and localized removal. The flow pushed only some of the bubbles away and was not as effective. However, this testing was done with a lot of bubbles. In a real experiment the current will be lower and bubbles will not be created as quickly. This means that using a constant flow on the sample surface would probably work to remove those small bubbles appearing during the test. The flow also showed to be less localized. The conclusion to draw from this is to design a flow system.

# 4 Final designs

This chapter will emphasize three different concepts for three different applications, one for use in the industry, on for use in the laboratory and one for an experiment with the Nano-indenter. Calculations will be followed up on the respective designs.

## 4.1 Industrial system design

The final design will emphasize to be a type of hybrid, though more accurate the box solution. In this chapter the different parts will be presented along with the final setup.

### *4.1.1.1 Cell design*

The cells are containers, and they are formed in a rectangular manner. This is for stability, and it makes it easier to connect attachments. The attachments need to have the highest local point by the venting system. Since hydrogen gas will rise to the highest point possible, the capillaries need to be sunk down into the frame of the cell. Otherwise a concentration of hydrogen gas can assemble and possibly damage the cell or the experiment.

**Figure 4.1 3d-model of one cell, see-through**

On the inside, the cells have rounded edges. This is from a maintenance perspective. Without sharp edges, the cells will be easier to clean. The production of this cell design in any polymer material can prove difficult. The cell mouth has a smaller radius than the main compartment. Without specially made tools, it is impossible to make from one piece of material. Therefore, one of the walls needs to be attached in a different manner. This is mainly using screws and some sort of sealing between the parts, since the electrolyte should not leak out of the cell. It is possible to argue that the cells could have a uniform radius from the sample to the end, and thus making it easier to produce. However, the thermal expansion of the electrolyte will be an issue. Using a glycerol based electrolyte this is a very relevant problem. The electrolyte can then either leak through faulty attachments, or end up clogging the venting system. Although not directly harmful to the equipment, it will make a sticky mess.

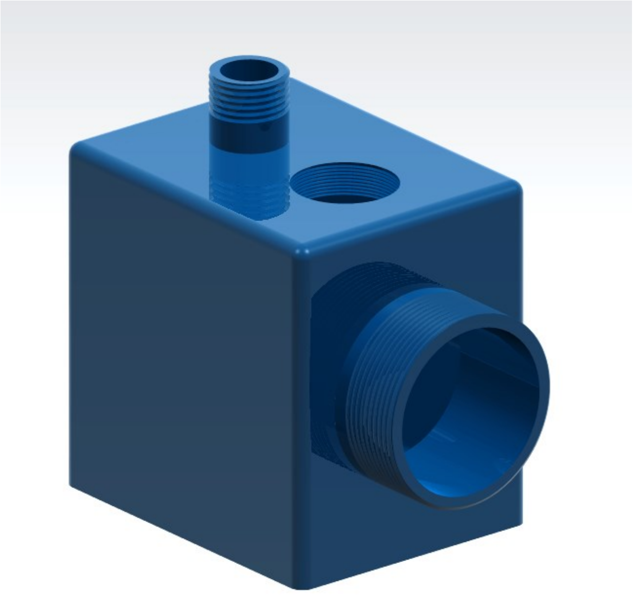

**Figure 4.2 3d-model of one cell with material**

Thermal expansion of glycerol has a value of 5 * $10^{-4}$ $K^{-1}$[24]. When calculated, the cell has proven to work for heating from 20°C to 100 °C. Even a larger volume of electrolyte can be filled in. A height of up to 35mm of the cell can be filled without a leakage. This is an advantage with the square cell, compared to a circular one, since there is more room at the edges of a square than in a circle.

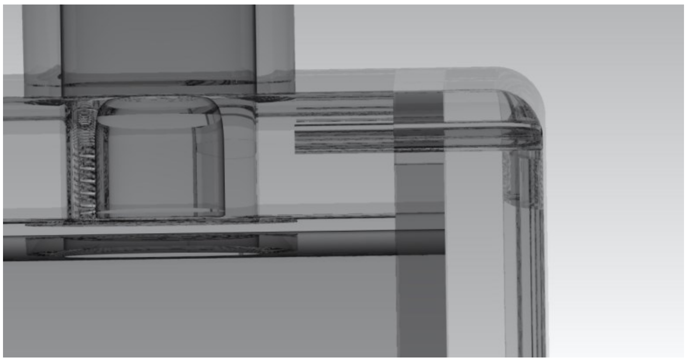

**Figure 4.3 Visualization of the screw hole and attachment for the back hole**

These calculations might seem unnecessary with a low thermal expansion coefficient, but since earlier testing experienced this problem, it had to be checked.

#### *4.1.1.2 Sample holder*

The sample holder will be the nut-solution. There have been made some small changes to the current design. The most important design change is to make a circular slot to place the sample. Making this slot have a larger radius than the standard size of the sample, it will allow for some irregularities in the sample radius, and less perfection is needed in cutting the sample. The slot will have a copper piece attached, around the edge that the sample is touching. This will ensure electrical contact when wired out of the sample holder as long as the sample piece is larger than the cell mouth.

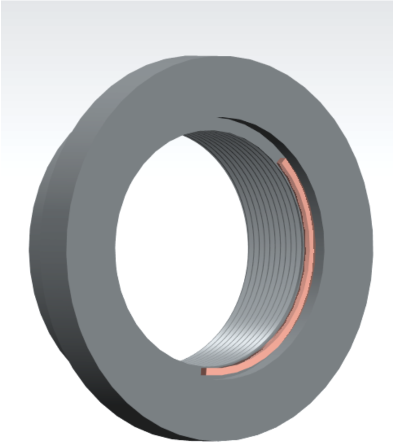

**Figure 4.4 3d-model of the part with electric contact**

The advantage of this sample holder compared to the others is the ability to tighten the cells pressure on the O-rings without compromising the angle by adjusting the nut. The O-rings pressure from the cell mouth to the sample piece is what seals the system. Without such a system, the sample holder threads and the cell mouth threads would need to be exactly machined to fit each other at a specific angle, and the system would be more vulnerable to wear. Another advantage is that sample thickness can be varied as much as the user wishes, as long as it is still sealed. The sample will not have its own designated slot that is restricted in the thickness direction since it is the cell mouths that press against the sample.

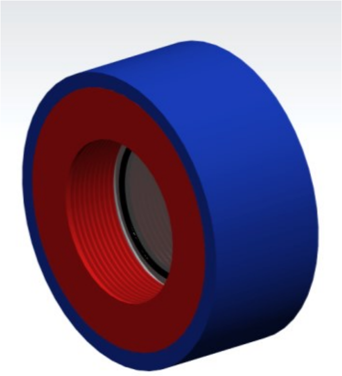

**Figure 4.5 The sample holder assembled. Different colors to visualize the different parts. Black parts are O-rings**

This is a three piece system, where two of the pieces are attached to the cell mouths. A nut is placed around one of them and then used to tighten the other part.

This system will make the exposed surface area of the smaller, and might need a smaller capillary, but this needs testing, both for the practical size of the capillary compared to the function.

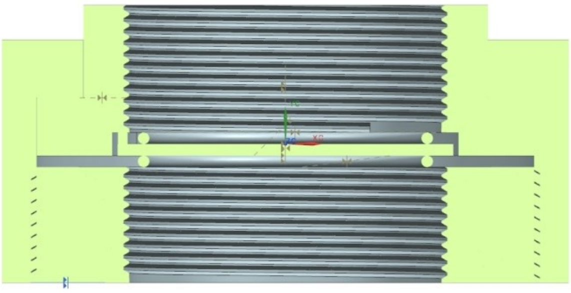

**Figure 4.6 Cross-section of the assembled sample holder**

#### 4.1.1.3 *Venting system*

The venting system is a bubbler. Using an electrical system would require more components and the mechanical systems would require too much inside pressure to let out gas. The pressure needed from the bubbler is governed by the amount of fluid that needs to be moved. This will allow for only small amounts of overpressure on one side to release the excess gas into free air. The design is created to use as little space as possible, meaning that it only functions in one direction without additional tubing. Other bubblers often have tubes connected in different directions, and this will take up room from something else outside the box. For a fluid glycerol should be used, since water may be spilt and contaminate the electrolyte inside the cells.

**Figure 4.7 3d-model of the bubbler**

Calculations for the liquid level in the bubbler are calculated by hydrostatic pressure.

$$P = \rho g h \tag{4.1}$$

P is the pressure, ρ is the density of the fluid, g is the gravitational constant and h is the height above the reference level. The results show that only a small difference in pressure ΔP from the inside of the cell to the outside is required. For glycerol at 20°C with an approximated density of 1261 $\mathrm{kg/m^3}$, only a difference in pressure of 24.74 Pa is needed to move the liquid 2mm. This value will increase proportionally with the height of the liquid column in the bubbler. Small mechanical valves can require several kPa for use. This proves that for the small amounts of hydrogen produced this will be able to do a satisfying job.

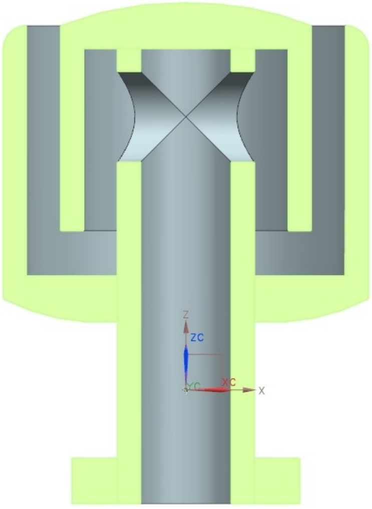

**Figure 4.8 Cross-section of the bubbler**

#### 4.1.1.4 *Heating*

The heating element is not a standard commercial product in itself. It consists of a glow plug attached inside a hole in a metal block. This block is attached to the faraday cage. When the plug is heated, the block can reach temperatures of at least 150 °C. The glow plug will be controlled by PWM to be able to reach the desired temperature. The temperature system will have a little delay, since the block itself needs to be cooled or heated. This requires a good control mechanism with several thermometers in the system. One could be needed in the block. One outside the cells and one inside the cells could be needed to see when a stable temperature is reached. Delay in the system might be the biggest problem with these heaters, and there could be applied smaller alternative heaters for better control. The heat loss of the system needs to be calculated to see the response of the system to temperature changes. The size of the metal piece will have a great impact on the amount of heat transferred, and also since the heat loss can't happen on the heated surface.

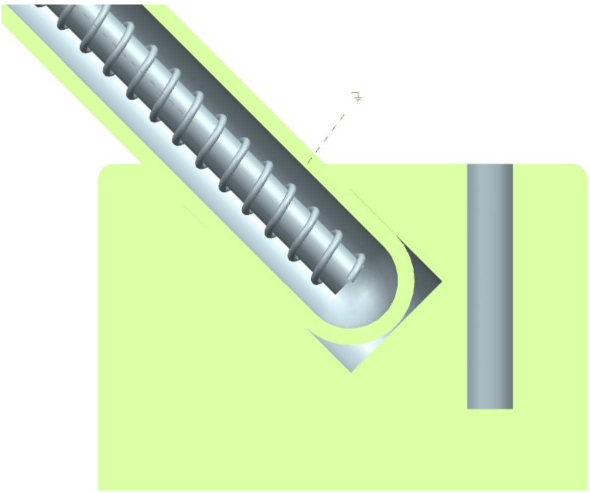

**Figure 4.9 Cross-section of the heater**

There could probably be a need for several heating elements, as one might not transfer enough heat into the system.

The heaters will be attached outside of the faraday cage in order to prevent noise from its electrical components. Another advantage is the lack of moving parts. This reduces wear and fewer things can be broken. If something is broken it can easily be replaced. The most danger for damage to the component is overheating of the glow plug. The aluminum will work as a heat bridge, but it may not be able to transport enough heat away. This sets demands for the glow plug and it should be carefully selected.

The air inside the faraday cage has a low heat transfer capacity and will work as an insulator for the cell. This will help with containing the heat loss from the cells themselves.

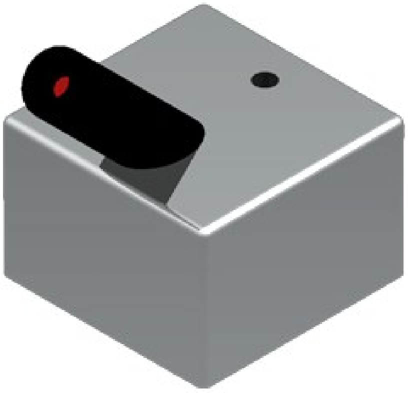

**Figure 4.10 The heater**

#### *4.1.1.5 Faraday cage*

The faraday cage, as presented earlier in chapter 3.1.5, is only a box with conductivity in all directions. They can be meshed or be solid. For this system a solid wall is to prefer to prevent heat loss and create a steady environment for the cells to be heated.

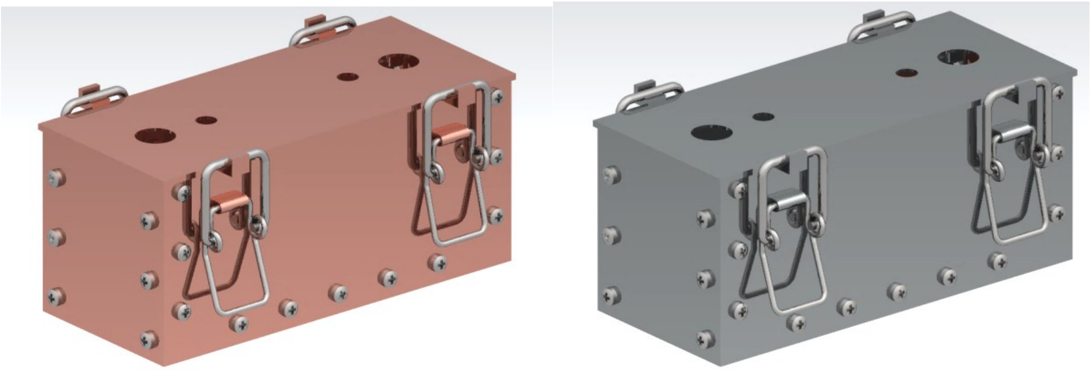

**Figure 4.11 Pictures of the suggested faraday cage. Left is in copper, right is in aluminum**

This concept requires the faraday cage to have holes in it for the bubblers, capillaries and wires. These will reduce the total shielding of the cage. What kind of EM radiation let into the faraday depends on their wavelengths. If the holes are smaller than the wavelength, it will not be a problem. This equipment is however larger than the smallest wavelengths it needs shielding for. That means it might be necessary to use metallic parts on the outside of the cell, to ensure conductivity, in a simple scenario, using conductive tape will work on the open areas.

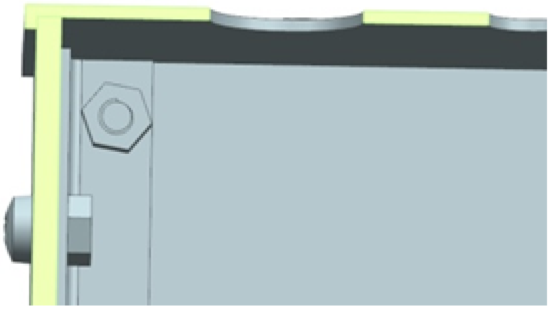

**Figure 4.12 Showing the edge of the lid on the faraday cage and the gaskets inside**

This type of faraday cage is easier to produce than one that is attached directly to the cell. It is only six metallic plates screwed together. It might require metallic gaskets over the connections to ensure conductivity, but in principle it should work. The lid is a separate unit for easy access to the cells. They have an edge to cover their connection and try to prevent holes. They are locked on with an easy lock system.

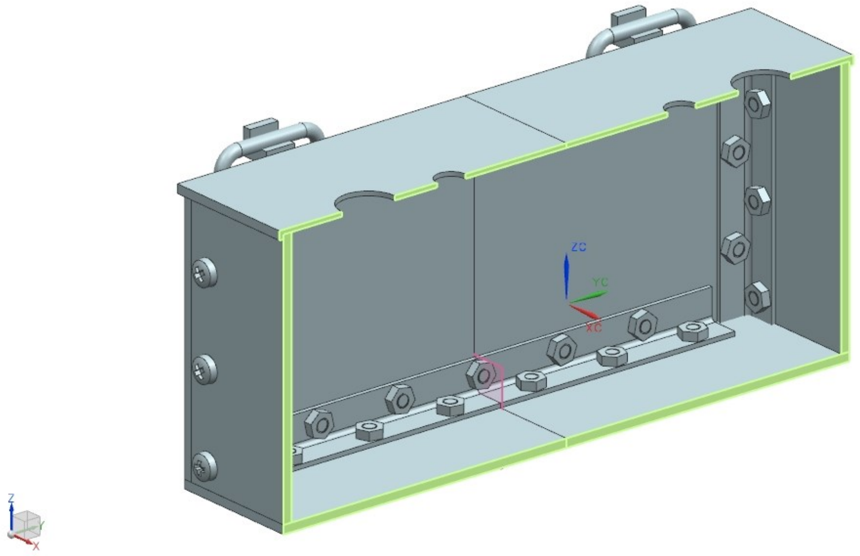

**Figure 4.13 Cross-section of the faraday cage**

To make the Faraday cage see through, it is possible to use conductive glass, for instance ITO-glass. This glass will then be a part of the Faraday cage's conductive field, and keep EM radiation out.

### 4.1.2 Main principle

The main principle of this system is to create an environment for the cell to do the testing. Creating the correct environments is crucial for reliable experiments. Some minor changes might need to be implemented after calculating effects and testing the systems. These changes can be insulation, more metal sheeting for shielding etc.

The size of the total system is 140x70x90mm. Depending on the number of heating elements needed, the size might be a little bit larger. Reference electrodes are not taken into account, as these will be designed by others and will have different size properties. The counter-electrode is not modelled, as this is reliant on the user and needed surface area. This can be put down besides the bubbler in the same mold when making the screw for the bubbler sealed.

The size lives up to the main tasks of creating a small system for use in hydrogen diffusion measurements. The size will not take up much space, but the total setup will be a little larger since it needs two potentiostats to work. With an external cage made of solid metal, the system will be more robust for outside force. Most of the design methods are made to prevent the use of moving parts. This also increases the robustness and reduces the expected maintenance greatly. Material selection will also be a factor when taking into account the cell. If the glass transition temperature is low, then viscous flow can occur and degrade the material or mechanical details like threads and holes during high temperature testing.

The system does not have working cooling system. This is hard to achieve, but it might work with using Peltier elements. This will not be followed up later in this thesis

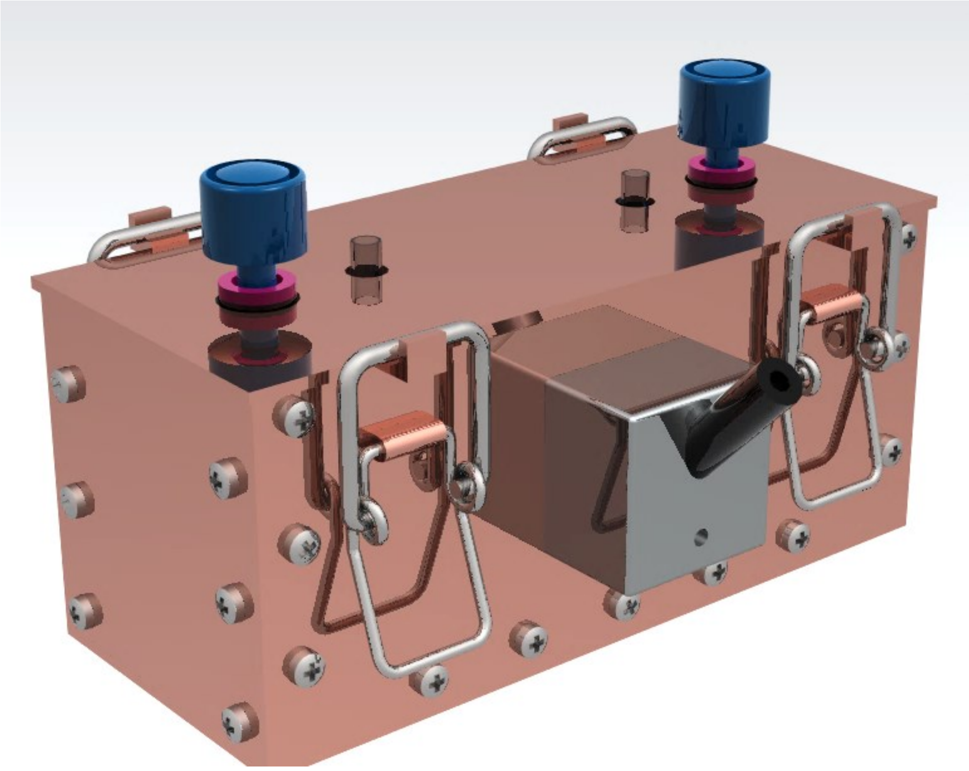

Figure 4.14 The whole system put together

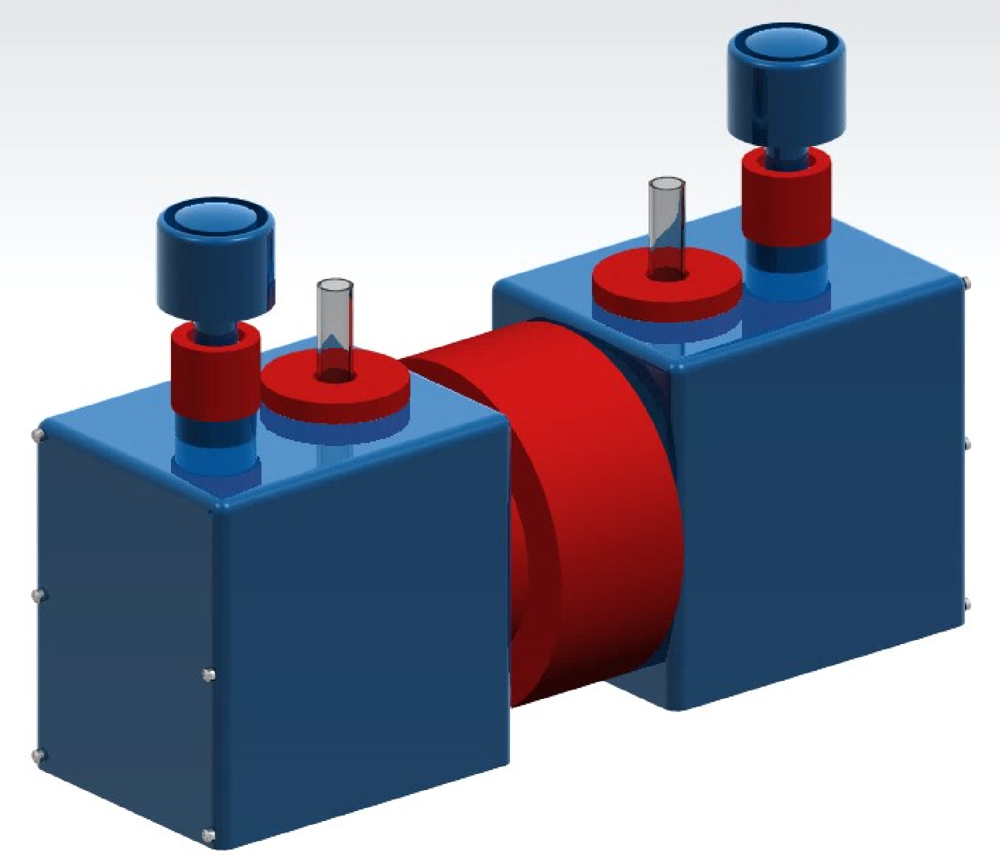

Figure 4.15 The cells assembled

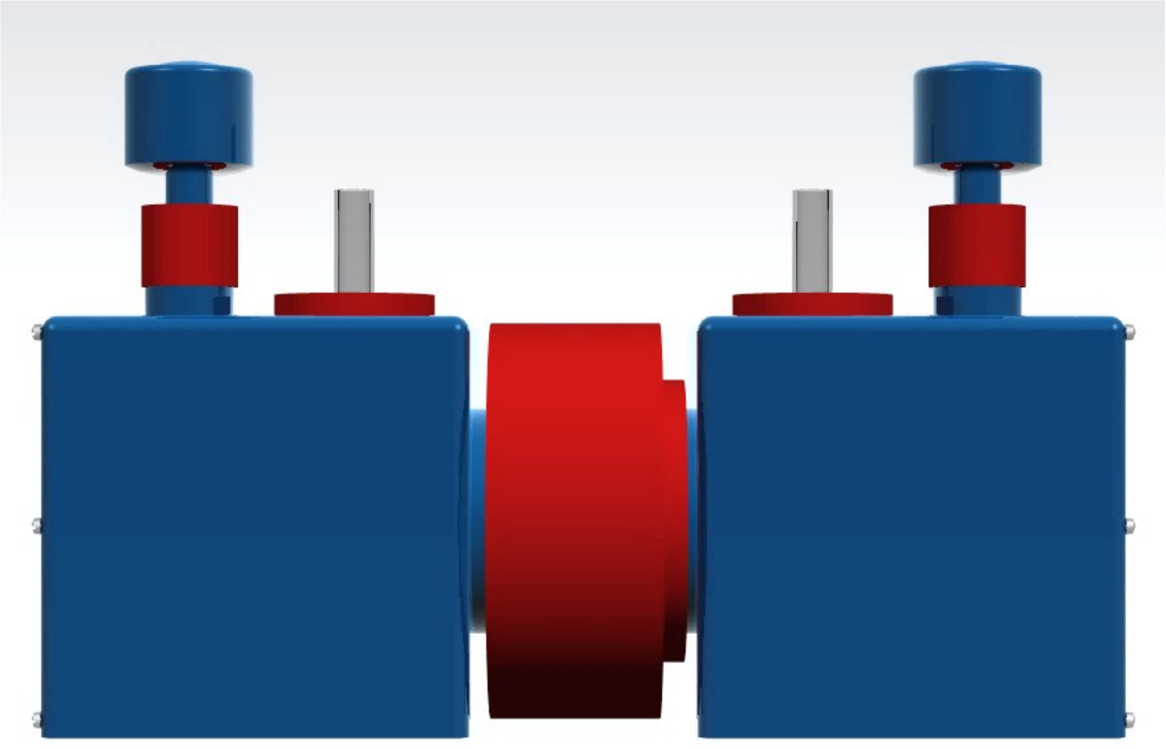

Figure 4.16 Side-view of the assembled cells

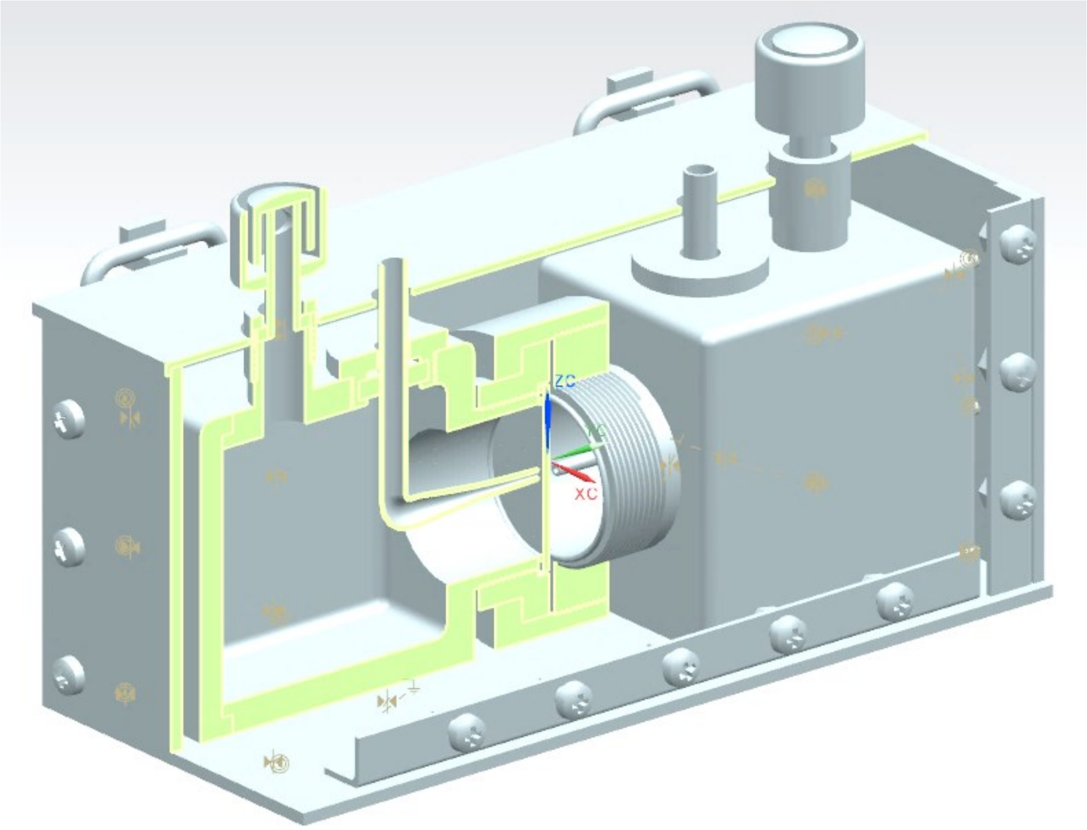

Figure 4.17 Partial cross-section of the assembled system

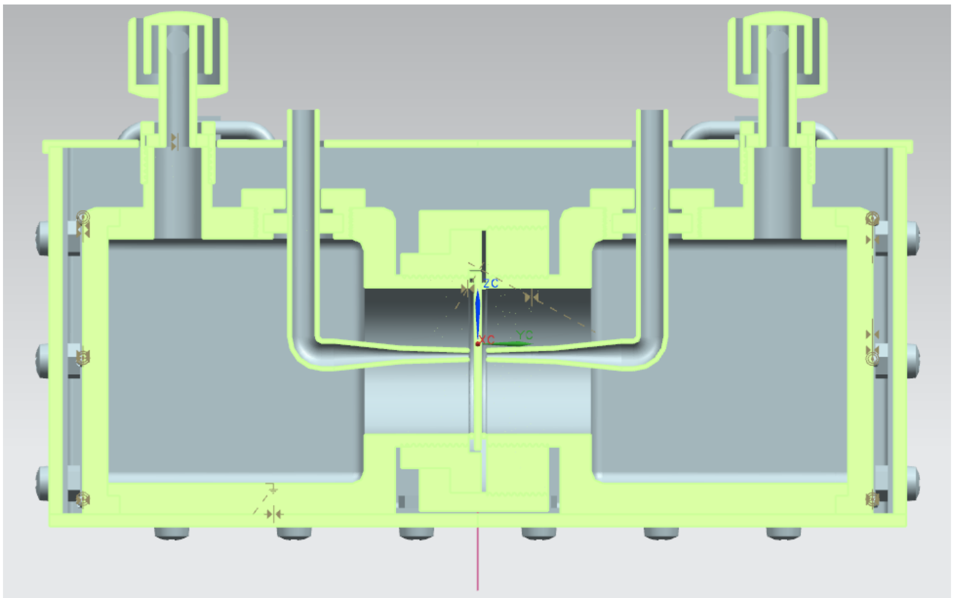

Figure 4.18 Side-view of whole cross-section of the system

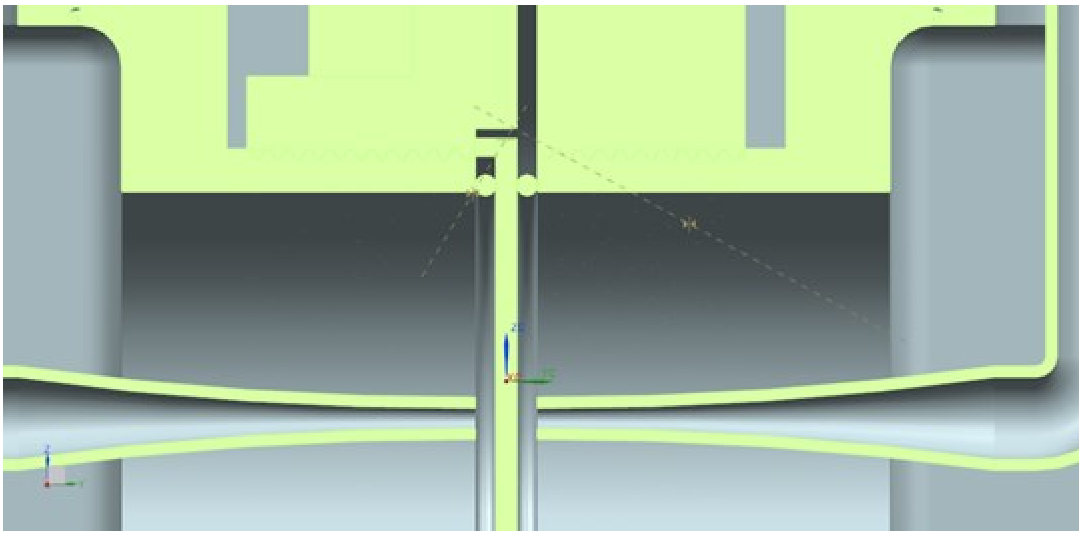

Figure 4.19 The sample piece in the system

Principle dimensions may be viewed in drawings in appendix D.

### 4.1.3 Material selection

#### *4.1.3.1 Cell and sample holder*

The materials in the cells and sample holders should be chosen carefully. Everything in contact with the electrolyte should be an inert material. This is to prevent corrosion inside the system. Corrosion might degrade the electrolyte and be detrimental to the experiment.

It would be possible to use a metal like titanium that will not corrode. It is not as susceptible to hydrogen damage or corrosion. This is a key when choosing materials to be used. Therefore many metals may not be used for these purposes. Austenitic steel and aluminum are usually not considered susceptible to hydrogen diffusion, and may seem like viable options for containers. They will have good heat transfer and shorten the time delay of the heating system. Aluminum has shown problems with stress corrosion cracking(SCC) from hydrogen[25, 26]. Usually it is immune while the natural $Al_2\ O_3$ oxides still exist, but when this layer is worn down aluminum will absorb $H_2$ at temperatures over 70°C[27]. Since the now used electrolyte is not tested, and other electrolytes may be used, the oxide layer could be dissolved without intention. Austenitic steels have an uncertainty with SCC[28]. Eventual SCC may only occur in the cell-mouth, since this is the only area subjected to a stress. Together with not being transparent, this is not a good choice. There is no need to risk it when other materials are available.

Glass is a viable option for the cells. This has been tested to work. The standard says that glass might not be a good option, since it can at high temperatures, above 50°C, release silica dissolutions in some environments [3, 29, 30]. This is mostly regarding different pH-values. For experiments at high temperatures it may not prove as useful. Some glasses are considered inert, and could work without interfering effects. Duran is used by the glass blower workshop at NTNU and could prove useful[31]. Glass is brittle, and will greatly decrease the robustness of the total structure. This might not be an issue when using a faraday cage, but the cells should either way be handled carefully.

Inert polymers might be a better option. Inert polymers do not react to the environment, in this case the electrolyte. Some polymers are more often used than others. Addition polymers are generally chemically inert polymers. Examples of this are the various forms of polyethylene and Teflon. The key is to use a polymer that is non-reactive to the electrolyte.

In the other the experiment in chapter 2.2.1.2 Kel-F (PCTFE) is used for the sample holder. Kel-F does not react with the electrolyte. However, it has a low glass transition temperature between 44°C and 77°C, depending on crystallinity[32, 33], which can be much lower than the test temperatures. This means that the mechanical features, such as threads, will be degraded much easier at these temperatures. The reason for its high inert properties is much the same as Teflon. Fluoropolymers have strong bonding between the carbon and flour atoms as well as the carbon-bonding, and are therefore highly chemical inert[34]. The reason for the use of Kel-F is that it is stronger and stiffer, making it easier to machine at room temperature[35].

Using a polymer material for the cells would be useful. Using a form of polyethylene could work, since it is inert to different chemical attacks, especially glycerol[36]. The machinability of the polymer is crucial as it needs to be able to have a certain force. This is a challenge and a lot of considerations must be taken into account. Melting temperatures, hardness and yield strength of the material play a role in this. It needs to be able to keep its form even if there is exerted force on it. Lower tolerances usually generate higher temperatures in machining. A polymer in the cell should also be transparent.

Ceramics might also be a good option for use, especially in the sample holder. A material like Macor has good machinability and low thermal expansion[37]. It is chemically inert and would fit well as the sample holder. The only consideration with using this is eventual wear to a weaker cell material. This is mainly for the part the sample is put on.

The other parts in the sample holder can be made from a cheaper material. POM (Polyoxymethylene) has been used and has proven successful. This can be a cheaper reactive material, since it only has chemical contact with air. The only properties that are needed to be worried about are the glass transition temperature and its machinability. A cheap metal like POM could be utilized.

#### *4.1.3.2 Faraday cage*

The faraday cages shielding abilities is determined by the conductivity of the material it's made of. The most conductive materials available are silver and copper. These are expensive, but would provide good shielding. For a cheaper cage aluminum could be used.

The thermal conductivity in these metals is also good. This is important with the heating system placed outside. This will create better heat transfer through the cage, and it will also spread the heat over a greater area and therefore prevent heat loss.

There is a relation between electrical and heat conductivity called the Wiedemann-Franz law. It says that the electrical and heat conductivity of a metal is proportional to the temperature.

$$\frac{\kappa}{\sigma} = LT \qquad (4.2)$$

Where κ is thermal conductivity, σ is electrical conductivity, L is the Lorenz number and T is the temperature. The law says that electrons cause the heat transfer in the metals, and therefore more free electrons lead to better heat transfer. This means that silver and copper are better heat transfers than aluminum.

### 4.1.4 Calculations of heat transfer

The calculations of the heat loss and heat transfer in the system have been done in a conservative manner. It is mainly done with numerical iterations of the heat equation by Euler's method. The assumptions made are:

- No heat conduction in the faraday cage
    - This is done mainly for easier calculations. It will in total lead to less heat loss from the cage since a larger area of the body will have a higher temperature than the air inside
- Constant temperature in the glow plug
- Air and glycerol heat the same in the whole volume. No local heating. Heat gradient uniform
- No local heat loss
- No convection, all fluids are at a standstill.
- Constant ambient temperature
- The model is simplified to a bare aluminum casing, a polymer cell and air in between.

The problem is set up as two solving temperatures, one for the air inside the faraday cage and one for the glycerol inside the cells. Specific heat capacity for aluminum is used as the transfer for the box, and Teflon for the cells.

The equations

$$\frac{dT_{air}}{dt} = \frac{1}{m_{air}c_{air}} * (g_{in} * (T_{element} - T_{air}) - g_{loss} * (T_{air} - T_{outside})) \tag{4.3}$$

$$\frac{dT_{glycerol}}{dt} = \frac{1}{m_{glycerol} * c_{glycerol}} (g_{cell} * (T_{air} - T_{glycerol}) - g_{cell} * (T_{glycerol} - T_{air})) \tag{4.4}$$

Where T is temperature, m is mass, c is specific heat capacity, and g is the heat transfer coefficient through the respective walls. The sample holder is disregarded as a source of heat. The heat transfer coefficient is related to the heat transfer rate and thickness of the layers. For detailed Matlab-script see appendix C. The equation might be wrong in (4.4), but should give an approximate picture of the situation. They are based upon the equations for a hot water tank from [38].

The goal with these calculations is to see that the heat loss is not so large that the temperature will not rise in the system. The other part is to see how much time is to be expected to warm up the cell to a certain temperature.

For the first calculations ambient and start temperatures were set at 20°C. The element temperature was set at 200°C.

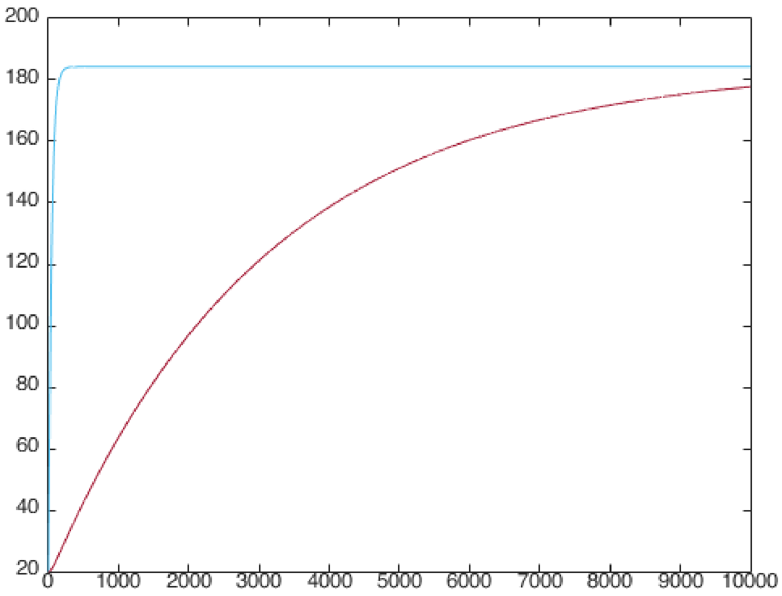

**Figure 4.20 Basic heating. The blue line represents the air, the red the electrolyte. X-axis is in seconds, y-axis is temperature in Celsius**

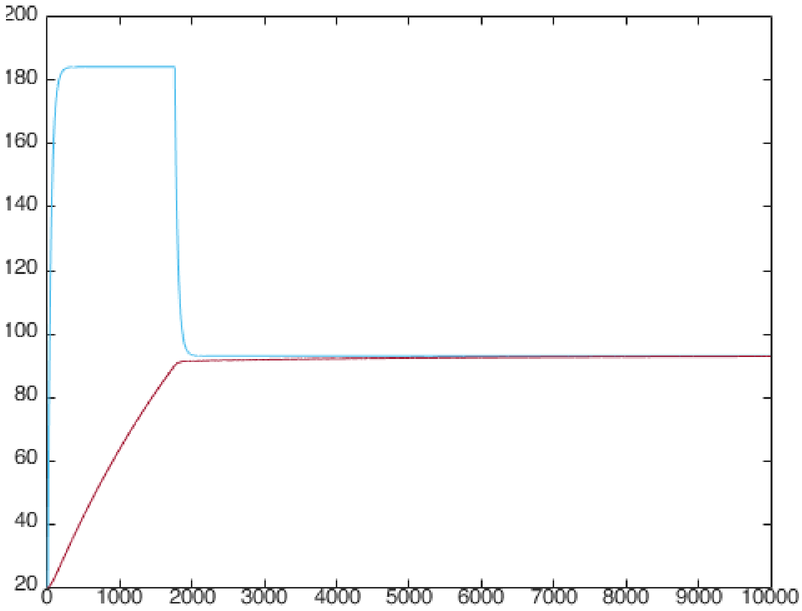

**Figure 4.21 Trying to control the system. Blue represents air, red is electrolyte. X-axis represents seconds, and y-axis temperature in Celsius**

In Figure 4.20 we can see that the temperature rises at a steady rate in the glycerol. This is what is expected when doing this numerical assessment of the system. The air rises quickly up to the designated temperature. The heat loss is there, but it is acceptable. Of course the temperature will never reach the highest point because of the boiling point of the glycerol. The highest testing temperatures will be at around 90°C, and the system will use approximately 40 minutes to reach it. This is the simplest setup of the calculations.

A more advanced setup with these two components is to adjust the element temperature to simulate a control system. This could either be done by time, hence number of iterations, or by temperature. Temperature is more convenient, as the control system would rely on thermostats. In the next presented the initial conditions are the same, but the temperature of the elements are changed when the glycerol reaches a certain temperature.

In Figure 4.21, the temperatures in the elements are adjusted to a 100°C when the glycerol reaches 90°C. This gives a more realistic picture of the temperature that will occur. It reaches a steady state quickly which is positive.

The next calculation is to show the delay in time for cooling of the cells.

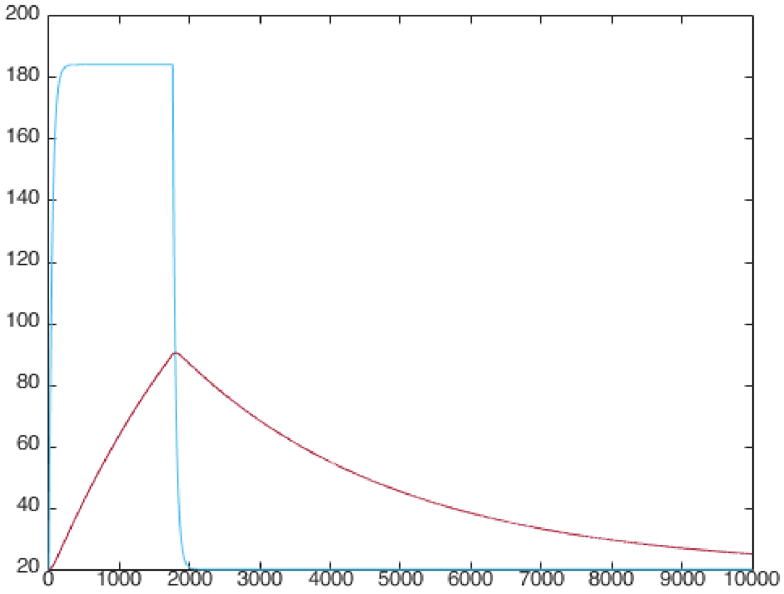

**Figure 4.22 This shows the slowness in cooling. Blue line is the air, red line is the electrolyte. X-axis is in seconds and y -axis is temperature.**

In Figure 4.22 when the glycerol reaches 90°C, the elements are dropped to 20°C. This shows that it will take some time before the system cools off. One problem that can have arisen is that the heat from the inside layers are not accounted for in the equations. The air should probably have some effect from the cooling of the electrolyte.

These calculations look good and the system will work, but the problem arises when the aluminum block for the heater is accounted for. These next calculations give the system a time delay for the temperature. This will greatly increase the time for cooling.

In Figure 4.23 the time delay is clearly shown. One thing done with these calculations to be able to show the cooling in a better manner, a convection transfer rate is used on the outside air. The air has an assumed speed of 2 m/s as the hot air rises and cold air flows to the element. Not using the convection transfer, the cooling was extremely slow. Probably it will be something between these values.

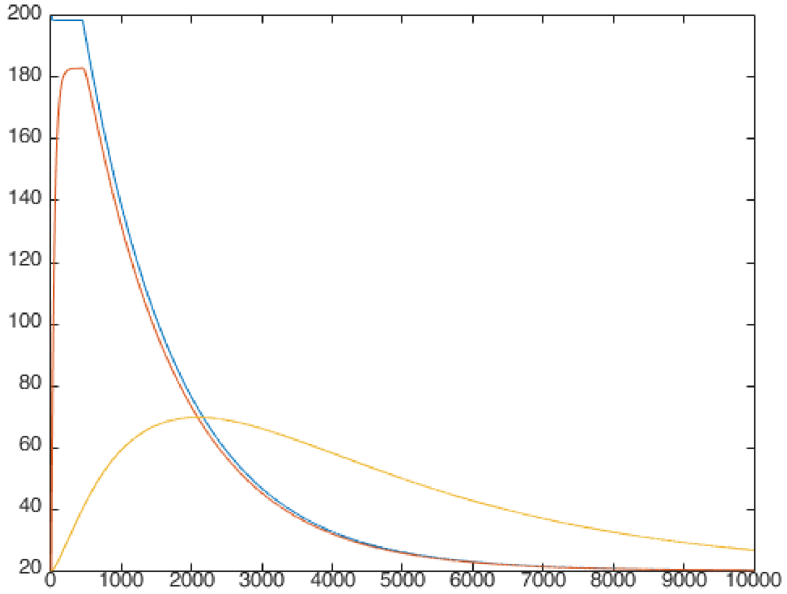

**Figure 4.23 The slowness for cooling of the block applied. Blue line is heating block, red line is air, and yellow line is electrolyte. X axis in seconds and y-axis in Celsius**

In this calculation the glow plug has a constant temperature. The glow plug will be adjusted using PWM from a microprocessor. It will require some time to cool off, but then more material data from the producer is needed.

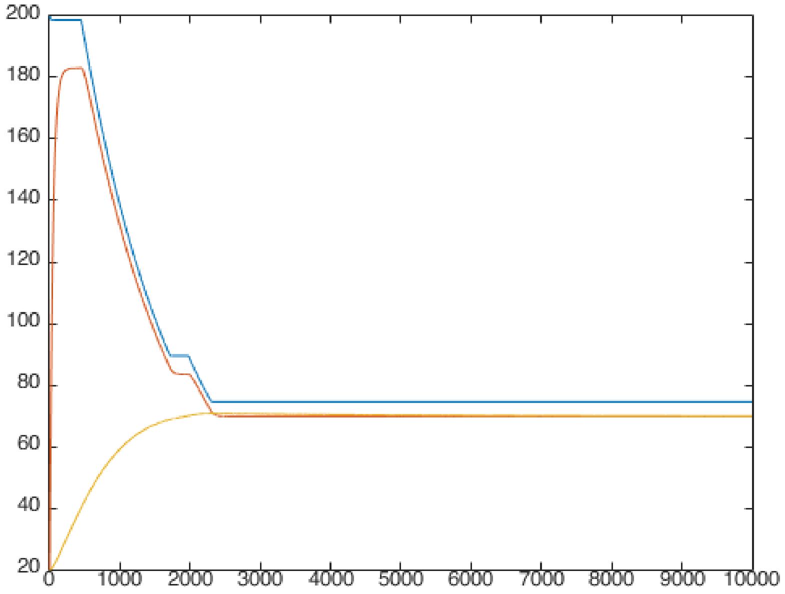

**Figure 4.24 Trying to control the system with the temperature from the glow plug**

In Figure 4.24 calculations are stepwise adjusted for the heating elements, to show how a control system could work to counteract overheating in the glycerol. This makes it reach a stable temperature earlier. The control system itself will need to have several temperature measurements to verify the temperatures before the time is taken into account.

In all, the calculations show that this system should work. Real life testing is required to verify this, as it surely will have some changes in the performance. The heat loss will be different because of the simplified model, but it is possible to believe that the performance will only be better.

## 4.2 The laboratory system

These designs are based upon improving the already existing equipment used in NTNU corrosion lab. The requirements given are that it should be made of glass, and use a flow of fluid to heat up the cells. The reason for this design is to be able to recreate the environment from the earlier experiments, and remove some of the problems that have arisen. It was decided to go for the double walled system, since this probably can give more uniform temperature distributions. The sizes of the cells are not clearly stated, but can be reviewed in the appendix D.

### 4.2.1 The design of double walls

The first design is based on the existing cell structure in glass in chapter 2.2.1.2. Some of the dimensions will need to be changed. The main principle is to add a double wall to the cells. Otherwise it has the same setup.

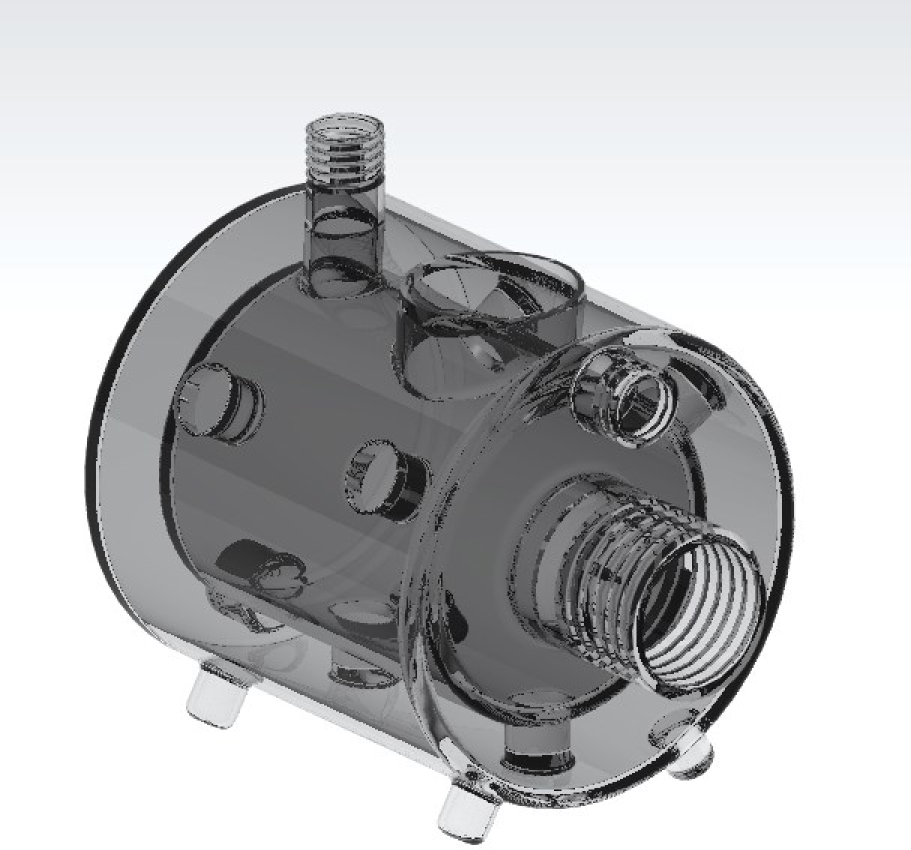

**Figure 4.25 First suggestion for the double walled cell**

This picture shows the first design of the cell. The cell mouth and the through holes for the electrodes need to be longer. This will require new capillaries, but they can be fitted to have another form that is better for this system.

After dialogue with the glassblowers, some changes needed to be made to make it constructible. The supports inside the walls were hard to make and not needed, the attachment for the capillary needs to have a top to be able to fit it. Another problem that arises is the placement of the inlet for the water flow. This needs to be high, but cannot be on the same side as the cell mouth, because a sample holder will not fit in between them.

After the discussion with the glass blowers, the design was modified. The inlet for water flow is moved, the supports inside the cell are gone and the capillary will have a screw attachment. It should now be ready for production.

**Figure 4.26 After interaction with the glass blowers, alterations were made to the double walled cell**

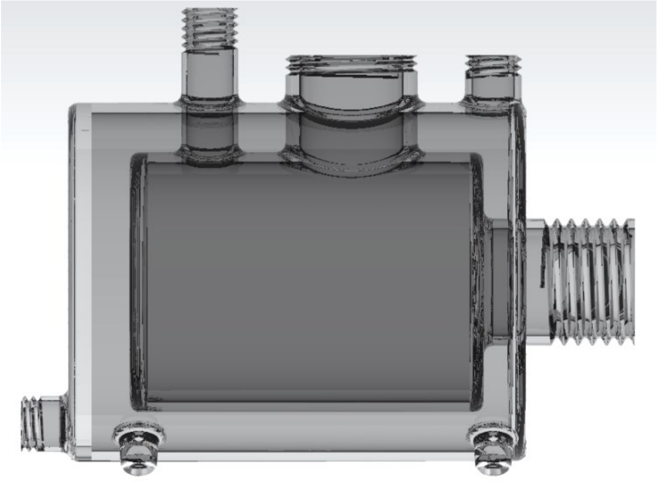

**Figure 4.27 Side view of the double walled cell**

#### *4.2.1.1 Trouble with thermal expansion?*

Thermal expansion is calculated for these designs. In the current form, the radius of the cell is 25.5 mm. The height needed to completely cover the sample is 35 mm. This gives this figure

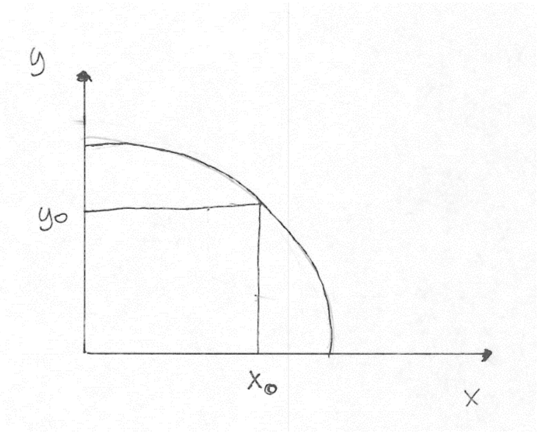

**Figure 4.28 Visualization of the electrolyte in the cell**

Symmetry causes only calculations of a quarter of the cylinder is needed. $y_0$ represents the height from the center of the cylinder to the top of filled electrolyte. In the following example $y_0 = 11.5mm$, $x_0$ can then be calculated by trigonometry.

$$\cos\theta_1 = \frac{y_0}{r} \tag{4.5}$$

$$90° = \theta_1 + \theta_2 \tag{4.6}$$

$$x_0 = r * \cos\theta_2 \tag{4.7}$$

With the initial values $x_0 = 22{,}76mm$

To calculate the volume of the electrolyte filled will be

$$A = \frac{1}{2} * \pi * r^2 + x_0 * y_0 + \int_{x_0}^{r} \sqrt{r^2 - x^2}\, dx \tag{4.8}$$

The solution for the integral when only considering one upper quarter of the cylinder:

$$A = x_0 y_0 + \left[\frac{x}{2} * \sqrt{r^2 - x^2} + \frac{r^2}{2} * \arcsin\left(\frac{x}{|r|}\right)\right]_{x_0}^{r} \tag{4.9}$$

The total area covered by the electrolyte can then be calculated by insertion, and it is 1589.4 mm$^2$ to the total area of 2042.8 mm$^2$.

These numbers are considered the thermal expansion. The length of the cell itself will not have an impact on the numbers if we don’t consider the cell mouth as well. This will be full of electrolyte that will expand. Since this has a volume, the cell as a whole will need to be considered by a volume as well.

Calculations with the same expansion coefficient as mentioned earlier in chapter 4.1.1.1 will not cause problems. Some more calculations were made to test how much liquid could be poured into the cell. This showed that the expansion will not be a problem until the height reached about 19 mm above the reference level. Since it was shown that this was not a big problem for the cylindrical cell, there will be done no more specific calculations on the next design.

### 4.2.2 Second design of double walls

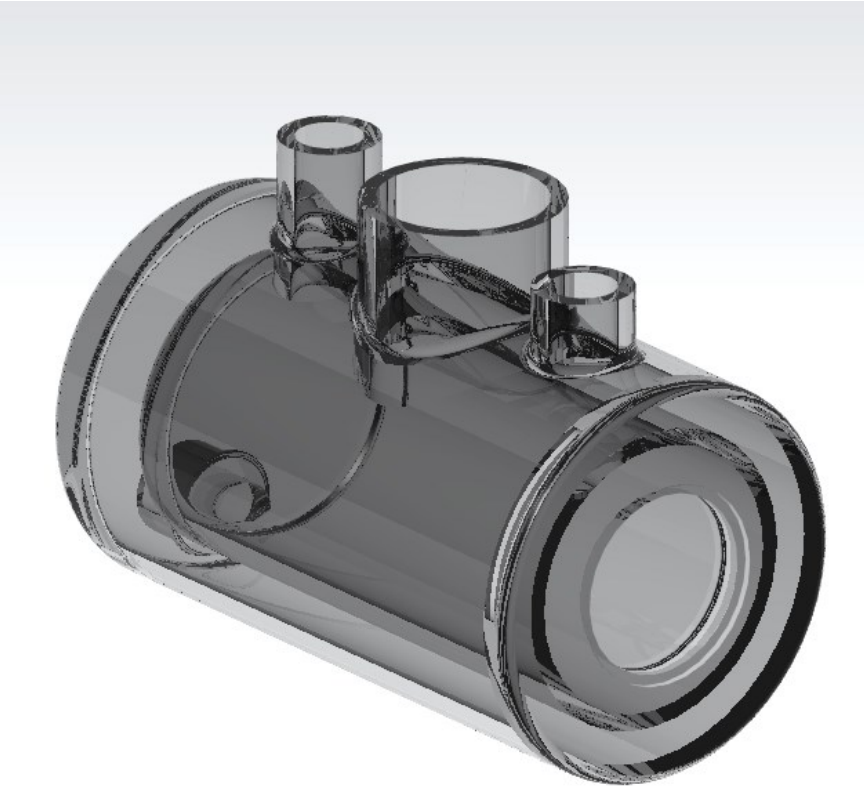

**Figure 4.29 Alternative to the double walled cell, focusing on pressure as the sealing mechanism**

A good advantage for a cell with double walls is that it doesn't need to be submersed. This means that a sample can have free edges since no corrosion will happen from the heating water. This will make the design of a sample holder simpler or not needed at all. Electrical contact will not be an issue either. The cell in the picture is designed to be pushed against another cell when having a sample in between. Utilizing the clamp solution for a sample holder would work. The main problem is that the cells are made of glass. Calculations on the wall thickness of the glass should be done to ensure that it has the needed strength to withstand the pressure applied to seal the cells. Thermal expansion still comes into play when using these cells, so the radius of the mouth opening should be smaller than the radius of the electrolyte compartment.

#### *4.2.2.1 Strength calculations for a clamp solution*

Using glass with a clamp solution has some risks. You run the imminent danger of the glass breaking. Glass is quite tough compression wise, and there should be no danger in the cylinder walls. The main problem will possibly arise at the end of the cylinder walls, where momentum forces from the sample placement can break the glass. The momentum forces will be directly related to the diameter of the sample placement and the diameter of the outside cylinder. Since this is a small structure, the momentum forces will probably not be so large that it would be a problem. This should be checked with relevant forces for the sealing of the tube.

FEA was done in the UGS Siemens NX 8 Nastran software. This should suffice for non-linear testing. The mesh of the model was set at 1 $mm^2$. To best simulate the forces only the outer ring of the outer cylinder was applied a force of 1000N. This is better since the clamp solution should have a flat uniform plate applying pressure on the cell. If there are any large deformations in the center back of the cell the plate will just push on the cylindrical walls and not the end wall. The constraints were set at the O-ring placement with fixed constraints in the x-, y- and z-direction. The material selected was toughened glass, with the material constants Young's modulus $E = 70$ GPa this is simplified from [39], Poisson ratio $\mu = 0.22$ and density $\rho = 2500$ $kg/m^3$. The material was considered isotropic in this case.

The quality of the result is important when doing FEA is the quality check. This compares stress and strain result to decide if the results are representable. These calculations give a quality of 94.966%. This is a bit low, but they are acceptable. The lack in quality often comes from quality of the meshing, with a more complex geometry the meshing needs to be better. It would be possible to get a better quality from the calculations by simplifying the geometry or refining the mesh. Higher quality will result in more accurate stresses, but the results from the FEA showed that it would not be necessary, especially compared with the computer power needed.

The final result showed that the highest elemental nodal stress, average stress of all elements contributing to the node, was 37.81 MPa at its maximum. The elemental stress, stress in the center of the element, was 24.12 MPa. All stresses are referred to as Von Mises stress. These stresses were situated around the sample placement, being mainly shear stresses. This was not what was expected, but clearly shows that the dimensions of the model were counteracting a large momentum. In the expected area the elemental nodal stresses are at the maximum 17.1 mPa, and the elemental stress is 11.2 MPa.

The difference between elemental nodal stress and elemental stress is seldom the exact value for the stresses in the point. The real case will be somewhere in between them. The strength of glass depend different conditions. Theoretical strength is high, but the actual strength is low. It can be the surface conditions, temperature, inclusions etc.[40] which are detrimental for the glass. This makes the ultimate tensile strength almost impossible to determine[41]. Flexural strength of soda-lime glass is 69 MPa[42]. It is possible to argue that a more modern day toughened glass will have higher restrictive strengths. Taken this into account, there should be no problem using these forces on the double-walled cell.

The force on the clamps should be adjusted according to the compression data for the O-rings. This can be calculated non-linearly by a software, but is easier tested on the specific O-ring.

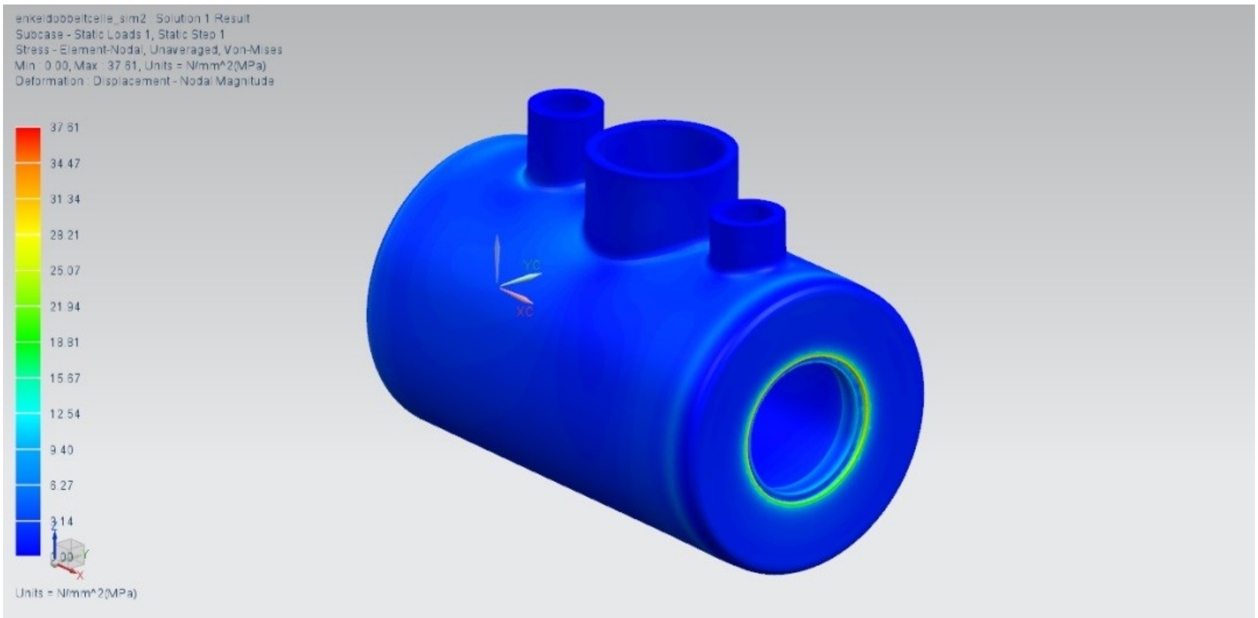

**Figure 4.30 Result of the FEA analysis**

### 4.2.3 Laboratory cell flow calculations

The laboratory cell requires a heated fluid to be pumped around the system to heat the cells up. This is presented earlier in chapter 3.1.3. This fluid will be considered as water for the rest of the thesis. This is because water is in abundance in almost any laboratory, it is cheap and has the temperature range required for the electrolyte to be heated to the desired temperature.

The cell heating compartment has a flow area than the tubes connected to it. This space needs to be filled up with water during the testing. This means that for the start of the test the volume flow rate at the outlet, must be less than the volume flow rate at the inlet. This will automatically be adjusted when the compartment is filled with water, so the velocities will be more or less equal at this point in time. To calculate this we need to use the Bernoulli equation

$$z_1 + \frac{P_1}{\rho_1 g} + \frac{v_1^2}{2g} = z_2 + \frac{P_2}{\rho_2 g} + \frac{v_2^2}{2g} \tag{4.10}$$

Where P is pressure, v is velocity, ρ is density, g is the gravitational constant and z is the height relative to a reference plane. It is important to note that the densities of the flows will be the same, as it is water in the whole compartment[22].

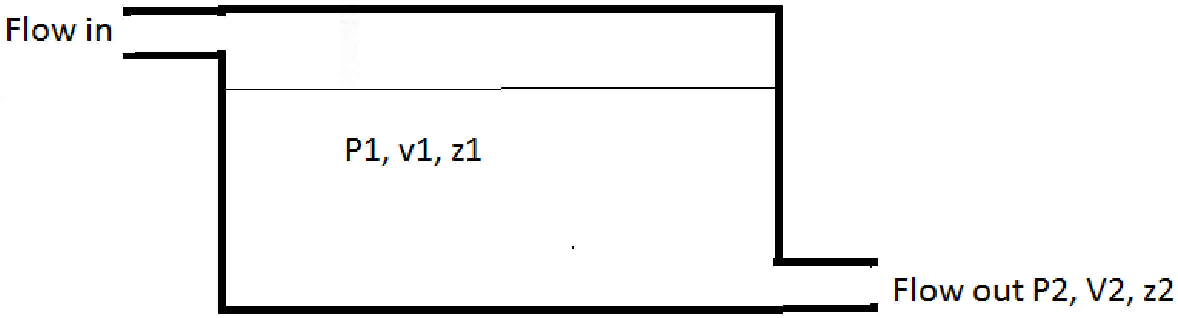

**Figure 4.31 Setup for the flow calculations of the double walled cell**

Before the compartment is filled, there is another situation. The conditions with subscript 1 in the figure are moved inside the container. The pressure P is the same as equation (4.1):

$$P = \rho g h \tag{4.11}$$

Where h is the height of the water level it will equal $P_2$. This is the hydrostatic pressure of the water inside the tank. Since the flows are not connected yet, the pressure from $P_1$ will not affect the pressure P2.The other conditions are that v1 = 0 and $z_1$ is equal to the height of the water. However, using the pressure and the z-values for pressure will create an error in the calculations and give the wrong results. The aim is to find is what the volume flow of tube 1 must be to be greater than the volume flow of tube 2.

The volume flow rate is

$$\dot{v} = v * A \tag{4.12}$$

For tube 1 this is largely controlled by the pump's capacity. The length of the tubes can usually affect the flow rate due to a head loss or pressure loss. This varies with the length and forms of the tubes, and will not be taken into account for this calculation since it can vary with each individual setup.

If the height of the compartment is 7 cm, and the diameter of the outlet tube is 1 cm, it will require a pump that has a capacity of 5.4 l/min to pump contain the water inside the compartment. This is how it would be if this was an open system, in other words, if the flow from tube 2 are poured out into an open reservoir. When the same water is reused, it will be another situation, since every part of the system must start being filled up and then a flow is applied. The use of a reservoir might be needed to start the continuous flow through the whole system. This reservoir can also be where the water is heated.

When water is completely filled in the cell, the flow should adjust itself by applying an extra pressure in the cell, increasing the speed out of the cell. If there is a loss of fluid inside, the same principle as before will be applied and the cells will be filled up again. The easy way to adjust the outgoing flow of the cells is to manipulate the area of tube 2. A smaller area means less flow out.

## 4.3 Nano-indenter cell

The third and final design is designed for another laboratory experiment.

The vertical cell is designed to be used in the Nano-indenter. This type of cell requires other considerations than a horizontal cell. The main issue in these cells will be the hydrogen bubbles that can be created during the testing. These bubbles will create an isolating layer under the sample piece. Then the experiment will not work. It is known that hydrogen bubbles will attach to the sample, and stay there until they are removed with an external force. The bubbles will not, after touching the metal, automatically continue to rise to the highest point. Several possible solutions will be presented in the next chapters.

Dimensions can be viewed in appendix D.

### 4.3.1 The design of the flow system

Since the cell is going to be used inside the Nano-indenter the main issue is to make it vertical, but there are also strict size requirements on the cell. The total height of the system cannot be higher than 60mm, since it will not fit if it’s larger. The anodic cell cannot be higher than 8mm, because of the length of the needle. The end of the anodic cell must be open to allow the needle to be inserted. Otherwise the same as previous demands must be considered. The only thing that can be neglected is the heating. The experiments will only be done in room temperature.

The principle of the design is simple. A flow is directed at an angle to the surface of the sample and the bubbles move away from the flow. A pump is used to create a closed circuit flow with an outlet for the electrolyte being pushed inside.

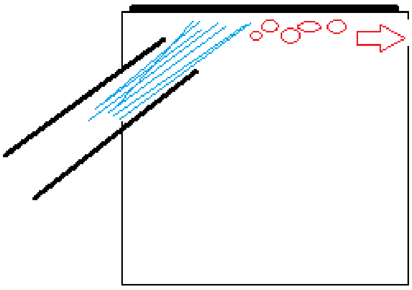

**Figure 4.32 Principle of the flow system**

There are however some design specifications that needs to be made during the development of the cell. A few iterations were made to improve the system in a stepwise focus.

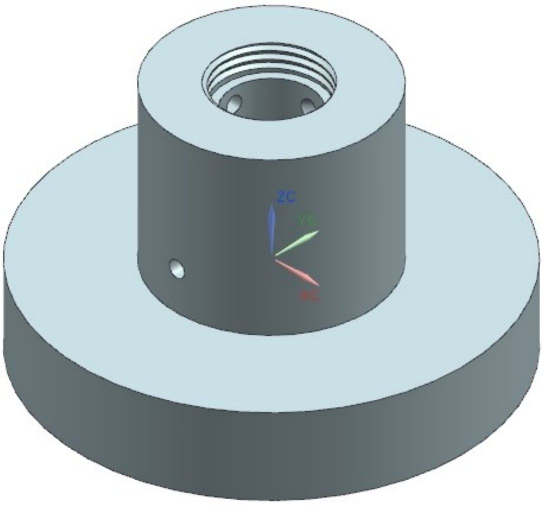

**Figure 4.33 First iteration model view**

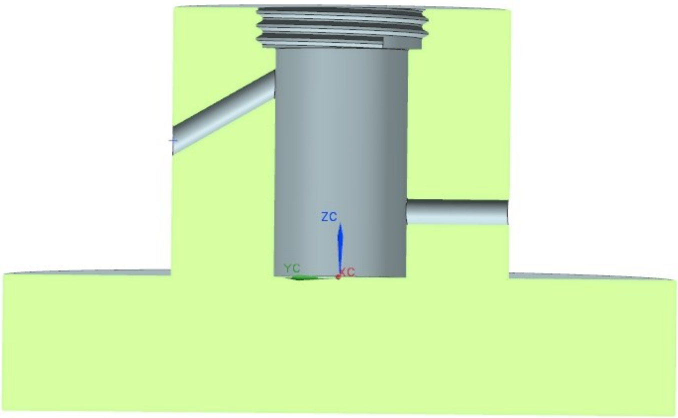

**Figure 4.34 First iteration cross-section view**

The first iteration was simple. It is the basic principle with a thread attachment for the anodic part of the cell. There is one entrance for the reference electrode, one for the flow, and one for removal of excess electrolyte. Some problems arise with this design. The gas will be contained in the cell and will continue circulating around the sample. Another problem that needs to be added is the attachment for the counter electrode. For the next iteration this needs to be fixed. The third problem is that it is hard to fill up the necessary electrolyte for touching the sample without spilling and making a mess. This is not the most important problem, but since it is going to be used in the Nano-indenter it should be fixed.

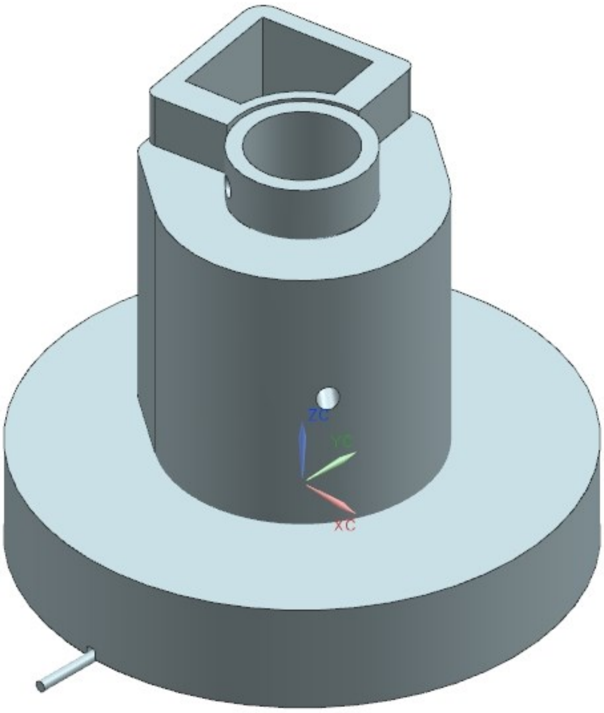

Figure 4.35 Second iteration model view

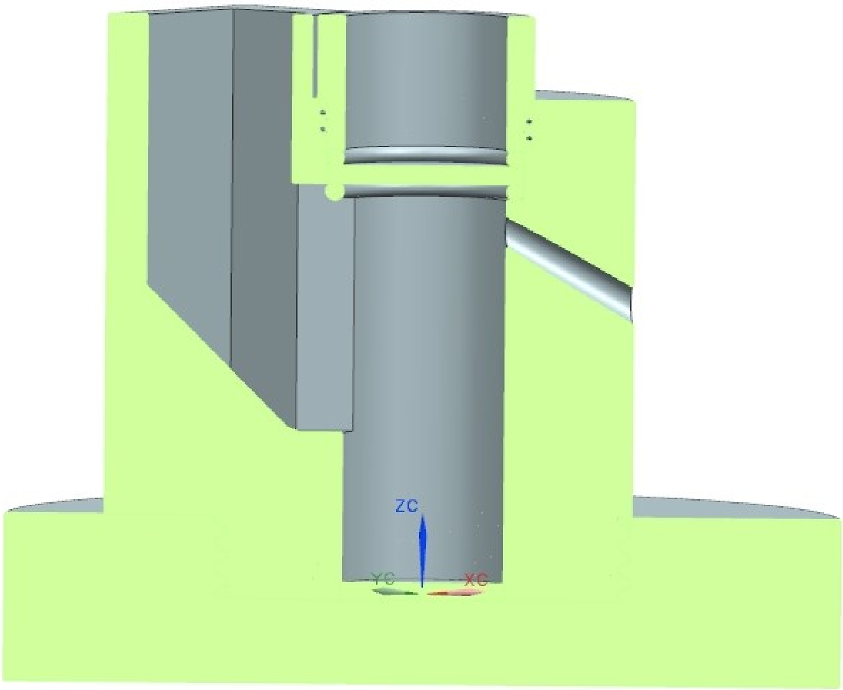

Figure 4.36 Second iteration cross-section view

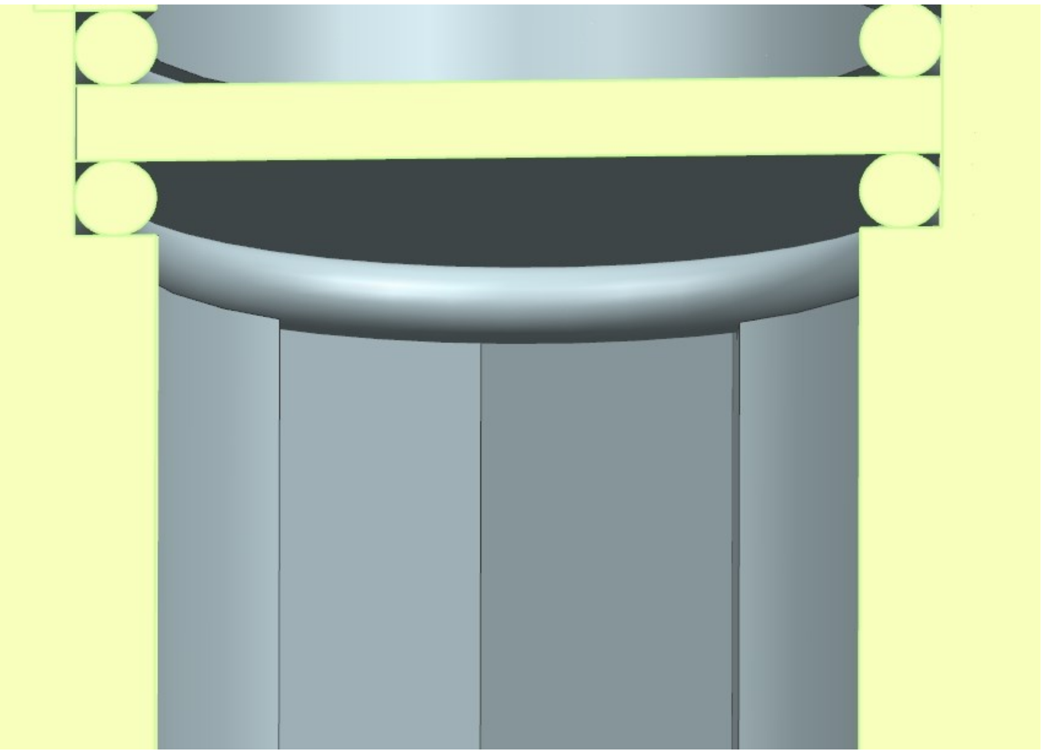

**Figure 4.37 View of the sample with O-rings in the system**

In this iteration there has been designed an outlet for the bubbles on the other side of the flow. As visible, the other parts of the cell are also included; the O-rings, the anodic cell, the sample, a counter electrode and a new base for placing it on. The outlet means that the bubbles will be pushed into an open area where they are free to move up and out of the cell. This open area can also be used for filling up the electrolyte and work as a reservoir for ensuring that there is always is enough electrolyte in the cell. The O-ring on the cathodic side is placed on the ledge as in the previous iteration. This ledge is however not all the way around the cell. By the hole, it is cut down. This will cause the O-ring to “hang”. This can cause a fluid to freely enter over and under the O-ring. Then it will be easier to remove the bubbles, and fill up the cell. It might cause a leakage on the top, but not into the anodic cell since this is sealed by its own O-ring. A new base is used to make it easier to produce and put the counter electrode down and wire it out.

Some problems arise with this iteration too. There might be leakage from the counter-electrode entrance. The area of the cell might also be a problem, as previous experiments have shown that it makes the experiment easier to do because of the area the electrode exposes. The third problem is the ability to produce it. Modern day production technology could have a hard time creating a slot inside a cylinder to connect it with the reservoir.

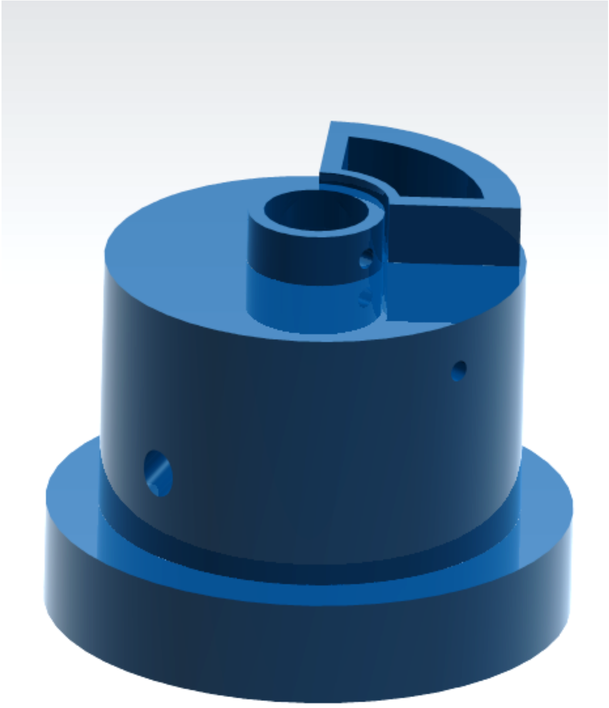

**Figure 4.38 Final iteration model view**

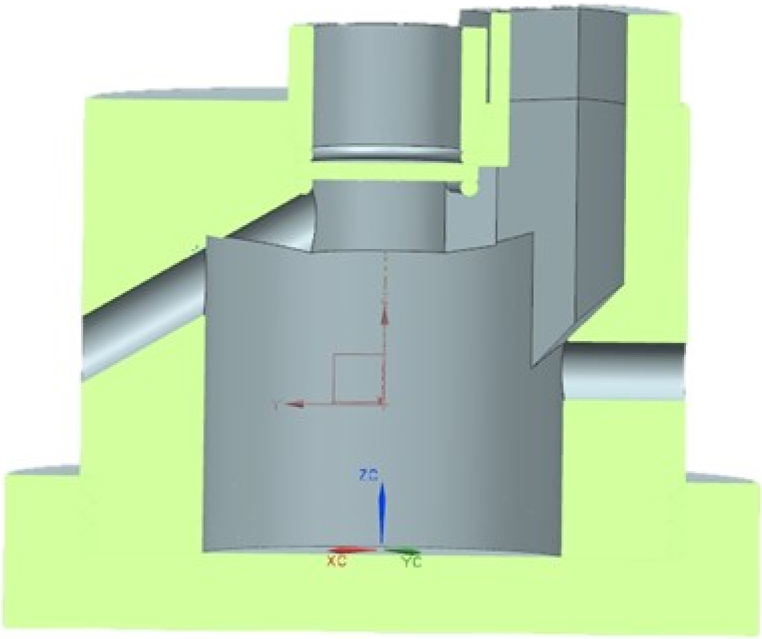

**Figure 4.39 Cross-section of final iteration**

In the last iteration the previous problems are fixed. The leakage from the counter-electrode is removed since the wire is lead out another way, though not modeled in the final part. The counter-electrode should shift its form. From being placed in the middle of the cell, it should be placed as a circle outside the sample placement. The end of the counter-electrode would be drawn up through the reservoir. Making another hole in the cell would make it leak because of hydrostatic pressure differences if the exit is lower than the height of the electrolyte. The advantage with this solution is that some of the produced hydrogen will be caught by the wall in the outer rim. Making this rim with an angle directing away from the sample will also be useful. Then the hydrogen bubbles here can be moved away from the center and the sample. It can even let out if small holes are drilled through to the rim. With the increased diameter of the lower part, the production should go smoothly as it only needs to work along one axis do dig out every hole.

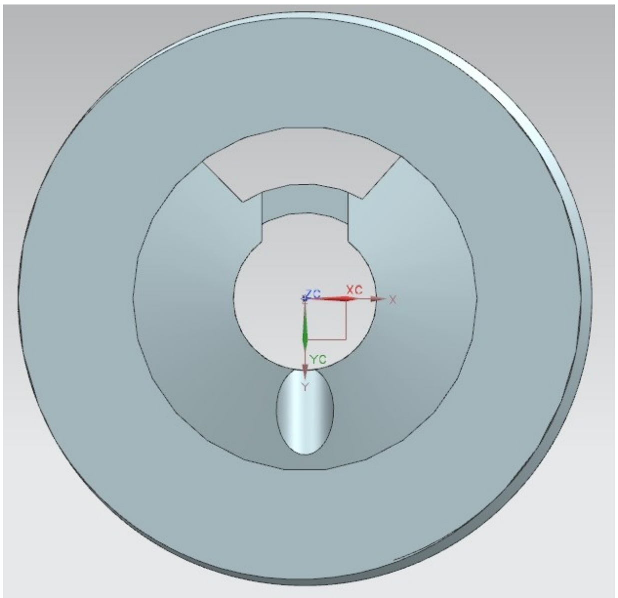

**Figure 4.40 This picture shows that it should be able to be produced, since there is only the need to mill along one axis.**

This solution will be the best to do the testing. Equipment is already in use for reference electrodes and should be continued for use. There is also a plate with a slot that fits the cell that is the initial design criteria for the base. This can be screwed down to the floor of the Nano-indenter to keep it stable.

There should not be any instability since the system is balanced on the base with the needle making indents close to the center of the structure. The tolerances for producing the system should be low. This does not apply to every dimension. For instance, the large diameter in the cathodic cell can be rather coarse. The tolerances that are important are the ones that impact the sample’s incline. The bottom of the base, the threads connecting the base to the main part and the ledge the sample is placed upon. If the sample is not even, the indents might have the wrong shape and can’t be measured.

As a final step a paper 3d-printer was used to create models in 1:1 scale. This creates cheap models for understanding the function better. It will make it easier to see adjustments needed before production. It also gives a sense on the scales used and which problems would arise from that. The problem when using the paper printer is that the resolution of the model is constrained by the paper's thickness so round edges is hard to make smooth. This also makes small details worse. Thin edges are also vulnerable since the final product must be dug out of a block of paper, and the small walls might be torn. Either way, the models gave good insight in how we should operate the system when testing.

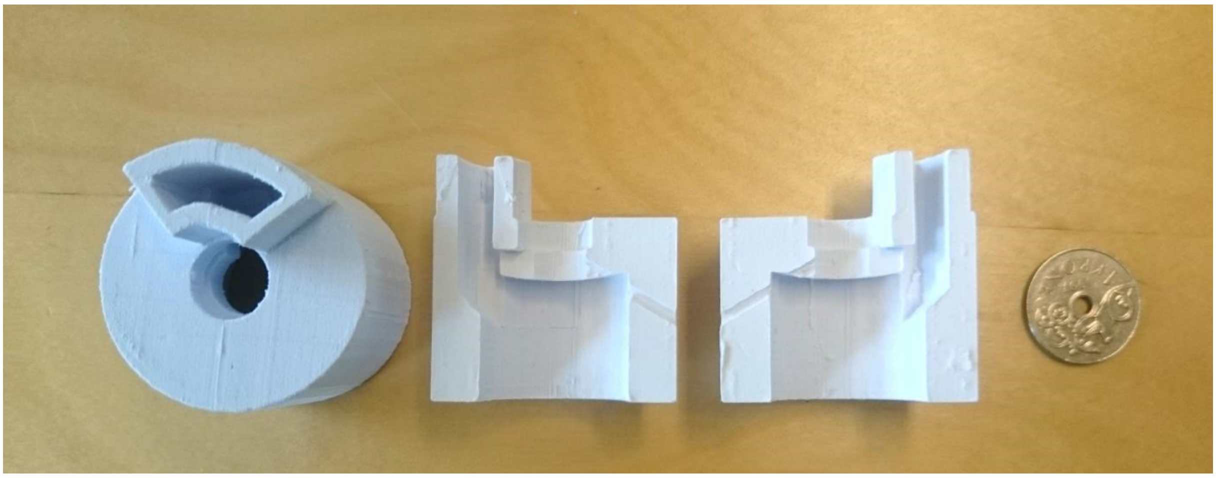

**Figure 4.41 Picture of the 3d-printed models. Coin for scale**

### 4.3.2 Flow in the Nano-indenter cell

The flow in the Nano-indenter cell should not change the experiment. It is to apply a force on the sample to move hydrogen bubbles. This flow has other characteristics than the water flow. The viscosity of the electrolyte makes the flow slower, but it can give more force. The aim is to have enough velocity in the flow, so that the bubbles are dispersed from the surface by the force extracted on it. For the force to be large enough, the area of the nozzle, the angle of the flow and the flow rate must be considered.

Without data on how strong the forces keeping the bubbles to the sample are, there are no comparison opportunities. This chapter will therefore be more of a guide on the equations and considerations needed.

A factor that might be degrading for this solution is erosion/cavitation. Although the speeds might not be high enough, this should be considered as a possibility. Especially if the surface of the cathodic side should be further examined. A SEM analysis might be a waste if this happens.

The force in the flow can be calculated by Newton's third law

$$F = \dot{m} * a \tag{4.13}$$

If no loss is assumed, a = 2v. The force will have an x- and y-component solved by simple trigonometry. The mass flow is given in cubic meters per second. The force then applied is for the same time interval.

The direction of the flow should be within the range of 20° and 70° to the surface. This is depending on the force needed. If a smaller force is needed, then the angle can be lower. This will push the bubbles harder towards the outlet. Due to the no-slip effect and the velocity being too low, it might not be able to push the bubbles away. If it is perpendicular to the surface, the bubbles will just be spread around the electrolyte and not pushed into the release.

Another way to maximize the force of the flow is to let it be at the same angle as the sample. Then shear forces from the flow can disturb the bubbles at the sample and releasing them, and then push them away from the surface. This shear stress is connected to the no slip effect of the boundary layer.

$$\tau = \mu * \frac{du}{dy} \tag{4.14}$$

τ is the shear stress, μ is the dynamic viscosity of the fluid, u is the velocity of the fluid by the boundary and y is the height above the boundary[22]. This states that the stress is highest close to a wall when y = 0. This is shown by a simple figure for flow velocity

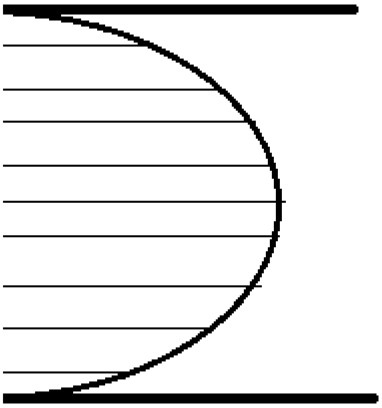

**Figure 4.42 Visualization of the no-slip effect**

Both of these methods are applicable to the cell. If the best result is to be achieved, it needs to be tested at hydrogen bubbles.

If the correct current or potential is applied, no bubbles should appear on the surface of the sample. In the case that they do, they will be few and small at the start. It is only if they are allowed to grow and become more they are a real problem. Exerting a constant force on the samples will remove the bubbles over time. Using this force is more of a safety net. The cells are not designed to be see-through. This means that the force needs to be applied at all times since it is impossible to see if and when bubbles appear on the surface.

First a positive displacement pump should be used. Having a peristaltic pump should suffice. The area of the tube is small, but making the nozzle smaller will increase the velocity of the fluid and in turn increase the force. The main tube has a maximum diameter, since the cell is so small. So the speed from this needs to be sufficient. The effectiveness of the pump will be based also on the piping from it, with regards to head and pressure loss.

# 5 Conclusion

During this thesis it has been presented 3 different design problems with each unique solution. Common for all of these cells is that they have not yet been produced during the process. This means that some work is still is needed to make sure that the cells work properly. This means creating prototypes and test them according to make sure they are reliable.

The industrial cell seems to be viable. It is built a like the earlier cells only smaller and more user friendly. The cell should be in a good size that it is still easy to handle but still so small that it will not be space consuming, Material selection is crucial for the function of the system. Choosing solid inert polymer materials for the cells and Macor for the sample holder will make the system become very robust for this application. A faraday cage built of copper with no mesh should prove good at keeping electrical noise out of the system. The heating system is the main problem. The calculations show that the suggested solution would work, but it should be tested in practice. It may show that it could be useful to have more isolation around the cells to prevent heat loss. This must be considered, but luckily it can easily be done after production of the cells with isolation materials. Production cost is not considered, and for an industry model this should be taken into account. A product is seldom more useful than what a customer would to pay for it. For instance, a specially designed bubbler for the application might run to an unacceptable high cost instead of using a mass produced component.

The laboratory system could prove viable. This depends much on the selection of the two solutions. The double walled with a sample holder seems to have less risks functioning than the one without, although calculated to not have any severe risk. It may come down to production costs and how easy it is to produce. This system should prove as effective as the current one as long as a flow is secured. It runs on the same principles as the industrial model for the heating, by creating an environment for the cell. Heating principles has not been added in the thesis, but it can be done as simple as a hot-plate on a reservoir. The calculations for the pump should be accurate without thinking of pressure and head loss. A pump of a bit higher capacity than the one calculated should be sufficient.

The Nano-indenter cell is the most risk filled design of the three. Since there are little experience on how to solve the problem, the outcome is unknown. The tests shown in this thesis were semi-successful, indicating that it was possible to remove the bubbles with a flow. With specialized equipment the tests can be run without the chance of human error, and under right conditions. Now the cell is designed to perform the flow solution, but it can easily be used with the suction instead. By using two pumps the tube for the flow can suck out from the cell, and the other pump can be used to constantly fill the reservoir. The cell itself can probably be produced without large problems. Without using heating as a parameter for the design, material choice is simple since Kel-F is under the glass transition temperature.

Regretfully, none of the systems were produced so real life testing could not be done. Physical prototypes of cheaper materials can be used for function testing, to make sure that everything works. This is the natural next step in the process for development of the systems.

I believe that the cells will work as expected if produced, but some initial problems may occur. These problems could be easy to fix, and make sure that the hydrogen permeation experiments can be done.

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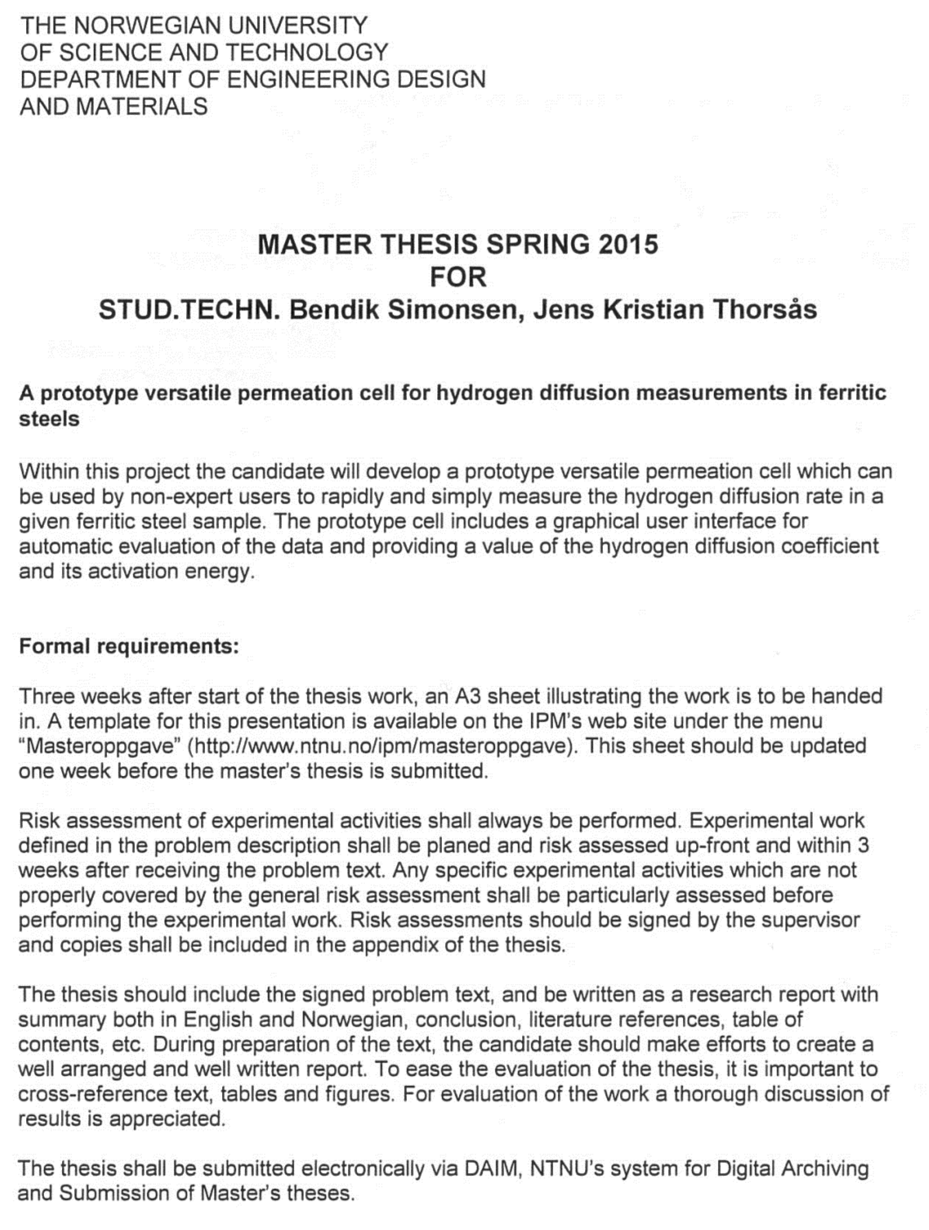
# Appendix A: Problem Text



THE NORWEGIAN UNIVERSITY
OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF ENGINEERING DESIGN
AND MATERIALS

## MASTER THESIS SPRING 2015
## FOR
## STUD.TECHN. Bendik Simonsen, Jens Kristian Thorsås

### A prototype versatile permeation cell for hydrogen diffusion measurements in ferritic steels

Within this project the candidate will develop a prototype versatile permeation cell which can be used by non-expert users to rapidly and simply measure the hydrogen diffusion rate in a given ferritic steel sample. The prototype cell includes a graphical user interface for automatic evaluation of the data and providing a value of the hydrogen diffusion coefficient and its activation energy.

**Formal requirements:**

Three weeks after start of the thesis work, an A3 sheet illustrating the work is to be handed in. A template for this presentation is available on the IPM's web site under the menu "Masteroppgave" (http://www.ntnu.no/ipm/masteroppgave). This sheet should be updated one week before the master's thesis is submitted.

Risk assessment of experimental activities shall always be performed. Experimental work defined in the problem description shall be planed and risk assessed up-front and within 3 weeks after receiving the problem text. Any specific experimental activities which are not properly covered by the general risk assessment shall be particularly assessed before performing the experimental work. Risk assessments should be signed by the supervisor and copies shall be included in the appendix of the thesis.

The thesis should include the signed problem text, and be written as a research report with summary both in English and Norwegian, conclusion, literature references, table of contents, etc. During preparation of the text, the candidate should make efforts to create a well arranged and well written report. To ease the evaluation of the thesis, it is important to cross-reference text, tables and figures. For evaluation of the work a thorough discussion of results is appreciated.

The thesis shall be submitted electronically via DAIM, NTNU's system for Digital Archiving and Submission of Master's theses.

The contact persons are Afrooz Barnoush and Martin Steinert.

| | |
|---|---|
| Torgeir Welo | Afrooz Barnoush |
| Head of Division | Professor/Supervisor |

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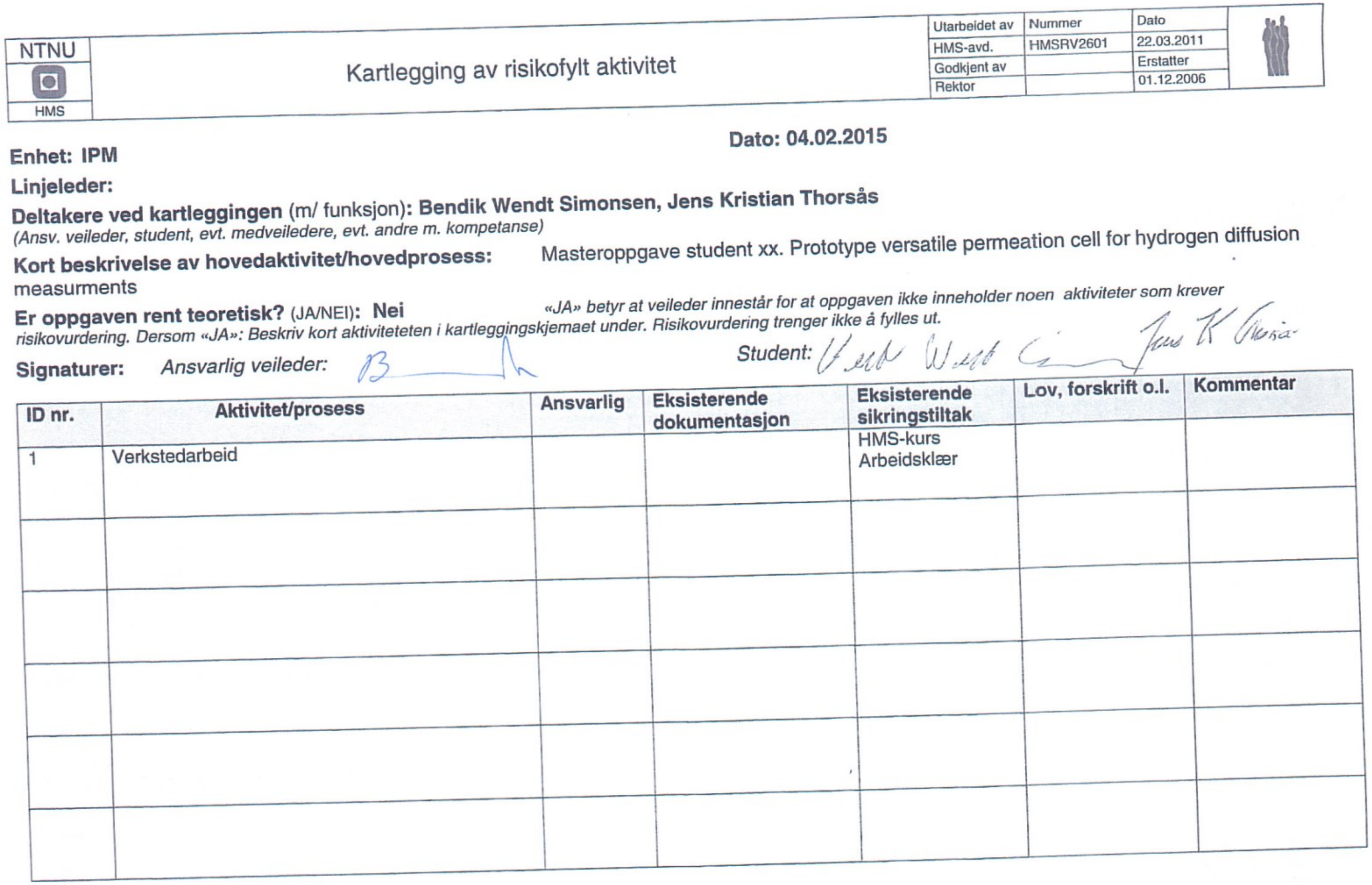
## Appendix B: Risk assessment

Original first, then updated without signature next.



| NTNU<br>HMS | Kartlegging av risikofylt aktivitet | Utarbeidet av | Nummer | Dato |
|---|---|---|---|---|
| | | HMS-avd. | HMSRV2601 | 22.03.2011 |
| | | Godkjent av | | Erstatter |
| | | Rektor | | 01.12.2006 |

**Enhet: IPM**

**Dato: 04.02.2015**

**Linjeleder:**

**Deltakere ved kartleggingen** (m/ funksjon): **Bendik Wendt Simonsen, Jens Kristian Thorsås**
*(Ansv. veileder, student, evt. medveiledere, evt. andre m. kompetanse)*

**Kort beskrivelse av hovedaktivitet/hovedprosess:** Masteroppgave student xx. Prototype versatile permeation cell for hydrogen diffusion measurments

**Er oppgaven rent teoretisk?** (JA/NEI): **Nei** *«JA» betyr at veileder innestår for at oppgaven ikke inneholder noen aktiviteter som krever risikovurdering. Dersom «JA»: Beskriv kort aktiviteteten i kartleggingskjemaet under. Risikovurdering trenger ikke å fylles ut.*

**Signaturer:** *Ansvarlig veileder:* *Student:*

| ID nr. | Aktivitet/prosess | Ansvarlig | Eksisterende dokumentasjon | Eksisterende sikringstiltak | Lov, forskrift o.l. | Kommentar |
|---|---|---|---|---|---|---|
| 1 | Verkstedarbeid | | | HMS-kurs<br>Arbeidsklær | | |
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| NTNU | Risikovurdering | Utarbeidet av | Nummer | Dato |
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| HMS | | HMS-avd. | HMSRV2601 | 22.03.2011 |
| | | Godkjent av | | Erstatter |
| | | Rektor | | 01.12.2006 |

**Enhet: IPM** **Dato: 04.02.2015**

**Linjeleder:**

**Deltakere ved kartleggingen (m/ funksjon): Bendik Wendt Simonsen, Jens Kristian Thorsås**
*(Ansv. Veileder, student, evt. medveiledere, evt. andre m. kompetanse)*

**Risikovurderingen gjelder hovedaktivitet:** Masteroppgave student xx. Prototype versatile permeation cell for hydrogen diffusion measurments.

**Signaturer:** *Ansvarlig veileder:* *Student:*

| ID nr | Aktivitet fra kartleggings-skjemaet | Mulig uønsket hendelse/ belastning | Vurdering av sannsyn-lighet | Vurdering av konsekvens: | | | | Risiko-Verdi (menn-eske) | Kommentarer/status Forslag til tiltak |
|---|---|---|---|---|---|---|---|---|---|
| | | | (1-5) | Menneske (A-E) | Ytre miljø (A-E) | Øk/ materiell (A-E) | Om-dømme (A-E) | | |
| 1 | Verksted arbeid | Skader på person | 2 | B | A | A | A | B2 | Opplæring maskiner, arbeidsklær, HMS--kurs |
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## Sannsynlighet vurderes etter følgende kriterier:

| Svært liten<br>1 | Liten<br>2 | Middels<br>3 | Stor<br>4 | Svært stor<br>5 |
|---|---|---|---|---|
| 1 gang pr 50 år eller sjeldnere | 1 gang pr 10 år eller sjeldnere | 1 gang pr år eller sjeldnere | 1 gang pr måned eller sjeldnere | Skjer ukentlig |

## Konsekvens vurderes etter følgende kriterier:

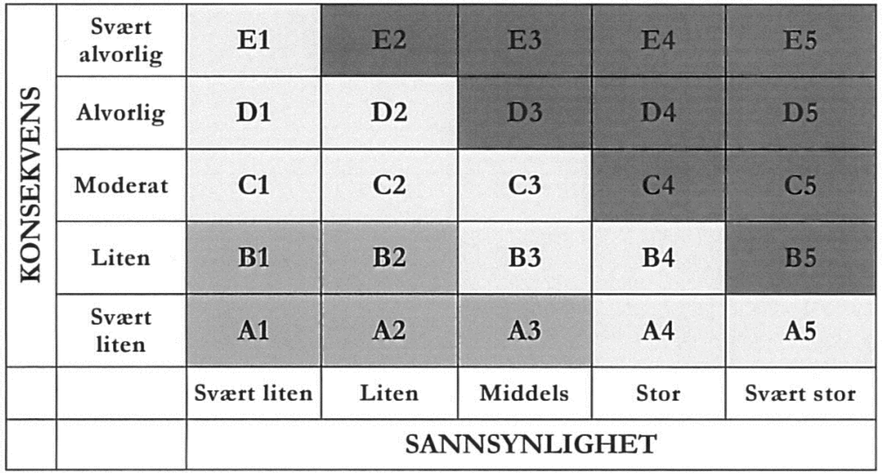
| Gradering | Menneske | Ytre miljø<br>Vann, jord og luft | Øk/materiell | Omdømme |
|---|---|---|---|---|
| **E**<br>**Svært Alvorlig** | Død | Svært langvarig og ikke reversibel skade | Drifts- eller aktivitetsstans >1 år. | Troverdighet og respekt betydelig og varig svekket |
| **D**<br>**Alvorlig** | Alvorlig personskade. Mulig uførhet. | Langvarig skade. Lang restitusjonstid | Driftsstans > ½ år<br>Aktivitetsstans i opp til 1 år | Troverdighet og respekt betydelig svekket |
| **C**<br>**Moderat** | Alvorlig personskade. | Mindre skade og lang restitusjonstid | Drifts- eller aktivitetsstans < 1 mnd | Troverdighet og respekt svekket |
| **B**<br>**Liten** | Skade som krever medisinsk behandling | Mindre skade og kort restitusjonstid | Drifts- eller aktivitetsstans < 1uke | Negativ påvirkning på troverdighet og respekt |
| **A**<br>**Svært liten** | Skade som krever førstehjelp | Ubetydelig skade og kort restitusjonstid | Drifts- eller aktivitetsstans < 1dag | Liten påvirkning på troverdighet og respekt |

**Risikoverdi = Sannsynlighet x Konsekvens**
Beregn risikoverdi for Menneske. Enheten vurderer selv om de i tillegg vil beregne risikoverdi for Ytre miljø, Økonomi/materiell og Omdømme. I så fall beregnes disse hver for seg.

**Til kolonnen "Kommentarer/status, forslag til forebyggende og korrigerende tiltak":**
Tiltak kan påvirke både sannsynlighet og konsekvens. Prioriter tiltak som kan forhindre at hendelsen inntreffer, dvs. sannsynlighetsreduserende tiltak foran skjerpet beredskap, dvs. konsekvensreduserende tiltak.

| NTNU | Risikomatrise | utarbeidet av | Nummer | Dato |
|---|---|---|---|---|
| HMS/KS | | HMS-avd. | HMSRV2604 | 08.03.2010 |
| | | godkjent av | | Erstatter |
| | | Rektor | | 09.02.2010 |

## MATRISE FOR RISIKOVURDERINGER ved NTNU



| | | | | | | |
|---|---|---|---|---|---|---|
| KONSEKVENS | Svært alvorlig | E1 | E2 | E3 | E4 | E5 |
| | Alvorlig | D1 | D2 | D3 | D4 | D5 |
| | Moderat | C1 | C2 | C3 | C4 | C5 |
| | Liten | B1 | B2 | B3 | B4 | B5 |
| | Svært liten | A1 | A2 | A3 | A4 | A5 |
| | | Svært liten | Liten | Middels | Stor | Svært stor |
| | | SANNSYNLIGHET | | | | |

**Prinsipp over akseptkriterium. Forklaring av fargene som er brukt i risikomatrisen.**

| Farge | | Beskrivelse |
|---|---|---|
| Rød | 🟥 | Uakseptabel risiko. Tiltak skal gjennomføres for å redusere risikoen. |
| Gul | 🟨 | Vurderingsområde. Tiltak skal vurderes. |
| Grønn | 🟩 | Akseptabel risiko. Tiltak kan vurderes ut fra andre hensyn. |

| | | | | |
|---|---|---|---|---|
| NTNU<br>HMS | Kartlegging av risikofylt aktivitet | Utarbeidet av<br>HMS-avd. | Nummer<br>HMSRV2601 | Dato<br>22.03.2011 |
| | | Godkjent av<br>Rektor | | Erstatter<br>01.12.2006 |

**Enhet: IPM** **Dato: 04.02.2015**

**Linjeleder:**

**Deltakere ved kartleggingen** (m/ funksjon)**: Jens Kristian Thorsås**
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**Signaturer:** *Ansvarlig veileder:* *Student:*

| ID nr. | Aktivitet/prosess | Ansvarlig | Eksisterende dokumentasjon | Eksisterende sikringstiltak | Lov, forskrift o.l. | Kommentar |
|---|---|---|---|---|---|---|
| 1 | Verkstedarbeid | | | HMS-kurs<br>Arbeidsklær | | |
| 2 | Laboratoriearbeid | | | HMS-kurs<br>Vernebriller | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

| NTNU<br>HMS | Risikovurdering | Utarbeidet av | Nummer | Dato |
|---|---|---|---|---|
| | | HMS-avd. | HMSRV2601 | 22.03.2011 |
| | | Godkjent av | | Erstatter |
| | | Rektor | | 01.12.2006 |

**Enhet:** IPM **Dato:** 04.02.2015

**Linjeleder:**

**Deltakere ved kartleggingen (m/ funksjon): Bendik Wendt Simonsen, Jens Kristian Thorsås**
*(Ansv. Veileder, student, evt. medveiledere, evt. andre m. kompetanse)*

**Risikovurderingen gjelder hovedaktivitet:** Masteroppgave student xx. Prototype versatile permeation cell for hydrogen diffusion measurments.

**Signaturer:** *Ansvarlig veileder:* *Student:*

| ID nr | Aktivitet fra kartleggings-skjemaet | Mulig uønsket hendelse/ belastning | Vurdering av sannsyn-lighet | Vurdering av konsekvens: | | | | Risiko-Verdi (menn-eske) | Kommentarer/status Forslag til tiltak |
|---|---|---|---|---|---|---|---|---|---|
| | | | (1-5) | Menneske (A-E) | Ytre miljø (A-E) | Øk/ materiell (A-E) | Om-dømme (A-E) | | |
| 1 | Verksted arbeid | Skader på person | 2 | B | A | A | A | B2 | Opplæring maskiner, arbeidsklær, HMS--kurs |
| 2 | Laboratoriearbeid | Skader på person eller utstyr | 1 | A | A | A | A | A1 | Vernebriller, klær, tilgang til førstehjelp |
| | | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |

## Sannsynlighet vurderes etter følgende kriterier:

| **Svært liten**<br>**1** | **Liten**<br>**2** | **Middels**<br>**3** | **Stor**<br>**4** | **Svært stor**<br>**5** |
|---|---|---|---|---|
| 1 gang pr 50 år eller sjeldnere | 1 gang pr 10 år eller sjeldnere | 1 gang pr år eller sjeldnere | 1 gang pr måned eller sjeldnere | Skjer ukentlig |

## Konsekvens vurderes etter følgende kriterier:

| **Gradering** | **Menneske** | **Ytre miljø**<br>**Vann, jord og luft** | **Øk/materiell** | **Omdømme** |
|---|---|---|---|---|
| **E**<br>**Svært Alvorlig** | Død | Svært langvarig og ikke reversibel skade | Drifts- eller aktivitetsstans >1 år. | Troverdighet og respekt betydelig og varig svekket |
| **D**<br>**Alvorlig** | Alvorlig personskade.<br>Mulig uførhet. | Langvarig skade. Lang restitusjonstid | Driftsstans > ½ år<br>Aktivitetsstans i opp til 1 år | Troverdighet og respekt betydelig svekket |
| **C**<br>**Moderat** | Alvorlig personskade. | Mindre skade og lang restitusjonstid | Drifts- eller aktivitetsstans < 1 mnd | Troverdighet og respekt svekket |
| **B**<br>**Liten** | Skade som krever medisinsk behandling | Mindre skade og kort restitusjonstid | Drifts- eller aktivitetsstans < 1uke | Negativ påvirkning på troverdighet og respekt |
| **A**<br>**Svært liten** | Skade som krever førstehjelp | Ubetydelig skade og kort restitusjonstid | Drifts- eller aktivitetsstans < 1dag | Liten påvirkning på troverdighet og respekt |

**Risikoverdi = Sannsynlighet x Konsekvens**

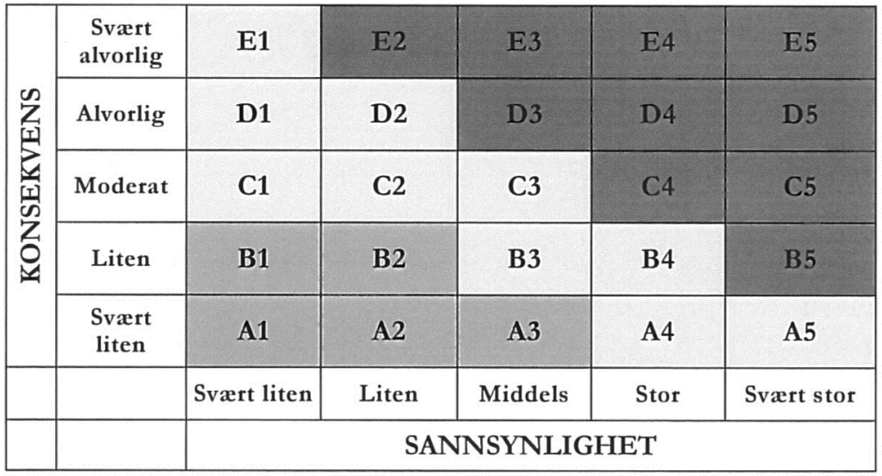
Beregn risikoverdi for Menneske. Enheten vurderer selv om de i tillegg vil beregne risikoverdi for Ytre miljø, Økonomi/materiell og Omdømme. I så fall beregnes disse hver for seg.

**Til kolonnen "Kommentarer/status, forslag til forebyggende og korrigerende tiltak":**

Tiltak kan påvirke både sannsynlighet og konsekvens. Prioriter tiltak som kan forhindre at hendelsen inntreffer, dvs. sannsynlighetsreduserende tiltak foran skjerpet beredskap, dvs. konsekvensreduserende tiltak.

| NTNU | Risikomatrise | utarbeidet av | Nummer | Dato |
|---|---|---|---|---|
| HMS/KS | | HMS-avd. | HMSRV2604 | 08.03.2010 |
| | | godkjent av | | Erstatter |
| | | Rektor | | 09.02.2010 |

## MATRISE FOR RISIKOVURDERINGER ved NTNU



| | | | | | | |
|---|---|---|---|---|---|---|
| KONSEKVENS | Svært alvorlig | E1 | E2 | E3 | E4 | E5 |
| | Alvorlig | D1 | D2 | D3 | D4 | D5 |
| | Moderat | C1 | C2 | C3 | C4 | C5 |
| | Liten | B1 | B2 | B3 | B4 | B5 |
| | Svært liten | A1 | A2 | A3 | A4 | A5 |
| | | Svært liten | Liten | Middels | Stor | Svært stor |
| | | SANNSYNLIGHET | | | | |

**Prinsipp over akseptkriterium. Forklaring av fargene som er brukt i risikomatrisen.**

| Farge | | Beskrivelse |
|---|---|---|
| Rød | 🟥 | Uakseptabel risiko. Tiltak skal gjennomføres for å redusere risikoen. |
| Gul | 🟨 | Vurderingsområde. Tiltak skal vurderes. |
| Grønn | 🟩 | Akseptabel risiko. Tiltak kan vurderes ut fra andre hensyn. |

## Appendix C: Matlab code

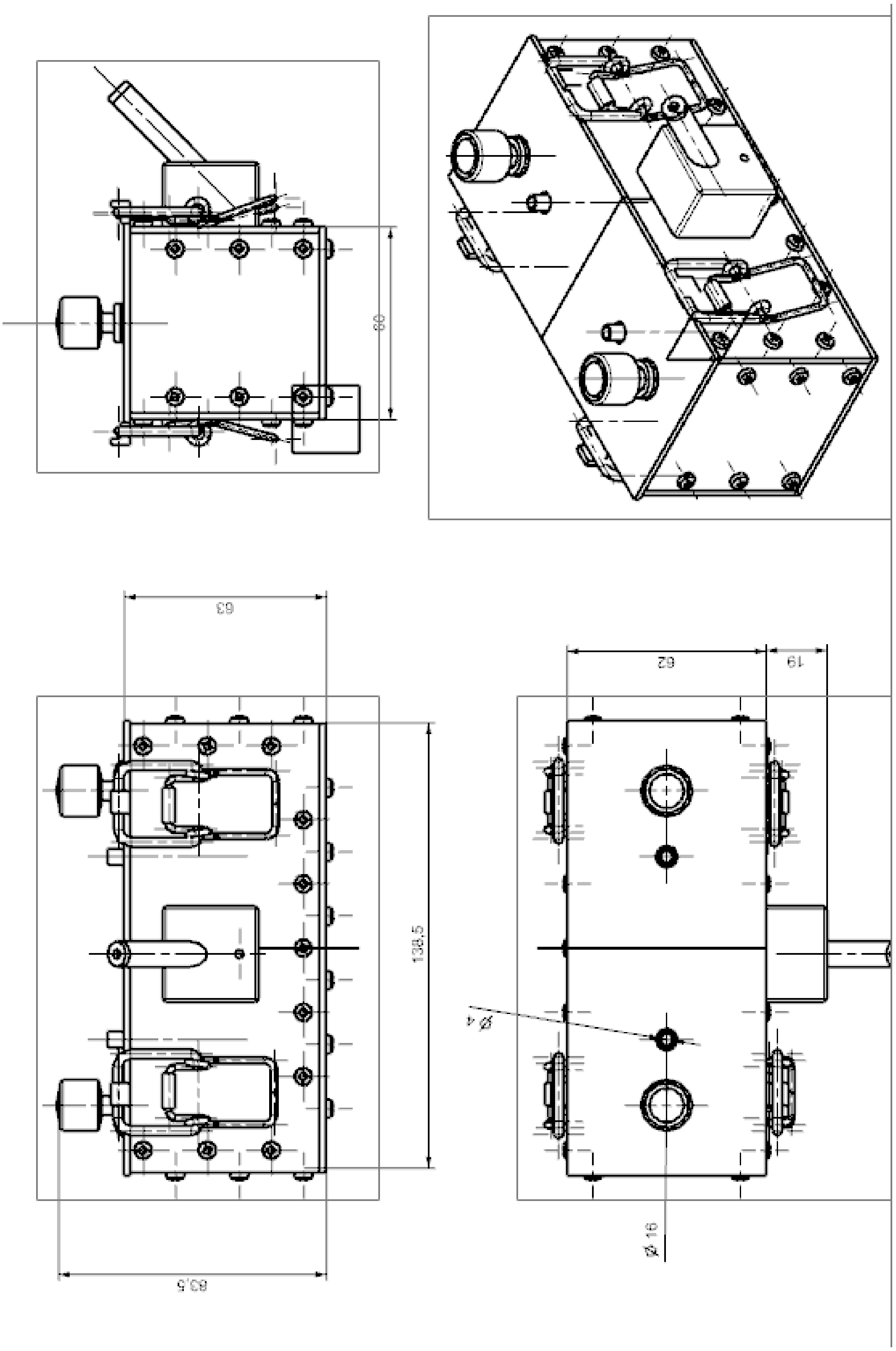
This is modified with to the last calculations. This should run fine in MatLab. Some commands are listed as not in use by % in front. This is mainly the different variants of the setup. Some code may need to be deactivated for use of the other calculations. Konstants have not been removed after some testing, and are still present in the code.

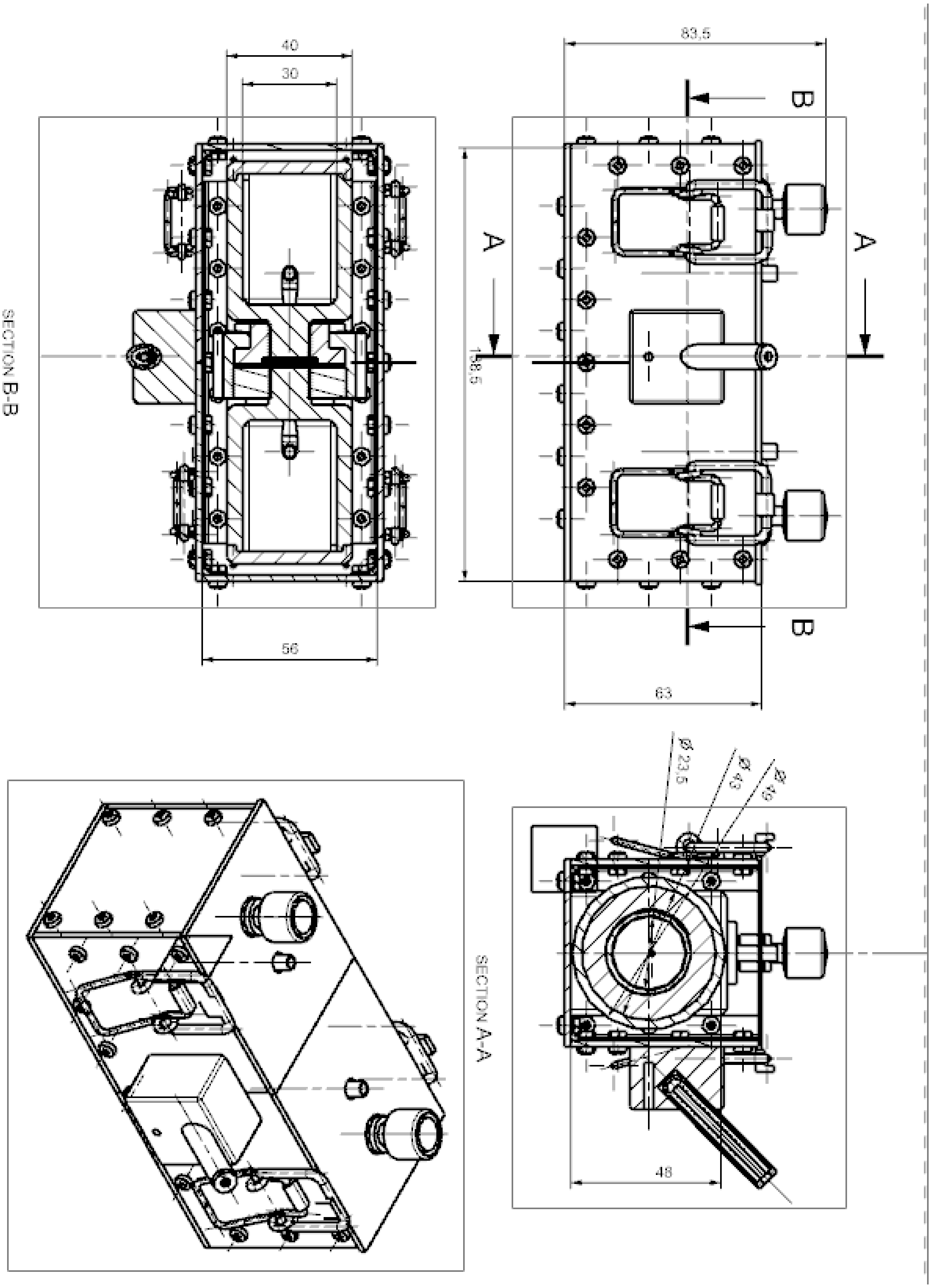
```
clear all;
clc; close all;

m   = (0.000588-0.000248)*1.2;      %kg air
m2  = 0.0001368*1181 ;              %kg glycerol
me  = 0.03*0.02*0.03*2700 ;         %kg aluminium

ca   = 1.0035*1000 ;                % J/(kg*K) air
cg  = 2430  ;                       % J/(kg*K) Glycerol
cw  = 4185.5 ;                      % J/(kg*K) Water
cal = 910 ;                         % Aluminium



e = 2 ; %number of heating elements

a1 = e*0.0009;                  %Area heating elements
a2 = 0.0448-a1 - 0.14*0.06;     %Area box(outlet)
a3 = 0.02632 - 0.14*0.06 ;      %Area cell
a4 = 0.02*0.03*4+0.03*0.03 ;    %Area element

b1 = 0.005 ;    %thickness air inside in m
b2 = 0.002 ;    %thickness aluminium in m
b3 = 1 ;        %thickness air outside in m
b4 = 0.005 ;    %thickness poly
b5 = 0.015 ;    %thickness glycerol
b6 = 0.015 ;    %thickness aluminum element

ha = 0.024 ;    %heat transfer rate air W/(m*K)
hal= 205 ;      %heat transfer rate aluminium
hp = 0.25 ;     %heat transfer rate teflon
hg = 0.28 ;     %heat transfer rate glycerol
hw = 0.58 ;     %heat transfer rate water

U1 = 1/(b1/ha+b2/hal) ;         %Overall heat transfer rate
U2 = 1/(b1/ha+b2/hal+b3/ha);
U3 = 1/(b1/ha+b4/hp+b5/hg) ;
U4 = 1/(b6/hal);
U5 = 1/(b6/hal + b3/ha);
U6 = 1/(b6/hal + 1/10);

%Alternate Us
% h = 10                        %Convection transfer rate air at 2m/s
% U1 = 1/(b2/hal+1/h)
% U2 = 1/(1/h + b2/hal + 1/h)

g1  = U1*a1;                % W/K
g2  = U2*a2;                % W/K
g3  = U3*a3;                % W/K
ge = U4*3.1415*0.01^2 ;
gu = U5*a4 ;
```

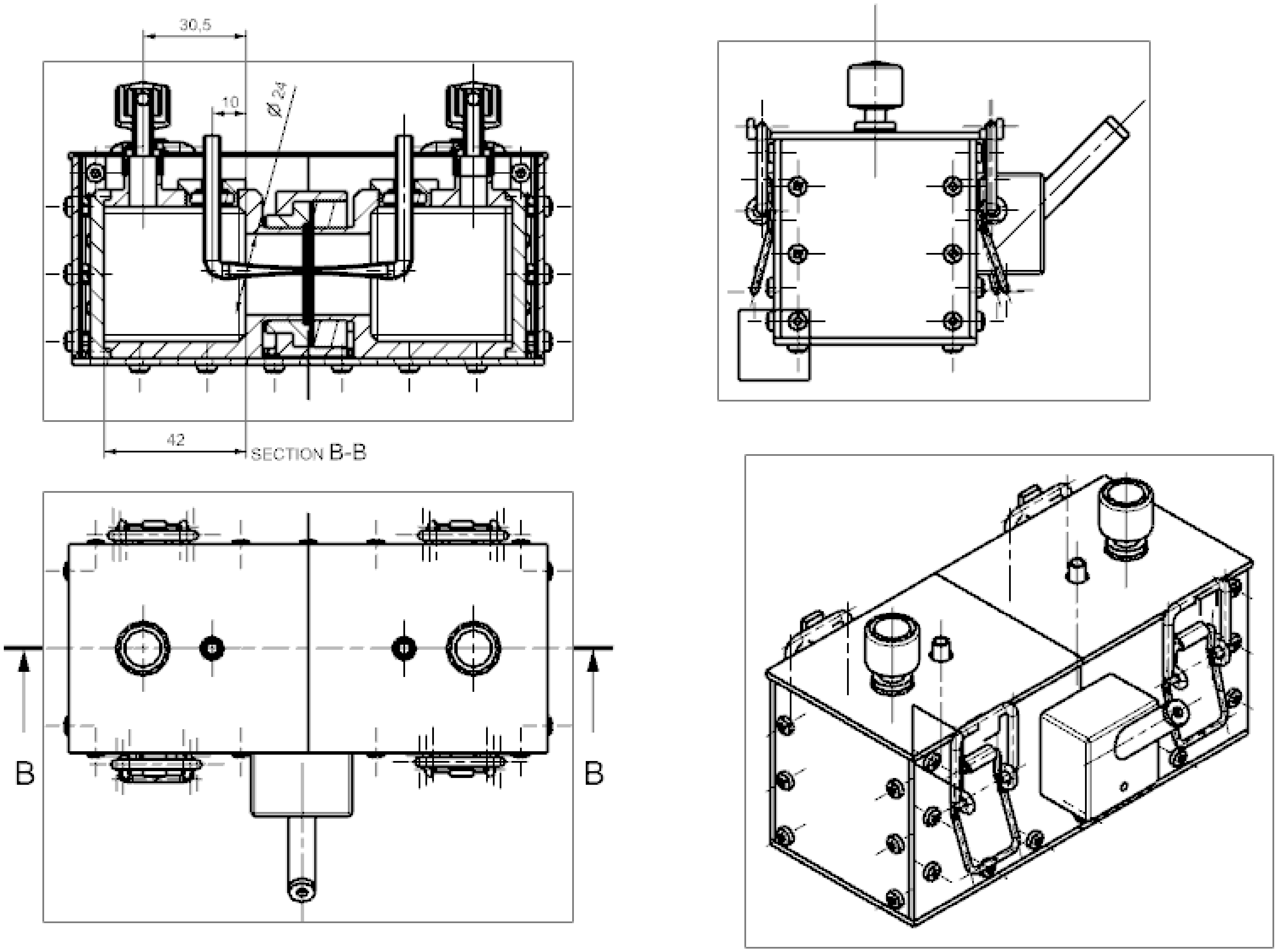
```
gu2 =U6*a4;

t   = 10000;                %Total sec
dt  = 1;  % seconds

T0  = 20;
T_T = 200;
T_O = 20;

T_E(1) = 200;
T(1) = T0;
T1(1)= T0;

for n=1:(t/dt)
 % if T1(n) > 90
 %      T_E = 20;
 % end
  %elseif 15000<n && n<30000
  %     T_E = 150;
  % elseif n > 30000
  %     T_E = 80 ;
  % end

 if T_T > T_E(n)
  T_E(n+1) =T_E(n) + dt*(1/(me*cal)*(ge*(T_T - T_E(n)) - gu2*(T_E(n)-
T_O)));
 else
   T_E(n+1) =T_E(n) + dt*(1/(me*cal)*(- gu2*(T_E(n)-T_O)));
end

   T(n+1) = T(n) + dt*(1/(m*ca))*(g1*(T_E(n)-T(n))- g2*(T(n)-T_O));
%Euler method

   T1(n+1) = T1(n) + dt*(1/(m2*cg))*(g3*(T(n)-T1(n)) - g3*(T1(n)-T(n))) ;
%Last may be wrong

   if T1(n) > 40 && T1(n) < 50
     T_T = 20;
  %elseif T1(n) == 50 && T1(n) < 70
     % T_T = 80;
  %elseif T1(n) > 70
    %  T_T = 75;
  end

end
time = 0:dt:t;
plot(time, T_E, time, T, time, T1)
```

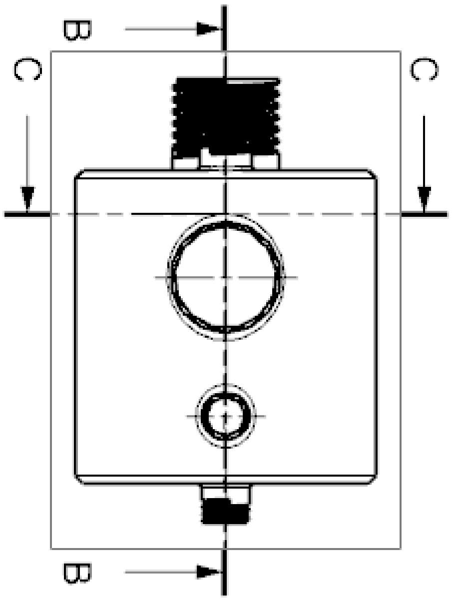
## Appendix D: Drawings from Siemens NX

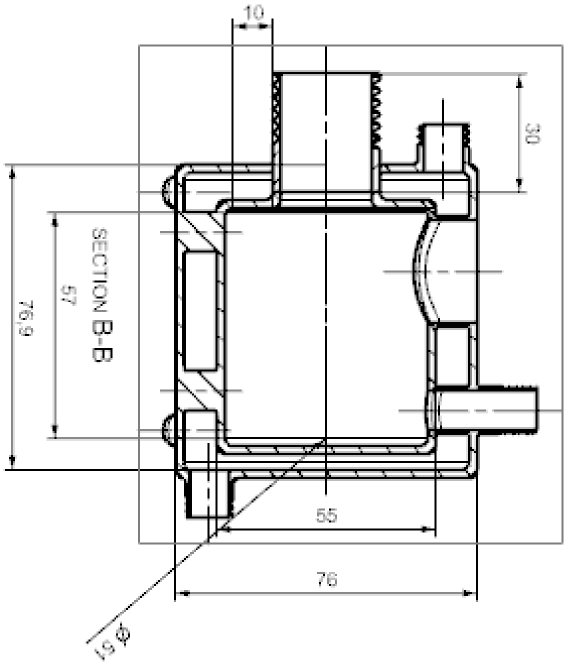
This appendix contains drawings of the different main models, with relevant dimensions. These are not meant as full machine drawings, but rather give the reader a understanding of the dimensions and forms involved. First is the industrial system, then the laboratory system and at last the cell for the Nano-indenter

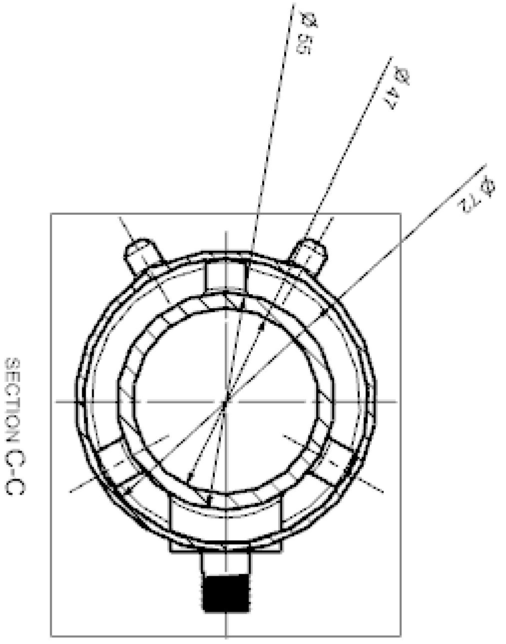


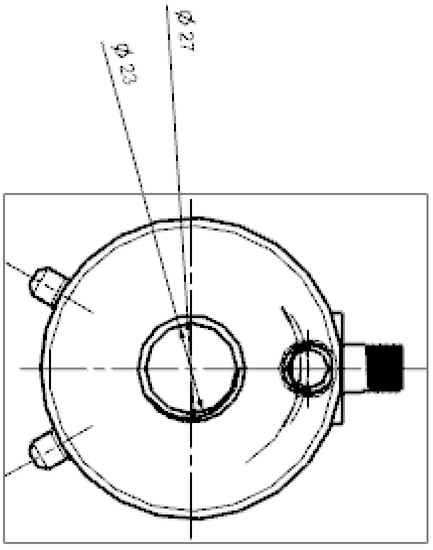

40
30
56
83,5
158,5
63
48
Ø 23,5
Ø 43
Ø 49
A
A
B
B
SECTION B-B
SECTION A-A

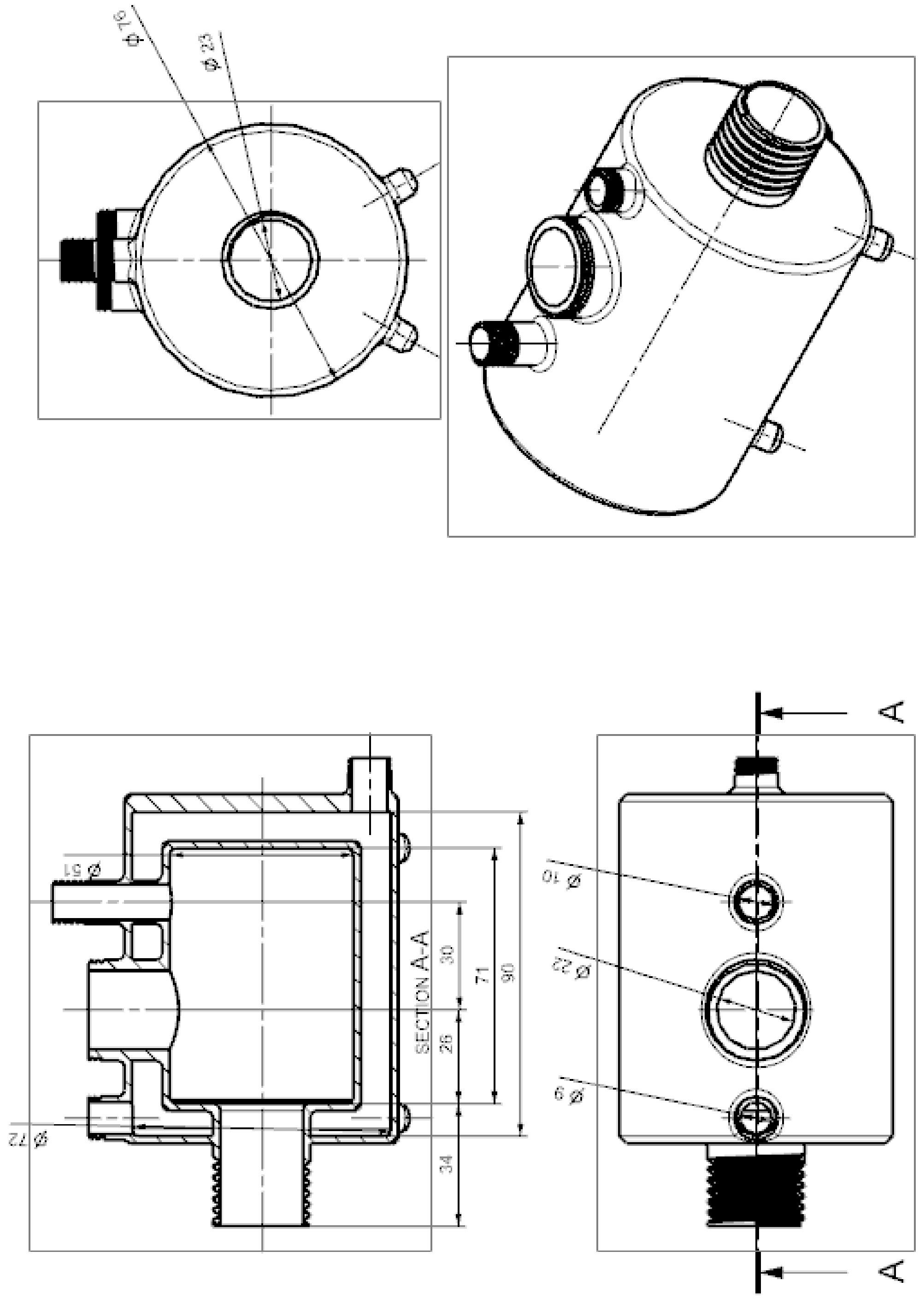

30,5
10
Ø 24
42
SECTION B-B
B
B

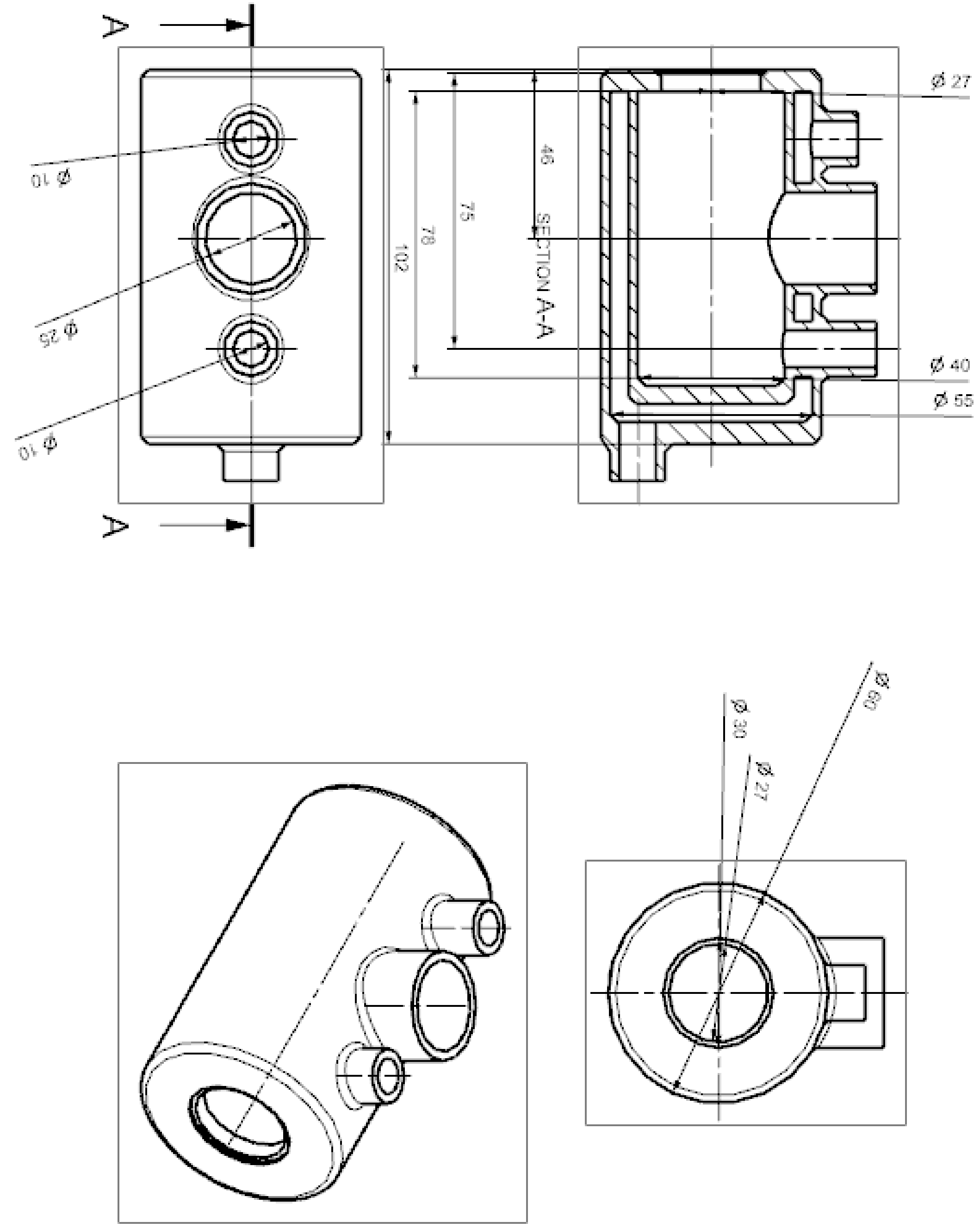

B
C
C
B

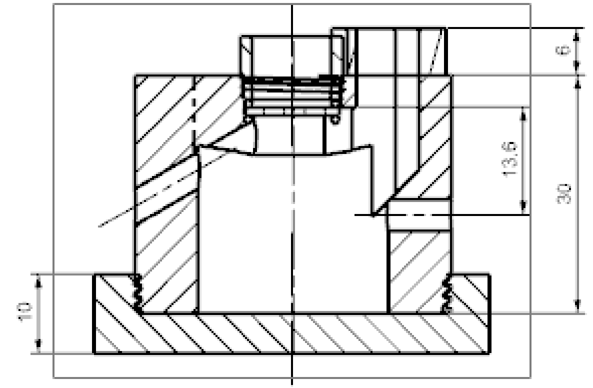

10
30
SECTION B-B
57
76,9
55
76
Ø 51


Ø 55
Ø 47
Ø 72
SECTION C-C


Ø 27
Ø 23


φ 76
φ 23
SECTION A-A
φ 51
φ 72
30
26
71
90
34
φ 10
φ 22
φ 9
A
A


A
A
⌀ 10
⌀ 25
⌀ 10
102
78
75
46
SECTION A-A
⌀ 27
⌀ 40
⌀ 55
⌀ 60
⌀ 30
⌀ 27



SECTION A-A