Design of a small-scale alkaline electrolyser for large-scale production

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Abstract

This thesis tackles the designing of a small-scale alkaline electrolysis cells (AEC) unit for large-scale production. This apparatus is applied for the production of pressurised hydrogen by employing solar energy. The goal is to minimise production costs while ensuring the safety of the unit operation throughout its lifespan. Although the employed technology is mature in the industry, large-scale production of such units still represents a novelty. Zero Emissions Fuel, ZEF, is currently carrying on the development of an electrolyser able to autonomously operate by two standard PV panels.

The study includes the designing of a bipolar electrolysis cell with thermoplastics and its optimisation for injection moulding. Likewise, methods for ensuring the leak-tightness of the unit are investigated and evaluated through distinct experiments. The concept development is focussed on the satisfaction of the main functional requirements for the AEC unit. Hence, operating conditions of stress, temperature and chemical corrosion he been taken into account to identify the material selection of each component.The proposed design is as twice as powerful compared to the previous development, within a much smaller and lighter form factor. Similarly, the unit cost has been reduced by a third.

Table of content

1.	Project brief	
1.1 1.2 1.3 1.4	Assignment Goals Challenges Approach	1 1 2
2.	Zero Emission Fuels	
2.1 2.2	A venture towards sustainable fuels Microchemical plant	7 8
3.	Alkaline electrolysis cells	
3.1 3.2	Alkaline water electrolysis (AWE) State of the art of the industry	15 18
4.	The state of the art ZEF	
4.1 4.2 4.3 4.4	Operation AEC components Prototype assessment Conclusions	24 26 28 30
5.	Cookies joining	
5.1 5.2 5.3	Joining methods Weld test Discussion	35 37 39
6.	Cell artightness	
6.1		

7. Geometry optimisation

7.1	Middle-cookie - V1	45
7.2	Middle-cookie iterations	47
7.3	Discussion	49

8. Pressure case

8.1	Case design	51
8.2	Material choice	54
8.3	Discussion	56

9. Ideation

9.1	Design focus	61
9.2	Criteria	63
9.3	Discussion	63

10. Concept development

10.1	Money-saver	66
10.2	The safe	68
10.3	Easy to assembly	70
10.4	Comparison	72
10.5	Discussion	73

11. Final proposal

11.1	Design features	77
11.2	Evaluation	80
11.3	Conclusion	80
11.4	Recommendations	81

12. Reflections

- 13. References
- 14. Appendices

List of figures

figure 1	CO2 emission from a factory chimney stacks	VI
figure 2	Double Diamond process (Design Council, 2005)	3
figure 3	Company logo	6
figure 4	Company mission	6
figure 5	Microchemical plant layout	9
figure 7	Current/voltage curves of a PV panel	10
figure 8	Microchemical plant concept (van Nunen, 2019)	11
figure 9	Process tree (Roozenburg and Eekels, 1996)	13
figure 10	Example of water decomposition through electrolysis.	14
figure 11	Alkaline water electrolysis	15
figure 12	Current density/ cell voltage curve	16
figure 13	Alkaline water electrolysis cells configurations	17
figure 14	High pressure alkaline electrolysis cell unit	18
figure 15	Scheme of a bipolar configuration adopted in industry	19
figure 16	Assembly of an alkaline electrolysis stack	19
figure 17	Diphragm coated fabric. Zirfon Perl UTP 500	20
figure 18	Electrode structures.	20
figure 19	Example of fuel cells bipolar plate	20
figure 20	Example of EPDM gaskets	21
figure 21	Current desing of ZEF AEC unit	22
figure 22	System diagram of the AEC unit	23
figure 23	Function diagram of the AEC unit	24
figure 24	Cookie-roll concept design	26
figure 25	Current pressure case design	26
figure 26	Current electrolysis stack design	27
figure 27	Current electrolysis cells design.	28
figure 28	Taxonomy of jopining techniques for thermoplastics (Yousefpour et al., 2004)	34
figure 29	Suitable welding processes	36
figure 30	Weld test samples	37
figure 31	Microscopic imaging of partially welded sample	38
figure 32	Microscopic imaging of superficially molten sample	38
figure 33	Microscopic imaging of not-affected sample	38
figure 34	Diagram of the experimental setup for diaphragm airtightness	40
figure 35	Mechanical behaviour of Zirfor Perl under compression	42
figure 36	Experiment observation of presence of bubbles along the edge	43
figure 37	State of the art of the middle-cookie geometry (V1)	44
figure 38	Thickness distribution in middle-cookie V1	44
figure 39	Design iterations of the middle-cookie	47
figure 40	Design iterations of the middle-cookie	48
figure 41	Middle-cookie V1 main dimensions	51
figure 42	Geometry division and force direction.	52
figure 43	Example of deep drawn shapes	55
figure 44	Example of structural ribs in thermoplastic forming	55
figure 45	Morphological chart with ideas evaluation	60
figure 46	Morphological chart and idea selection for concept development	65
figure 47	Assembly of concept #1	66
figure 48	Electrolysis stack of concept #1	66

figure 49	Exploded view of electrolysis cell of concept #1	67
figure 50	Assembly of concept #2	68
figure 51	Electrolysis stack of concept #2	68
figure 52	Exploded view of electrolysis cell of concept #2	69
figure 54	Assembly of concept #3	70
figure 53	Electrolysis stack of concept #3	70
figure 55	Exploded view of electrolysis cell of concept #3	71
figure 56	Assembly of the final proposal design of AEC	76
figure 57	Electrolysis stack of the final proposal design	77
figure 58	Exploded view of electrolysis cell of the final proposal (front and back)	78
figure 59	Elements integration in the electrolysis cell	79
figure 60	Back view of the final proposal	79

List of tables

table 1	Electrolysis specification comparison. Industry and ZEF (Carmo et al., 2013)(ZEF, 2019)	17
table 2	Higest requirements of the AEC unit operation	25
table 3	Costs of the state of the art of AEC	29
table 4	Middle-cookie V1 main dimensions	45
table 5	Simulation results of middle-cookie iterations. V2, V3, V4	48
table 6	Pressure case thickness per material	52
table 7	Clamping force require for the selected cases	53
table 8	Possible bolts configuration based on bolts' type and property class	53
table 9	Material compatibility (Graco, 2013) (Engineeringtoolbox, 2003)	54
table 10	Criteria and relative weights	63
table 11	Concepts evaluation with weighed objective (Appendix V)	72
table 12	Concepts cost comparison per component	72
table 13	Cost analysis of the final proposal compared to the state of the art	80



figure 1 CO2 emission from a factory chimney stacks

Introductrion

According to (Le Quéré et al., 2018) carbon dioxide emissions are Levels of CO2 in the atmosphere has been drastically increasing in the past decades mainly due to massive consumption of fossil fuels, for either transport and good means. Such unsustainable development has been proved to be the main cause of of atmosphere's temperature rising with direct effects on the environment and living organisms, including human beings. In these regards, Zero Emission Fuels (ZEF) is a growing startup in the field of sustainable energy.

Their goal consists in converting solar energy and air into methanol, which can be further adopted either as fuel for transport and for polymers production. Controversy to conventional chemical plants, which complexity and dimensions make them unlikely to properly operate with inevitable fluctuating energy supplies, ZEF's concept foresees a chemical plant small enough to operate with three standard photovoltaic (PV) panel of 300W and able to adaptively employ its energy supply and produce approximately 300g of methanol per day. In order to achieve such a goal, the methanol plant has been structured in multiple sub-units, each of which is responsible for a specific task, from capturing water and carbon dioxide from the air, to distilling high grade pure methanol. Hence, such a concept would result in a very adaptive alternative. In fact, by scaling up the number of these micro chemical plants it would be possible to proportionally increase methanol production with a consequent decrement of production costs. Although at this very moment most working principles have been proven through prototypes and tests, in order to step up and build the first integrated prototype, each subsystem has to be properly designed and optimised for being manufactured in big scale. Therefore, the project aims to further develop a subunit of the micro plant: the Alkaline Electrolysis Cell (AEC), which task is to decompose water into hydrogen and oxygen gases. The challenges involved in such development are mainly related to the requirements for the electrolysis cells to properly operate and integrate with the other plant's units. Nethertheless, its design requires further optimisation in order to make it suitable for mass production.

1. Project brief

1.1 Assignment

Design of a small scale alkaline electrolyser for large scale production

The assignment has been defined by ZEF's primary need for developing a cost-effective AEC unit. Cost represents the main objective to maintain the core of the business plan feasible, producing competitive high-grade methanol. The state of the art of AEC currently represents the most expensive unit of the entire chemical plant, accounting for almost 50% of the total cost. However, by adopting mass production techniques it is expected to lower the cost down to 127 (van Nunen, 2019). Indeed, as the micro-plant is envisioned to autonomously operate, the cost per ton of hydrogen is strictly dependent on the production costs of the unit itself. Therefore, the assignment foresees the designing of a reliable and low-risk assembly, integrating the required electrolysis components

1.2 Goals

The development and designing of a small scale electrolysis unit imply two main goals. In the first place, although it autonomously operates, the safety of its operation throughout its lifespan is of fundamental importance. Furthermore, costs need to match the defined target to make the business plan feasible.

1.2.1 Safe operation

The unit operation must be reliable over its estimated lifespan of 20 years without affecting other units' operation and not being harmful to users nor the environment. Indeed, as the unit must manage hazardous chemical compounds at severe conditions of temperature and pressure, AEC must avoid drastic events which could bring at either dispersion of dangerous elements or even violent burst. In this regard, a fault tree has been structured to define every possible event, pointing out the most dangerous conditions (Hoberman, 2019).

1.2.2 Cost

To be feasible for ZEF to implement such apparatus, AEC must be cost-competitive in terms of production methods. Hence, as operating expenses are gathered directly from the outer environment, CO2 and water from the air, costs strictly depend on the capital expenses. These costs include all production processes, including raw materials, manufacturing processes and assembly line. According to van Nunen (2019), for AEC to be feasible its cost needs to be below 127€ per unit.

1.3 Challenges

The challenges involved in designing a small scale electrolysis unit are strictly related to its operating conditions and the lack of similar development in literature and industry. Indeed, the unit should reliably operate at extreme conditions without the need for constant maintenance. On the other hand, the electrolysis industry only offers examples of large scale units.

1.3.1 AEC operation

In regards to the operational condition, the unit must withstand high pressure and temperatures as well as corrosive chemicals throughout its entire lifespan. Avoiding leaks at that pressure represents a serious challenge as it could result very dangerous as well as ineffective. Furthermore, the combination of high temperature and pressure in alkaline electrolysis creates great mechanical stress

Besides, the chemicals involved in the reaction, such as potassium hydroxide and pure oxygen, are very corrosive. As a result, they affect the mechanical properties of the material and therefore the ultimate lifespan of the product.

The development of manifold geometry for integrating electrolysis cells in series is not an easy task. Electrolysis components must be precisely included while providing the

1.3.2 Unique venture

The uniqueness of this unit represents an additional challenge. Indeed, the industry has been developing large scale units. Examples of smaller units have been developed only for laboratory purposes. Hence, since little information is available in the literature, it is expected to run investigations and tests to answer current unknowns.

1.4 Approach

The approach adopted for the development of such an assignment is the double diamond method (Design Council, 2005). Such a model, illustrated in *figure 2*, is composed in four phases, discover, define, develop and deliver which have been adopted in the report in respective sections.

1.4.1 Analysis

At first, brief research of the current development at ZEF introduces the company mission as well as the microchemical plant structure. A complete overview of the alkaline electrolysis technology has been conducted through a review of the literature and developments of previous teams at ZEF. This brings to an overall understanding of the current concept operation, clearly defining requirements, goals and challenges of the product development. As a result, the core components of the AEC unit have been defined as well as the unit' elements which require deeper investigations.

1.4.2 Investigation

In Section II of this thesis, further research has been conducted to better identify production requirements in terms of geometry and assembly. Furthermore, it is expected to run experiments and simulations specifically aimed to optimise the considered parts in terms of feasibility and costs. Similarly, materials suitable to withstand high pressure, high temperatures and chemicals are considered.

1.4.3 Concept development

Based on the insights of the research, creative ideas are developed from sub-functions and clustered to fulfil the product demands. Therefore, concepts are developed by making use of design tools such as morphological charts. Criteria are defined in such a way to properly evaluate the results and a final proposal is defined to be further detailed.

1.4.4 Final proposal

The final proposal consists of an AEC unit design which satisfies the requirements provided by the company, especially in terms of cost and operation. The proposed design will be mass manufacturable, easy to assemble and able to integrate with the other subsystems of the microchemical plant.

ZEF, a start-up currently active in the chemical field, is developing a chemical plant whose goal is to produce methanol from just the sun and air. This process, defined as "reversed burn", aims to combine hydrogen and carbon dioxide directly retrieved from the air to produce synthetic liquid fuel (ZEF, 2019). Hence, to deal with the intermittent reliability of solar energy, the chemical plant is scaled down to fit and operate with just three standard photovoltaic panels (PV) of 300W, reaching a maximum peak power of 900W. However, the mass production of a small scale electrolysis unit has never been tackled so far because of the easy maintenance and high efficiency of a single large scale unit.



figure 2 Double Diamond process (Design Council, 2005)

In the following section, a throughout analysis of ZEF's venture is exposed, lining out their mission and goals. Therefore, the envisioned solar farm production requirements are discussed as well as the structure of the chemical plant and the required subsystems.

Consequently, a deep analysis of alkaline electrolysis is presented. First, an explanation of the principle is given distinguishing different methods and configuration.

Therefore, the state of the art of industry development is investigated, retrieving common setups and approaches.

At last, a complete analysis of the state of the art of the electrolysis unit developed by ZEF is carried out. Hence, the main progress and limitation of the current concept are analysed to obtain a better unit optimisation.

the state of the art



figure 3 Company logo





Rely on renewable energy

Directly retrieve CO₂ from air



Produce liquid state fuel

figure 4 Company mission

2. Zero Emission Fuels

The assignment of the redesign of an alkaline electrolysis cells (AEC) unit, is a specific request of Zero Emission Fuel (ZEF B.V.). Such a system is part of a series of subunits of which the goal is to re-process carbon dioxide and water from the air into methanol. The peculiarity of this development lies in the fact that only renewable energy, specifically solar, is adopted to do so.

In the following chapter, a brief introduction of such a venture towards the development of the sustainable chemical industry is given. In the first place, the mission, goal and challenges of ZEF's microchemical plant are exposed. Hence, the reasons why methanol results in a viable resource are discussed. At last, the concept of the microchemical plant is briefly explained as well as its operation and envisioned life cycle.

2.1 A venture towards sustainable fuels

ZEF represents a novel venture in the field of synthetic fuels. Founded in 2016 by three cofounders, Hessel Jongebreur, Jan van Kranendonk and Ulrich Starke, the start-up has been tackling the challenge of synthesizing sustainable fuels without emitting carbon dioxide in the outer environment. Indeed, ZEF aims to reduce the amount of CO₂ in the atmosphere by collecting it from the air and reprocessing it into methanol, CH_3OH . This molecule is a truly versatile compound which can be adopted both as a fuel and as a building element for polymers. To do so, ZEF's chemical plant operates exclusively on renewable energy. Such disruptive reality challenges the current chemical industry development, assessing novel boundaries for sustainable alternatives to fossil fuels. Contrary to conventional chemical installations, which are specifically designed and built on demand, ZEF undertook the development of a small scale and integrated unit. Hence, the strategy of scaling down the unit size and increasing its number prompts three main advantages: decreasing development time and costs as well as allowing the unit to rely on renewable energy sources (Centi, Iaquaniello & Perathoner, 2019).

In the first place, such small scale elicits the possibility to operate actual dimension prototypes, allowing a thorough understanding of its operation and the development through multiple iterative processes. On the other hand, scaling up the number makes it possible to adopt large scale manufacturing methods, with a consequent reduction of capital costs. At last, conventional plants require a constant supply of energy to effectively operate. Contrary, because of its small dimensions, ZEF's micro plant results in a very dynamic alternative, able to operate with unreliable energy sources as the plant will autonomously adjust the methanol production on the energy availability.

2.1.1 Mission

ZEF vision is acting towards a possible alternative for mitigating global warming. To do so their mission stands on 3 main pillars: rely on renewable energy, directly retrieve CO_2 from air and produce liquid state fuel (*figure 4*). In this case, ZEF is capturing solar energy employing photovoltaic panels to power the micro plant. The reason for this is the drastic decrease in the cost of solar panels, dropping by about 60% in the past decade (Sendy, 2019). Furthermore, the units dynamically operate without having any power backup and without being connected to the grid. Hence, the system in development results completely autonomously, producing methanol on demand of the harvested energy.

Similarly, the plant directly gathers carbon dioxide from the environment. With this choice, ZEF wants to completely close the loop of CO_2 . Indeed, as the produced fuel will burn, releasing carbon dioxide in the environment, an equal amount of such a compound will be absorbed and processed into methanol. The plant output must be a liquid fuel as it is much easier to handle and transport compared to other states of matter such as gas and solid.

2.1.2 Goal

Therefore, ZEF's goal consists of developing a microchemical plant able to independently collect and reprocess carbon dioxide (CO_2) and water (H_2O) from air into methanol (CH_3OH). The chemical plants in development must operate in parallel in a solar farm in such a way to increase production by simply scaling up the number of units. Because of this reason, all plant's units must be mass-produced with viable processes to decrease costs.

2.1.3 Challenges

Given the disruptive venture of ZEF, several challenges are involved in the development of such micro plants. In the first place, reducing the sizes of the chemical plant has downsides in terms of energy efficiency. Relying on renewable energy represents an additional challenge. Indeed, the unit must autonomously manage the energy usage based on the intermittent supply consequently adapting system conditions. The last challenge consists of integrating all required sub-units compactly and effectively.

2.1.4 Why methanol?

Methanol is a very versatile compound. It is largely adopted both in the energy and chemical industry due to its simple composition as well as its liquid state at normal conditions (MGC, 2020). Energy industry adopts it due to its relatively high energy density, 22 MJ/kg, half of the energy density of common gasoline, 45 MJ/kg (EIA, 2013). Hence, it elicits the possibility of blending with other hydrocarbons to create green fuels for the current state vehicles. The use of methanol goes beyond the fuels market. Indeed, the chemical industry adopts methanol for the production of solvents and polymers for high-performance plastics as well as synthetic fibres.

2.2 Microchemical plant

As previously mentioned, the unit reprocesses simple compounds collected from the air into a more complex and valuable molecule: methanol. To do so, several steps are required, from directly absorbing carbon dioxide and water from the air, decomposing hydrogen from water through electrolysis and finally combining the gathered compounds, CO_2 and H_2 , within the methanol synthesis reactor. Hence, the micro plant must integrate each unit responsible for the relative chemical and physical process. In *figure 5* it is illustrated the plant layout with relative subunits.

Currently, the chemical plant foresees the inclusion of five main subunits: direct air capture (DAC), fluid machinery (FM), alkaline electrolysis cells (AEC), methanol synthesis (MS) and distillation (DS). Therefore, the plant is powered by three solar panels, while the energy management is guaranteed by the control unit (CO).

MICRO CHEMICAL PLANT SUBSYSTEMS



figure 5 Microchemical plant layout

2.2.1 Plant operation

ZEF is designing the plant in such a way to autonomously operate as it relies just on renewable energy, which in this case is defined to be solar. Indeed, the unit is not connected to the grid and it does not include any kind of energy storage, such as batteries, nor connection to the electrical grid. Therefore, the unit must smartly use the intermittent energy provided by the photovoltaic panel, managing the energy each unit consumption. The state of the art of the plant foresees three photovoltaic panels as a power source, implying a maximum power supply of 900W per plant. The basic principle of the plant operation foresees the harvesting of solar energy using photovoltaic panels, which provides the energy required to run all physical and chemical processes for methanol production. The first step consists of absorbing carbon dioxide and water directly from the air at DAC. Therefore, both CO_2 and H_2O are compressed up to 50 bar and stored in the respective buffer. This buffer feeds both AEC as well as the MS. Indeed, water is supplied to AEC, where it is decomposed through electrolysis to gather H2 at high pressure. Hence, carbon dioxide and hydrogen are supplied to the methanol reactor where the compounds are processed to generate methanol. As MS produces an equal amount of water and methanol, a final distillation phase is required for achieving high-grade methanol.



figure 7 Current/voltage curves of a PV panel

2.2.2 Solar farm

The ultimate operation of the microchemical plant is not as a stand-alone unit. Indeed, the plant is engineered to produce roughly 600g of methanol per day in optimal conditions. To compete within the methanol market, ZEF aims to scale up the number of the units and produce high-grade methanol at the price of 350 (ZEF, 2019). Therefore, the envisioned location is at the equatorial zone to provide as much as possible constant solar irradiation. The resulting methanol-solar farm includes 14000 units and it can harvest a maximum of 12MW of solar energy. As a result, the solar farm will produce roughly 4 ton of methanol per day, while absorbing 2 ton of carbon dioxide from the atmosphere.



figure 8 Microchemical plant concept (van Nunen, 2019)

2.2.3 Process tree

According to Roozenburg and Eekels (1996), a process tree represents a schematic diagram of all the processes present within the life cycle of a product. Therefore, it includes manufacturing, assembly, distribution, installation, operation, maintenance, use, reuse and disposal of the product. The diagram in *figure 9* takes into account the entire microchemical plant as a product. The reason for this is to consider all processes, including the subsystem integration which, in some concern, will affect the subunits certification, maintenance and replacement. Indeed, the pipelines operating at high pressure must be tested and certified together with specific equipment. Because of this, it is very unlikely to validate the pipeline on the field, hence, those elements will require a complete replacement.

PROCESS TREE



figure 9 Process tree (Roozenburg and Eekels, 1996)



figure 10 Example of water decomposition through electrolysis.

3. Alkaline electrolysis cells

Within the micro-plant, the AEC unit is in charge of decomposing water into hydrogen and oxygen. Reason for this is the need to supply high-pressure hydrogen to the MS. Hence, AEC deploys the technology known as alkaline water electrolysis (AWE) to efficiently run at the operating condition required for the microchemical plant. The following chapter gives a brief introduction of alkaline electrolysis, lining out operation and major requirements of such a technology. An investigation on the industry development aims to point out components and configurations of the current products. Furthermore, ZEF already developed a first AEC unit prototype defined as the state of the art of AEC. Hence, its analysis leads to the identification of main functions and operational requirements. At last, the main achievements and limitations of the state of the art are discussed to define the direction for optimising the current AEC design.

3.1 Alkaline water electrolysis (AWE)

Water electrolysis is an electro-chemical process adopted for decomposing water into hydrogen and oxygen through electricity. Literature offers several methods of such technologies, however, the unit developed by ZEF employs the alkaline water electrolysis (AWE) in a zero-gap configuration. AWE has been largely explored in the past century and it is considered a mature technology in the field of water electrolysis. Reasons for such a choice are the long operating lifetime, the possibility to use less noble metals, the high gas purity and the high efficiency up to 70-80% (Millet and Grigoriev, 2019). AWE is achieved by applying current between two electrodes submerged in an alkaline solution, defined





figure 11 Alkaline water electrolysis

as the electrolyte. The alkaline solution results to be very conductive and it allows electrons to move through it with little resistance. As current is applied from the cathode to the anode, positive and negative poles respectively, two reactions are triggered: reduction and oxidation. Reduction occurs at the cathode, negative pole, decomposing H_2O into H_2 and OH- ions. On the contrary, at the anode, positive electrode, oxidation happens, generating O_2 and ions H+. To keep the gases separated, a diaphragm, or separator, is commonly adopted in electrolysis. The diaphragm consists of a selective membrane constructed by a very fine polymer woven fabric which is coated with a specific compound. This separator electrically insulates the electrodes, avoiding any kind of short circuit. Furthermore, it allows ions to diffuse across it, but not gases. Such an element is of fundamental importance as it avoids the mixing of gases which can trigger a violent exothermic reaction at operating conditions, resulting extremely dangerous.

3.1.1 Electrical requirements

Electrolysis occurs when the voltage difference between the electrodes overcome the reaction potential difference as well as the resistance between the electrodes (Millet and Grigoriev, 2019). The electrolysis he potential difference is defined to be 1.23V. At this voltage, current flows, however little or no water decomposition is achieved. However, pure water results in a very poor conductor, hence alkaline catalysts are added in the solution to facilitate the reaction increasing its efficiency. In AWE commonly used electrolytes are potassium hydroxide (KOH) and sodium hydroxide (NaOH) (Keçebaş, Kayfeci and Bayat, 2019). Essential values for electrolysis are the cell's voltage V (V) and the current density J (A/cm²), (*figure 12*). Common ranges for these values are in between 1.8-2.4V and 0.2-0.4A/cm².



figure 12 Current density/ cell voltage curve

AEC specifications	Industry	ZEF	unit
cell temperature	60 - 80	90	°C
cell pressure	< 30	50	bar
current density	0.2 - 0.4	0.3	A∙cm-²
cell voltage	1.8 - 2.4	2	۷
power density	0,4 - 1	0,6	W∙cm⁻²
voltage efficiency	62 - 82	na	%
cell area	>40000	35	Cm ²
h2 production rate	<760	0,6	Nm³∙h⁻¹
lifetime	<90000	na	hrs

table 1 Electrolysis specification comparison. Industry and ZEF (Carmo et al., 2013)(ZEF, 2019)

3.1.2 AWE cells configurations

Furthermore, literature offers several configurations of electrolysis cells. The first distinction is between the traditional cell and zero-gap configuration shown in *figure 13*. Indeed, as a traditional cell is considered any electrolysis cells in which electrodes are placed far from the separator. Conversely, a zero-gap configuration consists of an optimised structure of the cell in which the electrodes are tightly placed against the diaphragm. Such setup results to be extremely efficient in terms of energy losses and cell dimensions. A zero-gap cell has very low ohmic resistance of the electrolyte as the distance between the electrodes is given by the diaphragm thickness. Furthermore, such a configuration allows reducing the dimensions of the cell itself, allowing the designing of much slimmer and compact cells.

An additional distinction of electrolysis cells can be done when using multiple cells configuration. In this case, literature distinguishes between monopolar and bipolar cell configurations (De Silva, 2017). The difference between is the electrical connection of the electrodes and therefore the overall voltage difference of the electrolysis stack. The monopolar configuration foresees all cells electrically connected in parallel. Therefore, each cell is directly connected to the power supply. On the other hand, bipolar cells are electrically connected in series and the total voltage of the electrolysis stack is proportional to the number of the cells. Monopolar stacks are easier to design and manufacture, however they are much heavier and larger compared to the bipolar configuration (Millet and Grigoriev, 2019).



Bipolar

Monopolar

figure 13 Alkaline water electrolysis cells configurations

3.2 State of the art of the industry

Nowadays, alkaline electrolysis is considered a mature technology for hydrogen production. Indeed, hydrogen has been widely adopted in industry for many applications, such as petroleum refinery, ammonia production and metal refining. (Zeng and Zhang, 2010) Furthermore, novel developments of fuel cells make hydrogen a very appealing alternative for energy conversion and storage as well as fuel for transportation means (Burheim, 2017).

Among all technologies for hydrogen production, alkaline electrolysis offers several advantages and it results to be the cleanest solution for hydrogen production. Although only 4% of the worldwide hydrogen production comes from water electrolysis, such a method could be truly advantageous as it does not have any CO₂ emissions, it produces very pure hydrogen, it can be scaled down in size and it can rely on renewables energies (de Souza et al., 2007). Furthermore, alkaline electrolysis can be achieved by using less noble metals for the electrodes, meaning lower costs, and it results reliable after several operating hours (<90000 hrs) (Carmo et al., 2013).

Literature offers several examples of alkaline electrolysis installations, however, according to Carmo et al. (2013) common electrolyser, as shown in *figure 14*, has an energy consumption within the range of 4.5-7.0 kWh. Indeed, small electrolysis stacks have been developed only for laboratory and research purposes (Kraglund et al., 2016)

3.2.1 Configurations

As previously mentioned, the current development of electrolysis plants has been conducted toward large units able to produce between 5-500 Nm3/h. Although both bipolar and monopolar units have been adopted in industry, the most common adoption is the bipolar configuration. Reason for this is given by the greater dimensions and weight of the monopolar configuration (Millet and Grigoriev, 2019). In *figure 15* is shown a basic structure of a cell configuration, including electrolysis components with relative channels for collecting hydrogen and oxygen. These elements are pressed fit together in to create a single cell. To stack multiple cells in series, bipolar plates allows the electrical connection, while designated channels separate the gases outputs as well as provide the reflow of the electrolyte in the cells.

Electrolysis requires specific values to efficiently operate, cells have similar voltage drop, 1,8-2,4V, and current density, 0,2-0,4 A/cm2 (Carmo et al., 2013). As discussed in paragraph 3.1.1, the range of these values does not change while scaling up or down the unit. Therefore, to increase hydrogen production it is possible to adjust the reaction surface and the number of total cells. In terms of operating pressure, the industry has been developing both low and high-pressure systems.



figure 14 High pressure alkaline electrolysis cell unit

Systems which operate at low or ambient pressure are the most adopted, as they require less maintenance and they result to be safer (Millet and Grigoriev, 2019). Converselly, pressurized units efficiently compress the gases without further processes. However, systems over 30 bar (3MPa) are very uncommon as they imply several issues in terms of leaks and high mechanical load.



figure 15 Scheme of a bipolar configuration adopted in industry



figure 16 Assembly of an alkaline electrolysis stack

3.2.2 Electrolysis components

The state of the art in industry adopts a few electrolysis components to stack together multiple electrolysis bipolar cells. These components are the diaphragm, the electrodes, the gasket and the bipolar plate.

3.2.2.1 Diaphragm

The diaphragm consists of a porous membrane, which selective permeability provides the exchange of ions between the cells' sides while avoiding the passage of gases. Literature offers several examples

of membranes, from coated metal mesh, polymer mesh and novel development with ceramics (Vogt et al., 2013). The most common separator in use for alkaline water electrolysis is Zirfon Perl 500 produced by AGFA shown in *figure 17*. It consists of a fine polymer fabric of PSU coated specific compounds which make it very hydrophilic. Reason of its wide adoption is the proprieties it provides in terms of lifetime and low thickness.



figure 17 Diphragm coated fabric. Zirfon Perl UTP 500

3.2.2.2 Electrodes

Electrodes are the elements where the actual reaction happens. Different materials and coating have been developed to achieve high efficiency of reduction and oxidation (Colli, Girault & Battistel, 2019). However, most interesting from a design perspective is the structure of the electrodes themselves. Indeed, several electrodes' structures have been found in literature: perforated plate stretched mesh, woven mesh, and metal foam as shown in *figure 18* (Santos, Sequeira & Figueiredo, 2013). The common integration of electrodes is through compression of the stack itself or by mechanical fastenings, such as screws. However, depending on the typology adopted, the connection to the bipolar plates differs. Common integrations methods of electrodes are through compression of the stack itself or by directly fastening it to the bipolar plate with screws.



figure 18 Electrode structures.

3.2.2.3 Bipolar plates

Bipolar plates are those elements which allow to electrically connect the cells in series. Because of this, bipolar plates are made out of conductive material, commonly machined out of stainless steel to endure the corrosive environment. This element connects anode and cathode between two cells in series. The bipolar plate provides all fluid connections to correctly collect gases as well as the mechanical strength which allows the tight compression of all elements. In *figure 19* are proposed examples of bipolar plates adopted in fuel cells. The reason of this example is the similar dimension



figure 19 Example of fuel cells bipolar plate

to the unit in development. In fact, fuel cells adopt the reverse process of electrolysis to generate electrity.

3.2.2.4 Gaskets

Gaskets are essential within the assembly of electrolysis cells as they fulfil both functions of electrical insulating the cells and ensuring a leak-proof system. Gaskets are always placed on the outer contour of the cell. A common material for this element is EPDM rubber as it can withstand the operating conditions as well as corrosion due to chemicals such as oxygen, hydrogen and the alkaline electrolyte. In *figure 20* are proposed possible integration of this rubber

flat gaskets





co-molded gaskets

figure 20 Example of EPDM gaskets

o'rings



figure 21 Current desing of ZEF AEC unit

4. The state of the art ZEF

The state of the art of the AEC, in *figure 21*, consists of a standalone unit designed and prototyped to embody all elements required for producing and storing high-pressure hydrogen. AEC includes further elements besides the alkaline electrolysis cells, such as the degasser unit and the hydrogen buffer. The first is in charge of purifying the water from carbon dioxide by adopting a stripping process (Kohl, 2014). Furthermore, the buffer consists of a simple empty volume which stores hydrogen before feeding the MS unit. Although several experiments have been run for assessing operational requirements, the prototype has never been operative due to safety reasons (Appendix I). Therefore, no hydrogen has ever been effectively produced and stored at the required pressure. Furthermore, the current unit has been engineered specifically for just one solar panel micro-plant concept and it is designed for an operative power of 200W. However, due to more recent analysis, the micro-plant is scaled up to run with three solar panels (van Numan, 2019). Consequently, the AEC unit must be scaled up to three folds to provide a sufficient supply of hydrogen for the methanol synthesis. Hence, the AEC unit will be designed to operate with 600W of power.



figure 22 System diagram of the AEC unit

4.1 Operation

The AEC unit starts at ambient pressure and it reaches the operating pressure by storing hydrogen in the relative buffer. Hence, it is designed in such a way to simplify as much as possible to control the system conditions by adopting a few sensors and actuators as shown in *figure 22*. A valve controls the water supply from the CO₂ buffer, in which water is already pressurised at 50 bar. As the reaction is triggered, hydrogen and oxygen flow up towards the top of the cells. The mixture of gas and electrolyte reaches the flash tanks above the cell where they separate. While hydrogen is stored in the respective buffer, oxygen is adopted for stripping carbon dioxide out from the supplied water. Ultimately, both CO₂ and O₂ are purged out of the system as soon as possible. Controversially, the electrolyte flows in the downcomers and then back into the cells through the bottom channels. At the downcomers, sensors detect the water levels of both hydrogen and oxygen sides. Such information is used to control the pressure balance of O₂ and H₂. Due to the conductivity of the alkaline solution, narrow channels identified as bridges electrically insulate the cells while allowing the correct flowing of the electrolyte in and out of the cells

•	avoid plastic deformation	give mechanical support the electrolysis stack
		fit the electrolysis stack
		provide axial compression
•	integrate unit to microplant	provide mechanical fastening
•	provide lifetime operation	withstand pressure and thermal condition
		endure to chemicals
•	provide system integration	embody electrical connections
		embody fluid connections
•	embody sensors and controls	detect electrolyte level
•	embody sensors and controls	detect electrolyte level detect unit temperatures
•	embody sensors and controls	,
<u>.</u>	embody sensors and controls	detect unit temperatures
·	embody sensors and controls provide leak tight system	detect unit temperatures
	2	detect unit temperatures detect system pressure
·	2	detect unit temperatures detect system pressure
·	provide leak tight system	detect unit temperatures detect system pressure ensure leak tightness ar 50bar
	provide leak tight system	detect unit temperatures detect system pressure ensure leak tightness ar 50bar embody electrolysis components in series
·	provide leak tight system	detect unit temperatures detect system pressure ensure leak tightness ar 50bar embody electrolysis components in series provide cell air tightness

figure 23 Function diagram of the AEC unit

4.1.1 Functions

To provide the correct operation, the state of the art of AEC has been developed in such a way to control the unit operation as well as integrate it within the microchemical plant. Therefore, each component of the unit has been engineered and designed in such a way to satisfy specific functions. In *figure 23* are reported the functions and sub-function of the AEC uni.

4.1.1.1 Requirements

The requirements for each sub-function and relative component have been defined in collaboration with the team. The outcomes of such evaluation are reported in Appendix IV. The most important requirements for the unit's operation are listed in *table 2*.

Requirement	Value	SI	Weight
ELECTROLYSIS STACK			
material corrosion	90	C	3
operating temperature	0.05	mm/year	3
membrane compression rate	1	MPa	3
ELECTROLYSIS CELL			
maximum linear tolerances	0.05	mm	3
number of cells	20	#	3
diaphragm clamping pressure	1	MPa	3
length/section ratio of bridge channels	> 10	-	3
PRESSURE CASE			
stress lower than material yield stress	5	MPa	3
linear tolerances	0.05	mm	3
closing clamping force	80	kN	3

table 2 Higest requirements of the AEC unit operation

4.1.2 Cookie roll concept

The current design of the AEC unit deploys what has been defined as the cookie roll concept (*figure 24*). Such concept foresees the use of modular elements, cookies, which can be piled up and press-fit together in a leak-tight stack. The inner geometry of the cookies varies depending on the functions to accomplish, while the leak tightness of the assembly is ensured by a series of o-rings between the parts. In such a way, it has been possible to integrate multiple subunits in a single element. Indeed, further, than the electrolysis stack, the state of the art includes a degasser unit, a hydrogen buffer as well as the relative flash tanks and downcomers. Because of this, the state of the art includes a total of thirty cookies. Besides the choice of adopting polymers for creating the electrolyzer geometry, such a concept very much resembles the bipolar configuration adopted in the industry.



figure 24 Cookie-roll concept design

4.2 AEC components

The current design is engineered in such a way to satisfy specific requirements, both from the unit operation and manufacturing processes. Because of this, the unit has been structured in two main elements, the pressure case, responsible for supporting the load given by the high pressure, and the cookies stack, whose function is to embody the electrolysis geometry and additional components, such as buffer and degasser in a leak-tight system.



figure 25 Current pressure case design
4.2.1 Pressure case

The pressure case consists of a stainless steel cylindrical container which embodies the cookie stack. It is composed of one single pipe and two closing lids. The closing mechanism is provided by collar clamps at the extremities as shown at (FIG.X). Pressure case is in charge of supporting the load given by the inner pressure of the unit. Hence, the lids are machined from a solid piece, while the pipe is extruded and welded at the extremities to accommodate the collar clamps.

4.2.2 Electrolysis stack



figure 26 Current electrolysis stack design

The electorlysis stack embodies all elements required for electrolysis to happen. Hence it embodies three distinct elements, the alkaline electrolysis cells, the degasser and the hydrogen buffer. is constructed by a total of thirty cookies machined out of high-density polyethylene (HDPE)(Appendix I). Each cookie has a specific geometry. The only exception is given by the middle-cookie, which consists of the modular element representing the electrolysis cells. The hydrogen buffer takes five cookies in total and it is directly connected to the hydrogen outlet. On the other hand, the degasser, composed of just two cookies, is connected to the water inlet from the CO2 buffer and the oxygen outlet of the electrolysis cells. Most of the cookies stack is made up of AEC, which accounts for 21 cookies in total, roughly 70% of the stack. Those are further distinguished into end-cookies and middle-cookies. As the term suggests, end-cookies are placed at both extremities of alkaline cells. Besides including all connections, they embody the downcomers, which collects the alkaline solution and feed it back into the cells. The middle-cookie, instead, includes electrolysis components, such as electrodes and diaphragm, in a zero-gap configuration. Furthermore, it embodies electrical connections as well as the flash tanks, in which the phase transition happens.

4.2.2.1 Seals

Within the cookie stack, seals are of fundamental importance to provide a leak-tight system and avoid any gas or fluid effusion. Therefore, within the assembly, two different types of seals have been identified, outer and inner seals (Appendix I). As outer seals are defined the seals towards the outer environment. Hence, they must withstand the operating pressure of 50bar. On the other hand, inner seals must avoid the gas effusion within the system, in which the pressure difference is almost negligible. Therefore, no actual gaskets have been adopted in this case. However, the middle-cookies have been created in such a way to fit one another providing a leak-tight assembly.

4.2.2.2 Connections

The unit includes several connections which have been distinguished into fluid, electrical and control connections. The unit includes four fluid connections, specifically for the water feed, KOH filling, hydrogen output and oxygen purge. Therefore, AEC has a polar connection to the power supply. At last connections of inner sensors, such as temperature and level sensors, have been clustered as control connections.

4.2.2.3 Sensors

Few sensors are also included to collect operational data of AEC. Based on this information the control unit can assess the real-time unit's condition and act responsively. Hence, temperature sensors are envisioned to detect the temperature of the stack. Specifically, temperatures are collected at the middle of the cells' stack and at the extremities of the stack itself. Furthermore, level sensors are placed in both hydrogen and oxygen downcomers. A pressure sensor is placed at the hydrogen buffer. Similarly, voltage and current sensors are responsible to detect the power absorption.

4.2.2.4 Actuators

Actuated valves have been embedded in the unit to control the mass flow within the system. Therefore, the unit includes three valves. One for the inlet water feed, one for the oxygen purge and one for the hydrogen outlet.

4.2.3 Electrolysis cells



figure 27 Current electrolysis cells design.

The electrolysis cell, defined as to the middle-cookie, consists of the most complex geometry within the stack. It embodies the required components for electrolysis, such as diaphragm and electrodes, as well as the electrical and fluid connections. Because of this, a single electrolysis cell is built up by coupling two middle-cookies. Indeed, the selective membrane takes place exactly in between these elements as shown in *figure 27*. Therefore, electrodes are placed close to the separator and the electrical connection is provided by four stainless steel elements through the cookie's wall. At the top and bottom of the cells, channels have been designed in such a way to convey the mixture of solution and gases from each cell side, to the flash tanks above. Furthermore, because of the high conductivity of the electrolyte, tiny channels, identified as bridges, electrically insulate the cells. (Appendix LIST of req)

4.3 Prototype assessment

The achievements ZEF team of the AEC brought to the development of a prototype designed and built in such a way to properly work as a ground test. Therefore, the entire assembly can be disassembled, adjusted and implemented with novel solutions. The prime objective of such a concept was to test and validate different configurations in terms of geometries, components and sensors (Amogh, 2019). A deeper analysis of the AEC unit and assembly developed by TEAM 3 has been conducted and confidentiality reported in Appendix I. The state of the art of AEC is far from being operative as it exposed several issues during the assembling and testing phases (Appendix I). As a result, the current development not only results to be very unreliable but also very dangerous to be operated. Furthermore, the state of the art greatly exceeds the target cost, resulting in not feasible in terms of production methods.

4.3.1 Safety consideration

In terms of safety few considerations can be done in terms of material selection, its geometry and assembling procedure. In the first place, the material which constitutes the cookie stack is HDPE which has been selected as a cheap thermoplastic. However, according to ZEF (2019), after a brief exposition to the electrolyte at operating temperature, the material quickly degrades with a drastic effect on its mechanical properties. Therefore, HDPE is not suitable to withstand the operating conditions of AEC. Furthermore, the electrolysis stack does not result safe. Indeed, because of the integration of the flash tanks above the electrolysis cells, a large quantity of pure gases is present at high temperature and pressure, leading to material degradation and eventual burst reactions. Issues related to this are the ageing of the material in contact with a relative decrease of its mechanical properties, as well as the extreme reactivity of oxygen. Given the extreme operating condition of the unit.

A further remark considers the placement of the bridge at the top side of the cell. Indeed, the channel is not at the very top of the cell, hence gas will remain trapped within the cell (Sriram, 2019). Consequently, electrolysis efficiency decreases and components can be corroded by the presence of gases. (Appendix I)

Similarly, the pressure case does not result in optimally designed. Indeed, its extremities present welds to accommodate the closing mechanism. However, due to hydrogen embrittlement, the material will degrade faster at higher concentration of carbon (Birnbaum, 2001). Therefore, it has been identified as a possible reason for the failure of the unit.

4.3.2 Cost analysis

The cost analysis of the state of the art of AEC is conducted by adding together the cost of raw material and relative manufacturing processes. However, the assembling cost has not been included in the estimation. The reason for such a cost assessment is to identify the most cost dependent elements. EDUPack database (2019) is adopted to retrieve costs of materials and relative manufacturing processes required to shape. In Appendix V are collected the tables developed for the calculations. As a result, the total cost of the prototype is 120€. The main part

Component Stat	e of the art (€)
• electroysis stack (material)	1.8
• electroysis stack (producion)	66
· electrolysis components	12
· pressure case (material)	15
· pressure case (production)	26
· total	120

table 3 Costs of the state of the art of AEC

of the total cost derives from the production method of the cookies as the current geometry design can be achieved only through machining it from solid pieces. As a result, the production of the cookies stack accounts for about 70% of the total cost of the unit and almost 90% of the production costs. Furthermore, the stainless steel pipe adopted as the pressure case consists of the half to the total raw material cost.

4.4 Conclusions

To conclude, the feasibility of the unit concerns its safe operation and costs. Given this preliminary analysis, the main design challenges are relative to the optimisation of the cookies geometry for injection moulding and the achievement of a leak-tight system. Therefore, this thesis will focus on the design of those components closely related to the safety and cost issues. Furthermore, few design constraints have been defined.

4.4.1 Design focus

The identified elements which require further optimisation are the leak-tight sealing of the cookie stack, the electrolysis cell design and the pressure case. Therefore, the design focus concerns the development of these elements as they represent the main current limitation.

4.4.1.1 Electrolysis stack

Alternatives for joining the cookies together in a reliable and leak-tight system will be investigated to develop a safe and reliable system.

4.4.1.2 Electrolysis cell

The electrolysis cell is embodied by the middle-cookie, which, among all cookies, has the most intricate geometry. The focus for this component will be the development of a manifold geometry for injection moulding to decrease the production costs and improve the integration of the components.

4.4.1.3 Pressure case

The pressure case will be taken into account as the current one results to be too expensive and not completely reliable. The dimensioning of the geometry will be investigated as well as the production methods.

4.4.2 Design constraints

As constraints are intended all those elements which have been already investigated and assessed by ZEF and, therefore, out of the scope of this thesis. In specific, those limits consider the unit's geometry, materials, embedded components and operation.

4.4.2.1 Geometry

The cylindrical shape of the unit has been defined. Indeed, AEC has a cylindrical shape as it is very effective either for mechanical properties and for assembly processes. Furthermore, the diameter will remain the same as the current concept.

4.4.2.2 Materials

The material choice is also limited. The reasons for that are the operating conditions of temperature, pressure and chemical. Indeed, the gases present within the system will act both on pressure case and cookies stack ageing the material and lowering material properties over time.

Regarding the pressure case, material alternatives are low carbon steel, composites and hightemperature resistant thermoplastics.

For the cookies stack the two given options are polysulfone, PSU, and polyphenylene sulfide, PPS. The latter requires some infill as it results too brittle without. Furthermore, glass is not an optimal infill material as it speeds up the aging process with KOH (Zhang, 2019).

4.4.2.3 Embedded components

The unit developed by ZEF includes further elements besides the alkaline cells. Indeed, it embodies a degasser unit, the flash tanks and the hydrogen buffer (Appendix I). Those elements are not

considered as a primary design focus. In the case of the degasser unit, it is still in development and it has too many uncertainties regarding its operation to be further developed. On the contrary, flash tanks and hydrogen buffer are considered too much dangerous to be embedded within the unit and therefore they are moved outside the assembly

4.4.2.4 Operation

Similarly, no changes in unit operation are investigated. Indeed, the design development will take into account all operational requirements assessed so far. Hence, the unit will embody a series of alkaline electrolysis cells in a zero-gap configuration. Furthermore, electrolysis components, such as electrodes, membrane and alkaline solution, are considered out of the scope in regards to their composition and suppliers. The development of such a small scale electrolysis unit implies the satisfaction of several requirements, bringing up likewise challenges. Few of them have been already assessed and resolved by ZEF and discussed as design constraints reported in section 3.2. However, several design uncertainties require further investigations to overcome the limitations in terms of costs and safety measures.

Leaks still represent one major challenge for the development of a reliable unit. Therefore, alternatives for effectively joining the components in a leak-proof assembly are present. The research includes an overview of the possible bonding methods for thermoplastic materials as well as a performed test with actual material and process.

Similarly, requirements for integrating the diaphragm within the electrolysis cell need to be further defined. Indeed, this component must be precisely placed in between the electrodes to avoid the effusion of gases across the two sides of the cell.

Furthermore, the middle-cookie is the only modular geometry within the unit, consisting of 70% of the cookie stack. By optimising this geometry for injection moulding it is expected to largely affect costs. Likewise, it embodies the electrolysis cell and relative components. For this reason, it is the most complex part of the entire assembly which must comply by severe requirements.

Ultimately, the case design is investigated in terms of stresses it must endure over its lifetime. First, mechanical stress defines the dimension of the casing, which must avoid plastic deformation. Therefore, materials are discussed based on the resistance to the chemical present. Hence, suitable manufacturing methods are discussed.



towards a new design

adhesive bonding solvent bonding
 adhesive agglutination

mechanical fastening riveting
 clamping
 bolting



5. Cookies joining

AEC supplies high-pressure hydrogen to the methanol synthesis. Therefore, the cookie stack must not present any kind of leak, requiring it to be both watertight and airtight. Furthermore, the unit must be completely shut as the electrolyte is a very corrosive compound and dangerous if dispersed in the environment. To achieve such hermetic geometry, the parts not only must not have any surface irregularity, but they must be reliably joined together. Both ZEF and the chemical industry foresee the use of gaskets tightly pressed in between the cells to achieve a leak-proof system. However, the current prototype never reached the desired operating pressure due to leaks. Reason for this is the lack of clamping force provided as well as the low accuracy of the assembly (Appendix I). Indeed, to effectively join the part in a shut system must overcome the combined force given by the inner pressure as well as the spring load of the gasket deformation. Literature offers several techniques for joining thermoplastics, distinguishing in three main branches: mechanical fastening, fusion bonding and adhesive bonding (Yousefpour et al., 2004)(*figure 28*). As previously discussed, ZEF employs a mechanical fastening method known as clamping. Therefore, further alternatives are investigated and discussed to find a more effective joining solution. Final decisions will be tested and evaluated and assessed in terms of feasibility.

5.1 Joining methods

According to Yousefpour et al. (2004) either adhesive bonding and mechanical fastening result to be ineffective techniques. In the first case, there is no effective adhesive to adopt for thermoplastic. Additionally, adhesives quickly degrade, especially in the presence of chemicals. In the second place, mechanical fastening techniques show difficulties regarding the stress concentration as well as different thermal expansion of components, issues very relevant at the operating conditions of AEC. Moreover, mechanical fastening does not provide any leak-tight bonds, requiring further elements such as gaskets to provide a sealed system. Due to these considerations, the only feasible alternative for creating leak-proof bonds is by adopting fusion bonding techniques.

5.1.1 Fusion bonding

Fusion bonding, commonly known as welding, consists of a joining technique in which the polymer is heated up a viscous state at the joining interface. In such a way, the polymer chains are free to move and inter-diffuse between the two elements. As the material cools down the bond is created. Thermal bonding is further clustered in three branches: thermal, friction and electromagnetic welding. As discussed in Appendix III, among all techniques exposed in *figure 28* feasible methods are represented by infrared, laser, ultrasonic and induction welding. The reason for this is the precision of the proposed technologies, which elicit the integration of the electrolysis components.

5.1.1.1 Advantages

The advantages of welding the cookies stack consist of ensuring a leak-tight bond, providing a mechanical connection of the parts as well as reducing the number of components. In the first place, the considered welding techniques ensure the creation of leak-tight bonds. Indeed, welding represents a much more reliable method compared to using gaskets. Furthermore, depending on the adopted technology, welds can offer a mechanical bond strength 40-70% of the mechanical properties of the material (Troughton, 2009). As a result, such a joining alternative keeps the stack connected slightly reducing the total clamping force required. Lastly, no gaskets are required for sealing the assembly. This will reduce the overall number of components and the risk of failure of the same due to chemical ageing or misalignment.

5.1.1.2 Disadvantages

On the other hand, welding rises the main disadvantage of disassembly the electrolysis stack. Because the assembly foresees the integration of electrolysis components within the cookies, it will be impossible to refurbish inner components in case of failure. Hence, as any of them fails the unit must be completely replaced and none of them could be reused or hardy reachable. Such a problem also affects production processes as even a miss-joint part compromises the overall assembly.

5.1.2 Suitable welding processes

Among the exposed welding techniques only a few are truly suitable for joining the cookies. Reason for this is the complexity of the geometry and the need to integrate electrolysis components. The welds must be placed at the contour and must not create any debris nor gaps. Therefore, the welding methods suitable for such connections are induction welding, ultrasonic welding, laser welding and infrared welding (*figure 29*). However, each technology has peculiar qualities and requirements to fulfil. In all the cases, it is present the challenge of welding multiple elements in one stack.

5.1.2.1 Laser welding

Laser welding foresees the use of a laser beam focused on the bonding interface of the components. Usually, the procedure is conducted by coupling a transparent material and an opaque base. However, it is also possible to weld transparent parts (Clearweld, 2019). The process is quite fast and precise, allowing the performing of different welding layouts.

5.1.2.2 Induction welding

Induction welding is a fusion bonding which adopts electromagnetic fields to heat ferromagnetic elements appropriately placed within the geometry. According to Troughton (2009), such a method allows very precise welding. Furthermore, induction welding allows the bonding of multiple elements simultaneously, resulting in a very effective solution for welding the cookies stack. On the other hand, the process could interfere with inner components damaging either the geometry and the components.

5.1.2.3 Infrared welding

Infrared welding is a process which foresees the heating up of the welding interface through infrared light. Such a method adopts the use of specific masks to heat localised areas, resulting in a very precise process. However, it is a very slow process as both elements need to reach the melting temperature of a large amount of material.

5.1.2.4 Ultrasonic welding

Ultrasonic welding is the cheapest and quickest alternative available. The technology foresees the use of ultrasonic pulse to melt the plastic at the desired interface.



laser welding



induction welding



infrared welding



ultrasonic welding

figure 29 Suitable welding processes

5.1.3 Selected process

Among the considered methods, laser welding is considered the most feasible for joining the

electrolysis stack in development. Reasons for this are the possibility to effectively include inner components as well as performing the weld with pre-aligned parts. Furthermore, laser welding is a very precise technique and it allows the welding of contours with great flexibility. Hence, it is possible to perform different types of welds, creating, for instance, outer and inner seals.

5.2 Weld test

To assess the feasibility of the laser welding a series of tests has been run in collaboration with AESON B.V and further reported in Appendix III. The scope of such an investigation is focussed on evaluating the performance of laser welding through the thick elements, the middle-cookie geometry, as well as through void cavities, such as the bridge channels. As illustrated in *figure 30* samples are oppositely machined and polished at the surfaces in such a way to provide the best permeability of the laser through the material. Therefore, the third-party company performed the welding as accorded.

5.2.1 Material

Due to high operating temperature and chemical corrosion (SOURCE), the material choice of the cookies stack is limited to just two thermoplastic polymers: polysulfone (PSU) and polyphenylene Sulfide PPS. However, to effectively perform laser welding the material must be transparent to the laser beam wavelength. This requirement excludes PPS because of its semi-crystalline structure. Hence, the polymer results opaque and the laser beam does not pass through-thickness higher than 2 mm (Troughton, 2009). Conversely, PSU is an amorphous thermoplastic and its microstructure allows easier penetration of light with a lower refraction rate.

5.2.2 Results



welded sample

figure 30 Weld test samples

broken weld

As shown in *figure 30* the welded samples show a visible contour at the interface. Although the not homogeneity of the weld, which appears inconsistent along the path, the pieces are firmly connected and not separable by hand. However, as the sample has been clamped to perform a tensile test, the weld broke showing a not effective bonding of the parts. The performed welds were not successful along the entire contour of the sample. Some areas seem to have reached the expected fusion of the material, however, they were too small and localised on a single spot. Through microscopic imaging it has been possible to identify three different surface characteristics: partially welded, superficially molten and not affected.

Partially welded 5.2.2.1

The connected areas are characterised by a fragile fracture of the thermoplastic. However, as shown in figure 31 the contour is not completely connected and areas with not effective bonding are present.



figure 31 Microscopic imaging of partially welded sample

5.2.2.2 Superficially molten

Although other parts of the contour show no effective welding, the surface results affected by the laser (*figure 32*). Indeed, the surface slightly melted as microbubbles are visible microscopically. However, the lack of temperature and pressure in the region did not allow any effective connection between the two parts.



figure 32 Microscopic imaging of superficially molten sample

5.2.2.3 Not-affected

Areas of the contour show no macro surface alterations. Indeed, although there is a visible burn trace of the laser beam in *figure 33* the surface texture did not reach the melting temperature and traces of previous polishing processes are still visible.



figure 33 Microscopic imaging of not-affected sample

5.3 Discussion

Although the performed tests are not completely successful, the preliminary tests show promising development. From the gathered results it is possible to assert that laser welding is a feasible technique to adopt. Indeed, as investigated it is feasible to perform welds through thick PSU components up to 10mm. However, further welding parameters must be optimised together with the geometry to achieve a consistent bonding along the wanted bonding area. Firstly, due to the high-temperature resistance of the polymer (Sastri, 2010) laser parameters, such as power and speed, must be further optimised. Secondly, to effectively focus the laser beam at the interface, very high precisely manufactured components are required. The provided samples have been manufactured by hand, therefore, the precision of the part may not be sufficient. Indeed, little surface imperfections could affect the welding performance resulting in a not completely homogeneous bonding. Because of this, the surface must be smooth at the interface with flatness tolerances of maximum 0,1mm at the interface (LPKF, 2018). At last, the conducted experiment took into account the bonding of just two parts. Hence, further tests are required to assess the feasibility of joining multiple elements.



figure 34 Diagram of the experimental setup for diaphragm airtightness

6. Cell airtightness

Besides the leak tightness of the stack towards the outer environment, the alkaline cells must embody airtight cavities to avoid hazardous reactions due to gas mixing. Therefore, as previously described in *4.2.3* the diaphragm must be placed in between the middle cookies to cover the entire electrodes' surface. Such selective membrane divides each alkaline cell in half avoiding the passing of gases while allowing the flow of ions between the electrodes. Therefore, it must not move, break or create any possible leak of gas between the anodic and cathodic sides of the cells. The common method adopted in industry for integrating such components is by tightly clamping the membrane between two bipolar plates (Millet and Grigoriev, 2019). Alternatives to co-moulding the membrane within the cookie are investigated and reported in Appendix II. Although the membrane is made of the same polymer as the electrolysis stack, it does not result suitable for injection moulding. Reasons for this are the presence of water in the membrane, the high temperature of the process and the difficulty of placing such a flexible material within the mould. Therefore, such direction has been discarded and further investigations regarding the clamping requirements are planned. Reason for this is the lack of information concerning the clamping forces required.

A brief investigation is conducted to assess the optimal clamping pressure over the diaphragm which provides the airtightness of the cells.

6.1 **Problem identification**

Within the current middle cookie geometry, the diaphragm is kept in place by the cookies and the electrodes. As it is shown in FIGX, the middle cookie design includes a clamping feature along the whole membrane's edge. In such a way the diaphragm is kept in place as the cookies are press-fit together. The compression of the d for the state of the art is 0.1mm. Such a mechanism consists of a flat surface, therefore, the pressure is homogeneous over the entire clamping area. However, providing a not correct clamping pressure could be very dangerous. In fact, by applying not enough pressure, gases can effuse across the cell. On the other hand, too much pressure could tear the diaphragm over time, creating harmful ruptures. To assess the required pressure to avoid any gas leaks an experiment is conducted. Similarly, the compression rate of the diaphragm has been verified retrieving the ideal dimensioning of the clamping mechanism

6.1.1 Zirfon Perl UTP 500

The diaphragm currently adopted is Zirfon Perl UTP 500 and it is supplied by AGFA. This product offers great performances, which allow increased efficiency and longer lifetime. Because of these reasons, this type of diaphragm is widely applied in the electrolysis industry (AGFA, 2019).

6.1.1.1 Diaphragm characteristics

Zirfon Perl consists of a fine woven mesh of polysulfone (PSU) coated with zirconia powder. Such a composition makes the diaphragm a selective membrane with a porosity of 50%. The pores are Ø 0,15 µm in diameter which allow the exchange of ions across the separator while avoiding any passage of gases. The total thickness of the separator is just 0.5mm, extremely efficient for zero-gap applications. The peculiar composition of this material makes it very hydrophilic. Zirfon Perl must be handled with care as it must not be crumpled or dried. Hence, it must be conserved in a humid environment in a temperature range between oC and 40C to prevent cracks (AGFA, 2019). Furthermore, the maximum operating temperature is 120C, far above the operating temperature of the electrolysis unit in the development.

6.1.1.2 Mechanical properties

Because there is no technical information regarding the mechanical behaviour of the material, the properties of the diaphragm have been assessed through a compression test with Zwick/ Roell equipment. As investigated, the membrane shows a linear behaviour at compression with a compression rate of 0,09mm/MPa (*figure 35*) Such data is used to retrieve the optimal compression rate based on the clamping pressure requirement.



figure 35 Mechanical behaviour of Zirfor Perl under compression

6.2 Clamping pressure

Additionally to the leak tightness of the stack at high pressure, the membrane must provide the airtightness of the cells at a lower pressure difference. Indeed, between the cathodic and anodic side of the cell, a slight pressure difference is applied. Reason for this is the difference in water level maintained at the downcomers which creates a pressure difference between the anodic and cathodic sides of the order of millibar (Appendix I). To ensure the safety of the unit, it has been defined as a requirement that the membrane must be airtight at 0.5 bar.

6.2.1 Experiment

To assess the required clamping pressure for airtightness of the diaphragm an experiment has been conducted by simulating the physical situation with the available equipment. Therefore, a specific ground test has been developed simplifying the geometry. The resulting setup in *figure 36* consists of two aluminium elements which are tightly fastened in the testing equipment, Zwick/Roell. The base has been developed to retain water in such a way to completely submerge the membrane. Conversely, the top part embodies the water connection as well as the air inlet. Furthermore, an additional part made out of PSU resembles the clamping surface. This element is directly screwed onto the top part and resemble the cell chamber. The experiment is conducted by placing the membrane on the bottom

element and submerged it with water. Therefore, the membrane is pressed with the predefined force and air pressure is applied inside the chamber. The airtightness of the setup is evaluated by observation. As no bubbles were formed at the clamp edge, the system is considered airtight. The test is run with different clamping forces from 20 to 500N



bubbles are present

bubbles are not present



6.2.1.1 Considerations

Due to lack of time and equipment, few considerations regarding the accuracy of the conducted test. Indeed, it has not been possible to conduct the test at the operating temperature. Therefore, it is warmly recommended to run a further investigation to determine more accurate and relevant data. Furthermore, although great care and accuracy have been put in machining the test setup, few mistakes and imperfections may still be present as it is handmade.

6.2.2 Results

As observed through multiple tests, the setup results airtight for clamping forces higher than 150N. Therefore, the general pressure required to make the membrane completely airtight is 0.85 MPa. Furthermore, because of the pressure provided over the clamping edge the diaphragm plastically deformed and a clear ring is evident on the surface.

6.3 Discussion

The test confirmed the possibility of making the separator air-tight with a pressure difference over it of 0,5bar. Specifically, the pressure to apply over the diaphragm must be higher than 0,85MPa. Therefore, given the compression rate retrived in *6.1.1.2*, the required compression of the diaphragm is of 0,08mm over the entire contour. Because the separator is present in each cell, the required clamping force is proportional to the number of the electrolysis cells included in the stack. Therefore, by reducing the clamping area it is possible to reduce the overall clamping strength.



figure 37 State of the art of the middle-cookie geometry (V1)



figure 38 Thickness distribution in middle-cookie V1

7. Geometry optimisation

The electrolysis stack developed by ZEF foresees the adoption of modular elements, cookies, piled together to create the required electrolysis geometry. However, the developed design is not optimal for mass manufacturing techniques. All the parts have been machined from solid pieces by using a computer numerical control (CNC) machine. The reason for this is the freedom of machining very complex geometries. However, such a process is very time consuming and expensive. To contain costs, a viable alternative consists of injection moulding the parts. This technology allows the production of relatively complex and very precise geometries while being truly cost-effective on a large scale. However, injection moulding requires specific requirements in terms of thickness, draft angles and undercuts to effectively form the components (RTP, 2017). The current cookie design does not completely satisfy those requirements. Specifically, the thickness of the part is too large and non-homogeneous through the whole geometry. Furthermore, tiny geometries, such as the bridges, within the cells are either very expensive and challenging to manufacture. Nevertheless, injection moulding elicits the possibility to integrate components in the forming process itself, simplifying further assembling steps.

Due to time limitations, the following chapter takes care of the manufacturability of the middlecookie. Reasons for this rely on the variety of challenges the middle cookie offers, specifically regarding the bridge channels and the integration of multiple components. Therefore, a preliminary analysis of the geometry under examination is exposed, pointing out the current issues and limitations. Hence, novel proposals are developed, discussed and further iterated.

7.1 Middle-cookie - V1

The state of the art of the middle-cookie in *figure 37* includes multiple cavities interconnected in such a way to separately collect oxygen and hydrogen as well as integrate electrodes and diaphragm in a zerogap configuration. However, the geometry presents some issues which affect the safe operation of AEC as well as its feasibility on a large scale production for injection moulding.

_			
•	material	S	HDPE
•	diameter	mm	97
•	thickness	mm	15
•	volume	mm³	58
•	cell area	mm²	35

table 4 Middle-cookie V1 main dimensions

A detailed analysis of the geometry has been reported in Appendix I. In *table 4* are collected the main dimensions of the state of the art of the middle-cookie. This preliminary component geometry is referred to as the first version, V1, of the electrolysis cell.

7.1.1 Design requirements

The following paragraph aims to describe the mismatched requirements of the geometry under examination. Specifically, these issues consider the thickness of the part, the lack of draft angles in the design, the connection and support of the electrodes as well as the manufacturing of the bridge geometry.

7.1.1.1 Thickness

The thickness represents the primary limitation for injection moulding the part. Besides features with present excessive thickness, higher than 10mm (*figure 38*) the geometry does not have a homogeneous distribution of material. Most of the material is localised at the outer rim, where the sealing is placed. Indeed, guidelines for thermoplastic moulding suggest the designing of parts with

as much as possible thickness uniformity. Furthermore, the thickness range must be in between 1 and 5 mm depending on the material in use RTP (2017). Reasons for this are to decrease cooling time and, therefore, production cost. Furthermore, this helps to avoid non-uniform shrinkages, which could lead to macro warpages of the part itself.

7.1.1.2 Draft angles

Draft angles are essential for injection moulding. Such a feature allows easy ejection of the part from the mould. According to RTP (2017), a minimum draft angle of 0,5° is required for effective part removal. Furthermore, the lack of draft angles in the current design exposed difficulties during the assembling procedure as the fitting element had a very tight tolerance to avoid leaks (Appendix I).

7.1.1.3 Electrodes supports and connection

The current design does not foresee any integrated support for the electrodes. Indeed, the electrodes are bent at the corners to fit the cell. However, such a method is not effective to provide a zero-gap configuration of the electrolysis cell. Furthermore, the current electrical connections are created from simple stainless steel rod, directly screwed through the cell wall. This method does not guarantee the leak tightness either a precise and reliable connection with the electrodes (Appendix I).

7.1.1.4 Bridges

The bridges consist of essential feature wich avoid current leaks between the electrolysis cells which must satisfy dimensional requirements diameter and length of 10 (Appendix IV). In V1 such a geometry is achieved by drilling the hole in an angled direction. The reason for this is providing the required length of such a channel as well as avoiding overlapping the diaphragm, as it could cause gas leaks. In terms of the injection moulding process, this feature implies several challenges since holes of such dimensions are not recommended. The tiny pins adopted for the creation of this geometry could easily deform and break due to fatigue.

7.1.2 Investigation goals

To design a feasible geometry of the electrolysis cell for injection moulding, the next iterations should resolve the discussed issues. It is required to have a much more homogeneous material distribution as well as including draft angles. Furthermore, the geometry will include elements for the correct alignment and support of both electrodes and membrane. Similarly, a co-injected electrical connection will simplify further integration and assembly procedures. Moreover, the novel proposals should integrate the bridge channels in a manifold and manufacturable geometry.

7.1.2.1 Preliminary bridges ideas

Given the challenge of integrating the bridges within the electrolysis cells, preliminary ideas are generated to evaluate feasible alternatives. Indeed, the difficulty of such geometry is given by its dimensional requirements. Furthermore, the position of such a connection must be placed at the very top of the cell to avoid eventual air gaps within the cells. The developed ideas foresee different methods for manufacturing the channels. Two preliminary ideas are achieved by adopting undercuts and on surface grooves as well as additional parts.

- Undercut and on-surface channel

This idea foresees the combination of an undercut to avoid overlapping the membrane and an on-surface channel geometry to provide the required length. However, such a method is achievable only through laser welding. Furthermore, dimensions of the channel are much limited and channels longer than 10 mm. Longer channels on the surface imply more material and, therefore, the larger thickness of the component.

- Additional element

This bridge design overcomes dimensional limitations of the previous ideas. According to a later

analysis (Sriram, 2019), the channels' cross-section must be larger than O1,5mm to avoid bubbles obstruction. The additional element elicit greater geometry freedom and it is directly welded to the middle cookie. However, this feature does not specifically require laser welding, ultrasonic welding can be chosen as a cheaper alternative.

7.2 Middle-cookie iterations

From the analysis of the V1 design, several iterations have been developed to optimise the geometry for the moulding process. The iterations are progressively identified as V2, V3 and V4 (*figure 39*). and further discussed in Appendix II. The following paragraph aims to evaluate the feasibility of the designs for injection moulding to assess the most viable. The main geometry's features are exposed, including the envisioned method for integrating the electrolysis components as well as the bridge geometry. Therefore, a simulation of the geometries is conducted to assess the good design of the cell. Such analysis takes care of the cooling time as well as eventual warpage and shrinkage of the geometry.



figure 39 Design iterations of the middle-cookie

7.2.1 Design features

As previously discussed in *4.4.2*, the flash tanks are removed from the electrolysis stack due to safety measurement and, therefore, from the middle-cookie geometry. Because of this, the top channels are much smaller, allowing to increase the reactive surface, which is almost two folds compared to V1 for the next iterations. Similarly, V2, V3 and V4 are as much as possible symmetrical, beside the electrical passthrough. They all include four bridges, two for each side of the cell to avoid current leaks. The cookie integrates a single electrical passthrough as well as supports for the electrodes.

7.2.1.1 Symmetry

Top and bottom channels have the same dimensions and the design is symmetrical. In V2 and V3 the electrical connection is shifted towards the bottom to allow the injection point right in the middle of the geometry. Conversely, in V4 the connection is moved towards the right side. Such a feature allows a more homogeneous flow of the plastic to the outer rim, especially towards the channels.

7.2.1.2 Bridges

The V2 and V3 design includes on-surface bridges with an undercut to avoid the membrane overlapping, as discussed at *7.1.2.1*. Hence, to match the dimensional requirements the channels extend on a waved path. Conversely, V4 adopts an additional element to create the channel. In this case, the design includes four elements welded to the electrolysis cell to shut the channel.

7.2.1.3 Seals

All designs foresee the use of laser welding for both outer and inner seals. Reason for this is the high precision and quality of the technology which can perform the sealing of the bridges channels layout.

7.2.1.4 Material

The chosen polymer for all the proposals is polysulfone (PSU). Reason for such a decision is the resistance such a polymer offers to chemical corrosion and mechanical performances at high temperatures. Furthermore, the sealing of the electrolysis stack is achieved through laser welding, which is only possible with PSU as discussed at *5.2.1*.



figure 40 Design iterations of the middle-cookie

7.2.2 Simulation

A finite element simulation has been run by Promolding B.V. to assess the feasibility of the developed geometry through injection moulding. The analysis of the part considers the time required for cooling as well as deformations in terms of surface displacement and geometry warpage. These criteria are very much dependent on the part thickness and topology. Furthermore, they give relevant insight into the cost and assembly feasibility of the middle-cookie.

7.2.2.1 Cooling time

Cooling time is the first indicator of a well-designed part as it is a direct symptom of thickness homogeneity. Furthermore, reducing cooling time largely affects the cycle time of the part drastically decreasing the costs. V2 required 89s to reach the temperature for ejecting the part from the mould, while V3 and V4 recorded better time with 33s. This result shows an improvement in the cooling time of about 65% compared to V2.

7.2.2.2 Sink marks

Sink marks are a consequence of material shrinkage after cooling. Usually, such marks represent exclusively an aesthetic defect. However, because of laser welding requirements, the surfaces must

Investigated parameters	V2	V3	V4
• cooling time (s)	89	32 (-64%)	31 (-65%)
 max marks displacement (mm) 	0.21	0.12 (-42%)	0.12 (-42%)
marks displacement at welding surface (mm)	0.07	0.05 (-28%)	0.05 (-28%)
• warpage	present	not present	not present

table 5 Simulation results of middle-cookie iterations. V2, V3, V4

be as flat as possible with a maximum flatness tolerance of 0,1mm (LPKF, 2018). Due to the great thickness of the outer rim, V2 shows deformation of 0,07mm at the welding surface with peaks of 0,2mm around the bridges. The V3 and V4 designs present a more homogeneous material distribution. Indeed, the sink marks at the same surface decrease to 0,05mm with a maximum displacement of 0,12mm, almost half of the previous version.

7.2.2.3 Warpage

Lastly, similarly to sink marks, warpage is still a consequence of the material shrinkage. However, the warpage analysis considers the three-dimensional deformation of the part, assessing whether it uniformly shrink or not. Also, in this case, V3 and V4 proposals showed great improvements compared to V2. Indeed, as shown in fig.X, V2 warped while all V3 versions show even shrinkages without evident deformation.

7.3 Discussion

The simulation results show great achievements between the V2 and V3, V4 designs. Cooling time has been drastically improved. Specifically, both V3 and V4 show a reduction of cooling time of about 65% compared to V2. However, cooling time results quite long for an injected moulded part, 32-34 seconds. The reason for this is the high temperature required to form such a high-performance thermoplastic as well as the dimensional requirements to withstand the operating stresses.

Furthermore, shrinkages and sink marks show evident improvements. Maximum displacement has been halved from V2 to V3 and V4 with slight improvements of the sink marks. Such an achievement ensure more suitability of V3 and V4 for laser welding

Unlike V2 geometry, no evident warpage is present in the V3 and V4. Despite the promising results, few elements of the parts result difficult to implement for injection moulding. In the first place, thickness homogeneity of the component can be improved to further reduce cooling time and therefore costs. Furthermore, the bridge channels of V2 and V3 are very challenging to manufacture due to the high complexity of the mould. Reason for this is the need for a slide per channel to perform the undercut, a factor which increases the mould cost, ejection time and risk of failure. V4 offers a viable alternative to reduce such an aspect, however it requires further assembling steps to create the bridges.

8. Pressure case

The pressure case is an essential component of the AEC unit. Its main function is to embody the cookies stack while providing mechanical support. Even small material displacements of the electrolysis stack, due to high temperature and pressure, could compromise the leak tightness of the unit as well as its safe operation. Because of this, the case must not deform under the pressure load and tolerances between the case and the stack must be as tight as possible.

Firstly, the case design and relative mechanical stresses due to pressure is further investigated. The analysis aims to define the safe wall thickness of the case in the case of different materials alternatives as well as the required clamping force to ensure the right fit of the cookies stack. Furthermore, the case must not fail in a brittle manner. Indeed, brittle fracture causes the sudden failure of the unit which has to be avoided under all circumstances. Therefore, the case must not be affected by any kind of corrosion by chemicals or environmental agents, which could modify material performances.

Lastly, suitable materials are proposed for the previous results. Likewise, production methods are investigated to define the most viable option in terms of cost and part accuracy.

8.1 Case design

The pressure case adopted for the state of the art consists of an extruded stainless steel pipe, of which the closing mechanism has been achieved by welding two collar clamps at the extremities. However, this design choice is not optimal not only for its functions but also for costs. As resulted from the investigation of the current design, the pressure case cannot effectively embody the stack due to dimensional requirements (Appendix I). Furthermore, the clamping mechanism adopted does not provide an easy and effective press fit of the electrolysis stack. At last, the choice of stainless steel severely increases the cost without adding additional functionalities.

The following paragraphs investigate the stresses the pressure case endures over its lifetime, both from a mechanical and chemical perspective. Therefore, materials suitable for the pressure case are discussed.

8.1.1 Mechanical stresses

The mechanical load of the pressure case resembles a pressure vessel. Indeed, assuming the complete leak tightness of the cookies stack, the stress is homogeneously spread over the entire case surface. Hence, given the cylindrical geometry, the investigated stress can be divided into radial and axial stresses. To satisfy the requirements, two essential elements must be ensured: the thickness of the case and the required clamping force for tight pressing the cookies stack.

8.1.1.1 Radial stress

To endure the radial load given by the inner pressure without plastically deforming, the case must be properly designed. Specifically, the case thickness must provide support to the electrolysis without overreaching the yield strength of the material. Hence, depending on the material the required thickness must be obtained. Because the case exhibits a rotationally symmetric geometry, it is possible to retrieve the thickness with the hoop stress formula (Pilkey, 2010). In this case, the formula in use is expressed as follows.



figure 41 Middle-cookie V1 main dimensions

$$\sigma = \frac{r \cdot P}{t \cdot S_f} \longrightarrow t = \frac{r \cdot P}{\sigma \cdot S_f}$$

Where t is the thickness of the material, p is the inner pressure, r is the radius of the cylinder, σ is the stress and S_f is the safety factor. As discussed at 4.4.2.2, possible materials for the pressure case are steel alloys, composite materials and thermoplastic polymer. Therefore, the required thickness of the case has been calculated for each material scenario (*table 6*). The calculation takes into account an inner pressure of 70bar, 7MPa, directly acting on the pressure case, without considering the mechanical load held up by the cookies stack itself. Furthermore, a safety factor of 2 has been included in the calculation.

Material	Thickness	Cost		
	(mm)	(€/dm)	(€/kg)	
ultra low carbon steel (ULC IF)	2,2	5,2	0,7	
 low carbon steel (AISI 1008) 	2,0	5,2	0,7	
 high carbon steel (AISI 1008) 	1,4	5,7	0,7	
fiberglass composites	1,2	50	24	
carbon fiber composites	1,1	62	31	
• polyphenyle sulphide (PPS)	10	6,5	5	
· polysulfone (PSU)	10	14	11	

table 6 Pressure case thickness per material

8.1.1.2 Axial load

Similarly, the case must ensure the pressfit of the cookies to avoid leaks. Therefore, the clamping force required not only has to overcome the force given by the internal pressure of 50 bar, but also provide additional compression force for sealing features, such as gaskets and diaphragm. The resulting force is given by the following formula.

As a result, the total clamping force required to ensure a leak tightness of a stack of 20 cells is in the order of 70kN. However, by adopting welding techniques to join the electrolysis stack it is possible to reduce the axial load of about 10-15%. As discussed in *5.1.1.1* and expressed in *table* 7, welding not only avoids the compression of gaskets but it also provides mechanical strength. Furthermore, because the force given by the inner pressure is proportional to the area, the geometry division severely affects the clamping force. Indeed, by splitting the cylinder with a vertical plane the cross-section always remains a circle of the same surface area. However, by dividing it with a horizontal plane the cross-



figure 42 Geometry division and force direction.

Forces	Case 1 (kN)	Case 2 (kN)	Case 3 (kN)
Inner pressure	55	55	167
Seal compression	11	-9	11
Membrane compression	6	0	6
Required clamping force	72	46	167

table 7 Clamping force require for the selected cases

section increases proportionally to the cylinder length (*figure 42*). Three cases have been distiguished fot the force calculation. The first two cases foresses a vertical dvision of the case. The difference between these case is the envisioned sealing method for the electrolysis stack. Case 1 includes gaskets, therefore it requries additional force to ensure the leak-tightness. For the case 2, the electrolysis stack is welded, drastically reducing the clamping force required. The third case has horizontal division. The result is essential to estimate the number of bolts to avoid plastic deformation of the same. In *table 8* are presented the possible bolt configuration, in terms of bolts' type and property class, for safely close the unit.

Bolt type (metric)	Property class (ISO 898)	Case 1 n	Case 2 n	Case 3 n
· M6	8.8	8	6	20
	9.8	8	6	18
	10.9	6	4	14
· M8	4.8	10	6	16
	5.8	8	6	16
	8.8	6	4	12
• M10	4.6	8	6	18
	4.8	6	4	12

table 8 Possible bolts configuration based on bolts' type and property class

8.1.2 Material corrosion

Furthermore, the case will be exposed to different elements and chemicals throughout its lifetime. This process, or material ageing, could negatively affect the mechanical properties of the material and its performances over time. As a consequence, the case could fail before the estimated end of life. Therefore, possible elements which could affect its lifetime operation are distinguished into the environmental agent and chemical ageing discussed as follows. The materials compartibility is collected in *table 9*

8.1.2.1 Chemicals

The case will not be directly exposed to any corrosive element. All chemicals are retained within the cookies stack, therefore, the case does not get in direct contact with the electrolyte, hydrogen nor oxygen during operation. However, hydrogen diffuses through the stack and the case itself due to the small dimension of the gas molecule H_2 . The consequence of such a process on materials is the effect of hydrogen embrittlement, especially relevant in metals. Indeed, at high temperature and pressure hydrogen combines with carbon present within metals producing methane. Since methane molecules cannot escape they accumulate creating voids in the material. Over time, this process severely decreases the material's strength and ductility to the failure point (Birnbaum, 2001). Furthermore, potassium hydroxide adopted as an electrolyte is very corrosive and it reacts differently with materials. Therefore, materials which would severely react with KOH, such as aluminium, are excluded. (Graco, 2013)

8.1.2.2 Environmental agents

The case consists of the outer element of the unit, therefore, it will bear environmental agents, such as air, humidity and sunlight. These factors can act differently depending on the material. Indeed, most steel alloys oxidize while thermoplastics are more sensitive to UV light. Therefore, during the material choice of the concept development additional treatments must be taken into account.

Material	0,2	H ₂	КОН	H ₂ O	UV
• ultra low carbon steel (ULC IF)	+	+	-	_	++
 low carbon steel (AISI 1008) 	+	-	-	-	++
• high carbon steel (AISI 1008)	+		-	-	++
 stainless steel 	++	+	+	++	++
fiberglass composites	+	++	+	++	_
carbon fiber composites	+	++	+	++	-
• polyphenyle sulphide (PPS)	+	++	+	++	—
• polysulfone (PSU)	+	++	++	++	-
· EPDM rubber	+	+	++	++	-

++ : Excellent + : Good - : Fair to Poor - - : Not recommended

table 9 Material compatibility (Graco, 2013) (Engineeringtoolbox, 2003)

8.2 Material choice

The metal used for the pressure case is currently stainless steel. Such a steel alloy has great resistance to the electrolyte as well as to the environmental conditions. However, it is a very expensive alloy. Hence, cheaper alternative materials have been investigated either among steel alloys as well as thermoplastics and composites.

8.2.1 Steel alloys

Among steel alloys, high carbon steel offers the best mechanical performance, requiring almost half of the thickness of low carbon alloys (*table 6*). However, the alloy has a high concentration of carbon, between which speeds up the process of hydrogen embrittlement. Conversely, low carbon steels have much lower carbon. specifically, ultra low carbon alloys without IF are the most suitable option in case of steel. Indeed, ULC IF are four times as cheaper as stainless steel and much more ductile, making them easy to form. However, these alloys are affected by environmental agents. Therefore, a protective coating, such as galvanisation, is required to ensure the lifetime operation. The considered manufacturing processes for the metal case is multi-stage deep drawing.

8.2.1.1 Multistage deep drawing and ironing

Deep drawing is a widely adopted method for creating geometries from sheet metals. The process consists of plastically deforming thin metal to the desired shape. This process is very fast and costeffective, resulting in an optimal technique for large scale production. Limit of such a technique is

given by the limit drawing ratio (LDR). LDR is equal to the ratio between the diameter of the starting blank diameter and the final one. Such a value is used to define the maximum length of the geometry to avoid fractures during production. Multistage deep drawing allows reducing the stress within the material through heating the part between each step. Furthermore, ironing is also adopted to increase the length of the part while reducing the wall thickness. Also in this case limits of the process has a limit ironing ratio (LIR) According to Parida et al. (2017), a 3-stage drawing process permits the formability of medium carbon steel with LDR= 2,06 and LIR = 3,55. Additionally, the ironing process will increase material properties due to strain



figure 43 Example of deep drawn shapes

hardening. Lastly, the ratio between the width and the length of the product as well as the radius of the corners must be 5 folds the sheet thickness (Thompson, 2015).

8.2.2 Thermoplastic polymers

High-temperature thermoplastic polymers could be an advantageous alternative for case development. Reason for this is the precision of the moulding process as well as the same or close thermal expansion of the material to the cookies stack. Furthermore, it elicits the possibility to create more complex geometries and embed further components within the moulding process, with a consequent reduction of the assembling time. Downsides of such materials are cost and stress conditions. Indeed, polymers which can withstand high temperatures, such as PPS, PSU and PEEK, are very expensive. Moreover, even though the considered thermoplastic are engineered to withstand high-temperature operations, given the extreme stress conditions, the material is very likely to deform due to creep over time.

8.2.2.1 Injection moulding

Injection moulding is the optimal process for shaping precise components with thermoplastics. Indeed, adopting the same production method elicits the production of components with equal quality and tolerances. According to RTP (2017), injection moulding requires relatively low thickness and as much as possible homogeneous of the geometry. However, as previously discussed, to withstand the mechanical stresses during operation the thermoplastic case must have thickness higher than 8mm. Therefore, to make it suitable for injection moulding, ribs must be included in the design in such a way to match both safety and mechanical and production requirements.



figure 44 Example of structural ribs in thermoplastic forming

8.2.3 Composites

Composites materials offer optimal mechanical properties as well as high-quality components. Furthermore, they are extremely light and do not suffer corrosion by environmental agents. These materials also behave very well at high operating temperatures. However, the main disadvantage of composites is the cost of both the material and the production processes, which is time-consuming and makes the material hardly recyclable. Furthermore, epoxy resins are vulnerable to UVs, making composite materials not optimal for external applications without any surface protection (Nikafshar et al., 2017).

8.2.3.1 Vacuum bag

The considered production process for composites material is vacuum bag. The reasons for this are the precision of this method as well as the possibility to create complex geometries such as flanges. Additionally, the process does not require expensive nor complex tools. However, it is very labour and time consuming, a factor which severely affects costs (Centea & Nutt, 2015).

8.3 Discussion

Among the considered materials ultra-low carbon steel represents the most viable alternative. The reasons for this are the low cost of the material compared to its mechanical properties, as well as the extreme ductility which allows the shaping of precise and long geometries through deep drawing. However, due to environmental conditions, carbon steel alloys require surface protection. Therefore, a galvanisation coating is required.

Conversely, plastic allows the production of more precise components. Furthermore, it is possible to embed components during the forming process, simplifying the assembling procedure. However, because of the operating conditions, a plastic case must have walls five times thicker than low carbon steels. Furthermore, plastic is very likely to deform over time due to creep.

Compared to thermoplastics, composites, such as carbon and glass fibres, offer far better mechanical properties, resulting in lighter and more robust alternatives. The forming process ensures the quality and precision to safely embody the electrolysis stack. However, composites are expensive to adopt. The cost derives both from the material and the forming process. Composites require manual labour resulting in a very time-consuming procedure. Lastly, composites suffer from material degradation due to sunlight exposition. Therefore, it is expected the mechanical properties will decrease over time.

This section presents the conceptual development. The scope is to elaborate the gathered information, either from the analysis and tests, into design proposals of the components under examination (4.4.1).

Ideas are developed to comply with the investigated issues and requirements. from the functional analysis of the components. Solutions are explained, described and assessed through univocal criteria. Therefore, a morphological chart collects and clusters the ideas to further develop the conceptual proposals.

Hence, preliminary concepts are achieved by matching the developed ideas in such a way to build coherent concepts. The results are further evaluated by adopting different methods. At first, a weighted objective evaluation is adopted to assess the concept through the defined criteria. Therefore, a cost analysis of the concepts considers materials and production methods. A final comparison with the unit requirements defines whether the developed designs are viable for the integration within ZEF's microchemical plant.



concept development



figure 45 Morphological chart with ideas evaluation

9. Ideation

Ideation phase aims to elaborate alternatives to solve problems and satisfy the functions of the considered product. In this case, the ideation phase is developed from the basic functions and subfunctions of the AEC (4.1.1). The goal is, therefore, to create multiple solutions for each subfunction. The resulting ideas are collected in a morphological chart and evaluated. In such a way it is possible to further select and cluster them to shape multiple concepts.

9.1 Design focus

As defined in *4.4.1*, the design focus considers the development of the electrolysis stack, the electrolysis cell and the pressure case.

9.1.1 Electrolysis stack

The main function of the electrolysis stack is to provide a leak-tight geometry which embodies all electrolysis cells and relative components. Therefore, these elements must be joint together in such a way to provide reliable and effective sealing over time. Furthermore, ideas alternative to cookie design as discussed together with alignment methods.

9.1.1.1 Material

The material choice for the electrolysis stack has been limited to just two options: PSU and PPS (4.4.2). These two thermoplastic polymers provide great performances at high temperatures as well as good chemical resistance.

9.1.1.2 Seals

The possible sealing methods investigated consists of welding together the electrolysis stack as well as integrating gaskets. EPDM gaskets are the most common adoption in the industry, however, by co-moulding the rubber (Caamano, 2002) could facilitate further assembling processes. Advantages of welding are the mechanical fastening and sealing effectiveness provided by fusing the material. Additionally, it elicits the creation channels between two flat surfaces (*5.1.1.1*). Conversely, with gaskets will be possible an easier disassembly of the unit for refurbishment and recycling.

9.1.1.3 Element subdivision

The current unit subdivision is through cookies. As discussed in (4.4.1.2) resembles the bipolar configuration adopted in industry. The main advantage is the inclusion of further elements besides the electrolysis cell, i.e. flash tanks and downcomers. However, by deconstructing the geometry it is possible to increase part quality and geometry freedom while decreasing the complexity of the assembly and cost. The great challenge of doing so is to ensure a leak-tight environment.

9.1.1.4 Sensors and connections integration

Sensors and connections must be integrated within the geometry ensuring the leak tightness of the parts and overall assembly. Therefore, both fluid and electrical connections are envisioned to be directly co-moulded during production. Furthermore, their placement can vary the unit accessibility, affecting assembling process, installation and maintenance. Conversely, for more fragile components, such as sensors, pockets must be specifically designed to include them.

9.1.2 Electrolysis cell

The electrolysis cell, or commonly referred to as the middle-cookie, consists of the component in charge of embodying all electrolysis components, such as membrane and electrodes. Hence, methods to safely integrate such components within the series of cells are proposed. Furthermore, the geometry must provide all fluid connections while avoiding any current leaks between the cells.

9.1.2.1 Diaphragm integration

As discussed in chapter 6, the integration of the diaphragm is essential for maintaining the airtightness between the cells and therefore ensuring the safe operation of the unit. Methods to integrate such a component foresees the placement of such a component directly between the cookies as well as inserting it in a frame which can simplify the assembly process. Furthermore, to reduce the clamping force it is possible to localise the pressure by including rib along the clamping surface.

9.1.2.2 Electrodes integration

As investigated in (3.2.2.2), multiple electrodes structures are currently in the industry. The most common options are represented by the perforated and expanded mesh, as they are cheap to produce and manage during assembly. Furthermore, these geometries permit an easy plating procedure, eliciting the adoption of cheaper materials. Woven mesh could result in a viable option as they can reach lower thickness while maintaining an equal reaction surface. However, it results hard to manage and fasten during the assembling without further support. Ultimately, metal foams result in an effective option to simplify the electrical connection. Indeed, depending on the electrodes' structure, the method of safely integrating them within the unit changes. Because expanded and woven meshes do not offer any precise or flat surface, the most reliable method is by directly welding them to the electrical connection. However, such a method can locally affect the quality of the plastic part. Differently, by properly designing the perforated mesh it is possible to fasten it through screws. Due to the compressibility of the metal foam, it is possible to just press fit it in between the middle cookies ensuring a reliable electrical connection and simplifying the assembling process.

9.1.2.3 Bridge channels

Therefore, the creation of these small channels has represented a great challenge for the optimisation of the middle cookie geometry. Indeed, as discussed in chapter 7, the integration of such small geometries can result quite troublesome, especially in terms of costs and part feasibility. The methods proposed include the integration of the bridges on the surface between the cookies, by exploiting the feature of laser welding for sealing the channel contour as developed for the middle cookie V3 (7.2.1.2). A feasible alternative is represented by adopting welded cover plates as investigated in the last middle cookie iteration, V4. Ultimately, it is possible to create the required geometry by properly deconstructing the functional geometries. In such a way it is envisioned to simplify the overall geometry complexity, however, it largely affects the sealing of the geometry.

9.1.3 Pressure case

The main functions addressed to the pressure case are supporting the electrolysis stack in terms of the mechanical stress as well as connecting the unit to the chemical plant. Hence, the correct dimensioning of the case is of extreme importance to provide the sufficient support of the cookie stack. Because of these reasons, the elements considered for the pressure case ideation are the material, the geometry subdivisions and the clamping mechanism.

9.1.3.1 Material and manufacturing

As discussed in chapter 8, multiple materials are suitable for the case design. Important factors in this choice are the corrosion resistance to chemicals and environmental agents to ensure a lifetime operation of 20 years (Appendix IV). Furthermore, the geometry must be feasible for large scale
production. Indeed, this drastically affects the overall cost of the unit. Steels alloys and composites offer the best mechanical properties compared to plastic, especially when exposed at severe pressure over high temperatures.

9.1.3.2 Geometry subdivision

As discussed in *8.1.1.2* the geometry division of the case affects the required clamping force. Furthermore, it also elicit different assembling procedure. The ideation phase includes two different geometry division. The vertical, as it is currently implemented in the state of the art, and horizontal.

9.1.3.3 Closing mechanism

The pressure case is closed by a clamping mechanism adopted for the state of the art of ZEF is collar clamps. Conversely, the industry has widely adopted threaded rods to employ the right pressure through the entire stack. Reason for this is the higher precision and strength provided by such an option. However, treaded rods are Hence, every concept adopts bolts to provide the correct clamping force.

9.2 Criteria

To further evaluate the proposed conceptual ideas, criteria have been retrieved from the project demands and requirements. As discussed in *1.2* the main design goals are to develop a cost-effective and safe unit. Cost and safety represent the most important criteria, therefore, they have been assigned the highest value, 3. Next, feasibility through the proposed production method has been weighted with 2. Similarly, lifetime is considered as criteria ad it is an essential demand for its safe operation, the given weight is 2. At last, the effectiveness of the

Criteria		Weight (pt)
	COST	3
•	SAFETY	3
•	FEASIBILITY	2
•	LIFETIME	2
•	ASSEMBLY	1

table 10 Criteria and relative weights

assembly is considered. In this case, the value assessed for this criterion is 1 (table 10).

9.2.1 Assessment

The developed ideas have been evaluated per each criterion. The scale adopted is given by the hierarchal satisfaction of each group ideas. I.e, in case of n ideas the scale goes from one to n. The reasons for this are avoiding equal values as well as having an adaptive scale for each group of ideas. Hence, the final score of each proposal is achieved by multiplying its heretical value times the relative criterion weight. The sum of the obtain scores per each criterion gives the total points obtained. Becasue of this, the maximum score a concept can get is 180 point.

9.3 Discussion

This primary evaluation of the ideas it has been employed to effectively select the ideas for the concept development. Indeed, by combining ideas which performed the best per each criterion, it has been possible to discard the least effective. Consequently, different concepts are developed by following the chosen criteria. Hence, the costs and feasibility are specifically addressed in the first concept, while safety and lifetime have been further developed in the second. The third concept aims to achieve an easy assembly of the unit.

10. Concept development

As presented in *figure 46*, by combining the ideas collected within the morphological chart, three distinct concepts have been developed. Each concept has been elaborated in such a way to address specific requests. While the first concept aims to reduce the overall costs of the unit, the second concept's objective consists of constructing a very safe apparatus. At last, the third proposal has been constructed in such a way to be easier to assemble and to embody further components. The proposed concepts embody the same number of connections, therefore, these elements have not been included in the concept development.



figure 46 Morphological chart and idea selection for concept development

10.1 Money-saver



figure 47 Assembly of concept #1

10.1.1 Electrolysis stack

In this case, the material choice for the cookie stack is PPS. The reason for this is the lower cost compared to the other alternative, PSU. Therefore, as the material choice excludes the adoption of welds for sealing the stack, EPDM gaskets represent the most viable option. Similarly to the state of the art, this concept adopts the cookie concept press-fit together. The electrolysis stack is composed of a total of 12 cells to further reduce material.



figure 48 Electrolysis stack of concept #1



figure 49 Exploded view of electrolysis cell of concept #1

10.1.2 Electrolysis cell

The geometry of the cookie envisioned for this concept is V4 discussed in (7.2.1). Reason for this is the much simpler geometry developed compared to the V3. In specific, channels have been developed in such a way to better satisfy dimensional requirements as well as avoiding undercuts. However, this geometry requires additional parts which are welded on the cell itself through ultrasonic welding. The membrane is clamped in place between the cells and ribs on the surface of the cookie aim to increase local pressure and reduce clamping force while matching the airtightness requirement. Electrodes are made out of metal foam, which greater surface area permits to reduce the number of electrolysis cells, and, therefore, the overall material usage and dimensions. Because of this, the electrical passthrough consists of a large surface onto which the electrodes are tightly pressed allowing an optimal current distribution as well as a good contact. However, bubbles can get stuck within the electrode, reducing efficiency while increasing the eventual corrosion processes.

10.1.3 Pressure case

Due to cost reasons, the pressure case is made out of low carbon steel alloys. Indeed, it consists of the cheapest option and it offers very good mechanical properties. Although high carbon steel alloys provide better mechanical properties, they have been discarded as they are affected by hydrogen embrittlement. Furthermore, low carbon steel is much more ductile easing the production. Hence, the production process consists of deep drawing, as it is very convenient in terms of time and cost. Furthermore, such a production method elicits the integration of a clamping mechanism without the adoption of any welds. However, due to the forming process, the envisioned geometry includes a single opening for both placing the electrolysis stack and embodying connections.

10.2 The safe



figure 50 Assembly of concept #2

10.2.1 Electrolysis stack

This concept adopts the cookie roll concept for the geometry subdivision. However, to ensure the absolute leak tightness of the electrolysis stack, the elements are bound together through a laser welding process. Because of this, the cookies must be made out of PSU (*5.2.1*)



figure 51 Electrolysis stack of concept #2



figure 52 Exploded view of electrolysis cell of concept #2

10.2.2 Electrolysis cells

The design of the electrolysis cell is represented by the cookie V3 (*7.2.1*). Such a geometry foresees the integration of the bridge channels completely sealed through laser weld, ensuring a complete leak-tight geometry. Similarly to the first concept, the membrane is clamped between the cookies. Therefore, the concept includes perforated electrodes tightly screwed to the electrical passthrough. In this case, the electrical connection consists of a solid insert placed in the middle of the cookie in such a way to provide a good current distribution and precision for the electrodes and cookies alignment.

10.2.3 Pressure case

The material selection for this second concept is composite materials. Reason for this choice is the great performances provided by such materials. Furthermore, composites are not severely affected by hydrogen embrittlement compared to steel alloys. In terms of the manufacturing process, composites elicit the production of very precise components, matching tolerances of injection moulding. However, the high cost is given both by materials in use and the forming process, which is labour intensive and it requires extensive time. Because of the production methods, the geometry has been subdivided into three parts, the main pipe and the closing lids.

10.3 Easy to assembly



figure 54 Assembly of concept #3

10.3.1 Electrolysis stack

Conversally to the previous concepts, the following concept proposal has been envisioned to adopt an alternative geometry subdivision of the electrolysis stack to the cookies roll concept. Reason for this choice is the possibility to increase geometry freedom making it easier to produce and assemble. Hence, a further element defined as the sleeve embodies the whole electrolysis stack in a leak-tight system. Indeed, such an element aims to reduce the number of high-pressure seals by including a



figure 53 Electrolysis stack of concept #3



figure 55 Exploded view of electrolysis cell of concept #3

single one through fusion bonding alongside the sleeve's edge. However, to provide a tight fit of the inner stack the components are tightly pressed together by a single central rod. At last, the electrolysis stack is slightly tilted. This implies two main advantages. First, the unique assembling alignment as well as the consequent increment of the electrolysis cell surface. Secondly, it elicits the possibility of integrating the downcomers within the pressure case, containing the amount of oxygen within the unit.

10.3.2 Electrolysis cells

Because of the different geometry subdivisions of the stack, the cells also have different features compared to the cookies concept. Indeed, the electrolysis cell is deconstructed in two elements, the cell which embodies the channel connection and the frame which embodies the diaphragm and electrode. The electrodes are made out of an expanded mesh and pressed to the electrical connection. In this case, the electrical passthrough is a simple metal ring pressed onto the electrodes. The bridges channel are created in while aligning the stack, therefore, additional parts are necessary to create the top channels.

10.3.3 Pressure case

This final concept has been developed in such a way to embody a thermoplastic case. Reason for this choice is to match both components tolerances and thermal expansion of the material. As investigated at (8.1.1.1), the case must have a thickness of 7-8 mm to deal with inner pressure. Hence, as such a dimension is not suitable for injection moulding, ribs have been designed in such a way to provide enough strength while matching production requirements. However, issues with such development are the operating conditions. Indeed, because of the stress and temperature the case must withstand, it is very likely it will deform over time due to creep.

10.4 Comparison

To evaluate the concepts two distinct approaches have been adopted. In the first place, they have been graded based on the developed ideas adopting the weighted objective method (SOURCE). Therefore, a costs analysis based on material and envisioned manufacturing process evaluates the viability of each concept.

10.4.1 Weighted objective evaluation

The adoption of the objective method (Roozenburg and Eekels, 1996) derives from the need to include several criteria with different importance or weights as discussed in *9.2*. Therefore, each concept has been assessed based on the satisfaction of these criteria. The total score has been achieved by summing up the scores of each idea linked ideas, as calculated in APPENDIX. Reported in *table 11*, is the final assessmentof each concept, which is 171 points for the first concept, 162 for the second and 128 for the last one. As discussed in *9.2.1*, the maximum score is of 220pts. Hence, the performace of each concept has been calculated base on this value.

Functional ideas	Money saver (pt)	The safe (pt)	Easy to assembly (pt)
• seals integration	34	20	30
 stack geometry 	21	21	12
diaphragm integration	26	27	13
electrodes integration	29	36	25
• bridge channels	17	16	17
· case material	26	24	16
case geometry	18	18	15
• total	171	162	128

table 11 Concepts evaluation with weighed objective (Appendix V)

10.4.2 Cost analysis

Furthermore, a cost analysis based on materials and production processes required has been carried on for each concept. Such an investigation has been carried on either to compare the developed concepts as well as assess the cost reduction achieved from the previous development. Indeed, as discussed in 4.3.2, the cost of the state of the art is of $154\mathbb{C}$. The developed concepts showed a remarkable reduction in cost (*table 12*). The first concept aimed to be the most cost-effective. The total cost of this concept is $74\mathbb{C}$, more than 50% less than the current concept. The safe is the most

Component	Money saver (€)	The safe (€)	Easy to assembly (\in)
• electroysis stack (material)	2.6	7.4	5.0
• electroysis stack (producion)	16	29	32
electrolysis components	43	30	31
• pressure case (material)	4.7	22	30
• pressure case (production)	8.0	31	10
· total	74	119	108

table 12 Concepts cost comparison per component

expensive among the developed concepts with 119€. At last, the easy to assembly concept cost is in between with 108€

10.4.3 Requirements

A further evaluation of the concepts with the given requirements (Apendix IV) has been conducted. Specifically, hard requirements (*table 2*) have been considered for this analysis as they are essential for the proper operation of the electrolyser. As resulted for this evaluation, none of the proposal is suitable for the integration within the chemical plant.

The first concept does not embody enough cells, while the safe concpet does not allow bridge channles cross-section larger than 1mm. Conversely, it is very likely the case of the third concept would deform over time due to temperature and stress conditions.

10.5 Discussion

The concept development brought to the definition of three concepts. Each of them aimed to tackle a predetermined objective of cost, safety and assembly. Such analysis showed that each developed concept is more cost-effective than the state of the art, *4.3.2*. In fact, in each case the cost stays below the target cost of 127€ (van Nunen, 2019). Besides cost, great improvement has been achieved in terms of form factor and requrements satisfaction.

The first concept, money saver, resulted by far the cheapest solution. The reasons for this are the cheap material and production method for the case as well as the reduction of the number of cells by adopting metal foam electrodes. As a result, this concept results in the most compact form factor. however, the reduction of electrolysis cells makes it non-optimal for the operation on PV panels. In fact, to properly match the energy supplied in terms of voltage the number of cells must be 20.

Conversely, the safe is the most expensive concept developed. In this case, 40% of the cost is given by the composite case. Such materials offer great mechanical proprieties and part quality resulting very light and ensuring the required tolerances. The sealing method through welds aims to completely shut the electrolysis stack, ensuring the leak tightness at high pressure as well as mechanical fastening of the stack itself. However, the possibility of laser welding multiple elements must be further investigated. Similarly, the final assembly cannot be easily disassembled, making hard eventual refurbishing and recycling process.

The last concept iteration proposes an alternative geometry to the cookie concept. The assembly reduces the number of high-pressure seals to just one. Furthermore, assembly construction aims to be more effective during the assembling process. Electrolysis components, diaphragm and electrodes, are pre-assembled in a frame to facilitate the final assembly. Similarly, the achieved shape of the cells ensures a unique assembly of the parts reducing risks of misalignment. However, to achieve this many components are necessary, increasing the overall assembly complexity.

The easy assembly concept employes thermoplastics for creating both the electrolysis stack and the pressure case. Due to this choice, it is very likely the case to deform over time due to creep.

Concluding, none of the proposed concepts can be a viable alternative for the next development of the AEC unit. Reason for this is the non-complete fulfilment of the requirements from each concept. However, the most effective direction is given by the first concept, the money saver. It consists of very cheap development. Therefore, a final proposal will be investigated in the next section to overcome the limitation exposed by this preliminary design. In this last section, the final proposal of the AEC unit is presented. The results from the concept development showed remarkable improvements regarding the AEC design. Specifically, dimensions have been drastically reduced compared to the previous design. Similarly, the cost has been halved compared to the state of the art (4.3.2)

However, the previous concepts were not completely compelling as none of them fully matched the satisfaction of the requirements. Therefore, the ultimate iteration of the electrolyser design is proposed.

At last, the recommendation of further developments as well as the personal reflections on the conducted work are given.



design proposal



figure 56 Assembly of the final proposal design of AEC

11. Final proposal

11.1 Design features

The final proposal has been developed to overcome limitations exposed in the previous concept evaluation. Specifically, the previous concepts did not completely satisfy the requirement. Therefore, this last design aims to further iterate the most compelling concept developed in the previous section. As discussed in SECTION, money saver is the most cost-effective among the proposed designs. Similarly, the only limitation of this concept the number of cells included, which is not sufficient to operate on PV panels. Furthermore, this last design iteration will include essential integration components such as fluid and electrical connections.

11.1.1 Electrolysis stack



figure 57 Electrolysis stack of the final proposal design

Similarly to the first concept, the electrolysis stack is made out of PPS, However, the number of the cells has been increased from 12 to 20 to match the unit requirements (Appendix IV). Furthermore, the sealing method foresees 2k moulded gaskets. Although this process is more expensive than the adoption of gaskets, as done for the money saver, it decreases assembly complexity and time. Likewise, the risk of misalignment of such an element will be reduced.

Similarly, electrical and fluid connection are comoulded to ensure the leakthightness of the assembly. Moreocer, electrical connection must be completely insultated. Ultimately, to provide the proper fit within the case, solid metal elements are included at both extremities.

11.1.2 Electrolysis cell



figure 58 Exploded view of electrolysis cell of the final proposal (front and back)

The electrolysis cell design has been slightly changed. The main difference with the cell proposed in 10.1.2 is the integration of the electrodes. Indeed, as previously described, the number of cells has been increased, hence, the large reaction surface provided by the metal foam is not required. Perforated mesh is included as electrodes, as adopted for the safe concept (10.2.2). Because of this, this element is directly screwed to the electrical passthrough, which has been also reduced in dimensions. The creation of the bridge channels as well as the diaphragm integration does not change compared to the money saver concept.



1st - 2k moulded gasket

2nd - welded bridge channels

3rd - electrodes integration

figure 59 Elements integration in the electrolysis cell

11.1.3 Pressure case

The pressure case is made out of ultra-low carbon steel. As described in *8.2.1*, such a material is required to achieve the dimension for embodying the longer electrolysis stack. The geometry is achieved by plastically deforming a single metal sheet. Because of this reason, the case presents only one opening in which the electrolysis stack is inserted. To make the case suitable for lifetime operation in an outside environment a galvanisation coating is required.

Furthermore, the connections for integrating the unit within the microchemical plant are proposed. Fluid connections are placed at the to avoid stagnation of gases. Dissimilarly, electrical connections are placed at opposite sides of the unit. The main reason for this is to provide a connection to the power supply as much safe as possible, without risk of inverting polarity nor creating shortcuts.



figure 60 Back view of the final proposal

11.2 Evaluation

Similarly to the previous concepts the final design has been assessed through with the same methods. Therefore, evaluation with the weighted objective method has been carried on as well as the cost analysis.

11.2.1 Weighted objective

The result from this evaluation is of 174pts. As expected, this value is very close to the score of the first developed concept, 171pts.

11.2.2 Cost analysis

The overall cost of the unit is of $80 \\million$, 10% more than the money saver. The reason for such increment is the increased number of cells, and, therefore material. The cost of the material and manufacturing processes are roughly the same. On the material side, the greatest contribution to the cost is given by the electrolysis components, electrodes and diaphragm, accounting of 80% of material costs. Indeed, the case material is $6 \\million$, 13%, and electrolysis stack is just $3 \\million$, 7%. Production costs show an opposite trend. The cost for producing the stack is $33 \\million$, representing 77% of the total production cost. The remaining percentage is mostly given by the case production $19 \\million$, 22%. As calculated, the shaping of electrodes and membrane is very inexpensive.

Component	State of the art (\in)	Final proposal (€)
· electroysis stack (material)	1.8	7
• electroysis stack (producion)	66	36
electrolysis components	12	31
· pressure case (material)	15	5
· pressure case (production)	26	9
• total	120	80

table 13 Cost analysis of the final proposal compared to the state of the art

11.2.3 Requirements

The final proposal fully satisfies the operational requirements of the AEC unit (Appendix IV). Conversely to the money saver, this last iteration includes 20 electrolysis cells, making it viable to operate within the microchemical plant. The ultra-low carbon steel case designed make it suitable for high pressure and temperature operation. Furthermore, the low presence of carbon within the alloy makes it truly viable alternative as it is less sensitive to hydrogen attack.

11.3 Conclusion

This final proposal shows remarkable improvements from the AEC state of the art both in terms of cost and safety. Such an achievement has been possible by properly select the materials as wells as by optimising the electrolysis cell and case geometry.

For the electrolysis stack, essential design choices are the material and the sealing method. Regarding the first point, the chosen material is PPS. Such a thermoplastic offers greater mechanical properties at high temperatures as well as much more resilience to chemicals compared to HDPE, currently adopted in the state of the art. Furthermore, to provide an easy and reliable sealing, the gaskets are directly embedded in the geometry of the cells.

Most of the design focus has been given to the electrolysis cell ad it is the most intricate and only modular component of the unit. The resulting geometry uses less material compared to the state of the art. Moreover, it shows a much more homogeneous thickness distribution, making it suitable for mass production. The reactive surface has been almost doubled, making possible to embody a 600W electrolysis unit. The bridge channel design is a more viable and effective solution. This solution allows adjusting the geometry with much more freedom without creating gases gaps within the cells. Similarly, the electrodes and membrane integration has been developed to ensure a zero-gap configuration without effusion of gases across the cells.

Regarding the pressure case, the developed geometry is more effective in terms of material and production methods. The material choice consists of a much cheaper alternative than stainless stells and the geometry has been designed in such a way to avoid welds.

Finally, the overall dimensions of the unit have been drastically reduced. Considering just the electrolysis stack, the state of the art is approximately 40cm long (Appendix I). The developed unit is just 18cm, resulting in a more compact and light form factor.

11.4 Recommendations

11.4.1 Test of PPS

The simulation of the electrolysis cell conducted in chapter 7 takes into consideration the use of PSU as material for the electrolysis stack. However, due to later consideration, laser welding has not been adopted in the final AEC design and the chosen material for the electrolysis stack is PPS. The reason for this is the cost of PPS, which is half cheaper than PSU. Therefore, further simulation of the electrolysis cell design must be conducted to verify its feasibility. Indeed, due to the semicrystalline structure of PPS, it is possible to have different behaviour in terms of shrinkages and warpage.

11.4.2 Simulation at operating conditions

A simulation of the entire assembly at the operating condition is essential. Mechanical stresses of the electrolysis stack and the pressure case are very much recommended to further optimise the unit. Similarly, simulations of the electrolyte flow and the bypass current are required.

12. Reflections

With this thesis, I propose a throughout redesign of a small-scale alkaline electrolysis unit. The challenge of such an assignment is given by the need to match high operating requirements while remaining cost-effective for large scale production. At this very moment, little research and development are available in the literature. This made the design process much difficult to elaborate as no effective validation and confrontation have been possible.

Although I do not have an engineering background, I decided to tackle this assignment because of two main reasons. At first, I am very much intrigued in any effort towards more sustainable developments. In this case, the designed electrolysis unit is custom made for ZEF's chemical plant. However, due to recent growth in the field of alternative and green energies, i.e. fuel cells, I expect this could be a stimulus for the future development for green hydrogen production.

Secondly, I truly wanted to challenge myself in designing and embodying a product specifically for production means. Although the straightforward construction of the examined unit, the project development involved many strong requirements to satisfy, with consequences on the material and production choice.

Throughout the thesis, I struggled with properly planning my tasks. As a result, it took me more time to complete the given assignment. I believe that the reason for this misjudgment is related to my lack of knowledge in some fields as well as my will of considering and detailing as many alternatives as possible.

Overall, I am satisfied by the result I have been able to achieve in the past months. Although the technicality of the project, which pushed me to discover novel knowledge and skills, I have been able to develop meaningful solutions by adopting design thinking approach and properly validate them.

apparatus

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13. References

Birnbaum, H. (2001). Hydrogen Embrittlement. Encyclopedia of Materials: Science and Technology, pp.3887-3889.

Burheim, O. (2017). Hydrogen for Energy Storage. Engineering Energy Storage, 147-192. doi: 10.1016/b978-0-12-814100-7.00008-0

Caamano, J. (2002). Hard rules for soft-touch overmolding. Retrieved 10 March 2020, from https://www.machinedesign.com/archive/article/21816978/hard-rules-for-softtouch-overmolding

Carmo, M., Fritz, D., Mergel, J. and Stolten, D. (2013). A comprehensive review on PEM water electrolysis. International Journal of Hydrogen Energy, 38(12), pp.4901-4934.

Centea, T., & Nutt, S. (2015). Manufacturing cost relationships for vacuum bag-only prepreg processing. Journal Of Composite Materials, 50(17), 2305-2321. doi: 10.1177/0021998315602949

Centi, G., Iaquaniello, G., & Perathoner, S. (2019). Chemical engineering role in the use of renewable energy and alternative carbon sources in chemical production. BMC Chemical Engineering, 1(1). doi: 10.1186/s42480-019-0006-8

Clearweld (2019). About Clearweld. [online] Clearweld.com. Available at: http://www.clearweld. com/concept.html [Accessed 16 Dec. 2019].

Colli, A., Girault, H., & Battistel, A. (2019). Non-Precious Electrodes for Practical Alkaline Water Electrolysis. Materials, 12(8), 1336. doi: 10.3390/ma12081336

De Silva, Y. (2017). Design of an Alkaline Electrolysis Stack. University of Agder, Department of Engineering Sciences.

de Souza, R., Padilha, J., Gonçalves, R., de Souza, M. and Rault-Berthelot, J. (2007). Electrochemical hydrogen production from water electrolysis using ionic liquid as electrolytes: Towards the best device. Journal of Power Sources, 164(2), pp.792-798.

Design Council (2005). The Double Diamond: A universally accepted depiction of the design process

Engineeringtoolbox. (2003). Metals and Corrosion Resistance. Retrieved 12 March 2020, from https://www.engineeringtoolbox.com/metal-corrosion-resistance-d_491.html

Graco. (2013). Chemical Compatibility.

Hydrogenics. (2019). Fuel Cells - Hydrogen Fuel Cell Description & Advantages. Hydrogenics. Retrieved 10 February 2020, from https://www.hydrogenics.com/technology-resources/hydrogentechnology/fuel-cells/

IRENA (2018), Hydrogen from renewable power: Technology outlook for the energy transition, International Renewable Energy Agency, Abu Dhabi.

Katsiropoulos, C., Moraitis, G., Labeas, G. and Pantelakis, S. (2009). Optimisation of laser welding process for thermoplastic composite materials with regard to component quality and cost. Plastics, Rubber and Composites, 38(2-4), pp.153-161.

Keasbaay, A., Kayfeci, M. and Bayat, M. (2019). Electrochemical hydrogen generation. Solar Hydrogen Production, pp.299-317.

Kohl, A. L. (2014). Stripping (chemical engineering). In AccessScience. McGraw-Hill Education. https://doi.org/10.1036/1097-8542.660700

Kraglund, M., Aili, D., Jankova, K., Christensen, E., Li, Q. and Jensen, J. (2016). Zero-Gap Alkaline Water Electrolysis Using Ion-Solvating Polymer Electrolyte Membranes at Reduced KOH Concentrations. Journal of The Electrochemical Society, 163(11), pp.F3125-F3131.

Kula, D., Ternaux, E., & Hirsinger, Q. (2013). Materiology. Amsterdam: Frame Publishers.

LPKF (2011). Cost Comparison. Is Laser Plastic Welding Economical?

LPKF (2018). Design guidelines for laser plastic welding

MGC. (2020). The Many Uses of Methanol From Clothing to Fuel: Products and Technology Highlights | Innovation | Mitsubishi Gas Chemical Company, Inc. Retrieved 19 February 2020, from https://www.mgc.co.jp/eng/rd/technology/methanol.html Millet, P. and Grigoriev, S. (2019). Water Electrolysis Technologies.

Nikafshar, S., Zabihi, O., Ahmadi, M., Mirmohseni, A., Taseidifar, M., & Naebe, M. (2017). The Effects of UV Light on the Chemical and Mechanical Properties of a Transparent Epoxy-Diamine System in the Presence of an Organic UV Absorber. Materials, 10(2), 180. doi: 10.3390/ma10020180

Parida, A., Soren, S., Jha, R., & Krishnamurthy, N. (2017). Multistage Deep Drawing with Ironing of Al-killed AISI 1040 Graded Medium Carbon Steel: a Parametric Study. Materials Research, 20(4), 1111-1120. doi: 10.1590/1980-5373-mr-2016-0586

Phillips, R., & Dunnill, C. (2016). Zero gap alkaline electrolysis cell design for renewable energy storage as hydrogen gas. RSC Advances, 6(102), 100643-100651. doi: 10.1039/c6ra22242k

Pilkey, W. (2010). Formulas for stress, strain, and structural matrices. Hoboken, NJ: John Wiley & Sons.

Roozenburg, N. and Eekels, J. (1996). Product design: Fundamentals and Methods, Chichester: Wiley.

RTP (2017). Part Design Guidelines for Injection Molded Thermoplastics. (2019).

Sastri, V. (2010). High-Temperature Engineering Thermoplastics. Plastics in Medical Devices, pp.175-215.

Schalenbach, M., Lueke, W. and Stolten, D. (2016). Hydrogen Diffusivity and Electrolyte Permeability of the Zirfon PERL Separator for Alkaline Water Electrolysis. Journal of The Electrochemical Society, 163(14), pp.F1480-F1488.

Selamet, O., & Ergoktas, M. (2020). Effects of bolt torque and contact resistance on the performance of the polymer electrolyte membrane electrolyzers. Retrieved 22 January 2020, from

Sendy, A. (2019). Price and efficiency of solar panels has changed over time. [online] Solar-Estimate. Available at: https://www.solar-estimate.org/news/how-has-the-price-and-efficiency-of-solar-panels-changed-over-time [Accessed 23 Oct. 2019].

Sriram, K. (2019). Thermal and flow characterisation of a small scale alkaline electrolysis system for hydrogen production.

Troughton, M. (2009). Laser Welding. Handbook of Plastics Joining, pp.81-95.

Troughton, M. (2009). Polyphenylene Sulfide. Handbook of Plastics Joining, pp.389-393.

Vogt, U., Gorbar, M., Schlupp, M., Kaup, G., Bonk, A., Hermosilla, A., & ZÃ¹/4ttel, A. (2013). Membranes Development for Alkaline Water Electrolysis. Presentation, Empa, Laboratory Hydrogen & Energy Überlandstrasse 129 CH-8600 DÃ¹/4bendorf / Switzerland.

Woosman, N., Cawley, W. and Verespy, J. (2004). Achievable Weld Strengths Using The Clearweld® process.

Yousefpour, A., Hojjati, M. and Immarigeon, J. (2004). Fusion Bonding/Welding of Thermoplastic Composites. Journal of Thermoplastic Composite Materials, 17(4), pp.303-341.

Yousefpour, A., Hojjati, M. and Immarigeon, J. (2004). Fusion Bonding/Welding of Thermoplastic Composites. Journal of Thermoplastic Composite Materials, 17(4), pp.303-341.

Zeng, K. and Zhang, D. (2010). Recent progress in alkaline water electrolysis for hydrogen production and applications. Progress in Energy and Combustion Science, 36(3), pp.307-326.

Zheng, X. (2019). How long will it last? An assessment of the useful life of plastics for the encapsulation of an alkaline electrolyser.

Appendix I. AEC state of the art



figure 1 Current desing of ZEF AEC unit

The following appendix aims to analyse and evaluate the state of the art of the AEC unit developed by ZEF. In specific, the investigation takes into consideration the "cookie roll" concept developed by team 2 and further optimised and prototyped by the TEAM 3. Although all components were prototyped, only partial tests of the design were conducted. Indeed, the current prototype exists in the form of manufactured components, but it has never been completely assembled by the previous team. Therefore, there is no proof of the effective operation of the AEC unit so far.

The investigation will be conducted, at first, through a literature review of the previous design, assessing main requirements for the chemical reaction to happen developed so far and integration of the AEC unit with the other subsystems of the microchemical plant. Therefore, a preliminary comprehension of AEC components is carried by reviewing the 3D CAD model of the overall assembly and further implemented with insights from the observation of the prototyped unit.

I.1.1 Objective

The scope of such investigation is to gather fundamental knowledge of the working principles of AEC as well as point out the current constraints of the concept. In the first place, the assessment of the main achievements and limitations of the previous design must be conducted. Hence, an understanding of the reasoning of such results through a literature review of the available documentation will complete the knowledge of the current system design principles. Non-working principles must be identified, evaluated and re-elaborated. In the second place, considerations on the developed assembly and component manufacturing must be conducted. Preliminary evaluation in terms of costs, manufacturability, assembly and risk must be lined out.

I.2.1 Approach

As previously mentioned the analysis of the state of the art of AEC has been conducted by combining the review of the literature produced so far by ZEF as well as observation of the prototyped unit of the cookie roll concept and through confrontations with actual developers of the unit in regards. Therefore, the overall alkaline electrolysis cells unit functionality has been lined out as follows. At first, the system boundaries of the unit within the plant are explained together with the operating principles and unit requirements. Furthermore, components are investigated in terms of manufacturing technologies as well as envisioned assembling procedure.

I.2.2 AEC unit

Within ZEF's microchemical plant, the AEC unit is in charge of decomposing water into hydrogen and oxygen to directly supply the H2 at high to the Methanol Synthesis (MS) unit. As shown in fig.X the alkaline cells get water supply from the CO2 and H2O buffer, in which water is pressurised with carbon dioxide up to 50 bar. However, because of the high pressure, water contains minimum levels of CO2, a factor which could decrease the overall electrolysis efficiency. Therefore, CO2 must be completely removed from the water before it contaminates the alkaline solution. In to do so, carbon dioxide is taken away through a stripping process within the unit known as the degasser.

Therefore, as electrolysis consists of an electrochemical reaction, hydrogen production and its efficiency depend on the power supplied at the opposite poles. Electrical energy is directly provided by the photovoltaic panel (PV) and managed by the control system (CO) to match production needs. Furthermore, the control system constantly monitors the AEC operation by gathering data about temperature, water level and inner pressure. Sensors are embedded in the unit as shown in the schematics below. Based on this data, CO controls inputs and outputs through actuated valves. As hydrogen is generated is stored in a buffer and supplied to the methanol synthesis based on its demand. At last, since electrolysis consists of an exothermic process, the AEC unit is expected to reach its optimal working temperature through its operation. Therefore, the excess of heat is transferred to other units: Direct Air Capture (DAC) and Distillation (DS). In such a way, the energy efficiency of the plant increases.

I.2.3 AEC state of the art

The state of the art of the AEC consists of a complex unit which embodies in itself multiple elements besides the electrolysis cells. Indeed, it includes the degasser unit and the hydrogen buffer. In to achieve such integration of elements, AEC has been designed by adopting what has been defined as cookie roll concept. Such an idea has been developed by team 2 and further optimised and built by team 3. The concept consists of a series of elements, called cookies, which could have different geometry depending on its function, but can fit together in a stack.

The cookie stack is further placed within a steel pipe which holds the pressure load as well as embodying the required connections for the integration of AEC to the plant.

I.2.3.1 Functional components

The current design has been developed in such a way to satisfy specific requirements, both from the unit operation and manufacturing processes. Therefore, the unit has been structured in two main elements, the outer case, responsible for supporting the load given by the pressure of 50bar, and the cookies stack, whose function is to embody the whole electrolysis geometry and components in a leak-tight environment. Therefore, these elements have been defined as functional components.

I.2.3.1.1 Pressure case

The current pressure case consists of a stainless steel pipe with collar clamps at the extremities. All

components are standard items and over-engineered to withstand the load. The pipe is 100mm in diameter, however, due to manufacturing processes, it largely varies from 97mm to 100mm.

Furthermore, the lids have been custom machined to accommodate fluid and electrical connections of the AEC unit.

I.2.3.1.2 Cookies stack

The cookie stack represents the actual geometry which embodies all required elements of the electrolyser. As shown in Fig.4 the stack is constructed by a total of 30 cookies. Each cookie is made



out of HDPE and it has a singular design. The only exception is given by the middle cookie, which consists of a modular element and it embodies the electrolysis cells.

I.2.3.1.3 Degasser and H2 Buffer cookies

At the opposite extremities of the stack, there are the degasser and the hydrogen buffer respectively. The degasser, as previously mentioned, bridges the water input to get rid of the diluted CO₂ by adopting a stripping process with the produced oxygen. It is composed of two cookies and it consists of an intricate pathway. Opposite of that, it is positioned the hydrogen buffer, which is a chamber directly connected to the hydrogen output.

I.2.3.1.4 AEC cookies

Therefore, in between the degasser and the hydrogen buffer, the alkaline cells are positioned. Different geometries of the cookies have been designed to integrate the required components. Therefore, the first couple of cookies at both extremities of the AEC stack are called end-cookies, while the rest of the cookies in between are defined as middle-cookie. In specific, end-cookies' design integrates the downcomers, the electrical connections to the power supply as well as the fluid connections. Hence, the design of the coupled end-cookies differs as they must provide different external connections. On the other hand, middle-cookies have the same geometry, as they must satisfy the same functions. The result is a modular component easy to scale up in number for increasing hydrogen production.

The middle-cookie has been designed in such a way to create an electrolysis cell by coupling two of identical parts. Indeed, the membrane is clamped exactly in between two middle-cookies, while the electrodes are placed tightly against it (picx). Therefore, electrical pass-throughs are included in the design to connect the electrodes at the sides of the cookie as well as support them against the membrane. The pass-through connections consist of stainless steel rods with M6 thread directly screwed in through the middle-cookie wall. Hence, the connections with the electrodes are given by lumps on the electrode surface at the pass-through position.

Furthermore, the middle-cookie embodies in its geometry the section of both top and bottom channels as well as the bridges which connect the cell to the channels. To provide leak-proof chambers, the geometry includes two types of seals. An outer gasket is placed all around the cookie geometry

and it should provide a leak environment at 50bar. On the other hand, inner seals are placed over the channels to prevent effusions and mixing of hydrogen and oxygen. In this case, the gasket must be leak-tight with a pressure drop of 0,5 bar as the pressure is equivalent within the system.

At both ends of the alkaline cells the end-cookies are placed. End-cookies are composed by the coupling of two cookies and they are called oxygen and hydrogen end-cookies as they include the respective gases output. Specifically, the oxygen end-cookie is next to the degasser while the hydrogen one at the opposite side is close to the hydrogen buffer. Both geometries include the downcomers, flash tanks in charge of ultimately separating the mixture of gases and alkaline solution which flows from the cells to the top channels. Furthermore, they embody the connections to the external power supply, having the negative and positive poles at the oxygen and hydrogen sides respectively.

I.2.3.2 Integration components

To integrate AEC with the rest of the plant's subsystems, further components have been included. Those have been identified as integration components and they include external connections, for electricity and fluids, as well as control elements.

I.2.3.2.1 Fluid connections

The unit has in total of four connections for fluids inlet and outlet. H2O input is directly supplied from the CO2 buffer to the degasser. Therefore, the KOH passthrough allows filling the cells with pure water solution before the unit commissioning as well as supply KOH for maintenance.

Oxygen is released in the outer environment together with CO2 at the degasser side, while hydrogen is supplied to the methanol reactor on the opposite side, from the H2 buffer.

I.2.3.2.2 Electrical connections

On the electrical side, the unit must be connected, in the first place, to the power supply. The cables, connected to the end-cookies cathode and anode, pass below the other components and exit at the opposite sides. The polarity of the connection is of fundamental importance. Indeed, in the case of polarity inversion also the reaction is reversed, with a consequent harmful mixture of gases within the cells. Further electrical connections include the wiring of sensors and actuators to the control unit.

I.2.3.2.3 Fastening support

The state of the art of the AEC unit exists just as a proof of concept. Therefore, fastening supports have not been integrated yet.

I.2.3.3 Control components

I.2.3.3.1 Sensors

Most of the sensors required for the AEC unit to operate are integrated within the cookie stack. Therefore, within the cookies, water level and temperature sensors are integrated (L2, L3, T5, T6.). For the water level, a pins sensors setup is adopted and two different sensors are implemented in both hydrogen and oxygen downcomer, in such a way to detect respective water level. Furthermore, two temperature sensors are placed at both end-cookies, while the last one is integrated at the very middle of the cookie stack. The only sensor which is not included within the stack is the pressure sensor (P5.), which is directly connected to the hydrogen output.

I.2.3.3.2 Actuators

The AEC unit includes only two actuated valves, one for water inlet from the CO2 buffer and the second for the purge of oxygen and carbon dioxide. Controversially, hydrogen output is directly actuated by the methanol reactor's demand. Hence, it has not been included in the unit design. Further input is given by the power supply. However, also, in this case, the power is managed by the integrated control of the chemical plant and therefore, not included.

I.2.4 AEC operation

The AEC unit adopts the technology of alkaline water electrolysis, AWE, cells, a mature technology which can efficiently operate with relatively low temperature and pressure. However, the difference

of conventional AEC, the unit in development at ZEF B.V. consists of a smaller scale electrolyser of 200W. However, due to more recent investigations, the unit must be scaled up three times reaching 600W. Furthermore, as the micro plant relies on renewable energy, AEC operates accordingly to the intermittent power source. As reaction occurs with a minimum voltage drop of 1,23V the number of cells proportionally defines the voltage required at the extreme poles. Furthermore, each cell embodies a zero-gap configuration. Such a setup is adopted to increase electrolysis efficiency as well as reducing cells' thickness. The diaphragm, tightly placed between the electrodes, divides each cell in half, avoiding the mixture of gases produced at the electrodes. Hence, as electrolysis happens a mixture of water and gases generated at the electrodes' surface flow upwards into channels. As the mixture reaches the top channels gas and solution separate. Hence, hydrogen is collected in the buffer and oxygen directed to the degasser. On the other hand, the alkaline solution flows to the downcomer and conducted back to each cell through the bottom channel.

Furthermore, although cells are electrically wired in series, the alkaline solution is conveyed in parallel in each cell. Therefore, as the alkaline solution results to be highly conductive, it is of fundamental importance to avoid any leak of current between the cells through the fluid. Indeed, this affects the water decomposition, decreasing or completely neutralizing the electrolysis reaction. Hence, each cell is electrically insulated by increasing the electrical resistance of the fluid within the channels. To do so very narrow channels have been placed at each cells' inlets and outlets. Those elements have been identified as bridges. Although bridges must be tiny, their dimensions must allow a sufficient solution flow of the solution through the system.

At last, AEC has been developed in such a way to reach the required operating pressure through the production of hydrogen itself. Therefore, a hydrogen buffer is used to temporarily store hydrogen avoiding large pressure losses as the gas is supplied to the methanol reactor.

As previously mentioned, oxygen is conveyed to the degasser, where it flows through the inlet water supplied by the CO₂ buffer in a long channel. Such a process aims to strip out carbon dioxide from water. Finally, both O₂ and CO₂ are purged out of the system. Hence, the control system manages the relative pressure between O₂ and H₂ by sensing the water level in the relative downcomers.

I.2.4.1 Unit specifications

The alkaline electrolysis cells developed by ZEF have been developed to run with specific operational requirements. The unit adopts potassium hydroxide, KOH, as a redox mediator, in a solution of 30% with water. Besides, the reaction occurs at a constant operating temperature of 90C. Therefore, electricity is applied to ensure a drop voltage of 2V per cell. Furthermore, the current density is defined to be 300 mA/cm². Additional requirements are defined by the chemical plant constraints. As the methanol reaction occurs at 50bar, hydrogen must be supplied at equal or higher pressure. Hence, the unit must ensure the production of hydrogen at that pressure.

I.2.5 Assembling procedure

At last, an observation of the assembly phase of the unit has been conducted. This process has been of fundamental importance for understanding the current components assembling procedure. The system observed included all previously listed components. However, the number of cells was reduced to 12 to fit the still pipe. The setup for the assembly has been carried out by two members of the team and it has been structured as follows:

- Preparation
- Arrangement
- Testing

I.2.5.1 Preparation

At first, all components have been collected and listed to avoid missing elements. Therefore, they have been clustered and ordered depending on their placement within the assembly itself.

I.2.5.2 Arrangement

The arrangement of all components consists of the most extensive phase of the entire assembly phase. Hence, the arrangement of the components started with the construction of the cookie stack. Starting from the hydrogen buffer side cookies were added including the respective elements such as gaskets, external connections and electrolysis components. To connect two cookies, they have been precisely aligned and firmly press-fitted against each other using a vice.

As all cookies were joined tightly, the entire stack has been placed within the stainless steel pipe. Hence, the pressure case is closed and all external connections

I.2.5.3 Testing

At last, the prototype has to be tested. The primary test consists of checking the leak tightness of the assembly. Therefore, as the unit does not present any leak, electrical connection and the operation of the control system is checked. At last, the unit must be fully commissioned and certified before the plant installation.

I.3 Discussion

As investigated the state of the art of the AEC unit consists of a custom made unit which embodies together multiple elements: the alkaline electrolysis cells, the degasser as well as the hydrogen buffer. Although few parts were purchased as standard components, most of the unit has been designed and manufactured on demand either by members of the team or supplied by the third party. Such an approach allowed the team to investigate, develop and evaluate several concepts of working principle.

However, the current design is not optimised for manufacturing processes yet. Hence, because of production time and costs, such design is not sustainable for mass production. Furthermore, due to safety reasons, the unit has never been operative. However, extensive investigations lead to the structure of a fault tree, which collects all possible failure events of the unit. (Hofman, 2019)

I.3.1 Prototype assessment

Through the research phase, many recommendations and directions in regards to the AEC state of the art have been listed. These decisions have been developed either from confrontation with the team and from the literature developed by the same. In the first place, the technology adopted for electrolysis remains the same as the previous design. Hence, the electrolyser embodies a series of alkaline cells in a zero-gap configuration. Similarly, operation conditions of pressure and temperature remain the same. Therefore the cylindrical geometry will be maintained as it results optimal for loading the mechanical stress given by the high pressure and it easily allows the piling of multiple elements. Also, the diameter has been defined to be within the range of 100-150mm. Furthermore, the integration of the unit within the plant follows the last concept development (van Nunen, 2019). Therefore, the unit must be scaled up to three folds to satisfy energy production requirements of the three panels chemical plant.

I.3.2 Identified issues

I.3.2.1 Cost

Few components design are not optimised for manufacturing processes, resulting in too expensive for production. First, the pressure case consists of a stainless steel tube. The chosen material offers great mechanical properties as well as good resistance to the alkaline solution in use. However, it is very expensive and the chemical resistance to KOH solution is not required as the electrolysis cells must not leak. As a result, the case consists of 50% of the total AEC cost (van Nunen, 2019).

Furthermore, the process adopted for prototyping the cookies is not sustainable. Indeed, machining

the parts through a 5 axis milling machine offers great geometry freedom, however, it consists of a very slow process. Injection moulding represents a more viable alternative to reduce costs and production time. However, components must be redesigned to match production requirements.

I.3.2.2 Assembling procedure

Similarly, the concept does not provide any easy assembling procedure. The overall process results to be time-consuming and not completely straightforward, requiring particular care and several attempts to assemble the stack. The high number of components and the intricate sequence of alignment makes the procedure very difficult to complete correctly. Indeed, the risk of misaligning components, especially membrane and electrodes is high, resulting in a non-reliable nor safe unit.

I.3.2.3 Material degradation

In terms of material, the current cookie stack is not optimal to endure alkaline electrolysis at high temperatures or pressure. Indeed, the mechanical properties of HDPE drastically degrade in the presence of KOH. Moreover, the pressure case will suffer from an embrittlement process due to hydrogen diffusion. Such material degradation process speeds up at welded spots, as there is a higher concentration of carbon within the alloy (Birnbaum, 2001). Likewise, oxygen is a very reactive molecule and it oxidizes many materials, compromising its properties.

I.3.2.4 Tolerances

Tolerances have been individualized as possible reasons for the failure of the unit. Indeed, the outsourced tube is not perfectly manufactured. As a result, it is tighter at the extremities and looser in the centre. The overall difference in diameter between extremities and centre is within the order of 2mm. Hence, the pressure case does not allow optimal support of the cookie stack. Due to that, the inner geometry could slightly deform and leaks might be created.

I.3.2.5 Gas mixture

The current AEC concept results to be not truly safe. Reason for this is the presence of gases within the unit. In specific, the unit includes the flash tanks within the assembly, therefore, it contains pure hydrogen and oxygen at high pressure. According to Hofmann (2019), such a combination of gases could cause several hazardous events such as auto ignition and detonation.

I.3.3 Design goals

Provide a leak-tight system

Develop geometry for injection moulding

Reduce the number of components

Simplify component arrangement

Appendix II. Injection moulded middle cookie

II.1 Introduction

To scale up production and lower the costs of the AEC unit, its components must be designed for mass manufacturing processes. In specific, the most complex elements to manufacture are represented by the cookies. The reason for this is represented by the intricate geometry required for embodying internal components and integrating the channels necessary for the reaction to happen. Currently, the cookies are prototyped by using a 5 axis CNC machine, which results way too slow and, therefore, expensive for large production. A more suitable alternative is the adoption of an injection moulding method for the manufacturing of the cookies. In specific, the focus of this research is on the middle-cookie as it shows the most complex geometry and it must embody several components.

II.1.1 Objective

The goal of the following investigation is to develop a manifold design of the middle-cookie for injection moulding. Therefore, its design must be reliable to produce and provide the integration of all electrolysis components. It is expected to iterate various geometries and design strategies to overcome the given challenges. Each concept will be evaluated either through confrontations with professionals in the field and actual simulation of the injection moulding process. The final scope is defining the injection moulding requirements for the middle-cookie design.

II.2 Research

II.2.1 Approach

The research is conducted in partnership with Promolding B.V., a company qualified in developing injection moulded parts. Hence, multiple meetings are set to investigate feasible alternatives for both the middle-cookie design and the overall assembly for components integration. In specific, experts from mould engineering and design, Rik Knopper and Eric Mejer, as well as specialists of the moulding process simulation were consulted. Each meeting was structured in such a way to focus on specific goals and details of the middle-cookie challenges.

To achieve the final scope of the first production of the middle cookie through injection moulding technology, few phases have been defined. In the first place, preliminary ideas were proposed, discussed and further elaborated for selecting the most feasible and viable alternative.

Therefore, optimisation of the resulting design is conducted through multiple iterations with actual simulations of the injection moulding process.

II.2.2 Preliminary ideas investigation

Primary ideas for integrating components within the middle cookie and further develop a manifold geometry of the same were stated as follows:

Is it possible to co-mould the electrolysis membrane with the cookie? Is it possible to co-mould the electrical passthrough with the cookie? How to injection mould bridges in the middle cookie? Which polymer does perform the best for injection moulding? II.2.2.1 Is it possible to co-mould the electrolysis membrane with the cookie?

At first, as the membrane must reliably separate the electrolysis cell in such a way to avoid any harmful mixing of gases within the system, a preliminary concept foresaw the possibility to co-mould it within the geometry. However, few doubts about the process were highlighted by both Eric and Rik. In the first place, the membrane contains moisture as it degrades if get dry (AGFA, 2017). Therefore, water evaporates during the moulding process creating bubbles and compromising the injected part. Furthermore, to avoid any leak of the mould, the clamping force between the two mould parts squeeze the membrane edges, occurring possible damages around it. Another doubt was expressed in regards to the zirconia coating of the diaphragm itself, which could have compromised the bonding of the membrane with the cookie and therefore not reliable over time. A final remark was given in terms of plastic shrinkage. Indeed, as the plastic cools down it eventually shrinks creating wrinkles on the membrane.

Because of those reasons, the concept of co-moulding the membrane has been discarded, as too many tests were required to assess its feasibility. Hence, alternative methods of integrating the membrane between the cells must be investigated and further developed

II.2.2.2 Is it possible to co-mould the electrical passthrough with the cookie?

On the other hand, the integration of a metal component results far easier. There are no problems of co-moulding electrical passthrough within the middle-cookie as it consists of a solid component which can withstand the injection moulding stresses much better.

II.2.2.3 How to injection mould bridges in the middle cookie?

To avoid the bypass currents through the cells the bridges which connect cells to the flow channels at the top and bottom must provide a high electrical resistance (Appendix I). Such a goal represents a great challenge as the channel in regards must have a ratio between length and diameter higher than 10. Therefore, for a diameter of 1mm, the length must be equal or higher than 10mm. Furthermore, top channels result to be more difficult to design as they must be placed at the extreme top of the cell to avoid retainment of gases. Hence Primary ideas were exposed and further discussed.

b)

Fig.1 - First concept for bridges to the top channels. a) Front view of the bridge channels. b) Isometric

Such small channels are troublesome both because of its tiny geometry and the undercut position. Indeed, to create them within the mould a pin must be inserted and removed before the opening of the mould. As the plastic flow generates stress on the pin it will inevitably bend because of its small dimensions. Further on, as the laser welding technique has been envisioned as the most effective solution (Appendix III), additional designs were developed. Specifically, the bridge geometry is created by grooves on the surface of the cookie itself. As two cookies are placed together the bridges are closed by the flat surface of the other cookie. Therefore, laser welding is essential to avoid any leakage over the groove contour as shown in Fig.2.

a) c)

Fig.2 - Second bridges geometry iteration.

b)

a) The bridge conveys the gases from the top of the cell to the top channel.

b) The bridge runs over the channel increasing cell dimension

c) The bridge runs over the entire depth of the cookie. In this case, two cookie geometries are required to avoid the interference of the channels.

However, the first iteration of such design still did not fulfil the requirements. In the first place, the so designed bridges take place over the membrane clamp. Hence, the geometry is not reliably leak-tight, creating a potential gap over the membrane for the gases to pass through. Hence a final concept has been developed to overcome such limitations. In Fig.3, the groove does not overlap with the membrane. To achieve that, an undercut is required.

Fig.3 - Final result of the bridge geometry to the top channel with undercuts (the two undercuts and bridges are on the opposite sides of the cookie)

Which polymer does perform the best for injection moulding?

The choices on the material are very limited. Reason for this is given by the chemicals the unit must endure over its lifetime operation. Therefore, the given options included were just PPS and PSU. At first, PPS has been selected as the optimal choice as it represents the cheapest solution. However, further considerations in terms of material bonding defined PSU as designed material as it allows the cookies to be laser welded, even through thick components (Appendix III). An additional consideration between PPS and PSU regards the typology of the polymer. PSU results easier to be injection moulded as it consists of an amorphous plastic while PPS is semi-crystalline. Such a difference slightly decreases the risk of warpage of the geometry itself while using the amorphous polymer.

II.2.3 Discussion

In the first place, difficulties in co-moulding the diaphragm within the cookie lead to the discard of such an alternative. Specifically, the main issues are represented by the presence of moisture within the membrane, risks of damaging it while clamping it within the mould as well as the possible warping of the same after the cookie cooling. Therefore, novel methods for integrating the diaphragm must be further investigated. Controversially, no issues have been assessed in co-moulding the electrical connections within the cookie design. However, as the cookie results of a round shape, it is optimal to place the injection runner as close as possible to the centre of the geometry, meaning that the passthrough should be slightly offset. Furthermore, bridges resulted in the most intricate elements for injection moulding. Reason for this is the little dimension of such geometry, which must have a defined ratio between length and cross-section.

Finally the choice of the material is PSU. The reasons for this is the possibility of sealing shut any contour. Indeed, although PSU has a higher cost per ton than PPS, it elicits the complete leak tightness of the cookie stack as well as creating the bridge channels geometry by employing laser welding.

II.3 Concept analysis

The collaboration with Promolding leads to the development of several conceptual designs of the middle cookie. Hence, the analysis of the developed design is run through computational simulation, assessing geometry feasibility, moulding time and possible defects. Finally, results from each design have been evaluated and further iterations of the cookie are developed whether necessary.

II.3.1 Simulation methodology

To assess the viability of the concepts, a finite element analysis (FEA) of the first design development has been investigated through. The simulation of the moulding process has been run at Promolding and the software in use was Moldex₃D. Furthermore, as the developed design envisioned to be laser welded the chosen material for the analysis is PSU. The simulation steps for injection moulding is structured as follows:

- Simulation preparation
- Mesh creation

- Cooling parameters
- Injection points
- Moulding simulation
 - Material parameters
- Simulation steps
 - Filling
 - Packing
 - Cooling
 - Warpage

II.3.2 V2 Concept

The V2 design consists of a middle cookie which integrates the same elements of the state of the art of AEC. However, the geometry has been adjusted implementing the insights of the analysis of the current AEC unit (Appendix I). Therefore, top channels have been reduced in size to reduce the volume of pure gases within the unit. A single element has been introduced for the electrical passthrough and placed just below the cookie centre. Similarly, supports for the electrodes have been placed over the entire electrode surface. Furthermore, the geometry includes the last bridge design discussed in paragraph 2.1.1.3. Hence, the geometry includes four undercuts cavities, one for each bridge channel, which increases mould complexity and costs.

Fig.4 - Cookie design V2 Clamped membrane Laser welded chamber Outer ring Inner channels and bridges Symmetric shape to simplify the mould Undercut for channels Top undercuts are wider to avoid gas retainment Curled bridges Electrodes support Shifted passthrough

II.3.2.1 V2 analysis

In the following paragraph, the results of the simulation conducted on the V2 are described. Specifically, the elements under investigation are weld lines, shrinkage and warpage.

II.3.2.1.1 Weld lines

Where the material ultimately joins together in the mould, therefore they represent the most fragile points where cracks will happen at first. As shown in the following image they are at the extremities of the cookie where fluid channels are placed.

Fig. 5 - simulated weld lines position. In colour are shown the angle of the weld.

II.3.2.1.2 Shrinkage and mark displacement

Secondly, the shrinkage of the material while cooling will produce displacements on the product surface. As shown in Fig. 6a), the considerable thickness of the cookie edge results in a not negligible shrinkage. Specifically, in the picture, it is shown the partial material with a volumetric shrinkage of 11%. Due to such a shrinkage, displacement on the surface is very evident. Indeed, in the second picture, the same areas display the greatest displacement.

a) b)

Fig.6 -

II.3.2.1.3 Warpage
At last, the simulation runs a warpage displacement. Here it is shown the deformation, the product warps due to inner tensions of the material. As is visible from the simulation, surfaces have remarkable warpage of 0.5mm from the lowest to the highest point. Reasons for this are represented by the outer rim of the cookies which results thicker than other geometries.

Fig.7 - Warpage of the cookie

II.3.2.2 Discussion

The results of the first simulation clearly show that the high thickness of the cookie's rim creates too much shrinkage and displacement specifically at the joining surface. Therefore, the alignment and bonding with laser welding techniques of multiple elements will not be possible. Furthermore, the thickness variation of the geometry should be reduced, as it creates undesired warpages. Such deformation is particularly evident at the undercuts as shown in Fig. 6/7. Reason for that is the large dimension of the undercut and the circular geometry of the channels, which does not properly follow the cell geometry.

II.3.3 V3 Concepts

Therefore, alternative designs have been developed adopting different strategies to improve the plastic flows within the mould as well as reducing the undesired deformations of the cookie by making the wall thickness more homogeneous.

The design goal of this iteration consists of:

- Improve surface flatness for laser welding
- Reduce volumetric shrinkage
- Reduce cooling time

In the first place, channels have been moved towards the edge, changing shape to follow the outer shape of the cookie. In such a way, it was possible to reduce the dimensions of undercuts, which now are placed in the middle of the cell and are the same for the bottom and top channels. Therefore, the overall thickness of the cookie has been reduced from 10mm of the V2 to 8mm of the V3. Ultimately, three concepts have been designed by adopting different strategies. The concepts have been defined as follows :

V3.1 Shifted wall V3.2 Outer shell

V3.3 Rib flow

II.3.3.1 Middle-cookie V3.1 - Shifted wall

The shifted wall concept aims to redistribute the material of the outer rim in such a way to reduce the overall thickness. Such geometry results easy to mould as it does not have additional undercuts and it allows easy alignment of the parts.

Fig.8 - Cookie design V3.1 - Shifted wall

II.3.3.2 V3.2 - Outer cut

Similarly, concept V3.2 reduces the outer rim thickness through a cut along the perimeter. In such a way it is possible to provide a homogeneous material distribution. However, the resulting geometry requires an additional mould slide to eject the part, increasing the mould complexity and costs.

Fig.9 - Cookie design V3.2 - outer cut

II.3.3.3 V3.3 - Rib flow

Controversially to V3.1 and V3.2, the rib flow version does not foresee a reduction of the outer wall thickness. However, it includes additional extrusions at the cell surface to increase the injection flow and, therefore, allow a quicker distribution of material within the mould.

Fig.10 - Cookie design V3.1 - Shifted wall

II.3.3.4 Results

To assess the improvements of the V3s, a second simulation has been run comparing all the developed designs including the previous V2. The results show remarkable improvements in terms of surface displacement, warpage and cooling time. On the other hand, weld lines show little or neglectable improvements. However, further investigations must be conducted to define whether they entail an actual problem.

II.3.3.4.1 Shrinkage and mark displacement

As shown in the following images, surface displacement has been drastically reduced. As a result, the surface for laser welding appears much more flat in all V3 concepts. Concept V3.3 shows larger marks as its edge thickness has not been reduced.

Fig.11 -

II.3.3.4.2 Warpage

Surface flatness has been improved as shown from the warpage simulation. As follows is listed the difference between the highest and the lowest value of warpage X-displacement at the surface per each concept:

V2 0,033 mm

V3.1 0,018 mm

V3.2 0,012 mm

V3.3 0,016 mm

The following picture graphically shows the location of minimum and maximum warpage points.

Fig.12 -

Also in terms of total warpage, the deformation results homogeneous, evenly shrinking in all directions without evident warpage.

Fig.13 -

II.3.3.4.3 Cooling

Cooling time consequently improved due to the decreasing of the overall wall thickness. Compared to V2 the simulation assessed a reduction of cooling time of about 60% for both concept V3.1 and V3.2 and around 40% for V3.3 design. Timing is listed as follows

V2 89s V3.1 33s

V3.2 32s

V3.3 53s

II.3.3.5 Discussion

The second results of the second simulation show great improvements in terms of cooling time and warping. Therefore, promising in terms of part quality and production time.

Specifically, the concept 3.2 has been rated as the most preferable for production as it shows the best overall performance during simulation. However, those changes in the geometry may implicate further complications, such as increasing in mould costs and production time. The concept V3.2 requires a more complicated mould compared to the other concepts as it requires an additional slide.

V2 V3.1 V3.2 V3.3 Sink marks [mm] Warpage [mm]

II.3.4 V4 Concept

An ultimate iteration of the middle-cookie has been conducted due to last consideration regarding the channel dimensions. According to Siram (2019), channels smaller than 1.5mm in diameter restricts the electrolyte flow. Especially, because of the gas formation, bubbles are likely to plug small channels. Therefore, as the cross-section of the channel increases, its length has to proportionally scaled. Because of this, any of the previous channel designs is not be feasible to implement as there is not enough space. This fourth iteration of the middle-cookie aims to:

- Include larger channels
- Reduce mould complexity
- Reduce volumetric shrinkage and cooling time

Therefore, the proposed bridge geometry takes place next to the top and bottom channels and it runs alongside the inner wall. This configuration does not allow a closed channel, Hence, a cover is required to close the cavity. Such a cover is a simple plastic component which is thermally fused with the middle-cookie.

Because of this, the mould geometry has been largely simplified as no undercuts are required anymore. Indeed, it is expected to reduce not only tooling costs but also ejection time of the part. Furthermore, with this last iteration, it is envisioned to reach a much better material distribution while moulding, positively affecting shrinkage marks and cooling time.

Appendix III. Thermoplastic bonding techniques

III.1 Introduction

One of the challenges of the AEC unit is being operative and reliable at a pressure of 50 bar. Therefore, it is of essential importance to avoid any leaks of the cells.

In the first place, any mixture of hydrogen and oxygen within the unit must be avoided, as it might cause hazardous reactions, such as auto ignition and detonation of the unit (Hoberman, 2019). Secondly, the alkaline solution in use contains 30% of potassium hydroxide.

The compounds result very harmfully and it must not be dispersed in the outer environment. As the unit foresees the assembling of several elements it is of fundamental importance to integrate a reliable and viable bonding of each component.

The state of the art of the AEC foresees a press-fit connection of all elements (Appendix I). Therefore, the concept includes a series of gaskets and grooves to prevent the effusion of fluids either towards the outer environment and in between cells. Therefore, the current system includes two different types of seal. Outer sales must provide the leak tightness of the system towards the outer environment, with a pressure difference of 50 bar, and inner sales, which must avoid any effusion with a difference in pressure of 0,5 bar. However, the developed design resulted to be unreliable as the assembly has never reached the desired pressure. Reasons for this are identified as a lack of clamping force of the assembly as well as not precise coupling of the prototype's parts.

III.1.1 Objective

The objective of the research is to investigate and define methods for reliably and effectively bonding the series of components which construct the inner geometry of the AEC unit. Hence such a connection not only must provide a mechanical joining but also avoid leaks at the operating pressure. The cookie geometry in consideration foresees a larger and stronger bonding towards the outer environment and smaller weld lines for inner chambers. Integration of electrolysis components must be guaranteed within the required tolerances.

III.2 Research

III.2.1 Approach

To effectively assess the previously stated questions a preliminary literature review of the state of the art of welding methods for thermoplastic is carried on. Therefore, be conducted in collaboration with AESON B.V. in such a way to effectively assess the feasibility of such technologies within the AEC development.

III.2.2 Literature review

Literature offers several alternatives for thermoplastic joining. Those are clustered into adhesive bonding, fusion bonding and mechanical fastening as illustrated in Fig1. However, according to Yousefpour et al. (2004) either adhesive bonding and mechanical fastening result to be ineffective techniques. In the first case, there is no effective adhesive to thermoplastics. In the second place, mechanical fastening techniques have issues in regards to the stress concentration as well as the mismatch of thermal expansion. Besides, the latter is the method currently in do not provide any leak tight bonds without the adoption of additional gaskets. Hence, fusion bonding represents the most effective direction.

Fusion bonding consists of a joining technique which foresees the heating of the polymer at the interface up to a viscous state. This procedure allows the polymer chains to inter-diffuse over the interface, hence ss the material cools down the joint is created. Such methods are commonly referred to as welding techniques. These methods are distinct into thermal welding, friction welding and electromagnetic welding The three differ on the method heat is generated at the interface. Friction welding adopts friction for generating heat at the interface. In such a case the two parts are placed against each other and pressure is applied. Thermal welding foresees the use of heating elements to heat the two components at the interface. Therefore, as the interface reaches the required temperature, the parts are pushed against each other. At last, electromagnetic welding makes use of metallic components to heat the interface through magnetic fields.

III.2.2.1 Discussion

A preliminary selection has been achieved by discarding those welding methods which are not feasible in terms of component integration. Among electromagnetic welding, only induction welding represents a feasible solution as its action can be localised in specific areas. However, the other methods, dielectric, microwave and resistance welding, are not suitable as they consist of very invasive approaches. Hence, inner components which contain metals will consequently heat up, with consequent damage of the geometry or the component itself. In regards to friction welding techniques, only ultrasonic welding represents a possible solution. In other cases, the displacement required for generating the heat is too large. Hence it will inevitably be ineffective with small details of the geometry, especially with the integration of components. At last, between thermal welding infrared and laser welding has been identified as the most suitable techniques to adopt.

Hence among all fusion bonding techniques discussed in the literature, four of them apply to join the geometry of the middle-cookie without having any troubles with the integration of further components.

- Infra-red welding
- Laser welding
- Ultrasonic welding
- Induction welding

III.2.3 Welding techniques investigation

Since facilities for fusion bonding require specialised equipment, ZEF B.V. established a partnership with AESON to discuss optimal bonding techniques for the geometry into account. AESON B.V. is a company expert in performing most of the fusion bonding techniques previously discussed. The reference person for this collaboration is Renzo van der Stolpe.

- Which joining method does elicit the joining of a series of elements?
- Which joining method does allow the integration of components?
- Which joining process is the most cost-effective?

III.2.3.1 Question investigation

Such collaboration has begun with an introduction meeting. Hence a brief explanation of Zero Emission Fuels' mission has been lined out as well as the operation of the AEC together with requirements and challenges (REPORT). A morphological chart has been structured to collect functional ideas. Hence, two preliminary concepts were developed to facilitate the understanding of the inner geometry of the AEC unit. Therefore, the discussion moved directly to bonding methods of the cookies stack.

III.2.3.2 Which joining method does elicit the joining of a series of elements?

In terms of multiple joining parts, among the chosen technologies only ultrasonic welding does not perform equally throughout the entire cookie stack as the transmission of the ultrasonic frequency diapers along with the assembly. Furthermore, although laser welding is commonly conducted by coupling a transparent layer upon an opaque one, it is possible to achieve the same result with all transparent elements by applying a thin layer of Clearweld (Woosman, Cawley and Verespy, 2004)

At last, infrared and induction welding do not imply any difficulties in welding multiple parts. In specific, induction enables the possibility of simultaneously bond the entire cookie stack.

III.2.3.3 Which joining method does allow the integration of components?

Among the proposed methods, only induction welding could show issues in terms of components integration. In fact, on the contrary to the other methods, induction welding is performed by heating ferromagnetic elements between the parts. Therefore, the placement of components must be done outside the range of the induction plate otherwise it could affect either the welding process as well as the component's functions. Furthermore, regardless of the chosen method, the design should provide precise alignments of components to effectively place all the parts without creating interference between the components. Indeed, depending on the bonding technique, the geometry could vary to accommodate each part.

III.2.3.4 Which joining process is the most cost/time effective?

In terms of costs, the driven factor is time. Indeed, among the selected technologies, expenditure for tooling is relatively high compared to other much simpler methods. Hence, their capital cost is roughly the same (EDUPack, 2019). Therefore, ultrasonic welding represents the quickest option. Laser welding results to be an equally fast process (LPKF, 2011). Similarly, induction welding results in an optimal solution to join simultaneously all the parts. At last, infrared welding represents the least likely procedure to adopt due to its slow process.

III.2.4 Discussion

Because of the previously discussed reasons, laser welding has been defined to be the optimal solution for joining the entire cookies stack. Indeed, among the selected methods, laser joining techniques results to be a very quick process while allowing the piling of multiple parts. Furthermore, it is a very precise tool able to perform different welded contours.

III.2.4.1 Further investigation

As laser welding has been defined as the most convenient solution to adopt for joining the entire cookie stack. However, since PSU is a high-performance polymer little data is present in literature. Furthermore, AESON never worked with such material and further investigations are required to resolve additional uncertainties. In the first place, the cookies are envisioned to be 8mm thick. Therefore, a preliminary analysis regarding the feasibility of laser welding through thick parts is conducted. Moreover, the geometry includes void cavities which allow the alkaline solution to properly flow within the unit. Hence, further research regarding the possibility to perform the weld through empty spaces will be investigated as well. Those explorations have been phrased as follows:

Is it possible to laser weld through thick parts?

Is it possible to laser weld through void cavities?

III.3 Experimental studies

The following experimental studies have developed in collaboration with AESON to find answers to the uncertainties expressed at 2.4.1. Those studies are specifically focussed on the feasibility of laser welding of PSU and the assessment of the limitation of such technology. To effectively weld two components using a laser beam, a few requirements must be matched. Hence, the material must be transparent to the laser's wavelength. Therefore, it is preferable to use amorphous polymers, such as PSU. Furthermore, the surface must result as smooth as possible to reduce any dispersion of energy of the laser. Therefore, all tests are prepared following the same procedure. The geometry is precisely machined to maintain the parallelism of the faces. Therefore, the surfaces are sanded through multiple grits from 320 to 4000. At last, a polish finish is achieved with a fine mesh cloth. In fig.A is shown the prepared samples before the welding procedure.

III.3.1 Test

To speed up the investigation phase the developed test aims to assess the feasibility of welding through thick components and void cavities simultaneously.

III.3.1.1 Setup

The tests setup consists of three disks cut from a PSU rod of 25,4mm as shown in Fig.x. The base disk of equal thickness of 5mm. The middle disk with different thickness 5, 7 and 13 respectively. The channel disk is 1mm thick. This last disk would have a cut of 1mm to simulate the bridge void. Therefore, the samples have been sent to AESON's facilities to be

III.3.1.2 Results

Through a preliminary observation, the samples clearly show the laser weld contour. The contour seems homogeneous along the circumference without showing evident weak points. Furthermore, the pieces result firmly joined together as any manual pulling has been ineffective. Therefore, it is correct to assume that it is possible to perform the laser weld through thick parts up to 13mm with PSU.

However, as the samples have been clamped in the pulling tool they came apart very easily, showing no effective bonding at the interface. Because of this, no data on the actual bonding strength has been assessed. However, through microscopic analysis of the laser contour, it has been possible to identify areas in which the weld was effective, areas where the laser slightly affected the polymer surface and others parts of the contour which have not been affected at all. FIGX

III.3.1.3 Discussion

At first, impression, although the provided samples were not properly joined, welding through thick parts and empty cavities seems possible. The reasons for this preliminary failure are few. In the first place, the precision of the surface of the component is essential. Indeed, as the provided samples had a large contact surface, even a little imperfection of the components results in an ineffective weld. Furthermore, parameters for welding PSU were still unknown to the company, therefore more tests are required.

III.3.2 Second test

As the previous welding test proves the possibility to perform weld through thick PSU components, the second test aims to identify the proper laser parameters to perform a good weld. Indeed, laser power and speed are of fundamental importance to effectively join two components without having incomplete bonding or material decomposition (Katsiropoulos et al., 2009).

III.3.2.1 Setup

The setup of the second experiment is very similar to the previous. Main differences regard the use of just two parts of equal thickness and the reduction of contact area to the welding surface as shown in FIG.X

III.3.2.2 Results

Results show great improvements to the weld. In the second test, many samples have been successfully joined showing no gaps. Indeed, from a rough preliminary test, the fusion between the two components appears consistent. FIGX

III.3.2.3 Discussion

With the second setup, it has been possible to achieve a good weld through the entire contour. Therefore, both surface tolerance and welding parameters were matched. However, it is necessary to design the parts in such a way they get contact just at the welding interface.

III.4 Conclusion

To conclude, it is correct to assert that the safest alternative to joining the cookies in a leak-tight manner is by adopting laser welding. Indeed, such technology elicits very precise welds through relatively thick parts. Likewise, laser welding does not affect the integration of further components and it provides a shut contour, as long as they do not interfere with the welding contour. However, Laser welding elicits the bonding of a series of elements in series, although no previous assessment of such an approach has been found in the literature.

Appendix IV. List of requirements

equirement	Value	SI	Weigh
ELECTROLYSIS STACK			
stress lower than material tensile stress	5	MPa	2
operating temperature	90	C	3
material degradation to chemicals	< 0.05	mm/year	3
electric resistance must be lower than	0.02	Ω	2
electrical poles must be insulated	-	-	1
supply water from CO ₂ buffer		cm³/min	2
purge oxygen towards degasser		mol/min	2
convey hydrogen to buffer		mol/min	2
safely release inner pressure		cm³/sec	3
hydrogen water level > oxygen water level	10	mm	2
cell temperature > flash tank	5	C	1
constant operating pressure	5	MPa	2
compression rate	20	KN	3
surface tolerances	0.02	mm	2
ELECTROLYSIS CELL		<u>.</u>	<u>.</u>
maximum linear tolerances	0.05	mm	3
number of cells	19-20	cells	3
diaphragm clamping pressure	1	MPa	3
maximum operating temperature	120	C	2
surface area greater than electrodes	>>55	cm ²	2
electrodes surface area	>55	cm ²	2
electrodes flatness tolerance	0.2	mm	2
low electrical resistance connectoin	0.02	ohm	1
convey gases and solution to flash tanks		cm³/min	1
convey solution to cells		cm³/min	1
length/section ratio	> 10	-	3
water level higher than cells	> 5	mm	2
maximum mol of oxygen at 50 bar		mol	3
PRESSURE CASE		- <u>-</u>	
stress lower than material yield stress	5	MPa	3
linear tolerances	0.05	mm	3
closing clamping force	80	kN	3
no permanent fastening	-	-	1
fastening strength		N	1

Appendix V. Cost analysis

Material	density (g/cm ³)	cost (€/kg)
· carbon fiber (twill)	2	31
 fibreglass (twill) 	2.1	24
 stainless steel 	7.8	2.7
ultra low carbon steel	7.8	0.7
 low carbon steel 	7.8	0.7
 carbon steel 	7.8	0.8
• HDPE	0.95	1.0
· PSU	1.24	11.0
· PPS	1.3	5.0
· EPDM	1.1	1.5
· Zifron PERL	1	400
 nickel foam 	0.6	120
 nickel mesh 	4	9.5

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			voli	volume	Weight			Cost			TOTAL	
	material	processes					material		processes			
			cm3		D	%		%		%		%
CASE			605.9	943.6	7360.1	80.4	15.2	55.0	25.8	27.9	41.0	34.1
pipe	stainless steel	extruded	440.0	440.0	3432.0	37.5	9.3	33.6	0.4	0.5	9.7	8.1
lid	stainless steel	machined	80.0	160.0	1248.0	13.6	3.4	12.2	4.2	4.6	7.6	6.3
clamps	mild steel	cast	74.0	296.0	2308.8	25.2	1.5	5.6	20.2	21.8	21.7	18.1
bolts	stainless steel	forging	7.2	28.8	224.6	2.5	9.0	2.2	0.4	0.4	1.0	0.8
washer	stainless steel	forging	2.3	9.2	71.8	0.8	0.2	0.7	0.1	0.2	0.3	0.3
nut	stainless steel	forging	2.4	9.6	74.9	0.8	0.2	0.7	0.4	0.4	0.6	0.5
COOKIE STACK			63.2	1151.6	1343.5	14.7	1.8	9.9	65.8	71.1	67.6	56.3
middle cookie	HDPE	5 axis machined	58.0	1102.0	1046.9	11.4	1.0	3.8	40.2	43.4	41.3	34.3
o-ring (cookies)	EPDM	injection	0.7	12.8	14.1	0.2	0.0	0.1	12.0	13.0	12.0	10.0
o-ring (outlets)	EPDM	injection	0.1	0.7	0.8	0.0	0.0	0.0	5.3	5.8	5.3	4.4
passthrough cookie	stainless steel	blanking	0.4	28.1	219.3	2.4	0.6	2.1	8.0	8.7	8.6	7.2
passthrough end	stainless steel	machined	4.0	8.0	62.4	0.7	0.2	9.0	0.2	0.2	0.4	0.3
ELECTROLYSIS COMPONENTS			3.2	72.0	451.9	4.9	10.6	38.4	1.0	1.1	11.6	9.7
membrane	coated PSU	blanking	1.7	16.2	16.2	0.2	6.5	23.4	0.7	0.7	7.1	5.9
electrodes	nickel expanded	blanking	1.5	55.9	435.7	4.8	4.1	15.0	0.3	0.4	4.5	3.7
							27.6		92.6		120.2	

			DA	volume	Weight			Cost			TOTAL	
	material	processes	unit				material		processes			
			cm3		6	%		%		%		%
ENCLOSURE			357.8	424.3	3309.5	<i>T.T</i>	4.7	9.3	8.0	33.3	12.7	17.0
case	low carbon	deep drawing +	1 70.0	170.0	1326.0	31.1	6.0	1.8	0.3	1.0	1.1	1.5
lid	low carbon	machined +	100.1	100.1	780.8	18.3	0.5	1.0	3.7	15.4	4.2	5.7
bolts	stainless steel	forging	7.2	57.6	449.3	10.6	1.2	2.4	0.3	1.2	1.5	2.0
washer	stainless steel	blanking	2.3	18.4	143.5	3.4	0.4	0.8	0.1	0.3	0.5	0.6
collar	stainless steel	machined	78.2	78.2	610.0	14.3	1.6	3.3	3.7	15.4	5.4	7.2
COOKIE STACK			26.2	313.8	679.4	16.0	2.6	5.2	15.8	65.4	18.4	24.7
cells	PPS	injection	22.0	264.0	343.2	8.1	1.7	3.4	8.0	33.2	9.7	13.1
o-ring (cookies)	EPDM	injection	0.7	7.8	8.6	0.2	0.0	0.0	7.3	30.4	7.3	6.9
passthrough cookie	stainless steel	machined	3.5	42.0	327.6	7.7	0.9	1.8	0.4	1.8	1.3	1.8
ELECTROLYSIS COMPONENTS			19.2	422.4	268.8	6.3	43.0	85.5	0.3	1.3	43.3	58.2
membrane	coated PSU	blanking	3.2	38.4	38.4	6.0	15.4	30.5	0.1	0.4	15.5	20.8
electrodes	metal foam	blanking	16.0	384.0	230.4	5.4	27.6	55.0	0.2	6.0	27.9	37.4
							50.3		24.1		74.4	

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			volt	volume	Weight			Cost				
	material	processes	unit				material		processes			
			cm3		δ	%		%		%		%
ENCLOSURE			378.9	522.8	1734.6	58.1	21.9	37.2	30.5	51.1	52.4	44.2
case	composite	vacuum	330.0	330.0	660.0	22.1	15.8	26.9	15.87	26.6	31.7	26.7
lid	composite	vacuum	37.0	74.0	148.0	5.0	3.6	6.0	6.35	10.6	9.9	8.3
bolts	stainless steel	forging	7.2	86.4	673.9	22.6	1.8	3.1	0.44	0.7	2.3	1.9
washer	stainless steel	forging	2.3	27.6	215.3	7.2	0.6	1.0	0.44	0.7	1.0	0.9
collar	stainless steel	forging	2.4	4.8	37.4	1.3	0.1	0.2	7.41	12.4	7.5	6.3
COOKIE STACK			26.8	536.0	769.6	25.8	7.4	12.6	28.7	48.0	36.1	30.4
cells	PSU	injection	26.0	520.0	644.8	21.6	7.1	12.0	13.33	22.3	20.4	17.2
welded seal	PSU	welded							7.94	13.3	7.9	6.7
passthrough cookie	stainless steel	machined	0.8	16.0	124.8	4.2	0.3	0.6	7.41	12.4	7.7	6.5
ELECTROLYSIS COMPONENTS			5.8	168.0	480.0	16.1	29.6	50.2	0.5	0.9	30.1	25.4
membrane	coated PSU	blanking	3.2	64.0	64.0	2.1	25.6	43.5	0.18	0.3	25.8	21.7
electrodes	perforated	blanking	2.6	104.0	416.0	13.9	4.0	6.7	0.35	9.0	4.3	3.6
							58.9		59.7	_	118.6	

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			ION	VOLUME	WEIGHT			COST			TOTAL	
	material	processes	unit	parts			material		processes			
			cm3	cm3	Б	%	ŧ	%		%		%
PRESSURE CASE			341.9	858.8	6698.6	78.4	29.9	46.0	10.6	24.6	40.5	37.5
case	Sdd	injection	330.0	660.0	5148.0	60.2	25.7	39.5	9.33	21.7	35.1	32.4
bolts	stainless steel	forging	7.2	100.8	786.2	9.2	2.1	3.3	0.51	1.2	2.6	2.4
washer	stainless steel	forging	2.3	64.4	502.3	5.9	1.4	2.1	0.25	0.6	1.6	1.5
bolts	stainless steel	forging	2.4	33.6	262.1	3.1	0.7	1.1	0.51	1.2	1.2	1.1
COOKIE STACK			163.1	601.0	1304.6	15.3	5.0	7.7	31.9	74.1	36.9	34.1
sleeve	PPS	injection	120.0	120.0	156.0	1.8	0.8	1.2	1.33	3.1	2.1	2.0
cells	Sdd	injection	15.0	300.0	390.0	4.6	2.0	3.0	13.33	31.0	15.3	14.1
channels	PPS	injection	10.0	20.0	26.0	0.3	0.1	0.2	1.33	3.1	1.5	1.4
damp	Sdd	injection	3.2	64.0	83.2	1.0	0.4	0.6	6.67	15.5	7.1	6.5
clamp membrane	PPS	ultrasonic				'			0.84	1.9	0.8	0.8
rod	stainless steel	forging	11.0	11.0	85.8	1.0	0.2	0.4	0.04	0.1	0.3	0.2
o-ring (cookies)	EPDM	2K injection	0.4	16.0	17.6	0.2	0.03	0.041	3.33	7.7	3.4	3.1
passthrough cookie	stainless steel	deep drawing	3.5	70.0	546.0	6.4	1.5	2.3	5.05	11.7	6.5	6.0
ELE CTROLYSIS COMPONENTS			6.2	184.0	544.0	6.4	30.2	46.3	0.5	1.2	30.7	28.4
membrane	coated PSU	blanking	3.2	64.0	64.0	0.7	25.6	39.3	0.18	0.4	25.8	23.8
electrodes	stretched	blanking	3.0	120.0	480.0	5.6	4.6	7.0	0.35	0.8	4.9	4.5
							65.1		43.1	_	108.2	

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			lov	volume	Weight			Cost				
	material	processes	unit				material		processes		107.7%	
			cm3	cm3	б	%		%		%		
ENCLOSURE			398.5	689.0	5374.2	82.4	4.8	12.7	9.1	21.5	13.9	17.4
case	ultra-low carbon steel	cast steel + galvanised	165.0	165.0	1287.0	19.7	6.0	2.3	5.1	11.9	5.9	7.4
lid	low carbon	machined +	224.0	448.0	3494.4	53.6	2.3	6.2	3.7	8.7	6.0	7.5
bolts	stainless steel	forging	7.2	57.6	449.3	6.9	1.2	3.2	0.3	0.7	1.5	1.9
washer	stainless steel	blanking	2.3	18.4	143.5	2.2	0.4	1.0	0.1	0.2	0.5	0.6
COOKIE STACK			22.1	398.3	606.1	9.3	2.7	7.2	32.8	77.2	35.5	44.3
cells	PPS	injection	18.0	360.0	468.0	7.2	2.3	6.2	13.3	31.4	15.7	19.6
channels	PPS	injection	2.7	10.8	14.0	0.2	0.1	0.2	2.7	6.3	2.7	3.4
channels welding	PPS	ultrasonic	ı						3.35	7.9	3.4	4.2
o-ring (cookies)	EPDM	2k injection	0.7	13.5	14.8	0.2	0.0	0.1	12.7	29.9	12.7	15.8
passthrough cookie	stainless steel	machined	0.7	14.0	109.2	1.7	0.3	0.8	0.7	1.7	1.0	1.3
ELECTROLYSIS COMPONENTS			6.2	184.0	544.0	8.3	30.2	80.0	0.5	1.3	30.7	38.3
membrane	coated PSU	blanking	3.2	64.0	64.0	1.0	25.6	67.9	0.2	0.4	25.8	32.2
electrodes	perforated steel	blanking	3.0	120.0	480.0	7.4	4.6	12.1	0.4	0.8	4.9	6.1
							37.7		42.4		80.1	

Appendix VI. Weighted objective evaluation

Seal integration	Welding (pt)	O'ring (pt)	Gasket (pt)	2K moulding (pt)
· COST	3	9	12	6
· SAFETY	6	3	9	12
· FEASIBILITY	2	8	6	4
· LIFETIME	8	4	4	4
· ASSEMBLY	1	2	3	4
· total	20	26	34	30

Stack geometry	Cookie concept (pt)	Welded sleeve (pt)
· COST	6	3
· SAFETY	6	3
· FEASIBILITY	4	2
· LIFETIME	4	2
· ASSEMBLY	1	2
· total	21	12

Diaphragm integration	Between cells flat	Between cells rib	Framed
	(pt)	(pt)	(pt)
· COST	9	6	3
· SAFETY	6	9	3
· FEASIBILITY	6	4	2
· LIFETIME	4	6	2
· ASSEMBLY	2	1	3
• total	27	26	13

Electrodes integration	Expanded mesh	Woven mesh	Perfororated mesh (pt)	Metal foam
	12	9	6	3
· SAFETY	6	3	12	9
· FEASIBILITY	2	4	8	6
· LIFETIME	4	2	6	8
· ASSEMBLY	1	2	4	3
• total	25	20	36	29

Channel geometry	Surface and undercut (pt)	Additional element (pt)
· COST	3	6
· SAFETY	6	3
· FEASIBILITY	2	4
· LIFETIME	4	2
· ASSEMBLY	1	2
• total	16	17

Case material	Low carbon steel (pt)	Thermoplastics (pt)	Composites (pt)
· COST	9	6	3
· SAFETY	6	3	9
· FEASIBILITY	6	2	4
· LIFETIME	4	2	6
· ASSEMBLY	1	3	2
• total	26	16	24

Case geometry	Horizontal (pt)	Vertical (pt)
· COST	6	3
· SAFETY	3	6
· FEASIBILITY	2	4
· LIFETIME	2	4
· ASSEMBLY	2	1
• total	15	18

Appendix VII. Bolts

BOLT PROPRETY CLASSES

Property class (ISO 898)	Proof strength (MPa)
· 4.6	225
· 4.8	310
· 5.8	380
· 8.8	600
· 9.8	650
· 10.9	830
· 12.9	970

BOLT

Size	Grade	Strength _{kN}	Case 1 #	Case 2 #	Case 3 #
• M6	4.6	6	21.2	14.9	49.2
	4.8	8	15.4	10.8	35.7
	5.8	10	12.5	8.8	29.2
	8.8	16	7.9	5.6	18.5
	9.8	17	7.3	5.2	17.0
	10.9	22	5.7	4.0	13.3
	12.9	26	4.9	3.5	11.4
M8	4.6	11	11.6	8.2	27.0
	4.8	15	8.4	5.9	19.6
	5.8	19	6.9	4.8	16.0
	8.8	29	4.4	3.1	10.1
	9.8	32	4.0	2.8	9.4
	10.9	41	3.1	2.2	7.3
	12.9	47	2.7	1.9	6.3
M10	4.6	17	7.3	5.2	17.1
	4.8	24	5.3	3.7	12.4
	5.8	29	4.3	3.1	10.1
	8.8	46	2.7	1.9	6.4
	9.8	50	2.5	1.8	5.9
	10.9	64	2.0	1.4	4.6
	12.9	75	1.7	1.2	4.0

Appendix VIII. Project biref



Procedural Checks - IDE Master Graduation

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chair Jos Oberdof		09 - 05 -	2019	signature	
CHECK STUDY PROGRESS To be filled in by the SSC E&SA (Shared Service The study progress will be checked for a 2nd tim	Center, Educ e just before	ation & Stude the green ligl	nt Affairs), a nt meeting.	fter approval of the p	project brief by the Chair.
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FORMAL APPROVAL GRADUATION PROJE		ase check the s	iteria belov	eam and study the p v.	arts of the brief marked **.
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Title of Project Designing of small scale alkaline cells (AEC) unit for mass production

Personal Project Brief - IDE Master Graduation

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Designing of small scale alkaline cells (AEC) unit for mass production	project title
	[]

Please state the title of your graduation project (above) and the start date and end date (below). Keep the title compact and simple. Do not use abbreviations. The remainder of this document allows you to define and clarify your graduation project.

start date 09 - 05 - 2019

05 - 12 - 2019 end date

INTRODUCTION **

Please describe, the context of your project, and address the main stakeholders (interests) within this context in a concise yet complete manner. Who are involved, what do they value and how do they currently operate within the given context? What are the nain opportunities and limitations you are currently aware of (cultural- and social norms, resources (time, money...), technology, ...).

Levels of CO2 in the atmosphere has been drastically increasing in the past decades mainly due to massive consumption of fossil fuels, for either transport and good means. Such unsustainable development has been proved to be the main cause of of atmosphere's temperature rising with direct effects on the environment and living organisms, including human being.

In these regards, Zero Emission Fuels (ZEF) is a growing Dutch start-up in the field of sustainable energy production. Their goal consists in converting solar energy and air into methanol, which can be further adopted either as fuel for transport and for polymers production.

Controversy to conventional chemical plants, which complexity and dimensions make them unlikely to properly operate with inevitable fluctuating energy supplies, ZEF's concept foresees a chemical plant small enough to operate with a standard photovoltaic (PV) panel of 300W and able to adaptively employ its energy supply and produce approximately 100g of methanol per day. Such amount of methanol would contain the equivalent energy required to run an economy car for about 1,7 km, or light a 60W bulb light for about 10 hours. In order to achieve such goal, the methanol plant has been structured in multiple sub-units, each of which is responsible of a specific task, from capturing water and carbon dioxide from air, to distilling pure methanol. Hence,

such concept would result in a very scalable alternative and by scaling up the number of these micro chemical plants it would be possible to proportionally increase methanol production while decreasing production costs. Although at this very moment most working principles have been proven through prototypes and tests, in order to step up and build the first integrated prototype each subsystem has to be properly designed and optimised for being manufactured on a big scale.

Therefore, this thesis project aims to further develop the sub-unit of the plant in charge of obtaining hydrogen from water: the Alkaline Electrolysis Cell (AEC). The challenges involved take in account designing the AEC unit for mass manufacturing in order to result cost competitive. Hence, technologies and methods for integrating components, reducing amount of parts required and simplifying the assembly phase.

Furthermore, safety and integrity of the unit throughout the years is essential, as it operate with hazardous chemical compounds, which must be carefully managed in order to do not be harmful for people and environment. Therefore, the design phase must take in account safety measurements and regulations, especially in the moment of commissioning and maintenance of the unit.

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IDE TU Delft - E&	SA Department /// Graduation project brief & study overview	r /// 2018-01 v30	Page 3 of 7
Initials & Name	O A Azzalini	Student number 4634756	
Title of Proiect	Designing of small scale alkaline cells (AEC) unit for mass	s production	



image / figure 1: Assembly exploded view of concept of the AEC unit developed by Team 3



image / figure 2: _____Assembled prototype of the AEC unit developed by Team 3

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PROBLEM DEFINITION **

Limit and define the scope and solution space of your project to one that is manageable within one Master Graduation Project of 30 EC (= 20 full time weeks or 100 working days) and clearly indicate what issue(s) should be addressed in this project.

At this very moment the AEC unit proof of concept subsist as working prototype, which has been structure in order to test and further develop the unit. Hence, it has been design and prototype in such a way it could be disassembled and modified. However, its over-complexity make it very unlikely to be mass produced and many components are not optimised for such process.

The designing and further optimisation of the AEC unit in consideration raises the following challenges

- the embodiment and integration of the unit for mass manufacturing technologies

- the development of an easy and effective assembly process of the AEC unit
- safety measurements while operating

In first place, as the scope is to scale up the number of produced units, the final design needs to be optimised for mass manufacturing processes, assessing feasible geometries and optimal materials. Production processes for each components and material must be considered and evaluated in order to provide an effective integration of essential components while matching the operational requirements.

Furthermore, components have to be redesign in such a way to simplify the overall assembly phase, reducing production time and costs. Firstly, the unit must be built together, hence it can be integrated in the chemical plant and operate with the other system's units.

Moreover, safety requirements must be considered, as the AEC unit contain hazardous elements at high temperature and pressure. Although the unit would autonomously operate, there would be few moments in which it would need human intervention, especially for commissioning and maintaining the unit. In these cases the operations required must be done in completely safety. In addition, the unit must not disperse any harmful substance in the environment.

ASSIGNMENT **

State in 2 or 3 sentences what you are going to research, design, create and / or generate, that will solve (part of) the issue(s) pointed but in "problem definition". Then illustrate this assignment by indicating what kind of solution you expect and / or aim to deliver, for instance: a product, a product-service combination, a strategy illustrated through product or product-service combination ideas, In case of a Specialisation and/or Annotation, make sure the assignment reflects this/these.

Design and embody ZEF's Alkaline Electrolysis Cell (AEC) for assembly and manufacturing processes. The design would take in account the current proof of concept, redefining and integrating components into a more compact and cost effective unit.

Since much research and development on the AEC unit have been carried on by ZEF in the past years, the first step would foresee the understanding of the current concept operation, clearly defining requirements, challenges and evaluating criteria of the subsystem in exam. Hence, a deep study of the current prototype would line out all components and expose limitations for optimal operation, mass production and assembly.

Therefore, multiple ideas for each sub-problems must be developed and quickly evaluated through mock-ups and focussed tests, which would define their feasibility and effectiveness.

From the preliminary analysis and ideas exploration few concepts would be assessed and evaluated by making use of accurate manufactured prototypes, computational simulation and actual tests, exposing concepts' feasibility of working principles, mechanical and assembly structure.

As follow the embodiment of the selected concept would further develop and detail the concept, assessing final geometry materials and required components.

At last the final proposal would consist in an AEC unit design, with relative tech docs, cost analysis and prototype. The proposed design would be mass manufacturable, easy to assemble and able to integrate with the other subsystem of the micro chemical plant. It is expected to deliver a accurate manufactured prototype of the final proposal, or at least main functional components.

IDE TU Delft - E&SA Department /// Graduation project brief & study overview /// 2018-01 v30

Page 5 of 7

Initials & Name OA Azzalini

Student number 4634756

Title of Project Designing of small scale alkaline cells (AEC) unit for mass production

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PLANNING AND APPROACH **

Include a Gantt Chart (replace the example below - more examples can be found in Manual 2) that shows the different phases of your project, deliverables you have in mind, meetings, and how you plan to spend your time. Please note that all activities should fit within the given net time of 30 EC = 20 full time weeks or 100 working days, and your planning should include a kick-off meeting, mid-term meeting, green light meeting and graduation ceremony. Illustrate your Gantt Chart by, for instance, explaining your approach, and please indicate periods of part-time activities and/or periods of not spending time on your graduation project, if any, for instance because of holidays or parallel activities.



The planning developed take in account 100 working days spread over 25 weeks, as I would work alongside graduation and I would commit 4 days per week on the project development.

1- The first period of 10 weeks would head to the midterm meeting. It would include the research, ideation, conceptualisation and a preliminary concept evaluation in order to propose a feasible proposal which would further embodied in the second period.

The research (2/3 weeks) would focus on the current concept developed by ZEF, understanding its operation principles and issues. Hence an investigation on technologies and requirements for mass production would follow assessing criteria for evaluation. The research phase would conclude with a list of requirements, challenges and goals. As follow a brief ideation of 2 weeks on defined requirement and functions would explore a wide range of solution which would then quickly tested, evaluated and finally collected in a morphological chart.

Therefore, 3/4 weeks would be required for combining most feasible and viable solutions from the chart in equally detailed concepts. At last, a couple of week for evaluating concepts would define the concept for embodiment. 2 - The second period would be entirely committed to the embodiment and refinement of the concept for assembly

and production. Hence, it foresee a couple of iteration of embodiment and evaluation phases in order to quick develop and test the working principles. The second period would conclude with a fully manufacturable proposal. First, a phase of 3/4 weeks would be required to completely embody the selected concept, defining components, material and architecture, detailing them for production and assembly.

Evaluations of the results would envision functional and accurate prototypes in order to highlight issues and improvement, which would be tackled in the next embodiment and optimisation iteration.

3 - The last period of 5 weeks before the final defence would mostly dedicated to the final report and presentation and the final evaluation and testing of the final design.

IDE TU Delft - E8	ASA Department /// Graduation project brief & study overview	/// 2018-01 v30	Page 6 of 7
Initials & Name	O A Azzalini	Student number 4634756	
Title of Proiect	Designing of small scale alkaline cells (AEC) unit for mass	s production	

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Personal Project Brief - IDE Master Graduation

MOTIVATION AND PERSONAL AMBITIONS

Explain why you set up this project, what competences you want to prove and learn. For example: acquired competences from your MSc programme, the elective semester, extra-curricular activities (etc.) and point out the competences you have yet developed. Optionally, describe which personal learning ambitions you explicitly want to address in this project, on top of the learning objectives of the Graduation Project, such as: in depth knowledge a on specific subject, broadening your competences or experimenting with a specific tool and/or methodology, Stick to no more than five ambitions.

I am personally fascinated and motivated in acting towards sustainable developments, as I really believe it represents the only direction to move on. In this regard, ZEF represents a truly disruptive venture in many ways, not only due to their mission of producing sustainable synthetic fuel from renewable energies, but also because of the entire project development, which is largely supported and carried on by interchanging teams of students .

First, I am very intrigued by the challenges such project provides and keen on participating in its development. My goal is to further refine personal design skills, specifically regarding embodiment and prototyping, I developed over the master course of IPD and effectively apply them to a concrete assignment. In particular I am very keen to effectively adopt design strategies for sustainability, such as cradle-to-cradle, biomimicry and LCA.

In second place, since I have already worked as intern at ZEF, I am looking forward being part of such cooperative and multidisciplinary team again. Indeed, as I would be one of the few designers within the team, it would be very insightful to gain novel knowledge and translate engineer requirements into a effective design.

Furthermore, this project would represent my first opportunity to design and fully embody a concept into a working product, collaborating with actual manufacturer and evaluating the resulting design in real operating conditions. Hence i am very keen in gaining further competences in engineering and manufacturing, investigating methods and possible alternatives for mass manufacturing, reducing costs and environmental impacts.

FINAL COMMENTS

case your project brief needs final comments, please add any information you think is relevant.

IDE TU Delft - E&SA Department /// Graduation project brief & study overview /// 2018-01 v30

Page 7 of 7

Initials & Name O A Azzalini Student number 4634756

Title of Project Designing of small scale alkaline cells (AEC) unit for mass production