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Ammonia2HeatStorage

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Ammonia2HeatStorage

Development of a long-term storage system through the combination of CLC and "green" ammonia by means of Membrane Distillation

(Entwicklung eines Langzeitspeichersystems durch die Kombination CLC und „grünem“ Ammoniak mittels Membrandestillation)

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Abstract

In order to increase the volatile share of renewables in the energy supply mix, the development of efficient energy storage technologies is becoming increasingly important. The requirements for such technologies are high flexibility, high freedom from losses and, in particular, compactness, i.e., storing as much energy as possible with small system volumes. In the recent past, chemical looping combustion (CLC) for long-term energy storage has been researched. The advantage of a CLC storage system is that, unlike, for example, sensible heat storage systems, heat can be stored chemically from several days or weeks to months without loss. Up till now, the CLC technology has been mostly used in combination with fossil fuels.

The CLC technology uses an oxygen carrier (OC), a metal, which is reduced/oxidized in cycles. The reduction can be achieved using biogas (CH₄), Hydrogen (H₂) or other fuels (e.g., synthetic gas, solid coal, NH₃, etc.) while the oxidation is done with air. For most of the OCs, both reactions are exothermic, and heat can be extracted from both. The aim of the project was to explore the viability of the CLC technology using the "green" NH₃ recovered from waste streams via Vacuum Membrane Distillation-VMD for the storage of renewable energies. The main success of the project **was a "proof of concept" of a lab-scale CLC prototype reactor which could be operated with NH₃.**

Thanks to the simulations of the mathematical model that BOKU developed within the project and the expertise of AEE INTEC in building and testing storage facilities **the project was successful in designing and testing a CLC reactor prototype operating with NH₃.** On the VMD side, the exploratory experiments together with an in-house VMD model development, **allowed to estimate the quantity, quality and energy needed for the recovery of ammonia from potential waste streams.** This report contains the findings consistent with the established project objectives, which were:

- A detailed thermodynamic model of the overall CLC/NH₃ system as well as an evaluation of the potential oxygen carrier materials.
- Ammonia quality, quantity and thermal energy consumption from the experimental VMD results from artificial and real water sources.
- Development, testing and proof of concept of a CLC/NH₃ reactor prototype
- Preliminary techno-economic potential assessment of the technology
- Definition of research questions for further development steps

The project was successful in achieving all the objectives, including a **CLC reactor using 1,8 kg of copper** as the OC and **operating with NH₃** that was built and tested fulfilling the proof of concept. The reactor was able to reach **temperature differences of more than 100 ° C** and **power densities** of around **164 kWh/m³** per cycle (reduction + oxidation) with NH₃ and **233 kWh/m³** with H₂. Also, **specific industrial application sectors** for the CLC/NH₃ storage tank were identified: the **steel industry/coke production, tanneries, biogas plants, rendering**, etc. In addition to these, there is also a considerable demand for high-temperature storage in so-called **"power-to-heat"** applications which could be tackled by a future CLC/NH₃ thermal storage.

Kurzfassung

Um den volatilen Anteil an Erneuerbaren im Energieversorgungsmix zu erhöhen, wird die Entwicklung effizienter Energiespeichertechnologien immer wichtiger. Anforderungen an solche Technologien sind hohe Flexibilität, niedrige thermische Verluste und insbesondere Kompaktheit, das heißt maximale Energiemengen bei gleichzeitig kleinem Systemvolumen zu speichern.

In jüngster Vergangenheit wurde begonnen **Chemical Looping Combustion (CLC) für langfristige Energiespeicherung** zu erforschen. Im Gegensatz zu bisher in Verwendung befindlichen Speichertechnologien kann durch den Einsatz einer Speichertechnologie auf Basis der Festbett-Chemical-Looping-Combustion (CLC) ein verlustfreier, kompakter und sicherer Hochtemperatur-Speicher realisiert werden. Dieser speichert Wärme chemisch verlustfrei wobei die Wärmeabgabe aus dem Speicher auf einem hohen Temperaturniveau von bis zu 1.000°C erfolgen kann.

Ziel des Projekts war es, die Eignung der CLC-Technologie für chemische Langzeitwärmespeicherung zu untersuchen. Im angedachten Systemkonzept wird statt fossiler Brennstoffe grüner Ammoniak (NH₃) eingesetzt, der mittels Vakuum-Membrandestillation (VMD) auf nachhaltigen Weg aus Abfallströmen gewonnen wird.

Das wichtigste Ergebnis des Projekts war der Bau und Test eines „Proof of Concept“-Prototyps im Labormaßstab. Detaillierte Reaktorsimulationen, mit einem eigens von der BOKU entwickelten Modell ermöglichten in Kombination mit der Expertise der AEE INTEC im Bereich des Prototypenbaus die Umsetzung dieses Ziels. Im Energielabor der AEE INTEC wurde im Zuge des Projekts ein CLC-Reaktor inklusive Teststand aufgebaut, der Experimente mit verschiedenen Speichermaterialien und Brenngasen ermöglicht. Versuchsreihen zur Validierung des „Proof of Concept“ wurden durchgeführt und mit den Simulationsergebnissen verglichen. Im Bezug auf die Ammoniak Produktion ermöglichten die Sondierungsexperimente zusammen mit einem von AEE INTEC entwickelten VMD-Modell die Abschätzung von Menge und Qualität des Ammoniaks aus Abfallströmen sowie der, zur Rückgewinnung benötigten Energie. Dieser Bericht enthält die Ergebnisse, die den festgelegten Projektzielen entsprechen, nämlich:

- Ein detailliertes thermodynamisches Modell des gesamten CLC/NH₃-Systems sowie eine Bewertung der potentiellen Redox-Systeme (verschiedene Sauerstoffträger-Materialien).
- Ammoniakqualität, -quantität und thermischer Energieverbrauch aus VMD Experimenten mit industriellen und synthetisch hergestellten Abwässern.
- Entwicklung, Umsetzung und „Proof of concept“ eines CLC/NH₃-Reaktorprototyps
- Abschätzung des technisch-ökonomischen Potentials der Technologie als chemischer Langzeitwärmespeicher
- Definition von Forschungsfragen für weitere Entwicklungsschritte

Im Rahmen des Projekts konnten alle gesteckten Ziele erfolgreich abgeschlossen werden, einschließlich des Aufbaus und der experimentellen Untersuchung eines „Proof of Concept“-CLC-Reaktors, welcher mit 1,8 kg Kupfer als Sauerstoffträger befüllt und mit NH₃ betrieben wurde. Der Reaktor war in der Lage, Temperaturdifferenzen von mehr als 100 °C und Energiedichten von etwa 164 kWh/m³ pro Zyklus

(Reduktion + Oxidation) mit NH₃ und 233 kWh/m³ mit H₂. Auf Basis der erzielten Ergebnisse konnten außerdem spezifische industrielle Anwendungsbereiche für den CLC/NH₃-Speicher identifiziert werden, die da wären: Stahlindustrie/Koksherstellung, Gerbereien, Biogasanlagen und die Lebensmittelindustrie. Zusätzlich besteht ein erheblicher Bedarf an Hochtemperaturspeichern in so genannten "Power-to-Heat"-Anwendungen, die von einem zukünftigen thermischen CLC/NH₃-Speicher adressiert werden könnten.

1 Introduction

1.1 CLC as storage technology

Chemical Looping Combustion (CLC)

In order to increase the volatile share of renewables in the energy supply mix, the development of efficient energy storage technologies is becoming increasingly important. The requirements for such technologies are high flexibility, high freedom from losses and, in particular, compactness, i.e., storing as much energy as possible with small system volumes. In the recent past, chemical looping combustion (CLC) for long-term energy storage has been researched. The advantage of a CLC storage system is that, unlike, for example, sensitive heat storage systems, heat can be stored chemically for several days and weeks to months without loss.

Heat of low temperature (< 100 °C) is mostly stored sensible in water, with a storage density of about 55 kWh/m³, based on the volume of water. However, sensible thermal storage systems will exhibit losses as the heat is stored at higher temperatures than the ambient temperature. A loss-free compact thermal storage system including the use of ammonia could be realized by using a technology based on fixed-bed chemical looping combustion (CLC). Since heat is stored chemically and without loss, CLC technology is ideal for storing heat for several days and weeks up to long-term storage or seasonal heat storage. In addition, initial literature research indicated that storage densities of up to 6 GJ/m³ could be achieved.

Figure 1 shows the classic approach of a CLC-reactor. It consists of two reactor modules operated in batch mode: an air-reactor and a fuel-reactor. In the air-reactor, reduced forms of the oxygen carrier (OC) are oxidized in an exothermic reaction with air. The oxidized forms of the OC are then reduced in the fuel reactor, using biogas (CH₄), Hydrogen (H₂) or other fuels (e.g., synthetic gas, solid coal, NH₃, etc.). The reduced OC can be then re-oxidized in the air reactor completing the loop/cycle. The final energy-balance will depend on the OC, the temperature and the pressure of the reactor (Mattison T. et al. 2018).

The **general chemical reactions** of the process can be described as follows:

$(2n + m) Me_xO_y + C_nH_{2m} \rightarrow (2n + m) Me_xO_{y-1} + nCO_2 + mH_2O$	Equation 1
$2Me_xO_{y-1} + O_2 \rightarrow 2Me_xO_y$	Equation 2

Equation 1 represents the reduction, where, Me_xO_y is the metal oxide (OC) and C_nH_{2m} is the fuel that reacts and reduces the metal oxide to Me_xO_{y-1} . Subproducts of this reaction are water (H_2O) and carbon dioxide (CO_2). Equation 2 represents the oxidation in the air reactor, where the reduced metal (Me_xO_{y-1}) is again oxidized again (Mattison T. et al. 2018).

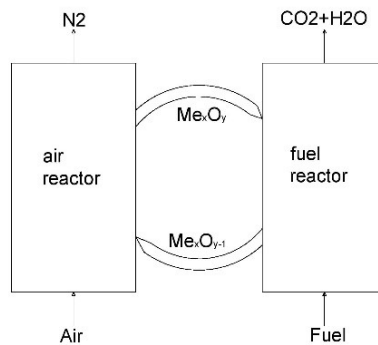


Figure 1: CLC combustion reactor basic principle (Proell T. 2011)

1.2 VMD as ammonia recovery technology

Fossil fuels are finite and cause serious environmental and supply issues. H_2 is foreseen as the future green fuel, however its use is limited by safety, costs and storage challenges. Ammonia is a safer, higher energy density, easier to liquefy and distribute alternative fuel. However, ammonia is currently produced through the highly energy-consuming and CO_2 producer Haber-Bosch process. Likewise, excessive production of agricultural, animal and industrial ammonia rich waste streams is the result of the increasing food demand. Due to its high solubility in water and chemical reactivity, ammonia is considered to be the cause of surface water eutrophication (Brian, C. et al, 2000). Additionally, acidic rain can be formed due to the oxidization of ammonia in the atmosphere, which influences the soil and groundwater (Brian, C. et al, 2000, Pearson J. et al, 2010). The recovery of ammonia from waste streams has the added benefit of reducing the (EU-regulated) treatment, transportation and disposal costs (i.e., N-pollution costs the EU between 70 and 100 billion € per year) (European Commission, Nitrogen Pollution and the European Environment: Implications for Air Quality Policy, 2013).

Ammonia is present in liquid waste streams in two forms: free ammonia (NH_3) and ammonium (NH_4^+). The free ammonia is gaseous, whereas ammonium NH_4^+ is an ionized form that remains soluble in water (M.M. Jafarpour et al 2010). There are different technologies to remove ammonia from wastewater streams, such as aerobic de-ammonification, reverse osmosis, air-stripping in combination with acid absorption, co-precipitation with phosphate and magnesium to form struvite, electro-chemical and biochemical treatment, etc (T. Duong et al 2013, J.P. Sheets et al 2015, A. Bonmatí et al 2003, L. Masse et al 2010, S. Uludag-Demirer et al 2005, M. Xie et al 2016). All these methods are 'destructive' processes and do not allow for the reuse of ammonia. **Membrane technologies are effective to remove and recover ammonia** from liquid streams, among these membrane distillation (MD) offers **the advantage of requiring mostly low-temperature thermal energy**. Also, the process **operates at atmospheric pressure** resulting in less demanding membrane characteristics and less severe fouling (M.A. Izquierdo-Gil et al 2004).

Within the ammonia2heatstorage project, various waste streams have been experimentally treated via VMD to recover free ammonia (NH₃). The open questions that we tried to answer were (1) what is the amount of ammonia that can be recovered from these waste streams, (2) what is the quality of the extracted ammonia and (3) how much thermal energy, chemicals and membrane area are needed to do so. One of the questions that unfortunately remained open after the project **is the effect of the quality of the VMD-extracted ammonia (i.e., amount of water vapor) in the performance of the CLC reactor.**

1.3 Objectives and methodology of the project

The project *Ammonia2HeatStorage* addresses the questions raised above following a modelling and experimental approach. The data generated experimentally and via modelling throughout the project, served to preliminary evaluate a series of KPIs for the assessment of the techno-economic potential of the proposed technology. However, during the course of the project, the consortium realized that many research questions will remain open and consequently a deep techno-economic assessment wouldn't be reachable at this stage. The efforts were directed to the main objective of the exploratory project which was **to serve as a proof of concept for the operation of a CLC with NH₃ as fuel.**

The project was structured in four tasks:

- Thermodynamic modelling of the CLC -NH₃ reactor
- Design, building and testing of a CLC -NH₃ prototype
- VMD experiments for ammonia extraction potential
- Techno-economic potential of the proposed technology

The tasks were defined among the two partners and the workflow was established from the beginning via regular workshops to discuss and share results. These meetings were the basis for the exchange of information and culminated in a final CLC prototype design and experimental plan. In these meetings BOKU would explain their modelling results and share their experience in CLC handling and AEE INTEC would discuss the final CLC design, the operation conditions, the suitability of materials and the risk management of such a system.

Key aspect of the project (CLC prototype)

The final CLC prototype design and experimental set-up was fixed by March 2020. However, the COVID-19 situation forced the consortium to delay the procurement and building of the prototype and search for alternatives to produce experimental data and gain experience in handling CLC reactor set-ups. For that reason, the consortium decided to perform preliminary tests in an existing reactor, the layout of which was as close as possible to the proposed Ammonia2HeatStorage design. These experiments took place in TU Graz and helped the consortium not only to characterize the oxygen carrier and gain hands-on experience but also to generate experimental data to preliminary validate the mathematical model.

The structure of the report is as follows: Chapter 2 explains the materials and methods used during the project: the mathematical model developed (section 2.1), the VMD experimental procedure (section 2.2) and the construction and testing of the CL prototype (section 2.3). Chapter 3 contains the main results of each of the technical activities carried out in the project, this chapter is again divided into results from the thermodynamic modelling (3.1), results from the ammonia recovery via VMD (3.2) and final design, testing results and model validation of the CLC prototype at AEE-INTEC (3.3). Chapter 4 summarizes the main conclusions of the project, including a detailed assessment of the potential of the proposed technology and a preliminary economic analysis. Chapter 5 gathers further research question that arose during the project and finally, Chapter 6 gives a general outlook.

2 Materials and methods

2.1 Reaction engineering/thermodynamic basic investigations

Within this project, a mathematical model of a fixed bed CLC reactor has been developed by BOKU. The simulation is implemented in the software Matlab and the free software Oktave Gnu. The model shows the gas movement through the reactor, the heat development inside the system and the conversion of the OC. The simulation gives the possibility to test ammonia and hydrogen with an oxygen carrier to find the best operating setup, without the need for immediate practical testing. The model has been validated through the tests on a copper-based OC that AEE performed in WP3. The main objectives of the developed model are to investigate:

1. The operation time
2. The degree of oxidation X_s after a single operation and repeated cyclic operation
3. The gas breakthrough curve
4. The heat development in the reactor, and the amount of heat generated
5. The feasibility of **NH₃** as a fuel and its comparison to **H₂**

The calculations are based on a dynamic solution of a 1-dimensional mass and energy balance, via partial differential equations. The approach follows an explicit Euler scheme.

The details of the model, its architecture and detailed evaluation can be found in **DLs 2.1-2.2** and **2.3**

2.2 VMD experimental procedure

In previous projects, AEE developed a **mathematical model** to simulate the performance of VMD systems for ammonia extraction. The model was validated with artificial solutions of ammonium sulphate (AS) of different concentrations and published in the Journal of Membrane Science (Scheepers D.M. et al., 2020).

With the help of the model, we were able to **study the influence of the operational parameters** on the VMD performance for ammonia separation **and potentially optimize it**.

Additionally, **a series of VMD experiments with different water sources** have been performed at AEE. The experiments were targeted at assessing the potential of different waste water streams for maximum ammonia extraction. All the VMD experiments were performed with a flat sheet polytetrafluoroethylene microporous commercial membrane. The gaseous ammonia and water vapour permeating the membrane were trapped in an external condensing device (bubbler) containing sulfuric acid in excess and measured accurately.

The **water streams used in the experiments were:**

- AS solution

As mentioned before an ammonium sulphate solution at different equivalent ammonia concentrations was used to validate the model, accordingly all the other streams were compared to this artificial ammonia stream. Ammonium Sulphate (technical grade) and deionized water were used to prepare it.

- WWTP

Centrate water from waste water treatment plant is an interesting stream for ammonia removal, as it reduced the nitrogen load in the main basin and improves the respective C:N ratio for the WWTP. The specific water used in these experiments has slightly lower concentrations than expected (1g/l) due to a specific configuration at the site.

- Digestate (slaughterhouse)

Digestate is another important stream for N removal, as easy handling of digestate is limited due to its high ammonia content. Here, specifically digestate of a slaughterhouse was tested. More details on the experimental procedure can be found in **DL 3.1**

2.3 CLC Storage prototype and experimental procedure

2.3.1 Preliminary CLC experiments at TUGraz

Even though chemical looping combustion as a base technology has been covered in research works in the past, the proposed setup for this project is unique and measurement data for comparison was not available to the consortium. For that reason, the project team decided to perform preliminary tests in an existing reactor (at TUGraz), whose layout was as close as possible to the proposed Ammonia2HeatStorage design. The experiments were performed under supervision and with support of TU Graz associated scientists.

As the setup can only supply, control and measure Hydrogen (= reduction fuel) and nitrogen, but not oxygen/air (= oxidation fuel) to the tubular reactor, only the reduction half of the CLC cycle could be investigated. As the second half of the reaction (oxidation step) was not carried out, cyclic experiments

were not possible. Therefore, samples of pre-oxidised material were subjected to reduction with diluted Hydrogen (diluted with nitrogen N₂). More details on the experimental procedure can be found in **DL 3.1**

2.3.2 Development and production of a CLC reactor

To be able to design, develop and manufacture the CLC reactor the general framework conditions during the operation had to be formulated upfront. The framework conditions include the expected pressure and temperature during operation as well as the dimensions and furthermore safety aspects. The requirements for a first design of the reactor were obtained due to the experiments performed at TU Graz as well due to the first simulation results out of WP2. Based on the given boundary conditions a **first design** of the CLC reactor could be **realized**. Additionally, in order to adequately assess possible operational hazards and risks, a dedicated **HAZOP study** was performed for the prototype in Gleisdorf. Finally, and based on the initial design study (which included already the boundary conditions) and the performed HAZOP study as well as input from the manufacturer the final **CLC-reactor was built together with the set-up for its safe testing**. More details on the reactor design and construction can be found in **DL 3.1**

2.3.3 CLC Experiments at AEE INTEC

A very similar experimental procedure as that followed during the experiments in TUGraz was performed. Additionally, **the set-up built in Gleisdorf allows for the second half of the reaction (oxidation step) and cyclic experiments were possible**. More details on the experimental procedure can be found in **DL 3.1**

3 Main results

3.1 Fundamental thermodynamic simulations

The next section summarizes the results obtained and compares different temperatures as well as the efficiency between both fuels used. These results allow predictions about conversion rate, duration and heat development for a practical test. The reactor model assumes small proportions; this leaves some uncertainties about upscaling the system even though it gives an excellent first impression of the reaction dynamics.

3.1.1 Reduction with Hydrogen H₂

The reduction of the copper-based OC with hydrogen is tested abundantly in prior studies because of the high reactivity of copper, even though only one active CLC reactor over 10kW is in operation with a copper-based OC. The institute of carbon-chemistry in Spain uses a fluidized bed regime on copper-based OC and CH₄ as fuel (Adanez, J. et al 2012). CH₄ has much higher reaction enthalpies than H₂. The excellent conversion properties of H₂ and the simplicity in the reaction were the main reasons for the testing.

Moreover, it allows a good comparison to the reduction with ammonia since the reducing agent is always hydrogen.

First simulations were done at an inlet fuel gas temperature of 700°C. The enthalpies for the reduction count 96.99 kJ/mol. The model worked fine and reflected the kinetics predicted by Abad (Abad, A. et al 2007). The theoretical approach (all of the OC reacts) assumes a rise of 97.4 °C, while the model predicts a rise of ~94 °C. Satisfying results obtained were the conversion of the fuel as well as the reduction of the OC. These correlate well with the literature and confirm the accuracy of the simulation. The simulation shows an even usage of the OC as well as the distribution of temperature. c_{crit} is reached after full conversion of the OC. For the single operation, the inlet gas temperature was varied to understand the influence and allow a suggestion for practical experiments. The temperature does influence the reaction slightly. The breakthrough curves of the gas as well as the conversion of the OC show similar results for all temperatures, even though higher operating temperatures lead to a higher temperature difference.

Table 1: Summary of the results of the single operation with H₂ as fuel for different temperatures

Comparison of reduction with H₂ for different temperatures					
Temperature [C°]	500	600	700	800	900
Heat [J]	38285.5	38956.6	39619.4	40240.2	40831.7
Tmean [°C]	591.3	692.9	794.5	895.9	997.3
time of operation [s]	3030	2990	2960	2930	2910
dT max [°C]	103.23	103.86	106.4	107.41	108.9
P [Watt]	12.64	13.03	13.38	13.73	14.03

Moreover, the starting temperature has a significant influence on the operation time. The reduction of the reactor with fuel at 100 vol % H₂ took ~50 min. The time varies for the different temperatures of about 5 min at this small scale. To conclude the gas breakthrough curve is equal for all temperatures. Higher temperatures lead to a slightly stronger increase of temperature and reduce the reduction time. The gas and reactor need to be heated up more, which results in higher energy input.

3.1.2 Oxidation

To hold the costs of operation low, air is used for the oxidation of the CLC reactor. For the model, the constituents of air are 21 vol % oxygen and 79 vol % nitrogen, neglecting the other, most prominently Ar and CO₂. The reactor produces most of the heat during oxidation as the reaction enthalpy is - 150.70 kJ/mol and around 53.71 kJ/mol higher than for reduction. The temperatures are varied in the same manner as for the reduction with H₂. This test assumes a wholly reduced OC in an adiabatic system. The oxidation takes longer than the reduction.

The air temperature for the first experiment was 700°C. The Oxygen carrier does not oxidate completely after one experiment. The outlet signal is not reliable; therefore, a second break condition is added, that C_{crit} was only valid if the X_s of Vol 40 was higher of that in Vol. 41.

The same temperature variation were tested as for the reduction. The time of operation decreases strongly, while the operation at 500 °C took ~73 min, it takes 50 min at a temperature of 900°C. On the contrary to the reduction with H₂, the temperature difference decreases with higher temperatures. The maximal temperature rise occurred at a temperature of 500 °C. Also, the mean temperature is higher (~5°C) for lower temperatures. Since the gas moves slower, the heat can diffuse and heat the solid material in contact. The heat generated nonetheless remains significantly higher for high temperatures due to the shorter operation time.

Table 2: Summary of the results of the single oxidation for different temperatures

Comparison of reduction with O ₂ for different temperatures					
Temperature [C°]	500	600	700	800	900
Heat [J]	60261.78	59875.86	58567.10	58294.44	57887.55
Tmean [°C]	643.66	742.74	839.62	938.97	1038
time of operation [s]	4360	4110	3500	3170	3090
dT max [°C]	180.84	178.67	167.44	164.2	163.2
P [Watt]	13.82	14.57	16.73	18.39	18.73

This contradicts the observations made by Abad (García-Labiano, F. et al 2004, Abad, A. et al 2007), who measured a higher influence on the reduction reaction. Although were the test made with a TGA, which measures only a small part of OC. The gas propagation is similar even for reduction, achieving 99% oxidation of the OC. The reactor does heat up very fast at the beginning of the reactor and during reduction underlining the high reactivity of copper.

3.1.3 Reduction with NH₃

For the prior discussed experiments, different literature for comparison and kinetics are available. Ammonia poses a new fuel for investigation. The idea derives from the Project Ammonia2Heat, with the idea to utilize ammonia obtained out of sewage sludge and biogas residues. The considerations taken for the thermodynamics are explained in prior sections. Ammonia decomposes in an endotherm reaction reducing the energy output. The observations make clear that ammonia is not as efficient as pure hydrogen. But since it can diminish the purification costs of a WWTP, it poses a possible available alternative to load a CLC reactor.

The first experiments consider a fuel temperature of 700°C. The model assumes a 99 % conversion of ammonia within the first 10 cm. Practical test must confirm these assumptions since most experiments use a catalyst for the decomposition. The experiments took around 3800 seconds (~ 70 min). The

additional time compared to the reduction with H₂ also arises due to the mixture of fuel with steam (ratio NH₃ : H₂O = 50:50). This choice was made to limit the temperature loss at the front part of the reactor. Vol.1 at the example of 700 °C reduces nearly four times slower compared to the reduction with H₂, in 420 seconds. Because of the low concentration of the reacting agent in the first volume element, as ammonia needs to decompose first. The mean temperature at the end of reaction rises ~65°C, 30 °C less than during reduction with H₂. After an initial increase due to the reduction reaction, heat loss prevails according to the endotherm decomposition in the front part of the reactor. A heat front moves with the reaction through the reactor. The reactor heats up similarly to the reduction with H₂, with the explained difference at the front. However, higher absolute maximum is reached with ammonia as fuel. This can be explained according to the longer reaction time and the axial heat dispersion.

The reduction was repeated for the same temperature variations as the oxidation and reduction with H₂. The temperature shows a similar dependency on the starting temperature as the reduction with H₂, meaning an increase of mean temperature and dT_{max}, as well as a decline of operation time. However, the temperature shows less influence on the operation time for NH₃. The reaction takes 64 min for 500°C to reach c_{crit}. It takes 14 min longer than the reduction with H₂. This proof the functionality of the model also for ammonia, although it shows a minor efficiency. The reaction time also decreases for higher temperatures, with a difference of 120 seconds (2 min).

Table 3: Summary of the results of the single operation with NH₃ as fuel for different temperatures

Comparison of reduction with NH₃ for different temperatures					
Temperature [C°]	500	600	700	800	900
Heat [J]	26372.39	27085.50	27664.38	28398.46	28964.75
Tmean [°C]	562.87	664.57	765.95	867.7	969.05
time of operation [s]	3840	3780	3780	3720	3720
dT max [°C]	108.4	107.21	109.89	111.87	111.8
P [Watt]	6.9	7.2	7.3	7.6	7.8

Without copper as OC and a high reaction enthalpy also for reduction, it is questionable if ammonia is feasible, as the temperature could decrease too much. Ammonia seems to work as a reducing agent for the practical experiments. Still, the question remains if ammonia decomposes under high temperatures completely as assumed, which could be guaranteed by using a catalyst. Nickel could pose a promising candidate since it is a widely used and known catalyst and is also tested abundantly as OC for CLC. The advantage of copper is the strong exotherm reactivity during reduction, which nickel does not have.

Since ammonia is a very requested chemical for agriculture as fertilizer it seems wasteful to use it as fuel. Producing green ammonia can reduce the very energy-demanding production of conventional ammonia production via the Haber Bosch Process, which contributes to high emissions on a global scale. Nevertheless, long term storage mediums are an additional option in the sustainable energy/heat supply

mix. Furthermore, ammonia has gained interest as a storage medium for H₂. But it is still at the very beginnings, and the effectivity is questionable (Valera-Medina, A. et al 2018). But if the fertilizer market is saturated or the law restrictions don't allow further usage of nitrogen fertilizer, it can be an interesting option to limit high concentration in the groundwater and find usage for ammonia.

3.1.4 Comparing the results of the simulations for the single operation

To create a better overview between the single operations they are compared in the time of operation, the temperature difference at t_{end} and the heat generated in diagrams below. In Figure 2 the time of operation is illustrated, showing a decline for all simulations with higher temperatures. While little changes of time for the reduction simulations are noted, especially for the reduction with ammonia, the oxidation times show a strong decrease. A change from 20 min between 500°C and 900°C is noted. The results of the experiments conducted by García Labiano (García-Labiano, F. et al 2004), could not show the same influence of the temperature on the operation time. In contrast, their experiments showcased a more decisive influence of the temperature on the operation time for the reduction with H₂. The temperature in this model showed a higher impact on the oxidation reaction. It must be noted that different concentrations were used for the reduction reaction, and experiments were made in a TGA with a tiny amount of OC.

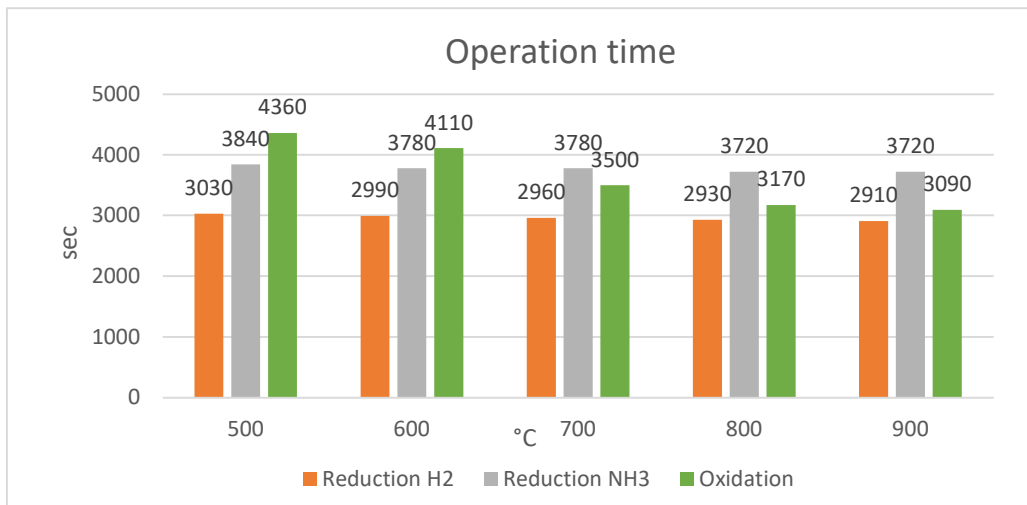


Figure 2: Comparison of operation time of single run simulations

The mean temperature difference, depicted in Figure 3, was measured over the whole length of the reactor at t_{end} . It showed a temperature change during the reduction of ~94°C and during oxidation ~ 140 °C. This correlates very well with the reaction enthalpies. Surprisingly, the temperature difference decreased for the oxidation at higher temperatures, while for the reduction reaction, showed an increase in difference with the rise of temperature.

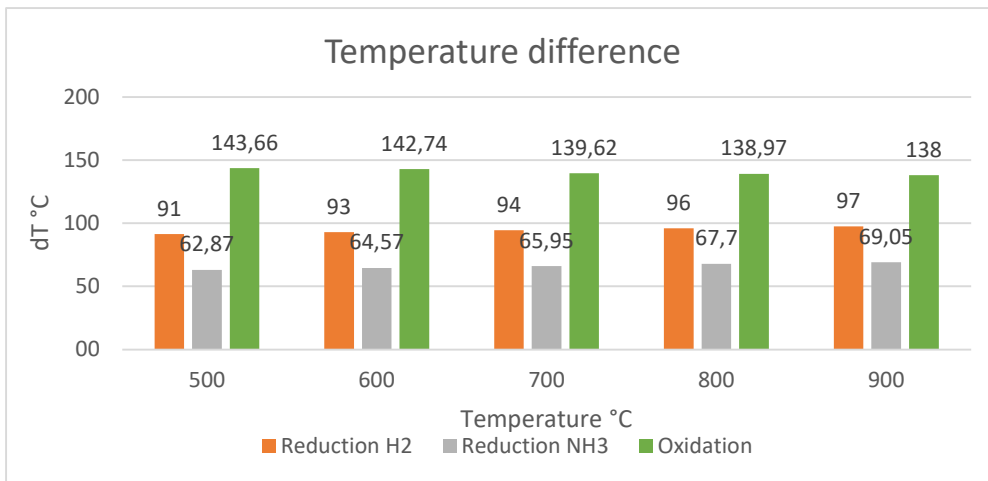


Figure 3: Comparison of the temperature difference at t_{end} for single run simulations

The heat generated, illustrated in Figure 4 for the reduction with ammonia (7 watts) is half of the heat generated by the reduction with hydrogen (13 watts) and showed a slight increase with higher temperatures. While a substantial increase of heat generated could be noted for the oxidation (~5 watt), this can be attributed mainly due to the reduction of the operation time.

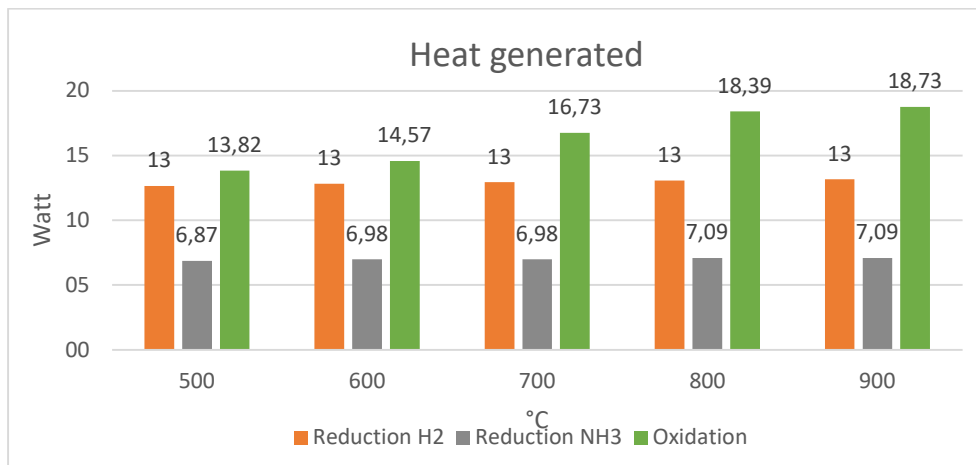


Figure 4: Comparison of the heat generated for different temperatures fuels/air

3.1.5 Cyclic operation

The cyclic operation is vital for a good understanding of efficiency. In a single operation, the OC does not convert fully. This leads to a loss of heat in the reactor. Two approaches are considered, where in the first scenario the fuel and air are injected from the same side, while in the second scenario, the air and fuel are injected from the opposite side. Both cyclic operations left a part of the OC unused during the oxidation reaction and showed advantages and disadvantages. 16.77 Watt are extracted during oxidation from the reactor, and 15.89 Watt during reduction to maintain it isothermally. The heat gets extracted continuously over the whole length of the reactor. The same entry parameters were used for both experiments to allow a fair comparison.

Same side

Table 4: Summary of the cycles with injection from the same side including duration, T_{mean} , T_{max} , T_{min}

	1. cycle	2. cycle	3. cycle	4. cycle	5. cycle	6. cycle	7. cycle	8. cycle	9. cycle	10. cycle
max. Tox [°C]	825.6	806.1	797.5	789.9	786.1	783.1	781.7	780.6	779.1	778.5
max. Tred [°C]	788.7	763.7	753.2	754.0	753.0	758.5	755.3	751.3	755.3	752.1
min.Tox [°C]	582.4	594.9	604.0	609.5	610.7	610.0	607.6	605.2	603.2	600.4
min.Tred [°C]	619.0	633.8	643.7	644.7	641.2	638.9	637.5	636.4	635.3	634.8
mean T oxi [°C]	698.1	696.8	694.7	692.1	689.5	687.0	684.9	683.0	681.1	679.8
mean T red [°C]	690.6	690.2	689.2	687.2	684.8	682.3	680.0	678.1	676.2	674.6
t [s]	6410	6360	6370	6360	6360	6350	6340	6350	6350	6330
t [min]	106.8	106.0	106.2	106.0	106.0	105.8	105.7	105.8	105.8	105.5

Opposite side

Table 5: Summary of the cycles with injection from the opposite side including duration, T_{mean} , T_{max} , T_{min}

	1. cycle	2. cycle	3. cycle	4. cycle	5. cycle	6. cycle	7. cycle	8. cycle	9. cycle	10. cycle
max. Tox [°C]	836.8	822.4	812.7	809.2	805.7	801.8	800.4	795.7	794.7	794.1
max. Tred [°C]	788.7	797.9	802.4	804.3	807.2	807.0	808.6	809.7	808.2	807.0
min.Tox [°C]	573.0	578.3	582.2	583.9	585.5	585.5	586.5	586.6	584.8	583.2
min.Tred [°C]	619.0	599.0	589.9	585.1	581.5	578.9	576.2	572.5	570.4	570.5
mean T oxi [°C]	698.7	698.0	696.9	695.6	694.1	692.6	691.0	689.3	687.8	686.5
mean T red [°C]	690.6	690.1	689.2	688.1	686.9	685.7	684.5	682.9	681.1	679.6
t [s]	6410.0	6410.0	6420.0	6430.0	6430.0	6430.0	6420.0	6420.0	6440.0	6440.0
t [min]	106.8	106.8	107.0	107.2	107.2	107.2	107.0	107.0	107.3	107.3

The mean temperatures after oxidation of the two different approaches of each cycle are compared in Figure 5. Scenario 2 seems to have a more balanced utilization of the OC. Moreover, it generates more heat than scenario 1 though the difference is not substantial, (7 °C after 10 cycles). The degree of oxidation is very similar for both experiments. Moreover, the OC is worn down faster in scenario one where the OC gets heated up and cooled down twice as much. This further favor scenario two, since the OC is a valuable material, and its lifetime should be kept as long as possible. The main advantage of scenario one is the lower construction costs. Hence the additional piping and control system increases the construction costs significantly. The economic analysis is not part of this work, but an injection from opposite sides seems favorable seen from a technical perspective.

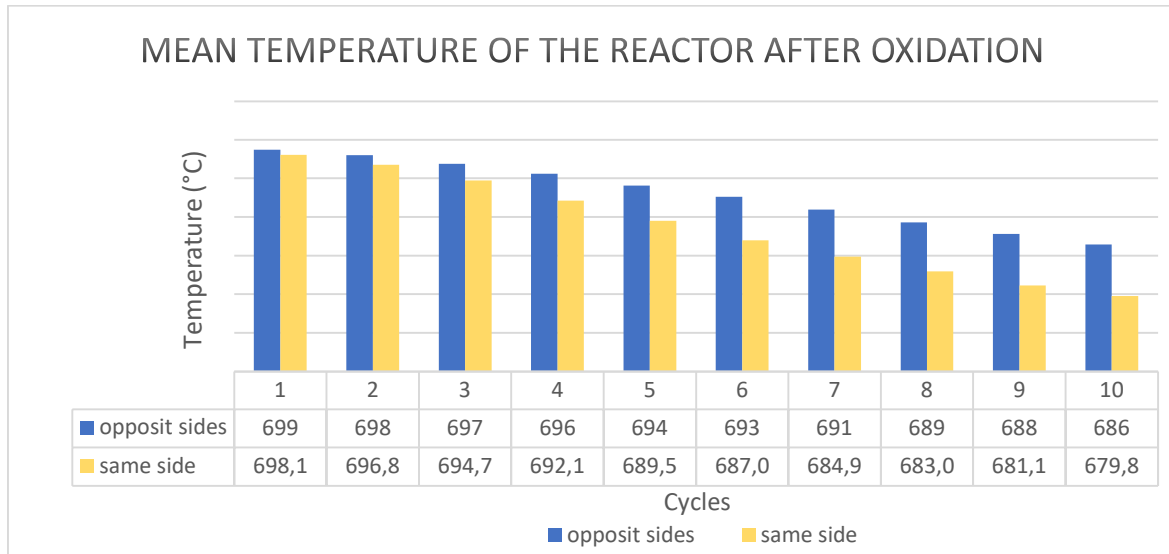


Figure 5: T_{mean} of each cycle of the 2 different approaches (1. Injection same side 2. Injection opposite sides)

3.2 Ammonia Recovery via MD

MD is a thermally driven separation process, where a porous hydrophobic membrane acts as a barrier to separate a warm solution from a cooler solution (B.R. Bodel et al 1968). The separation process is driven by the component’s partial pressure difference between the feed and permeate membrane interface (X. Yang et al 2017). Only vapour/gaseous species can cross the membrane pores towards the permeate side and depending on the configuration condensed or extracted as gases.

In VMD the NH_3 can be recovered in gaseous form. Since only gaseous species can be separated via MD, it is necessary that the ammonia is present in its volatile free form (NH_3). The volatile free ammonia fraction is pH and temperature dependent. These two parameters (temperature and pH) **will determine the energy and chemical consumption** of the MD process.

Not only ammonia but all volatile species at the operation conditions of VMD (e.g., 30-60 °C and under vacuum pressure) will cross the membrane, this includes water. **Since the ammonia is contained in rather diluted aqueous solutions, the amount of water transported through the membrane becomes important and will determine the concentration of ammonia gas downstream the VMD process.**

3.2.1 Optimization of VMD operating parameters to maximize ammonia recovery

With the help of the model, we studied the influence of the operational parameters on the VMD performance for ammonia separation. Table 6 summarizes the relative effect of each of the operational parameters used in VMD on the performance of the process in term of ammonia flux, selectivity and thermal consumption.

Table 6: relative effect of the VMD operational parameters have in the performance of the ammonia recovery (Scheepers D.M. et al., 2020)

Operational parameter \ Performance Parameter	Ammonia flux (J_{NH_3})	Selectivity (S_{NH_3})	Specific thermal energy consumption (STEC)
$\uparrow T_{feed}$	$\uparrow\uparrow$	\downarrow	\uparrow
$\uparrow P_p$	\downarrow	$\uparrow\uparrow$	\downarrow
$\uparrow c_{NH_3}$	\uparrow	$\uparrow\uparrow$	$\downarrow\downarrow$
$\uparrow \dot{V}_{feed}$	\uparrow	\uparrow	\downarrow
$\uparrow L$	\downarrow	\uparrow	\downarrow

In order to maximize the recovery of ammonia and therefore the ammonia flux, VMD is limited by the ammonia feed concentration. This is of particular importance when working with the low ammonia concentrations found in waste waters ($\sim 1 \text{ g l}^{-1}$) as it is the bottleneck of the process. Feed temperature and vacuum pressure can enhance the flux but they also reduce the selectivity, in other words, **there is a trade-off between ammonia flux and ammonia selectivity.**

The selectivity or the ammonia concentration in the gas stream is important not only because the higher the selectivity the lower the specific thermal consumption of the VMD process, but also because the posterior use of the recovered ammonia might be sensitive to the water content. One of the questions that unfortunately remained open after the project **is the effect of the quality of the VMD-extracted ammonia (i.e., amount of water vapor) in the performance of the CLC reactor.**

3.2.2 Quantification of chemical consumption per recovered ammonia

In order to maximize the potential flux of ammonia it is clear that a $\text{pH} > 9$ would be desirable. However, the consumption of chemicals to maintain the pH increases exponentially. On the other hand, if we use a higher temperature, we could compensate the amount of chemicals used. For example, at 80°C and a pH of 8 we would have the same potential flux as if we were operating at 40°C and a pH of 9. The final conditions will depend on the temperature of the available waste heat, the chemical costs and the quality (selectivity) of the required ammonia.

Buffering effect of the water matrix

When working with real wastewaters it is important to assess the buffering capacities of the streams themselves. It is clear that for the VMD ammonia technology, high N-NH_4 concentrations, low buffering capacities and low total suspended solids streams work best. The following figure show the amount of NaOH per litre of solution needed to reach a certain level of pH for the different waste streams used at AEE for the VMD experiments. The streams range from $< 1 \text{ g/l}$ to $> 5 \text{ g/l}$ N-NH_4 concentrations. The results are compared to the artificial AS solutions prepared above, in order to assess the buffering effect of the water matrix.

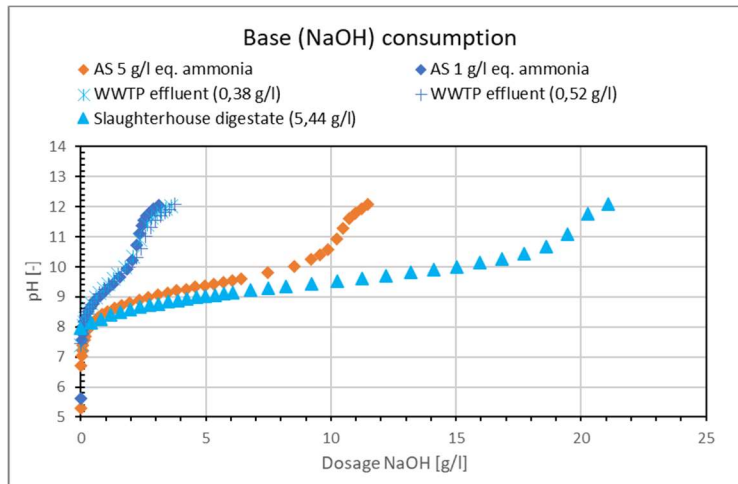


Figure 6: Base dosage (g/l of NaOH) to reach certain values of pH for different wastewater streams and their comparison with ammonium sulphate solutions equivalent to 1 and 5 g/l N-NH₄. Buffering effect of the different water matrices.

The buffering **effect** of the WWTP effluent is especially **remarkable** at pH > 10 even though its N-NH₄ content is lower (i.e., 0.38-0.52 g/l) if compared to the 1g/l AS solution. **This effect is aggravated** in the **higher N-NH₄ concentration** streams (i.e., 5.4 g/l) when compared to the 5 g/l AS solution. In general, the amount of NaOH to reach the same pH level is between **60-80% more** when compared to the artificial N-NH₄ concentration equivalent AS solution.

3.2.3 Experimental VMD results of different streams

The results obtained with the different waste streams are compared to those obtained with the ammonium sulfate (AS) solutions of different ammonia concentrations, in order to show the effect of the complex matrices of the real waste water streams on the different performance parameters of the VMD process. All the experimental results have been obtained at a pH of 11-12, a flow rate of 150 l/h and different T_{feed} and P_{vacuum} values and represented against the driving force (TMP). Therefore the ammonia flux and selectivity is not limited by the free ammonia available and only the operational parameters play a role. Most of the experimental results can be found in the **DL 3.1**. In this report we have selected some of them.

3.2.3.1 Ammonia flux (J_{NH_3})

In the following graph the J_{NH_3} results have been plotted against the driving force (TMP) vapour pressure difference through the membrane.

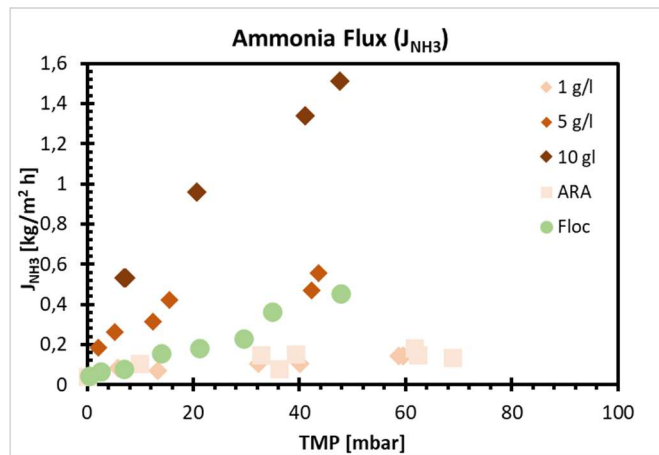


Figure 7: Ammonia flux (J_{NH_3}) results as a function of the driving force (vapor pressure difference or TMP) for all the VMD experiments. Comparison between the AS or artificial water streams (1, 5 and 10 g/l) and the real waste waters (i.e., digestate flocculated and WWTP).

The ammonia flux J_{NH_3} follows again a more or less linear tendency if plotted against the driving force (TMP). Those experiments performed with the digestate samples (flocculated) showed a comparatively lower J_{NH_3} . Again fouling could be the cause of the comparatively lower flux. Also, again, the experiments performed with the WWTP water compared to those done with the AS solution showed practically the same J_{NH_3} .

3.2.3.2 Ammonia Selectivity (S_{NH_3})

The ammonia selectivity S_{NH_3} which represents the ratio between the ammonia flux and the total flux follows a rather logarithmic trend if plotted against the driving force (TMP). Since the total and ammonia fluxes for those experiments performed with the digestate samples (flocculated) showed a comparatively lower flux, the resulting S_{NH_3} is practically the same compared to those done with the AS 5 g/l solution. The WWTP experiments showed practically the same S_{NH_3} values compared those done with the AS 1 g/l solution. The relative effect of the ammonia concentration on the S_{NH_3} is clear, the selectivity is increased by one order of magnitude from 1 to 10 g/l. Unfortunately, the experimental results confirm an existing tradeoff between S_{NH_3} and J_{NH_3} .

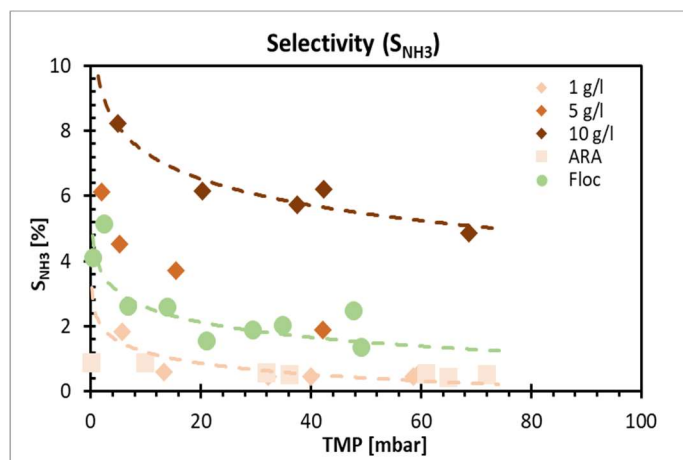


Figure 8: Ammonia Selectivity (S_{NH_3}) results as a function of the driving force (vapor pressure difference or TMP) for all the VMD experiments. Comparison between the AS or artificial water streams (1, 5 and 10 g/l) and the real waste waters (i.e., digestate flocculated and WWTP).

3.2.3.3 Specific Thermal Consumption (STEC)

The last graph shows the relationship between the thermal consumption (STEC) and the selectivity. The interesting information of this last graph is the maximum S_{NH_3} that can be expected from each stream depending on its ammonia concentration.

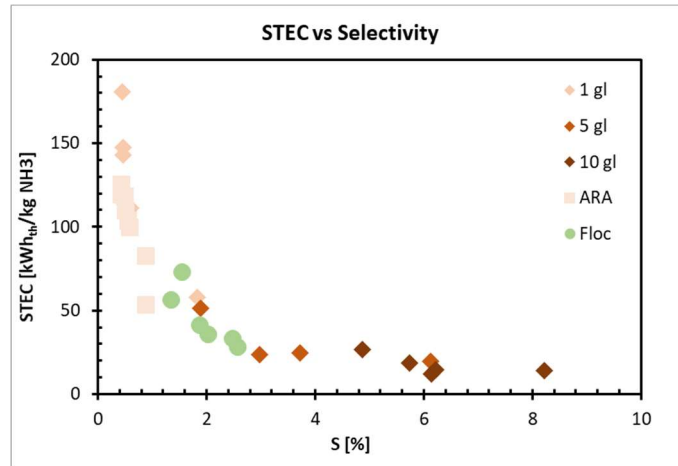


Figure 9: Specific Thermal energy consumption (STEC) results as a function of Selectivity obtained for all the VMD experiments. Comparison between the AS or artificial water streams (1, 5 and 10 g/l) and the real waste waters (i.e., digestate flocculated and WWTP).

3.2.4 Techno economics on the VMD side

Data has been evaluated based on the VMD model and the experimental results obtained. The calculations have been performed **by fixing a target ammonia production of 1 kg/h from two different waste streams of 1 and 10 g/l ammonia concentration.**

In order to obtain the target production, the **RR of the modules is investigated as a function of the feed temperature and the membrane area.** Once the RR per area and temperature is known, then **the number of required modules in parallel to produce 1 kg/h is calculated** together with their corresponding total membrane area which is represented in the graphs. Based on that, the **volume of feed (m³/h) and the corresponding chemical consumption and thermal consumption (STEC) is calculated.** The **Capex is calculated based on the total membrane area** needed for the targeted ammonia production. Other general assumptions for the techno-economic evaluation are shown in the table below.

Target production	g/h	1000
Capex of MD units	Eur/m ²	286
Flow rate MD unit	l/h	140
MD unit area per frame	m ²	0,4
Price of chemicals (NaOH)	Eur/ton	200
NaOH dose ¹ @ 1 g/l N-NH ₄	g/l	3
NaOH dose ² @ 10 g/l N-NH ₄	g/l	23
Maintenance	% of CAPEX	6
Electrical consumption	kwh/kg	0,1-0,3 ³

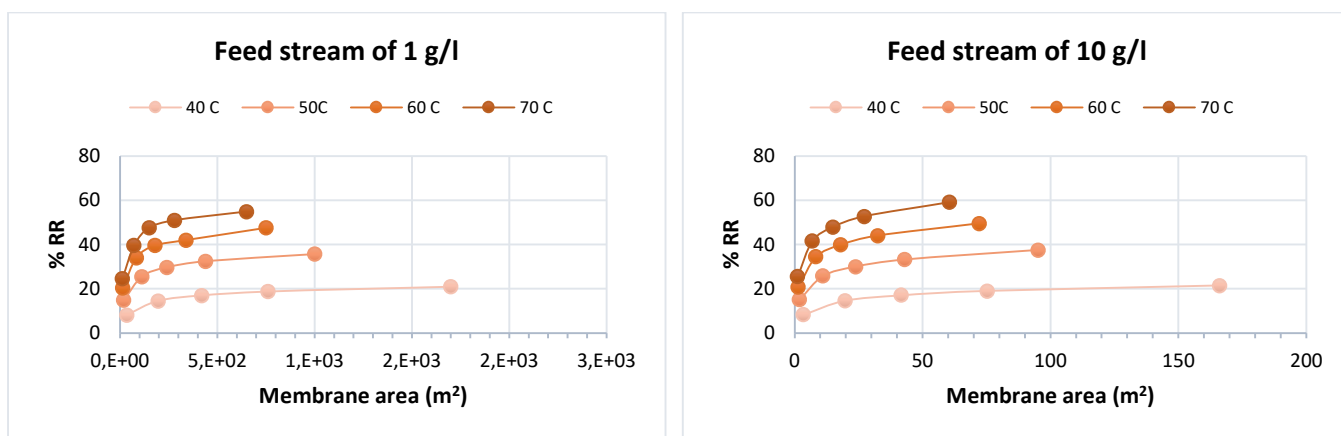


Figure 10: Recovery Ratio (%) as a function of feed temperature and total membrane area (including modules in parallel to achieve a production of 1kg/h for two streams of 1 and 10 g/l of ammonia respectively.

¹ For a pH of > 11

² For a pH of > 11

³ Depending on membrane area and membrane modules in parallel

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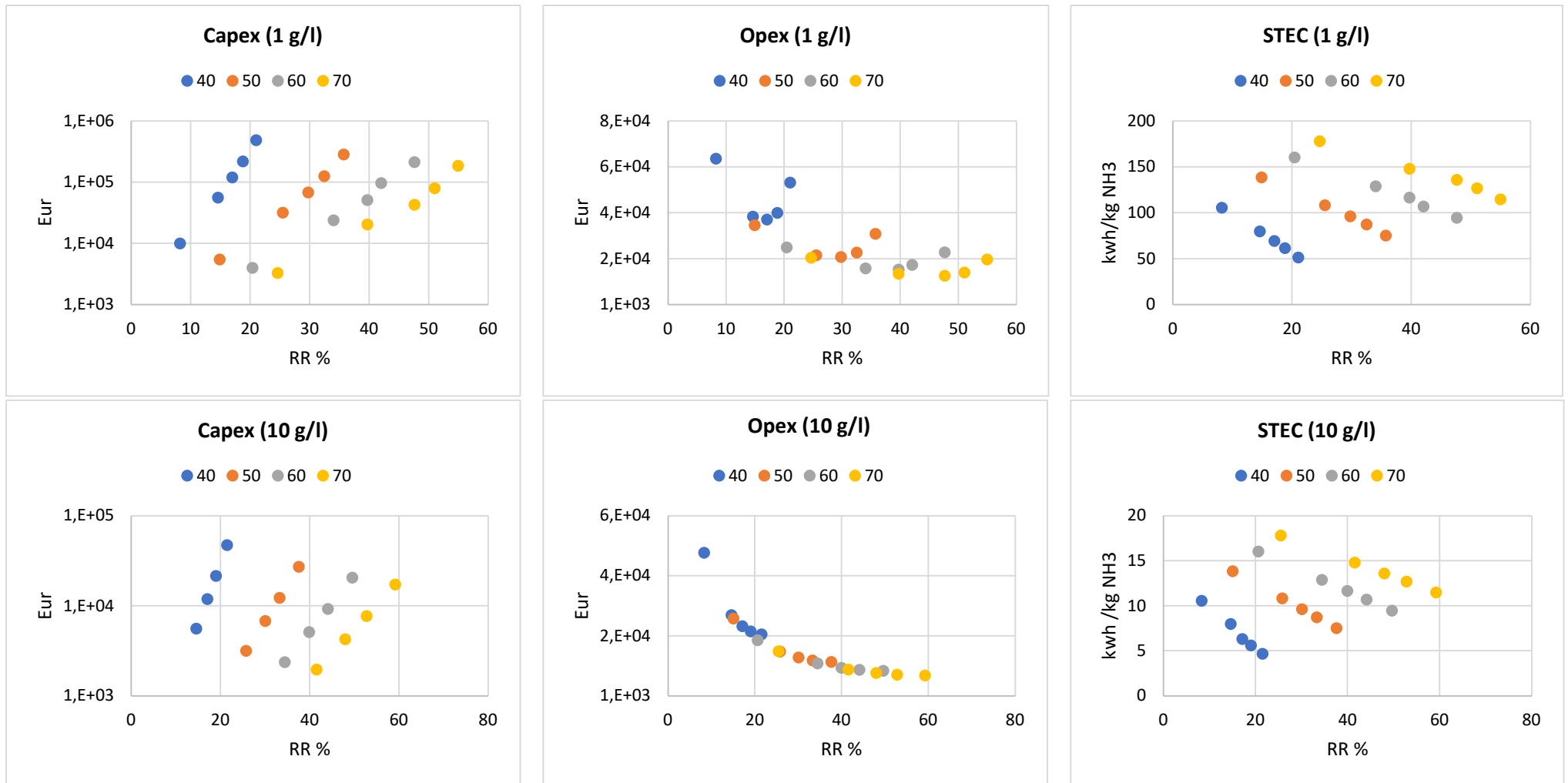


Figure 11: Capex, Opex (chemicals and maintenance) and Specific thermal consumption (STEC) to achieve a production of 1kg/h as a function of the Recovery Ratio (%), feed temperature and ammonia feed concentration (i.e., 1 and 10 g/l).

3.3 CLC reactor tests and validation

3.3.1 Preliminary test at TUGraz

These experiments were very useful not only to get familiar with the system and the expected behaviour and evaluate the time and temperature range of the reaction and select the experimental conditions suitable for a stable reduction reaction but also to interpret the graphs and evaluate the results.

For the evaluation, the **reaction time** was determined via the **breakthrough curve**, which is derived from the volumetric Hydrogen concentration at the reactor outlet (gas analyser for H₂, see Figure 12). The time dilation as well as the Hydrogen mass balance clearly show that the desired reaction is taking place within the reactor. Time dilation for all experimental breakthrough curves is in the range of minutes, whereas the retention time of a filled, inactive reactor is just 35 seconds (experimentally determined with the same setup). The results of the breakthrough curves for all three experiments are shown in Figure 12.

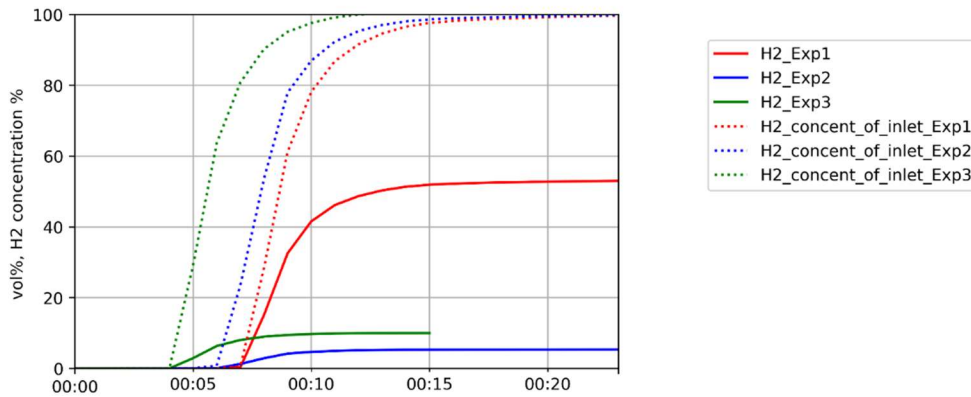


Figure 12: Breakthrough curves for all three preliminary CLC experiments at TUGraz

Obtaining sharp breakthrough curves with a **high slope and low drag was an important goal of the project**, as it is necessary for controlled charging and discharging of the reactor. All three experiments clearly show these breakthrough curves, which means that the chosen experimental conditions are suitable for a stable reduction reaction within the reactor. Therefore, **the baseline total flow rate (860 ssc/min) is taken as a starting value for the experiments in Gleisdorf**, as the Ammonia2HeatStorage prototype has similar size properties. Furthermore, the varying of the H₂ flux (higher total flow rate or higher concentration) have a clear influence on the breakthrough curves, producing higher slopes. The expected temperature increase of the exothermic reduction of the copper oxide could be observed at the respective temperature sensor in the bed (temperature sensor in sample, see Figure 13).

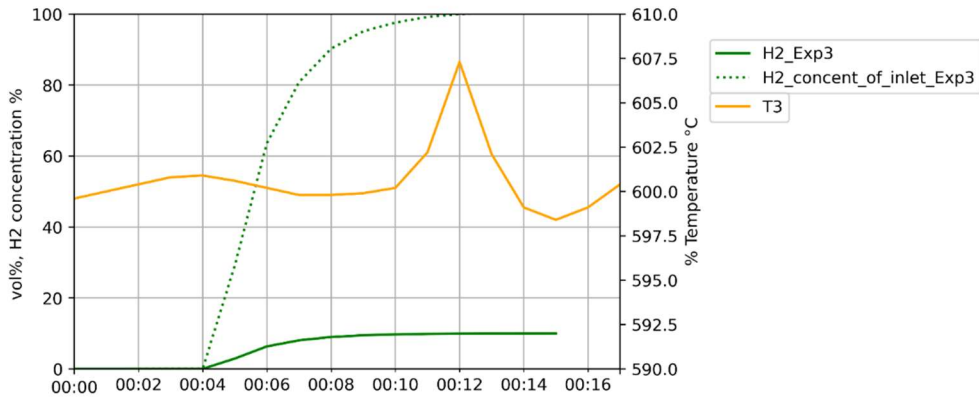


Figure 13: Temperature increase of the exothermic reduction of the copper oxide during the 3rd preliminary CLC experiment at TUGraz

Mass balances were performed taking into account the reacted mass of Hydrogen. A mass-based OC conversion rate was determined from these values. This **conversion rate was used to compare the Gleisdorf reactor** setup to the one at the TU Graz for the Hydrogen experiments. For the TU Graz experiments, satisfactory **OC conversion rates between 86% and 98% could be achieved.**

3.3.2 CLC-reactor design

Based on the initial design study (which included already the boundary conditions) and the performed HAZOP study (see DL 3.1) as well as input from the manufacturer a detailed CLC-reactor design was created. The specs of the reactor can be seen in Table 7. The material chosen for the CLC reactor is a special steel with high temperature and acid resistance.

Table 7: Overview of the final reactor dimensions and design parameters and picture of the actual CLC reactor (right)

	Unit	Value
Total length of the reactor	mm	855,8
Length of the middle section	mm	630
Length of the lower section	mm	25
Length of the upper section	mm	80
Max. length of the active zone	mm	300
Outer diameter of the active zone	mm	44,7
Inner diameter of the active zone	mm	42,4
Wall thickness	mm	3,2
Volume of active zone	l	0,42 ⁴
Reactor material	-	1.4841
Temperature sensors inside the reactor	#	6
Oxygen carrier material	-	10% of CuO/Cu 90% of Al2O3
Density of the OC	kg/l	~ 4,18
Possible mass of the OC inside the reactor	kg	1,8



⁴ Based on the maximum length of the heat able and controllable zone.

The test bench setup fundamentally consists of the CLC-reactor, pipe system, pressure bottles for NH₃, N₂, and air, as well as a condenser and the collecting vessel. Figure 14 shows the piping and instrumentation diagram, the P&ID, of the test stand including the installed measuring and control equipment. A picture of the test rig is shown in Figure 15.

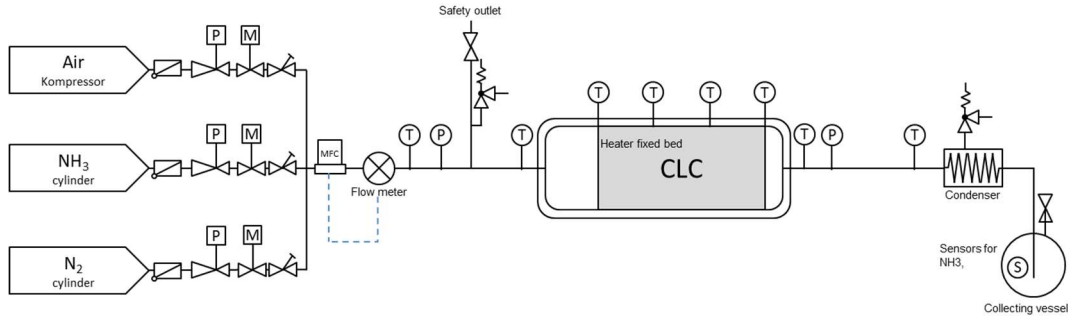


Figure 14: P&ID of the test stand including the installed measuring and control equipment

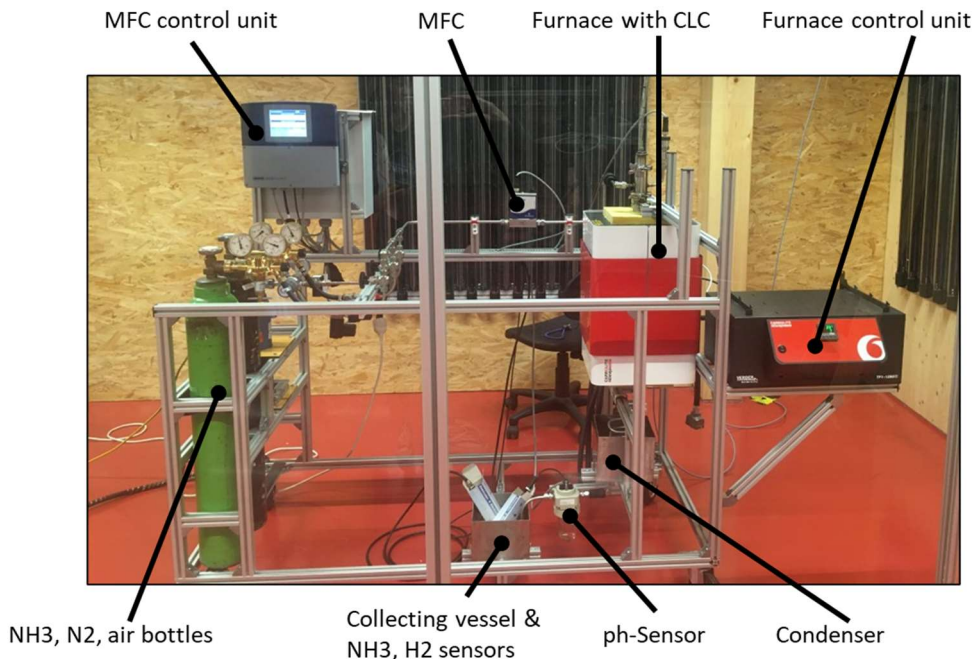


Figure 15: Picture of the CLC test bench setup including description of the placement of the installed components

Extensive details on the measurement system, control strategy and data acquisition can be found in **DL 3.1**.

3.3.3 Proof of concept and validation

A series of experimental cycles with the Gleisdorf prototype were performed with hydrogen and ammonia as reducing agent. Details of the experiments can be found in **DL 3.1**. The measurement results obtained during the experimental cycles were compared to the simulation results. In particular, the comparison is

performed for the measured and simulated **heat output**, **temperature lift** and **power output** as well as **reaction duration**. The results are shown in Table 8. **Simulation runs are marked in blue.**

Table 8: Overview of the measured and simulated heat output (P_{avg} , P_{peak} , Q_{sum}), the corresponding temperature level and lift as well as the duration time of the experiments

	T_Ofen_Soll °C	P_avg W	P_peak W	Q_sum Wh	T_peak_inc °C
Oxidation	600	15,4	88,9	27,0	101,5
Oxidation	650	23,7	97,3	23,7	106,7
Oxidation	650	25,7	94,2	25,7	105,4
Oxidation	550	21,2	113,4	26,5	107,5
Simulation Oxidation	600			28,2	152,0
Reduction 10vol% NH ₃ in N ₂	650	3,0	30,6	7,1	25,1
Reduction 10vol% NH ₃ in N ₂	650	3,4	24,7	8,4	21,7
Simulation Reduction NH3	600			10,9	58,0
Reduction 10vol% H ₂ in N ₂	550	10,5	23,1	24,6	28,8
Reduction 10vol% H ₂ in N ₂	650	7,8	32,6	18,2	25,9
Simulation Reduction H2	600			17,7	94,0

The emitted heating power of the experiments was calculated on the basis of the measured heating input needed to maintain a predefined reactor temperature. Therefore, additional experiments upfront were performed to determine the heating power needed to keep the reactor at a certain, pre-defined temperature. Based on these results, it was possible to calculate the heat loss of the setup (P_{ofen_loss}) as a function of the average reactor temperature (T_{ofen_avg}). Equation 3 shows the obtained heat loss equation. The difference between the measured and the expected heating input finally results in the heating output during oxidation and reduction experiments. The emitted heating energy of the experiment is then calculated as a function of the duration of the experiment.

$$P_{ofen_loss} = 0,701 \cdot T_{ofen_avg} - 102,83 \quad \text{Equation 3}$$

As an example of the explained characteristics during an oxidation experiment, Figure 16 shows the temperatures in the reactor (T_Reaktor_1 to T_Reaktor_7), the predefined setpoint temperature at 600°C (T_Ofen_Soll) and the heating power (P_ofen). In the diagram, the increase of the temperature of the temperature sensors 1 to 7 by the oxidation can be seen well. As the temperature in the reactor increases due to the oxidation, the heating power decreases. As explained, this reduction of the heating power is used to calculate the heat output of the reaction. Nevertheless, due to the small size of the reactor and the consequent high heat loss power, compared to reaction power, energetic calculations are very difficult.

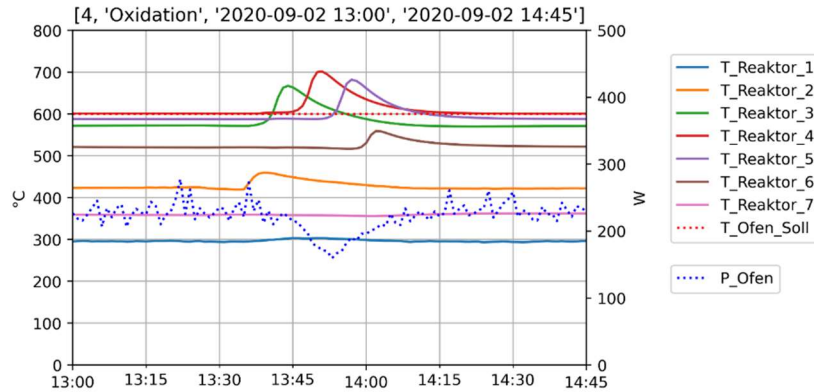


Figure 16: Graph showing the temperatures in the reactor (T_Reaktor_1 to T_Reaktor_7), the predefined setpoint temperature at 600°C (T_Ofen_Soll) and the heating power (P_ofen) during an oxidation experiment

Based on the described method, also the maximum power output can be calculated as well. The determined maximum outputs of different runs are presented in Figure 17. Shown are the maximum power outputs during four oxidation runs (in gray) at temperatures between 550°C and 650°C as well as results obtained during reduction with NH3 (in orange) and obtained during the reduction with H2 (in blue). The maximum power output during oxidation was in average 93 W, during reduction with NH3 in average 23 W and with H2 in average 27W.

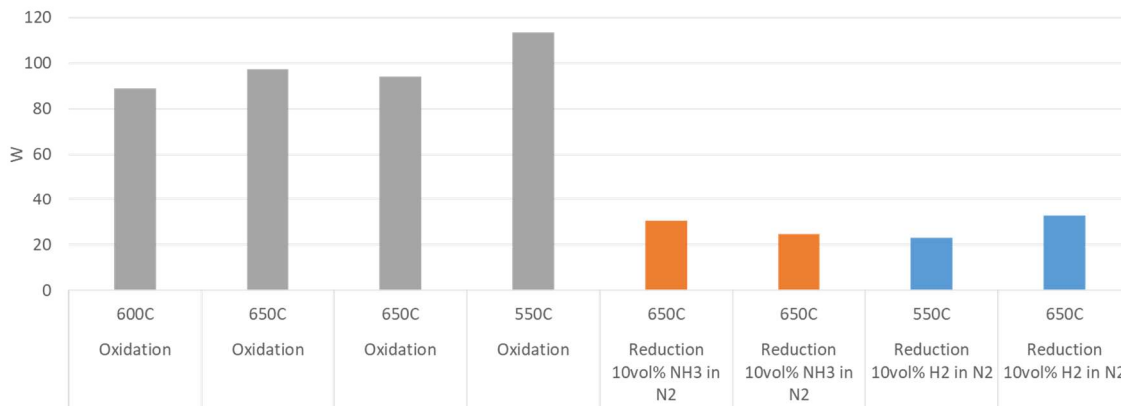


Figure 17: Maximum power outputs during four oxidation runs (in grey) and during two reduction runs with NH3 (in orange) and with H2 (in blue)

Figure 18 shows a comparison of the obtained heat output obtained at different temperatures during oxidation as well as during reduction with NH3 and H2. In blue the experimental data is shown in orange the corresponding simulation results are given. During the oxidation a heat output was reached with 24,7Wh at 650°C in avg., 27 Wh at 600°C and 26,5Wh at 550°C. The simulation results indicate an energy output of 28,2Wh at 650°C. The difference between the experimental results and the simulation is in the order of around 12,2%. Looking at the reduction runs, it was found that in average 7,8Wh could be measured with NH3 and 21,4Wh with H2. In comparison, the simulation results showed around 10,9 Wh for the reduction with NH3 and 17,7 Wh with H2 in average. Considering the size of the reactor and the expected errors due to the difference between the order of the heat losses exceeding 200W, the comparison achieved is very positive.

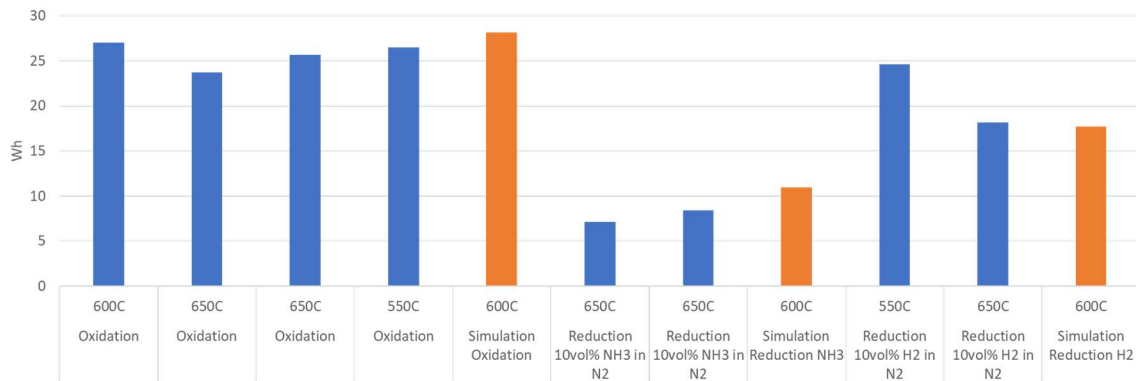


Figure 18: Heat output in Wh during four oxidation runs and during two reduction runs with NH3 and with H2 (all in blue) as well as the simulation results (in orange)

Based on the volume of the reactor, the energy density on fixed bed level can be calculated. The specific energy density in kWh/m³ based on the results of the experiment as well as for the results of the simulation are shown in the following Figure 19. As it can be seen in the graph during oxidation an energy density was reached with 125 kWh/m³ at 650°C in avg., 136 kWh/m³ at 600°C and 134 kWh/m³ at 550°C. The simulation results indicate an energy density of 142 kWh/m³ at 650°C. In regard to the reduction runs, it was found that in average 39 kWh/m³ could be measured with NH3 and 108 kWh/m³ with H2. In comparison, the simulation results showed around 56 kWh/m³ for the reduction with NH3 and 89 kWh/m³ with H2.

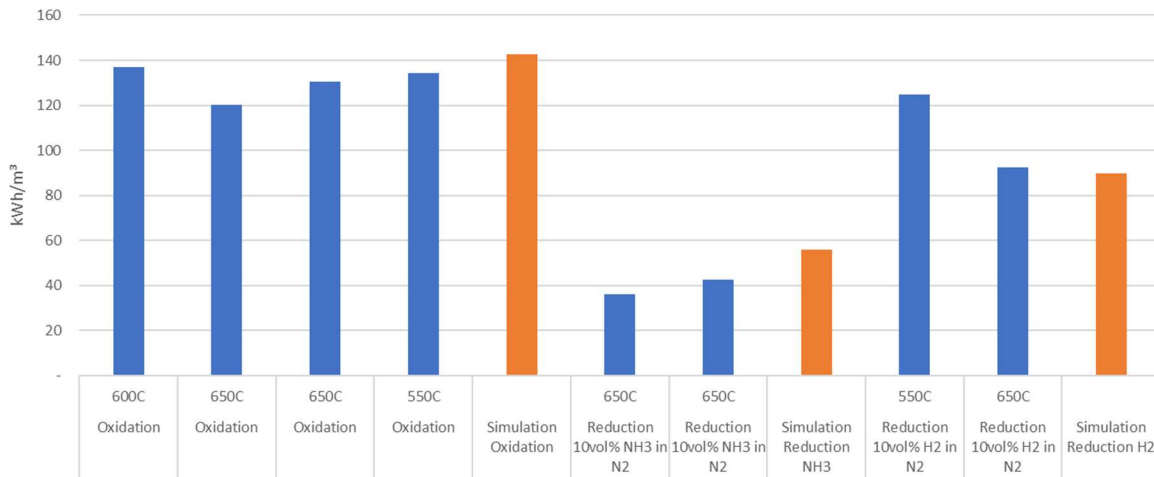


Figure 19: Energy density in kWh/m³ (fixed bed level) during four oxidation runs and during two reduction runs with NH3 and with H2 (all in blue) as well as the simulation results (in orange)

A comparison of the achieved temperature lift during the experiments and on the based on the simulation results is shown in the following **Error! Reference source not found.**Figure 20. According to the simulation, a maximum temperature lift of 152K was expected during oxidation, during reduction with NH3 94K and for during reduction with H2 a lift of 58K. In comparison to the simulation, the temperature lift measured during the experiment are generally lower, being 106K during oxidation and 58K with NH3 and a lift of 94K when H2 was used. The lower temperature increase during the experiments can be explained due the fact of increased heat losses which are not possible to fully being extracted. Nevertheless, the results show a comparable increase and ratio between oxidation and reduction runs and give a good

indication of the expected discharge temperature lift in future a full-size reactor is used. An analysis of the obtained storage density incl. an outlook on the expected value in comparison with other storage technologies can be found in section 4.3.

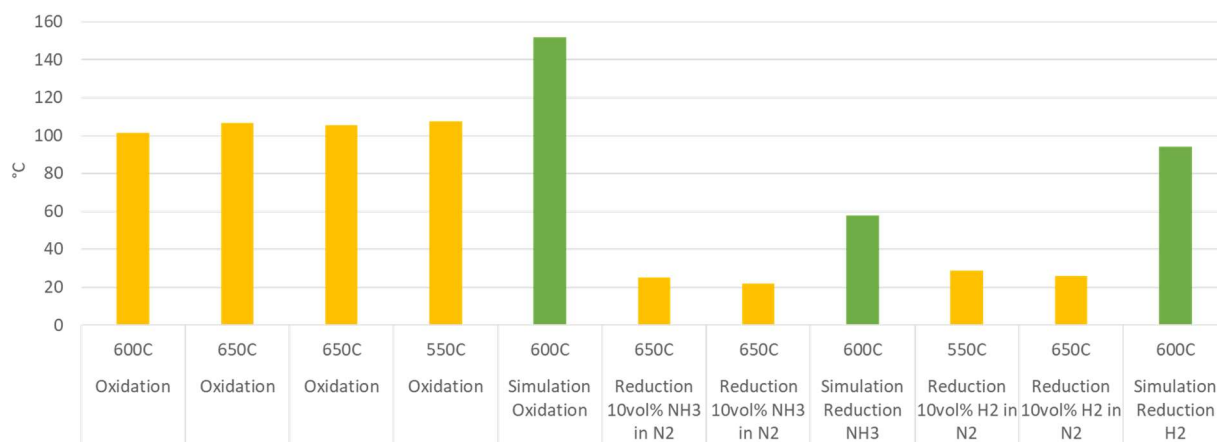


Figure 20: Temperature lift during four oxidation runs and during two reduction runs with NH₃ and with H₂ (all in yellow) as well as the simulation results (in green)

It was possible to **show a good comparison between the experiments and the simulation** results for the most important parameters such as the **energy output** of the oxidation and reduction reactions, the **energy density** as well as the **associated temperature increase**. It was shown that due to the small size of the reactor and the consequent high heat loss power, compared to reaction power, energetic calculations are very deficient. Nevertheless, a very good correlation between the experimental results and the simulation results could be achieved.

4 Conclusions

4.1 The CLC-NH₃ from a thermodynamic point of view

The results from the simulations of the CLC system can be summarized as follows:

When operated with H₂

- The temperature showed little influence on the reaction dynamics. A small reduction of the operation time could be observed, and additional heat was generated. The degree of oxidation remained the same for all temperatures.
- This leads to the conclusion that it is not reasonable to run the CLC reactor at high temperatures since the gas and the reactor must be heated up at desired temperatures resulting in much higher energy input.
- For the oxidation reaction, the temperature showed significant influence on the reaction time; this also results in higher heat output. The degree of oxidation remained similar for all simulations leaving a small part of OC at the reactor end unused.

- Therefore, it could be meaningful to operate at higher temperatures, although it must be cleared how much additional energy is necessary to heat up the air and reactor and to compensate for higher heat loss to the environment.
- Furthermore, higher temperatures lead to more chemical/physical stress on the OC, although CLC proved its stability over more cycles in prior experiments, conducted by Labiano and Abad (García-Labiano F. et al 2004, Abad, A. et al 2007). The attrition and sintering processes rise at high temperatures reducing the lifetime of the OC.

When operated with NH₃

- Ammonia was assumed to decompose with a certain reaction rate for the simulations. Experimental validation of the NH₃ decomposition was achieved by comparison to the experimental results from WP3.
- The influence of the endothermic NH₃ decomposition reaction was clearly visible. After the temperature rose at the beginning due to the dominance of the exothermic reduction of H₂ with the oxygen carrier, the reactor further on showed a decrease to the initial temperature at the front part. Nevertheless, the temperature of the rear part of the reactor increased similar to the experiments with H₂, resulting in a mean temperature rise of 66 °C.
- The influence of the temperature resulted similarly to the influence observed for the reduction with H₂. Small improvements for the operation time and the heat output could be observed. It can be suggested to run it at lower temperatures starting at 600 °C, since an improvement to 500 could be seen and the decomposition of NH₃ is more likely.
- The heat output was half the amount (~6 watts) of the output with H₂.

The cyclic experiments give a first impression of the energy output under continuous operation. The degree of oxidation and the usage of the oxygen carrier showed an excellent conversion rate for both experiments. However, scenario 2 (injection of fuel and air from opposite sides) generated more heat than scenario 1 (injection of fuel and air from the same sides) under the same conditions. The usage of the OC was more uniform for scenario 2 and left the assumption of a longer lifetime of the OC. This must be verified through practical experiments. Looking only at the reactor performance a better working system for scenario 2 is predicted. The lower construction costs strongly favor scenario 1. Since the additional piping and control system is connected with high costs, an economic analysis should provide information about which scenario is more economical.

4.2 Potential of the VMD technology for ammonia recovery

There are different technologies available to remove ammonia from wastewater streams e.g., aerobic de-ammonification, reverse osmosis, air-stripping, co-precipitation with phosphate and magnesium to form struvite, ion exchange, electrochemical treatment, etc. However, most of these technologies do not allow for the reuse of ammonia in its free form (NH₃). Also, they have low ammonia transfer coefficients, hence

requiring longer operation times and large amounts of electrical energy e.g., conventional aerobic activated sludge processes require 11– 14 kWh per kg of total N removed which is typically more than 50%, and up to 70% of the total electrical consumption of a WWTP. Membrane technologies, including MD, are effective in removing ammonia from liquid streams. Additionally, MD has the following advantages in comparison to conventional membrane separation technologies include: low operating temperatures, allowing for its coupling with waste heat (largely available in the industrial sector) and atmospheric pressure operation, resulting in less demanding membrane characteristics and less severe fouling. The results of the project allowed us to define some KPIs of the VMD technology for ammonia (NH₃) recovery from waste streams.

- **T of operation:** 30-60°C The feed temperature will be determined by the quality of the ammonia required downstream since the selectivity of the process depends greatly on the feed temperature/vapour pressure difference. The greater the feed temperature, the higher the ammonia flux but the lower the selectivity.
- **Treating capacity (m³/day):** although there are no specific ammonia removal VMD modules, all the market available DCMD, AGMD and V-AGMD modules are suitable for this application. Their treatment capacity is completely scalable since MD is deployed as a modular technology. Complete ammonia removal/recovery will depend on the membrane area (one pass, continuous) or the recirculation time (batch operation). Recently, an Indian company named ROCHEM has been identified as one of the few companies working in ammonia removal via DCMD at industrial scale. The treating capacity per membrane area of these modules is around 16 l/h m² (0,4 m³/m²).
- **Membrane area/m³:** 10 to 25 m²/ m³
- **Ammonia production capacity (kg NH₃/day):** according to our calculations, VMD modules could be easily scalable to produce 1 kg NH₃/h with recovery ratios up to 70% at a reasonable cost.
- **Energy consumption (thermal):** the thermal consumption per kg of ammonia produced is related to the selectivity (expressed as ratio of flux of ammonia/flux of water) of the process which is in turn limited by the ammonia concentration in the feed to be treated and the feed temperature. A general number of 60 kWh/kg NH₃ is normally reported for stripping processes including VMD (Beckinghausen A. et al., 2020). However, as shown in the experimental results and the modeling the Selectivity and Thermal consumption depends greatly on the ammonia feed concentration (g/l).
- **Energy consumption (electrical):** Electrical specific consumption not assessed in optimized conditions. In our calculations we have used a value of 0,1-0,3 kWh/kg NH₃. It has been alleged to be below 1.3 kWh_e in large V-AGMD systems in batch operation.
- **Chemical consumption:** as explained in previous sections, in order to separate ammonia (NH₃) from waste or process water streams it is necessary to increase the pH of the solution > 9. To achieve basic conditions NaOH, KOH or lime is used and the amount needed depends greatly on the initial ammonia concentration and the water buffer capacity. In general, consumptions between 60-80% of the estequiometric ones can be expected. For very clean streams with ammonia concentrations varying from 1-10 g/l, consumptions between 1 to 3-5 g/l to reach pH~9 can be expected.

- **Recovery Ratio (RR):** the RR is the % of the total ammonia present in the feed stream that can be actually recovered in the permeate side. Ammonia removal ratios as high as 90% via MD have been reported in literature. However, there is a limitation in the amount of ammonia that can be recovered in the permeate side and it depends on the **driving force** and the **ammonia concentration**. For this reason, the RR is related to the membrane area where both driving force and ammonia concentration in the feed are reduced along the length.
- **Ammonia quality:** The quality of the ammonia obtained via VMD is here expressed in terms of the Selectivity. Experiments and modelling have shown how this S depends greatly on the TMP and the ammonia feed concentration and how there is a trade-off between ammonia flux and ammonia selectivity.

Economical:

- **Membrane/module costs:** a reasonable capex for MD systems, based on manufacturer data, is in the range of 2000 Eur/ MD module or ~300 Eur/m²
- **Maintenance:** This KPI is key for the Opex calculation of the technology. For membrane technologies a 10% of the CAPEX is normally assumed, since MD is a low maintenance membrane technology a 6% can be assumed.
- **Pre-treatment necessities:** there is a general lack of information about the limits this technology has in terms of tolerable stream characteristics such as TS (Total solids), BOD, fat and oils content, surfactants, etc. This KPI is especially relevant when dealing with high leaded streams such as bio-streams containing ammonia (i.e., digestate) and it can also play a role in the quality of the permeate and of course on the cleaning/replacement ratios.

Others:

- **Advantages of ammonia removal:** The presence of ammonia in waste and process water is toxic and strictly regulated but conventional WWTPs use cost effective methods to remove it before disposal. However, the ammonia pollution is costly for the EU, not only in terms of WWTPs but also from a health and environmental point of view. The legislators are becoming more restrictive in terms of ammonia disposal and the policies will steering towards a circular economy.

4.3 Potential of CLC-NH₃ as a storage technology

In the following section a set of Key Performance Indicators (KPIs) are presented and used to evaluate the Chemical looping storage technology and compare it to other technologies. However, since the development is in its early stages, in some aspects only an outlook or assessment can be given. The assessment will be given on material characteristics of the oxygen carrier as well as on the reaction gas and not on system or integration level since this is not developed nor defined in this point in time. As a result, KPIs which cannot be distinct in this point in time will form upcoming research questions for a future research project.

- **Storage Density:** Since storage density is depending on the definition of system boundaries and operating limitations it is necessary to give clear definitions. According to Wilhelms (Wilhelms C. et al., 2010) there are three different definitions which will outline the storage density of a thermal storage:
 - Physical storage density
 - Effective storage density
 - Actual storage density

Considering the actual focus is on reactor level the physical storage density is more likely a KPI on material level and therefore skipped at module level since this cannot be predicted at this point in time. Furthermore, the effective storage density relates to the Installation space occupied by the storage system as well as its balance of plant components which will be related to the use case of a future storage system.

Nevertheless, it is possible to predict a range of the storage density on material level based on the outcome of the simulation results and experimental results and compare those to elaborated storage technologies. During the experimental results a storage density of up to 175 kWh/m³ was reached during a full cycle (combining oxidation 136 kWh/m³ at 600°C and reduction 39 kWh/m³ measured with NH₃). The simulation results indicated a storage density of up to 231 kWh/m³ (142 kWh/m³ at 650°C for oxidation and around 56 kWh/m³ with NH₃ reduction). During the experiments, an oxygen carrier was used with a reactive material content of 10% and a porosity of around 40%.

By changing to an oxygen carrier with a higher effective reaction ratio, correspondingly higher storage densities could be achieved and via using the simulation method, developed in the project, it is furthermore possible to calculate the projected storage density. For the simulation, materials characteristics were used, which has already been investigated in other research projects and are therefore known. The materials used are known to have effective reaction fractions of up to 50% and by optimizing the grain sizes, the porosity can be increased up to 30%. In combination, storage densities of up to 1544 kWh/m³ can be predicted at the material level. A comparison of the storage densities of the CLC reactor (achieved with the simulation with the material used in the A2S project as well with the modified OC) with typical storage densities of a water storages, TCM storages and PCM storages are shown in Figure 21. The graph clearly shows the very high potential of the CLC storage technology in terms of the storage density compared to other heat storage technologies currently in use or under research.

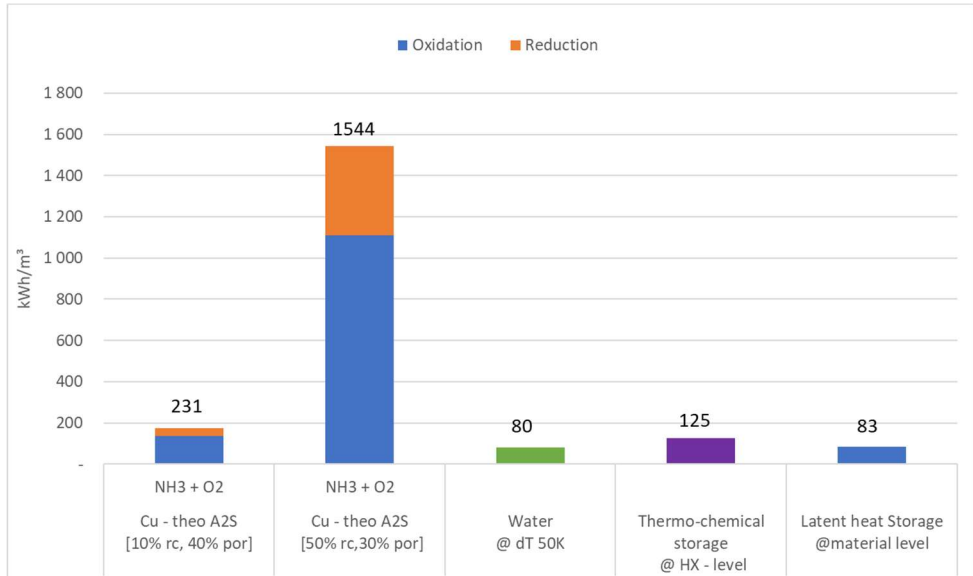


Figure 21: Comparison of the storage density at material level for different storage technologies

Figure 22 shows furthermore the storage density as well as the corresponding storage temperature of different storage technologies. As it can be seen, a possible chemical looping storage technology with a potential storage density of up to 6.000 MJ/m³ and at a temperature level of up to 900°C outruns storages based on sensible (e.g., water), latent (PCMs) and thermochemical storage technology by far.

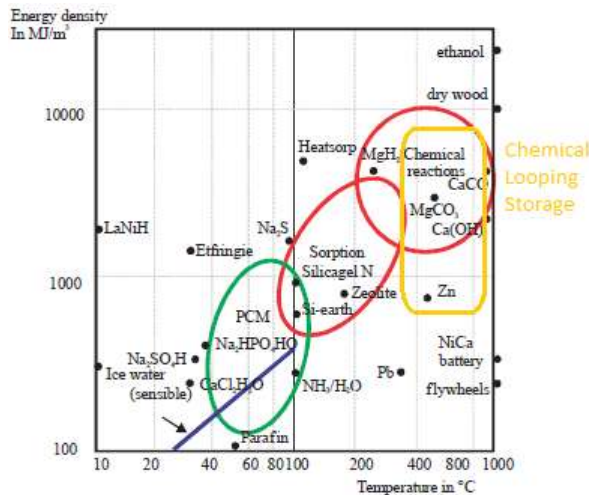


Figure 22: Storage density and temperature range of different storage technologies (CLC storage density added to graph based on N'Tsoukpo, K.E. et al 2009)

- **Temperature of operation:** The operation temperature of the storage directly determines the possible application scenario. Low temperature storage materials and technologies are mainly used for domestic applications such as hot water preparation and space heating. Storage technologies capable of providing at higher temperature, e.g., >450°C, such as the chemical looping storage technology can consequently be used in a higher variety of applications such as power generation and industry applications in which higher temperatures are needed.

- **Cycle efficiency:** The main field of application of heat storage is storing energy for short and / or long term and providing the stored energy according to the demands of the heat sink. This process can be rated by the round-trip efficiency. The cycling efficiency of a chemical looping storage benefit directly of the storage principle which is based on chemical reaction. Resulting in no heat losses in between the oxidation and reduction cycles. Nevertheless, sensible heat losses have to be taken into account during oxidation and reduction and could reduce the cycle efficiency if the heat cannot be used in one cycle or the other. This KPI can at this point in time not be calculated since the “proof of principle”-reactor does not have a typical heat sink as well as heat source and therefore this KPI have to be determined either by future system tests or detailed system simulation. At this point in time, it cannot be distinct and poses a question for a future research project.
- **Power Output:** The power output, similar to the temperature of operation, directly determines the possible application scenarios. Due to the fact that the oxygen carrier will in any case metal based, high heat transfer rates can be assumed with a high certainty. Accordingly, it can be stated, that a storage system based on the chemical looping principle will not be limited by heat transfer from the reactive material. The mass transport will stronger be determined by the reactor design but in this point in time no limiting factors towards was identified either.
- **Modulation capabilities and response time:** The interface between the heat distribution system of the referenced building and the thermal storage is mainly described by the submitted heat flux. From this objective modulation range, speed and Respond time are the most interesting properties in terms of system integration. This KPI have to be determined either by future system tests or detailed system simulation. At this point in time, it cannot be distinct and poses a question for a future research project.
- **Auxiliary power infrastructure:** A thermal storage includes all balance of plant components (such as: actors, pumps, controls, etc.). This leads to the need of additional power supply besides the energy flux of renewable energy. Therefore, additional heat and / or energy fluxes are trespassing the boundary of the black box. These additional fluxes have to be described in terms of amount, kind and power in a future system and this KPI have to be determined either by future system tests or full system simulation.
- **Cycling stability (mechanical and chemical stability of the storage material resp. oxygen carrier):** Chemical stability of the oxygen carrier factor is an important factor. The chemical stability of the storage shall be support high cycle stability, a long-life time and safe and robust operation of the heat battery. Each storage material will have its own characteristics that need to be taken into account. The oxygen carrier properties should support a safe and environmentally friendly operation of the storage system. During experiments no degradation of the mechanical and chemical stability was found. Nevertheless, based on the number of cycles undertaken the question of the cycling stability cannot be distinct and poses a question for a future research project.
- **Safety aspects and environmental impact:** The view of the end customer concerning is, that the thermal storage as well as the storage material and reactive gases have to be non-toxic during operation as well as in case of failure and furthermore to be generally environmentally friendly. At

this point in time, although no so-called show stopper was identified, the safety and environmental aspects of such a chemical looping storage system could not be fully distinct and therefore further specific knowledge of the storage technology as well as on the used materials are required and need to be addressed in a future research project. Examples of safety aspects and environmental impact which need to be addressed are:

- Flame point and explosive window
 - Heat release
 - Reaction sensitivity
 - Recycling capability
 - Safety aspects on system level
 - Environmental aspects on system level
 - Material and safety data sheet (MSDS) according to EU guidelines
 - REACH register number according to EU guidelines, if available
 - Export list number of the EU – requirement is not be listed
 - Melting point
 - Dissociation temperature and pressure
 - Heat capacity: pure material, diluted material, bulk material
 - Heat conductivity: pure material, diluted material, bulk material
 - Storage enthalpy – temperature or pressure difference
 - Acidity: pure material, diluted material, bulk
 - Corrosiveness
 - Purity: possible impurities, impact of impurities due to material degradation and storage process
 - Etc.
- **Technology readiness level:** Technology Readiness Levels (TRL) are a method of estimating technology maturity of Critical Technology Elements (CTE) of a program during the development process. They are determined during a Technology Readiness Assessment (TRA) that examines program concepts, technology requirements, and demonstrated technology capabilities. TRL are based on a scale from 1 to 9 with 9 being the most mature technology. The use of TRLs enables consistent, uniform, discussions of technical maturity across different types of technology. The European Commission has published within the HORIZON 2020 – WORK PROGRAMME 2014-2015 - General Annexes (Extract from Part 19 - Commission Decision C (2014) (4995) a high-level description of technology readiness levels (TRL). This description is the baseline to assess the technology readiness at the end of the project. Where a topic description refers to a TRL, the following definitions apply, unless otherwise specified:
- TRL 1 – basic principles observed
 - TRL 2 – technology concept formulated
 - TRL 3 – experimental proof of concept
 - TRL 4 – technology validated in lab
 - TRL 5 – technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies)
 - TRL 6 – technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies)
 - TRL 7 – system prototype demonstration in operational environment

- TRL 8 – system complete and qualified
- TRL 9 – actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space)

Based on the presented outcome and achieved results of the project it can be stated that goal of the project to achieve the technology readiness level of 2 to 3 was fully achieved. The next step would be a research project to lift the chemical looping storage technology from TRL 2/3 to TRL 3 / 4 resulting in of a fully functional high temperature storage system using CLC technology on a laboratory scale including knowledge of the coupling of the CLC storage system with VMD as well as knowledge of the technical possibilities of heat extraction from the CLC storage system.

4.3.1 SWOT analysis

Through the SWOT analysis below, the strengths and weaknesses of the new technology have been analysed and pointed out:

Table 9: SWOT table of the CLC-VMD-storage technology

Strengths	Weaknesses
+ Loss-free storage of heat + High storage densities + Output temperature level >500°C + Usage of waste streams	I. Continuation, no further development without projects on the topic:
Opportunities	Threats
+ Novel technology + High demand for loss-free high-temperature storage in industry as well as in the course of the change in energy supply + Simple, inexpensive design:	II. Current low TRL and associated need for research III. Effect of the VMD ammonia quality (water vapour content)

Strengths:

Loss-free storage of heat: The chemical looping storage technology is based on chemical reaction and therefore no sensible heat losses between the different oxidation and reduction cycles will occur.

High storage densities: Based on the knowledge gained during the project it can be stated that very high storage densities can be reached, compared to other thermal storage technologies

Output temperature level >500°C: Based on the knowledge gained during the project it can be stated that output temperatures above 500°C can be reached.

Usage of waste streams: Using NH₃ as a reactive gas will lead to the possibility to use waste streams for energetic utilization at concentrations which are too low to be used for other purposes.

Opportunities:

Novel technology: Until now, CLC has only been considered as a carbon capturing method in Austria. The "Ammonia2HeatStorage" technology represents a radical innovation leap in CLC storage development and the use of green ammonia of "green ammonia" and its separation by MD. The project results open

up research institutions but also Austrian industries the starting point to build up an international technology leadership and to and to play a leading role in the development of the technology.

High demand for loss-free high-temperature storage in industry as well as in the course of the change in energy supply: In order to increase the volatile share of renewables in the energy supply mix, the development of efficient energy storage technologies is becoming increasingly important. The requirements for such technologies are high flexibility, high freedom from losses and, in particular, compactness, i.e., storing as much energy as possible with small system volumes. The combination of high storage densities compared with high output temperatures above 500°C were shown in the project and proof the possibility of a new promising storage technology.

Simple, inexpensive design: The simple design approach with a fixed bed reactor offers the opportunity not only for an inexpensive reactor but an overall simple and cost-effective storage solution. Based on known plant engineering techniques, it can be assumed that a complete prototype system and a functional, marketable product can be developed in a relatively short time. No new technology needs to be developed for implementation. Moreover, the operating framework conditions (pressure, temperature, safety) are not new in the industry.

Weaknesses:

Continuation, lack of acceptance in the industry: The risk of a lack of acceptance in the industry (user) is not willing to invest in a novel technology.

Threats:

Current low TRL and associated need for research: A technology development with the aim of realizing the (technical) potentials identified in the project is probably not feasible on its own and in any case requires cooperation with other research institutions as well as industries including appropriate research funding.

4.4 Potential of the CLC-VMD-storage-concept and real application in industry

Within the scope of the potential assessment carried out in the project, it was possible to define first specific areas of application for a "CLC storage tank" to be developed in the future in combination with a VMD. These are, in particular, industrial processes in which, on the one hand, sufficiently high ammonia concentrations are available in the process waste water and, on the other hand, there is a heat demand in the respective industrial processes. The industrial sectors that, based on the potential survey, are directly eligible for the use of the **CLC storage** technology combination are:

Steel industry or coke production (gas tower condensates and phenol-cyan wastewater): The wastewater streams of the steel industry can be problematic in wastewater treatment plants (WWTP) precisely because of their high ammonia content. However, for membrane technology, the higher the ammonia concentration, the better the performance. In addition, the steel industry produces problematic

materials for disposal, especially mill scale, which could be used as a low-cost storage material, adding value to applications in this particular sector.

Biogas plants: Ammonia removal by MD reduces the need for aeration in the denitrification steps (lower electricity consumption) and also produces more biogas (by increasing the proportion of primary sludge disposal). At the same time, a biogas plant uses about 28% of the biogas produced for its own needs (heating). If all the biogas produced can be used externally or sold, an alternative heat source must be ensured. This is where the proposed heat storage solution comes in: Ammonia can be used as a seasonal heat storage in combination with CLC technology.

Rendering and slaughterhouses: These industries require thermally intensive processes such as continuous pasteurisation based on hot water/steam (> 170°C, 8 bar). Several ammonia-containing wastewater streams have been identified and could be of interest for utilisation (e.g., in slaughterhouses blood and wastewater or rendering blood wastewater and concentrate).

Fertiliser production and chemical industry: Ammonia can be generated from the urea synthesis process as well as in the wastewater from the production of ammonium nitrate. The A2HS concept is ideally suited to the needs of the chemical industry, where high-temperature processes (i.e., production temperature >150°C, e.g., ammonium nitrate production with temperatures in the range 100-180°C, other secondary processes such as CO₂ stripping: 180°C or NH₃ recycling up to 170°C) are used and problematic ammonia-rich waters are produced on a daily basis.

Tanneries: In tanneries, thermal energy is used to dry and produce hot water to treat the leather and can account for up to 30% of total energy consumption. The temperature levels here are somewhat lower (~70°C), but the ammonia potential is very significant. The waste stream identified as interesting here is the so-called lime-containing wastewater, which is produced in the conventional delimiting and pickling processes. Up to 70% of the ammonia found in the total wastewater of tanneries is said to be due to the use of ammonium salts in these operations.

Table 10 provides an overview of the potential assessment, the industrial sectors and their corresponding wastewater ammonia concentrations and the heat and temperature requirements of these processes. Furthermore, the decoupling of heat to a temperature level of up to 1000°C makes power-to-heat applications and loss-free long-term heat storage possible fields of application for a future CLC high-temperature storage facility.

Table 10: Potential sector of application/industrial sectors, their wastewater ammonia concentrations and temperature ranges of application

Industrial sector	Ammonia in waste water [kg/d]	Temperature range of application [°C]
Steel industry and coke production		
Gas tower condensates	3.195	>1000°C
Phenol-cyan waste water	1.239	>1000°C
Animal processing plants / slaughterhouses	76	70°C for pasteurization Steam production (T>170°C) for fat treatment and meat sterilization
Tanneries	32	70°C for pasteurization; hot water production, wet degreasing (40-70°C)

Biogas plants		
Sludge from biogas plants	178	Fermentation at mesophilic (35-45°C) and thermophilic temperatures (50-60°C)
Fertiliser production		
Urea synthesis process	33	>350°C CO ₂ -stripping >180°C NH ₃ -recycling up to 170°C
Artificial fertiliser production div.	32	Ammonium nitrate production 100-180°C.

The energy supply is changing and the course is already being set today for a sustainable energy system with up to 100% renewable energy. In addition to the industrial sectors mentioned, it can therefore be assumed with a high degree of certainty that the development of efficient energy storage technologies will become increasingly important in order to increase the volatile share of renewables in the energy supply mix. The requirements for such technologies are high flexibility, loss-free storage and, in particular, compactness, i.e., storing the maximum amount of energy with small system volumes.

Further research could develop a compact, loss-free, high-temperature heat storage system based on the key technology "chemical looping combustion" using "green" ammonia obtained from wastewater and waste streams by means of vacuum membrane distillation technology - VMD, which has the potential to bring about a radical, cross-industry paradigm shift compared to storage technologies currently in use. In addition to numerous industrial processes, there is also a considerable demand for high-temperature storage in so-called "power-to-heat" applications.

4.4.1 Economic Analysis of a potential future CLC-VMD-storage-concept

To evaluate possible future cost of a CLC-VMD-storage-concept a cost estimation for the VMD as well as for the CLC storage itself was performed.

The overall investment cost of a chemical looping storage will be mainly determined by:

- Reactor resp. storage system cost (incl. heat extraction and VMD-coupling)
- Oxygen carrier cost

Due the fact of the low TRL level, only very rough cost estimations can be given. The final reactor cost will not only be determined by the chosen reactor design itself but also by the size, the integration design, the coupling design of the CLC storage system with VMD as well as of the design of the heat extraction from the CLC storage system. Based on the knowledge gained, the cost estimation will be given on the actual design and will then be used to calculate a rough investment cost estimation per m³ resp. per kWh.

The reactor cost will be determined by material cost and labour cost to produce the reactor. Based on the actual system reactor cost, reactor cost of roughly 5000€/m³ are estimated. Additional cost for control and monitoring can be estimated with 1.500€ as well as 1.500€ for heat extraction and VMD-coupling.

Synthetic oxygen carrier can be purchased at 9.500€/m³ resp. 430€/m³ with a porosity of 40% in the fixed bed. Adding the storage cost to the oxygen carrier cost the invest cost of the storage cost will lead to

~40€/kWh (with an OC storage density of 237kWh/m³) resp. down to ~5€/kWh (with an OC storage density of 1.550kWh/m³). Even though those numbers are very rough and in an early stage of research, compared to other storage technologies it can be assumed possible/achievable, to build up an economically competitive product in short period of time.

5 Further research needs

The following further research questions are to be addressed in a next research project:

On the CLC side

- Further investigations on reaction-technical and thermodynamic basic processes including further redox systems.
- Calculation of mass and energy balances of a chemical looping combustion high-temperature storage system.
- Further evaluation and finding of suitable and affordable redox systems (material properties)
- Experimental investigation and determination of operating parameters (initial temperature, power, mass flow and concentration of reaction gases, oxygen carrier characteristics, etc.) of a fully functional high temperature storage system using CLC technology on a laboratory scale
- Knowledge and design of the technical concept of the coupling of the CLC storage system with VMD
- Knowledge and design of the technical concept of the technical possibilities of heat extraction from the CLC storage system.
- Optimization of the heat extraction and operation (charge/discharge) of the storage system specific to the application (end user)
- Determination of storage KPIs based on a fully functional high temperature storage system using CLC technology e.g., temperature of operation resp. output temperature, cycle efficiency, power output (min, max, avg, starting, etc.), modulation capabilities and response time, auxiliary power infrastructure, cycling stability (mechanical and chemical stability of the storage material resp. oxygen carrier), safety aspects and environmental impact:

On the VMD side

- Experimental investigation of different wastewater and waste streams to gain knowledge on the ammonia quality (specifically the water content but also possible volatile contaminants such as sulphur or fatty acids) effect in the CLC technology
- Experimental investigation of the possibilities for upgrading the produced VMD-gaseous ammonia to increase its concentration
- Membrane and membrane materials investigations towards better ammonia selectivity

- Investigation of coupling schemes (i.e., RO+MD; ED+MD, etc.) for pre-concentration of the ammonia streams prior the VMD process to increase the quality of the VMD-gaseous ammonia produced.
- Experimental evaluation of the membranes life span for better assessment of the VMD system's Opex
- Experimental investigation of the possibilities to directly couple the VMD and CLC

6 Outlook

The possibility of chemical energy storage in a fixed bed chemical looping reactor was investigated on a low TRL level within this project. Wet ammonia from VMD was considered as reducing agent and air as oxidizing agent. The project has shown that both half cycles are feasible when using a manufactured oxygen carrier material based on copper oxide. It was shown in the experiments that ammonia decomposition was not a limitation to the process and, therefore, the simulations in which an ammonia decomposition rate fast enough to not limit overall conversion was chosen, were proven valid. From the state of knowledge after this feasibility project, we can state the following as outlook and recommendation:

- As the resources within this project did not allow for a systematic alignment of simulation model validation and the experimental campaign, it would be interesting to use these two now existing infrastructures (model and prototype) and get to a more reliable prediction of quasi-continuously operated fixed bed CLC devices.
- Dedicated simulations of large-scale devices should be considered based on the findings, where the question of efficient heat exchange with the oxygen carrier filling and long-term energy losses through heat radiation and the gas connections can be assessed on a realistic basis.
- As the reliance on waste ammonia as fuel limits the potential application of CLC heat storage, a screening for other “waste gas streams” as potential reducing agents could be made. This could be focused on industrial branches with a demand for high temperature heat storage.
- A combination with the provision of pure CO₂ for subsequent storage or utilization out of the reduction half-cycle of the CLC process could be investigated if nitrogen-free carbonaceous reducing agents are used.

7 Contact

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