Solar [photo-electrochemical] waste water treatment for H2 and NH3

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AEE INTEC – Water & Process Technologies

Resource Valorization

Nutrient Recovery (NPK)

Products from Ligno-Cellulosic Materials/Waste Streams

Intensified Conversion Processes & In-Situ Separation

Optimized Process Systems for
- Biorefineries, Pulp&Paper
- Biogas plants
- Food industry

Closed-loop recycling

Solar water treatment

Recycling of High Value Chemicals

Zero Liquid Discharge in Industry

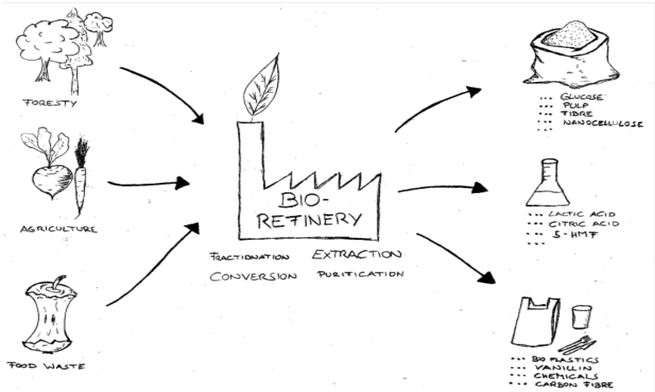
Waste & Process Water Valorization

Cooperative F&E Projects, EU Projects, Industry research

International expert networks - IEA:
- SHC Task 62 Solar Water and Waste Water Management
- IETS Task 17 Membranes in Biorefineries
- IETS Task 11 Industrielle Bioraffinerien – Net Zero GHG Emissions

EFCE Working Party for Process Intensification

Plattform Green Chemistry Austria



Design and Experimental Development of Component, Process, System and Control

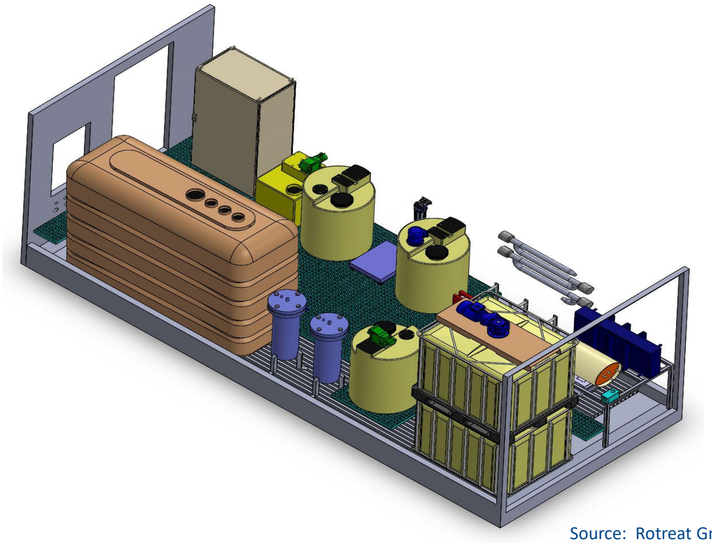
Simulation, Model and Algorithm Development

Laboratory and Pilot Testing, Upscaling, Monitoring and Demonstration

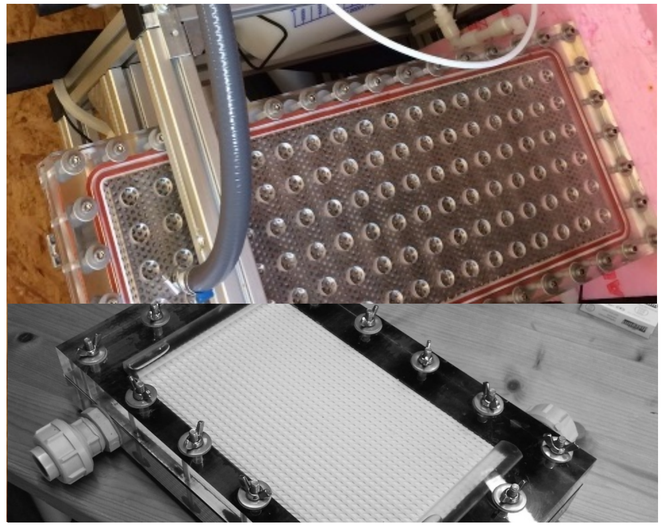
Sustainability Analysis, System Integration

Ammonia Separation via (solar?) Membrane Distillation

Source: iStock



Source: Rotreat GmbH



Source: AEE INTEC

> Focus

Removal and valuable material production from ammonium from waste streams.

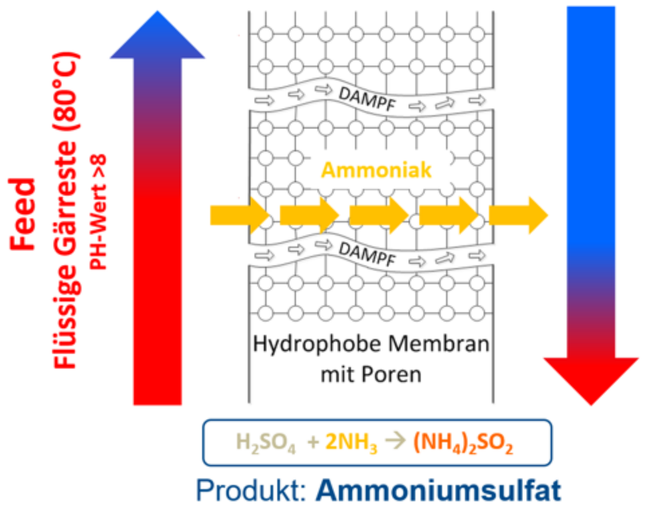
Application area: wastewater treatment plants, biogas plants, biorefineries, industry with highly organic- or N-polluted wastewater

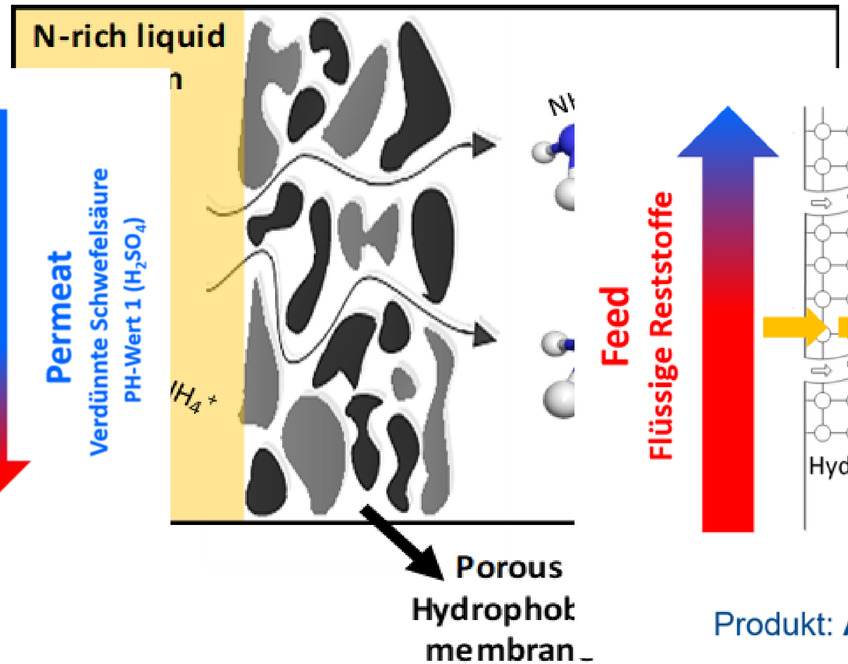
> Objective

- Recovery and utilization of ammonia as:
  - Energy vector (fuel, thermal storage).
  - Chemical (fertilizer, protein recovery, CO_2 storage, pre-treatment (bio-based industry) etc.)
- Reduction of disposal costs and waste water production (circular economy)
- Ultrapure water / distillate production

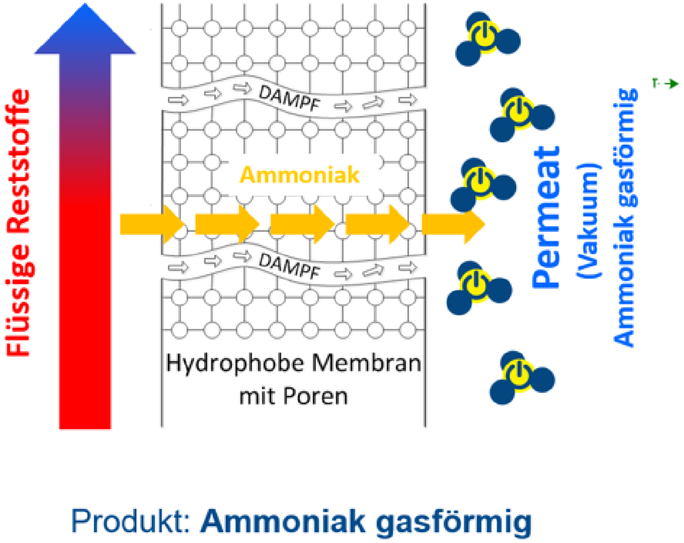
Ammonia Separation via Membrane Distillation

Direct Contact MD





Vacuum MD



Only ammonia in **free form (NH_3)** passes the membrane → **pH > 8 and/or temperature**

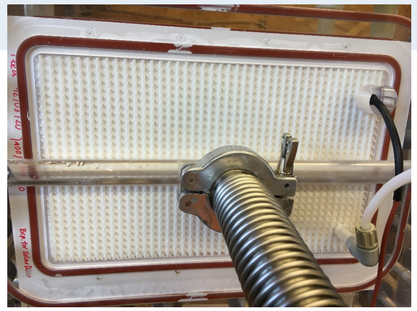
- Ammonia is condensed/reacted in a liquid solution
  - **Water** → ammonia water (other uses)
  - **Acid** → AS, AN, Urea, etc. (fertilizer)

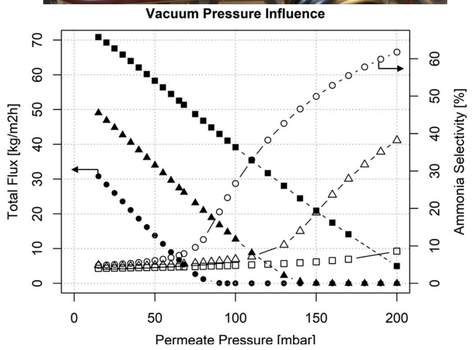
- Vacuum in permeate side
- Ammonia is collected in **gaseous form** (‚wet‘)

MD projects @ AEE INTEC

Ammonia-to-Power

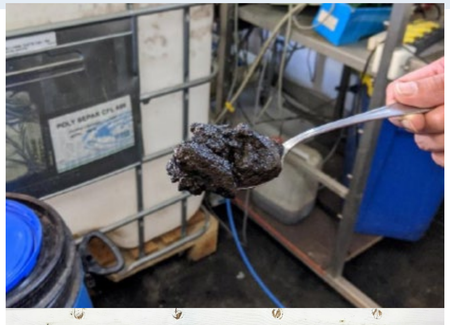
- Efficient extraction of **NH_3 in a gaseous** from waste liquid streams by means of **VMD**
- **Power + Heat** generation via SOFC **fuel cell**

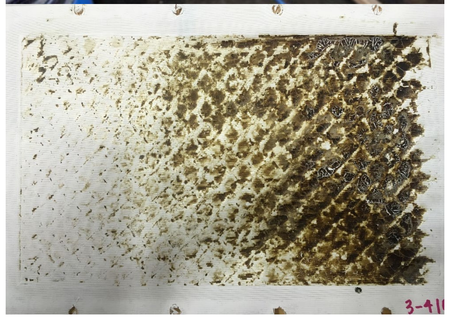




Nutricoal

- Efficient extraction of NH_3-NH_4^+ from **slaughterhouse** liquid streams by means of **VMD/DCMD**
- Production of a AS solution to be sprayed in carbon activated coal from solid residues (bones, etc.): fertilizer with slow release.





Ammonia-to-Heat Storage

- Efficient extraction of NH_3 in a gaseous from liquid streams by means of **VMD**
- Use: **Thermochemical storage**

Thermaflex

- Efficient extraction of NH_3 and fertilizer production from WWTPs **pilot** by means of **DCMD**
- Integration in District Heating Hub

Ammonia-to-Power

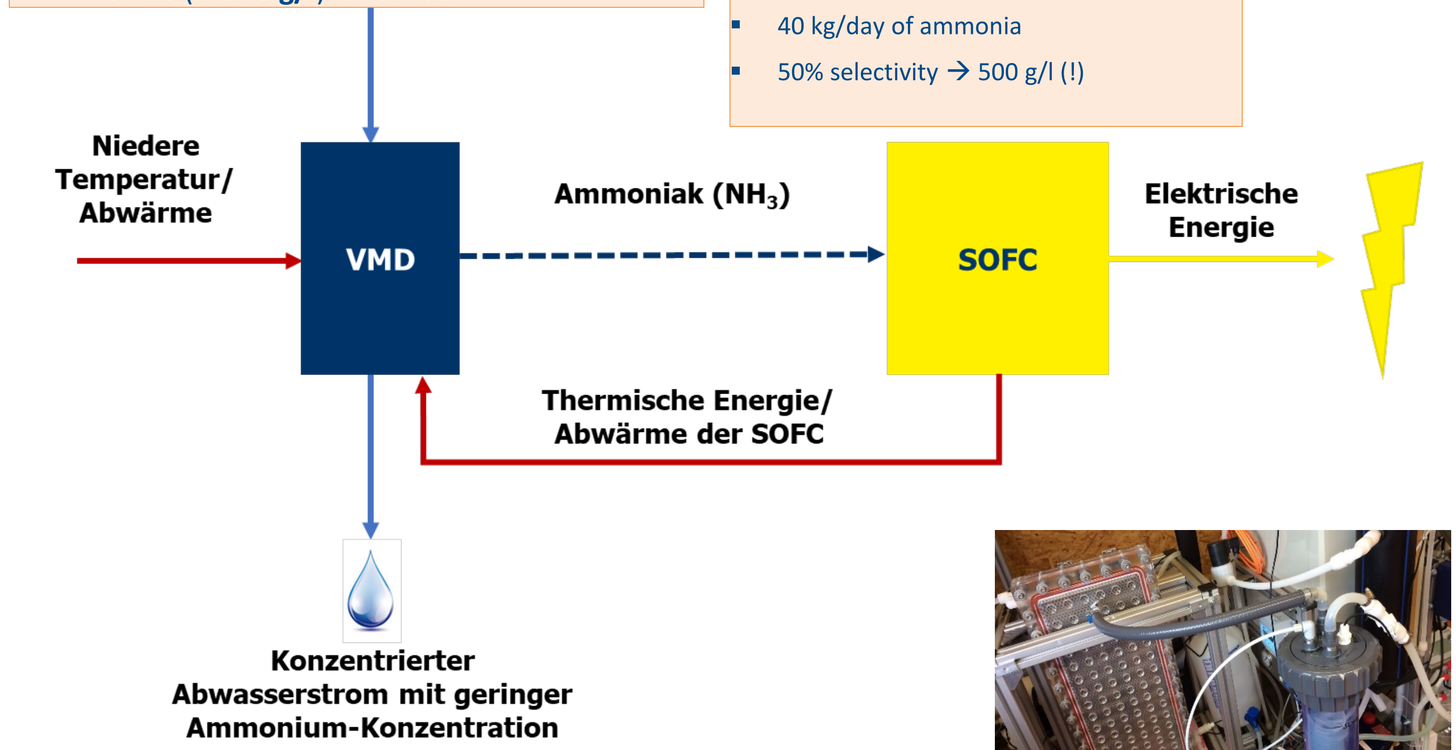
Ammonia-to-Power System

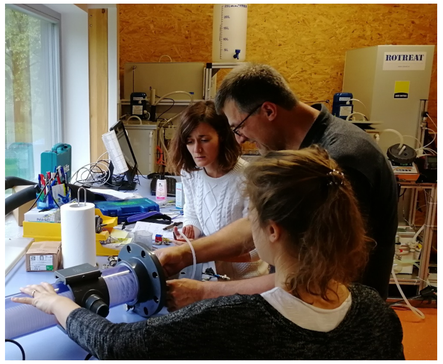
- **Streams:**
  - WWTP centrate water (<**1 g/l**) → CF: 500
  - Digestate (max **6 g/l**) → CF: 83
  - Urine (max **8 g/l**) → CF: 62

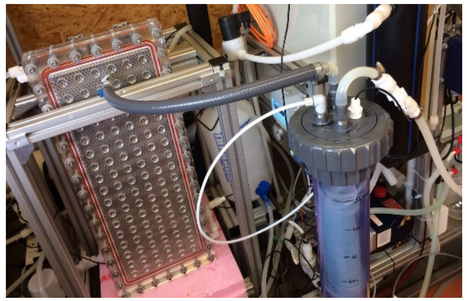
Target

Ammonia gas to be fed to a SOFC (VMD)

- 40 kg/day of ammonia
- 50% selectivity → 500 g/l (!)







Ammonia-to-Power

ELSEVIER

Journal of Membrane Science
Volume 614, 15 November 2020, 118399

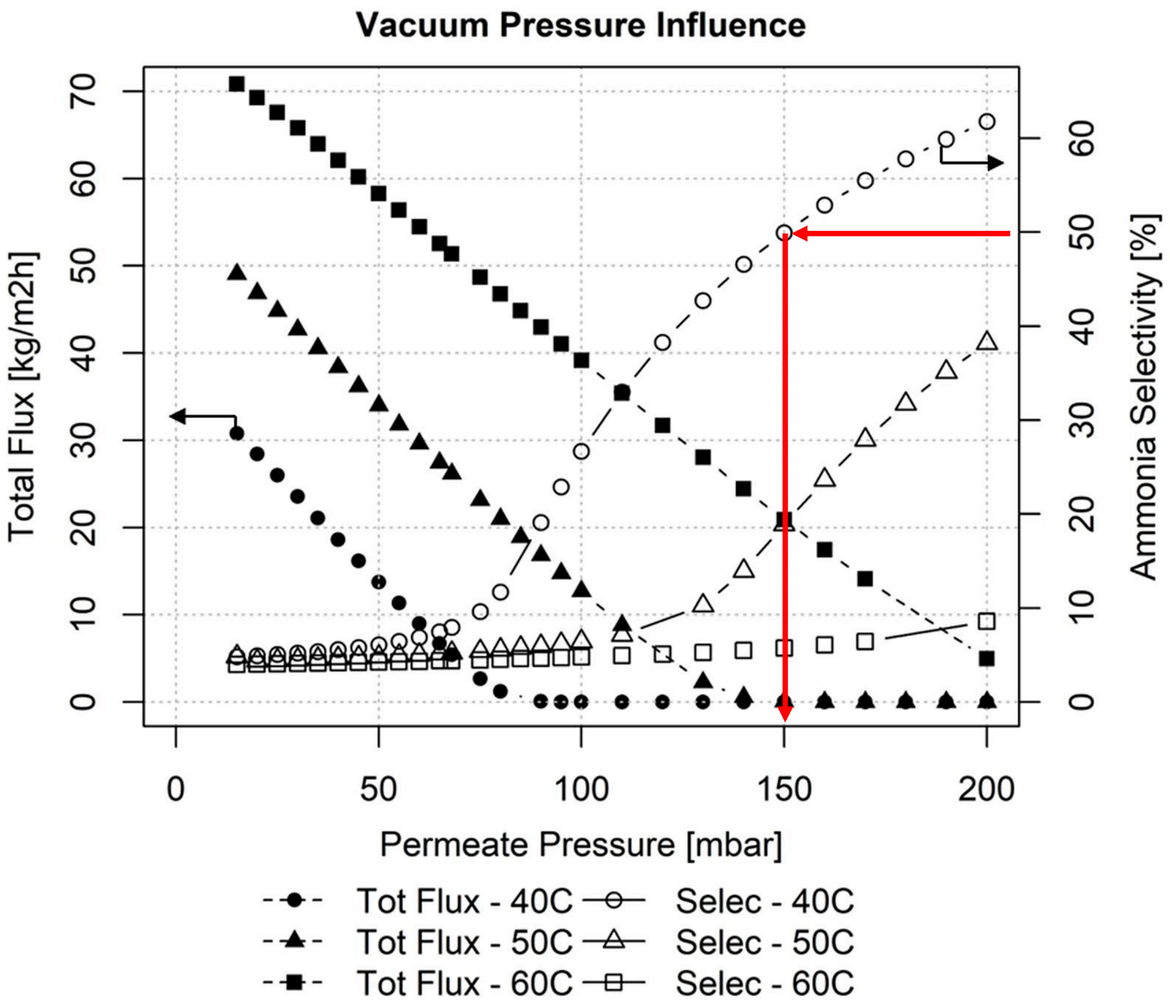
Vacuum membrane distillation multi-component numerical model for ammonia recovery from liquid streams

D.M. Scheepers MSc. [a, b], A.J. Tahir MSc. [a], C. Brunner [a], E. Guillen-Burrieza PhD [a]

Operation parameters influence in the VMD performance

- **NH4+ concentration, Temperature, Vacuum pressure,** Flow rate

- Low vapor pressure differences increase **S** but at the cost of the **Ammonia flux**
- Big trade-off between **Selectivity** and **Ammonia flux**
- 50% very unlikely at these concentrations…



Ammonia-to-Power

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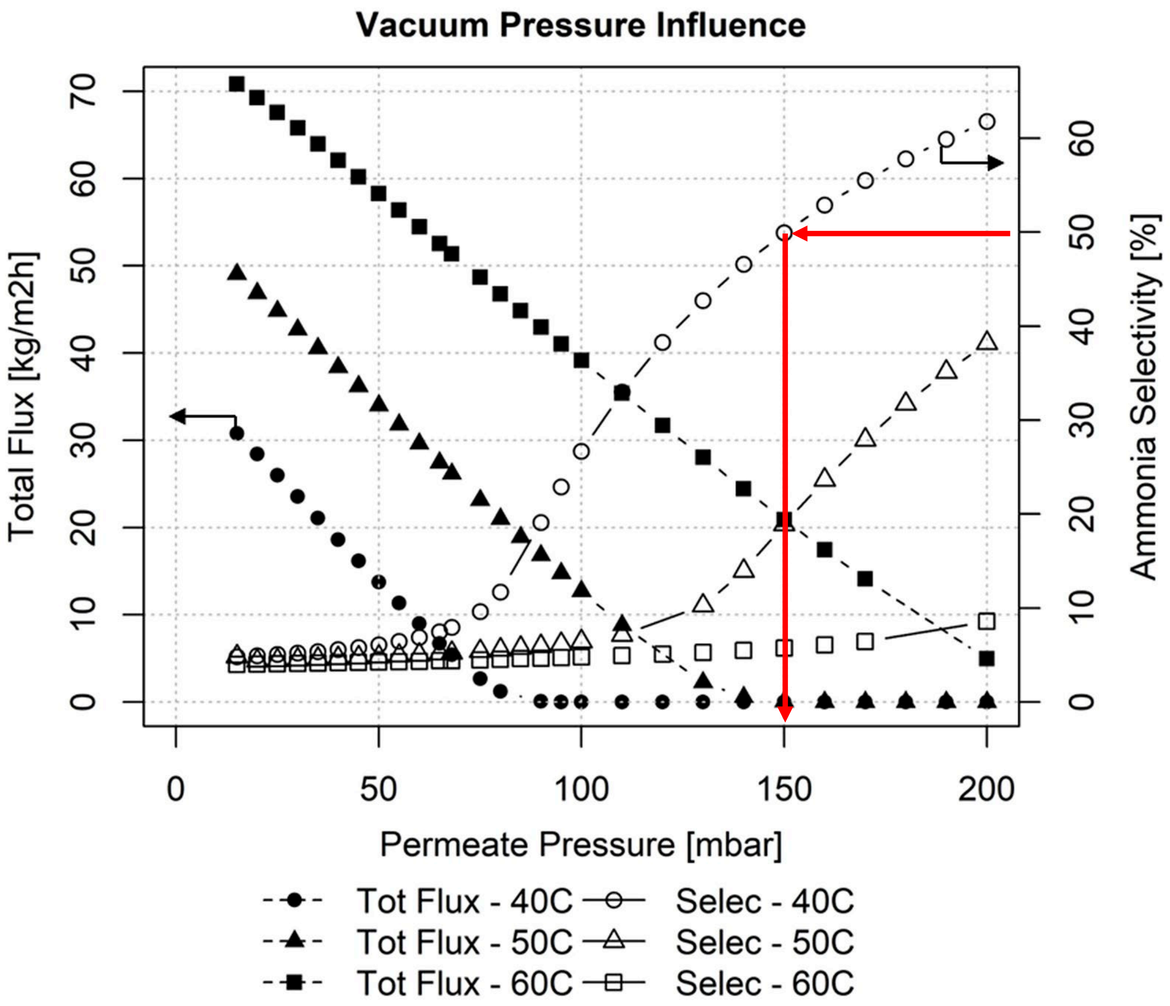
New strategies:

- **Decoupling water and ammonia flux**
- **Functionalized membranes**
- **Optimized operating parameters, low T operation**
- **What is the real SOFC requirement?**
- **stable performance?**
- **….partly proven in DCMD….VMD to come 2022!**



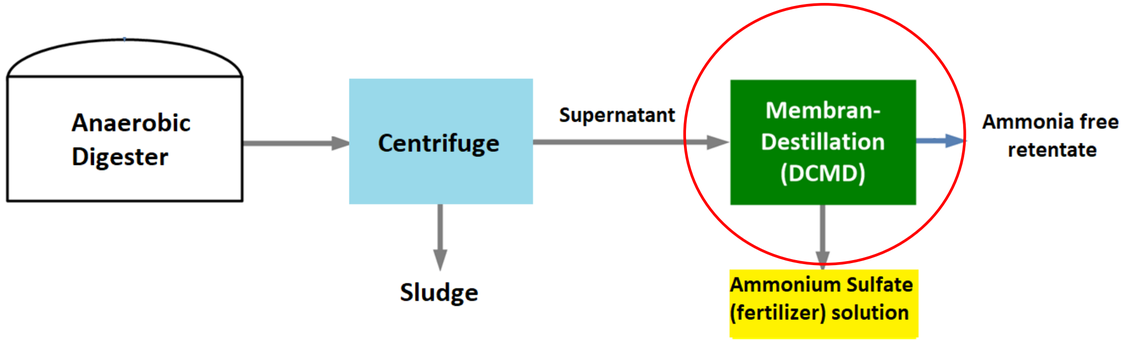
ThermaFLEX project MD results

- **Objective:** remove NH_3 from WWTP digestate supernatant with a **net benefit**
  - Reduce N/DN basin → target removal 99%
  - Produce a fertilizer (AS solution)
  - ~40 m^3/day ~ <1 g/l N-NH_4 → ~30 kg NH_3/day
- **Challenges:**
  - Highest product concentration and removal possible.
  - Fouling/cleaning (?)
  - Reduced **Opex:** chemicals
  - From lab to pilot
  - Continuous operation 24/7

2 m^2 **4 m^2** **14 m^2**

Very scalable plate modules of different sizes

Point of integration

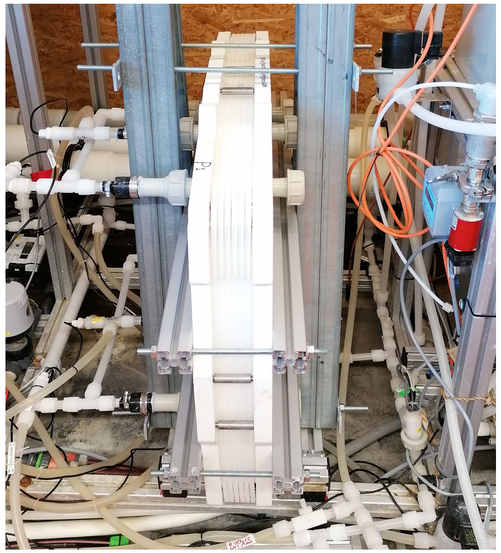


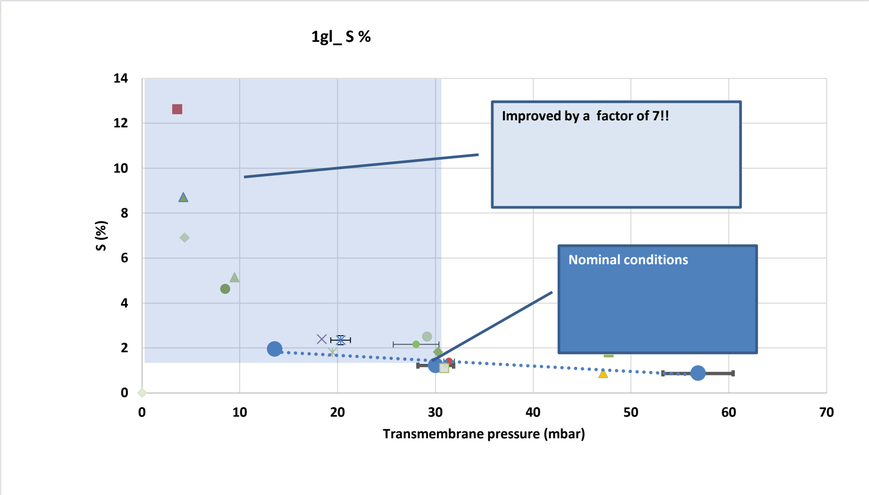
ThermaFLEX project MD results

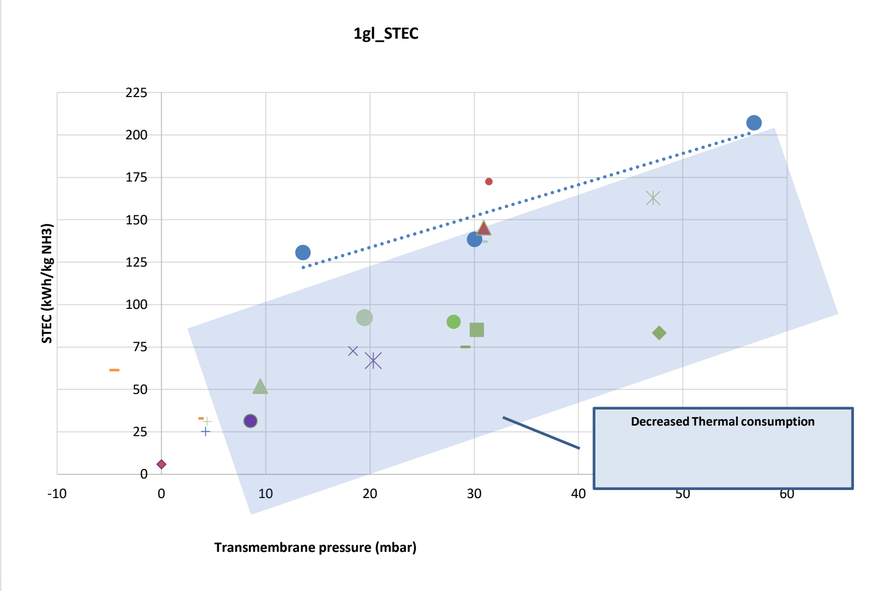
<u>In the lab:</u> optimize performance (2 m^2 module):

- Artificial water (AS)
- Played with operational parameters:
  - velocity, pH, T, acid dosing, etc.
- Increased **Selectivity by a factor of 7** w/o reducing the ammonia flux and decreasing specific thermal consumption (STEC) accordingly
- Reached **<u>100% selectivity</u>** (improved operational conditions) in lab scale
- Mathematical model for performance optimization
- Chosen **optimized conditions for PILOT**

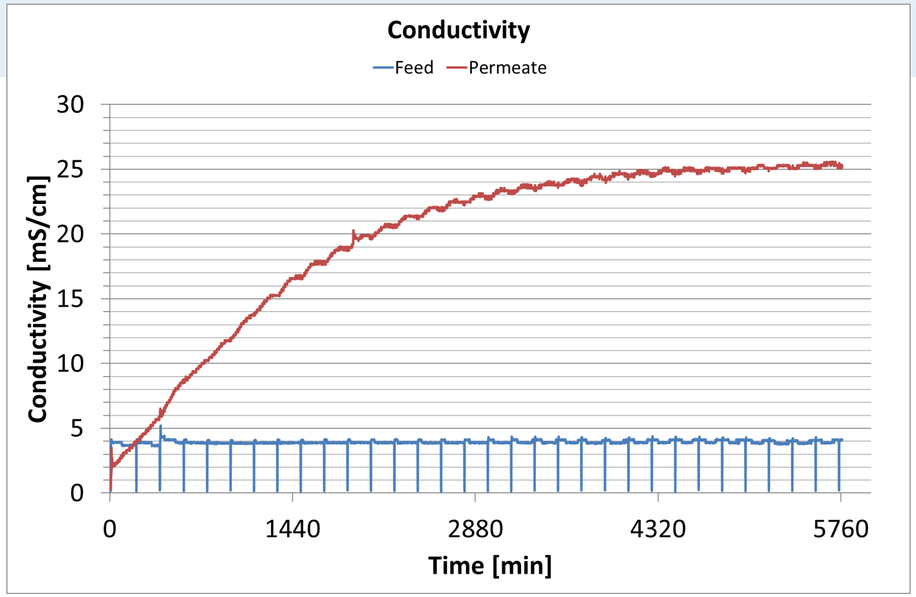
2 m^2







ThermaFLEX project MD results



<u>Pilot plant</u> at ARA Gleisdorf (centrate water < 1 g/l):

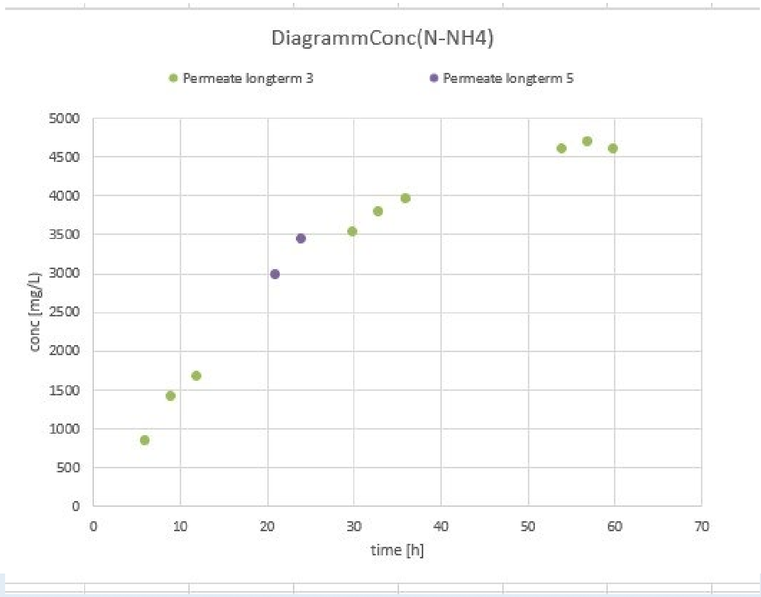
- **We are now operating in continuous mode for > 72 h steady**
- **Water capacity ~ 1 m^3/day, 14 m^2 membrane area**

<u>Performance average values are the same:</u>

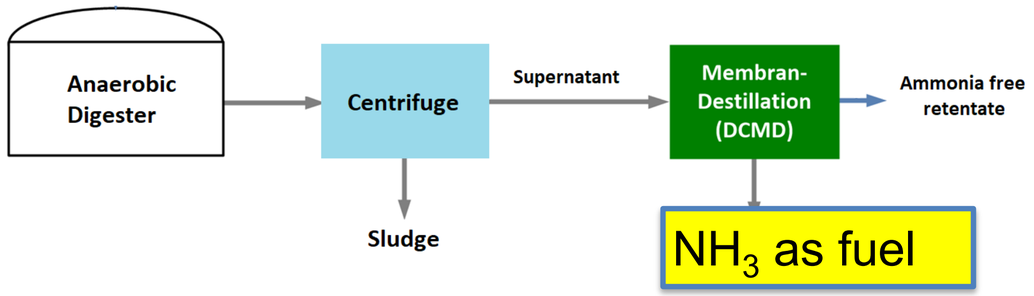
- **<u>Recovery of ammonia > 95%</u>**
- **<u>Removal of ammonia > 99%</u>**
- **<u>Ammonia in effluent: 4-2 mg/l</u>**

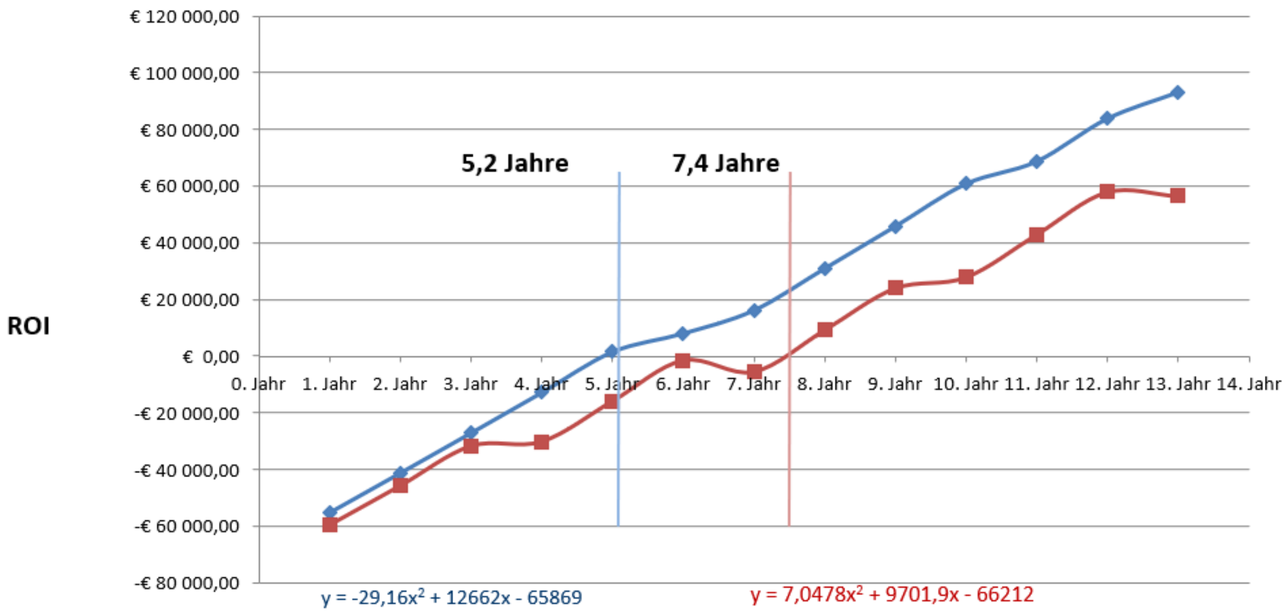
Continuous operation (T operation < 40°C):

- **Permeate ~ 30 g/l AS**
- **16 kWh_{th}/kg-NH_3 (~19 kWh_{th}/kg-N)**
- **More than 2 weeks w/o cleaning necessity**
- **Cleaning: citric acid less than 2 hours (not optimized)**



Business Case – thermal energy freely available WWTP





Modullebensdauer:	5 a
Membranfläche:	Standard

Modullebensdauer:	3 a
Membranfläche:	+50%

Task 62 – Solar Water Decontamination and Disinfection Systems (Subtask B)

- Comprehensive description of the state-of-the-art and potential applications of **solar water decontamination and disinfection systems** in industrial water management.
- **Membrane solar photocatalytic systems** for industrial wastewater treatment and reuse.
- Solar driven new **thermochemical technologies** (low-medium temperature up to 300ºC for specific industrial wastewater treatment.
- **Design of new solar collectors** for hydrogen production and industrial water decontamination and disinfection.
- Integration of water decontamination and disinfection technologies driven with solar energy with membrane separation technologies **for recovery of nutrients and products/wastes with added value**.

SUBTASK B
Solar Water Decontamination and Disinfection Systems

Source: CIEMAT

IEA SHC Task 62 – Solar photocatalytic generation of H_2

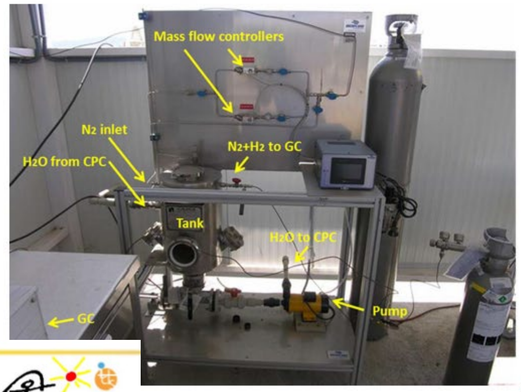
Isabel Oller, CIEMAT

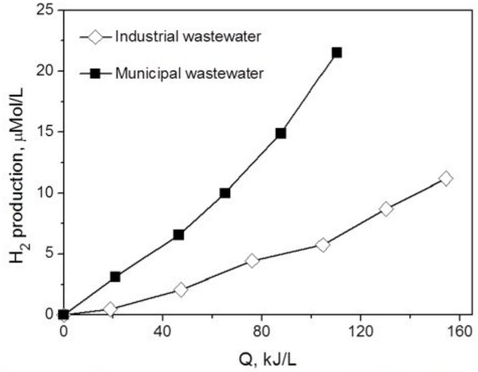
Solar photocatalytic generation of hydrogen (decarbonisation systems)

-16 Pyrex glass tubes (inner Diameter 28.45 mm, outer diameter 32.0 mm, length 1530.0 mm) mounted on a fixed platform tilted 37 (local latitude).
- Total area irradiated of 2.1 m^2
- Total irradiated volume of 14.24 L.
- Total slurry volume of 25 L
- Catalyst loading in the range of 0.2-1 g/L.

$$C_xH_yO_z + (2x-z)H_2O \xrightarrow[h\nu \geq E_g]{photocatalyst} xCO_2 + \left(2x - z + \frac{y}{2}\right)H_2$$

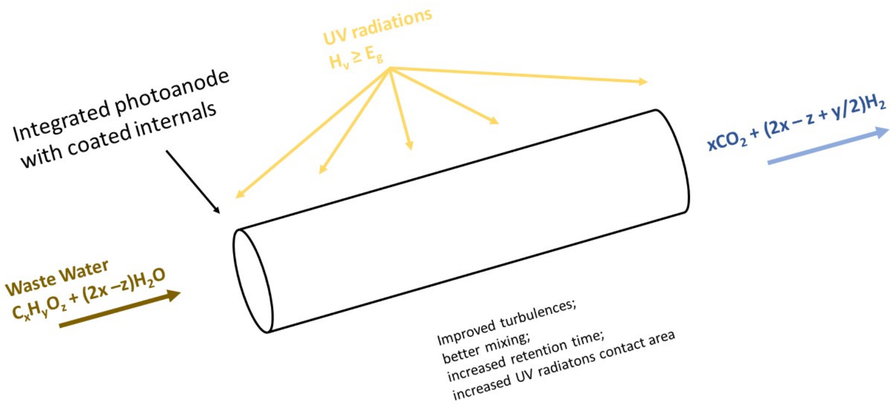
Solar photocatalytic generation of hydrogen

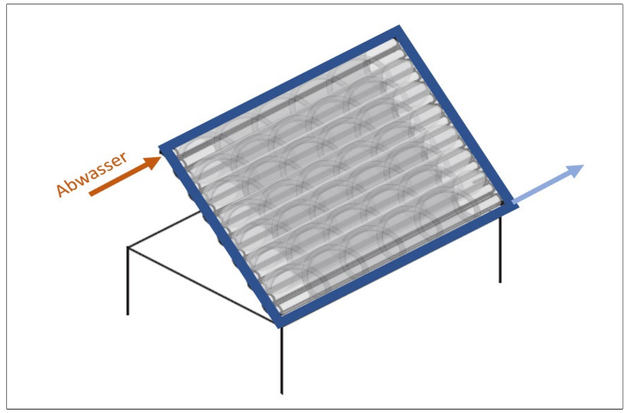




H_2 production vs. energy accumulated into the photoreactor (305-550 nm) as a function of the type of real wastewater used. 25 L of 0.2 $g \cdot L^{-1}$ Au/TiO_2 slurries..

Solar photo-electrochemical waste water treatment





> Target

Development of a solar reactor for efficient photo-electrochemical H2 production and simultaneous waste water treatment under direct sunlight:

- Simultaneous removal of several waste water compounds (solvents, organic pollutants etc.), removal rates > 50%
- Waste water components as electron donors for H2 production
- Increase of system efficiency Solar-to-Hydrogen ratio by 25%

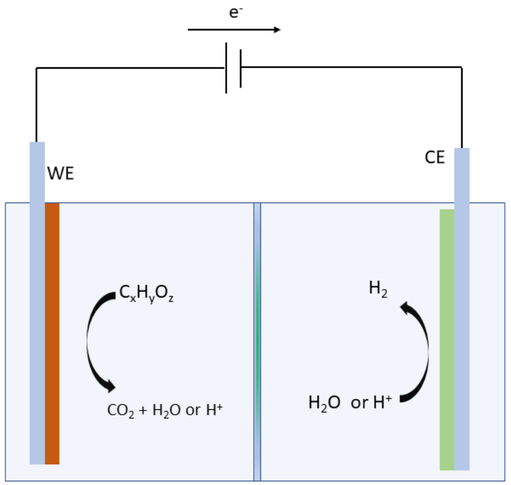
> Approach

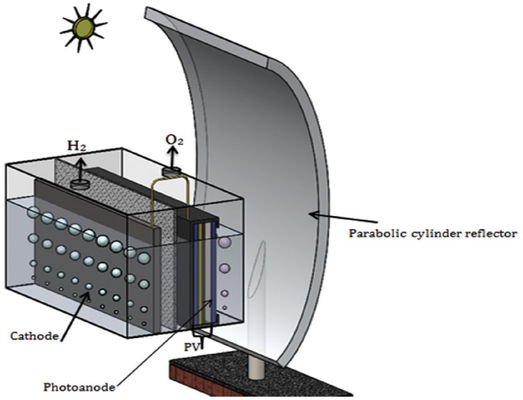
- Optimization of catalyst morphology
- Identification of limiting processing steps in contaminant removal to optimize decomposition
- Optimizing process parameters (voltage, pH, decomposition rate)
- Novel rheology for optimized mass and energy transfer
- Reactor development as CPC system with concenrated sunlight intensity

Source: AEE INTEC 2,

Coupling waste water treatment with H2 production

- Several studies on photo-electrochemical waste water treatment and simultaneous hydrogen production
- Waste water components as electron donors for H2 production
- Examples of single componentes under research (Gupta, 2018):
  - Saccharides (cellulose from paper industry, WWTP)
  - Phenols (refineries, pulp industry, agriculture)
  - Organic acids
  - Ammonia
- Solar-to-Hydrogen in current research: 5-15% (Roeb M., et.al, 2020)

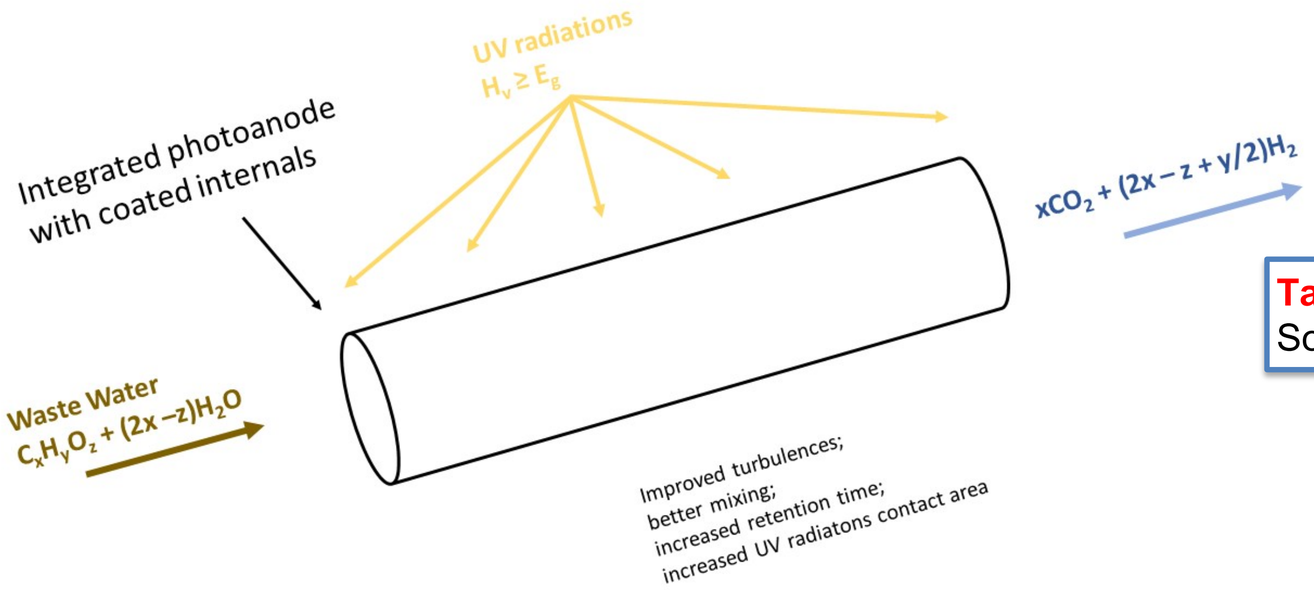




Urbain F, Smirnov V, Becker JP, Lambertz A, Yang F, Ziegler J, et al. Multijunction Si photocathodes with tunable photovoltages from 2.0 v to 2.8 v for light induced water splitting. Energy Environ Sci 2016.

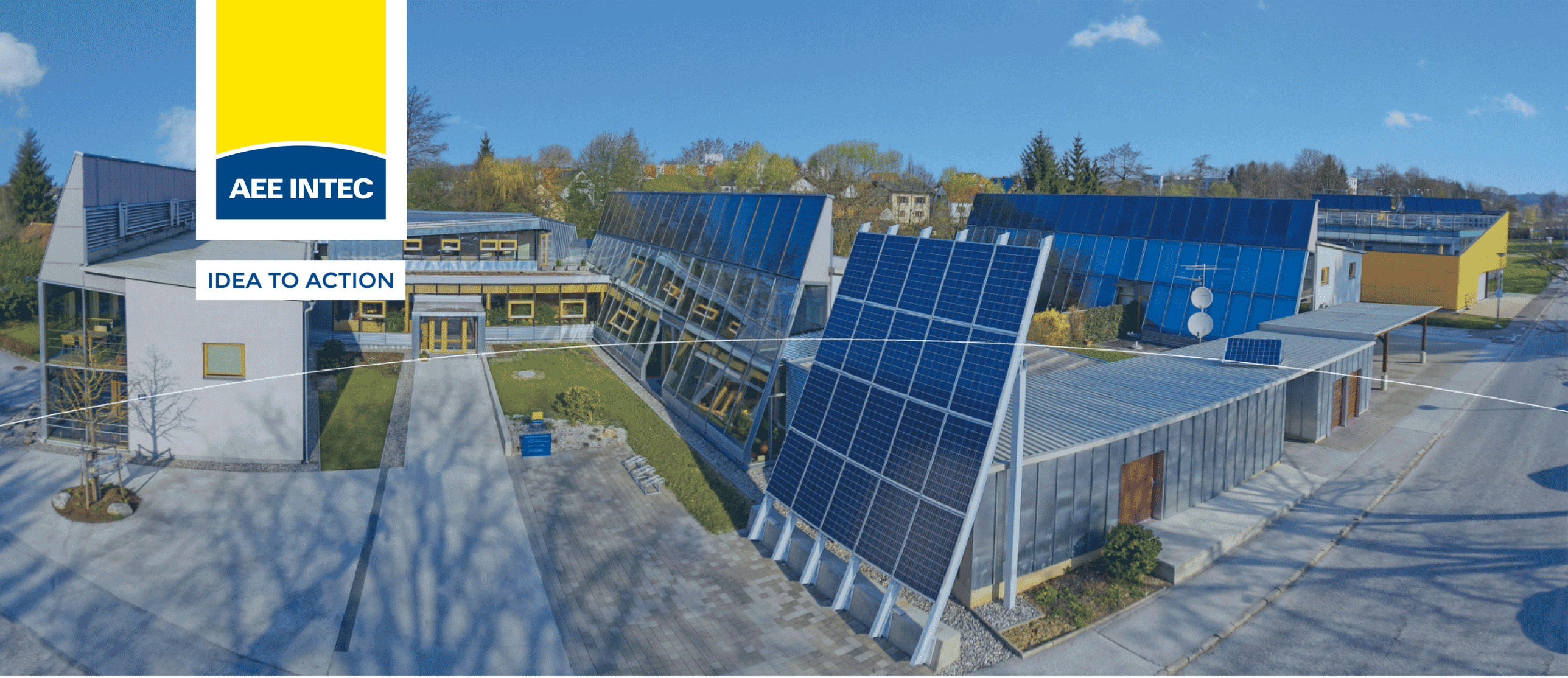
Novel process engineering approach to increase Solar-to-Hydrogen ratio

Multi-component waste waters:
- Vegetable production/Glass house
- -pharmaceutical waste water
- Pulp&paper (EDTA)
- microplastics
- ……



Target:
Solar to Hydrogen > 25%

Advantages based on improved reactor design:
- High mixing of viscous streams, even catalyts particles (or coated internals)
- Better light penetration – enhanced path light -> catalyst
- Short reaction times due to intensifed mass and energy transfer
- Decoupling of residence time and particle velocity
- Continuous process – net flow/residence time control based on available sunlight
- Shorter reaction times



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