CASALE

PLANTS FOR
A NEW PLANET.
SINCE 1921.

PIERDOMENICO BIASI,
SUSTAINABLE CHEMISTRY AND ENGINEERING IN INDUSTRY
21ST NOVEMBER 2024

Ammonia Synthesis: a 100 years journey

OUTLINE

- CASALE AND ITS JOURNEY TO SUSTAINABLE SOLUTIONS
- AMMONIA SYNTHESIS AND ITS HISTORY
- STEPS FROM GREY AMMONIA TO GREEN AMMONIA
- AMMONIA REACTOR AND CATALYST
- FROM LAB TO IMPLEMENTATION
- SUMMARY

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CASALE AND ITS JOURNEY TO SUSTAINABLE SOLUTIONS

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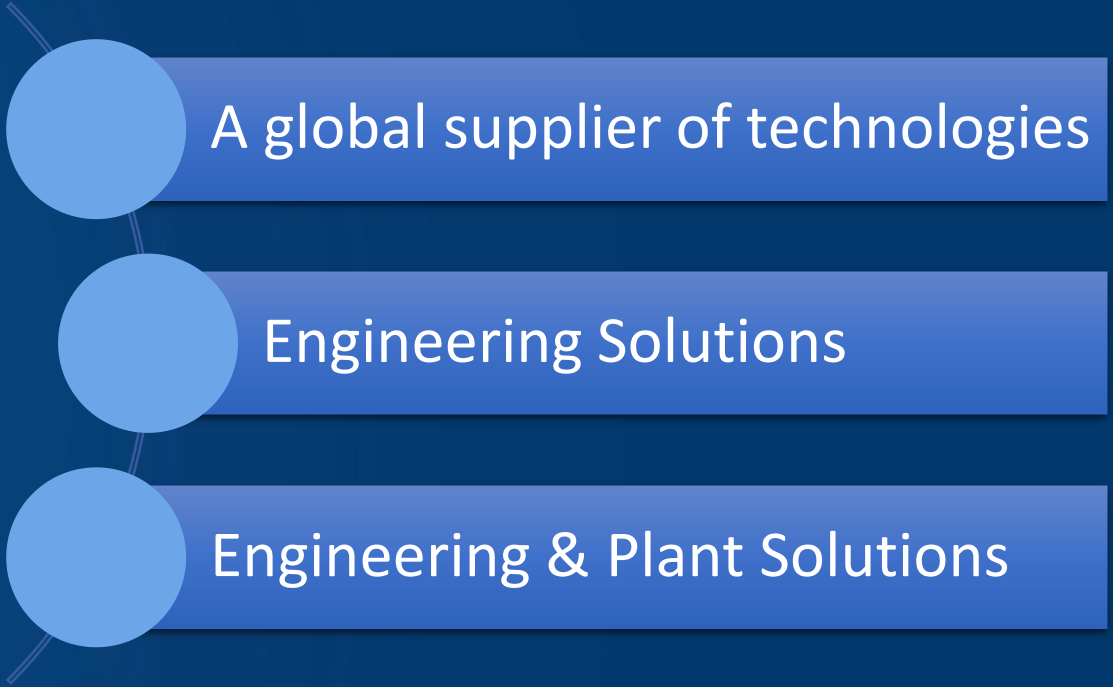
CASALE: Swiss Company with Global Footprint



A global supplier of technologies

Engineering Solutions

Engineering & Plant Solutions

SYNGAS **AMMONIA** **METHANOL** **UREA** **MELAMINE** **NITRIC ACID**

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...WITH 100 YEARS OF HISTORY

1921
FIRST AMMONIA TECHNOLOGY

1980s
UREA AND METHANOL TECHNOLOGIES

2013
MELAMINE TECHNOLOGY

2014
NITRATE, PHOSPHATE, COMPLEX FERTILIZER

CASALE

420 SPECIALISTS FOCUSED ON DELIVERING VALUE

CASALE

LUGANO - SWITZERLAND

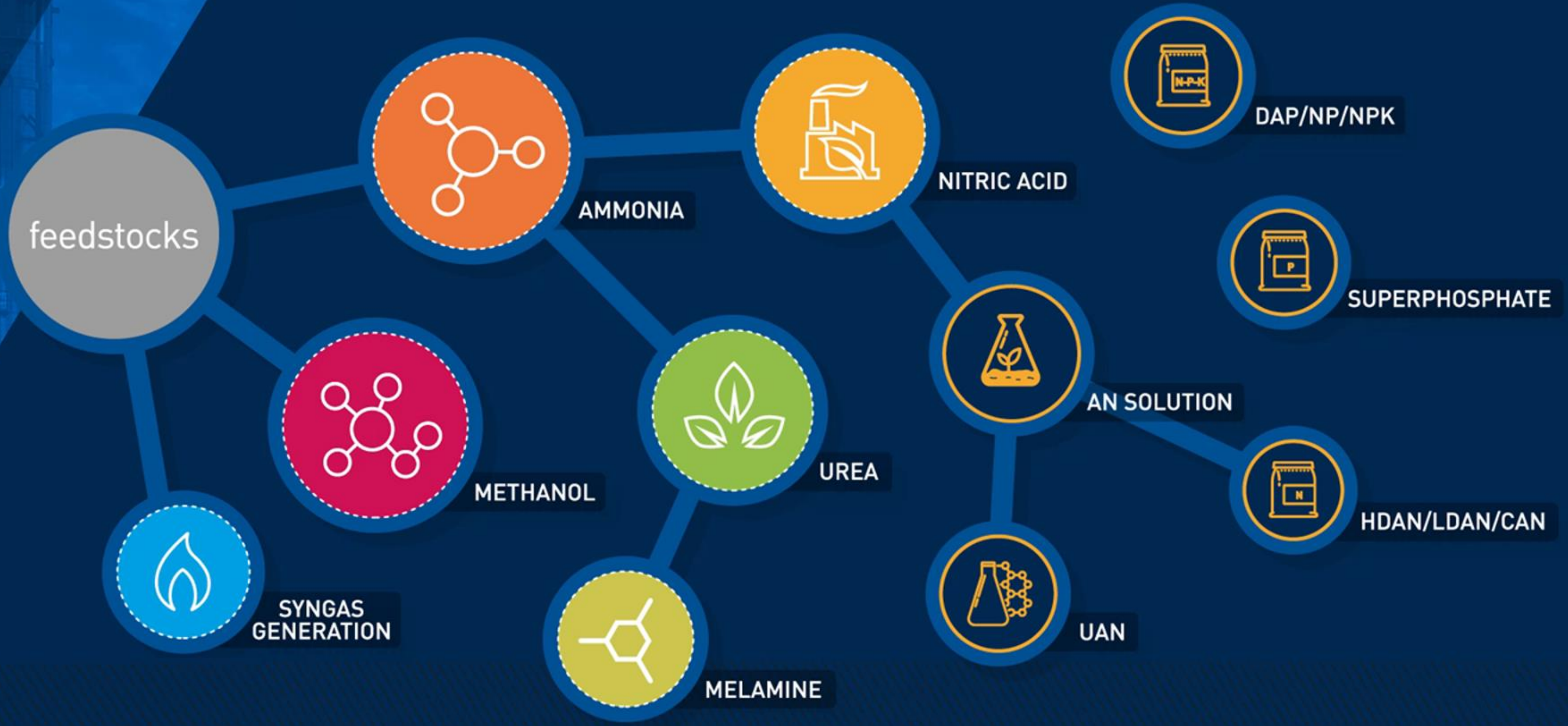
260 PROFESSIONALS

CASALE PROJECT

PRAGUE - CZECH REP.

160 PROFESSIONALS

Casale delivers technologies to the ammonia chain covering >95% of current markets.



feedstocks

AMMONIA

METHANOL

SYNGAS GENERATION

NITRIC ACID

UREA

MELAMINE

AN SOLUTION

UAN

DAP/NP/NPK

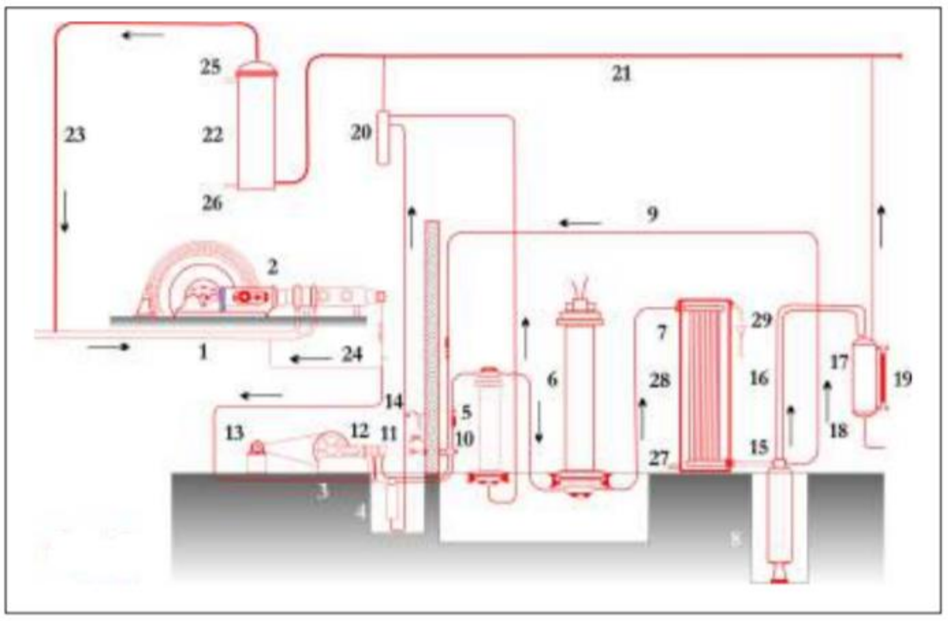
SUPERPHOSPHATE

HDAN/LDAN/CAN

CASALE

Decarbonisation in Casale since 1920

- Casale is the oldest Licensor in the green ammonia field presently in the market
- Casale built the first fully green ammonia plant about 100 years ago in Italy
- The electrolysers were fed by hydroelectric power producing hydrogen that was supplied to a dedicated synthesis loop
- 100 years of CASALE SA: a scientific perspective on catalytic processes: *https://www.sciencedirect.com/journal/catalysis-today/vol/387/suppl/C*



PFD of the ammonia synthesis loop by Casale in 1920'

Fiat car with engine fuelled with ammonia. Casale patent in 1935

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AMMONIA SYNTHESIS AND ITS HISTORY

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Ammonia Synthesis

- Synthetic ammonia was industrially produced for the first time in Germany in 1913 by Badische Anilin und Soda Fabrik (BASF) in their factories using the HaberBosch process
- Ammonia is a colorless inorganic compound of nitrogen and hydrogen with the formula NH_3.
- At ambient conditions it is gaseous with a characteristic pungent odor. Ammonia is irritating to the skin, eyes, nose, throat, and lungs.
- Ammonia is the most abundantly synthesis chemical produced in the world (ab. 180 million tons in 2021)

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Ammonia Synthesis

- Ammonia synthesis accounts for around 2% of the total energy consumption annually in the world.
- Ammonia is the basic building block of the world nitrogen industry; consumption of ammonia for nitrogen fertilizers accounts for nearly 80% of the world ammonia market.
- Nitrogen fertilizers are the most widely used fertilizers in the world, accounting for close to 60% of all fertilizers.
- With the exception of mainland China, where most of the ammonia is produced from coal gasification, most of the world’s ammonia is produced from natural gas.
- During 2023–28, world apparent consumption of ammonia is forecast to increase at about 4.0% per year.
- Ammonia reactor is designed based on the activity of the catalyst (majority of reactors and processes are designed based on catalyst deactivation).
- Ammonia synthesis was selected 2 time for the Nobel Prize.

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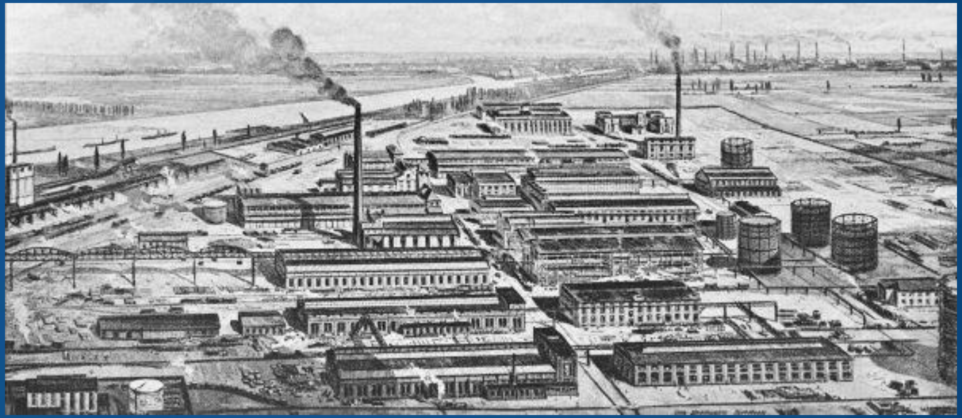
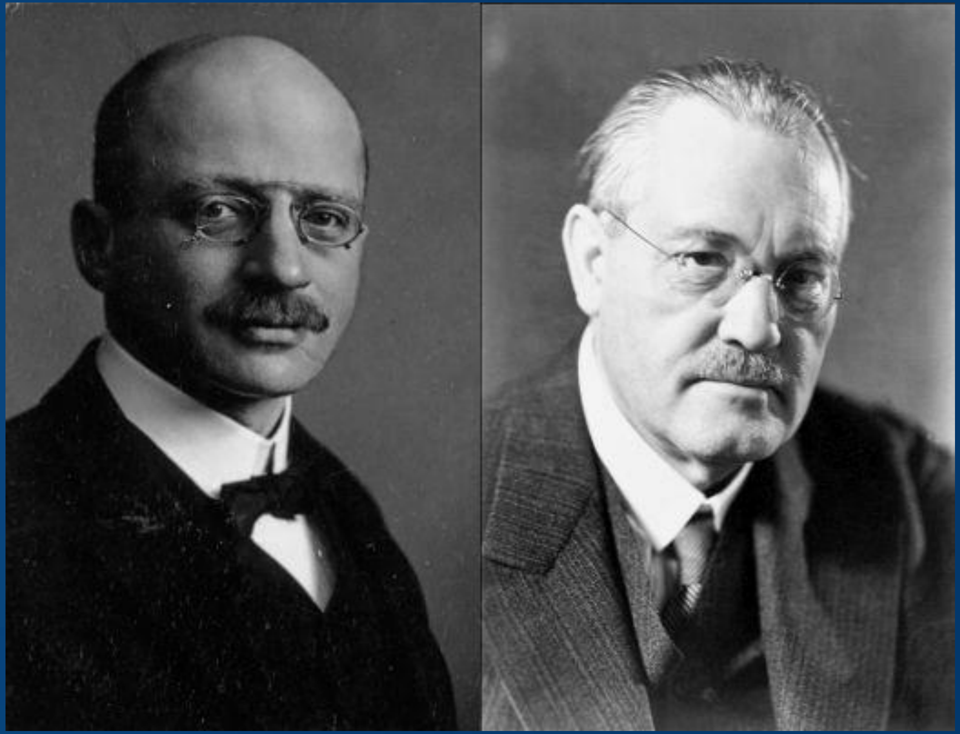
Ammonia Synthesis

Carl Bosch:

“Ich glaube, es kann gehen“ (“I think it can work”)



BASF plant in Oppau at the time of the first ammonia production using the Haber-Bosch process. (Image: BASF)



Picture taken from: https://www.chemietechnik.de/anlagenbau/id-100-jahre-ammoniaksynthese-geschichte-der-ammoniaksynthese-269.html

Synthetic ammonia was an exclusive process from BASF

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Ammonia Synthesis

Research in Ammonia Synthesis in 1913

- “[...]large-scale technical production [of ammonia] would not have been possible without the availability of large quantities of a cheap catalyst. [...] This task could be solved successfully by Alwin Mittasch who in thousands of tests found that a material [...] exhibited satisfactory activity.” Gerhard Ertl, Nobel Lecture, Angew. Chem. Int. Ed. 2008, 47, 3524

Catalyst was the paramount for the ammonia synthesis

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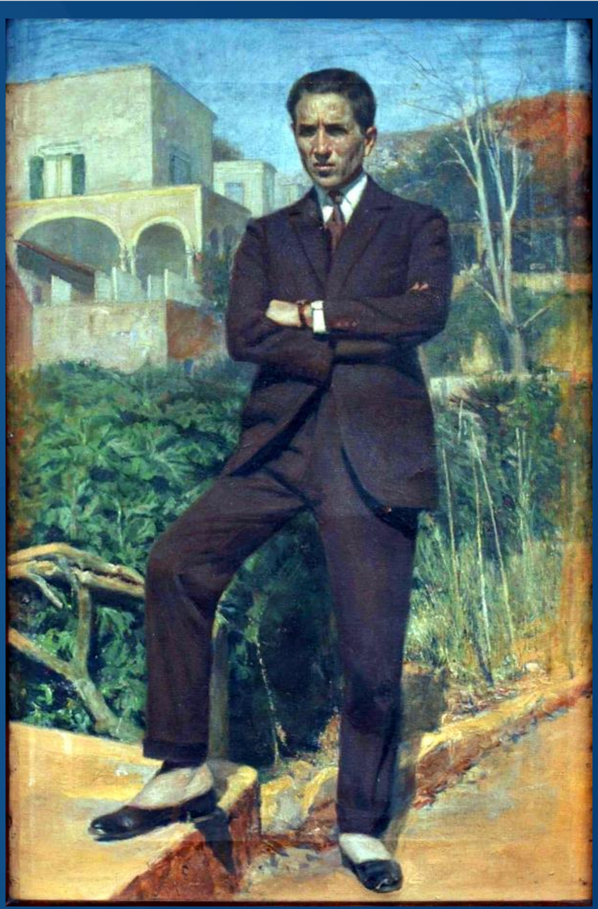
Ammonia Synthesis

- A. Travis, Luigi Casale's enterprise: Pioneer of global catalytic high-pressure industrial chemistry.

  Catalysis Today, Volume 387, 1 March 2022, Pages 4-8



Luigi Casale needed a catalyst because BASF was not licensing it

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Ammonia Synthesis: First Casale Process

- Pressure was 400 bar to avoid being inside BASF patent
- Reactors were done from the cannons of the first world war
- Catalyst was not the best in class since the high pressure in the process did not require the most active catalyst

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Ammonia Synthesis: Main Technology Players

- Casale
- Topsoe
- Johnson Matthey
- KBR
- Mitsubishi Heavy Oils
- ThyssenKrupp
- Linde

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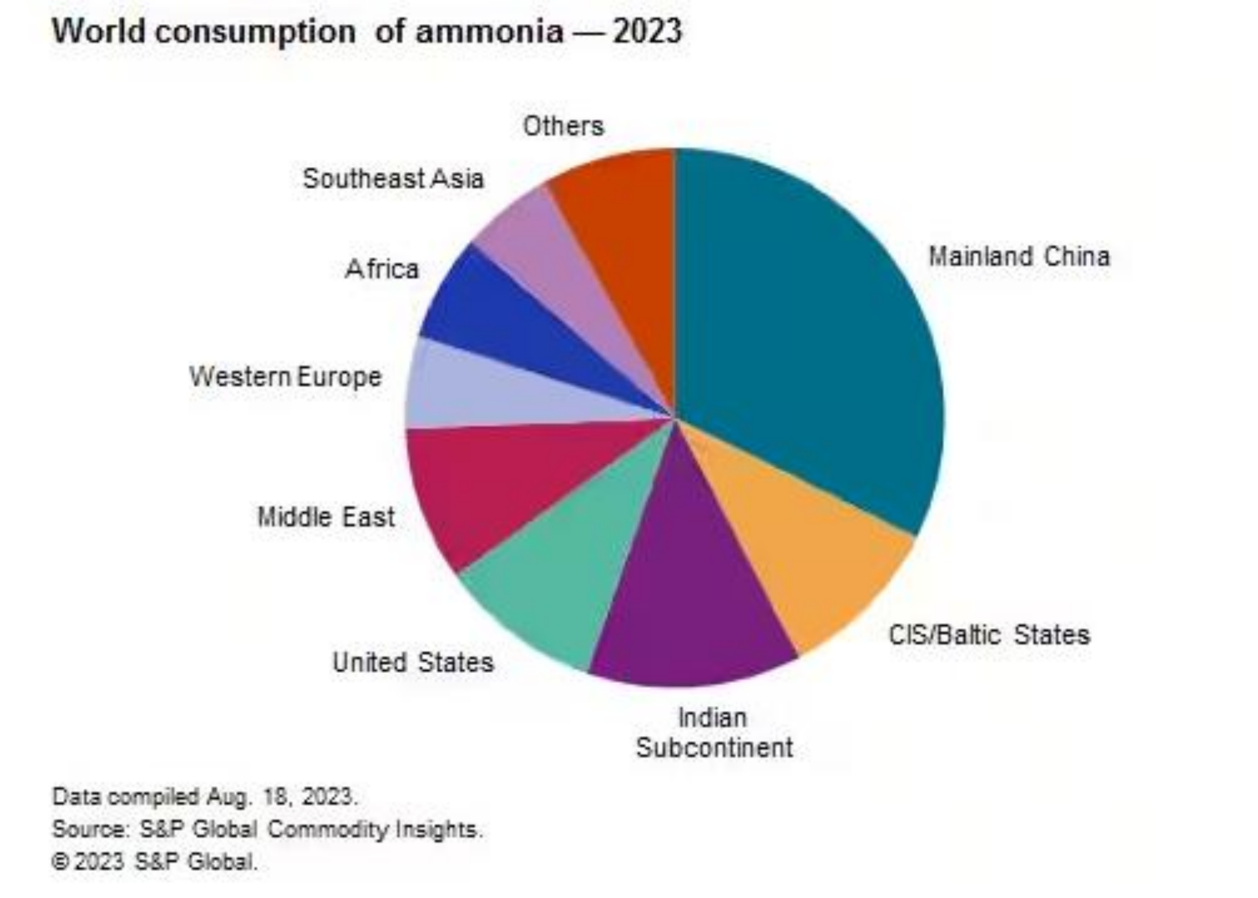
Geographical Share of Ammonia Consumption



Data compiled Aug. 18, 2023.
Source: S&P Global Commodity Insights.
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Share of Ammonia world consumption

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Ammonia Synthesis

- Ammonia is produced in the reaction between hydrogen and nitrogen in a fixed bed reactor.
- The gases, in stoichiometric proportions, are heated and passed under pressure over a catalyst.

$$N_2(g) + 3\,H_2(g) = 2\,NH_3(g) + \text{Heat} \quad \Delta H° = -46\,kJ\ mol^{-1}$$

- Catalyst is needed to promote the reaction
- High temperature (350°C-500°C) and pressure (70-150 bar) are needed (exothermic reaction)
- 2000 MTD (metric tons a day) is a standard plant size for commercial ammonia synthesis
- Economics, energy efficiency and sustainability (emissions) are the main drivers for the ammonia synthesis

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Ammonia Synthesis

- N_2 is obtained from atmospheric air
- H_2 is produced from a variety of feedstocks, mostly from natural gas, coal or naphtha
- At the beginning H_2 was also produced by water electrolysis
- Before World War II, 90% of ammonia production was derived from coal and coke gasification
- By 1960 most of the ammonia was produced using cheaply available natural gas and naphtha through the steam-reforming process
- Since 1975, after the oil crisis, the primary feedstock of most of the new plants is natural gas
- Nowadays, coal gasification is used in some locations like China due to the abundance of coal and lack of natural gas in such area

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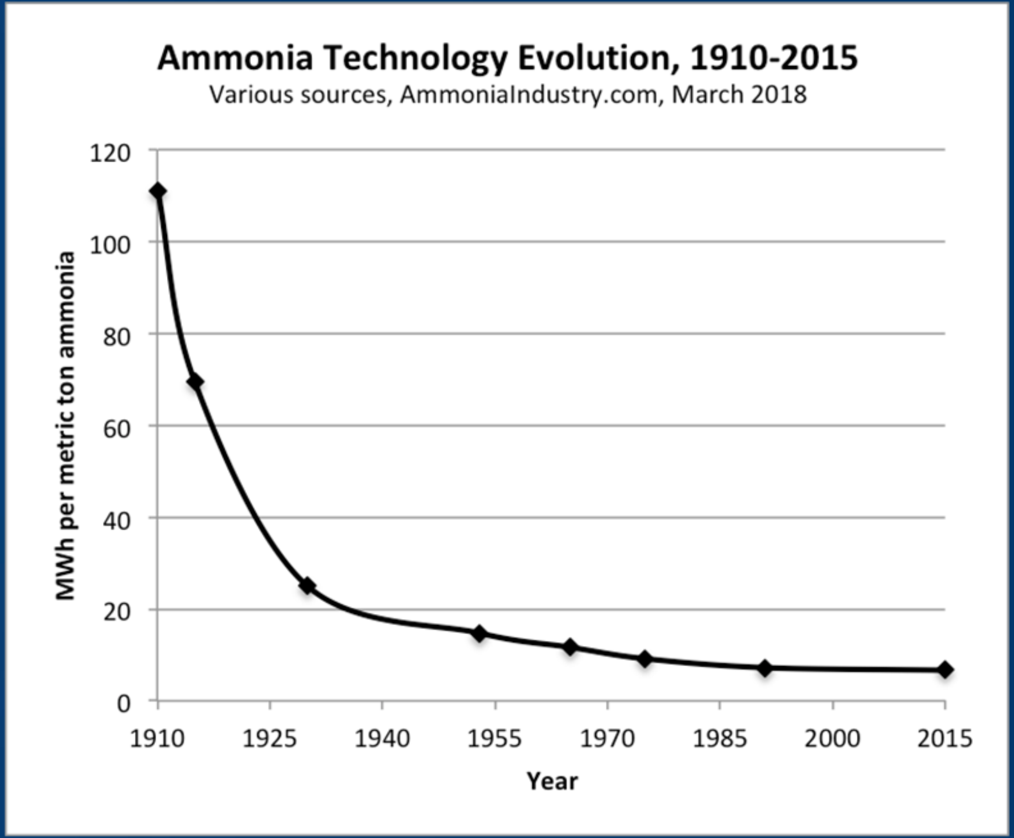
Ammonia Synthesis

- Today's ammonia synthesis catalyst is essentially the same as developed by Fritz Haber and Alvin Mittasch one century ago…

- The goal is a breakthrough catalyst, that can generate a significant change in the established process
- A new NH_3 synthesis catalysts with high activity at low temperature, say 100°C lower then at present
- higher resistance to poisoning from oxygenates

Ammonia Technology:



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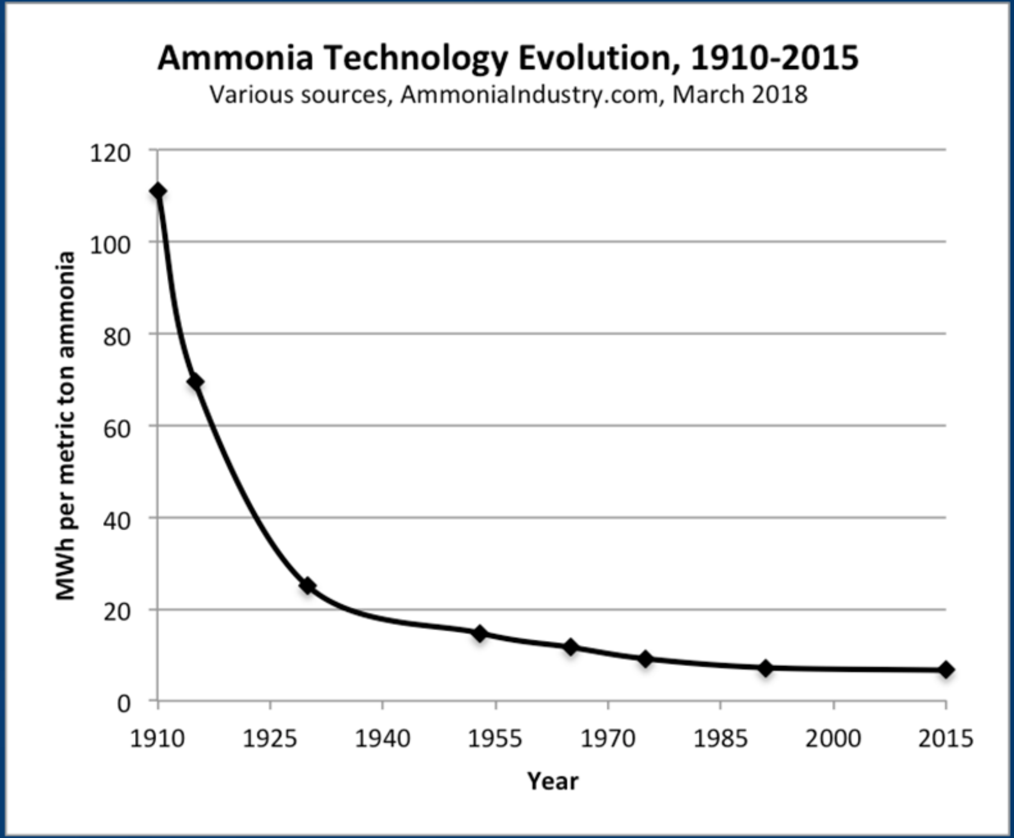
Ammonia Synthesis

- The advantages would be:

- A drastic increase in conversion per pass, meaning decrease plant energy consumption by 3 % and the cost of the plant as well
- Greatly facilitating the design and operation of green ammonia plants
- Ammonia production causes 1.5% of the total GHG emissions worldwide, so these advantages are very important overall

Ammonia Technology:



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Ammonia Synthesis: Definitions

- The core of the ammonia production process is still Haber-Bosch synthesis, a process developed over one hundred years ago in the first decade of the 20th century that combines nitrogen with hydrogen to produce ammonia over iron as the catalyst.

- The production of one of the two key components; hydrogen can make the ammonia “grey”, “blue” or “green” depending on the feedstock and production process. Blue low-carbon ammonia is essentially like conventional grey ammonia coupled with carbon capture, which can reduce its carbon emissions by more than 90%. Green ammonia uses green hydrogen produced by water electrolysis, powered by renewable energy, making green ammonia production virtually carbon dioxide–free.

- Industries and countries committed to net-zero are moving towards blue and green ammonia as they emerge as strong candidates for long-term energy carriers, vectors providing a route for greenhouse gas emissions reduction as low- or zero-carbon fuels. For example, Japan is focused on testing cofiring ammonia in coal-based power plants with the aim of converting entirely to ammonia in the future.

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Ammonia Synthesis: Definitions

Green, Blue and Grey ammonia

- **Green ammonia** production is where ammonia is made from renewable energy inputs. One way of making green ammonia is by using hydrogen from water electrolysis and nitrogen separated from the air.
- **Blue ammonia** is conventional ammonia e.g where the process of making ammonia started by natural gas for which its by-product CO_2 has been captured and stored.
- Finally **grey ammonia** is ammonia produced from natural gas without any CCS.

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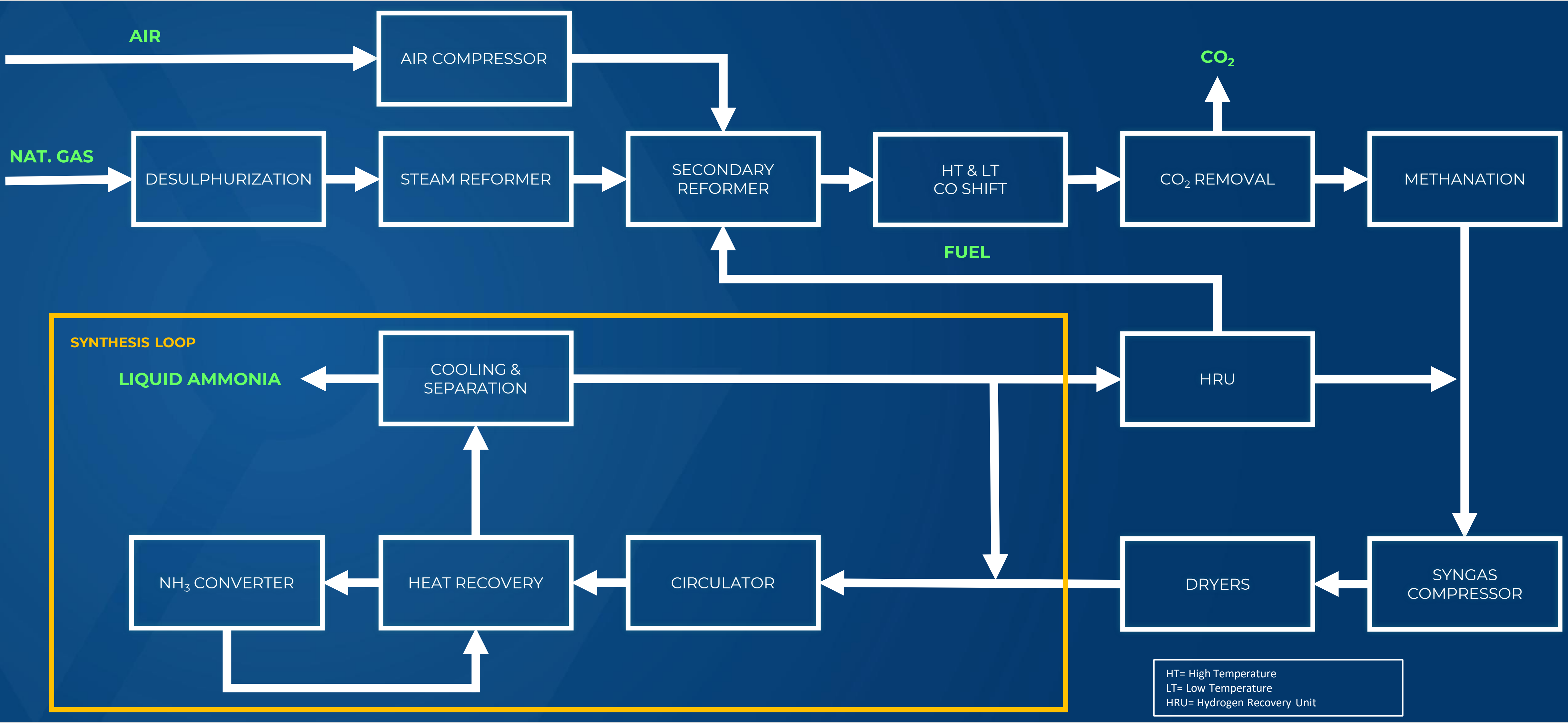
Grey Ammonia Process Scheme



HT= High Temperature
LT= Low Temperature
HRU= Hydrogen Recovery Unit

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Steps involved in the Ammonia Synthesis

Reactions

- SMR: $CH_4 + H_2O = CO + 3\ H_2$ - heat
- HT and LT CO Shift: $CO + H_2O = CO_2 + H_2$ + heat
- II Reforming $H_2 + ½\ O_2 + 2\ N_2 = H_2O + 2\ N_2$ + heat
- Methanation: $CO + 3\ H_2 = CH_4 + H_2O$ + heat

  $CO_2 + 4\ H_2 = CH_4 + 2\ H_2O$ + heat
- Ammonia Synthesis: $6\ H_2 + 2\ N_2 = 4NH_3$ + heat

Reactions

- Desulphurization
- CO_2 adsorption

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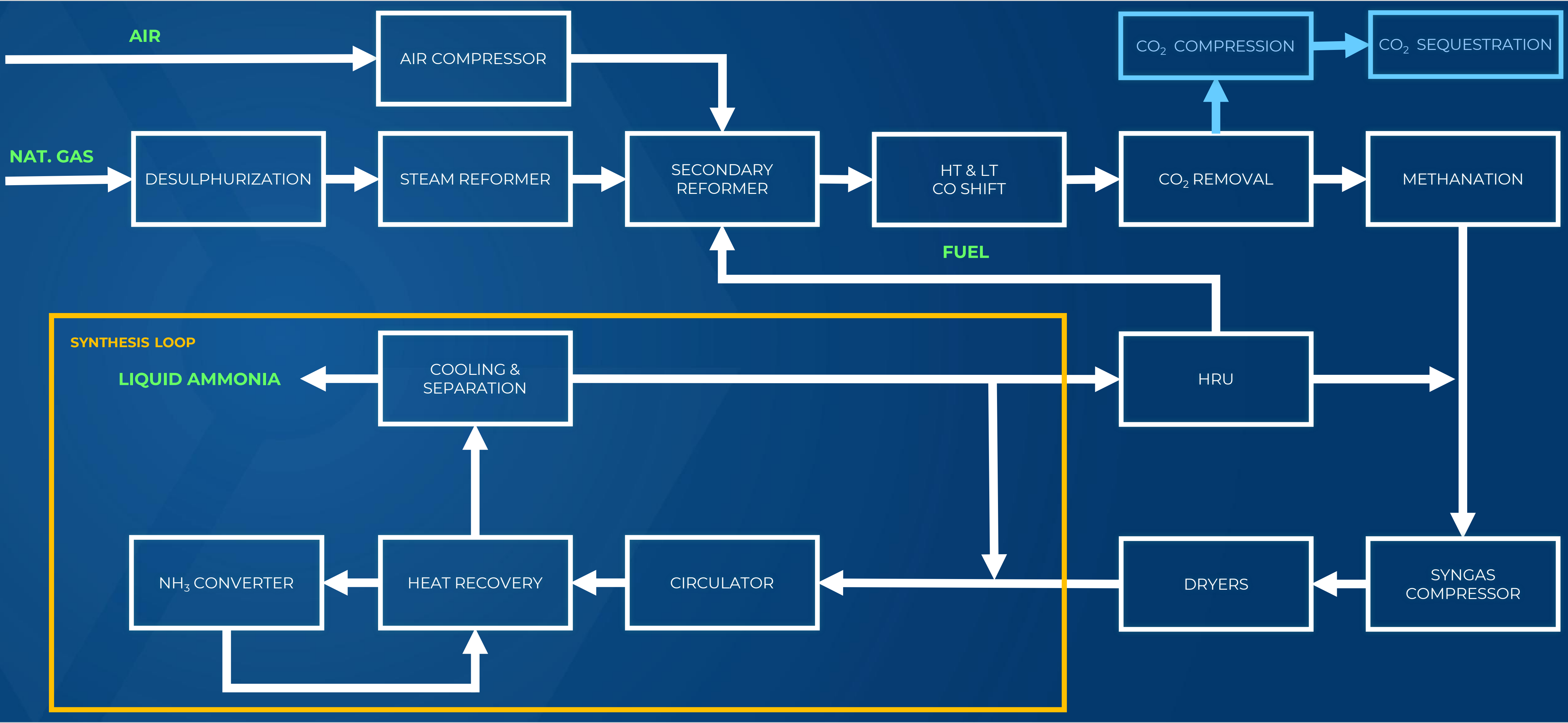
Blue Ammonia



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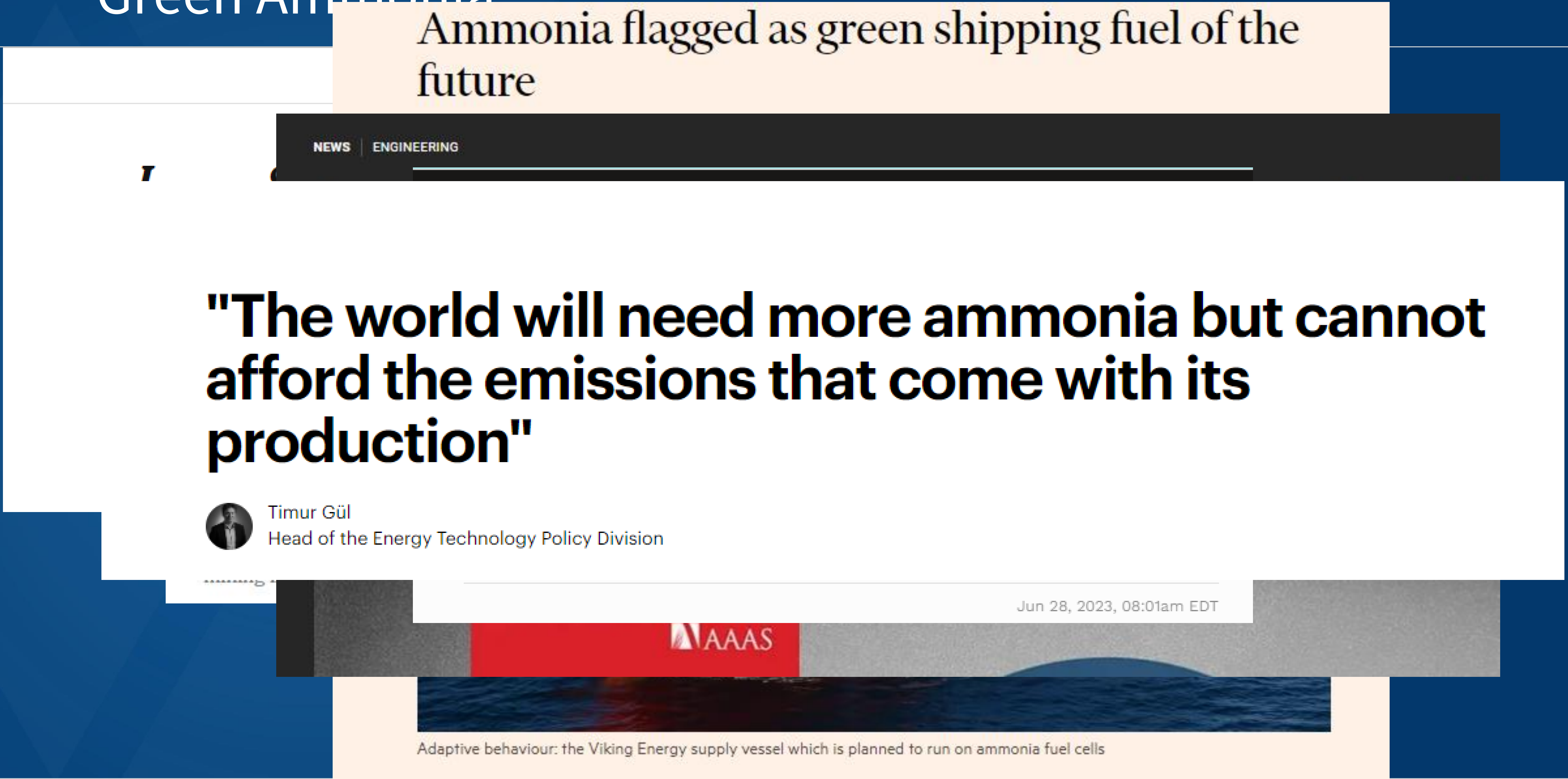
SHAPING THE FUTURE

NOTHING STAYS THE SAME FOREVER

CASALE

Green Ammonia



Ammonia flagged as green shipping fuel of the future

NEWS | ENGINEERING

"The world will need more ammonia but cannot afford the emissions that come with its production"

Timur Gül
Head of the Energy Technology Policy Division

Jun 28, 2023, 08:01am EDT

Adaptive behaviour: the Viking Energy supply vessel which is planned to run on ammonia fuel cells

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Green Ammonia

Casa
Indus

Converting

We are pleased to a
execution of the Ba
facility to be establ
green hydrogen and
fertilizer markets w

NEWSROOM

RTI International Awarded $10 million from U.S. Department of Energy's ARPA-E to Demonstrate Renewable Ammonia Production and Use

May 06, 2021

New project aims to re-imagine next-generation processes for producing and using low-carbon energy carriers like ammonia

The project will integrate the most promising breakthrough technologies developed in ARPA-E's Renewable Energy to Fuels Through Utilization of Energy-Dense Liquids (REFUEL) program into a modular, demonstration facility capable of producing 1 metric ton of low- and zero-carbon ammonia per day. The technologies include Casale and RTI's low-temperature, low-pressure synthesis along with flexible process control strategies that can vary ammonia production to meet available intermittent electricity, and the University of Minnesota's (UMN) elevated temperature ammonia separation. The demonstration facility will be located at the UMN West Central Research and Outreach Center (WCROC), Morris, MN, and will leverage the site's existing hybrid wind and solar generation in the fully integrated process.

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Picture taken from: https://revisesociology.com/2017/09/20/rise-fall-detroit-industrialisation/

Picture taken from: https://revisesociology.com/2017/09/20/rise-fall-detroit-industrialisation/

From Grey to Green

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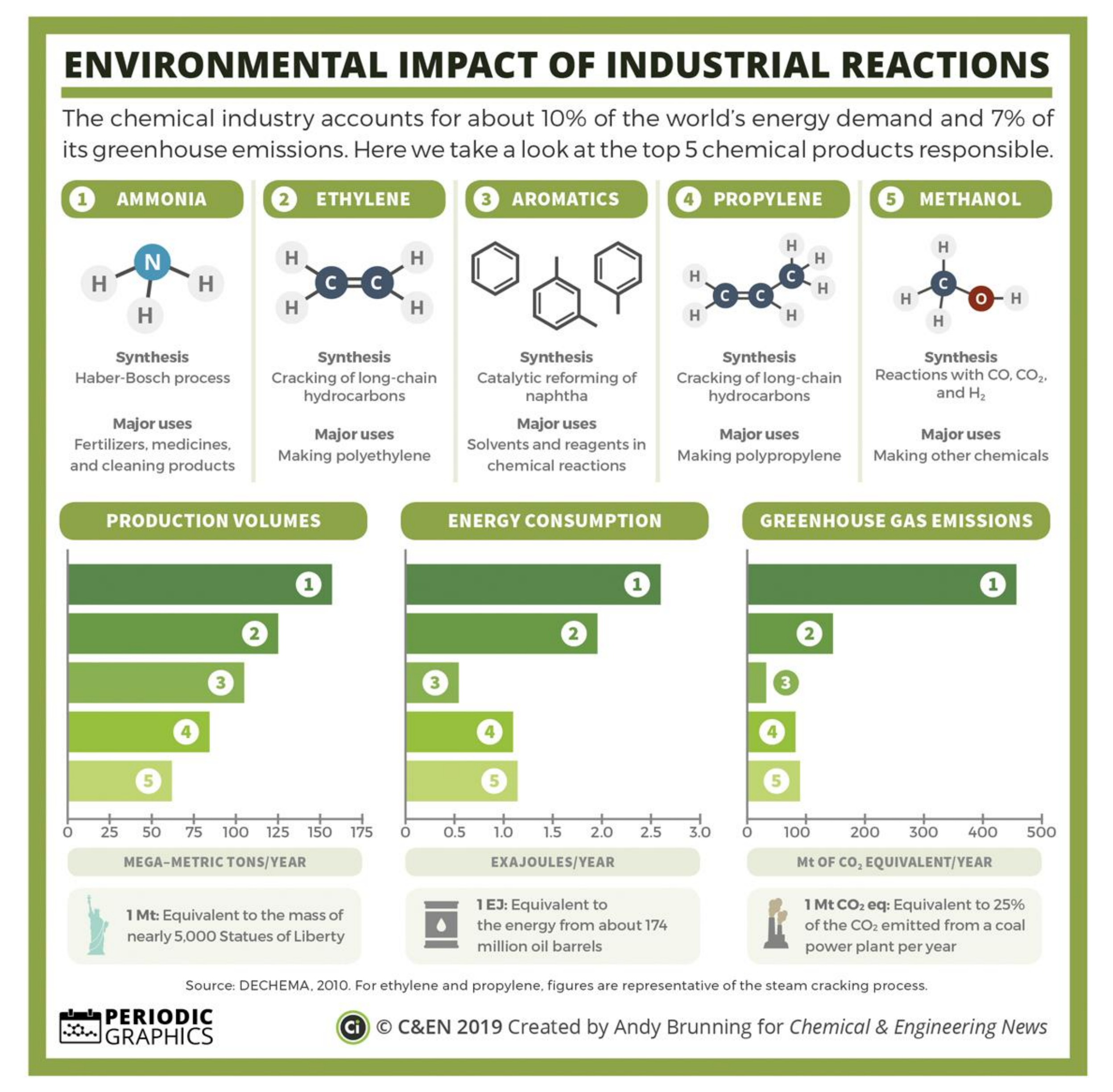

ENVIRONMENTAL IMPACT OF INDUSTRIAL REACTIONS

The chemical industry accounts for about 10% of the world's energy demand and 7% of its greenhouse emissions. Here we take a look at the top 5 chemical products responsible.

① AMMONIA

Synthesis
Haber-Bosch process

Major uses
Fertilizers, medicines, and cleaning products

② ETHYLENE

Synthesis
Cracking of long-chain hydrocarbons

Major uses
Making polyethylene

③ AROMATICS

Synthesis
Catalytic reforming of naphtha

Major uses
Solvents and reagents in chemical reactions

④ PROPYLENE

Synthesis
Cracking of long-chain hydrocarbons

Major uses
Making polypropylene

⑤ METHANOL

Synthesis
Reactions with CO, CO_2, and H_2

Major uses
Making other chemicals

PRODUCTION VOLUMES

MEGA-METRIC TONS/YEAR

1 Mt: Equivalent to the mass of nearly 5,000 Statues of Liberty

ENERGY CONSUMPTION

EXAJOULES/YEAR

1 EJ: Equivalent to the energy from about 174 million oil barrels

GREENHOUSE GAS EMISSIONS

Mt OF CO_2 EQUIVALENT/YEAR

1 Mt CO_2 eq: Equivalent to 25% of the CO_2 emitted from a coal power plant per year

Source: DECHEMA, 2010. For ethylene and propylene, figures are representative of the steam cracking process.

PERIODIC GRAPHICS

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C&EN June 17, 2019 | A version of this story appeared in Volume 97, Issue 24

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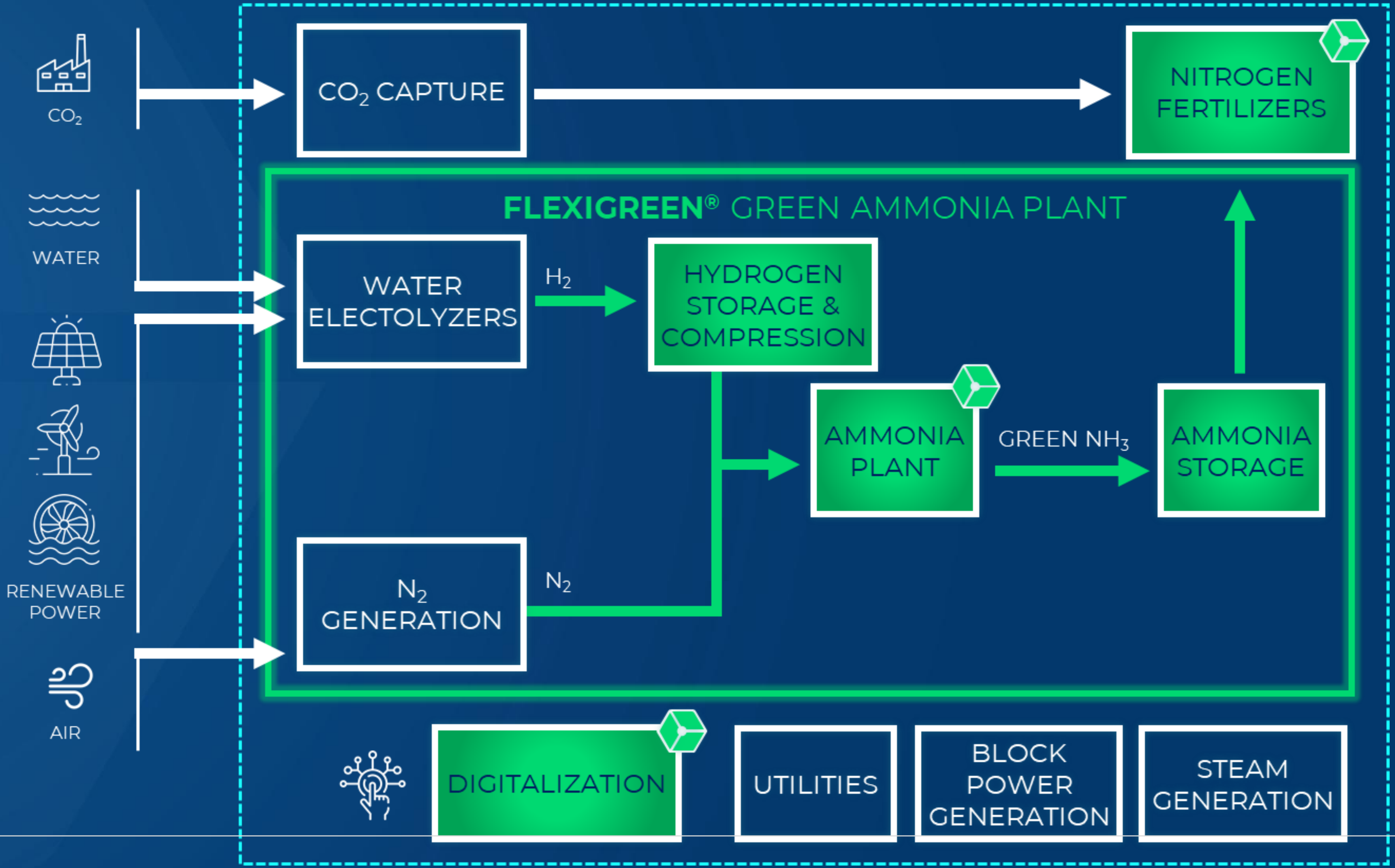
FLEXIGREEN® PRODUCTS: GREEN AMMONIA PLANTS

Integration of proprietary and third-party technologies

Different schemes according to plant capacity, tailored for green ammonia

3 Basic Engineering
>110 proposals
80+ projects from H2+N2



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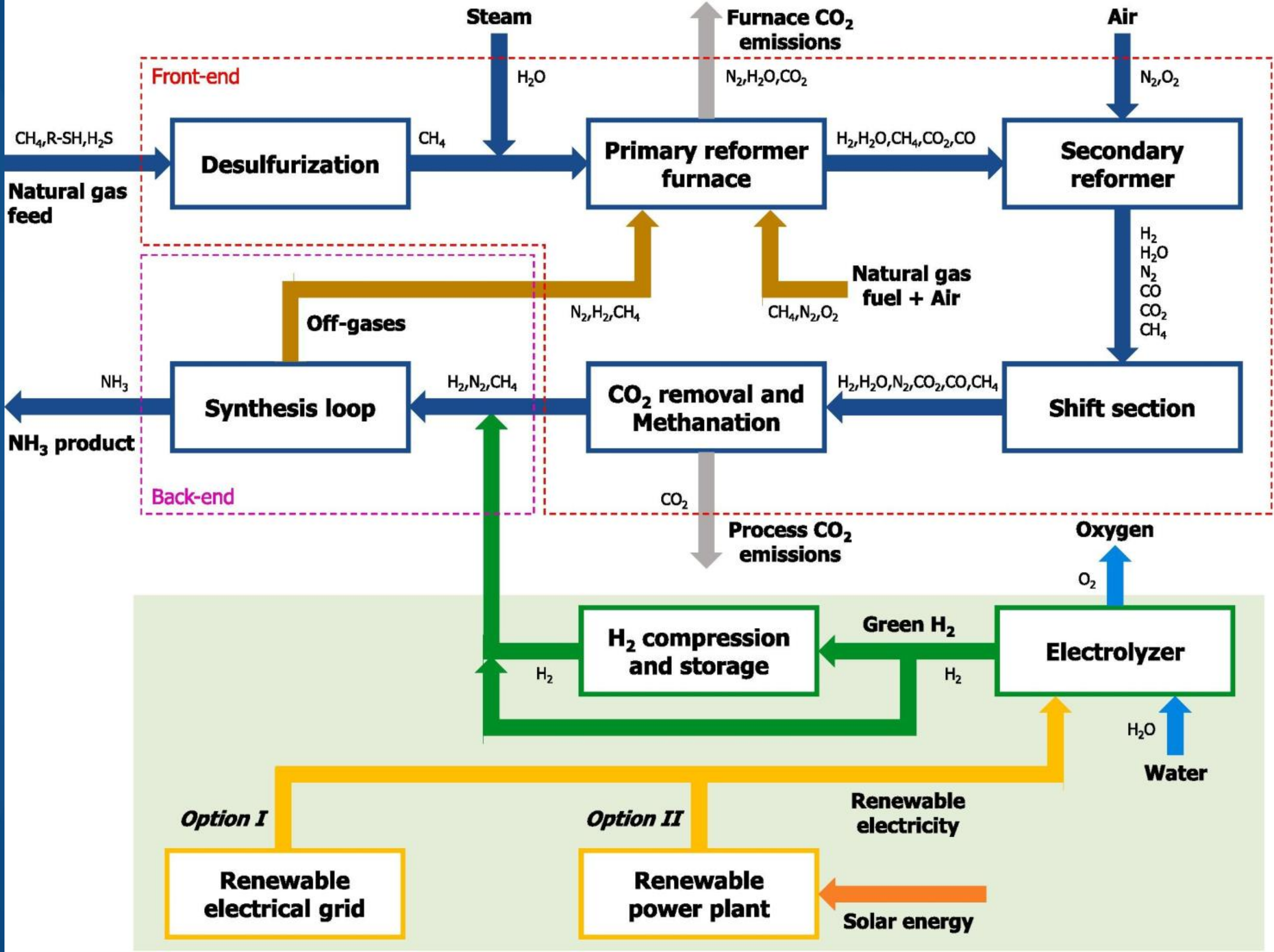
Hybridization of Ammonia Process Scheme



Towards the decarbonization of ammonia synthesis – A techno-economic assessment of hybrid-green process alternatives. A. Isella. R. Ostuni and D. Manca. https://doi.org/10.1016/j.cej.2024.150132

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GOING GREEN:

RENEWABLE ENERGY SOURCES

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Renewable sources for power production

SOLAR

WIND

HYDRO

GEOTHERMAL

BIOMASS

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Principal RES technologies available at utility scale

Technology	Efficiency	Min size	Scale up/Numbering up	LCOE	Capacity factor	Emissions
	%	W	-	\$/kWh	%	$g_{CO2\text{-}equiv}$/kWh
PV	12-25	10-80	Numbering-up	0.19-1.3	10-25	23-45
CSP	N.A.	N.A.	N.A.	0.114-0.358	20-50	10-80
WIND	35	hundreds	Scale up and numbering up	0.05-0.3	25	4.6-55.4
HYDRO	90	thousands	Scale up	0.01-0.2	40	0.3-13/4.2-152
TIDAL	80	thousands	Numbering up and scale up	N.A.	20-35	5-20
GEOTHERMAL	40-55 electric 80-90 thermal	thousands	Scale up	0.04-0.14	90-95	10-40
BIOMASS	10-30	7000-8000	Scale up	0.08-0.29	85-95	63-70

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Solar energy

Solar radiation is the most abundant renewable resource on earth

- Sun light is available everywhere, but it varies due to geographical conditions
- Solar radiation is influenced by seasonal climatic variations
- Available only during daylight
- Non-dispatchable source
- Clean source
- Site restrictions: shadowing
- Sun resource availability can be found in many databases
- Resource assessment: possibility of extrapolation of existing data concerning an area

Different technologies to exploit sun energy are available:

- Photovoltaic
- Concentrating solar power
- Thermodynamic solar panels

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Photovoltaic (PV)

- Conversion of sunlight into electricity using semiconducting materials that exhibit photovoltaic effect
- A PV module consists in a number of cells, it can be directly connected to the user or an inverter is needed
- Usually a PV plant is coupled with a battery storage system
- Size can be increased by numbering up: a single panel nominal power is 20-300 W, in a PV field up to thousands of MW can be installed
- Safety issues: wind effect on PV array

Pros

- Very flexible technology: from few watts up to large solar fields
- Cheap equipment and easy installation
- Possible installation in the proximity of utilization if ground is available
- Low civil engineering constraints

Cons

- Low capacity factor
- High land utilization
- Visual impact
- Non dispatchable: need of battery storage
- Voltage regulation and energy conversion are needed
- Need of specific materials for PV cells

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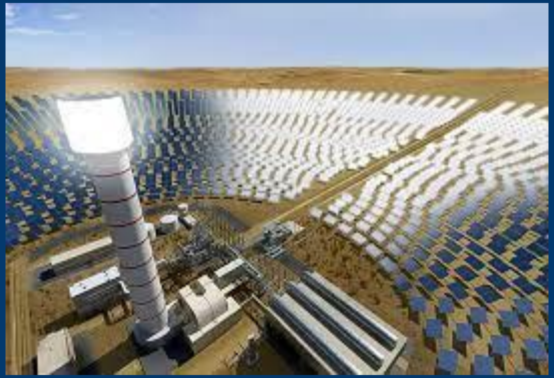
Concentrated solar power (CSP)

- CSP systems generate solar power by using mirrors or lenses to concentrate a large area of sunlight into a receiver. Electricity is generated when the concentrated light is converted to heat (solar thermal energy), which drives a heat engine (usually a steam turbine) connected to an electrical power generator or powers a thermochemical reaction.
- Different types of concentrator can be used: parabolic trough, power tower, linear Fresnel, parabolic dish.
- The efficiency is still low (up to 25%) but is facing a fast increase of capacity installation as it is becoming more cost efficient.



Pros

- Easy installation and operations
- Can be coupled with a storage system, reaching a lower LCOE
- Can be coupled with other energy sources as supplement
- More predictable energy source (compared to PV)

Cons

- High land utilization, need of remote locations
- Visual and ecological impact
- More expensive than PV and wind
- Small scale is not convenient
- High costs for thermal storage materials

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Wind energy

- Site-specific resource, very abundant in some locations
- At least one-year data are needed for a local resource assessment
- High short-term and seasonal variability: wind power changes during the day and during the year
- Clean source
- Site restrictions: soil roughness and obstacles
- Resource assessment: extrapolation of existing data requires use of a dedicated software and a thorough assessment of site specifications

Can be installed:

- Onshore: on land
- Off-shore: in the sea

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Wind turbines - Onshore

- Wind turbines converts kinetic energy of the wind that hits the blades into electric energy
- Production is intermittent: the turbine works in a specific wind velocity range (cut-in is 3-5 m/s, cut-off is 20-25 m/s)
- The minimum size for an efficient turbine is 50-100 kW
- Wind farms have to be installed in remote locations to avoid obstacles and to mitigate noise and visual impact
- Size can be increased by both scaling up and numbering up
- Safety issues: electrical moving parts can be dangerous, difficult erection and laying down of the machines

Pros

- Good energy efficiency
- Efficient land utilization
- Low CO_2 equivalent emissions (in LCA)
- Low operating costs

Cons

- Visual impact and affects bird's population
- Noise
- Hydrogeological and faunal impact
- Less flexibility than PV on size variations
- Difficult maintenance operations
- Non dispatchable source: storage is needed

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Wind turbines - Offshore

- Installing wind turbines offshore allows to exploit higher wind potential and reduce visual impact
- In the sea the wind is not affected by obstacles and has lower seasonal effect
- Nowadays installation depths are limited to 40-50 m, otherwise with floating turbines more than 100m depths can be achieved
- Technologies for offshore floating installations are already established from oil & gas sector

Pros

- Higher wind speed at same heights
- Higher equivalent working hours
- Lower to no visual impact
- No noise impact

Cons

- Need of stronger machines to resist gravity and buoyancy forces
- Corrosion problems
- Need of subsea electric cables for grid connection
- Installation and maintenance is more difficult

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Hydro power

Electric power generation from hydro potential is the most significant renewable source in the world in terms of energy production.

- It consists in the generation of mechanical power through a conversion of a water potential. The mechanical power is then transformed in electric power by a hydroelectric turbine
- It is the oldest way for power generation as it needs cheap equipment, it is highly effective and easy to regulate
- Is a dispatchable source and its production is usually predictable. Rainfalls, rivers and terrains can influence the production
- Highly site specific: a hydraulic head is needed
- Size can range from less than 100 kW up to tens of GW

Hydro plants can be classified as:

- **Run-of-river** plants: with filling rate of less than 2 hours
- **Storage** plants: pond plant (filling rate 2-400 h), reservoir plants (more than 400h).

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Pump Hydro

Energy storage can be performed with:

- **Pumped storage hydroelectricity** (PSH): a pump recirculates the water from the bottom pond to the top one during the night, when cheaper energy is available, so that the water can be used again the day after
- **Top power** plants : non-pumping plants that exploit just once the water flow of their source.

Pros

- Dispatchable and programmable source when integrated with storage, can meet peak electricity demand
- Low environmental impact (for low-medium size plants)
- Long lifetime, becomes inexpensive in the long run
- Simple equipment is needed
- High efficiency
- Easy to regulate

Cons

- High CAPEX required for construction
- Long civil works both for construction and maintenance
- Highly site specific
- Some safety issues could arise especially for large scale
- Visual impact

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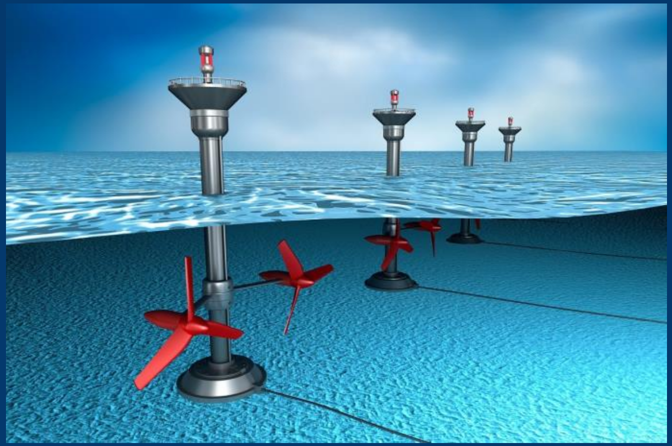
Tidal

- Tidal energy is produced by the natural rise and fall of tides, caused by the gravitational interaction between Earth, the sun, and the moon
- Tidal turbines work like wind turbines, but they're turned by the flow of water rather than air. These turbines drive generators, and underwater cables transmit the electricity into the grid
- Tide-powered turbines can work anywhere there's a strong enough tidal current—natural or artificial. They can either float or rest on the sea floor, and they can operate singly or in arrays (groups).



Pros

- Renewable unexploited resource with no carbon emission
- Predictable
- Abundant power output
- High efficiency
- Long lifetime

Cons

- Few suitable locations exist
- Expensive equipment
- Not mature technology
- Impact on sea life
- Corrosion issues
- Production predictions may not be precise, so electricity supply may fall short of the demand

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Geothermal

- Exploitation of energy stored as heat under earth's surface, coming from primordial internal energy or radioactive isotopes decay
- The average heat flux is 50 mW/m2 on land and 100 mW/m2 on sea-bed
- It can be considered renewable only if the vapor mixture is reinjected in a reinjection well nearby
- Depending on the temperature of the reservoir, it can be exploited to generate both thermal and electric energy,
- To produce electricity direct or indirect Rankine cycles. Indirect organic Rankine cycles are the best options for a size smaller than 20 MW, otherwise steam or ammonia can be used as cycle fluid.

Pros

- Dispatchable and constant energy source
- GHG emissions are present but significantly lower in comparison to natural gas cycles
- Low OPEX, saving on fossil fuels

Cons

- Highly site specific: few suitable locations exist
- High investment costs for exploration and well drilling
- If a direct cycle is used the equipment encounters corrosion problems
- The reservoir can be depleted
- Toxic or polluting gases can be emitted from the reservoirs

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Biomass

- Biodegradable fractions of organic products and residuals can be liquefied or gasified to be used as fuel for energy production
- Biomass can have animal and vegetable origin or come from industrial and municipal waste
- The size can be variable: from large scale to compact local installations
- Biofuels allow to reduce dependence from fossil fuels but energy efficiencies that can be reached are still low (max 30%).

Pros

- Dispatchable and constant energy source
- Renewable source that exploits unused materials
- GHG emissions are present but significantly lower in comparison to fossil fuels
- Size flexibility
- Low production costs for biomass

Cons

- Some biomass can have season variability
- Toxic or polluting gases can be emitted
- Possible impact on forests and surrounding environment
- Land utilization
- Low efficiency when converting to electricity
- High O&M costs

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Challenges & Impact of Green Intermittency

Unsteady, time variable input of green kWh	Need for higher process flexibility
System flexibility needed to cope with fluctuation of renewables	Plant suffers from operational discontinuities of power
Requires additional electrolysers and imposes operating costs (green kWh)	Uncertainty in the levelized cost of production for green portion
Necessity of large H_2 buffer storage	High costs and large footprint
Nitrogen to convert green hydrogen is not co-produced by the electrolysers	Fluctuation of front-end operating conditions to supply additional nitrogen
Equipment not designed to withstand frequent fatigue cycles	Potential damage of existing equipment

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ELECTROLYZERS

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Electrolyzers

Electrolysis is a chemical reaction where an electric current passes through a substance, causing it to decompose into its basic components.

Name	**Electrolyte**	**Electrical efficiency [%]**	**H2 purity [%]**	**Stack lifetime [thousand hours]**	**Capital cost [$/kW]**
Alkaline	KOH or NaOH	65-70	99.8	60-90	800-1200
Proton exchange membrane	H^+ conducting polymer	70-80	99.99999	20-60	1100-2000
Solid Oxide	Ceramic (e.g. YSZ)	60-90	99.9	<20	> 2000
Molten Carbonate	$LiCO_3$/$NaCO_3$ in matrix	60-70	-	30-40	-
Anion exchange membrane	Polymer	70	99.99	>5	-

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Alkaline

Alkaline electrolyzers contain water and a liquid electrolyte solution such as potassium hydroxide (KOH) or sodium hydroxide (NaOH). When current is applied to an alkaline cell tack, the hydroxide ions (OH-) move through the electrolyte solutions from the cathode to the anode of each cell. The hydrogen gas bubbles are generated at the cathode, and the oxygen gas is generated at the anode.

- Main characteristics

Electrolyte	Current density	Pressure	Temperature	Hydrogen purity	Raw materials	Catalyst	Lifetime
30%wt KOH solution or 25% wt NaOH solution	2000-4000 A/m^2	<3.3 MPa	80-90°C	>99.8 %	Deionized water and alkali	Pt alloys or Ni based	10 years

- Manifacture cost is relatively low vs PEM
- pH has a high impact on kinetics: need to find a suitable catalyst to improve kinetics in acid conditions

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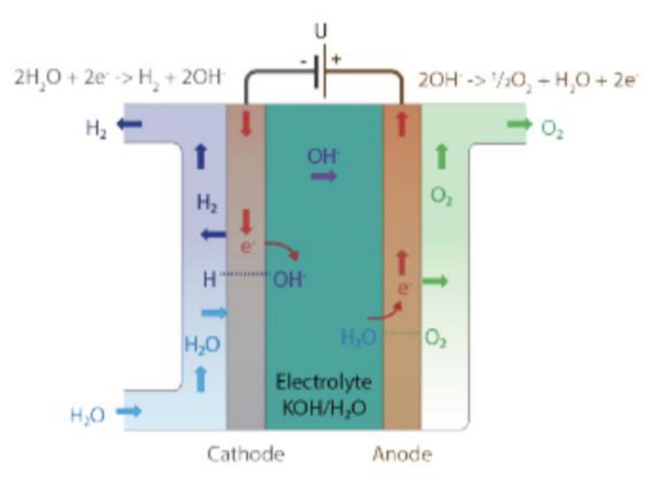
Alkaline

Advantages:

- High hydrogen production capacity
- Higher durability than PEM due to an exchangeable electrolyte and lower dissolution of anodic catalyst
- Using Ni alloys allows to reduce costs with respect to use of pure Pt
- High tolerance for impurities



Drawbacks:

- Low efficiency
- Limited hydrogen purity
- Liquid alkaline electrolyte may lead to corrosion problems or leak
- Limited part load
- Global reaction is favoured in acid solutions: need to find a catalyst materials where kinetics can be improved in acid conditions
- Ni catalysts are less efficient than pure Pt
- Limited operating temperature and pressure range

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Proton exchange membrane (PEM)

PEM electrolyzers contain a proton exchange membrane that uses a solid polymer electrolyte. When an electrical current is applied to its cell stack during water electrolysis, the water splits into hydrogen and oxygen. The hydrogen protons pass through the membrane to form H_2 on the cathode side.

- Main characteristics:

Electrolyte	**Current density**	**Pressure**	**Temperature**	**Hydrogen purity**	**Raw materials**	**Catalyst**	**Lifetime**
Solid polymer (e.g. Nafion)	10000-20000 A/m^2	<5 MPa	50-80°C	99.99 %	Deionized water	Pt or Ir on carbon	3-4 years

- Manifacture cost is high, precious materials are needed
- High energy density, small volume and weight: suitable for mobile applications

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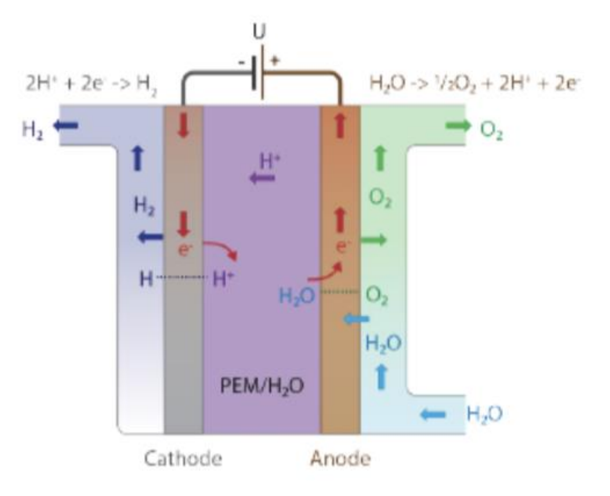
Proton exchange membrane (PEM)

Advantages:

- High efficiency
- Fast response time, quickly adjusts to changes in energy supply (suitable for RES coupling)
- Good partial load range
- Compact size
- Can work under pressure
- Low operating temperature
- High hydrogen purity can be achieved



Drawbacks:

- High capital costs, expensive materials are needed
- Limited hydrogen production capacity
- Dependence on platinum material
- Acidic corrosive environment can cause catalyst degradation
- Low durability

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Solid Oxide (SOEC)

Solid oxide electrolyzers, or solid oxide electrolysis cells (SOECs), are solid oxide fuel cells that run in regenerative mode. A SOEC uses a solid oxide, or ceramic, electrolyte. When current is applied, and water is fed into its cathode, the water converts into hydrogen gas and oxide ions. While the hydrogen gas is captured for purification, the oxide ions move to the anode and release electrons to an external circuit to become oxygen gas.

- Main characteristics:

Electrolyte	**Current density**	**Pressure**	**Temperature**	**Hydrogen purity**	**Raw materials**	**Catalyst**	**Lifetime**
solid ceramic material	30000-40000 A/m^2	0.1-100 MPa	500-800 °C	99.99 %	Deionized water, carbon dioxide	Ni, YSZ, Perovskite	2-3 years

- The solid electrolyte allows to reach higher efficiencies as no leakages happen and the operating temperature is higher
- Large volume and wight: suitable for stationary applications

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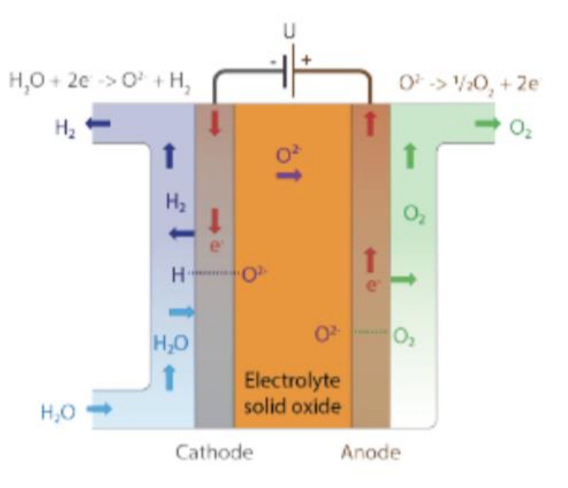
Solid Oxide (SOEC)

Advantages:
- High efficiency due to favourable kinetics at higher temperatures
- High hydrogen purity can be reached
- High current densities at low voltages
- Long term stability
- Flexibility on fuels and geometry
- Lower cost for materials compared to PEM
- Possibility to work under pressure

Drawbacks:
- Technology is not yet established at industrial level
- Bulky system design
- Low durability due to high operating T and ceramic brittleness
- High operating temperature leads to longer start-up times
- Catalyst can be poisoned by C deposition



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Molten carbonate (MCEC)

When the MCFC is run in reverse, it operates as a molten carbonate electrolysis cell (MCEC) to produce fuel gas, like hydrogen or syngas. The electrolysis cell includes nickel-based porous electrodes, where electrolysis of water takes place and molten carbonate electrolyte (e.g., $LiCO_3$ or $NaCO_3$ in matrix). Carbon dioxide as well as water must be present in the inlet gas, since CO_2 is a reactant when producing carbonate ions.

- Main characteristics:

Electrolyte	Current density	Pressure	Temperature	Hydrogen purity	Raw materials	Catalyst	Lifetime
Carbonate	30000-50000 A/m^2	MPa	600-700°C	Low	Deionized water and carbon dioxide	Ni based	5 years

- Using molten carbonate fuel cell for reverse operation is a promising technology but it is still at low TRL

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Anion Exchange Membrane (AEM)

Anion Exchange membrane (AEM) works in an alkaline environment and is designed to allow only anions to permeate and impermeable other gases. The method requires non-noble metals such as nickel, cobalt, iron as a catalyst.

- Main characteristics:

Electrolyte	**Current density**	**Pressure**	**Temperature**	**Hydrogen purity**	**Raw materials**	**Catalyst**	**Lifetime**
Polymer pre treated with KOH	50000-60000 A/m^2	1-30 bar	50-60 °C	99.99	Deionized water	Ni, Co, Fe	< 1 year

- Potentially low-cost and efficient technology for hydrogen production
- The process is still at R&D level due to the fast degradation of the available membranes

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AMMONIA SYNTHESIS REACTORS

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TAILORED SOLUTIONS

NEW PLANTS

SMALL - WORLD SCALE - MEGA

HIGH ENERGY EFFICIENCY

INTEGRATED PRODUCTIONS

PLANT REVAMPING

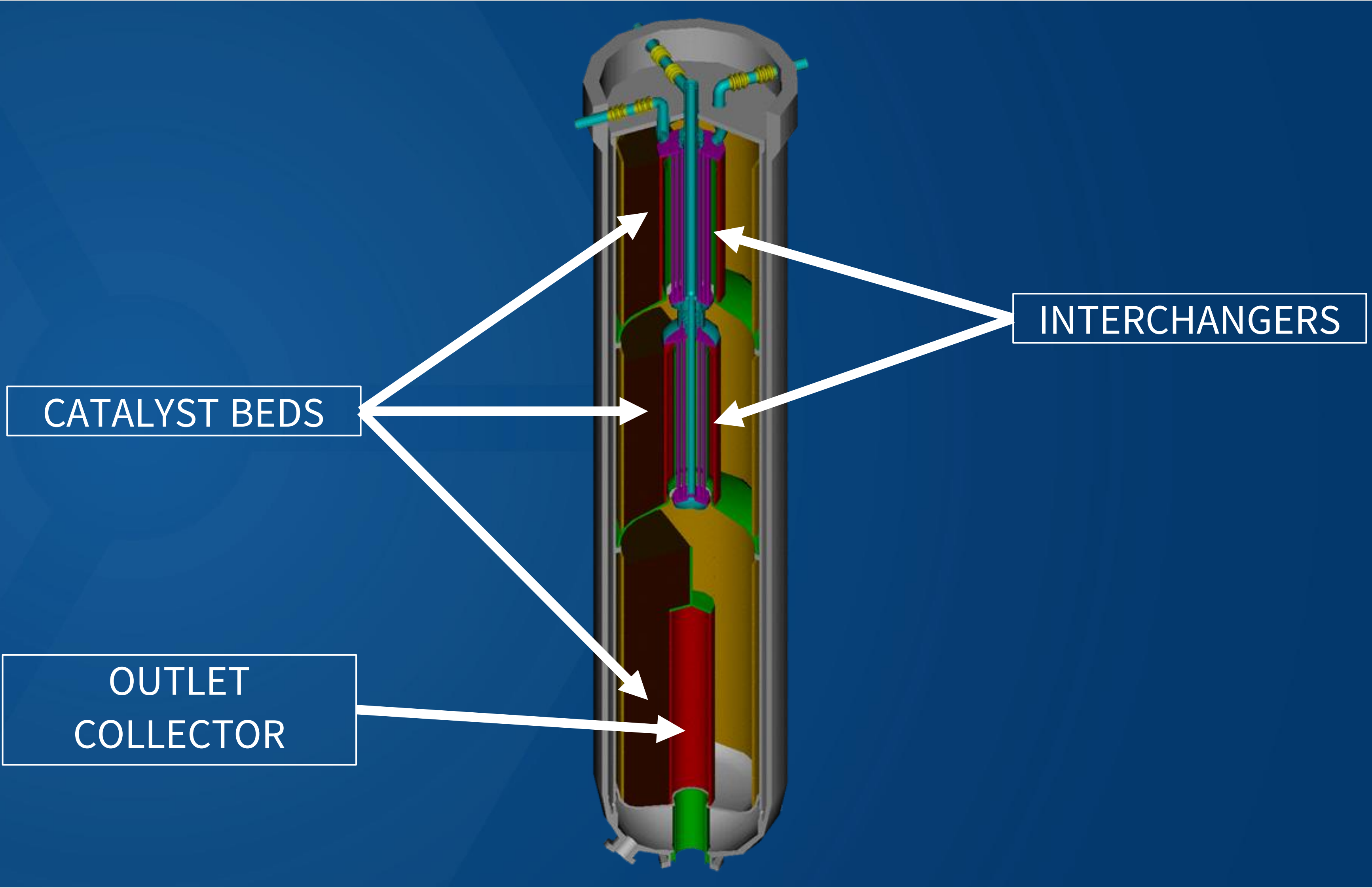
CAPACITY INCREASE (UP TO +100%)

ENERGY SAVING (5% - 30%)

REDUCTION OF CARBON FOOTPRINT

CASALE

Ammonia Converter



CATALYST BEDS

INTERCHANGERS

OUTLET COLLECTOR

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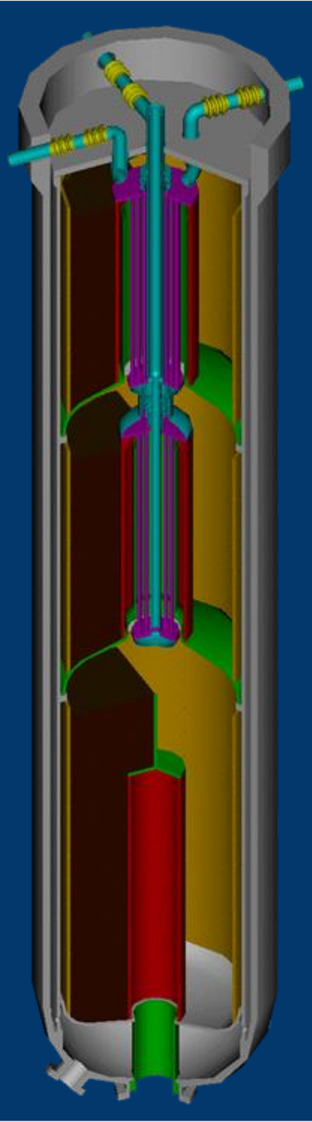
Ammonia Converter Internals

- Optimal catalyst distribution in multi-bed cartridge
- Maximum filling of catalyst inside the cartridge
- Highest efficiency of each bed
- Low pressure drop
- Simple mechanical construction
- Easier catalyst loading/unloading



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Ammonia Converter Internals

AXIAL-RADIAL DESIGN:

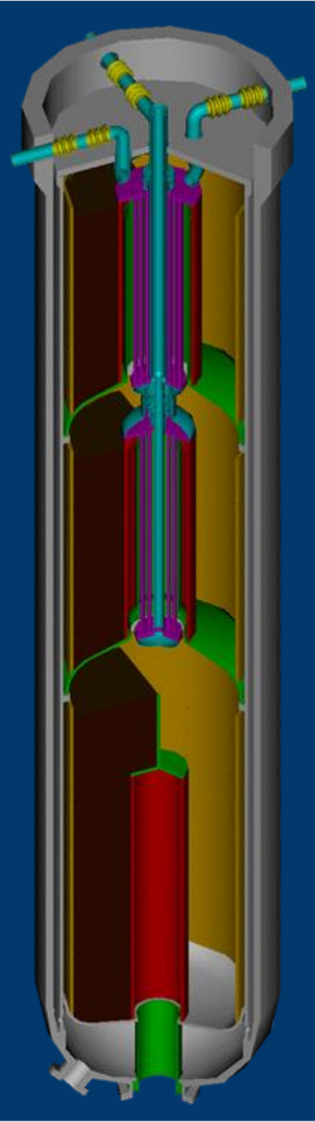
- full catalyst utilization in each catalyst bed
- Low pressure drops for the given mass/volume of the catalyst

THREE-BEDLAY-OUT:

- maximum conversion

TWO INTERCHANGERS:

- optimal thermodynamic configuration



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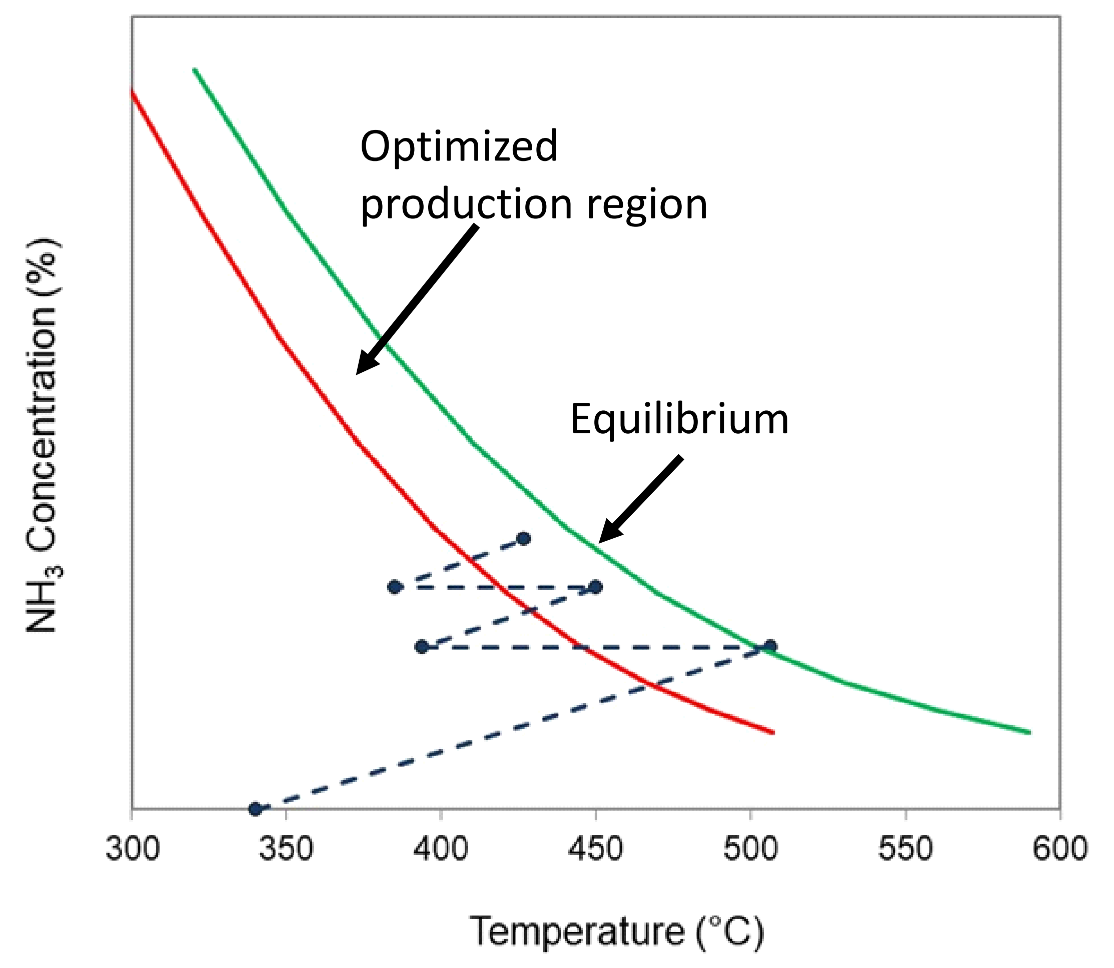
Ammonia Converter Thermodynamics: Adiabatic Operations

AXIAL-RADIAL DESIGN:

- Axial-Radial concepts is based on a different approach compared to axial reactors



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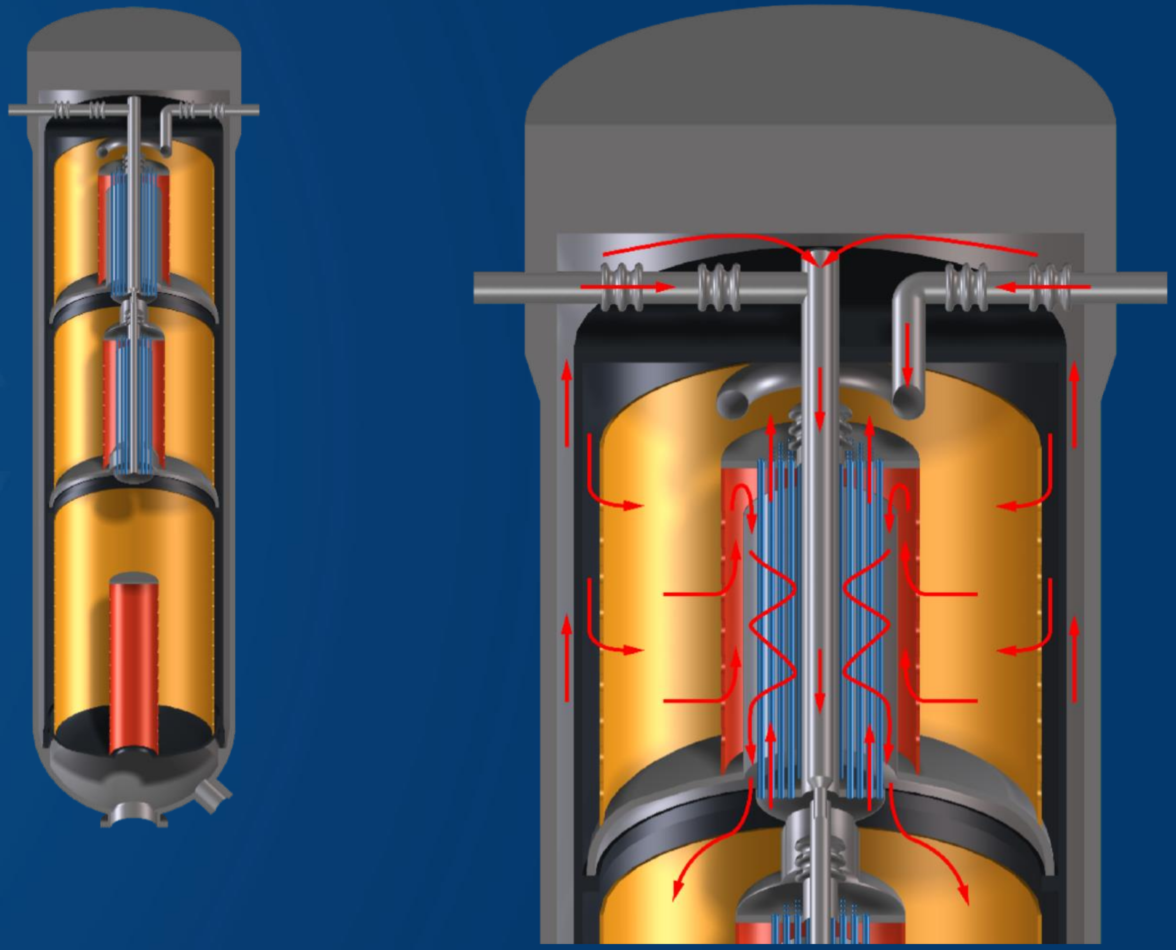
Ammonia Converter Thermodynamics: Adiabatic Operations

AXIAL-RADIAL DESIGN:

- Axial-Radial concepts is based on a different approach compared to axial reactors



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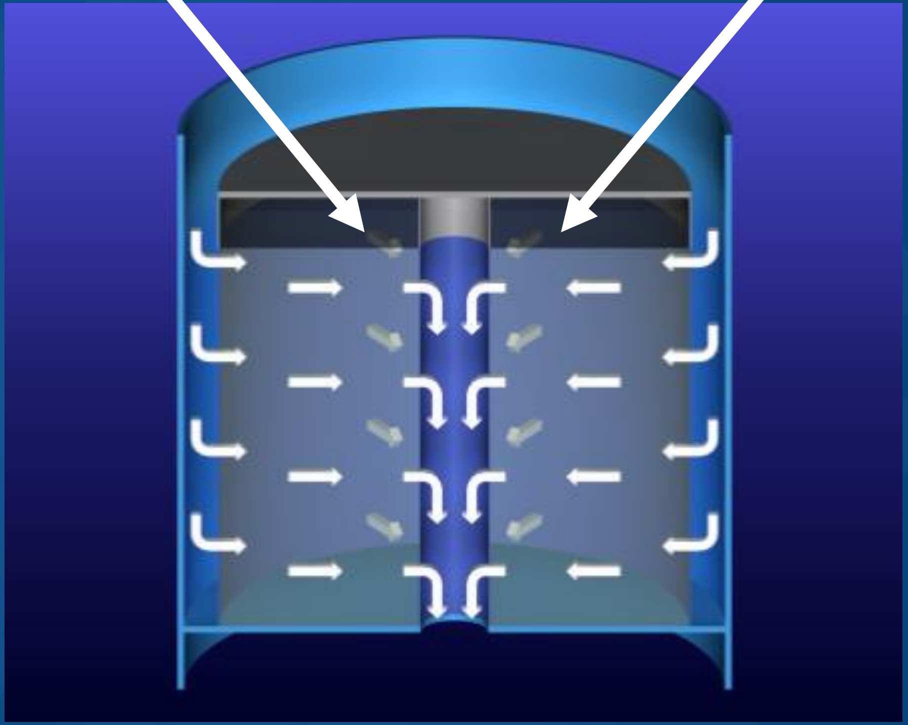
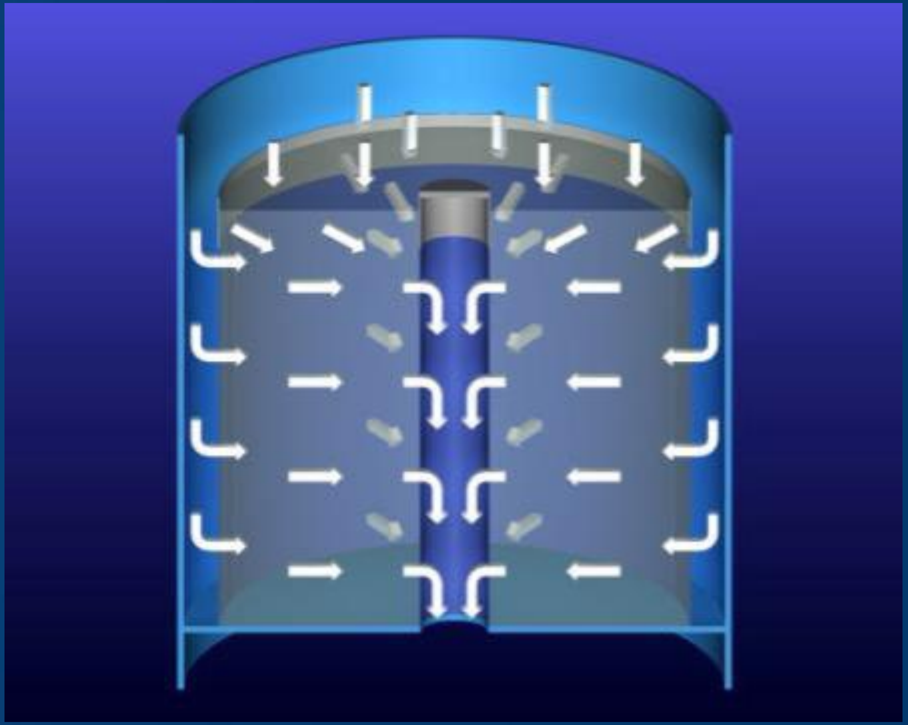
Ammonia Converter fluidodynamics

Unused catalyst portion 5-10% of the total volume



pure radial



Casale axial-radial

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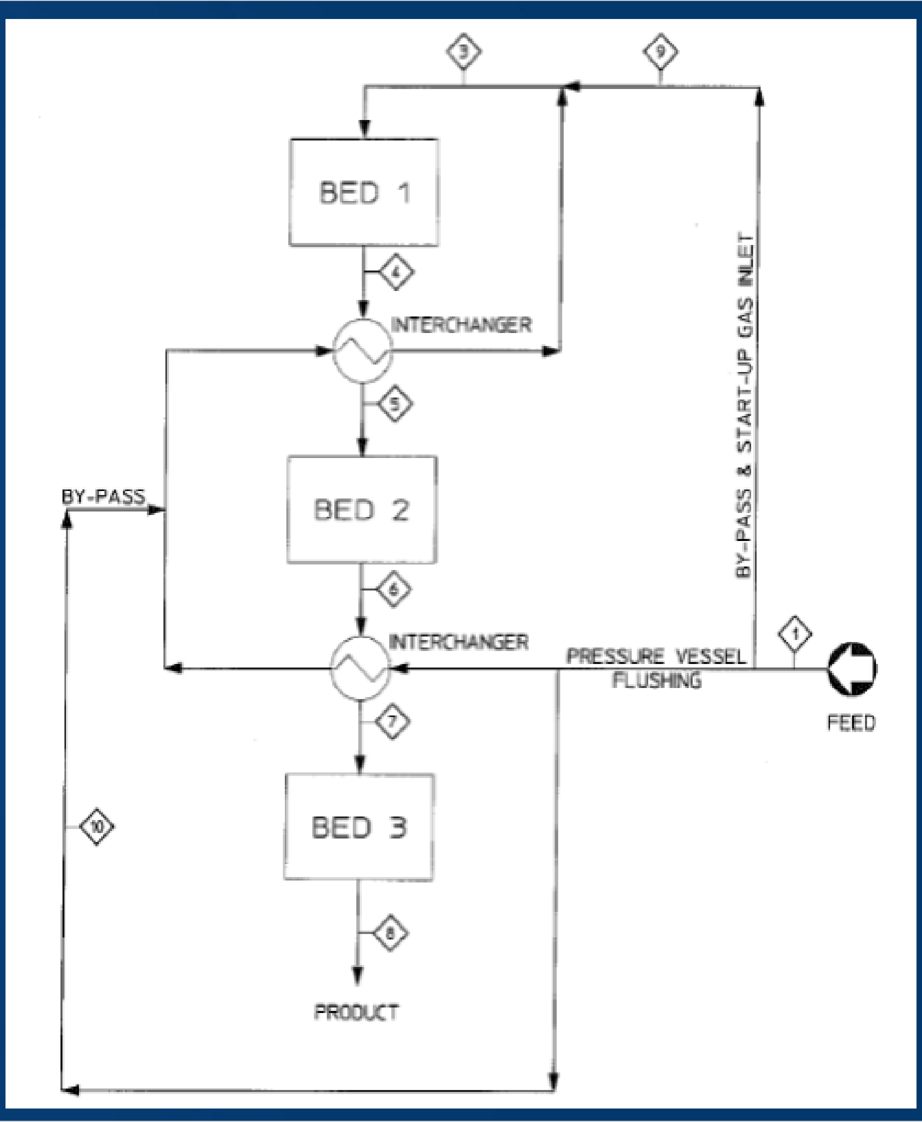
Ammonia Converter Internals

AXIAL-RADIAL DESIGN:

- Each bed inlet temperature is controlled independently and easily in any situation and any plant load, allowing to run the converter always in optimized conditions



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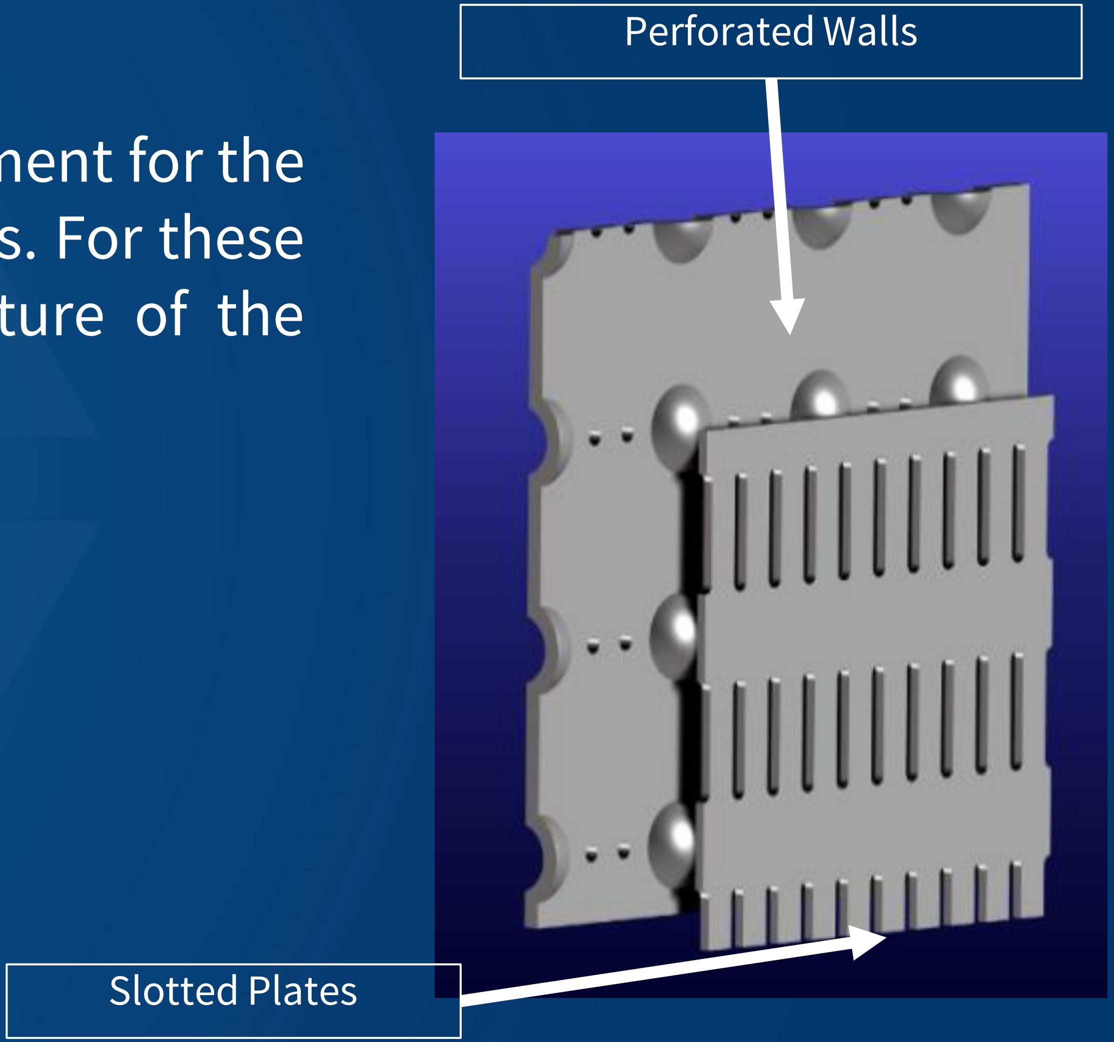
Ammonia Converter Special Features

Collectors / Slotted Plates

- The slotted plates act as a containment for the catalyst and also as gas distributors. For these reasons their design is a key feature of the reactor.



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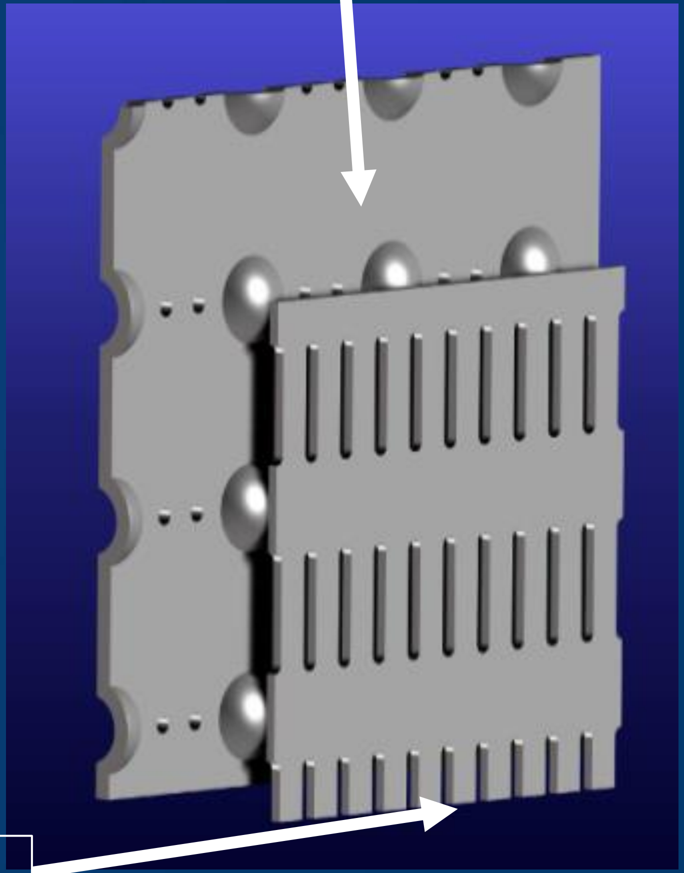
Ammonia Converter Special Features

Collectors / Slotted Plates

- Slotted plates consist in stainless steel solid plates with cuts (slots) disposed in parallel rows.
- The geometry of the cuts allows an optimal flow of the gas while keeping the catalyst inside the bed
- The blind regions between two adjacent rows of slots are kept in front of the distribution holes, acting as impingement of the gas, avoiding catalyst fluidization even at the highest loads



Perforated Walls

Slotted Plates

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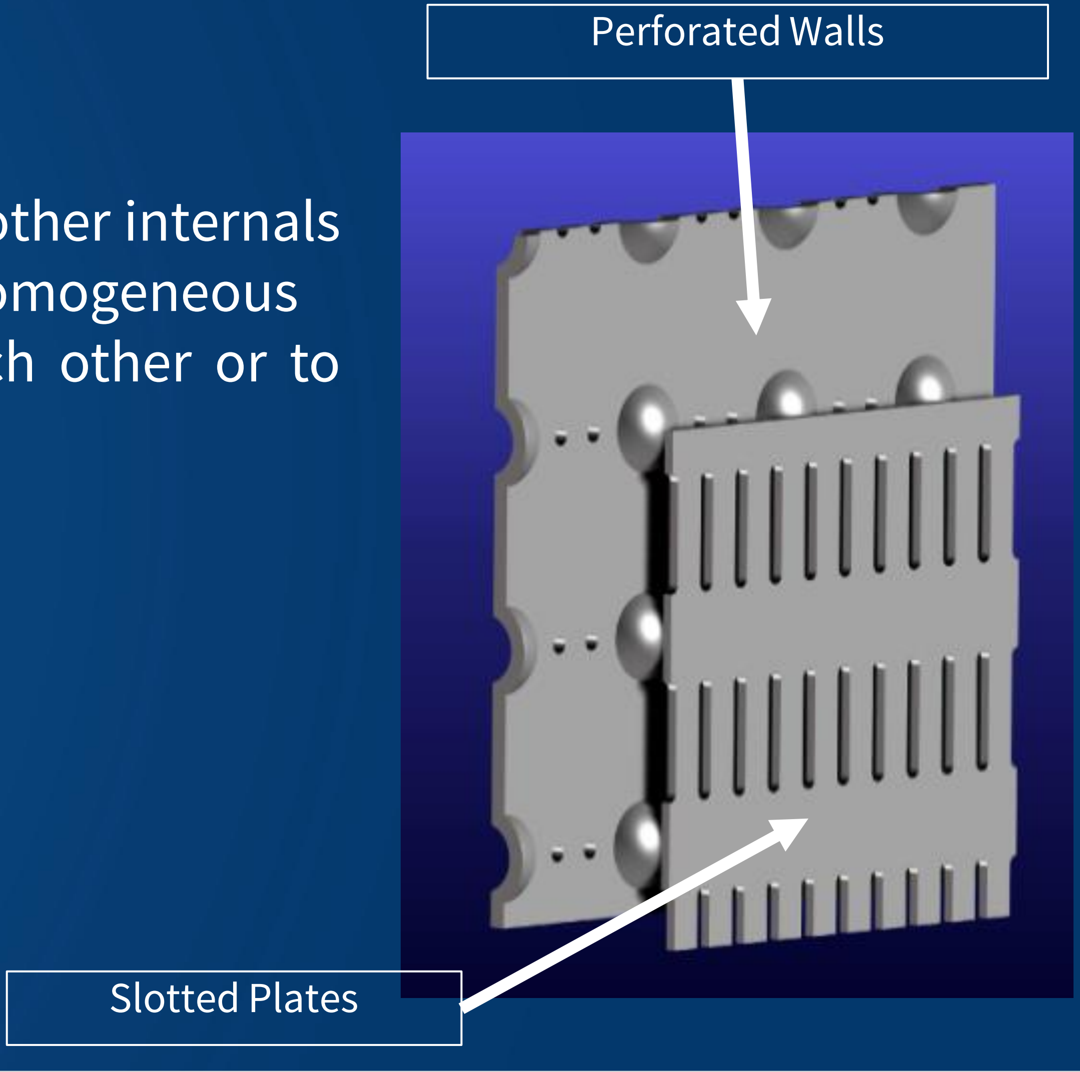
Ammonia Converter Special Features

Collectors / Slotted Plates

- Slotted Plates are solid, monolithic plates
- Slotted Plates are made of the same material of other internals (AISI 321), therefore all welds on collectors are homogeneous
- Slotted Plates panels can be easily welded each other or to solid plates in a reliable way

Materials

- AISI 321
  - stabilized with Titanium
  - no risk of carbides precipitation
- INCONEL 600
  - For thin elements such as
  - tubes, expansion joints



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Ammonia Converter Assembly Sequence

1. Pressure vessel
2. Introduce the new cartridge in the H.P. vessel

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Ammonia Converter Assembly Sequence: Cartridge

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Ammonia Converter Assembly Sequence

1. Pressure vessel
2. Introduce the new cartridge in the H.P. vessel
3. Catalyst loading on 3rd bed

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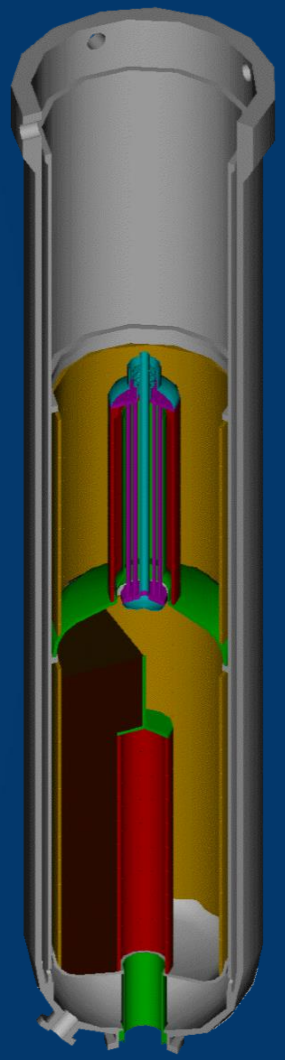
Ammonia Converter Assembly Sequence

- Pressure vessel
- Introduce the new cartridge in the H.P. vessel
- Catalyst loading on 3rd bed
- Install 2nd bed with interchanger



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Ammonia Converter Assembly Sequence: Second Bed Installation

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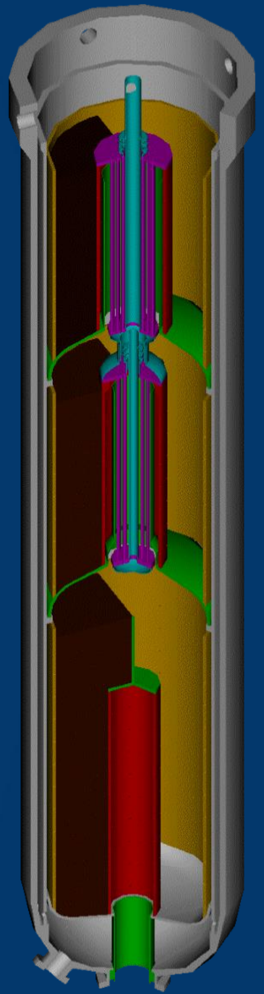
Ammonia Converter Assembly Sequence

1. Pressure vessel
2. Introduce the new cartridge in the H.P. vessel
3. Catalyst loading on 3rd bed
4. Install 2nd bed with interchanger
5. Catalyst loading on 2nd bed
6. Install 1st bed with interchanger
7. Catalyst loading on 1st bed



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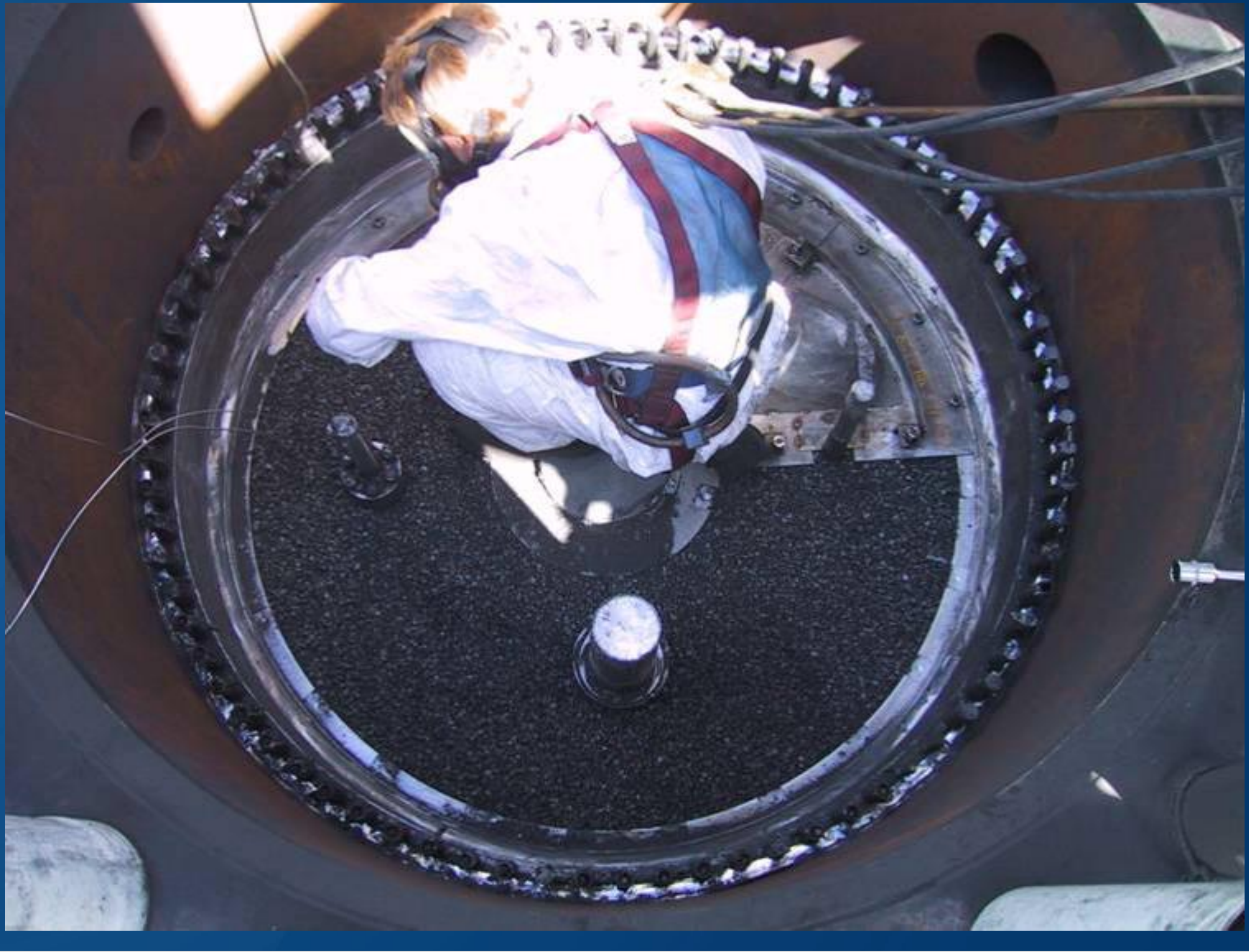
Ammonia Converter Assembly Sequence: First Bed Closure



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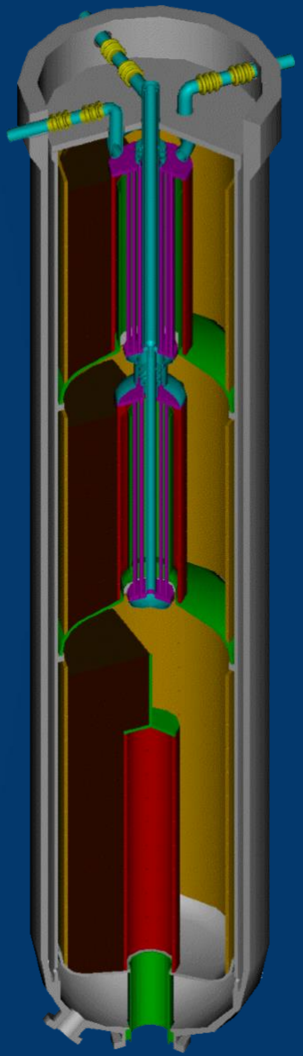
Ammonia Converter Assembly Sequence

1. Pressure vessel
2. Introduce the new cartridge in the H.P. vessel
3. Catalyst loading on 3rd bed
4. Install 2nd bed with interchanger
5. Catalyst loading on 2nd bed
6. Install 1st bed with interchanger
7. Catalyst loading on 1st bed
8. Install cartridge cover and sealing stuffing boxes
9. Connection of start-up and bypass line to the H.P. vessel



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Ammonia Converter Assembly Sequence: Cartridge Top Cover

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EVOLUTION OF AMMONIA SYNTHESIS CATALYST

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Ammonia:

- Introduction of Ammonia Synthesis
- Features of the catalysts
- Evolution of the catalysts
- Industrially used catalysts
- Size of the catalyst
- From lab to reactors
- R&D strategies

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Ammonia: Catalyst

- Why Iron?
- Promoters
  - K+
  - Ca
  - Mg
  - Si
  - Al

- Promoters in a range of 4-10 wt.%
- The reduction step
- Are the promoters necessary?

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Ammonia: Catalyst Promoters

- Promoters
- K+
- Ca
- Mg
- Si
- Al

- The promoters are fundamental for the catalyst activity
- Promoters modify: electronic structure, resistance of the catalyst, spaces between nanocrystal

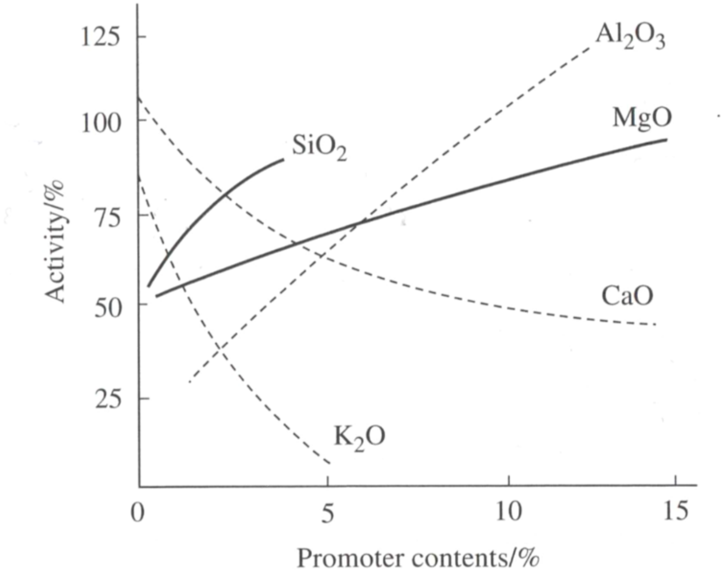

Fig. 3.43 Influence of promoter contents on activity of catalyst

Ammonia Synthesis Catalyst: Innovation and Practice. Huazhang Liu, World scientific, 2013. https://doi.org/10.1142/8199

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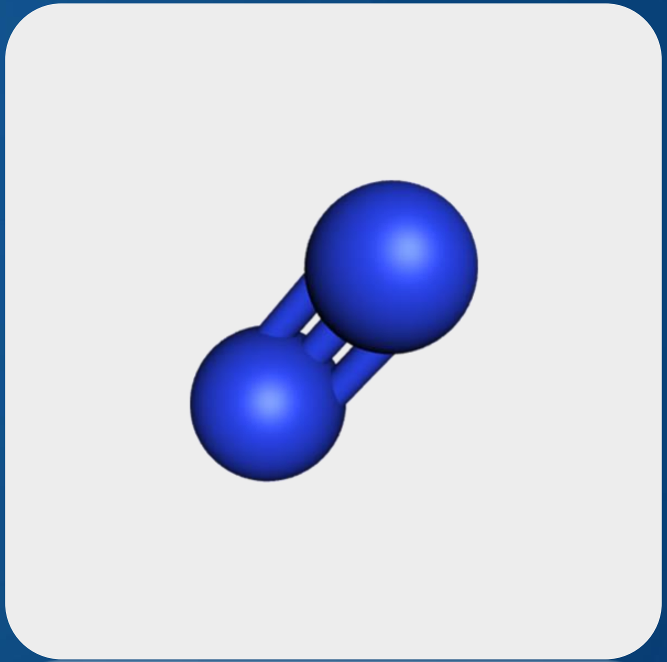
Ammonia: Catalyst

- Iron crystallographic phase is important
- N_2 triple bonds to be broken
- How to produce the catalyst?



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Ammonia: Evolution of the Catalyst

- Magnetite precursor (oxidized)
- Fe_3O_4
- Magnetite precursor (prereduced)
- Fe_3O_4
- Wustite precursor (oxidized)
- $Fe_{1-x}O$
- Wustite precursor (prereduced)
- $Fe_{1-x}O$
- Magnetite+Co
- Ru/C
- Is it the future?

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Ammonia: Industrially used catalysts (1)

- Main types of ammonia synthesis catalysts in the world

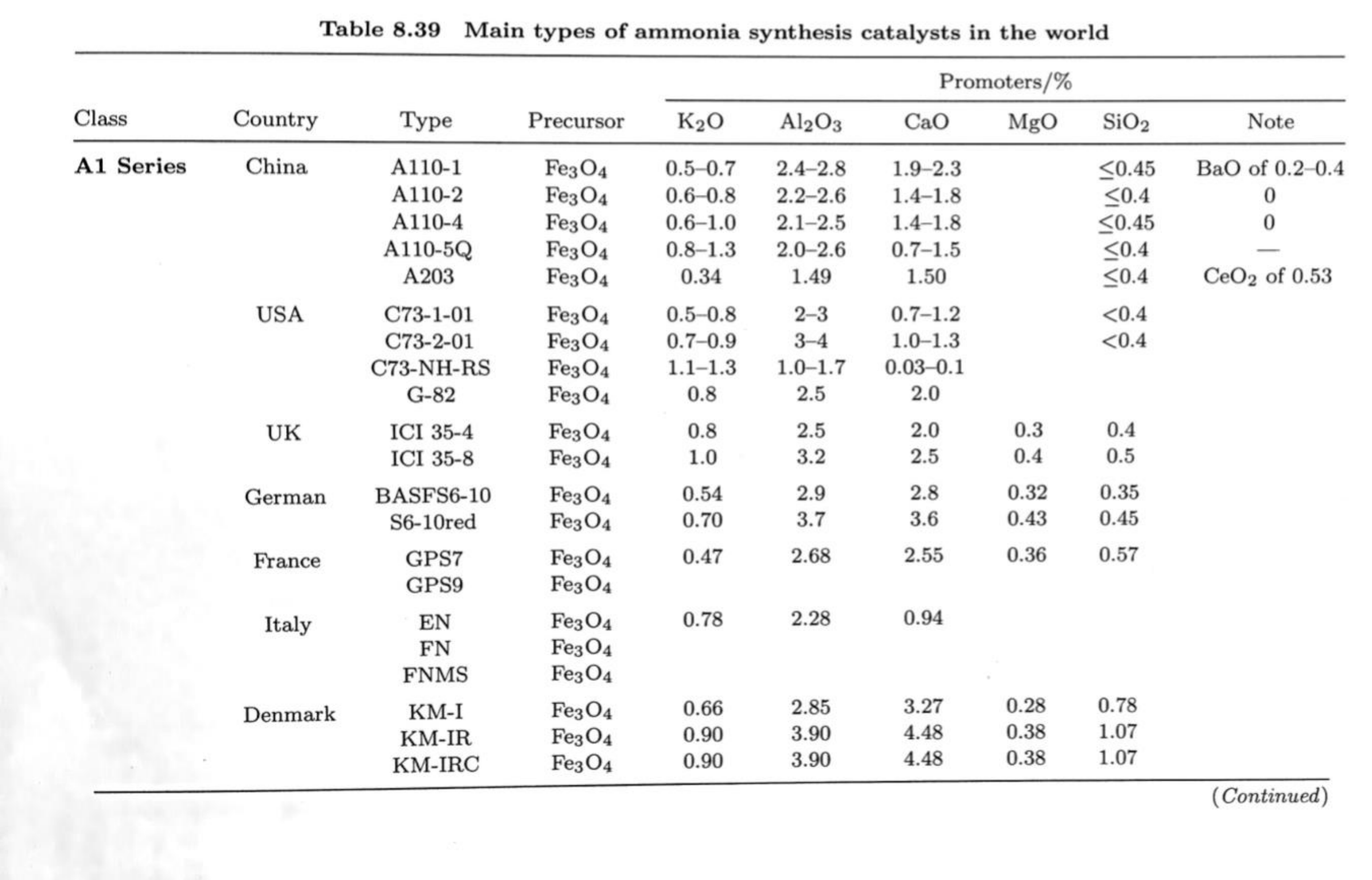

Table 8.39 **Main types of ammonia synthesis catalysts in the world**

Class	Country	Type	Precursor	Promoters/%					Note
				K_2O	Al_2O_3	CaO	MgO	SiO_2	
A1 Series	China	A110-1	Fe_3O_4	0.5–0.7	2.4–2.8	1.9–2.3		≤0.45	BaO of 0.2–0.4
		A110-2	Fe_3O_4	0.6–0.8	2.2–2.6	1.4–1.8		≤0.4	0
		A110-4	Fe_3O_4	0.6–1.0	2.1–2.5	1.4–1.8		≤0.45	0
		A110-5Q	Fe_3O_4	0.8–1.3	2.0–2.6	0.7–1.5		≤0.4	—
		A203	Fe_3O_4	0.34	1.49	1.50		≤0.4	CeO_2 of 0.53
	USA	C73-1-01	Fe_3O_4	0.5–0.8	2–3	0.7–1.2		<0.4	
		C73-2-01	Fe_3O_4	0.7–0.9	3–4	1.0–1.3		<0.4	
		C73-NH-RS	Fe_3O_4	1.1–1.3	1.0–1.7	0.03–0.1			
		G-82	Fe_3O_4	0.8	2.5	2.0			
	UK	ICI 35-4	Fe_3O_4	0.8	2.5	2.0	0.3	0.4	
		ICI 35-8	Fe_3O_4	1.0	3.2	2.5	0.4	0.5	
	German	BASFS6-10	Fe_3O_4	0.54	2.9	2.8	0.32	0.35	
		S6-10red	Fe_3O_4	0.70	3.7	3.6	0.43	0.45	
	France	GPS7	Fe_3O_4	0.47	2.68	2.55	0.36	0.57	
		GPS9	Fe_3O_4						
	Italy	EN	Fe_3O_4	0.78	2.28	0.94			
		FN	Fe_3O_4						
		FNMS	Fe_3O_4						
	Denmark	KM-I	Fe_3O_4	0.66	2.85	3.27	0.28	0.78	
		KM-IR	Fe_3O_4	0.90	3.90	4.48	0.38	1.07	
		KM-IRC	Fe_3O_4	0.90	3.90	4.48	0.38	1.07	

(*Continued*)

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Ammonia: Industrially used catalysts (2)

- Main types of ammonia synthesis catalysts in the world

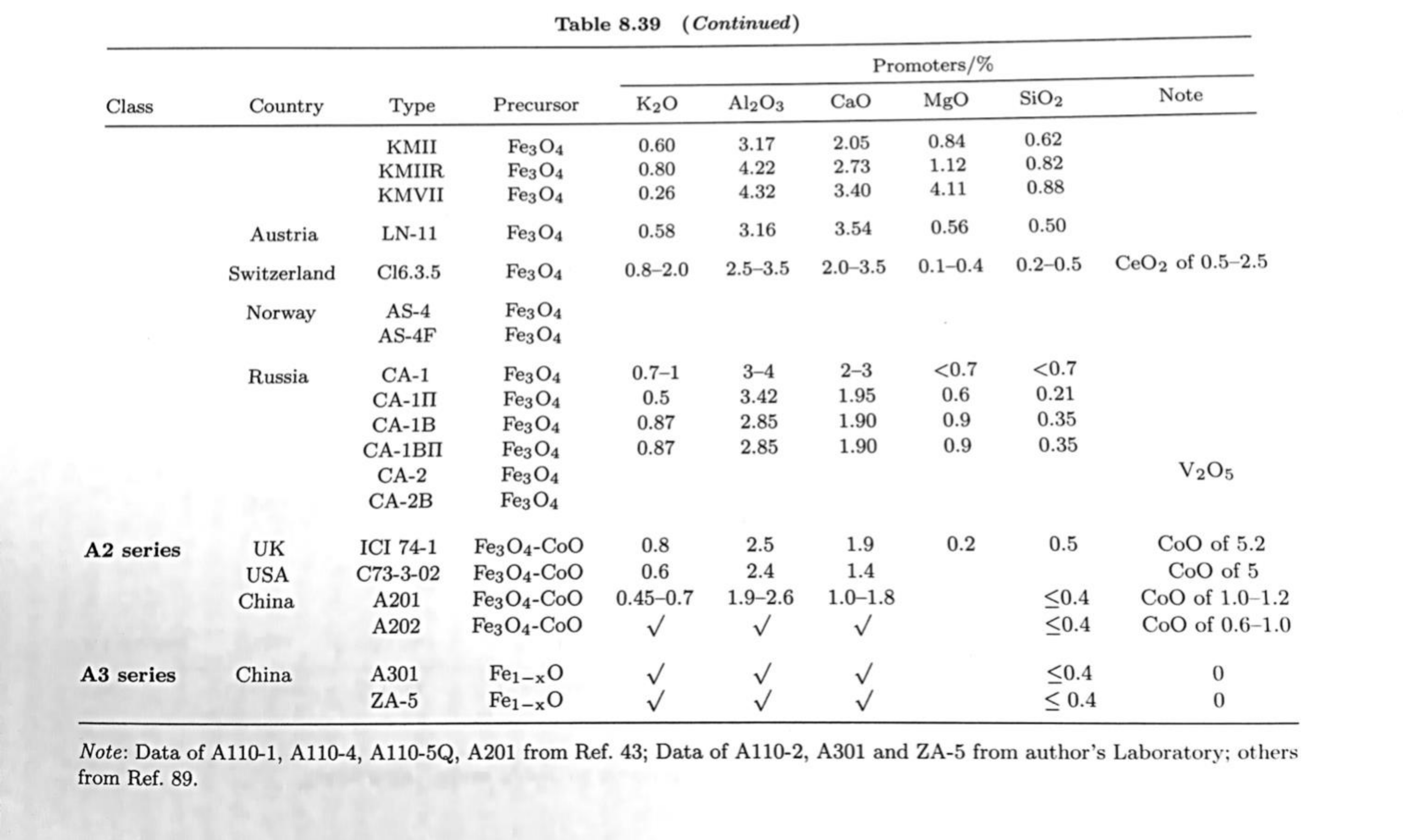

Table 8.39 (*Continued*)

Class	Country	Type	Precursor	Promoters/%					Note
				K_2O	Al_2O_3	CaO	MgO	SiO_2	
		KMII	Fe_3O_4	0.60	3.17	2.05	0.84	0.62	
		KMIIR	Fe_3O_4	0.80	4.22	2.73	1.12	0.82	
		KMVII	Fe_3O_4	0.26	4.32	3.40	4.11	0.88	
	Austria	LN-11	Fe_3O_4	0.58	3.16	3.54	0.56	0.50	
	Switzerland	Cl6.3.5	Fe_3O_4	0.8–2.0	2.5–3.5	2.0–3.5	0.1–0.4	0.2–0.5	CeO_2 of 0.5–2.5
	Norway	AS-4	Fe_3O_4						
		AS-4F	Fe_3O_4						
	Russia	CA-1	Fe_3O_4	0.7–1	3–4	2–3	<0.7	<0.7	
		CA-1П	Fe_3O_4	0.5	3.42	1.95	0.6	0.21	
		CA-1B	Fe_3O_4	0.87	2.85	1.90	0.9	0.35	
		CA-1BП	Fe_3O_4	0.87	2.85	1.90	0.9	0.35	
		CA-2	Fe_3O_4						V_2O_5
		CA-2B	Fe_3O_4						
A2 series	UK	ICI 74-1	Fe_3O_4-CoO	0.8	2.5	1.9	0.2	0.5	CoO of 5.2
	USA	C73-3-02	Fe_3O_4-CoO	0.6	2.4	1.4			CoO of 5
	China	A201	Fe_3O_4-CoO	0.45–0.7	1.9–2.6	1.0–1.8		≤0.4	CoO of 1.0–1.2
		A202	Fe_3O_4-CoO	√	√	√		≤0.4	CoO of 0.6–1.0
A3 series	China	A301	$Fe_{1-x}O$	√	√	√		≤0.4	0
		ZA-5	$Fe_{1-x}O$	√	√	√		≤ 0.4	0

Note: Data of A110-1, A110-4, A110-5Q, A201 from Ref. 43; Data of A110-2, A301 and ZA-5 from author's Laboratory; others from Ref. 89.

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Ammonia: Ru/C Catalyst Pros and Cons

- PROS
  - High Activity
  - Less Catalyst Volume
  - Different catalyst compared to competitors
  - Low pressure

- CONS
  - Drawback 1
  - Drawback 2
  - Drawback 3

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Ammonia: Ru/C Catalyst Cons

- Ruthenium is one of the rarest metals on Earth.

- Ruthenium is found as the free metal, sometimes associated with platinum, osmium and iridium, in North and South America, and in South Africa. There are few minerals, such as laurite, ruarsite and ruthenarsenite. All are rare and none acts as a commercial source of the metal. Ruthenium is also associated with nickel and deposits (from which it is recovered commercially). World production is 12 tonnes per year and reserves are hestimated to be around 5.000 tonnes.

- https://www.lenntech.com/periodic/elements/ru.htm

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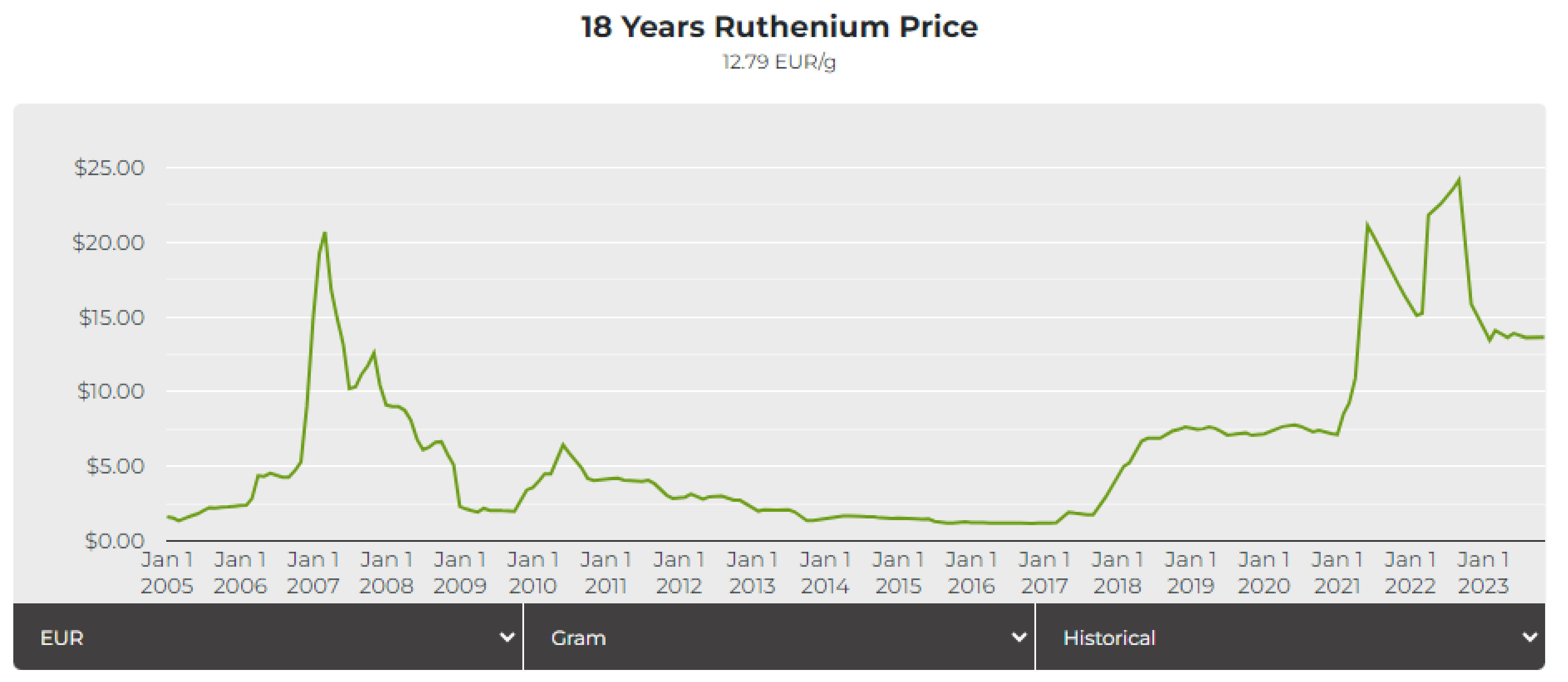
Ammonia: Ru/C Catalyst Cons

- https://www.mining.com/markets/commodity/ruthenium/ (accessed 29.11.23)



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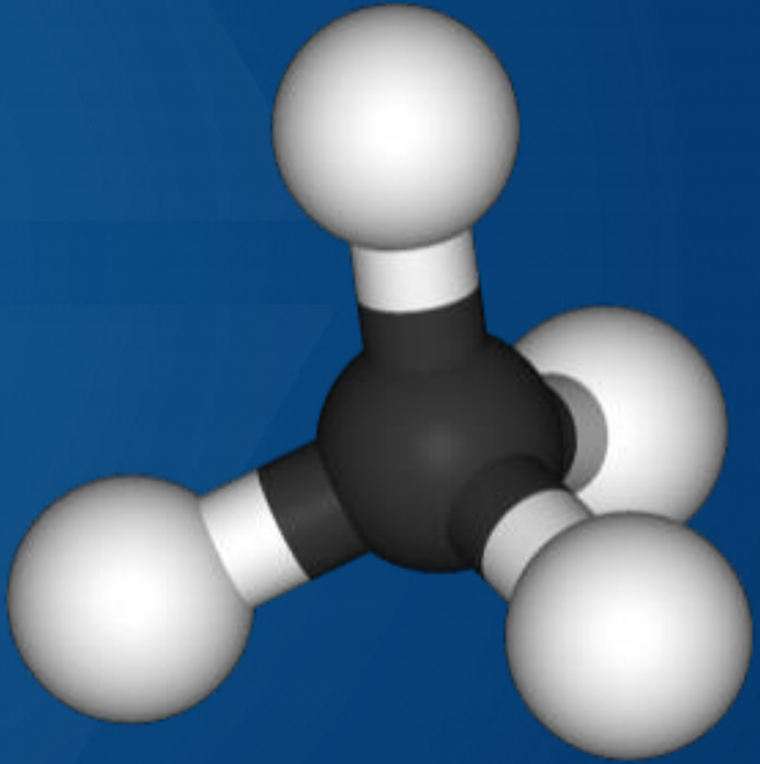
Ammonia: Ru/C Catalyst Cons

- Formation of Methane from Hydrogen and the carbon support



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Ammonia: Ru/C Catalyst was not feasible in the past

- Due to the numerous drawbacks of the catalyst it will not be used at large scale for all the existing plants
- Alternatives must be found

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Ammonia: size of ammonia synthesis catalyst

- Ammonia synthesis catalyst had a mean diameter between 6 and 10 mm for axial reactors.
- The size changed when the technology changed: from axial to radial reactors
- Casale improved the radial reactors introducing the axial-radial reactors
- Now the optimal size range of the catalyst is 1.5-3 mm

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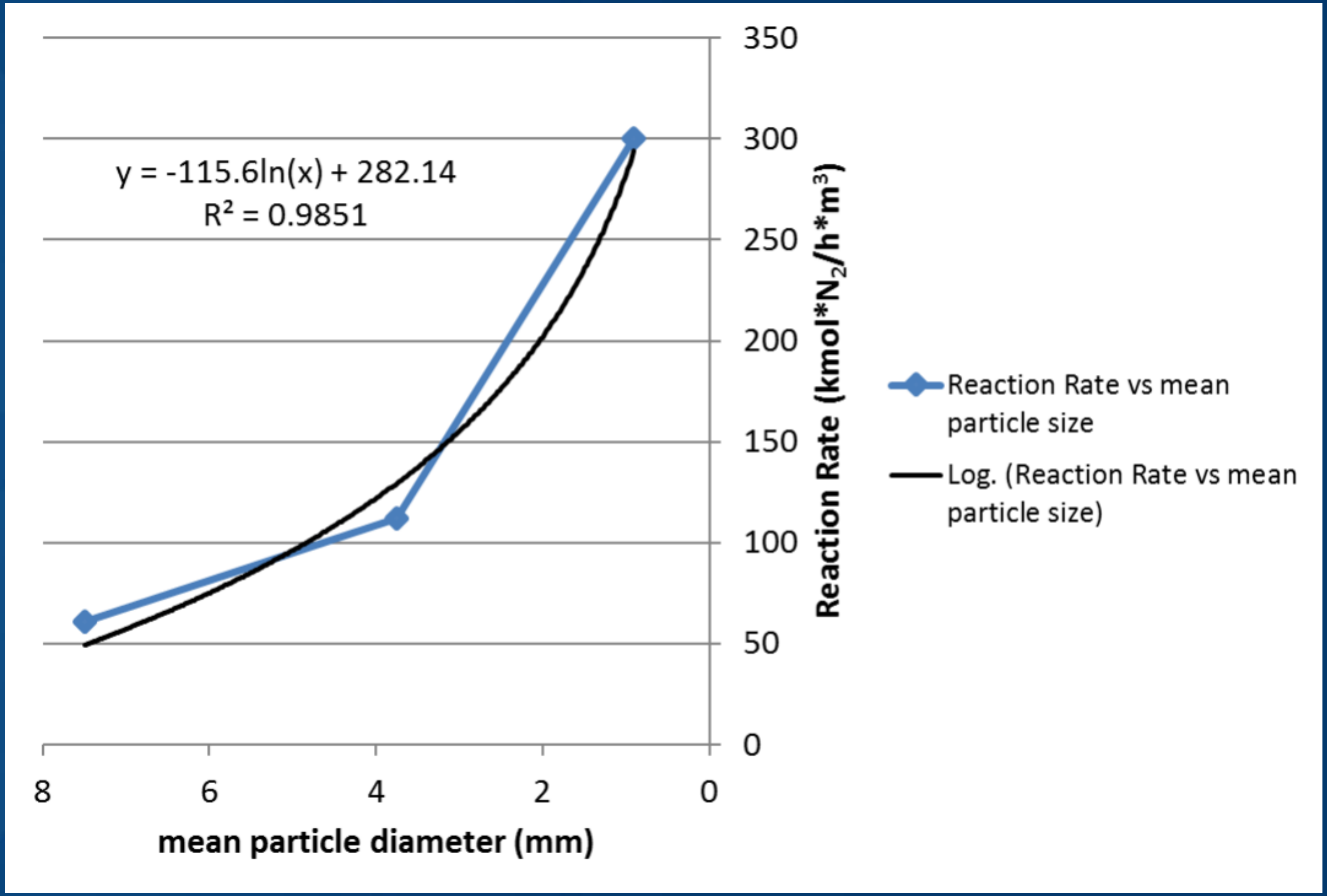
Ammonia: size of ammonia synthesis catalyst

- Reaction Rate vs Size: From axial to radial reactors



Reaction rate versus mean particle size of ammonia synthesis catalyst (adaptation from table 8.3, in the Catalyst Handbook (Twigg, 2nd edition page 412).

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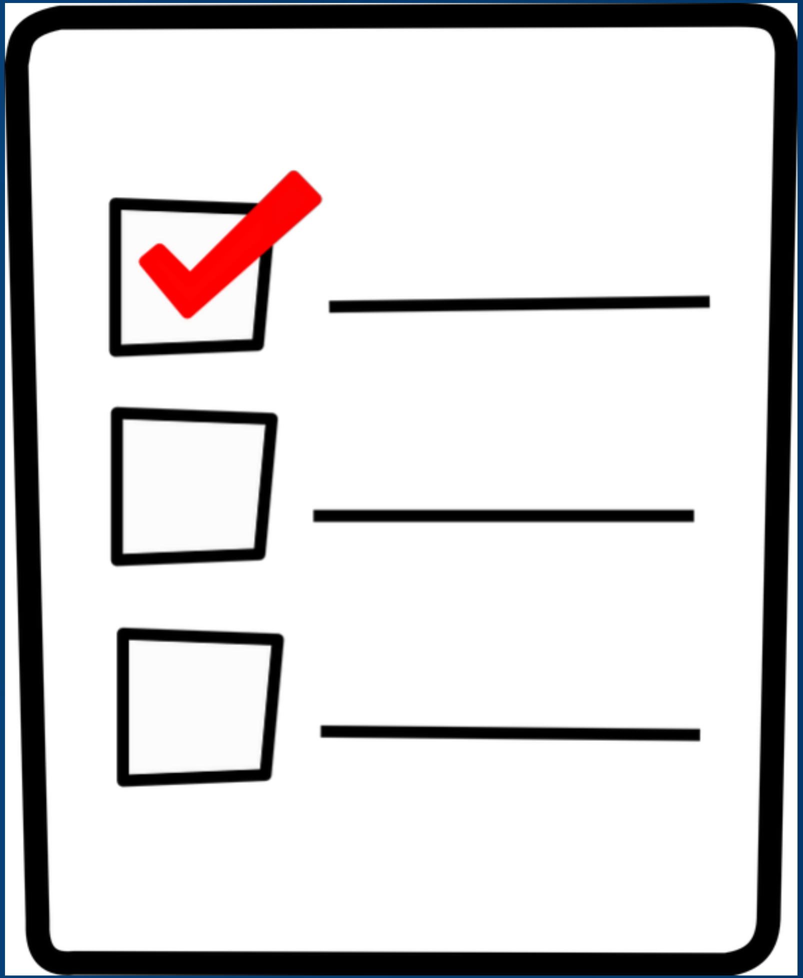
Ammonia: size of ammonia synthesis catalyst

- Pressure drops
- Catalyst in the reactor
- From axial to radial reactors
- Cost of the equipment



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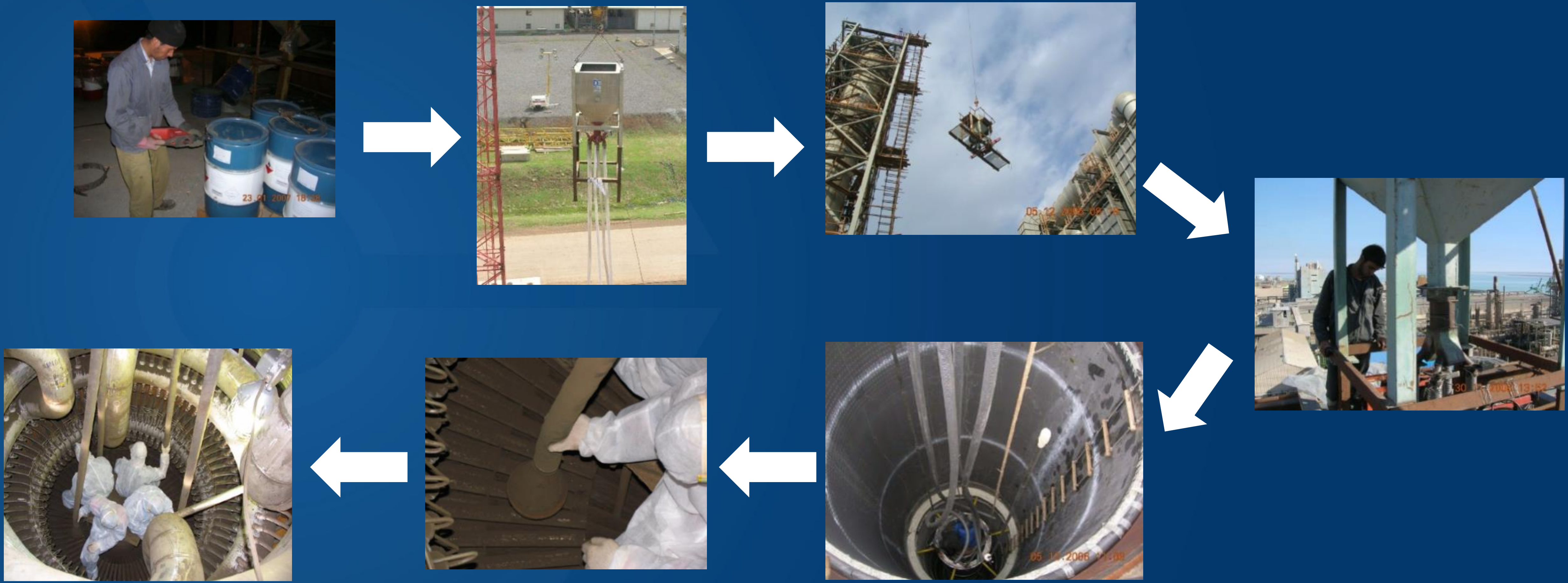
Ammonia: catalyst loading is crucial for catalyst life



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Ammonia: from lab to reactors

- Powder form
- Different synthesis strategies
- Control over every parameter
- Catalyst screening
- Reduction strategies for the catalyst

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Ammonia: from lab to reactors

- Ageing
- Poisoning
- Life time
- Catalyst Comparison
- Kinetics

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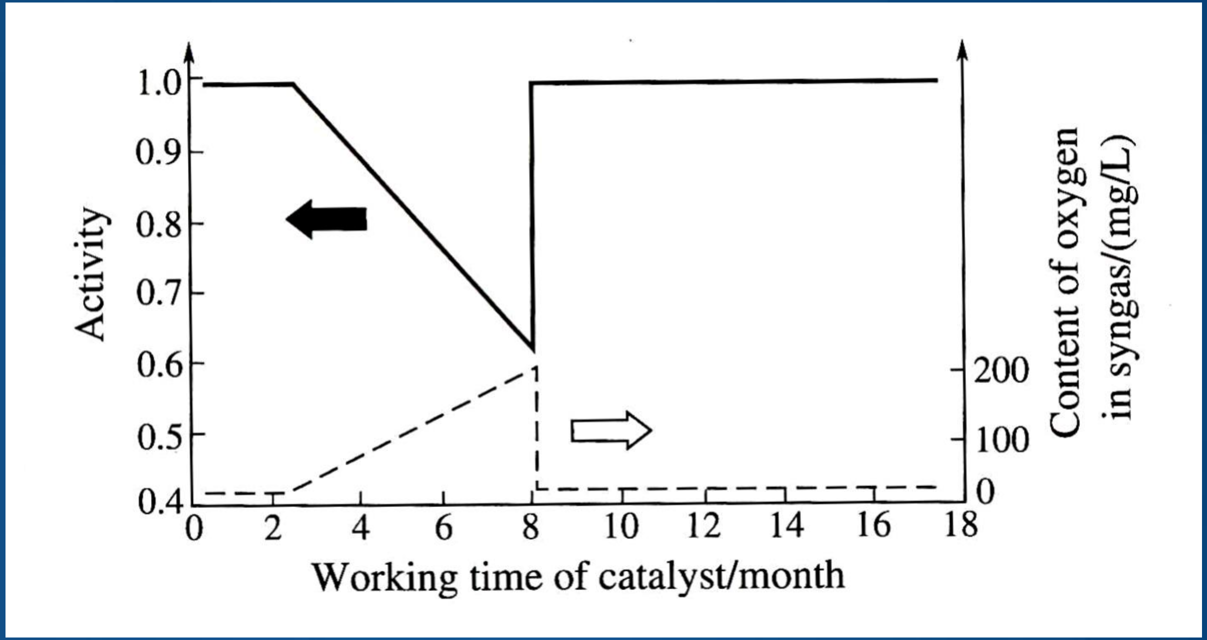
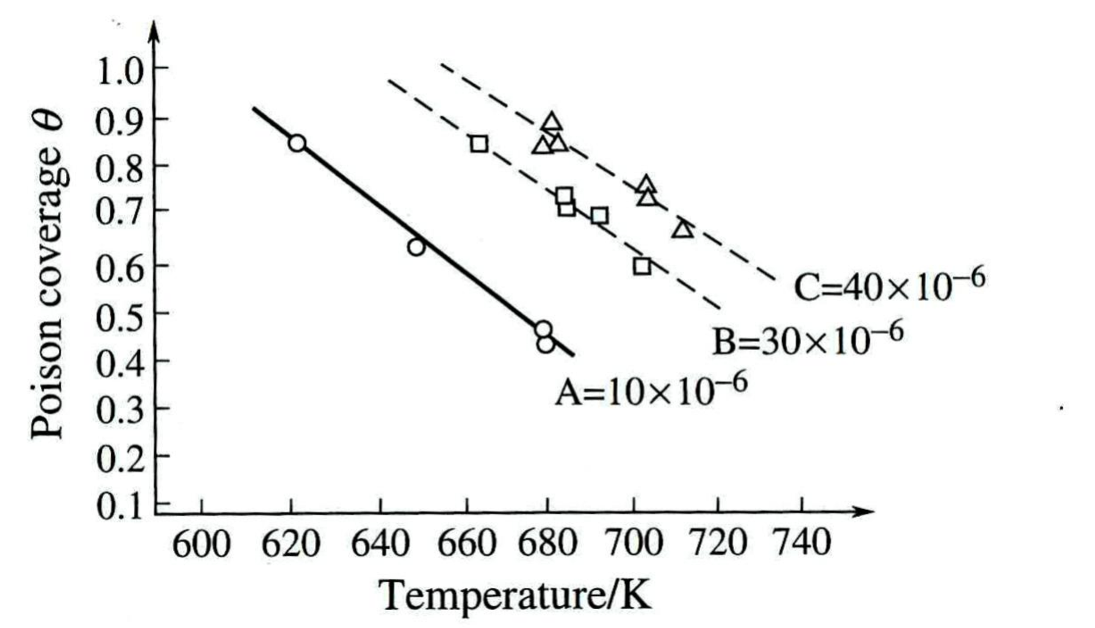
Ammonia: from lab to reactors





- Oxygen, water and other oxygenates poison the catalyst

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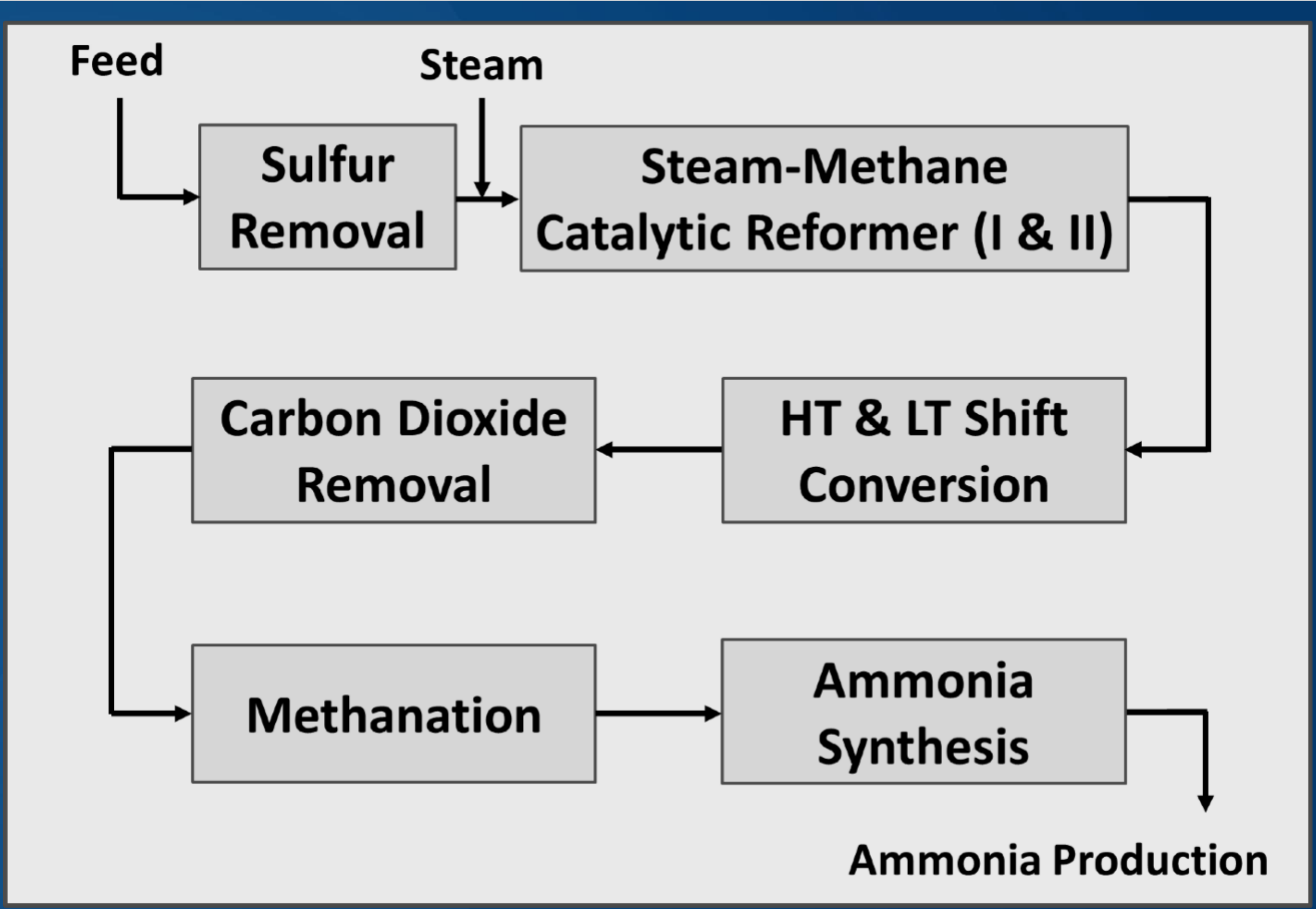
Ammonia: Ammonia synthesis catalyst is like a baby…it has to be protected



Hydrogen and Nitrogen have to arrive pure to the ammonia synthesis converter

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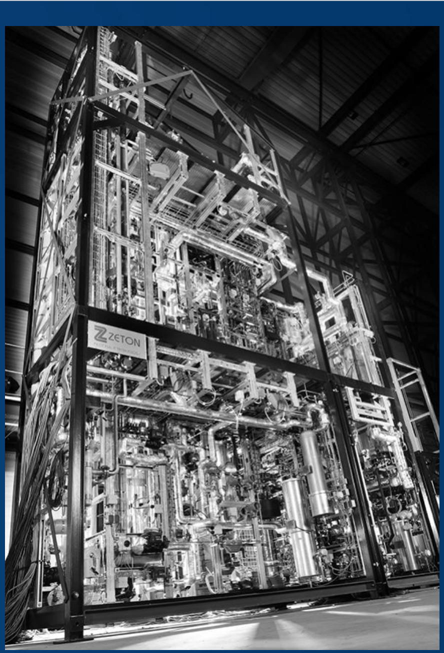
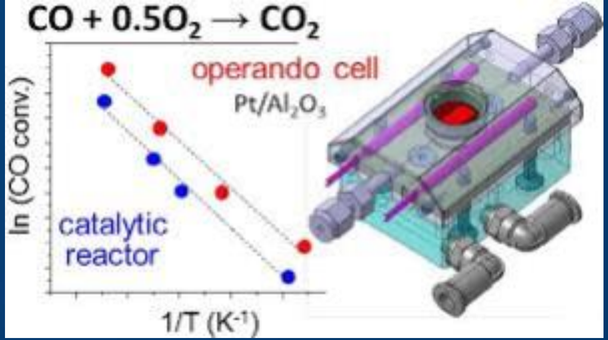
Ammonia: from lab to reactors

BENCH-SCALE



PILOT



OPERANDO

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FROM LABORATORY TO IMPLEMENTATIONS: A CASE STUDY

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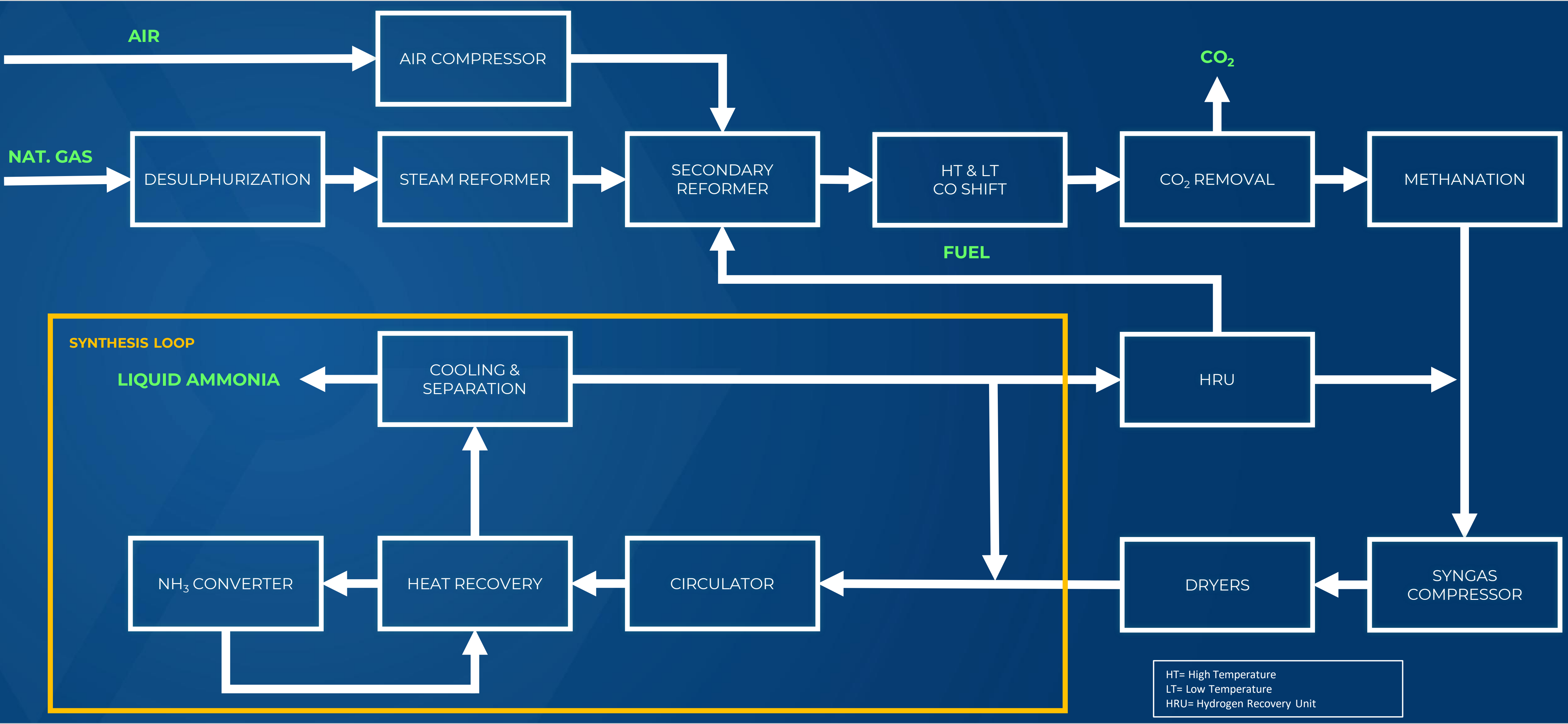
Grey Ammonia Process Scheme



HT= High Temperature
LT= Low Temperature
HRU= Hydrogen Recovery Unit

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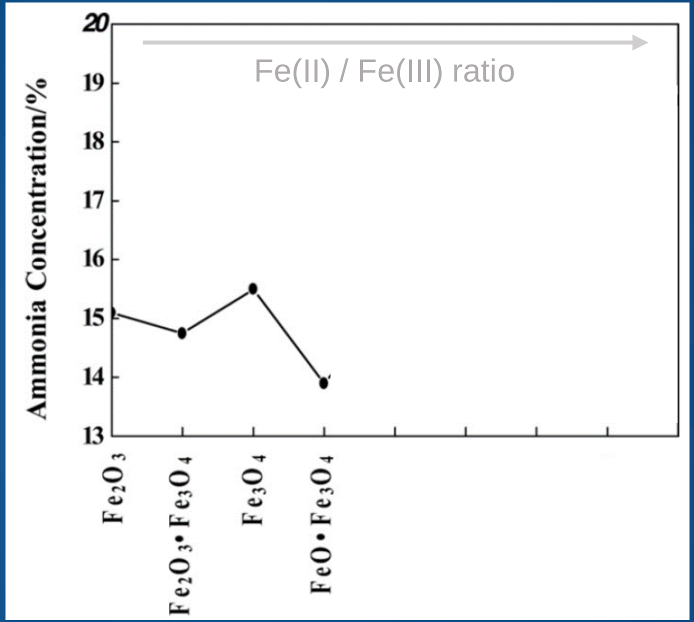
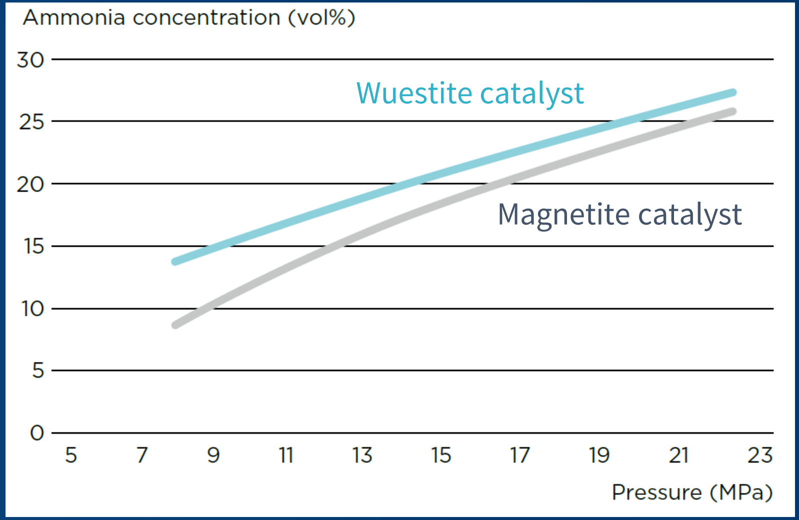
Ammonia: Catalysts for ammonia synthesis

Impact of Fe oxide precursor



H. Liu, W. Han, *Catalysis Today* 297(**2017**) 276-291

Wuestite vs. magnetite catalyst



- Since the early 20th century, catalysts have been based on **Magnetite Fe_3O_4** with a mix of promoters such as K_2O and Al_2O_3

- 1986: First catalyst based on **Wuestite $Fe_{1-x}O$**

  → more active, especially at low p / T

- 2002: Clariant's own wuestite-based catalyst **AmoMax® 10**

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Ammonia: Catalyst activation

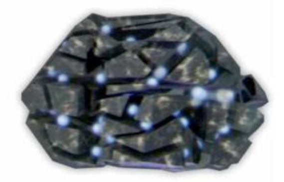
- Active phase is formed by reducing the catalyst directly inside the converter

$Fe_{1-x}O$
<< 0.5 $m^2\,g^{-1}$

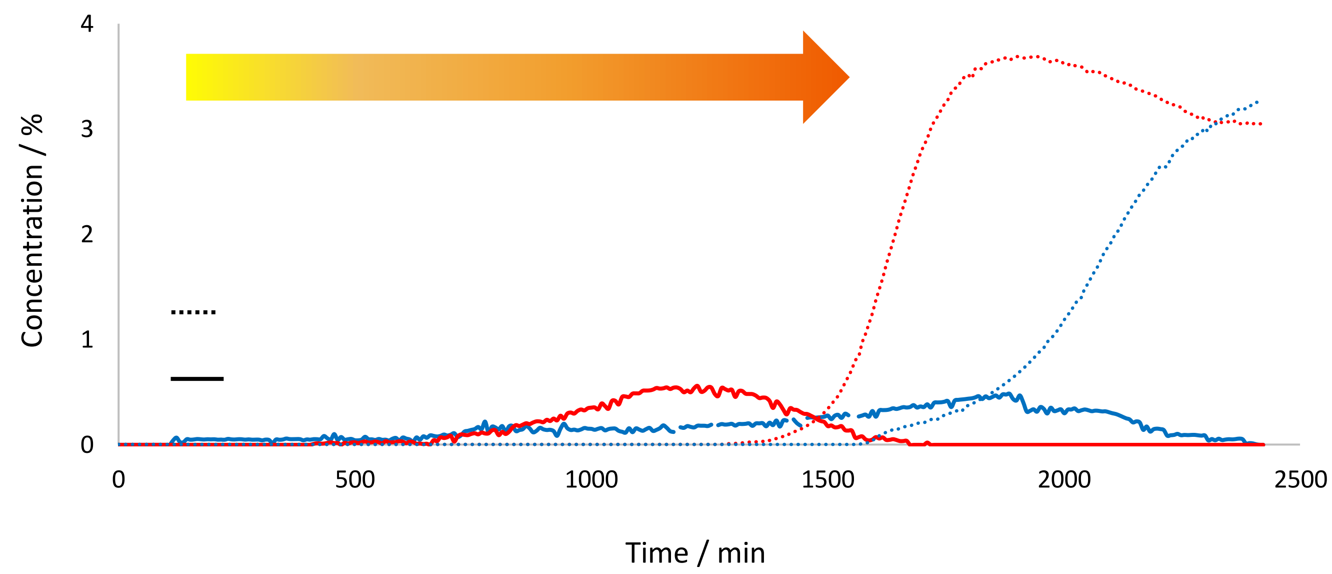
+ H_2

- H_2O

α-Fe
10 – 20 $m^2\,g^{-1}$



Reduction profile in lab experiment under realistic conditions



Compared to conventional, Fe_3O_4-based catalysts, AmoMax® 10 has a lower oxygen content

- ✓ 25% less water evolved with AmoMax® 10
- ✓ H_2O release and NH_3 production at lower temperature
- ✓ Faster reduction

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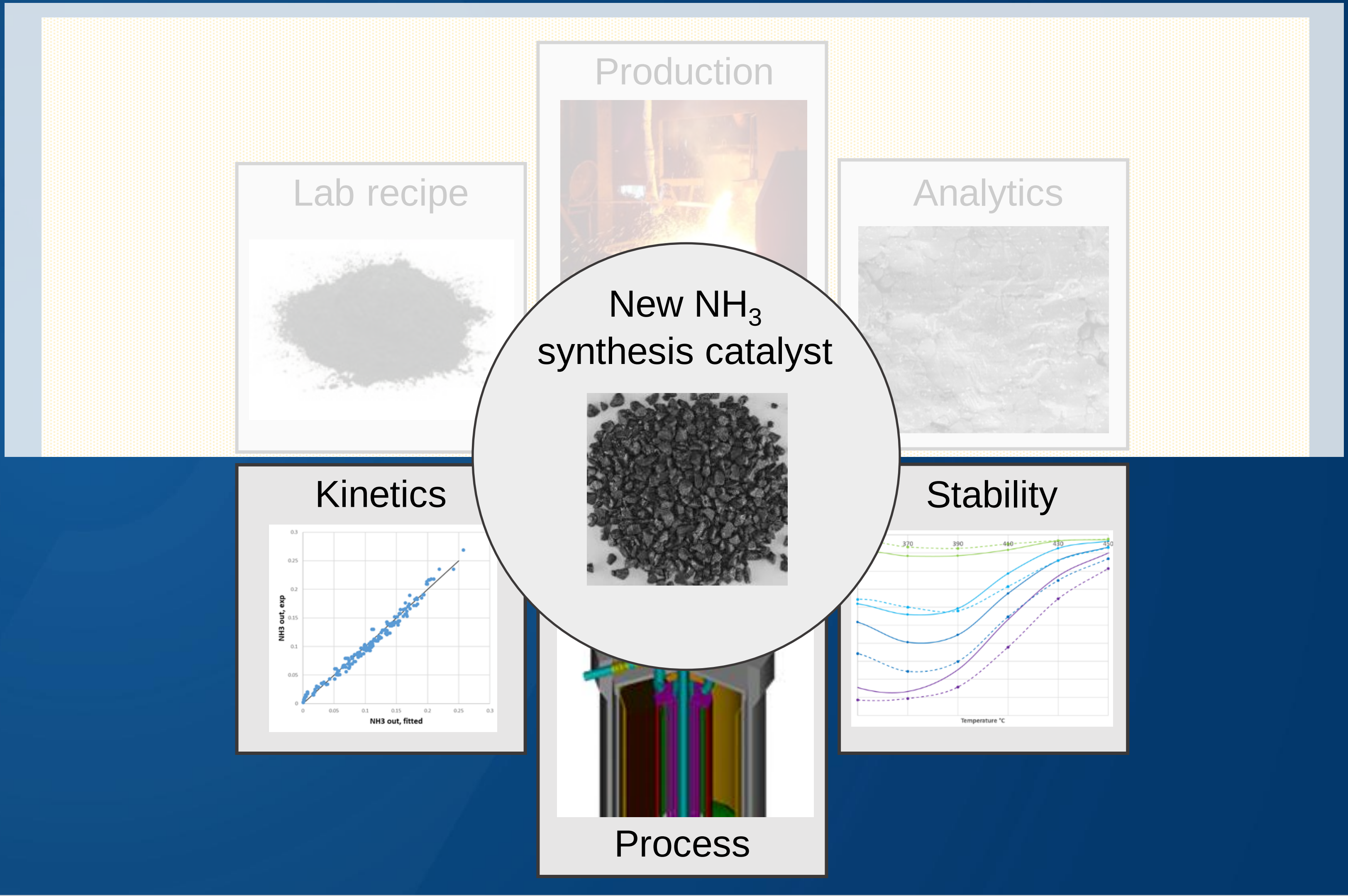
Ammonia: Developing a new ammonia synthesis catalyst



Catalyst Manufacturer

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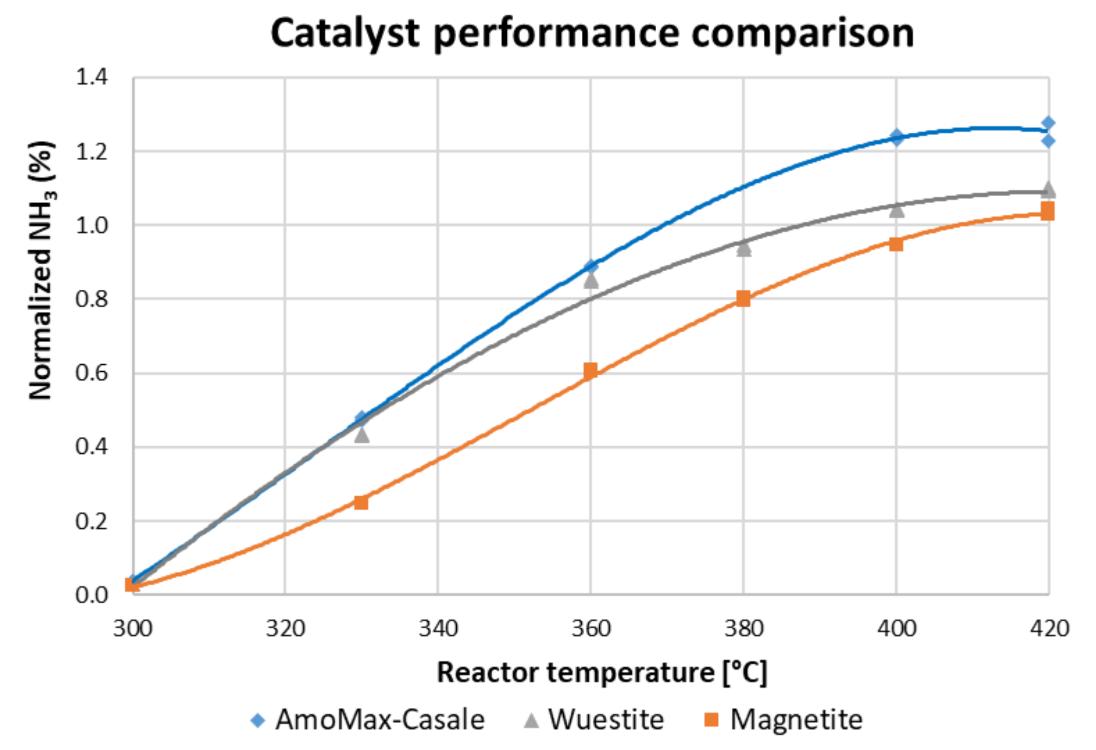
Ammonia: Catalyst testing

- Tubular reactor, tests performed on granules
- Pressure: 150 bar and $H_2 : N_2 = 3$
- Temperature: 300, 330, 360, 380, 400 and 420°C
- Inert dilution with 0%, 7% and 14% CH_4



✓ New formulation outperforms Wuestite-based reference catalyst

✓ Increased gap in performance compared to magnetite catalyst

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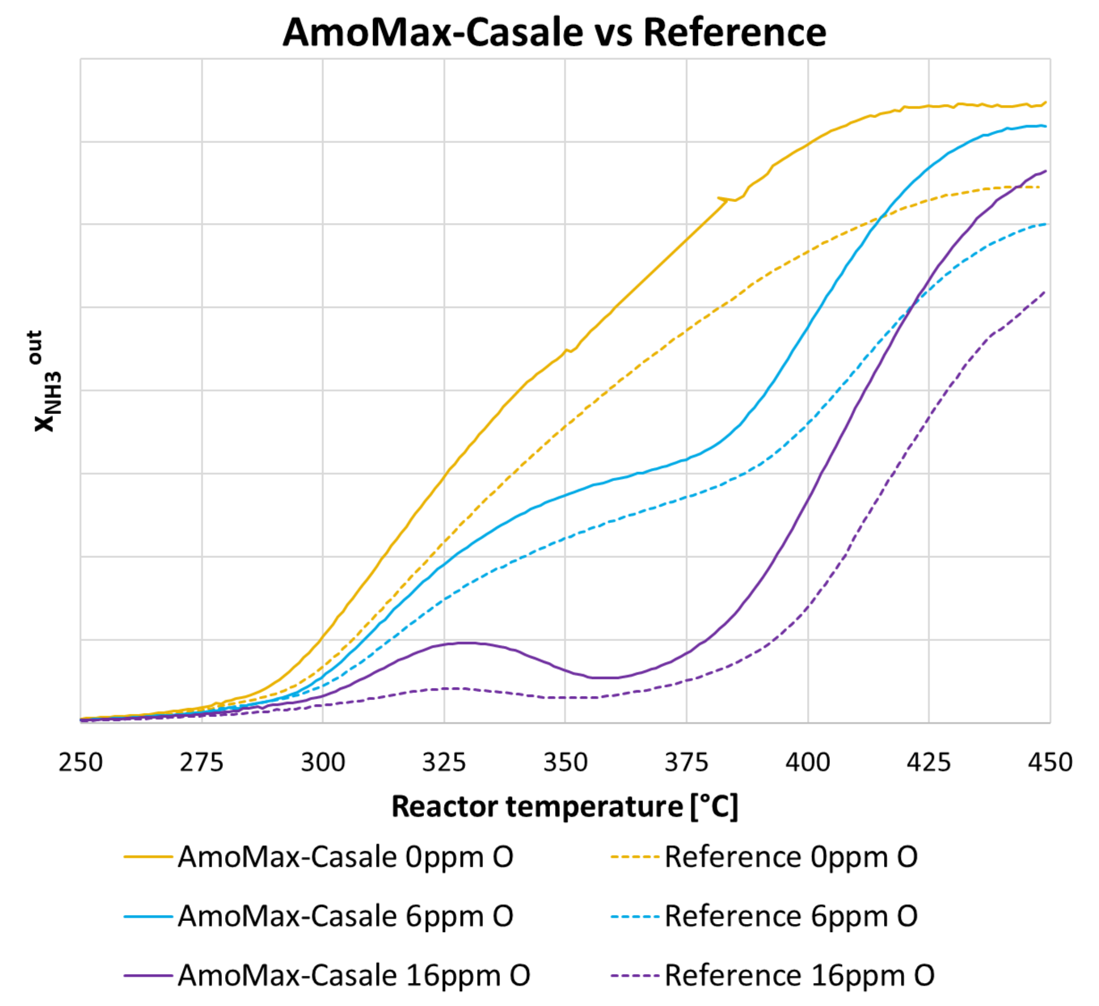
Ammonia: Catalyst testing and performance in poisoning conditions

The performance with different O_2 concentrations in the feed was tested at different temperatures:

- Oxygen poisoning behaviour of new catalyst is similar to reference
- The deactivation observed due to Oxygen poisoning is similar to what is observed in plant
- New catalyst offers superior performance regardless of Oxygen concentration



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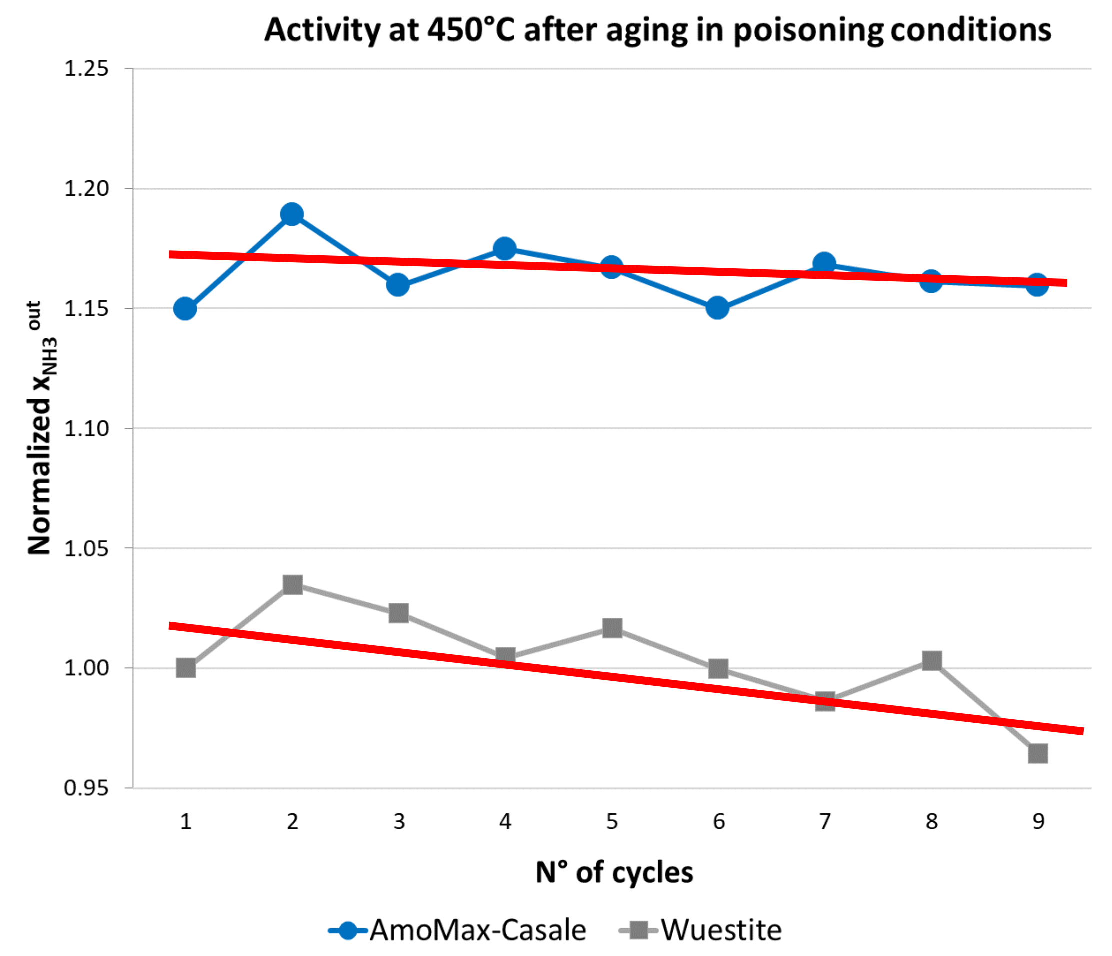
Ammonia: Catalyst testing and stability check after poisoning conditions

Catalyst performance was tested after each poisoning treatment to check the stability

The activity was followed over time at fixed testing conditions without oxygen poisoning and after a stabilization period.

AmoMax®-Casale has proven to be very stable compared to Wuestite-based reference catalyst



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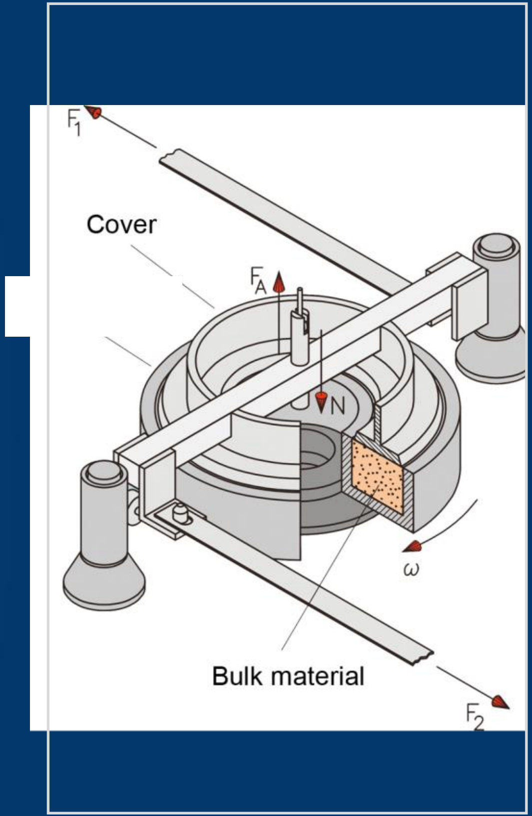
Ammonia: Mechanical catalyst validation

- Evaluation of powder produced during loading: weight loss due to wall friction with collectors
- Experimental testing of pressure drop
- Check the mechanical stress on the reactor collectors: shear stress test to determine friction coefficients
- Ensure that no bed fluidization occurs

Casale wall tester

Industrial pilot plant for pressure drop measurement



Shear stress test unit

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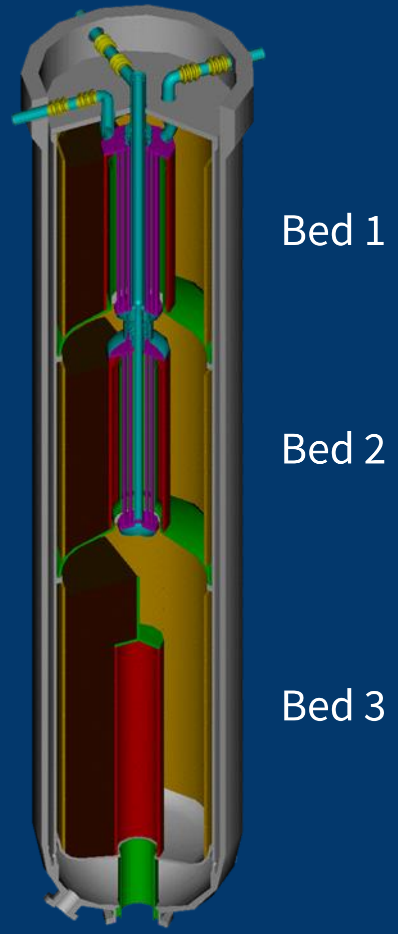
Ammonia: Process Simulation

- Different configurations were tested to determine the optimal reactor design and conditions to run the new catalyst
- The best configuration uses AmoMax®-Casale only in bed 3, since it is the most limited by catalyst kinetics, operating at lower temperature

Case Study

- Real case revamping with AmoMax®-Casale lead to an expected **decrease of the ammonia plant energy consumption** up to **40’000 kcal/MT$_{NH3}$**
- In case of ammonia plant capacity limited by synthesis loop, the use of AmoMax®-Casale provides roughly **1.5% capacity increase**



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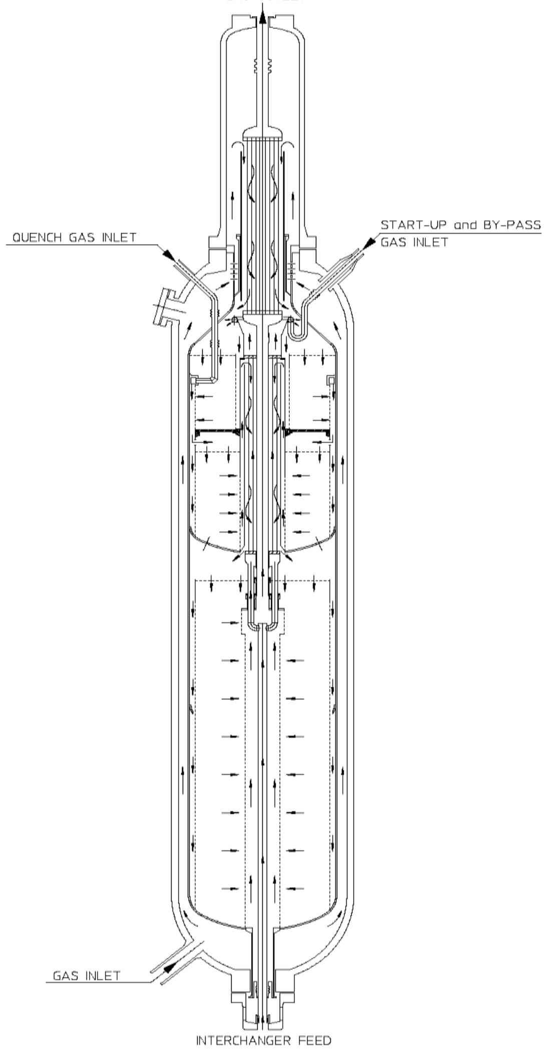
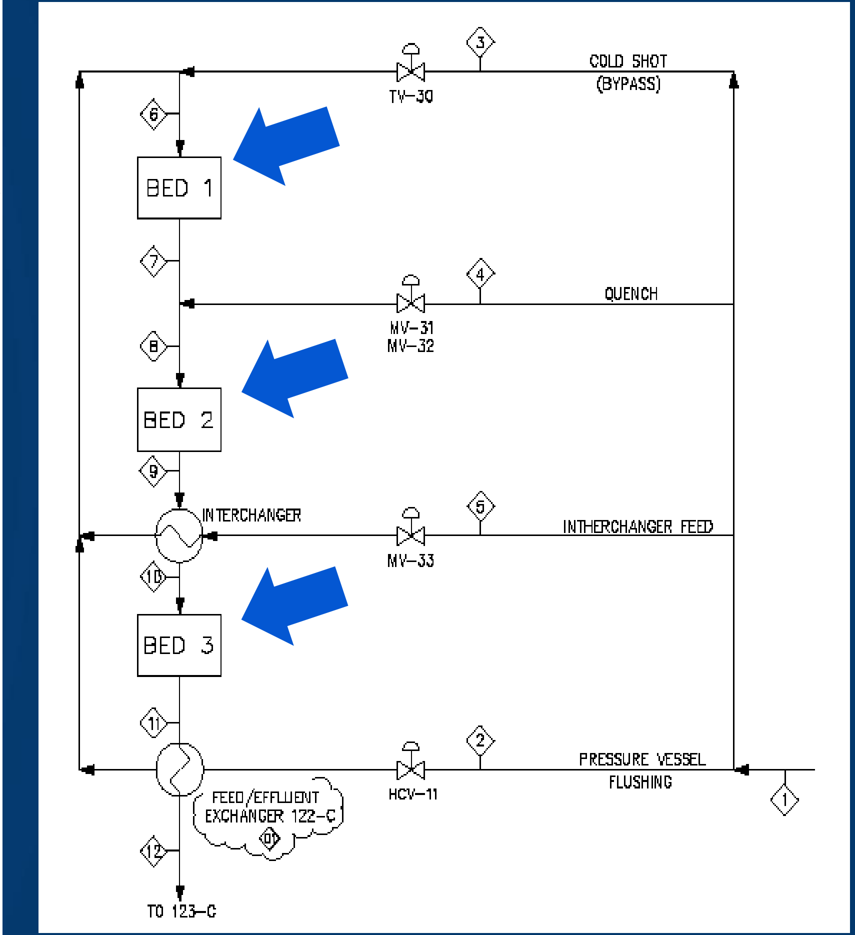
Ammonia: First industrial reference of AmoMax®-Casale

- Revamping of a bottle shape KBR converter
- AmoMax®-CASALE used in 3rd bed
- Same design used for a standard magnetite and Wustite-based catalyst
- Interchanger feed from bottom





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Ammonia: AmoMax®-Casale at SOR exceeded expectations

- Capacity is at 75% at this point, due to external factors
- **AmoMax®-Casale catalyst performed better than expected**, despite water carry over and oil loss that affected the activation phase
- Inlet pressure has been reduced by **18.5 bar**

Conditions	AmoMax®-Casale	Before revamping
Life	SOR	MOR/EOR
Capacity	75% (not optimized)	75%
Inlet pressure (bar)	**110**	**128.5**
NH_3% in	1.28	1.63
NH_3% out	**14.46**	**12.27**
ΔP (bar) ΔP (psi)	2 29	4.5 64
Recirculation (lb/hr)	725’000	753’000

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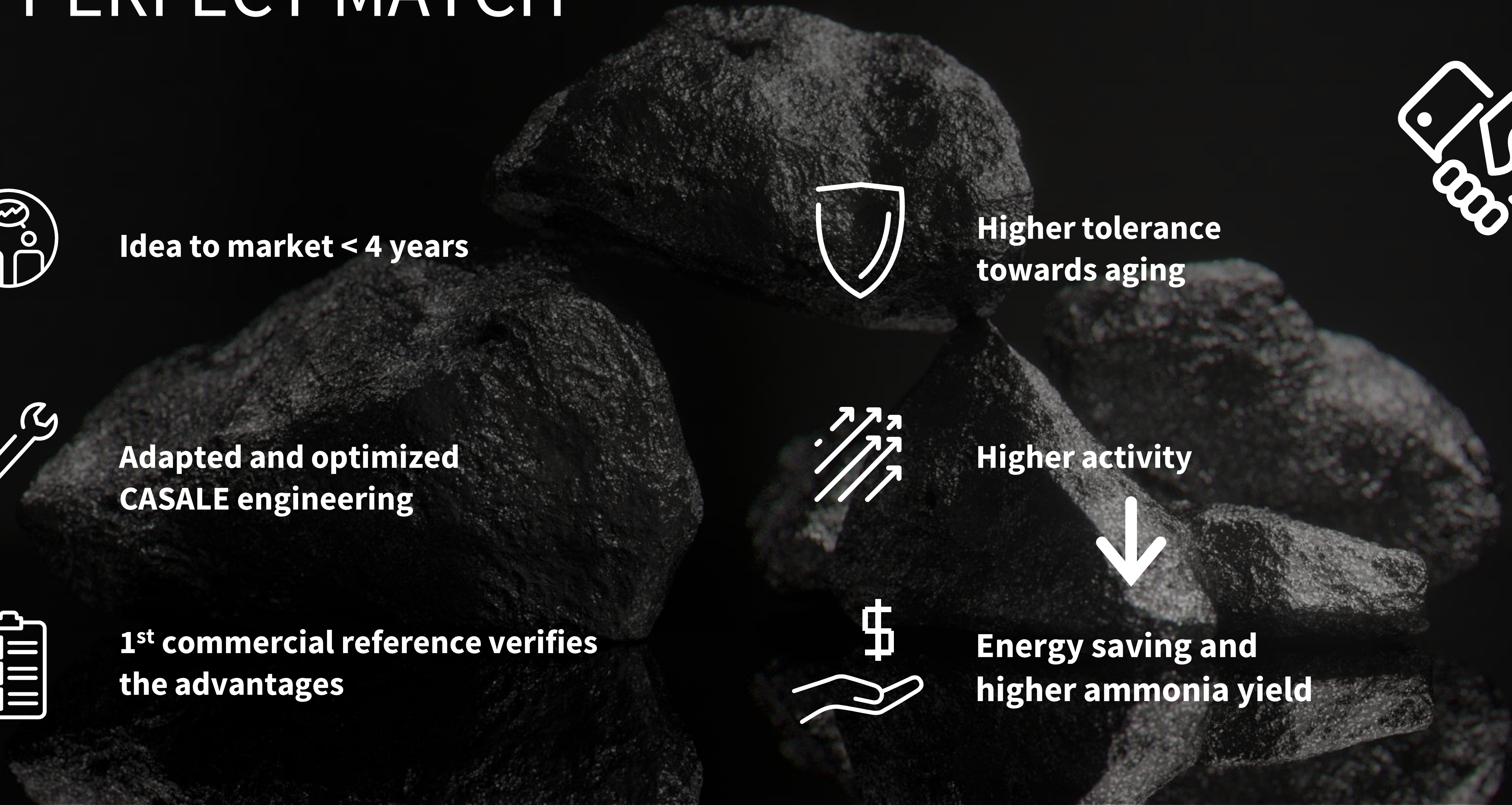
CASALE Technology and AmoMax®-Casale THE PERFECT MATCH



- Idea to market < 4 years
- Adapted and optimized CASALE engineering
- 1st commercial reference verifies the advantages

- Higher tolerance towards aging
- Higher activity

↓

- Energy saving and higher ammonia yield

FROM LAB TO IMPLEMENTATIONS: …..AND THEN TO GREEN

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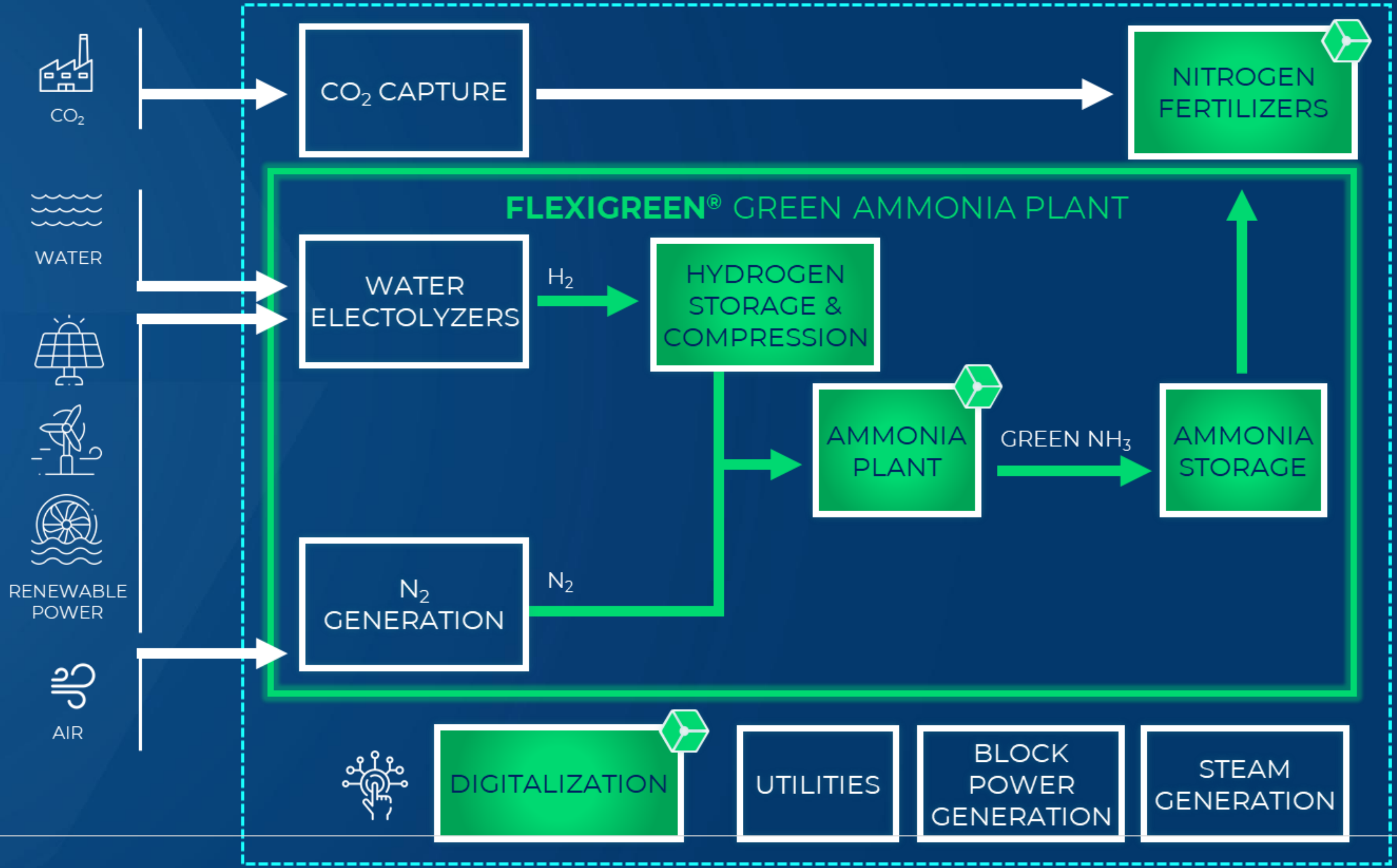
FLEXIGREEN® PRODUCTS: GREEN AMMONIA PLANTS

Integration of proprietary and third-party technologies

Different schemes according to plant capacity, tailored for green ammonia

3 Basic Engineering
>110 proposals
80+ projects from H2+N2



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WHAT DO WE NEED TO OVERCOME THE CHALLENGES OF RENEWABLE ENERGY SOURCES?

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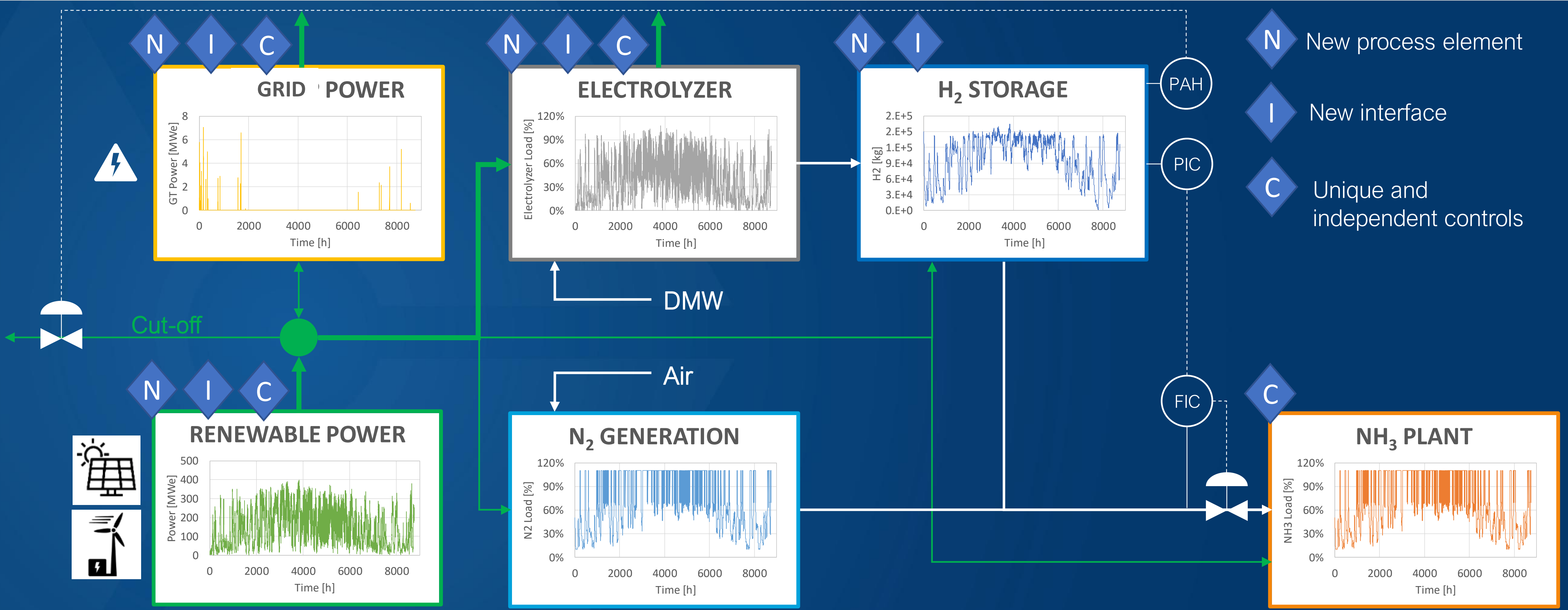
Plantwide control system embraces conventional elements & newcomers



N New process element

I New interface

C Unique and independent controls

Intermittency of renewables imposes ammonia loop to be more flexible, process to suffer from operational discontinuities and impairs levelized cost of ammonia (LCOA)

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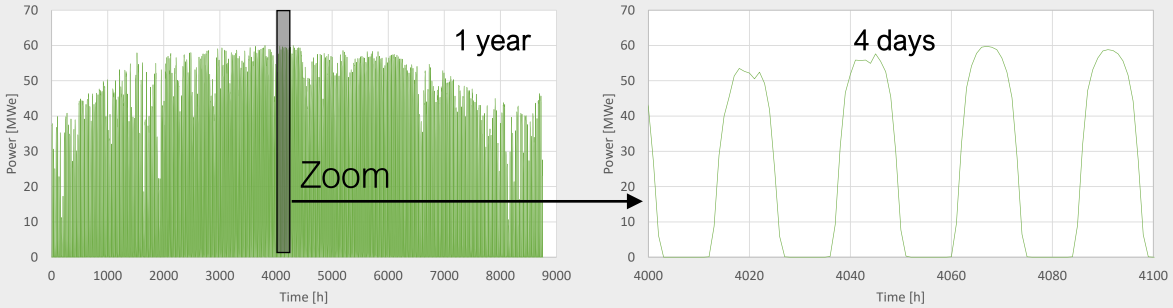
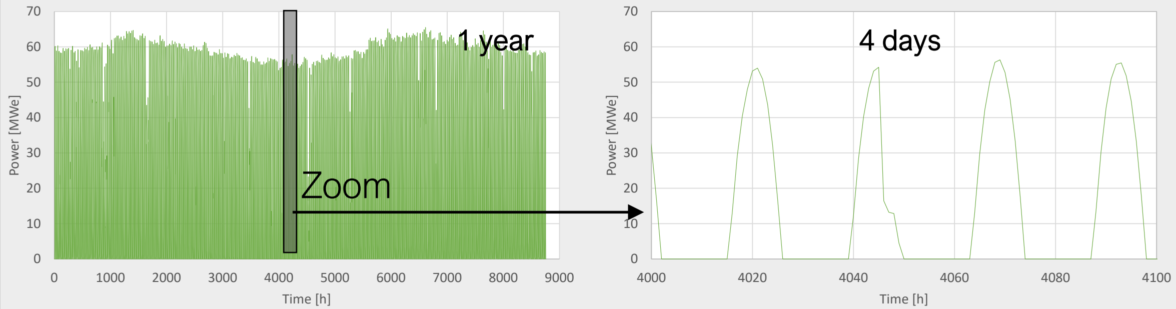
Employing real power profiles to capture their impact on the green ammonia

Solar PV in US



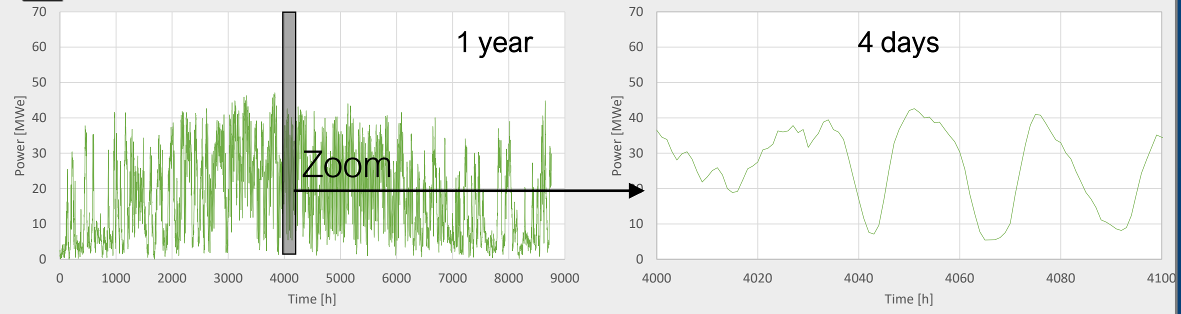
Capacity Factor Peak / average power = 30%
Very high «seasonal» variation of peak power.

Solar PV in Chile



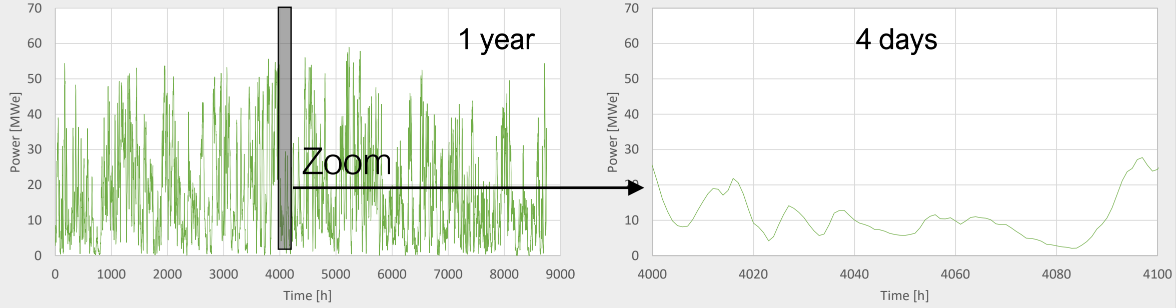
CF = 27%. Even power peaks, moderately «seasonal»

On-shore Wind in US



CF = 38%

On-shore Wind Norden (EU)



CF = 30%

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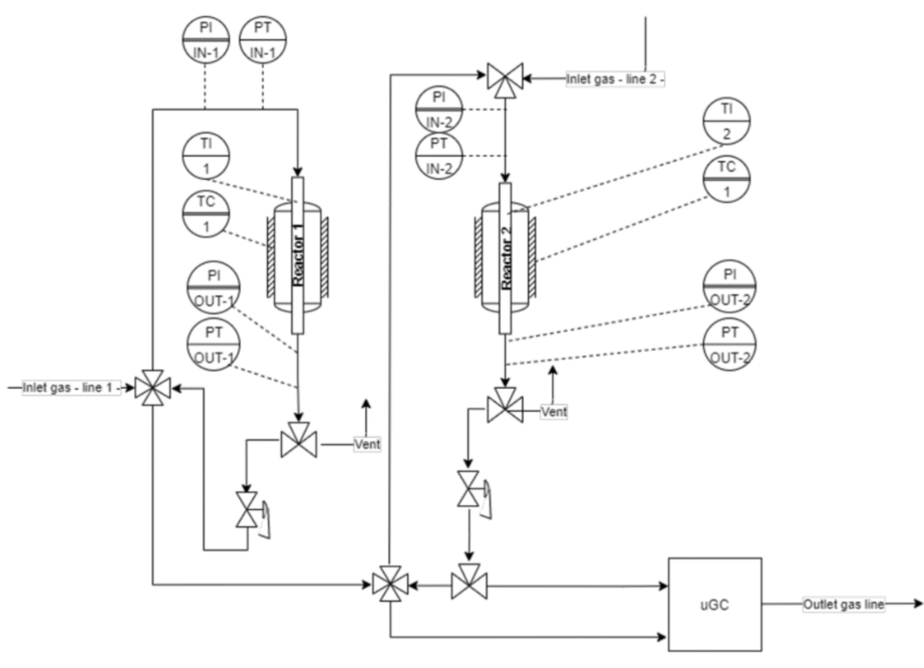
Non-stationary conditions cat tests with novel set-up

- In this work, a novel experimental setup has been implemented to perform a lab scale investigation of the Amomax-Casale catalyst behavior under non-stationary conditions, based on tailor-made experiments.



- This unique solution, with no references in the scientific literature for lab scale applications, is characterized by a custom adiabatic reactor that allows us to evaluate the heat of reaction more effectively.

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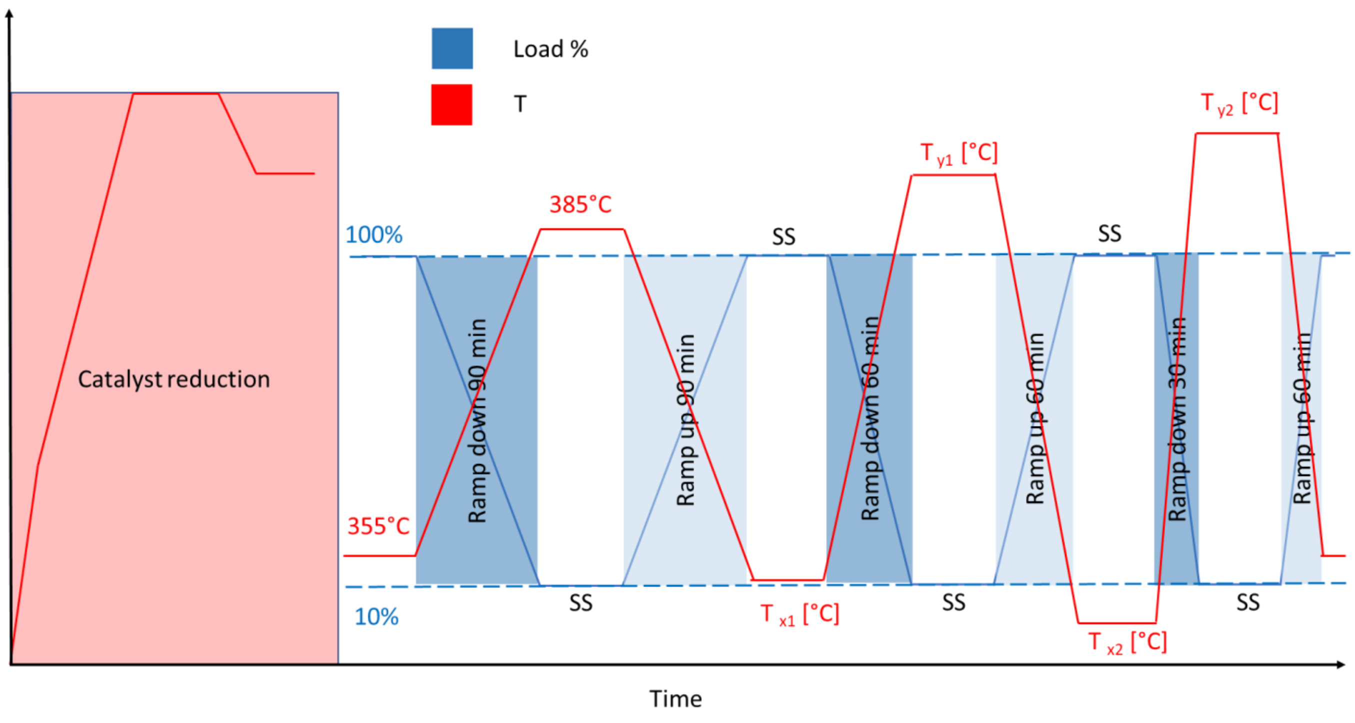
Catalyst testing under conditions of fluctuating renewables



- Sequence of ramp-up and ramp-down stages where inlet gas total flow rate is changed between 10% to 100% of the maximum load capacity with time steps of 90, 60 and 30 min.
- Inlet gas T (range 300-385°C) and operating P (range 140-70 barg)
- Data analysis of the cycles helped to identify the behaviour of the catalyst in non-stationary conditions

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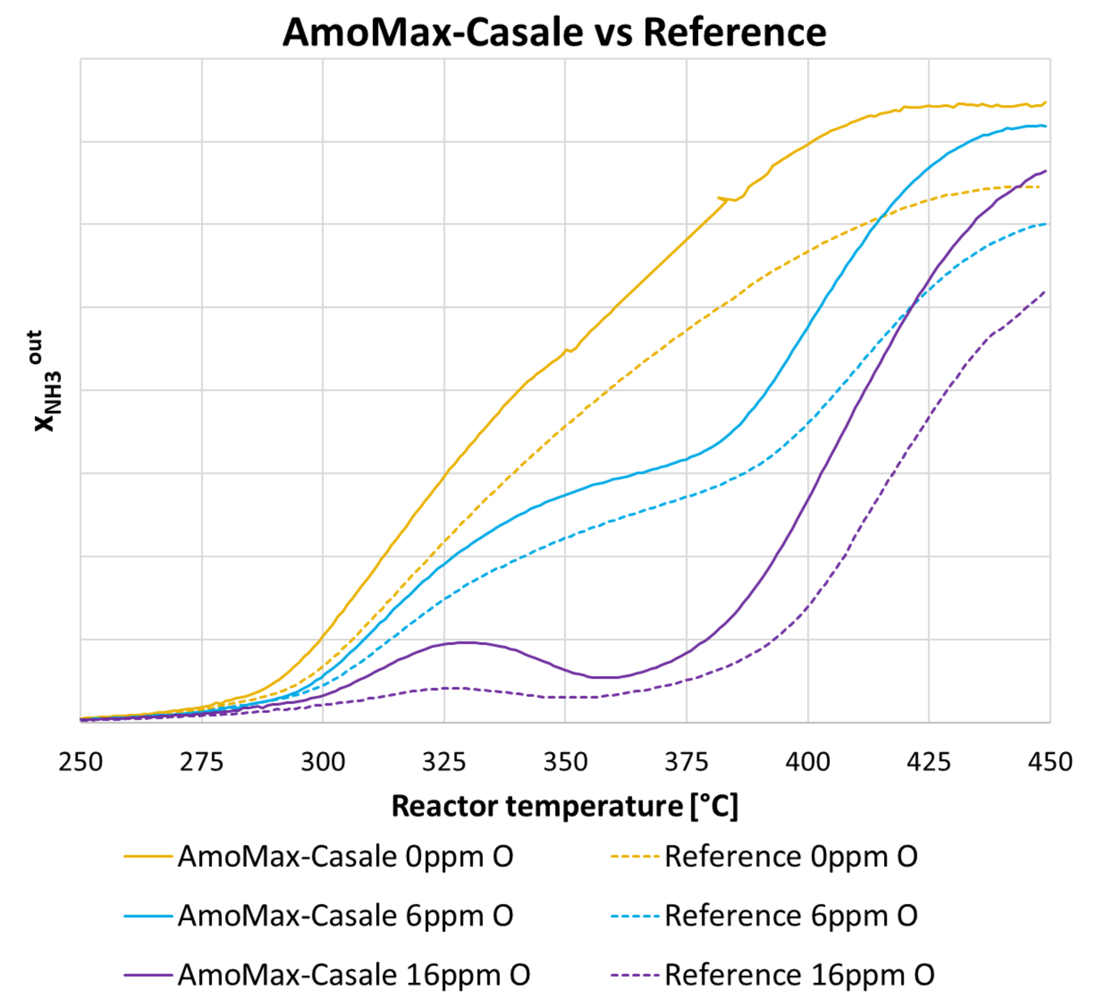
Catalyst testing: performance in poisoning conditions

- The performance with different O_2 concentrations in the feed was tested at different temperatures:
- Oxygen poisoning behavior of new catalyst is similar to reference
- The deactivation observed due to Oxygen poisoning is similar to what is observed in plant
- New catalyst offers superior performance regardless of oxygen concentration



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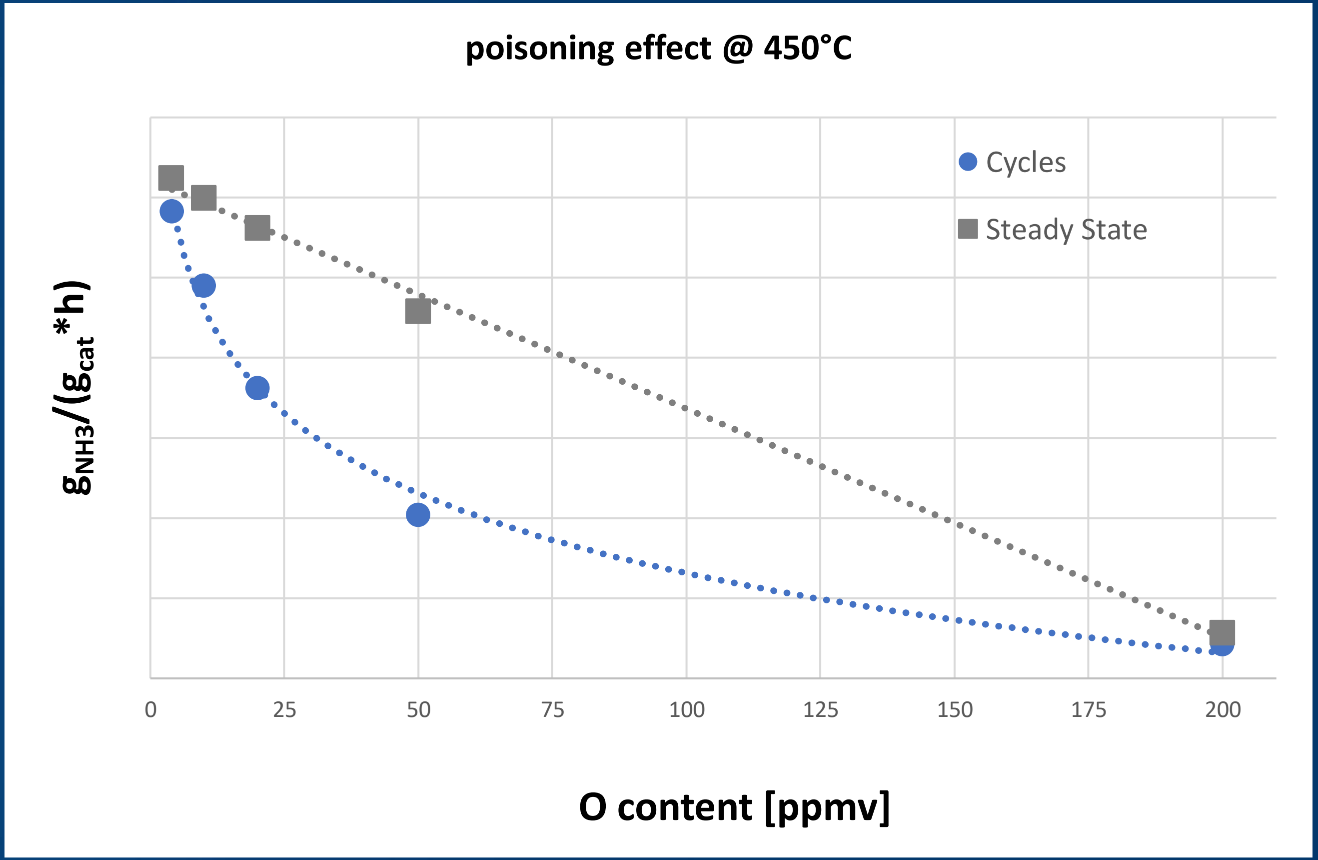
Multiple cycle series and oxygen poisoning effect

- Cycles: T =250°C-450°C @ 3°C/min and back, GHSV = 20’000 h^{-1}, H/N = 3, P = 100 bar.
- Steady State @ T = 450°C, GHSV = 20’000 h^{-1}, H/N = 3, P = 100 bar.

- Ammonia production at the end of each ramp up stage (10 min of steady state) is lower than values achieved after long-lasting single steady state stages (500 min steady).



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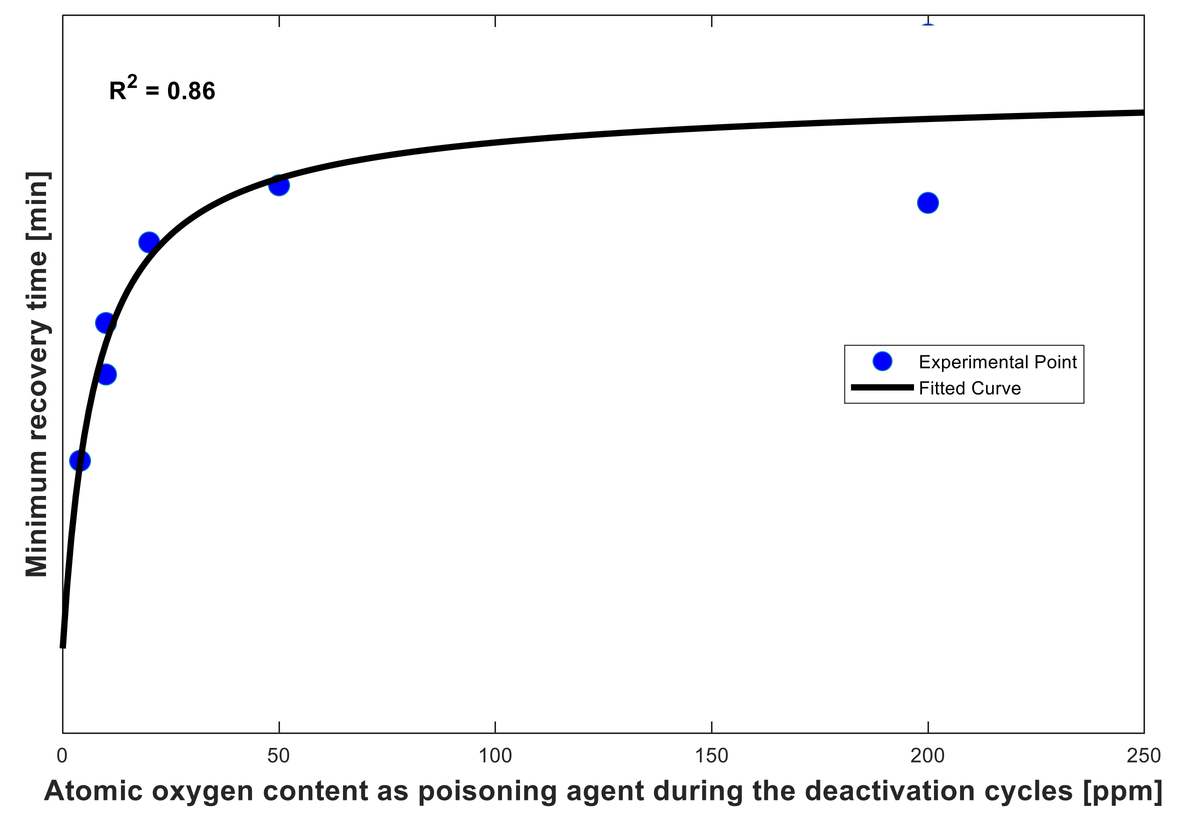
Amomax-Casale: Analysis of the recovery stages

- Cycles: T =250°C-450°C @ 3°C/min and back, GHSV = 20’000 h^{-1}, H/N = 3, P = 100 bar.
- After every multiple cycle sequence under poisoning conditions, to check if the catalyst can restore the initial activity, a steady state stage @ T = 400°C and clean feed is made
- A treatment with a clean syngas feed @ 450°C for minimum 7 hours always restores the initial catalyst activity.



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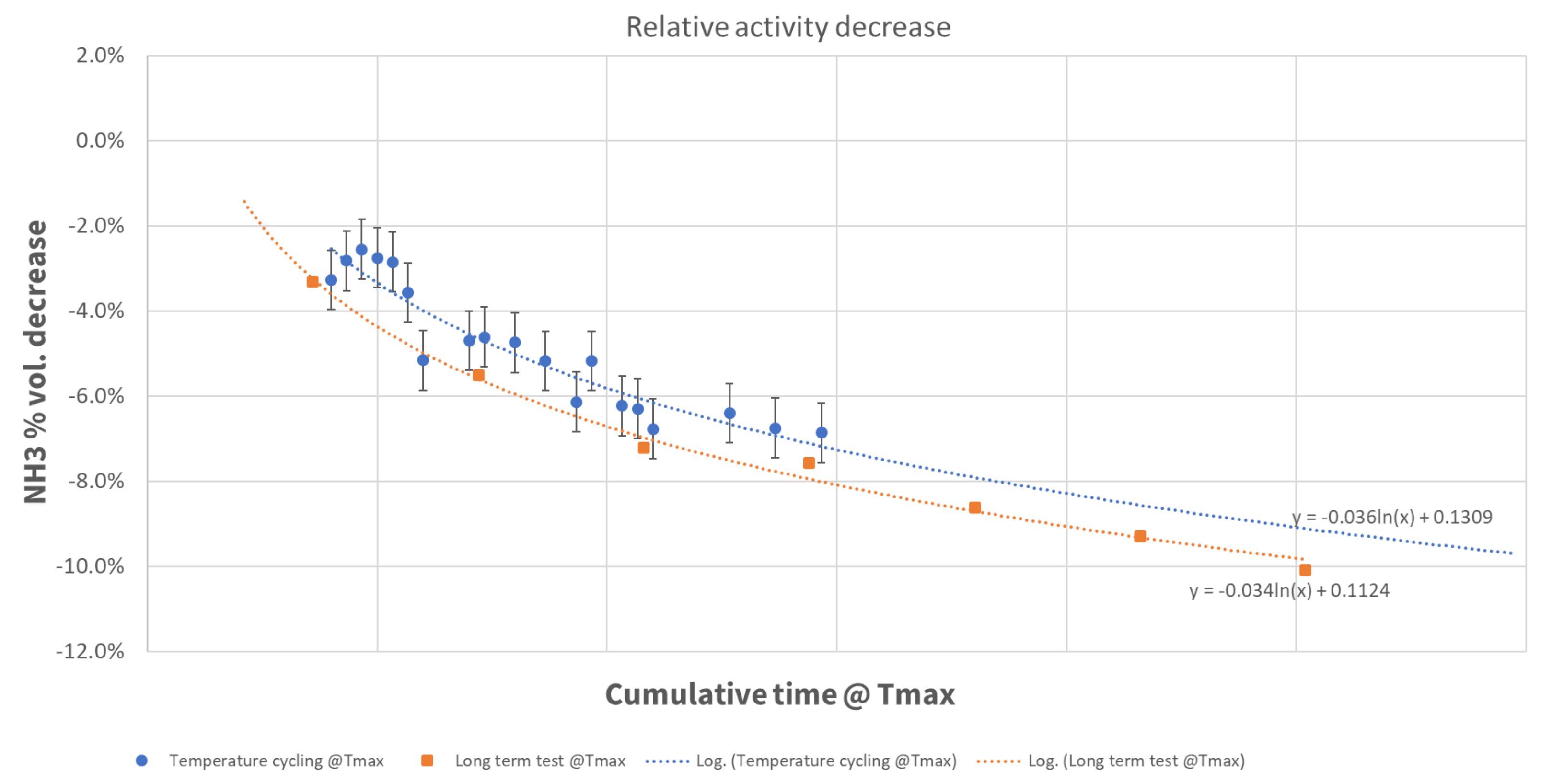
Amomax-Casale: cycling vs cumulative time deactivation

- The plot in the figure reports the decrease of NH_3 vol. % in the experiments executed with:
- temperature cycles (blue)
- long-term stability (exposures for X hours at the desired temperature, orange).

- The overall cycles made continuously with the Tmax selected were more than 600:



The data obtained during the cycling tests and steady state in clean conditions for the Amomax-Casale are aligned: it can be observed that the velocity of catalyst deactivation is equal.

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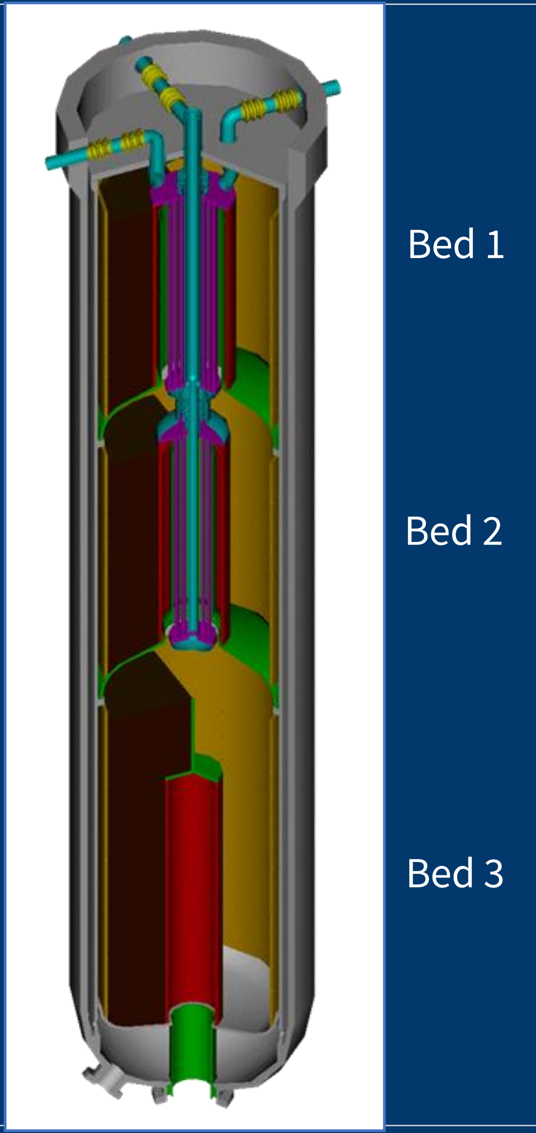
Implementation on reactor design and process configuration

REACTOR DESIGN AND CONFIGURATION

- Casale’s reactor design was tailor made for green ammonia conditions in order to overcome the challenges listed above. Experimental data helped to understand the issues of the catalyst and the strategies to maximize its performances:
  - → Risk reduction of reaction switch-off
  - → Maximization of ammonia production

PROCESS SIMULATION

- Different configurations were tested to determine the optimal reactor design and conditions to run the new catalyst
- The best configurations with the AmoMax®-Casale were found and were used to optimize the control policies of the reactor:
  - → Higher resilience to load fluctuations
  - → Reduction of potential mechanical damage



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SUMMARY

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Summary

- Ammonia Synthesis is a multidisciplinary and evolving topic
- What we have learned?
- What we bring home?
- What we need to do in the future?

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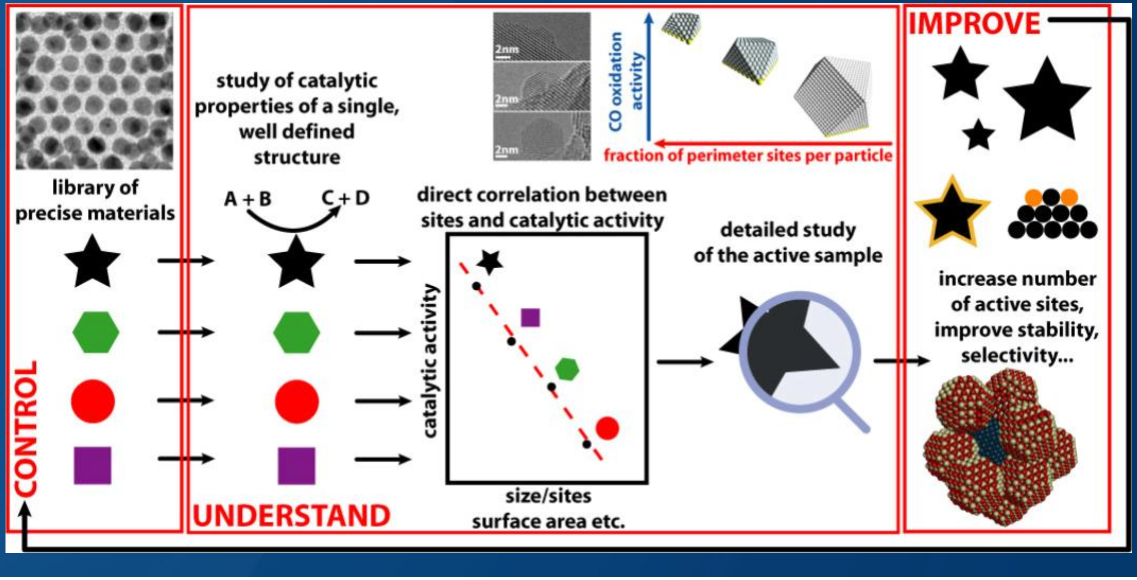
Ammonia Synthesis Now

Research in Ammonia Synthesis in 1913…and NOW…

- "[...]large-scale technical production [of ammonia] would not have been possible without the availability of large quantities of a cheap catalyst. [...] This task could be solved successfully by Alwin Mittasch who in thousands of tests found that a material [...] exhibited satisfactory activity." Gerhard Ertl, Nobel Lecture, Angew. Chem. Int. Ed. 2008, 47, 3524



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We need to understand the basis

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Thanks for your attention

PIERDOMENICO BIASI *p.biasi@casale.ch*

CASALE

PLANTS FOR
A NEW PLANET.
SINCE 1921.