Developing A Nanotechnology To Support Green Ammonia Production

Associate Professor Franck Natali
School of Chemical and Physical Sciences
Te Herenga Waka—Victoria University of Wellington

WEDNESDAY SEPTEMBER 6, 6:00PM – 7:00PM

THE FIVE CLIMATE GRAND CHALLENGES

FROM 51 BILLION TONS PER YEAR TO ZERO

MANUFACTURING: 30%

How We Make Things

AGRICULTURE: 21%

How We Grow Things

TRANSPORTATION: 16%

How We Get Around

BUILDINGS: 7%

How We Live

ELECTRICITY: 26%

How We Plug In

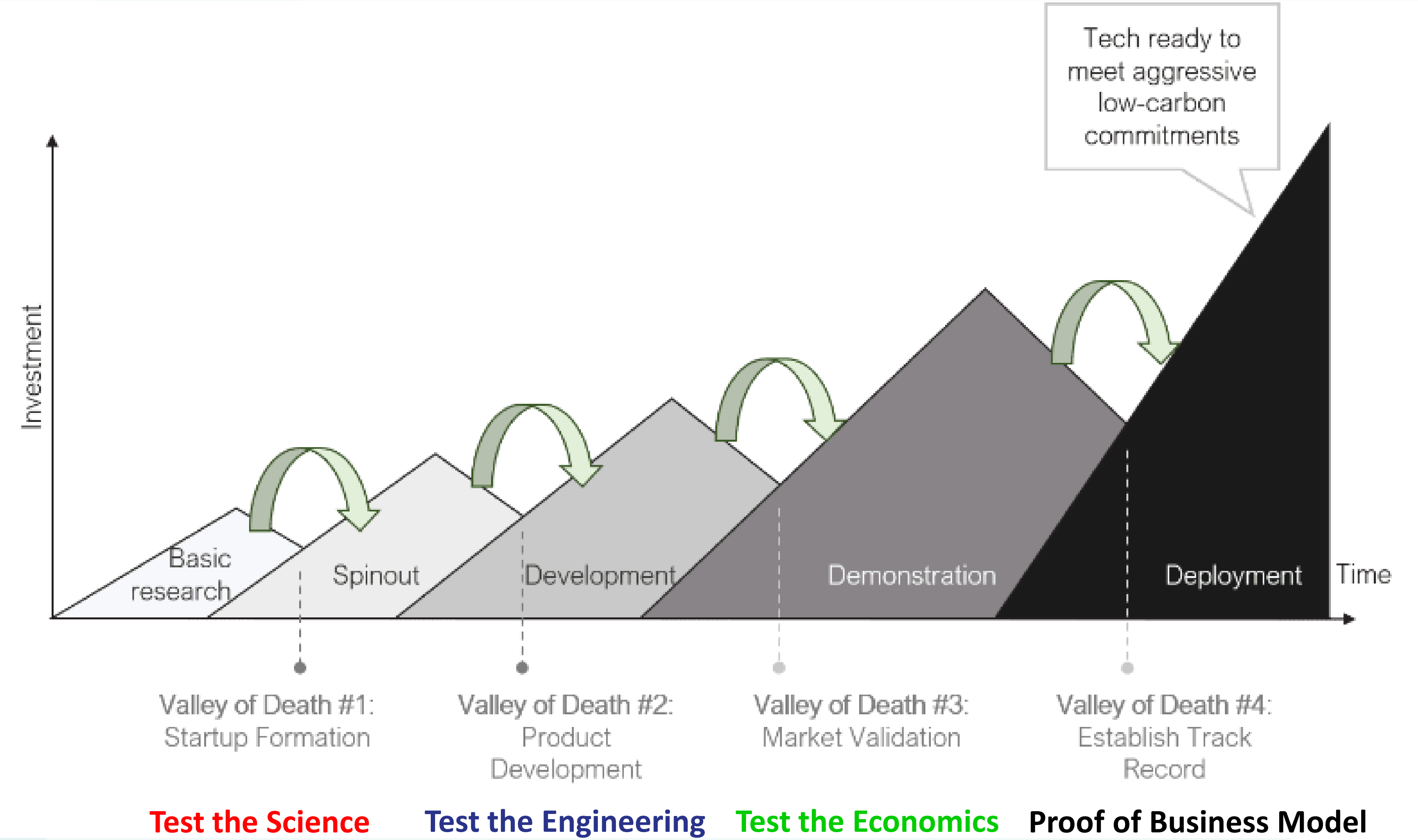
Courtesy of Breakthrough Energy Program

HEAVY INDUSTRY MANUFACTURING

FROM 51 BILLION TONS PER YEAR TO ZERO

HEAVY INDUSTRY MANUFACTURING

LIFECYCLE OF CLIMATE-TECHNOLOGY



Source: Third Derivative and breakthrough Energy Business Fellows Harshita Venkadesh

HEAVY INDUSTRY MANUFACTURING

FROM 51 BILLION TONS PER YEAR TO ZERO

HEAVY INDUSTRY MANUFACTURING

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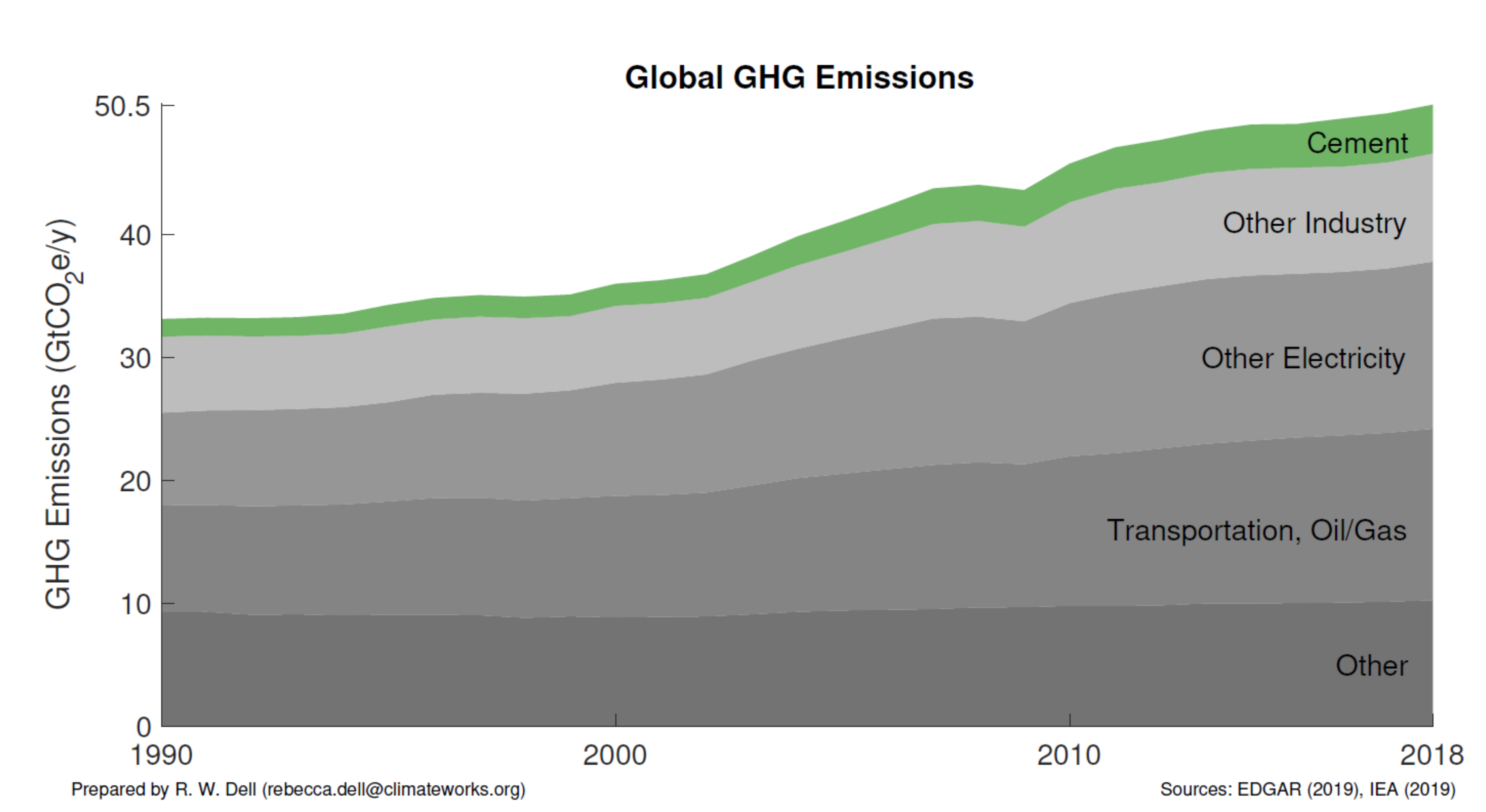
FIRST EXAMPLE: CEMENT

HEAVY INDUSTRY MANUFACTURING

CEMENT

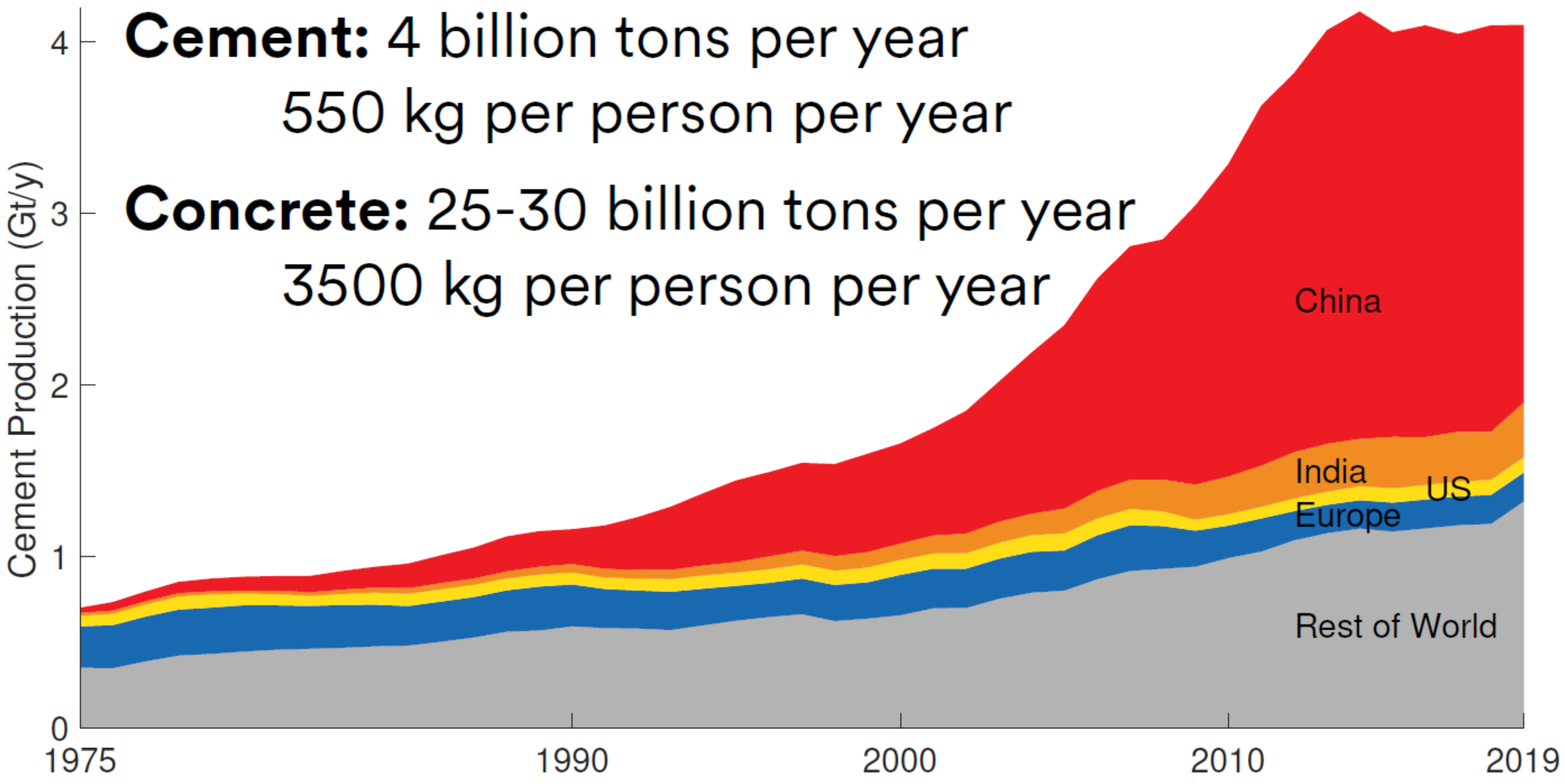
Cement is responsible for about 7% of greenhouse gas emissions.



HEAVY INDUSTRY MANUFACTURING

CEMENT

That’s because we use an astonishing amount of it!

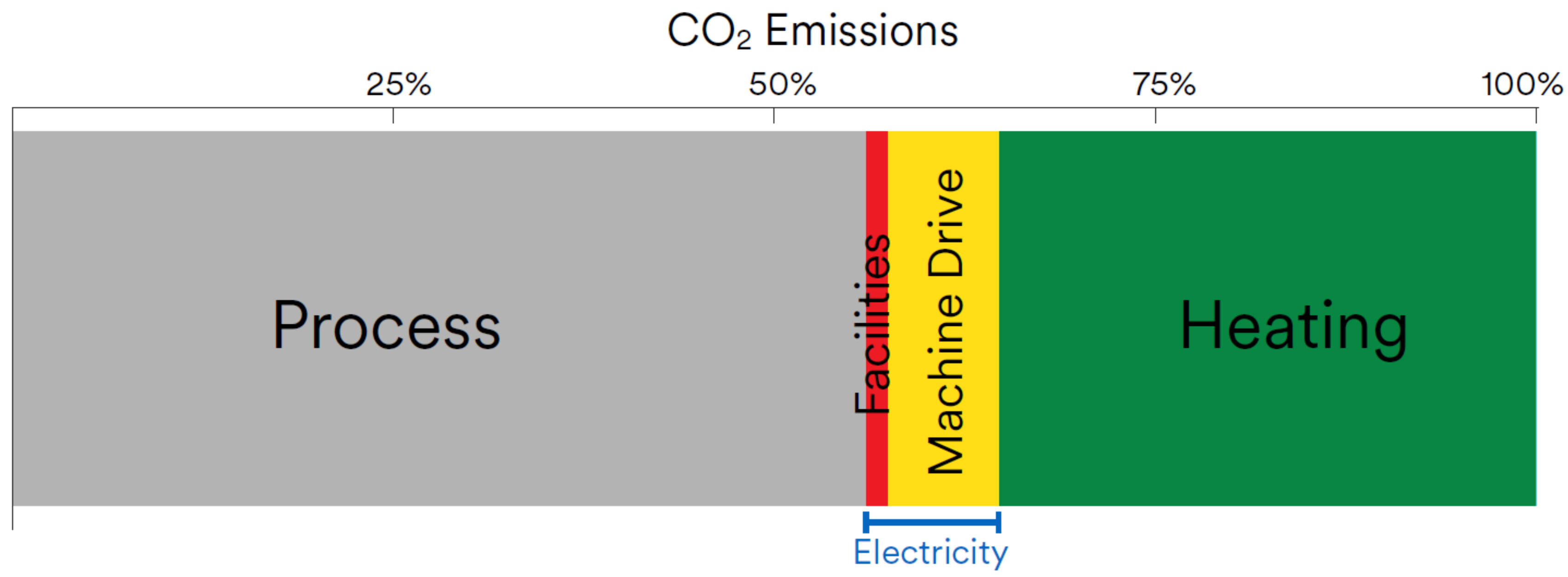


Source: USGS (2021)

HEAVY INDUSTRY MANUFACTURING

CEMENT

Producing cement emits nearly 1 ton CO_2 for each ton of cement!



$$CaCO_3 + heat \rightarrow CaO + CO_2$$

$CaCO_3$ =calcium carbonate (Limestone)

CaO = calcium oxide (Cement)

HEAVY INDUSTRY MANUFACTURING

CEMENT

Cement is extremely cheap!

HEAVY INDUSTRY MANUFACTURING

FROM 51 BILLION TONS PER YEAR TO ZERO

SECOND EXAMPLE: AMMONIA

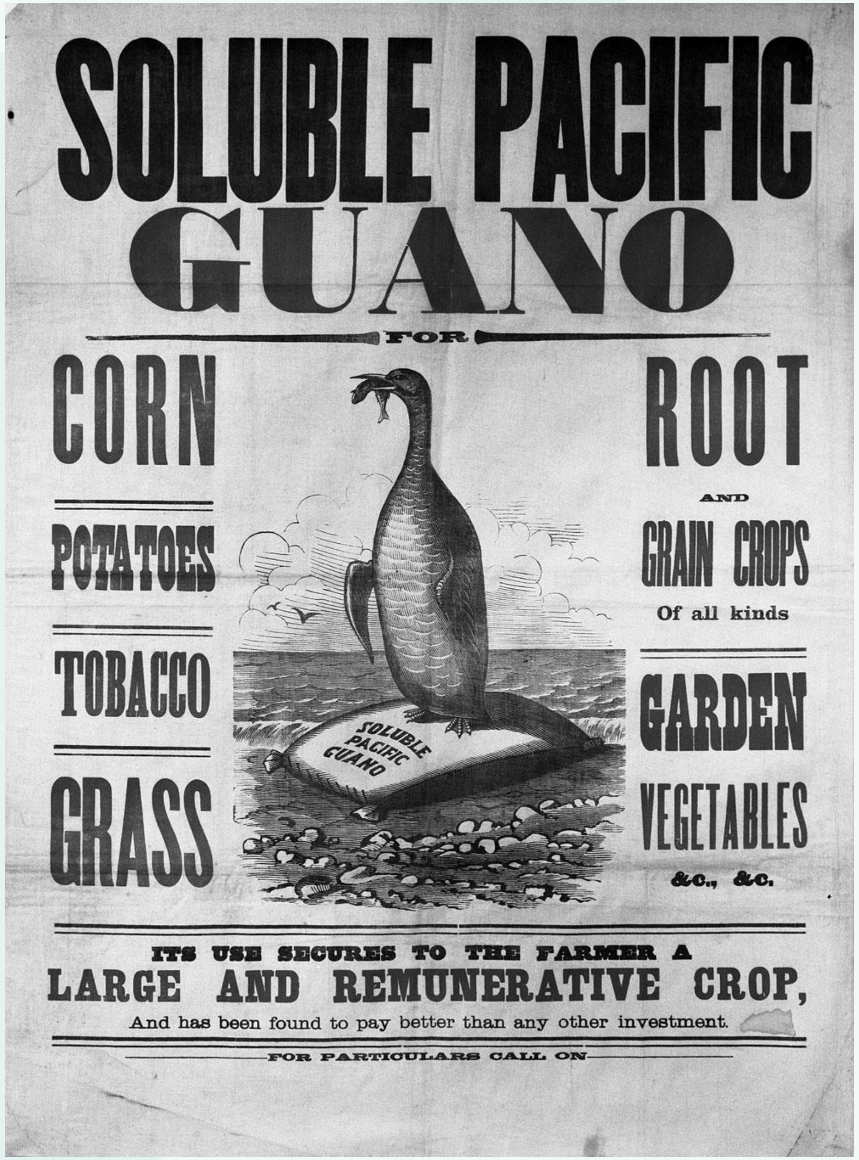
HEAVY INDUSTRY MANUFACTURING

AMMONIA=FERTILISERS

Tractor applying conventional anhydrous ammonia fertilizer on a field (US)

HEAVY INDUSTRY MANUFACTURING

BEFORE AMMONIA-BASED FERTILISERS: GUANO

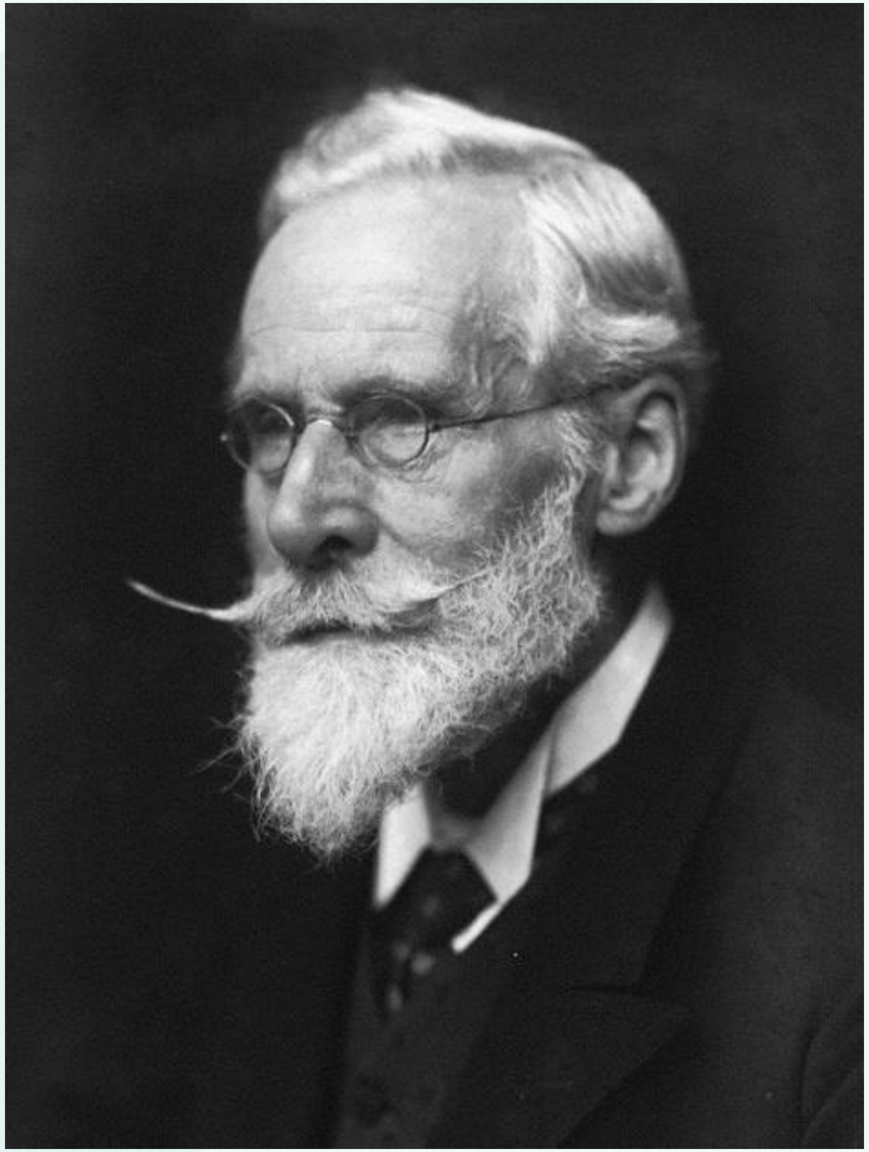


More Precious than Gold: The Story of the Peruvian Guano Trade by David Hollett

~1840-1880: Seabird excrement imported from Chincha Islands

HEAVY INDUSTRY MANUFACTURING

BEFORE AMMONIA-BASED FERTILISERS: LIMITED NATURAL RESSOURCES



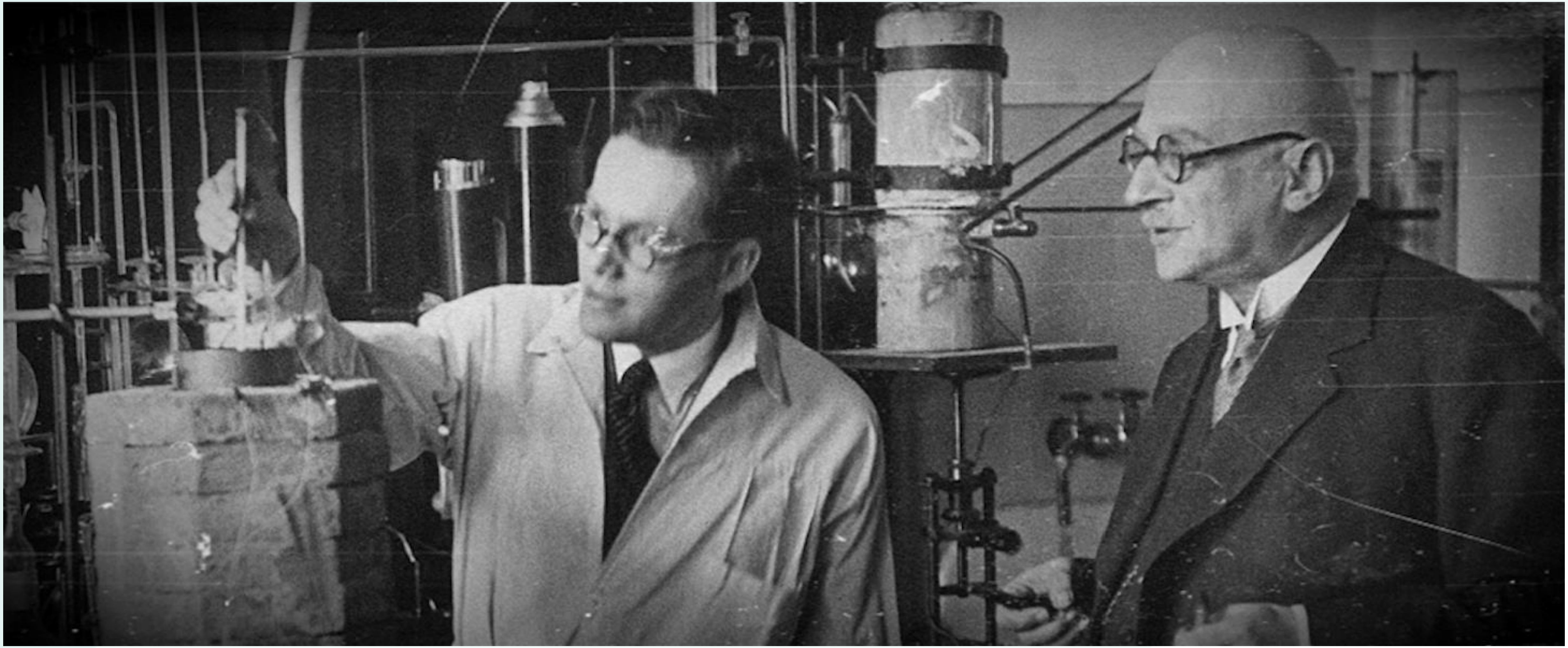
"My chief subject is of interest to the whole world - to every race, to every human being. It is of urgent importance to-day, and it is a life- and -death question for generations to come. I mean the question of food supply. Many of my statements you may think are of the alarmist order; certainly they are depressing, but they are founded on stubborn facts. They show that England and all civilized nations stand in deadly peril of not having enough to eat. As mouths multiply, food resources dwindle. Land is a limited quantity, and the land that will grow wheat is absolutely dependent on difficult and capricious natural phenomena"

Sir William Crookes, Bristol, 1898.
President of the British Academy of Sciences

HEAVY INDUSTRY MANUFACTURING

AMMONIA: SYNTHETIC FERTILISERS

Haber-Bosch: ammonia production process (1920-1930)



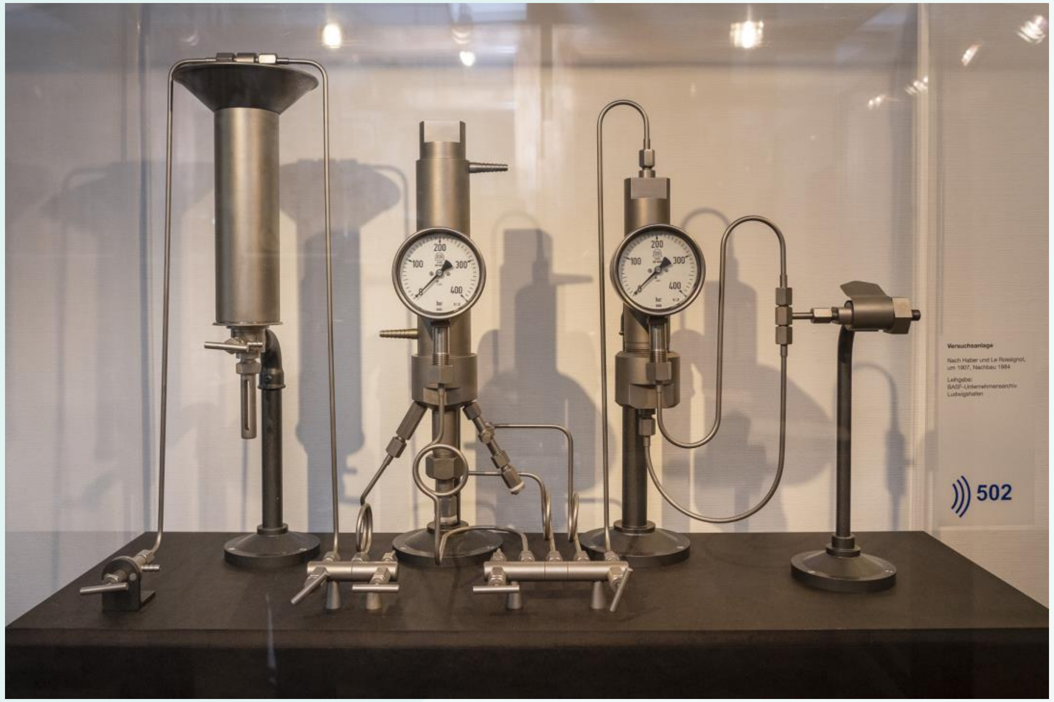
HEAVY INDUSTRY MANUFACTURING

AMMONIA: SYNTHETIC FERTILISERS

Haber-Bosch process

"Of all the century's technological marvels, the Haber-Bosch process has made the most difference to our survival" Vaclav Smil

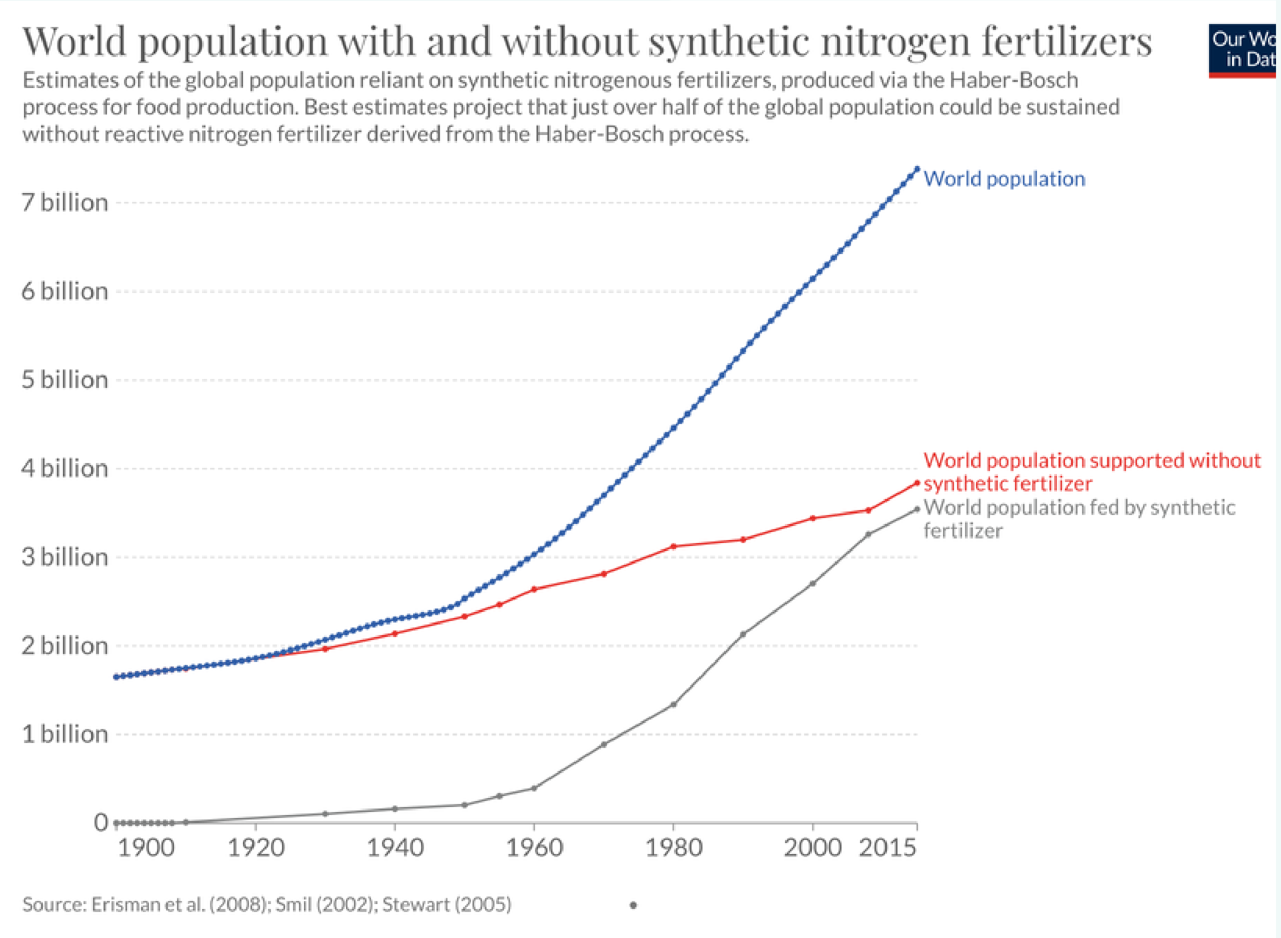
~1920 – Tea spoon of ammonia per day



~2000 – >> 5000 tonnes of ammonia per day

HEAVY INDUSTRY MANUFACTURING

AMMONIA: SYNTHETIC FERTILISERS



Major types of nitrogen-based fertiliser with % nitrogen content:

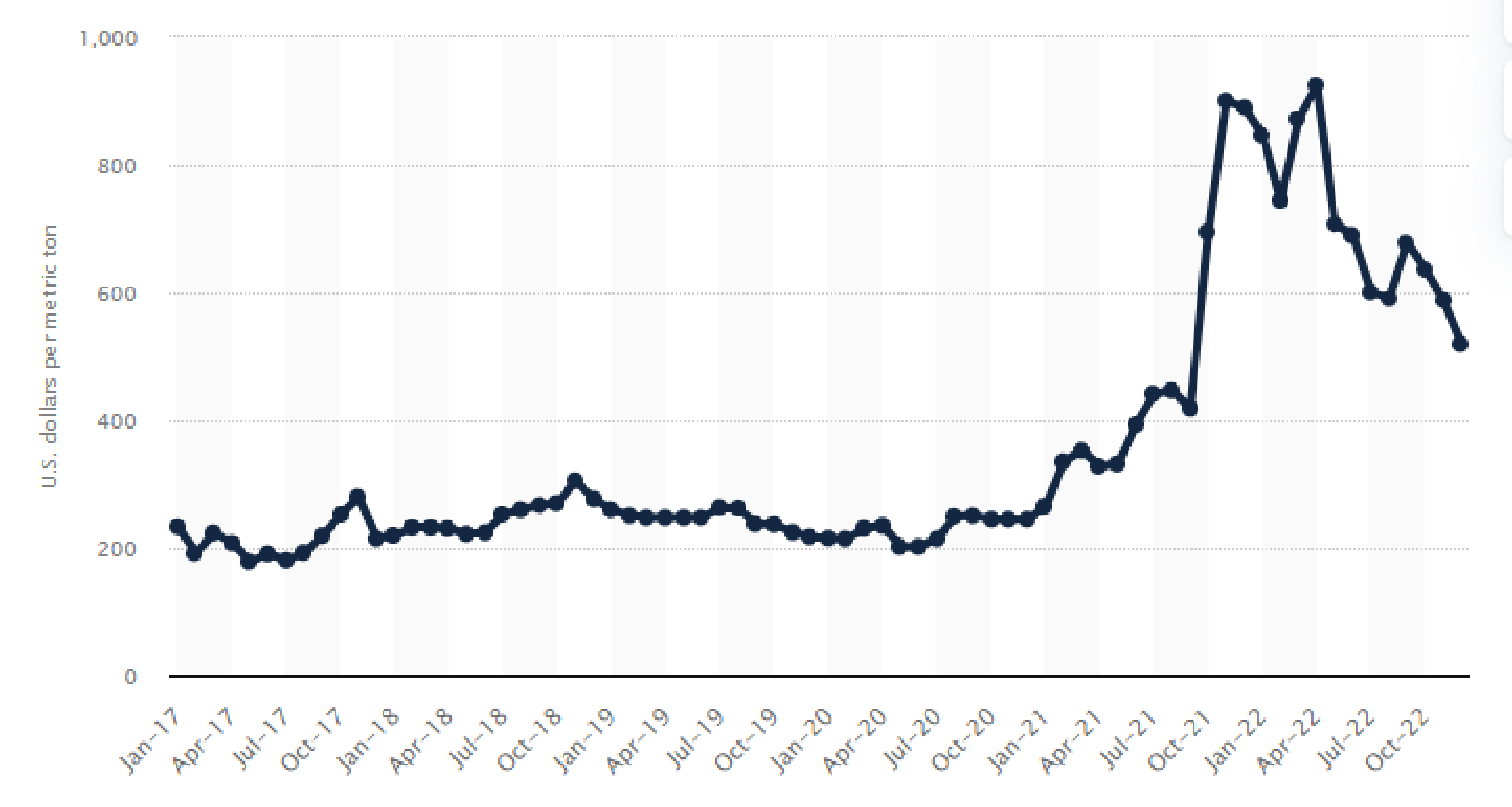
- Urea (46%), anhydrous ammonia (82%), ammonium nitrate (34%), ammonium sulfate (21%), nitrogen solutions (30%), diammonium phosphate (18%).
- Choice is function of cost and equipment available.
- Most common globally is urea.
- Manure (~1% N). Poultry manure has highest N content

If crop yields would have stayed at 1900 levels, we'd need 10x more land for agriculture than we use today

HEAVY INDUSTRY MANUFACTURING

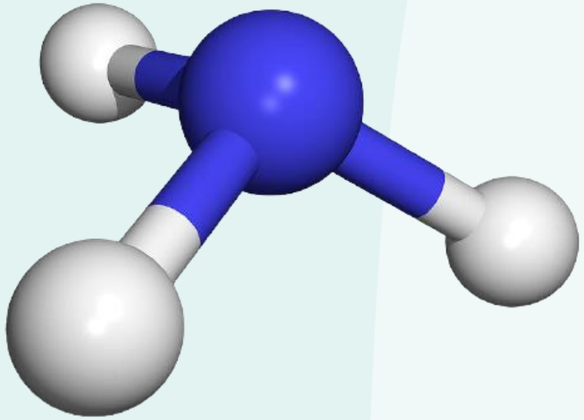
AMMONIA: SYNTHETIC FERTILISERS

Monthly prices of Urea fertilizer worldwide from January 2017 to December 2022



HEAVY INDUSTRY MANUFACTURING

AMMONIA PRODUCTION

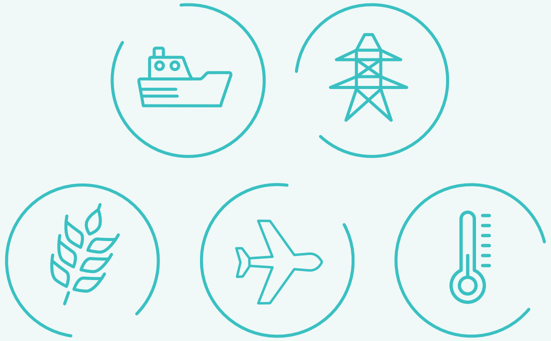


Ammonia: NH_3

↑

$N_2 + H_2$

NH_3 is one of largest chemical processes (Haber-Bosch) on the planet



For every tonne of NH_3 produced, three tonnes of CO_2 are emitted

~ 1 billion tons of CO_2 per year

HEAVY INDUSTRY MANUFACTURING

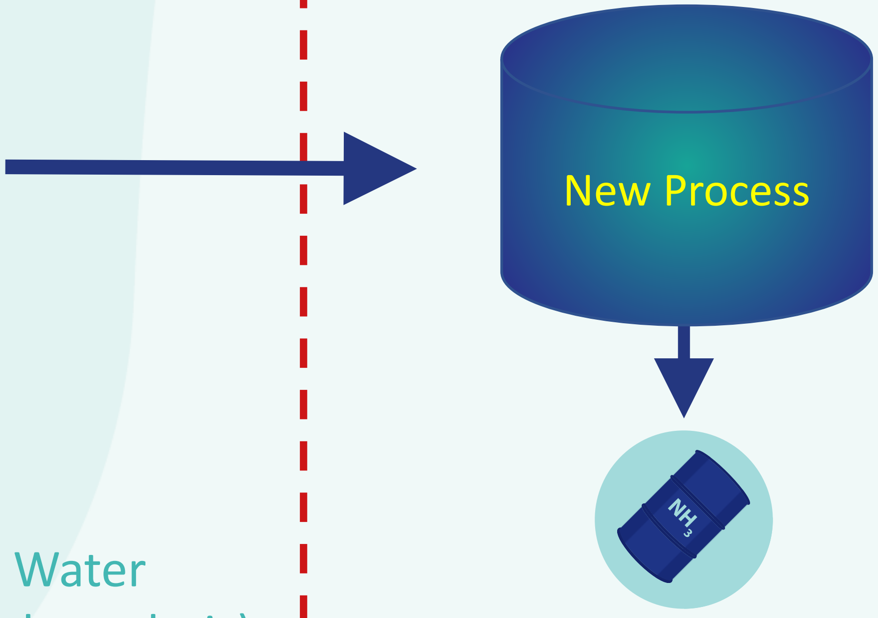
THE GREEN AMMONIA CHALLENGE

Nitrogen From Air

+

Hydrogen from Water
(Renewable energy electrolysis)

NEED Lower temperature
Lower pressure synthesis



$

Catalyst developments

Breaking the N-N bond is very difficult

Haber-Bosch Process Needs:

- Iron or ruthenium catalyst
- T = 400-450 °C
- P = 200-300 atm

Much interest in developing new catalysts to avoid these harsh conditions

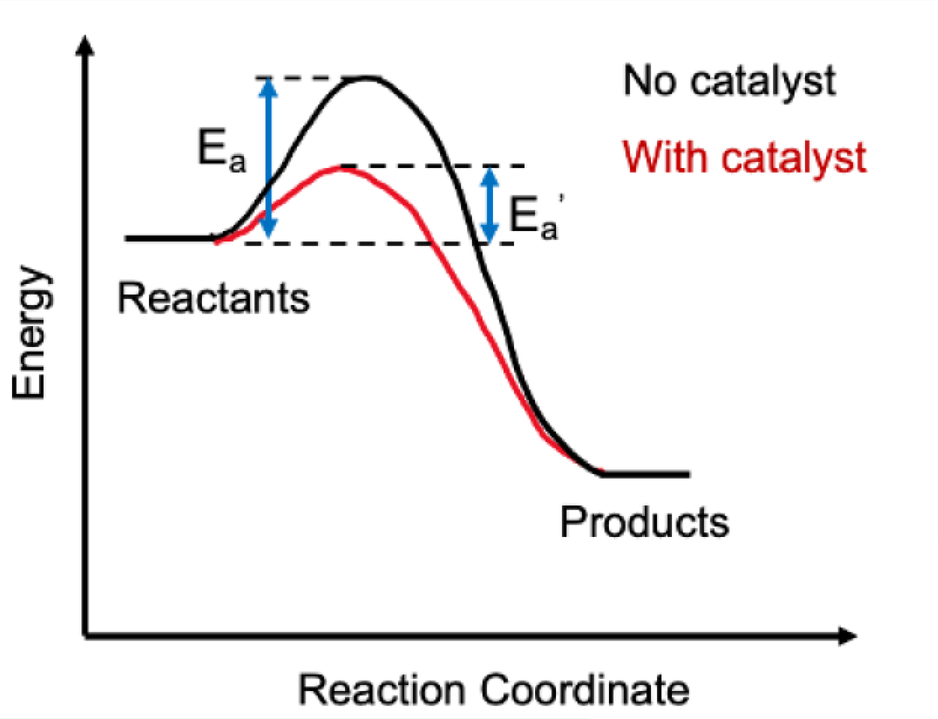
AMMONIA PROCESS AT THE ATOMIC SCALE

THE CATALYST: THE CHALLENGE

Iron catalysts

Role Catalysts

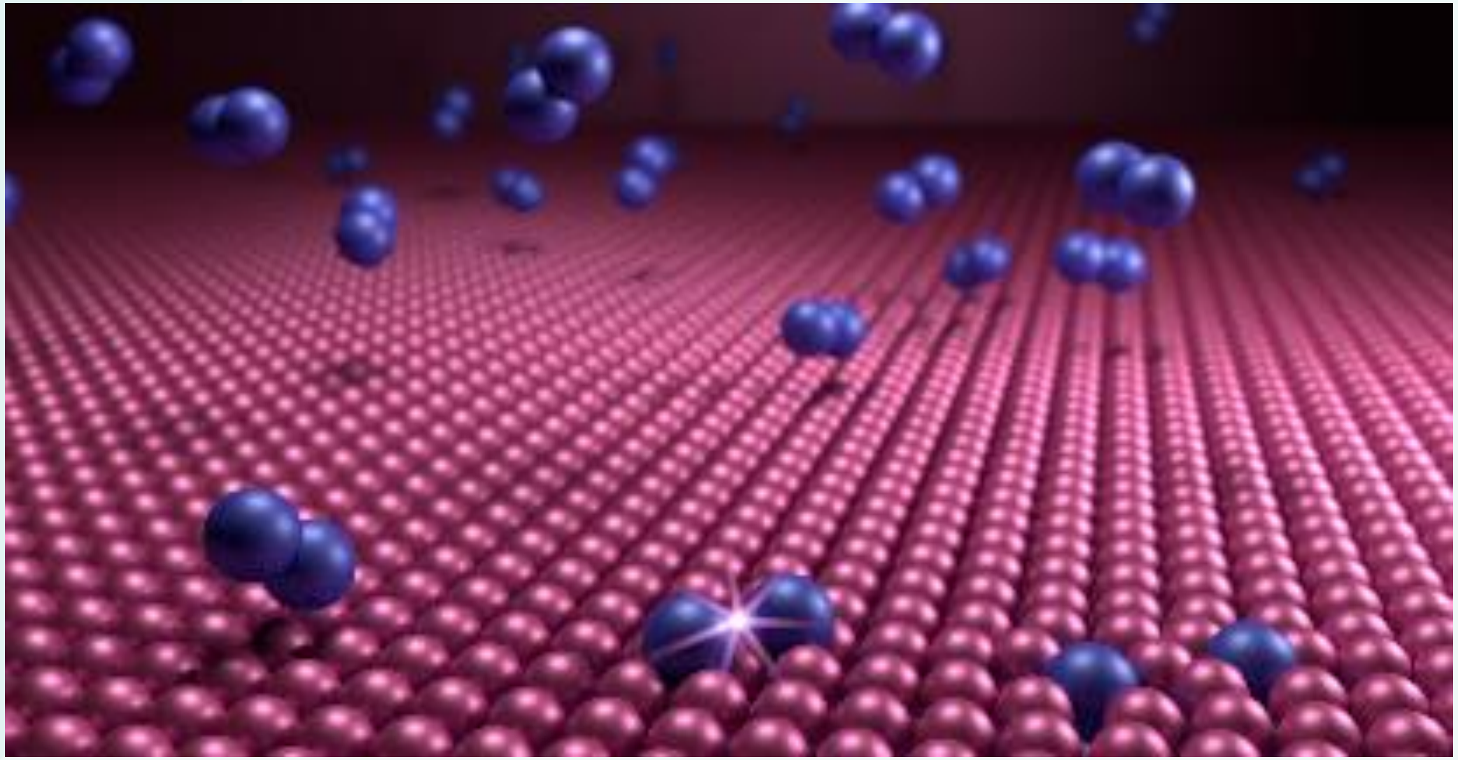
Alternative pathway for the reaction to follow that has that lower activation energy; easier and faster for the reactants (H_2 & N_2) to form the product (NH_3).



AMMONIA PROCESS AT THE ATOMIC SCALE

THE CATALYST: THE CHALLENGE

The Scientific Journey: Find (= fabricate) a material (=catalyst) that can break (=dissociate) molecular nitrogen at mild temperature and pressure



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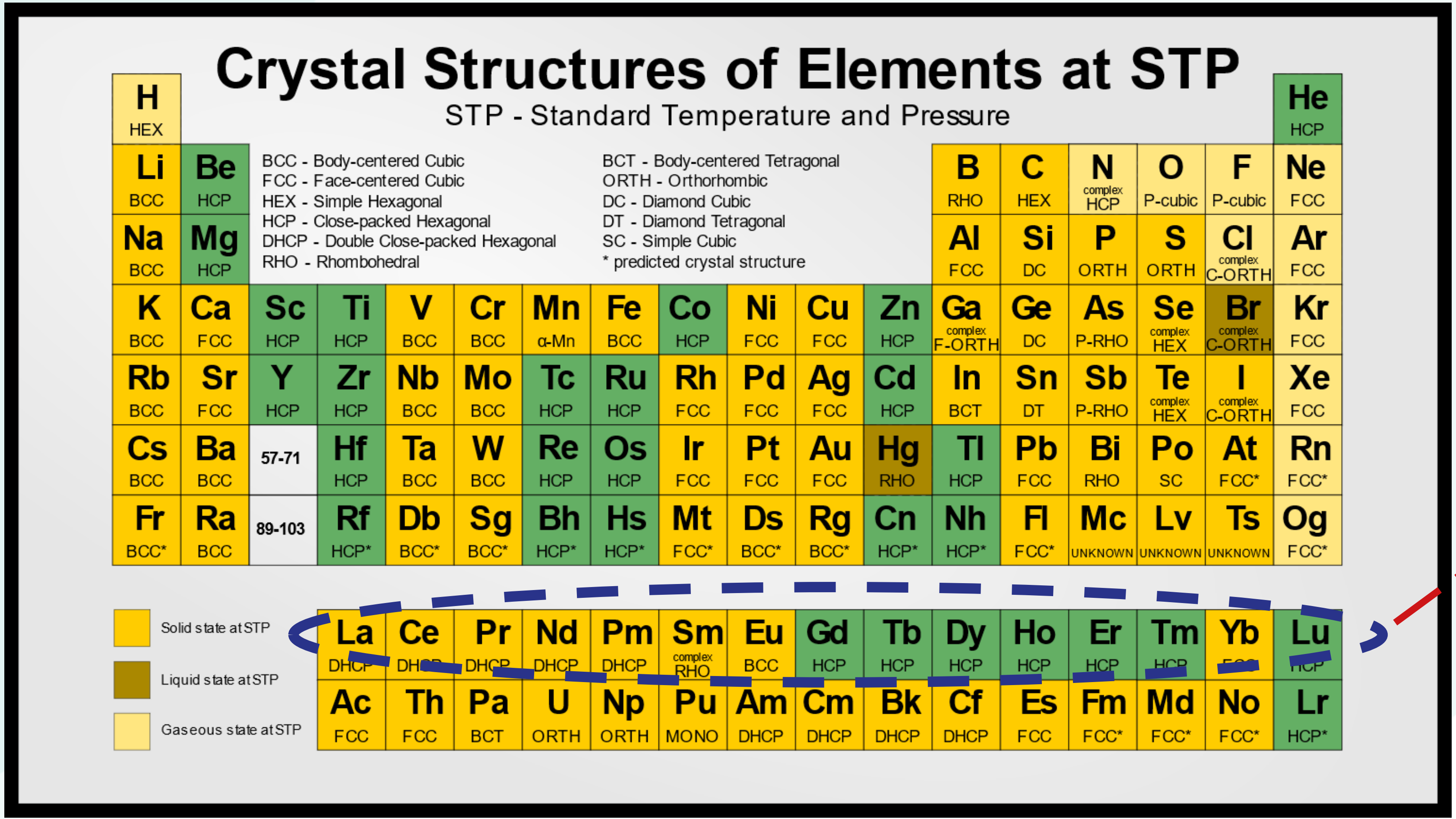


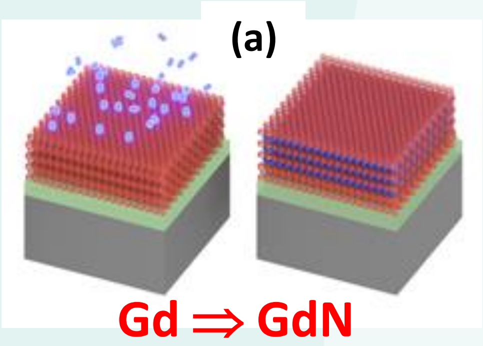
Lanthanide Materials

AMMONIA PROCESS AT THE ATOMIC SCALE

FACILE DISSOCATION OF N_2 BY LANTHANIDE SURFACES

In-situ and real time monitoring of the nitridation of lanthanides - exptl results

- Steps by steps: (2) Exposure to N_2 AND (3) Formation of Gadolinium Nitride surface layer



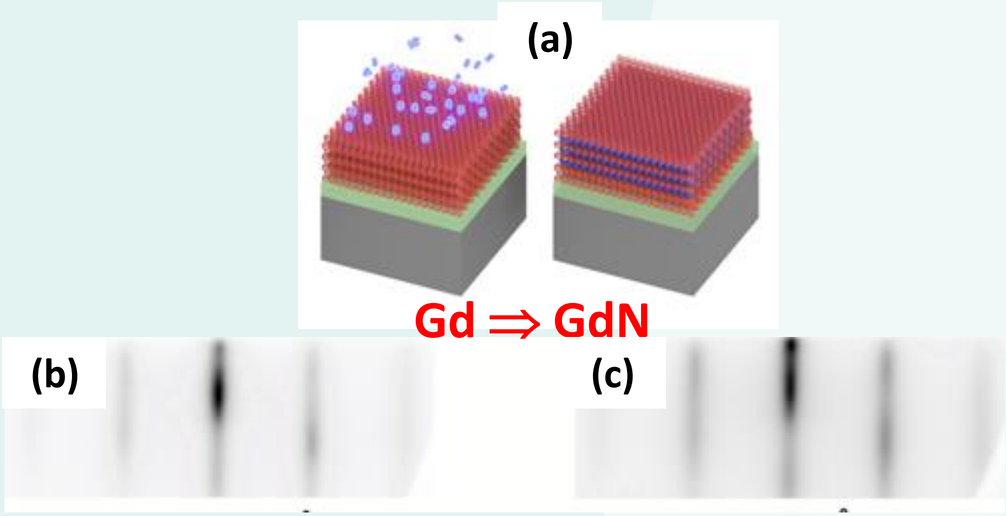
- (a) Exposure of the Gd surface to N_2; at ambient temperature and N_2 partial pressure of 3 x 10^{-5} mBar.

AMMONIA PROCESS AT THE ATOMIC SCALE

FACILE DISSOCATION OF N_2 BY LANTHANIDE SURFACES

In-situ and real time monitoring of the nitridation of lanthanides - exptl results

- Steps by steps: (2) Exposure to N_2 AND (3) Formation of Gadolinium Nitride surface layer



- (a) Exposure of the Gd surface to N_2; at ambient temperature and N_2 partial pressure of 3 x 10^{-5} mBar.
- (b) and (c) RHEED patterns of Gd before (a) and after (c) exposure to N_2.
  Streak spacing increases, indicating a contraction of the surface Gd lattice spacing; a_{GdN} = 3.53 Å.

AMMONIA PROCESS AT THE ATOMIC SCALE

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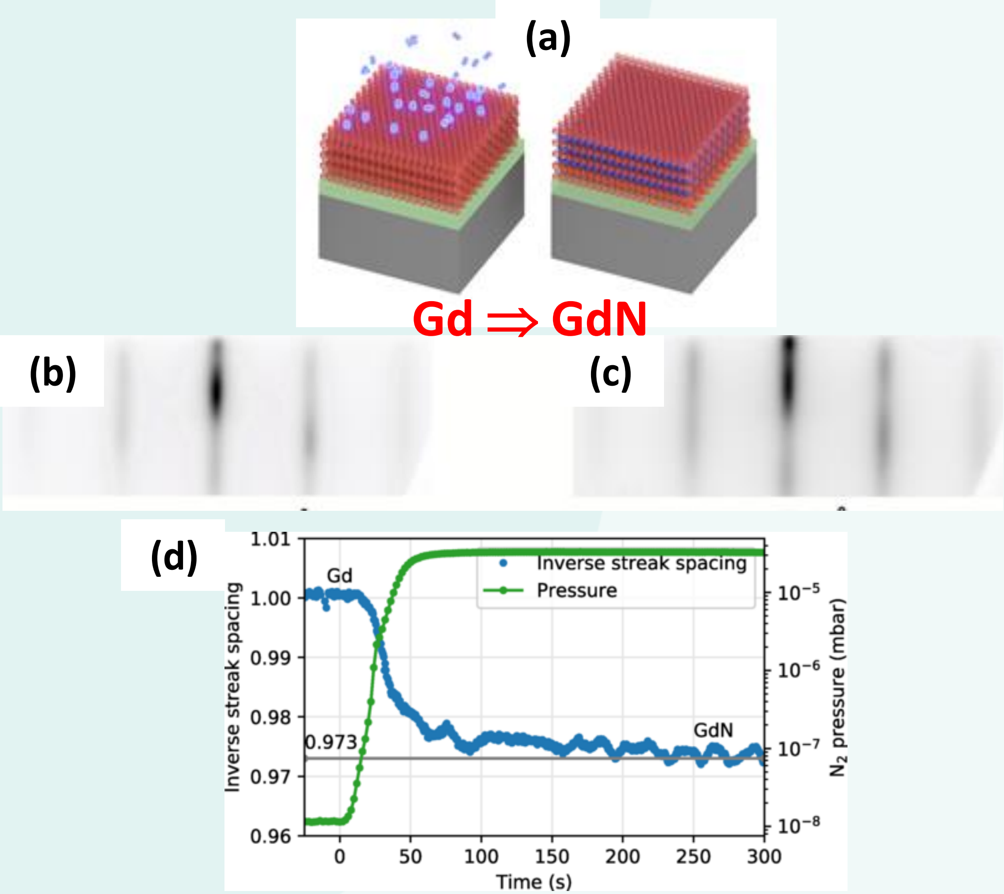
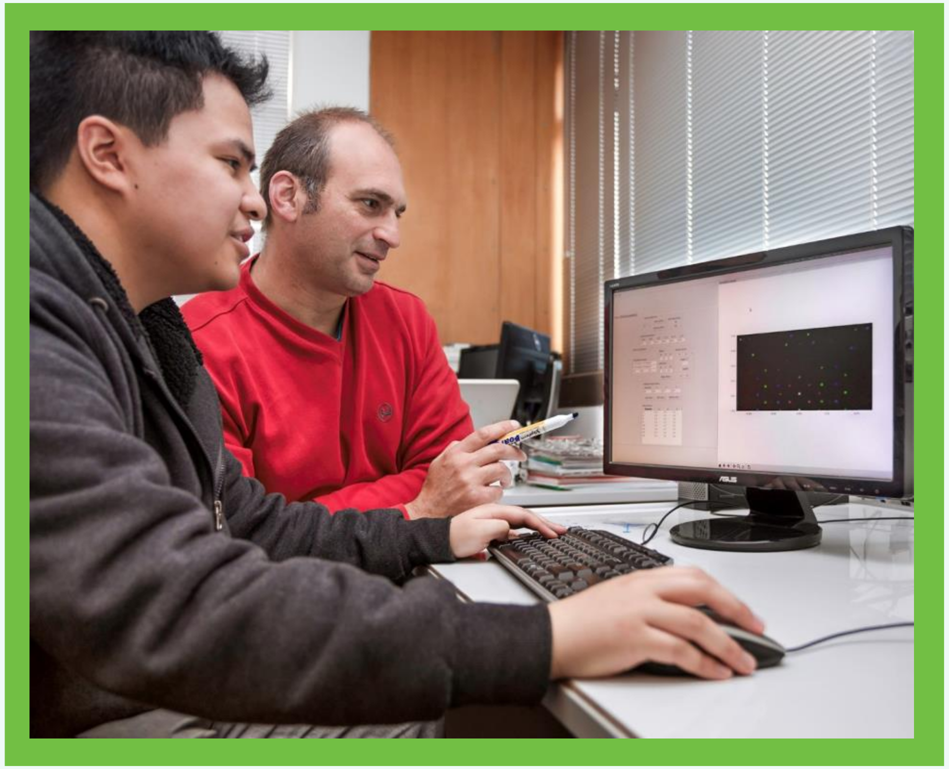


- (a) Exposure of the Gd surface to N_2; at ambient temperature and N_2 partial pressure of 3 x 10^{-5} mBar.
- (b) and (c) RHEED patterns of Gd before (a) and after (c) exposure to N_2.
  Streak spacing increases, indicating a contraction of the surface Gd lattice spacing; a_{GdN} = 3.53 Å.
- (c) full nitridation of the surface within 300 seconds; relatively fast process

AMMONIA PROCESS AT THE ATOMIC SCALE

TUAKANA-TEINA

SUPPORTING & GROWING PHD STUDENTS & SUPERVISORS



"It's been really interesting to work on a project that has real-world application, and to see first-hand how commercialising research can get it out of the lab and into the hands of others where it can make a difference."

JAY CHAN, PHD STUDENT (2014-2018) – Funded Royal Society of New Zealand (Marsden Grant)

Electron diffraction Software Licensed to US-based Company (>X00,00NZD - 2021)

AMMONIA PROCESS AT THE ATOMIC SCALE

TOWARDS AMBIENT TEMPERATURE AMMONIA SYNTHESIS

Ammonia Synthesis – exptl results

PHYSICAL REVIEW MATERIALS **4**, 115003 (2020)

Facile dissociation of molecular nitrogen using lanthanide surfaces: Towards ambient temperature ammonia synthesis

J. R. Chan,[1,*] S. G. Lambie,[2] H. J. Trodahl,[1] D. Lefebvre,[1] M. Le Ster,[3] A. Shaib,[1] F. Ullstad,[1] S. A. Brown,[3] B. J. Ruck,[1] A. L. Garden,[2] and F. Natali[1,†]

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(Received 7 May 2020; revised 22 September 2020; accepted 29 October 2020; published 30 November 2020)

A combined experimental and computational study is reported on a hitherto unrecognised single lanthanide catalyst for the breaking of molecular nitrogen and formation of ammonia at ambient temperature and low pressure. We combine *in situ* electrical conductance and electron diffraction measurements to track the conversion from the lanthanide metals to the insulating lanthanide nitrides. The efficiency of the conversion is then interpreted using DFT+*U* calculations, suggesting a molecular nitrogen dissociation pathway separate from that well established for transition metals. Finally, we show that exposure of the lanthanide surfaces to both molecular nitrogen and hydrogen results in the formation of ammonia.

Bluesky Research To Business Academic

THE JOURNEY

<2020

RESEARCH INTO SEMICONDUCTORS
Quantum computer memory elements

2020

BIG, BUT NOT FOR EVERYONE
Production NH3 at ambient temperature and low pressure

KIWINET PSAF ACCELEARTOR
Ammonia reactor to upscale production

EXTERNAL VALIDATION BY THIRD PARTY OF LIQUIUM'S CATALYST EFFIENCY

2021

BREAKTHROUGH ENERGY FELLOWSHIP
New clean technologies for heavy industries

2022

BEST PRACTICE IN EQUITY STAKES FOR ACADEMIC & UNIVERSITY!

INCORPORATION OF LIQUIUM & $1.5M SEED FUNDING SECURED

"Without BLUESKY research, you only invent what you know"

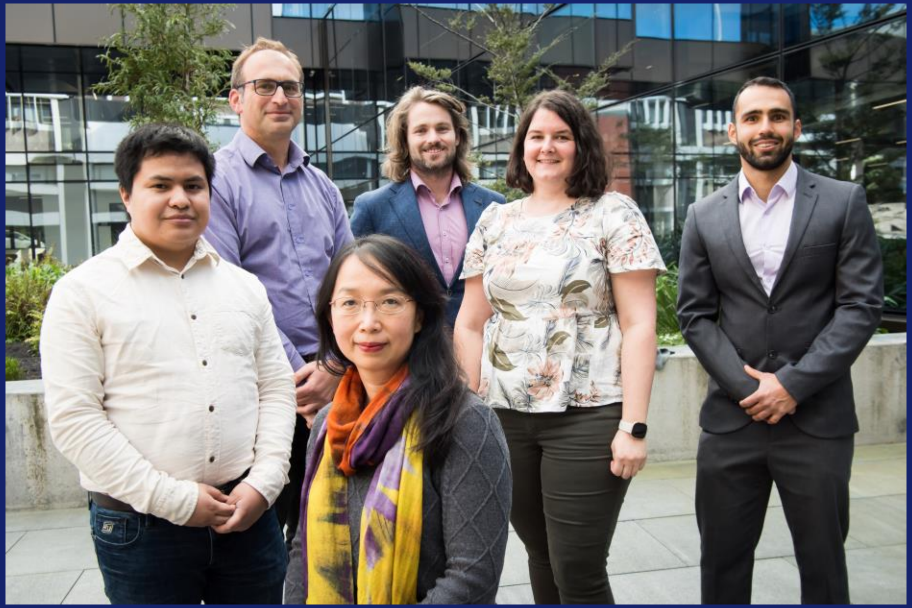
liquium
Clean liquid fuel
for heavy industry

What makes an industrially relevant catalyst?

liquium

Materials showcase

Team showcase



- 5 Graduate Students from Victoria University of Wellington,
- 1 Graduate Student from University of Canterbury, Paul Geraghty (Liquium's CEO),
- Pipeline for graduate students,
- Populating the deep tech sector.

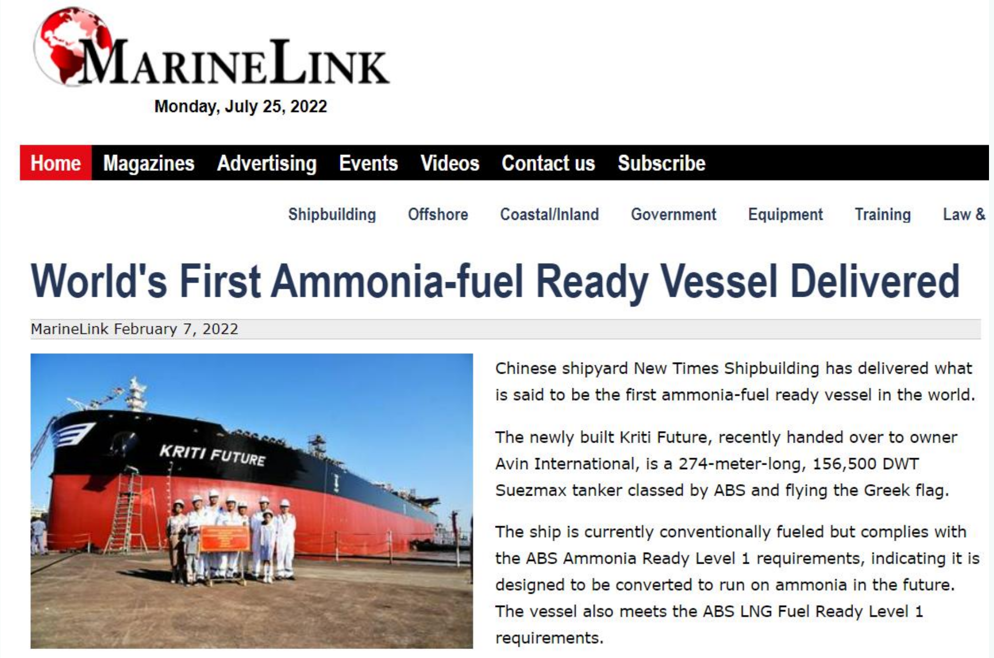
INNOVATION & IMPACT POTENTIAL

MARKET AND END USERS

INNOVATION & IMPACT POTENTIAL

MARKET AND END USERS

Proposed design of the vessel
Image credit: Nihon Shipyard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Monday, July 25, 2022

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World's First Ammonia-fuel Ready Vessel Delivered

MarineLink February 7, 2022

Chinese shipyard New Times Shipbuilding has delivered what is said to be the first ammonia-fuel ready vessel in the world.

The newly built Kriti Future, recently handed over to owner Avin International, is a 274-meter-long, 156,500 DWT Suezmax tanker classed by ABS and flying the Greek flag.

The ship is currently conventionally fueled but complies with the ABS Ammonia Ready Level 1 requirements, indicating it is designed to be converted to run on ammonia in the future. The vessel also meets the ABS LNG Fuel Ready Level 1 requirements.

ACKNOWLEDGEMENTS

"SCIENCE IS PEOPLE" - Alan MacDiarmid Nobel Prize (2000, Chemistry)

"A PLACE WHERE TALENT WANTS TO LIVE" - *(Sir Paul Callaghan)*

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Breakthrough Energy

liquium

the ROYAL SOCIETY of NEW ZEALAND TE APĀRANGI

UNIVERSITY of OTAGO Te Whare Wānanga o Otāgo NEW ZEALAND SAPERE AUDE

MINISTRY OF BUSINESS, INNOVATION & EMPLOYMENT HĪKINA WHAKATUTUKI

KiwiNet

We STILL need to go from 51 Billion tons of emissions per year to Zero