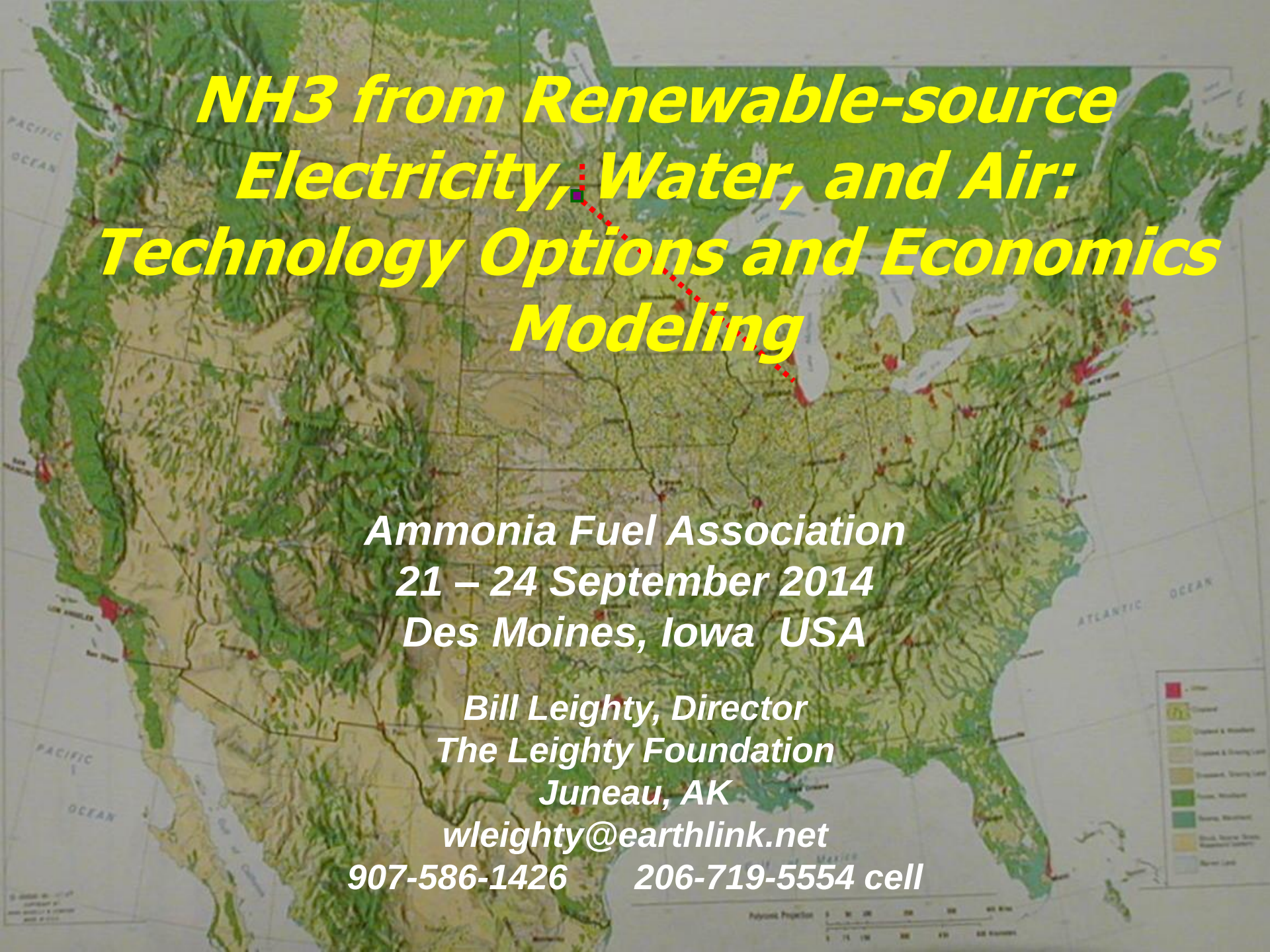


NH3 from Renewable-source Electricity, Water, and Air: Technology Options and Economics Modeling

Ammonia Fuel Association
21 – 24 September 2014
Des Moines, Iowa USA

Bill Leighty, Director
The Leighty Foundation
Juneau, AK
wleighty@earthlink.net
907-586-1426 206-719-5554 cell

Mendenhall Glacier, Juneau, AK

June ‘71

Mendenhall Glacier, Juneau, AK

10 October 10

Mendenhall Glacier, Juneau, AK
10 October 10

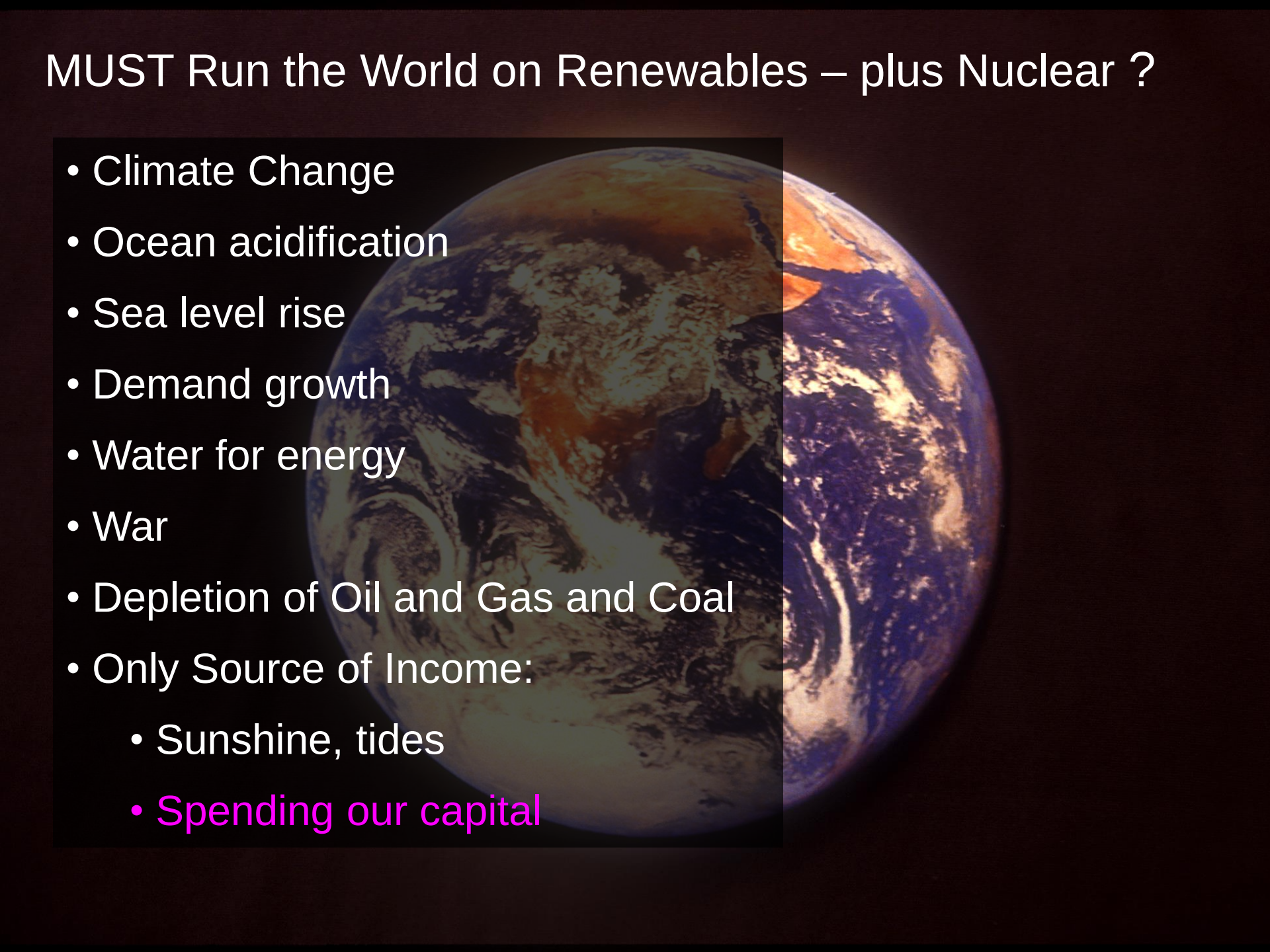
Rapid climate change

Spruce bark beetle kill, Alaska

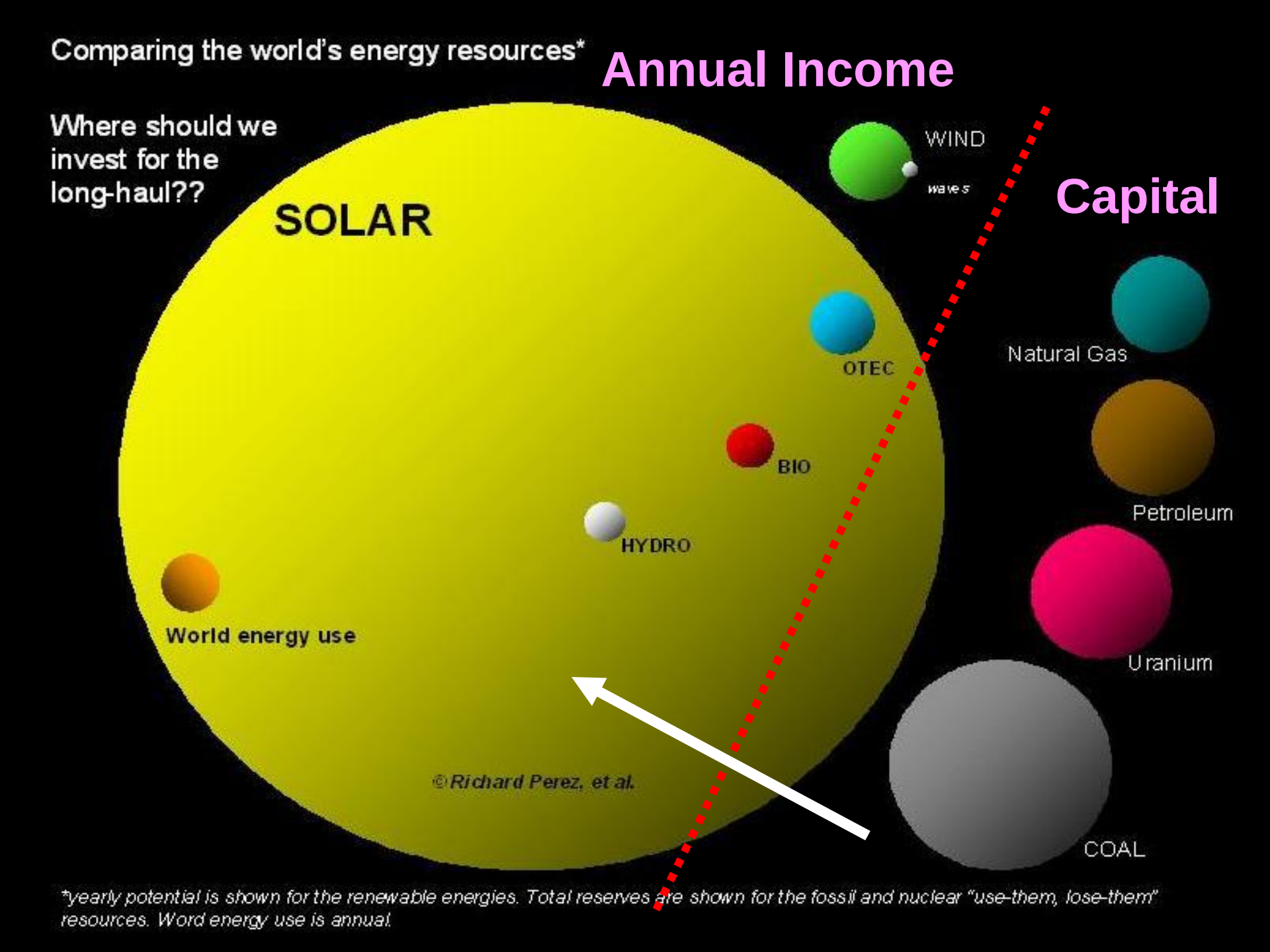
Shishmaref, Alaska

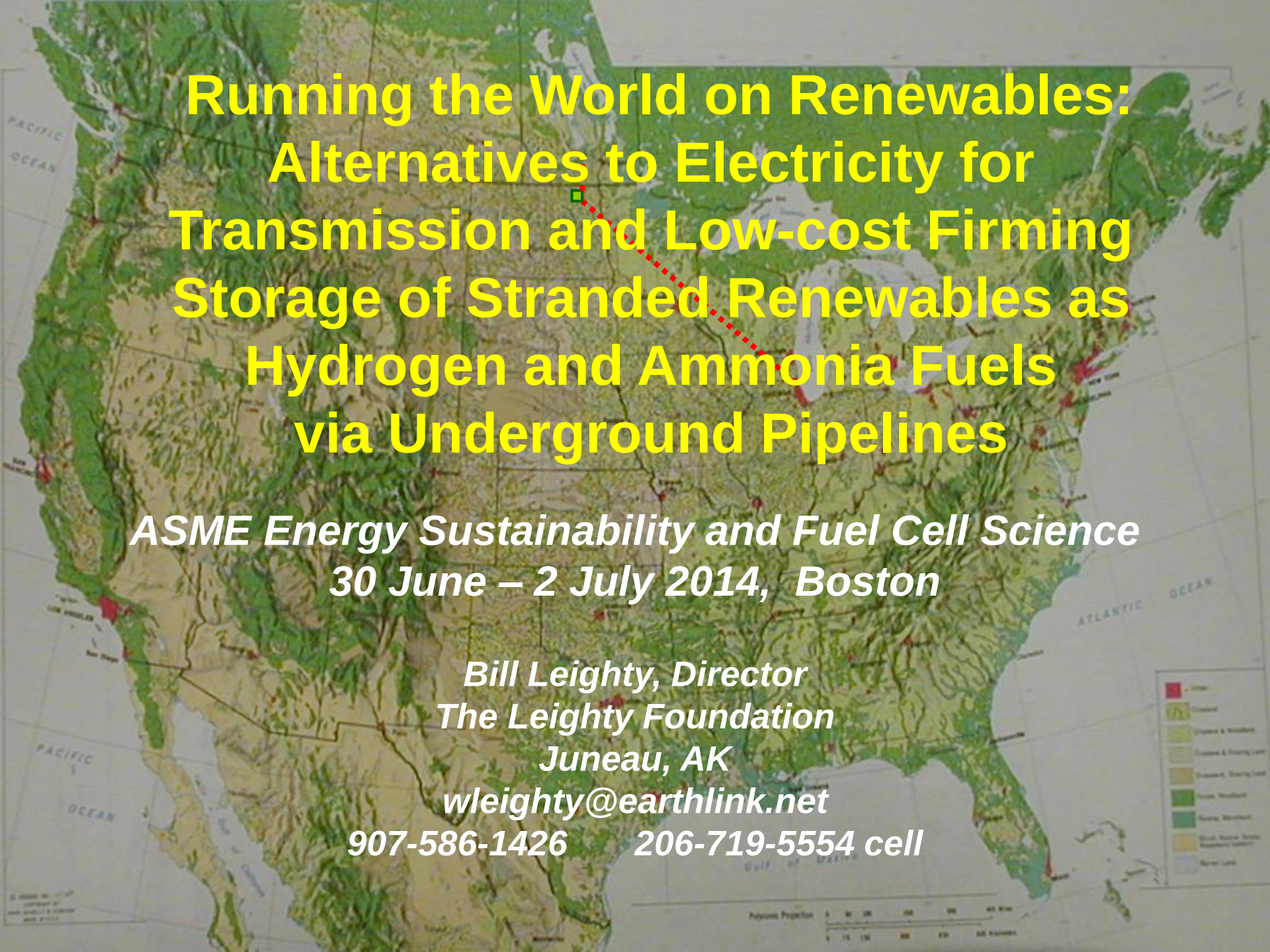
Winter storms coastal erosion

MUST Run the World on Renewables – plus Nuclear ?



- Climate Change
- Ocean acidification
- Sea level rise
- Demand growth
- Water for energy
- War
- Depletion of Oil and Gas and Coal
- Only Source of Income:
  - Sunshine, tides
  - Spending our capital


Comparing the world's energy resources*
Annual Income
Where should we invest for the long-haul??
SOLAR
WIND
waves
Capital
OTEC
Natural Gas
BIO
Petroleum
HYDRO
Uranium
World energy use
© Richard Perez, et al.
COAL
*yearly potential is shown for the renewable energies. Total reserves are shown for the fossil and nuclear "use-them, lose-them" resources. Word energy use is annual.



Running the World on Renewables: Alternatives to Electricity for Transmission and Low-cost Firming Storage of Stranded Renewables as Hydrogen and Ammonia Fuels via Underground Pipelines

ASME Energy Sustainability and Fuel Cell Science
30 June – 2 July 2014, Boston

Bill Leighty, Director
The Leighty Foundation
Juneau, AK
wleighty@earthlink.net
907-586-1426 206-719-5554 cell

Trouble with Renewables

- **Diffuse, dispersed: gathering cost**
- **Richest are remote: "stranded"**
  - **High intensity**
  - **Large geographic extent**
- **Time-varying output:**
  - **"Intermittent"**
  - **"Firming" integration + storage required**
- **Distributed AND centralized**

Trouble with Renewables: Big Three

1. Gathering and Transmission
2. Storage: Annual-scale firming → dispatchable
3. Integration
   - Extant energy systems
   - Electricity grid
   - Fuels: CHP, transportation, industry

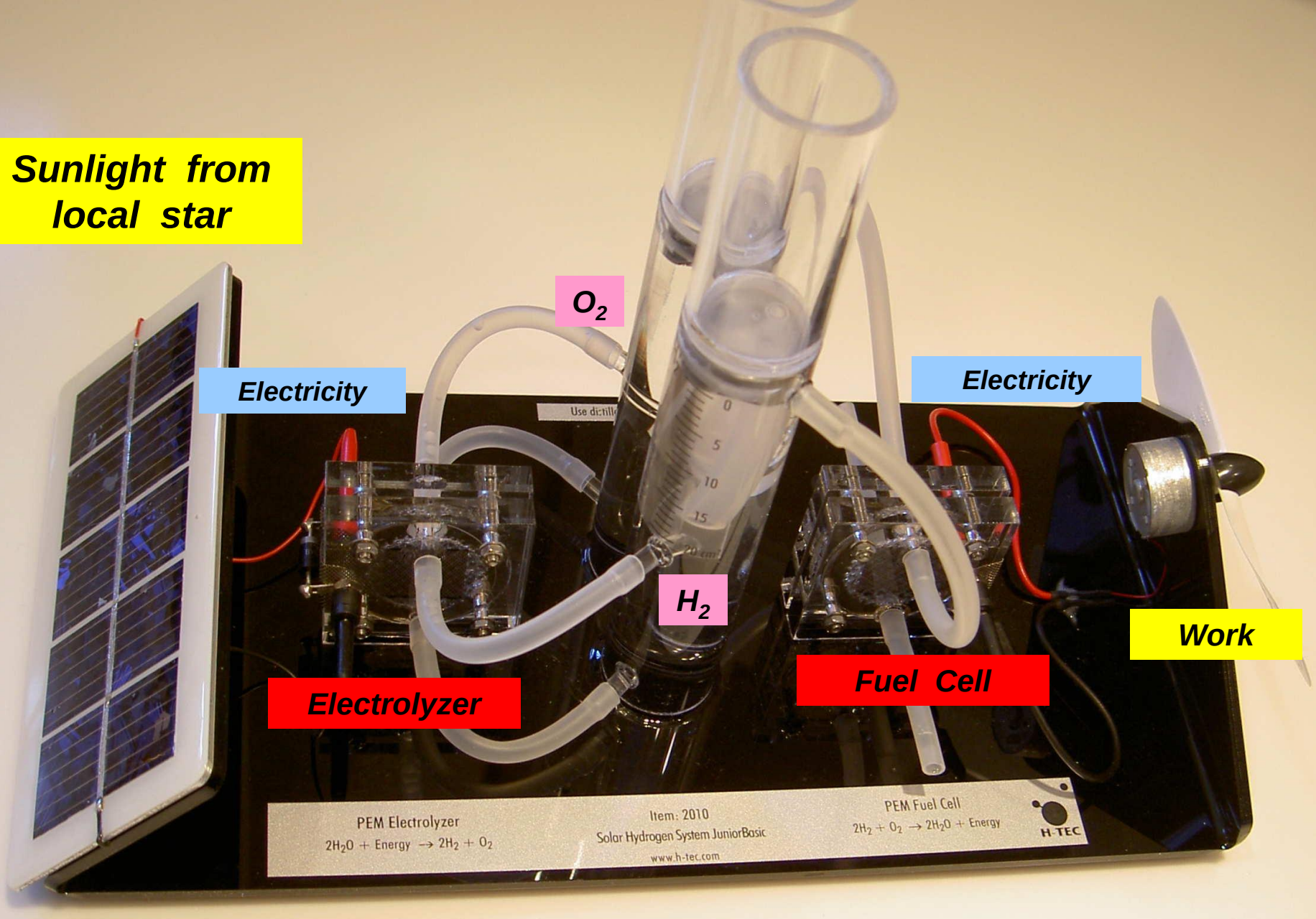
Beyond "Smart Grid"

- **Next big thing; panacea**
- **Primarily DSM**
- **More vulnerable to cyberattack ?**
- **Adds no physical:**
  - **Transmission, gathering, distribution**
  - **Storage**
- **Run the world on renewables ?**
- **Must think:**
  - **Beyond electricity**
  - **Complete energy systems**
  - **ALL energy**

"Transmission"

- **Electrofuels**
  - **CHP on-site: Combined Heat and Power**
  - **Transport**
  - **Industrial**
- **Renewable-source electricity**
- **Underground pipelines**
- **Carbon-free fuels: hydrogen, ammonia**
- **Low-cost storage:**

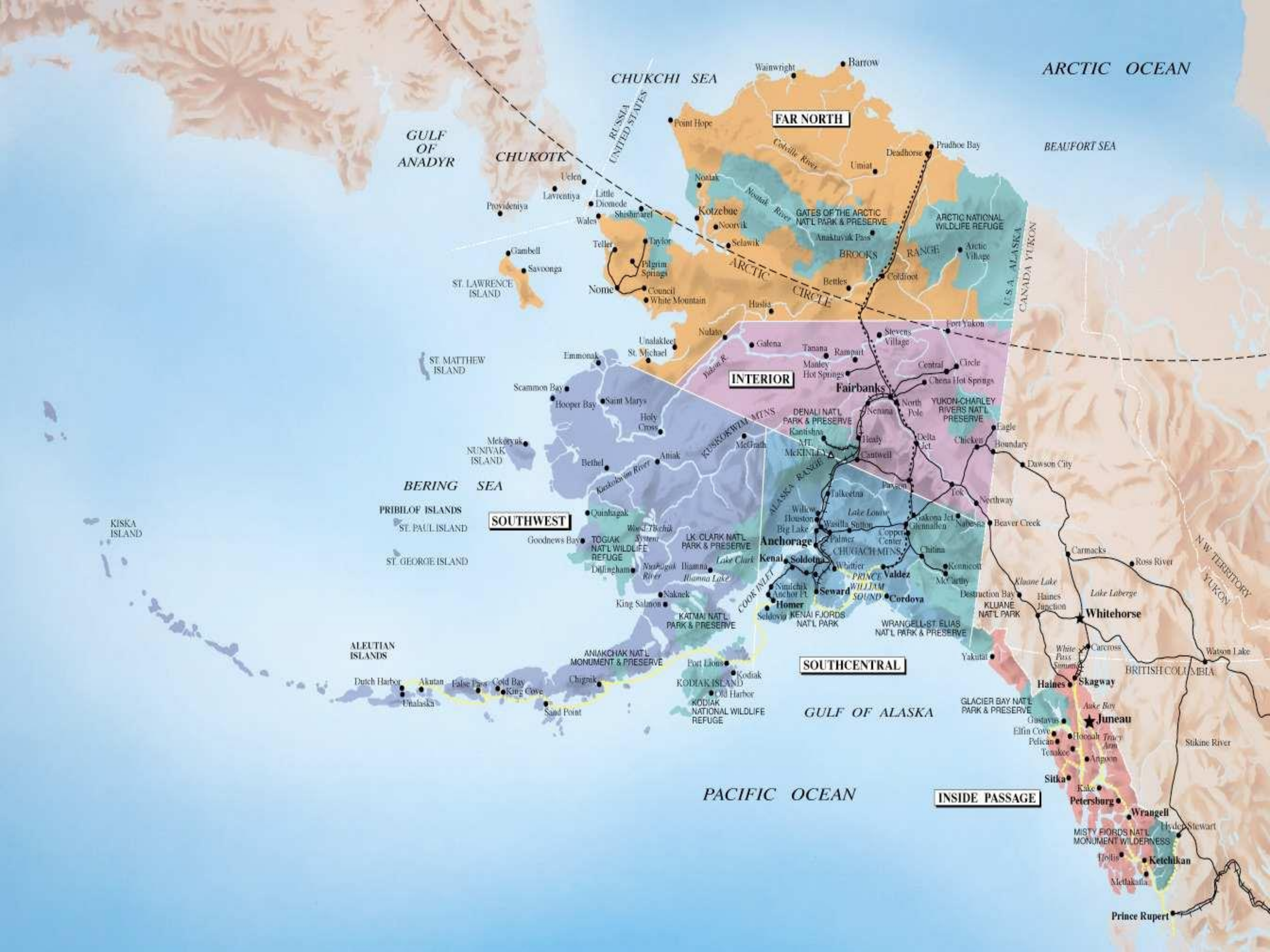
  $ 0.10 – 0.20 / kWh capital
- **RE systems, GW scale**

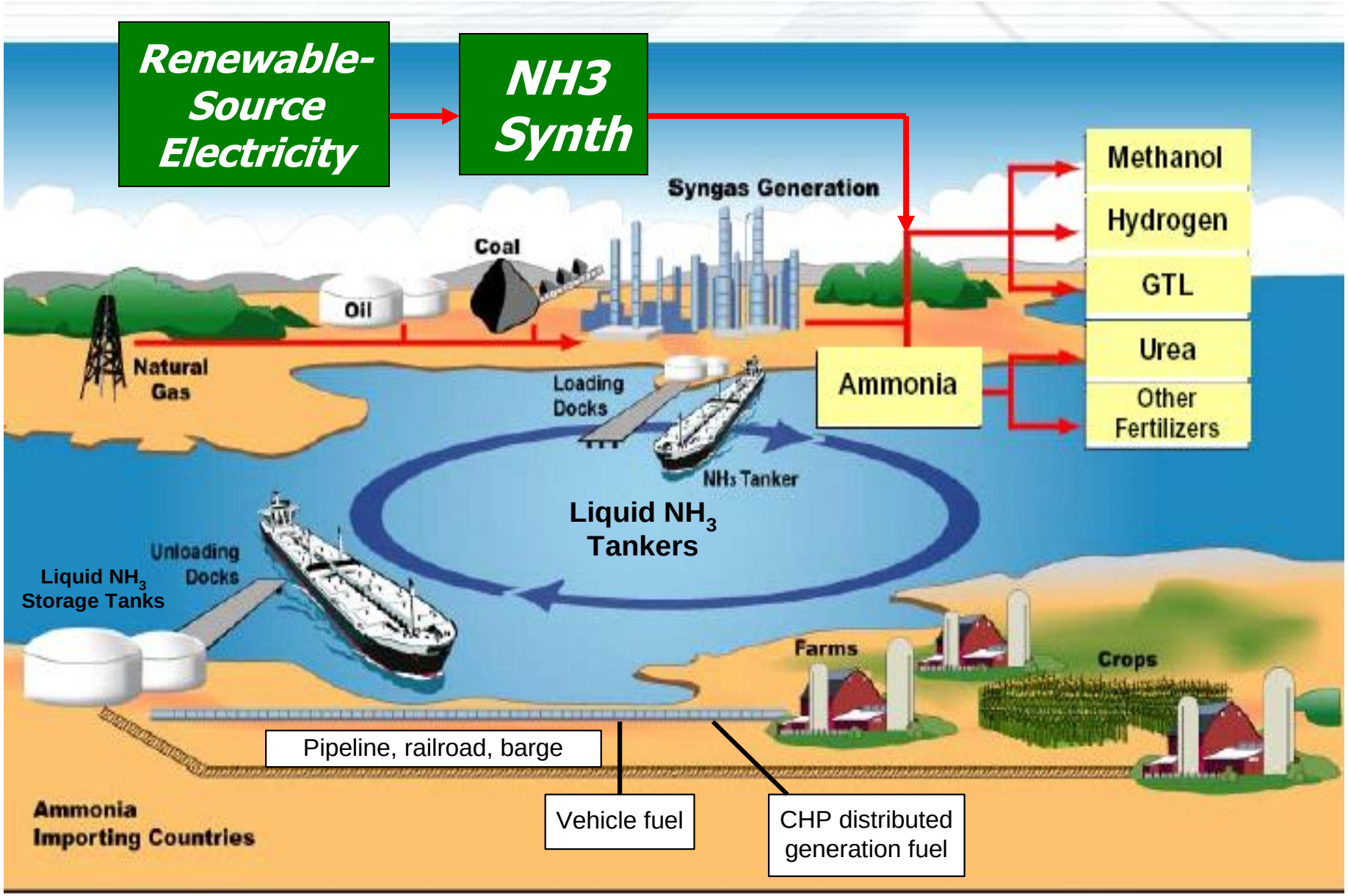


Solar Hydrogen Energy System

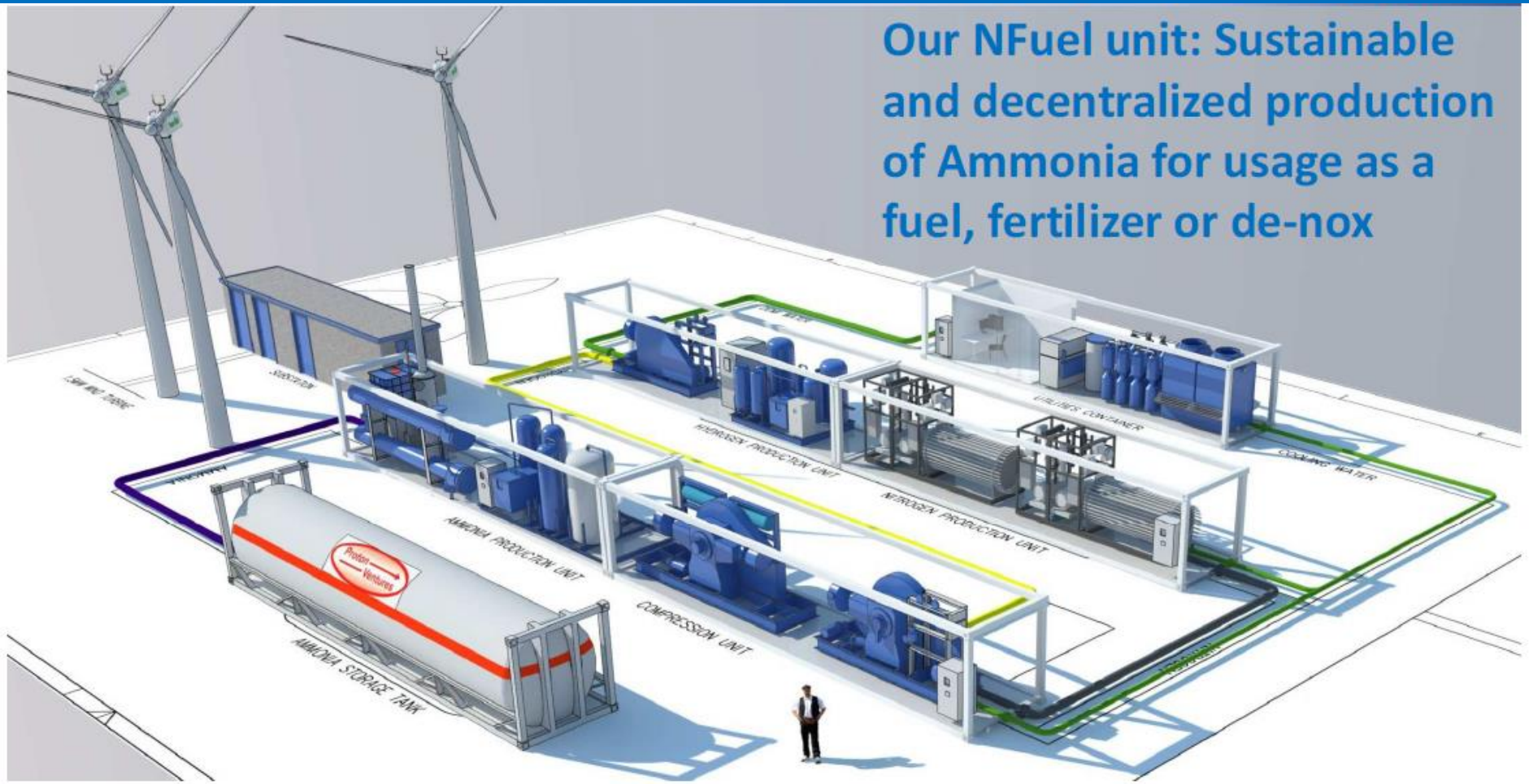
Landscape: RE-source NH3

- Alaska demo project: AASI
- Complete RE systems:
  - Generation, harvesting
  - Gathering + Transmission
  - Annual-scale firming storage
  - Integration: distribution + end-use
- Artificial Photosynthesis: UK, July ‘14
- Ag Ventures, Iowa: Wind → NH3 study
- Synthesis tech survey
  - From H2
  - From electricity
- ICE gensets conversion to NH3: demand demo

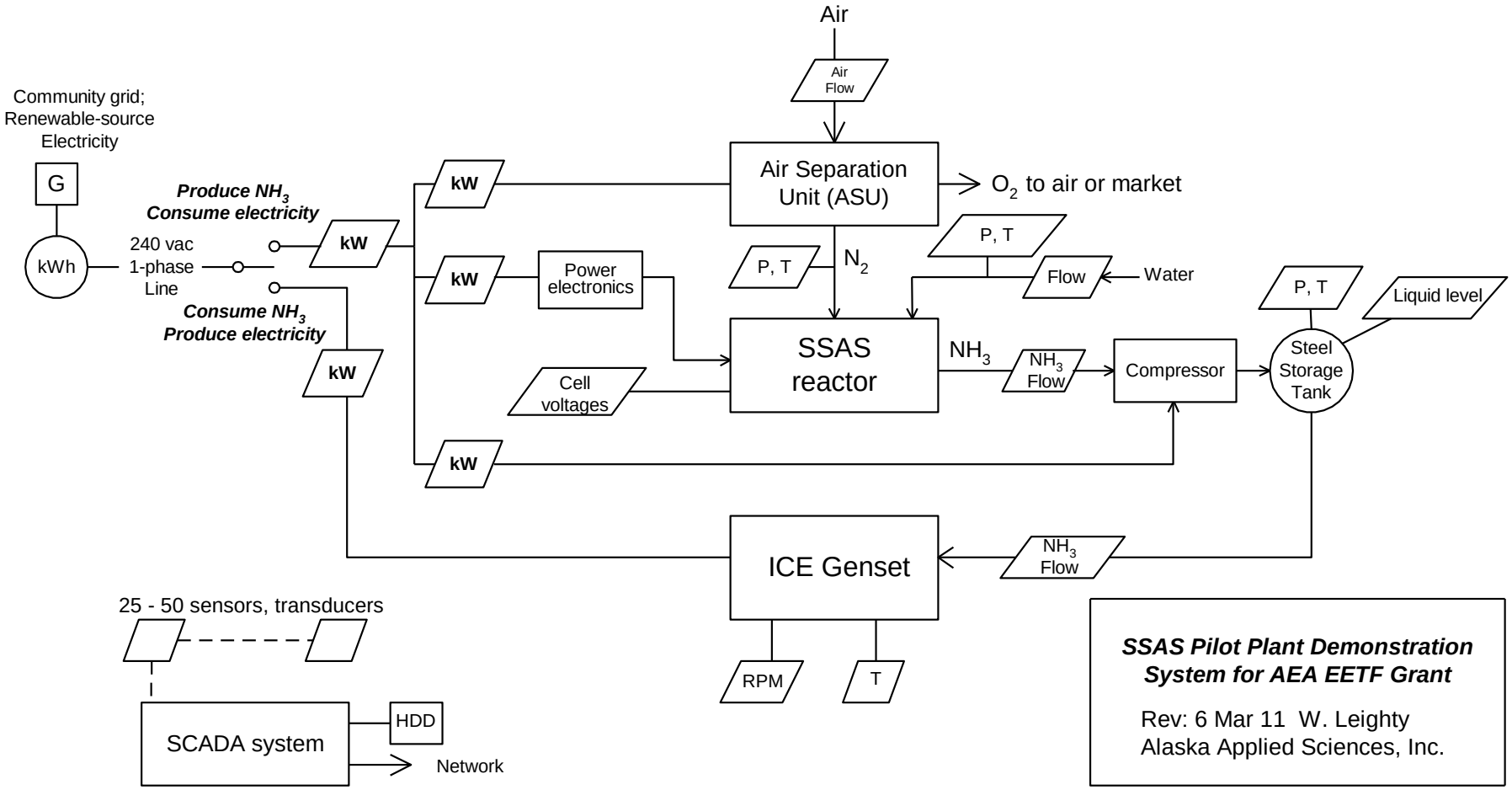

ARCTIC OCEAN
CHUKCHI SEA
BEAUFORT SEA
GULF OF ANADYR
CHUKOTK
RUSSIA
UNITED STATES
FAR NORTH
INTERIOR
SOUTHWEST
SOUTHCENTRAL
INSIDE PASSAGE
BERING SEA
PACIFIC OCEAN
GULF OF ALASKA
Barrow
Wainwright
Point Hope
Prudhoe Bay
Deadhorse
Umiat
Colville River
Noatak
Noatak River
Kotzebue
Noorvik
Selawik
GATES OF THE ARCTIC NAT'L PARK & PRESERVE
Anaktuvuk Pass
ARCTIC NATIONAL WILDLIFE REFUGE
Arctic Village
BROOKS RANGE
ARCTIC CIRCLE
Bettles
Coldfoot
U.S.A. ALASKA
CANADA YUKON
Uelen
Lavrentiya
Provideniya
Little Diomede
Shishmaref
Wales
Teller
Taylor
Pilgrim Springs
Nome
Council
White Mountain
Gambell
Savoonga
ST. LAWRENCE ISLAND
Huslia
Nulato
Unalakleet
St. Michael
Emmonak
Galena
Yukon R.
Fort Yukon
Stevens Village
Tanana
Rampart
Manley Hot Springs
Central
Circle
Chena Hot Springs
Fairbanks
North Pole
Nenana
YUKON-CHARLEY RIVERS NAT'L PRESERVE
DENALI NAT'L PARK & PRESERVE
Kantishna
MT. McKINLEY
Healy
Cantwell
Delta Jct.
Eagle
Boundary
Chicken
Dawson City
ST. MATTHEW ISLAND
Scammon Bay
Hooper Bay
Saint Marys
Holy Cross
KUSKOKWIM MTNS.
McGrath
Mekoryuk
NUNIVAK ISLAND
Bethel
Aniak
Kuskokwim River
ALASKA RANGE
Paxson
Tok
Northway
Talkeetna
Willow
Houston
Big Lake
Wasilla
Sutton
Lake Louise
Gakona Jct.
Glennallen
Nabesna
Beaver Creek
Anchorage
Palmer
Copper Center
CHUGACH MTNS.
Chitina
Kennicott
McCarthy
Kenai
Soldotna
Whittier
Valdez
PRINCE WILLIAM SOUND
Seward
Cordova
Ninilchik
Anchor Pt.
Homer
Seldovia
COOK INLET
KENAI FJORDS NAT'L PARK
WRANGELL-ST. ELIAS NAT'L PARK & PRESERVE
PRIBILOF ISLANDS
ST. PAUL ISLAND
ST. GEORGE ISLAND
KISKA ISLAND
Quinhagak
Goodnews Bay
TOGIAK NAT'L WILDLIFE REFUGE
Wood-Tikchik System
LK. CLARK NAT'L PARK & PRESERVE
Lake Clark
Dillingham
Nushagak River
Iliamna
Iliamna Lake
Naknek
King Salmon
KATMAI NAT'L PARK & PRESERVE
ALEUTIAN ISLANDS
ANIAKCHAK NAT'L MONUMENT & PRESERVE
Chignik
Dutch Harbor
Unalaska
Akutan
False Pass
Cold Bay
King Cove
Sand Point
Port Lions
Kodiak
KODIAK ISLAND
Old Harbor
KODIAK NATIONAL WILDLIFE REFUGE
Carmacks
Ross River
N.W. TERRITORY
YUKON
Kluane Lake
Destruction Bay
KLUANE NAT'L PARK
Haines Junction
Lake Laberge
Whitehorse
Yakutat
White Pass Summit
Carcross
Watson Lake
BRITISH COLUMBIA
Haines
Skagway
GLACIER BAY NAT'L PARK & PRESERVE
Gustavus
Auke Bay
Juneau
Elfin Cove
Pelican
Hoonah
Tracy Arm
Tenakee
Angoon
Stikine River
Sitka
Kake
Petersburg
Wrangell
Hyder
Stewart
MISTY FIORDS NAT'L MONUMENT WILDERNESS
Hollis
Ketchikan
Metlakatla
Prince Rupert



KBR
Energy and Chemicals



Proton Ventures BV, Netherlands
www.protonventures.com



PROJECT: Complete RE – NH_3 Synthesis + Storage System

- **> NH3 synthesis from RE electricity, water, air (N_2)**
- **> Liquid NH_3 tank storage**
- **> Regeneration + grid feedback**
- **> SCADA instrumentation → UAF - ACEP**

Pilot Plant Budget

EETF via AEA	**$ 750 K**
Technology in-kind	**$ 100 K**
WindToGreen in-kind	**$ 100 K**
AASI in-kind	**$ 50 K**
TOTAL	**$ 1 M**

EETF Emerging Energy Technology Fund, State of Alaska
AEA Alaska Energy Authority, State of Alaska
AASI Alaska Applied Sciences, Inc.

Landscape Survey: RE-source NH3

- WindToGreen, LLC tech survey
- “Better catalysts”
- New methods, pathways, to NH3 synth
- All “Non-Haber” tech is at TRL 1-3
- Electrolysis + Haber-Bosch (EHB) lowest risk
- Long-term, costly effort for RE-NH3
- High cost of RE-NH3: competition, C-tax ?

Landscape: RE-source NH3

- Sources: Electricity or Hydrogen ?
- Markets:
  - Transportation Fuel
  - Ag Fuel
  - N-fertilizer
  - Distributed Generation (DG) Fuel
  - Industrial Fuel + Feedstock
  - “Run World on Renewables”

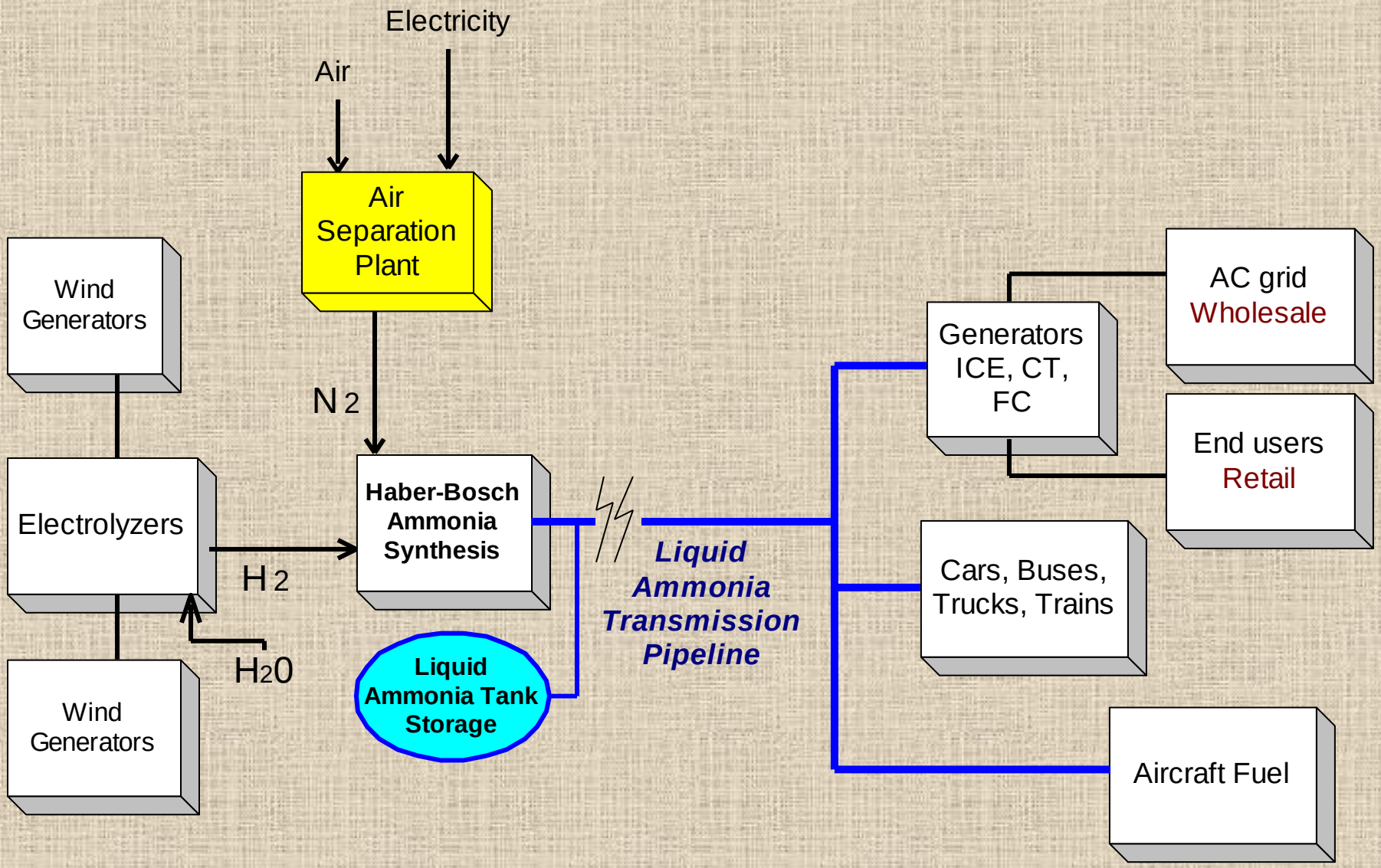
RE Systems: Carriers and Storage Strategies

- Electricity
- Gaseous Hydrogen (GH2)
- Liquid Hydrogen (LH2)
- Anhydrous Ammonia (NH3)
- Toluene (C7H8) ←→ Methylcyclohexane (C7H14)
- Artificial Photosynthesis (AP)

Global Artificial Photosynthesis Project
The Royal Society, Chicheley Hall, UK July 8 – 10, 2014
Tom Faunce, Australia National University, Convenor
Leighty for NH3 Fuel Association: "What Shall We Do With The Photohydrogen?"

Chicheley Hall, The Royal Society, UK

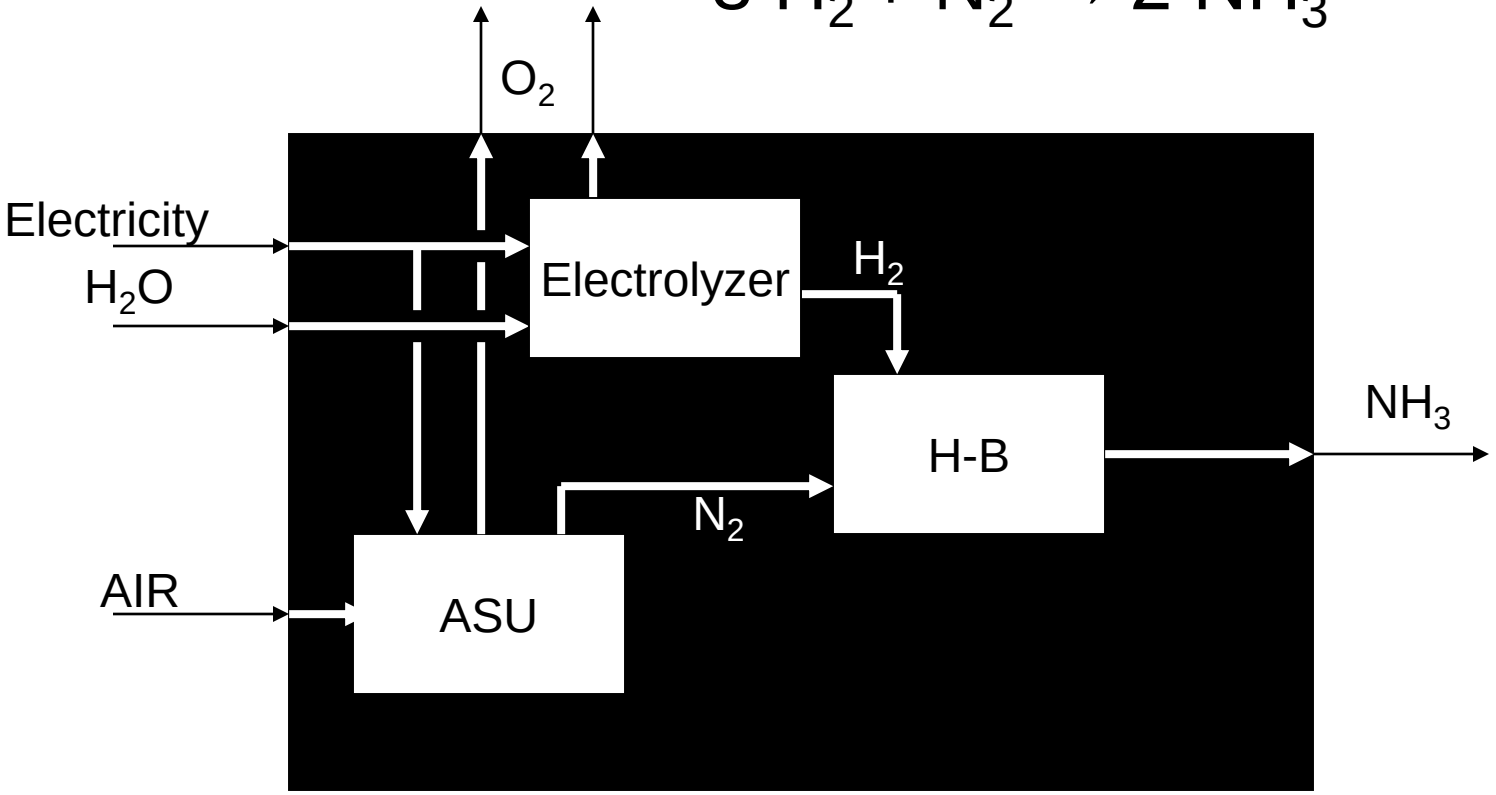
RE Ammonia Transmission + Storage Scenario




Norsk Hydro
Electrolyzers
2 MW each
Ammonia from
hydrogen
from zero-cost
off-peak hydro

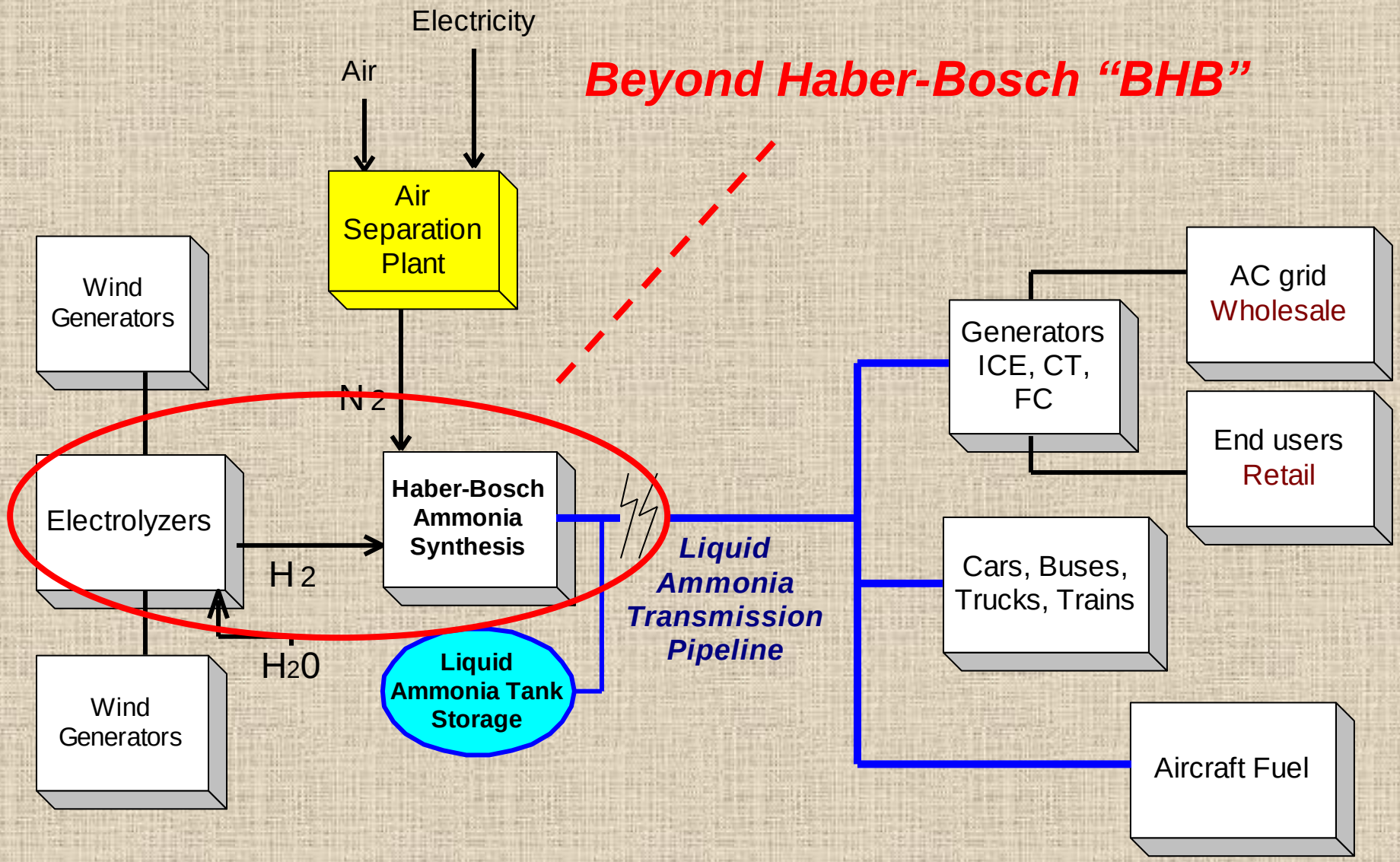
Inside the Black Box: HB Plus Electrolysis

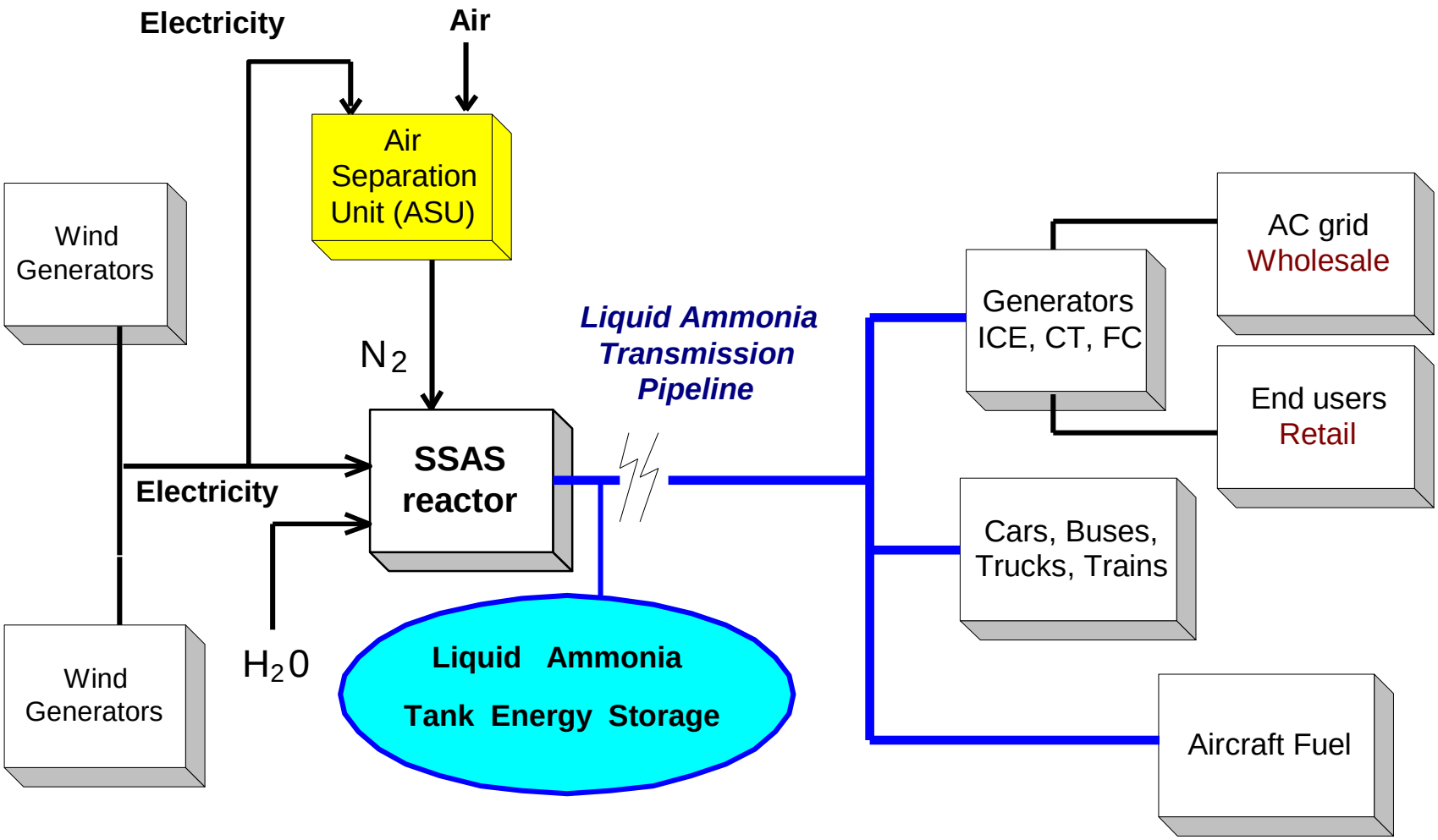
$$3\ H_2O \rightarrow 3\ H_2 + 3/2\ O_2$$
$$3\ H_2 + N_2 \rightarrow 2\ NH_3$$



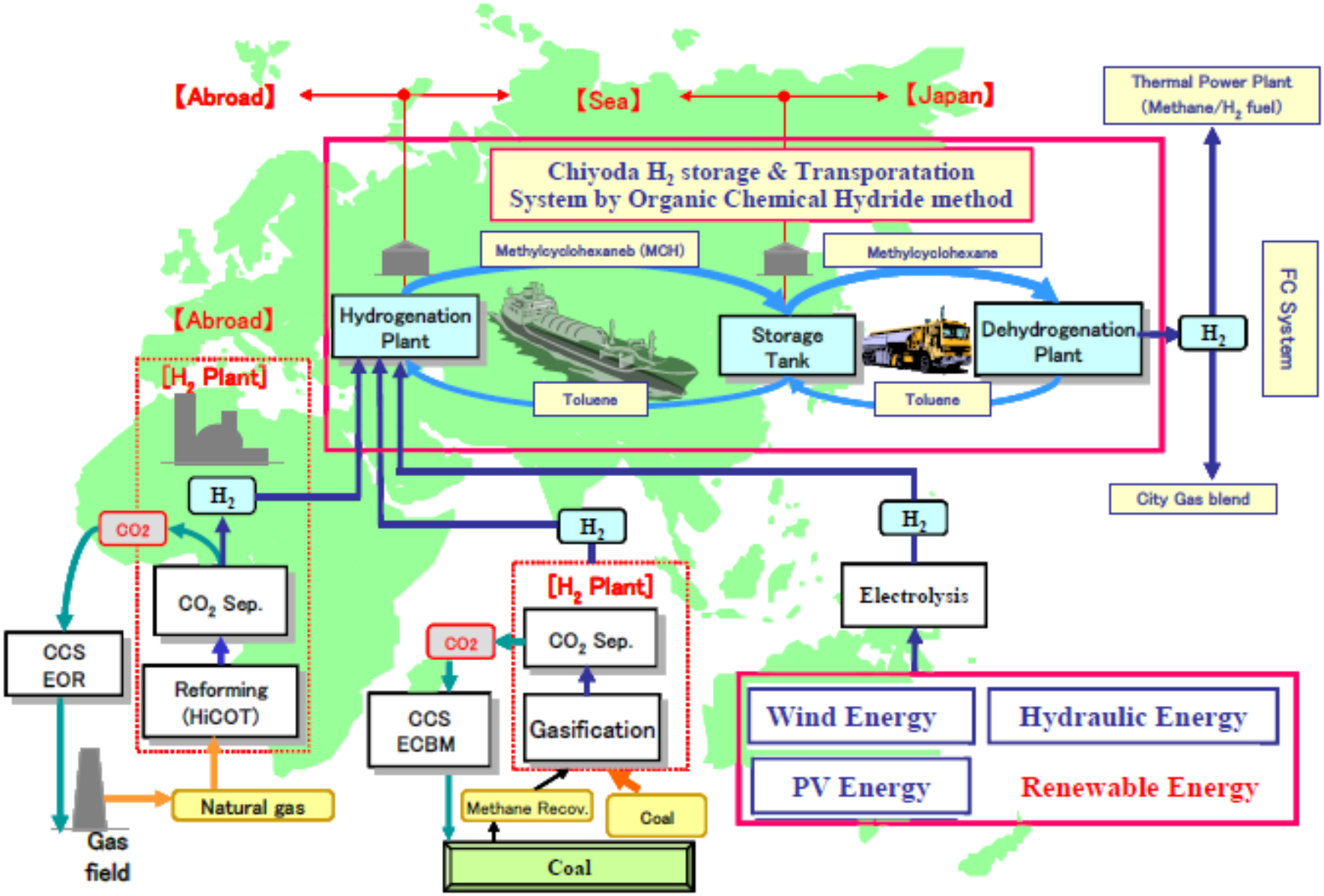
Energy consumption ~12,000 kWh per ton NH_3

RE Ammonia Transmission + Storage Scenario





Beyond Haber-Bosch "BHB"



C-emissions-free Hydrogen transport and storage: Chiyoda Chemical, Japan
Toluene (C_7H_8) ←→ Methylcyclohexane (C_7H_{14})

NH3 Synthesis Technologies

- WindToGreen, LLC 2013
  Technology Advisory Group
- Landscape assessment
- Literature search
- Followup

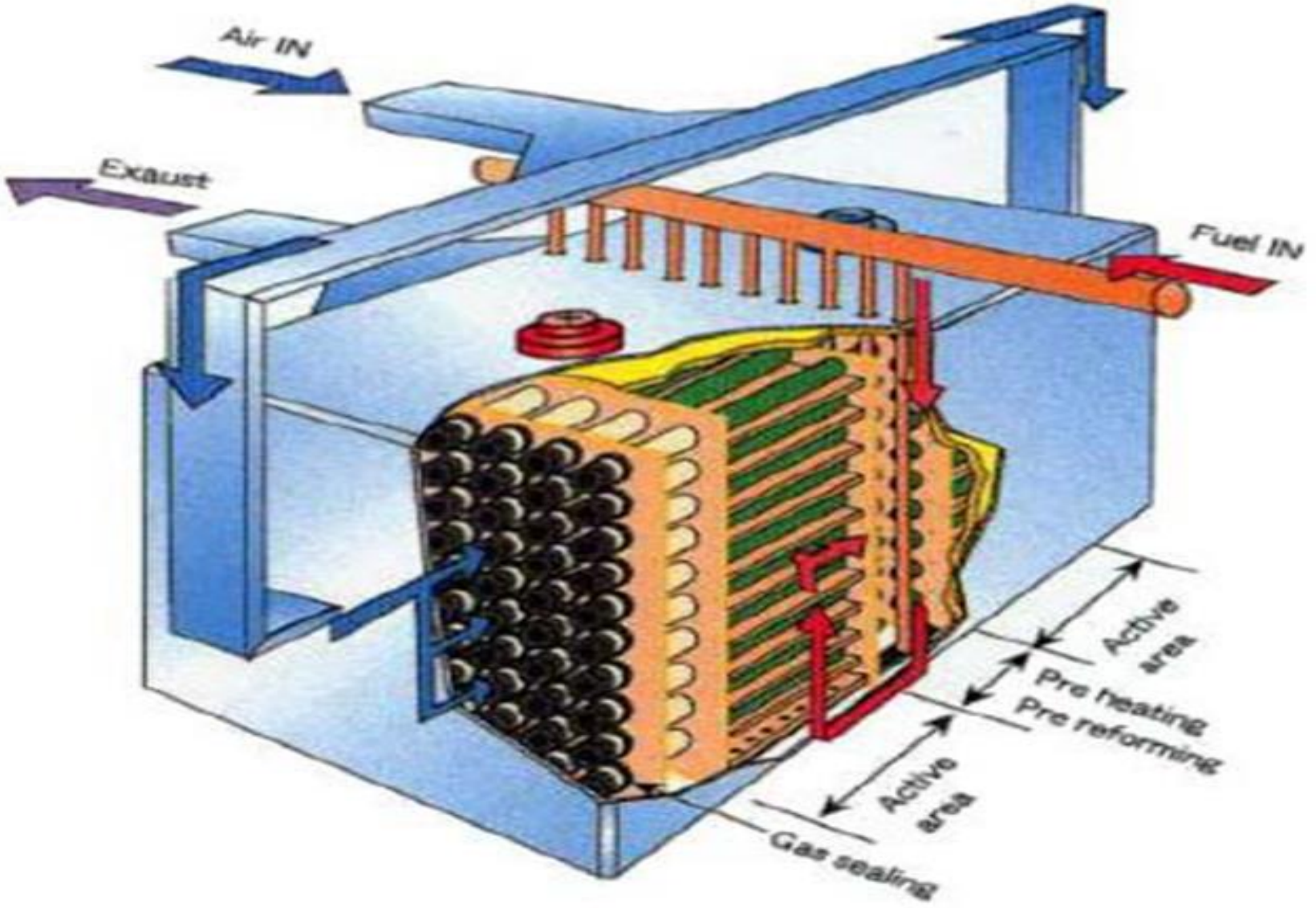
NH3 Synthesis Technologies

- H-B and electrolysis plus H-B (EHB)
- Polymer membrane: nano
  - Nanoparticle catalyst impregnated polymer membrane
  - nanostructure catalyst
  - nanostructured polymer membrane
  - Other nanoparticles catalysts and nanostructure catalyst carriers
  - Composite electrolytes
- Polymer membrane “Nafion” not compatible with NH3
- Ammonia-Compatible Polymer (UMN)
- Membrane Electrode Assembly (MEA): PEM fuel cell

NH3 Synthesis Technologies

- Proton Conducting Ceramic (PCC) electrolytes:
  Examples ($BaCeO_3$, $CaZrO_3$, $SrZrO_3$, $LaGaO_3$)
- Other PCC: MP_2O_7 Intermediate-temp PCC + M-N catalysts (LANL)
- Oxides:
  - Complex perovskite-type
  - Pyrochlore-type
  - Fluorite-type
- Oxygen ion conducting ceramic electrolyte
- Plasma
  - Non Thermal (NTP)
  - Microwave

Beyond Haber-Bosch "BHB"

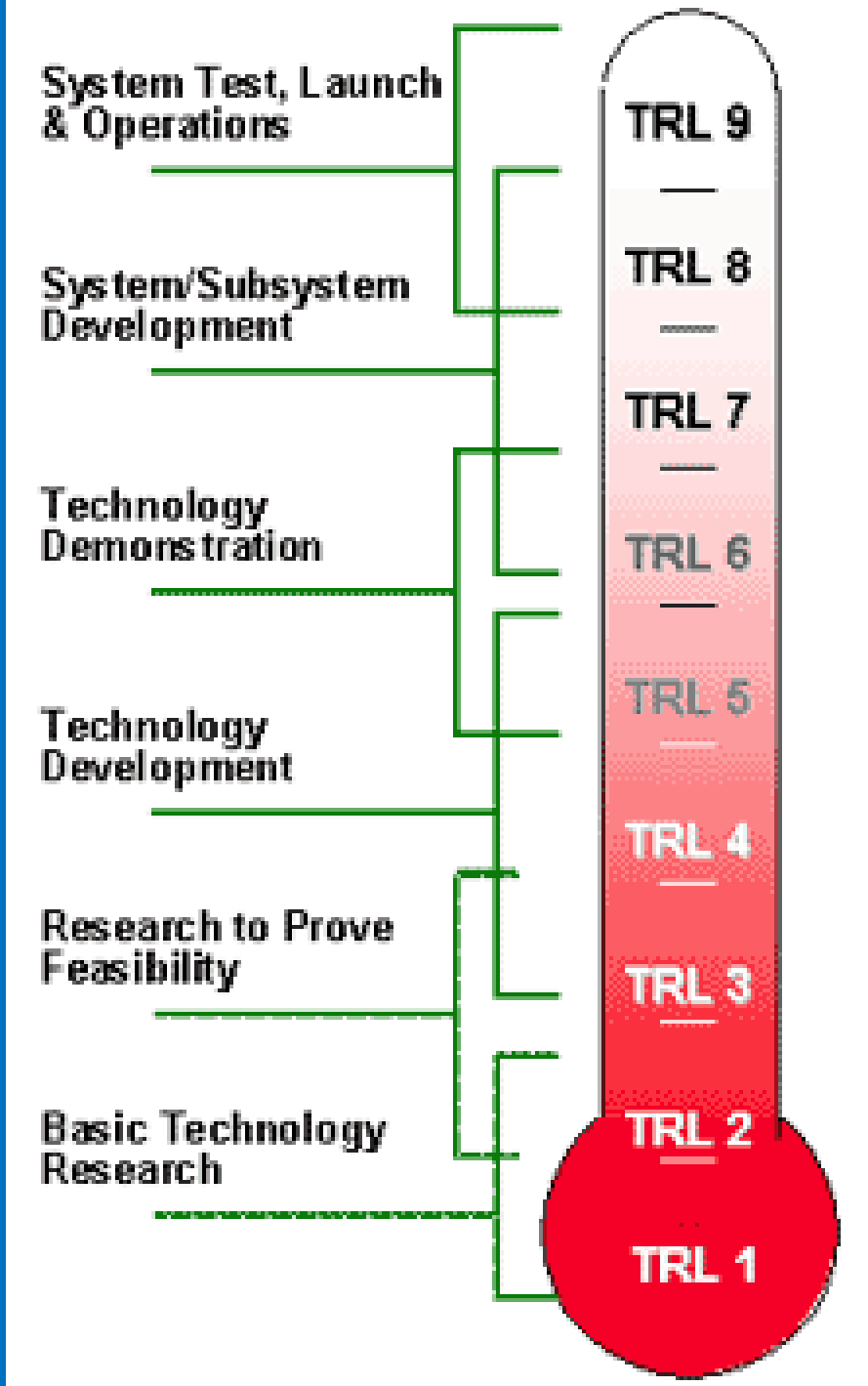


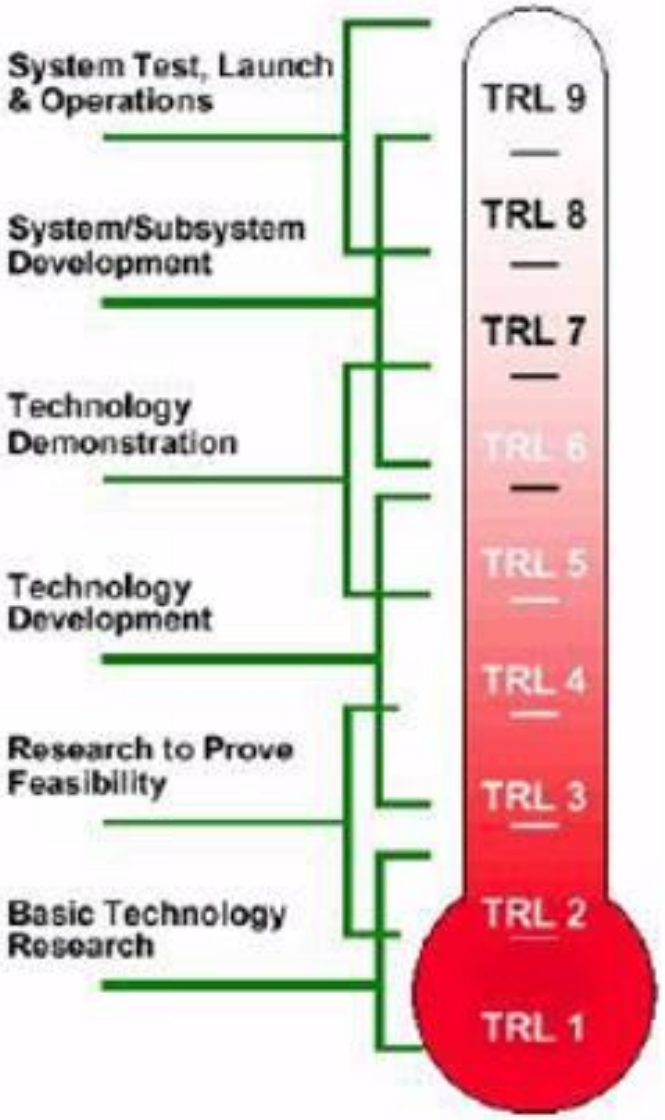
NH3 Synthesis Technologies

- Molten salt electrolyte
- Ionic Liquid electrolyte
- Diamond nanoparticles catalyst, substrate:
  U. Wisconsin Madison (R.J. Hamers)
- Solar-assisted two-stage metal nitride redox, low-P NH3 synth, from ETH, Zurich
- N2 Cleavage and Hydrogenation by a Trinuclear Titanium Polyhydride Complex
- Cyclic Pressurization (ICE)
- Lithium (proprietary)

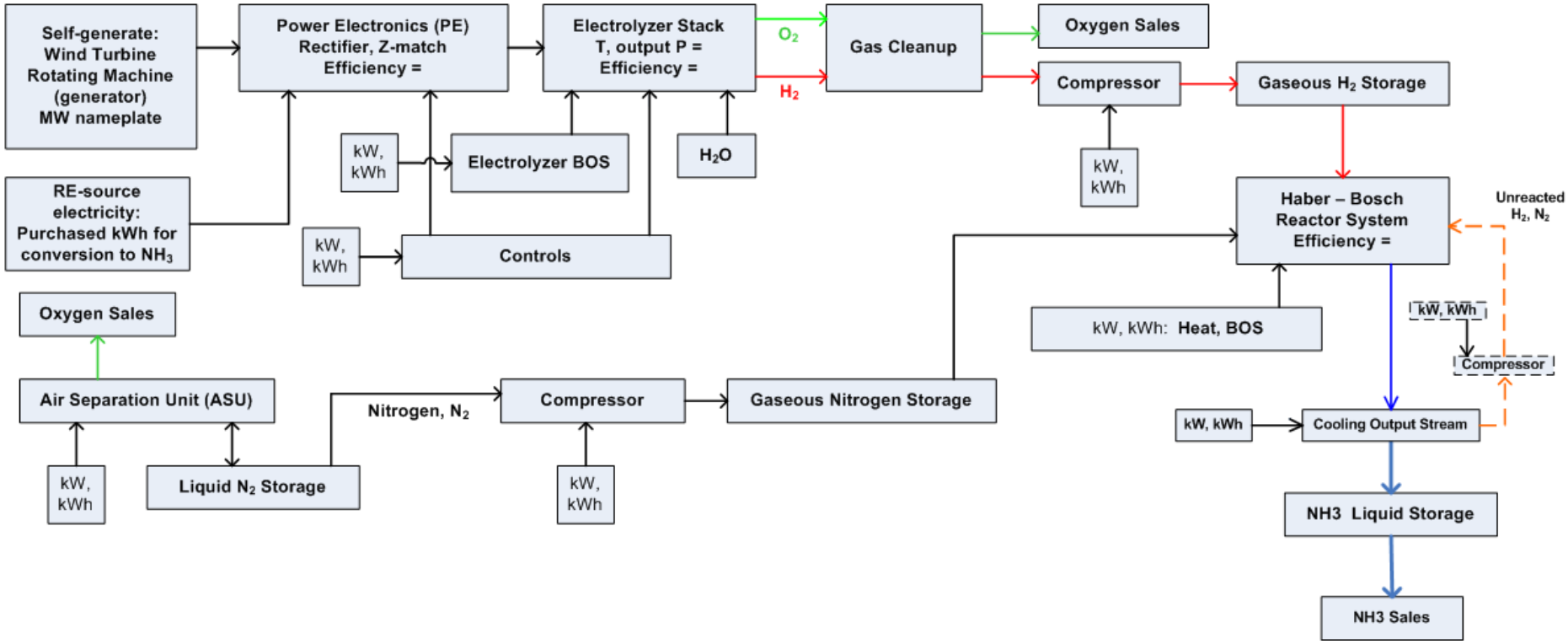
H2 generation to feed H-B

- Artificial Photosynthesis (AP)
- Catalyst pseudo-random search: JCAP
- Biology: algae, other
- Gasification
- Nanoptek: light or electricity input → H2
- Other


System Test, Launch & Operations
System/Subsystem Development
Technology Demonstration
Technology Development
Research to Prove Feasibility
Basic Technology Research
TRL 9
TRL 8
TRL 7
TRL 6
TRL 5
TRL 4
TRL 3
TRL 2
TRL 1



Actual Technology qualified through successful mission operations
Actual Technology completed and qualified through test and demonstration
Technology prototype demonstration in a simulated operational environment
Prototype demonstration in a relevant environment
Technology basic validation in a relevant environme
Technology basic validation in a laboratory environment
Analytical and experimental critical function and/or characteristic proof of concept
Technology concept and/or application formulated
Basic principles observed and reported



Electrolysis + Haber-Bosch (EHB) system
For RE-source Electricity, Water, and Air inputs

Review of electrochemical ammonia production technologies and materials

S. Giddey, S.P.S. Badwal, A. Kulkarni

CSIRO Energy Technology
Victoria, Australia

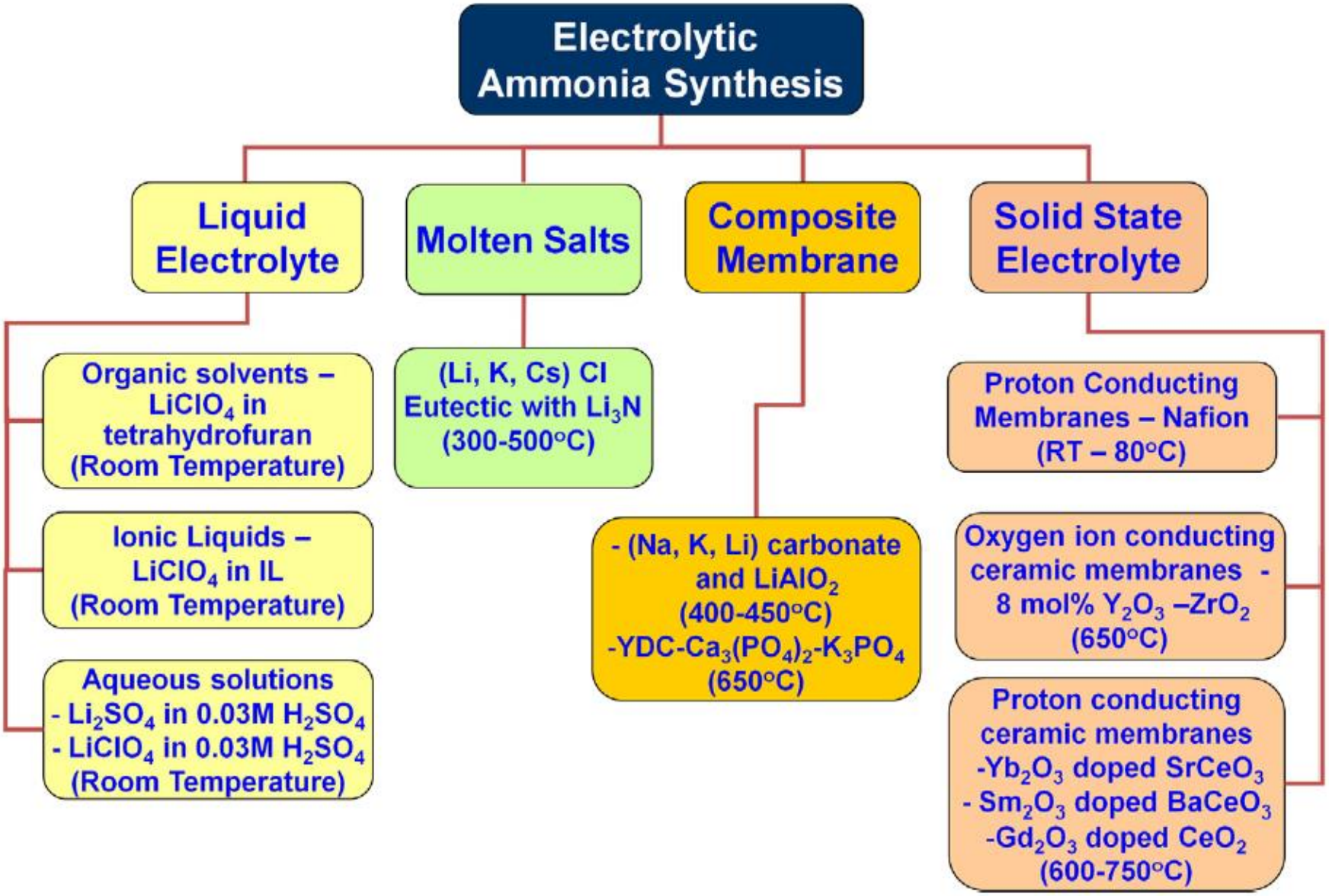
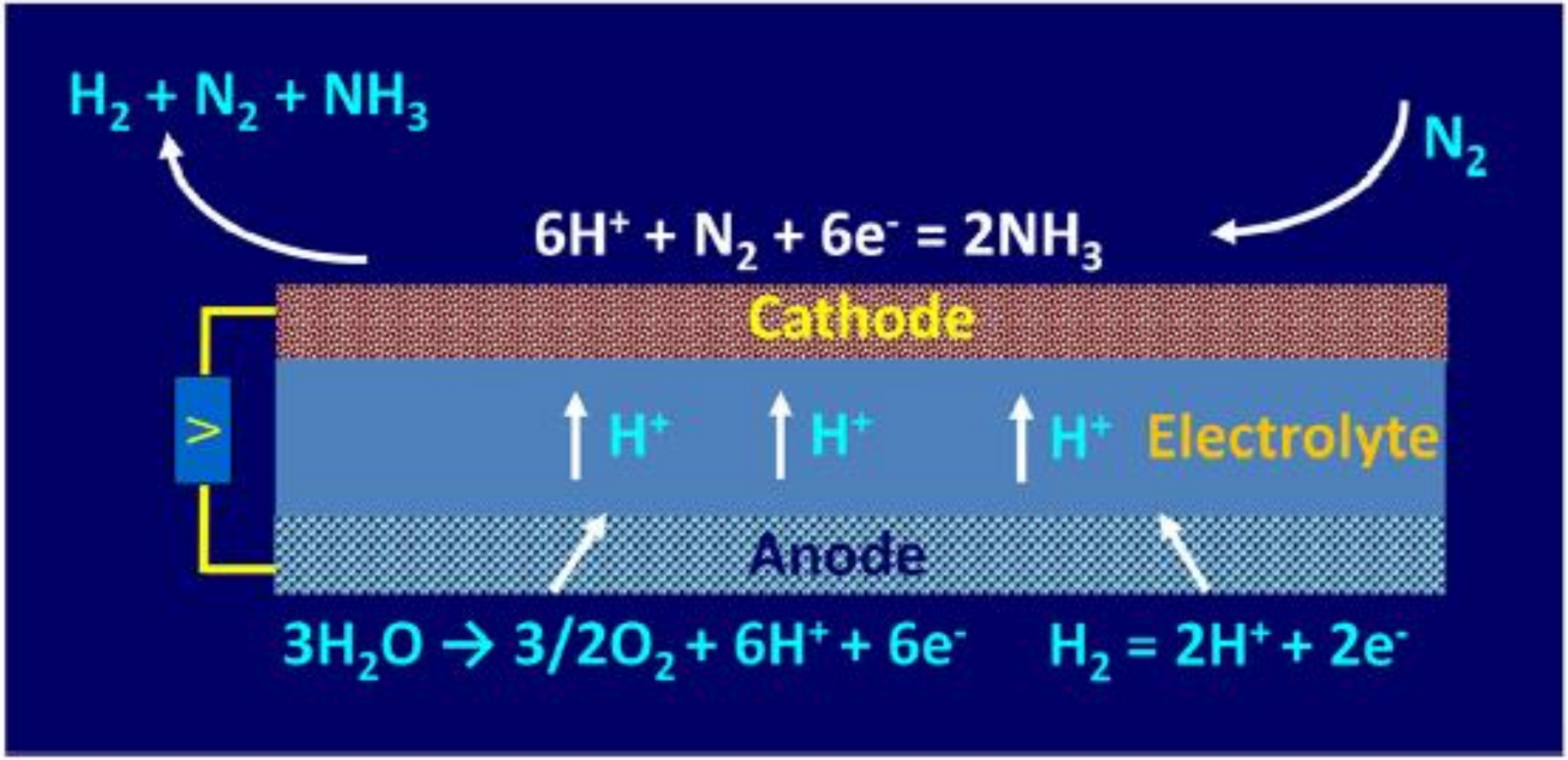
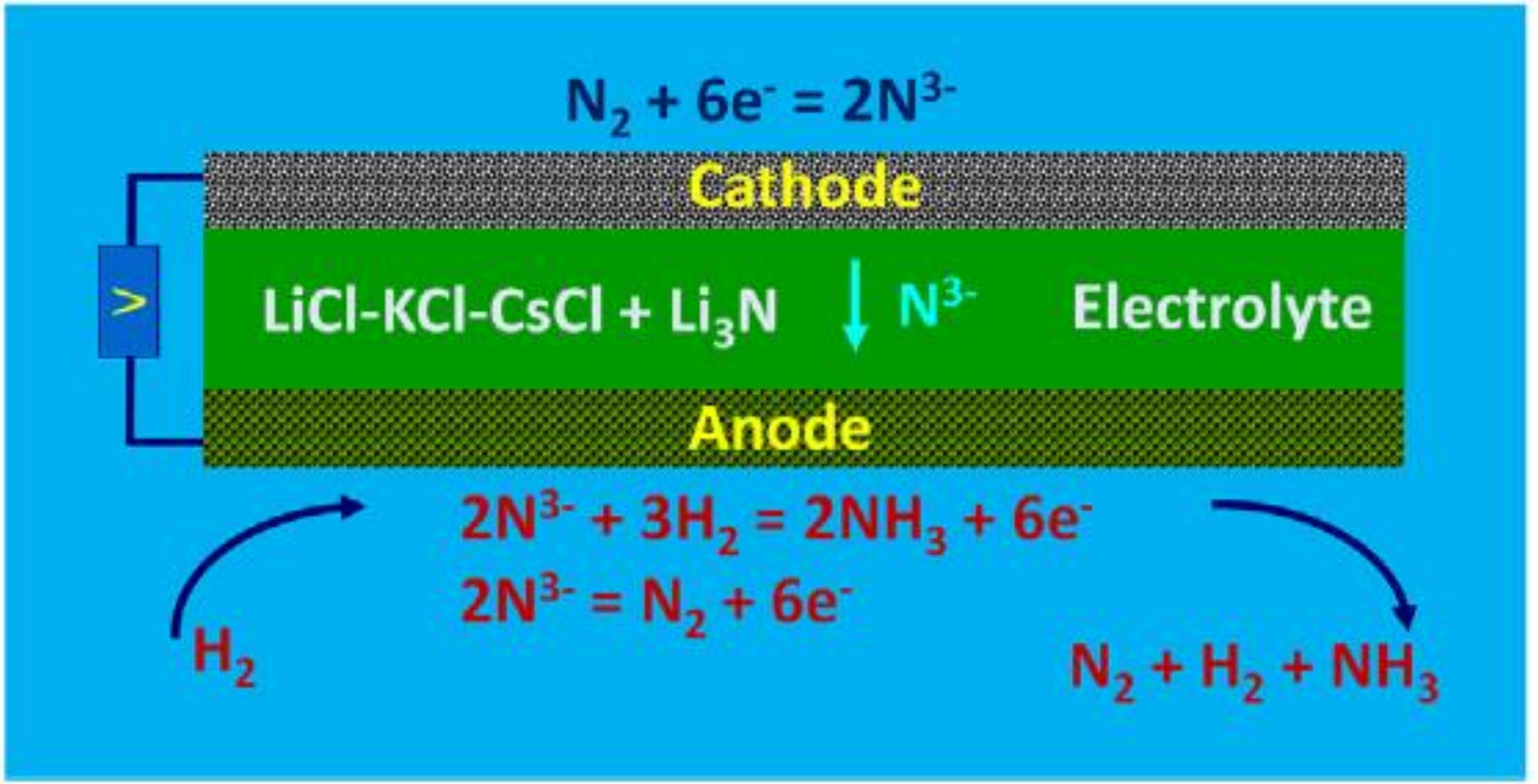


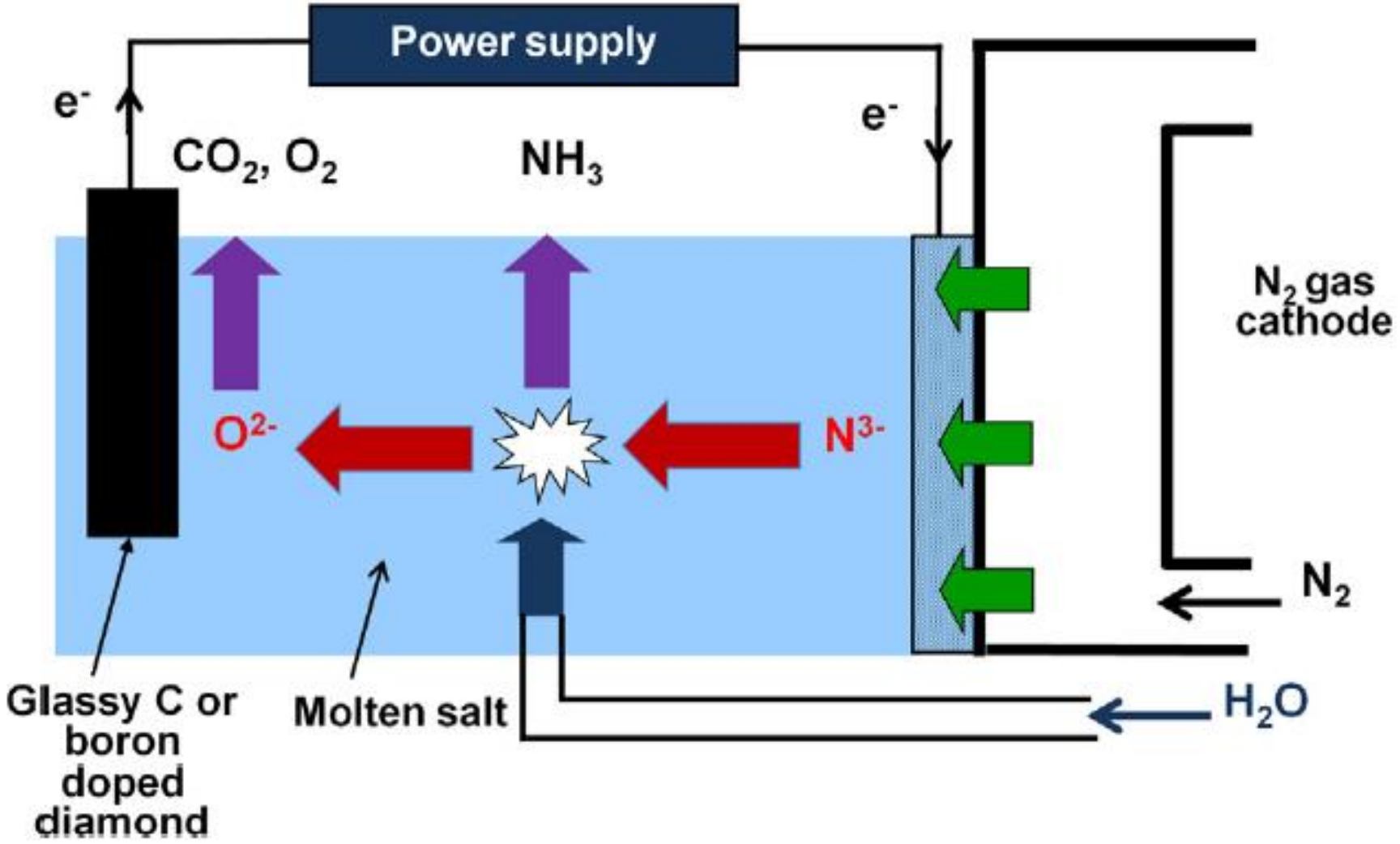
Fig. 2 – Various electrolytic options under consideration for ammonia synthesis.



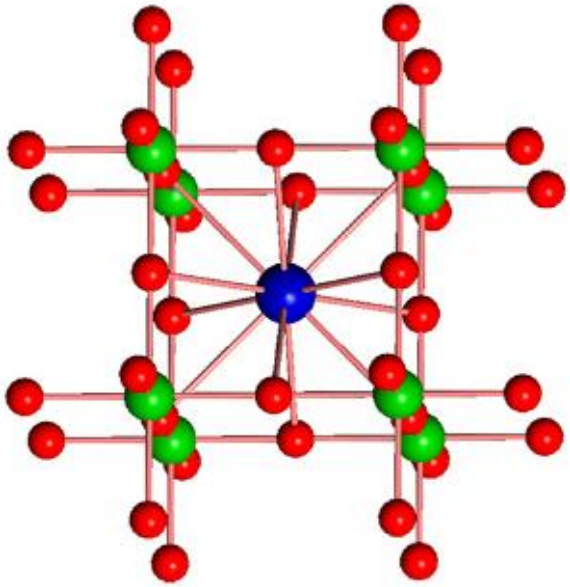
NH3 Synthesis by Proton Conducting Solid Electrolyte



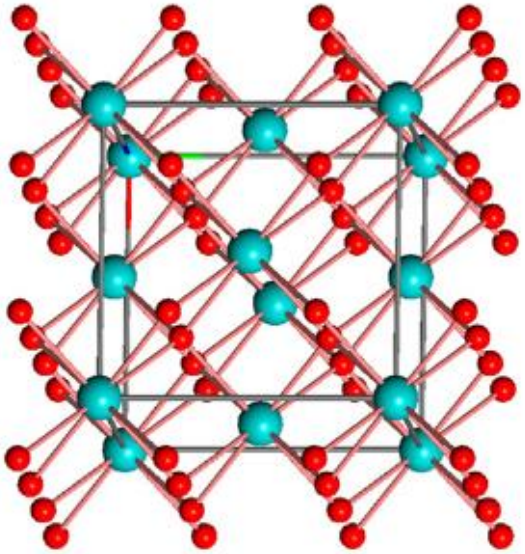
NH3 Synthesis by Molten Salt Electrolyte



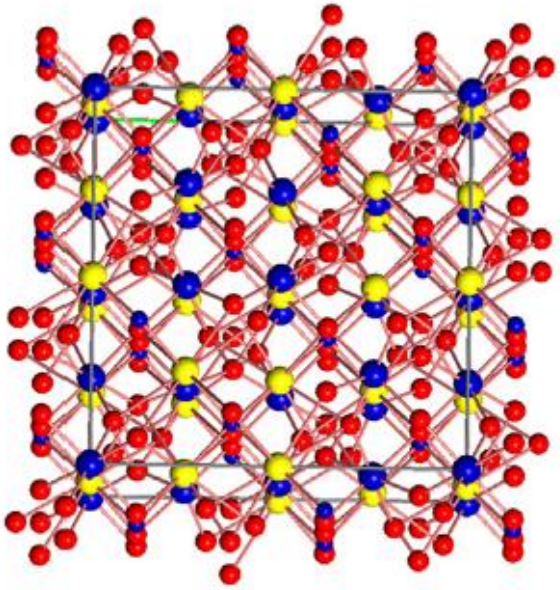
NH3 Synthesis via Molten Salt Electrolyte With Water as Hydrogen Source



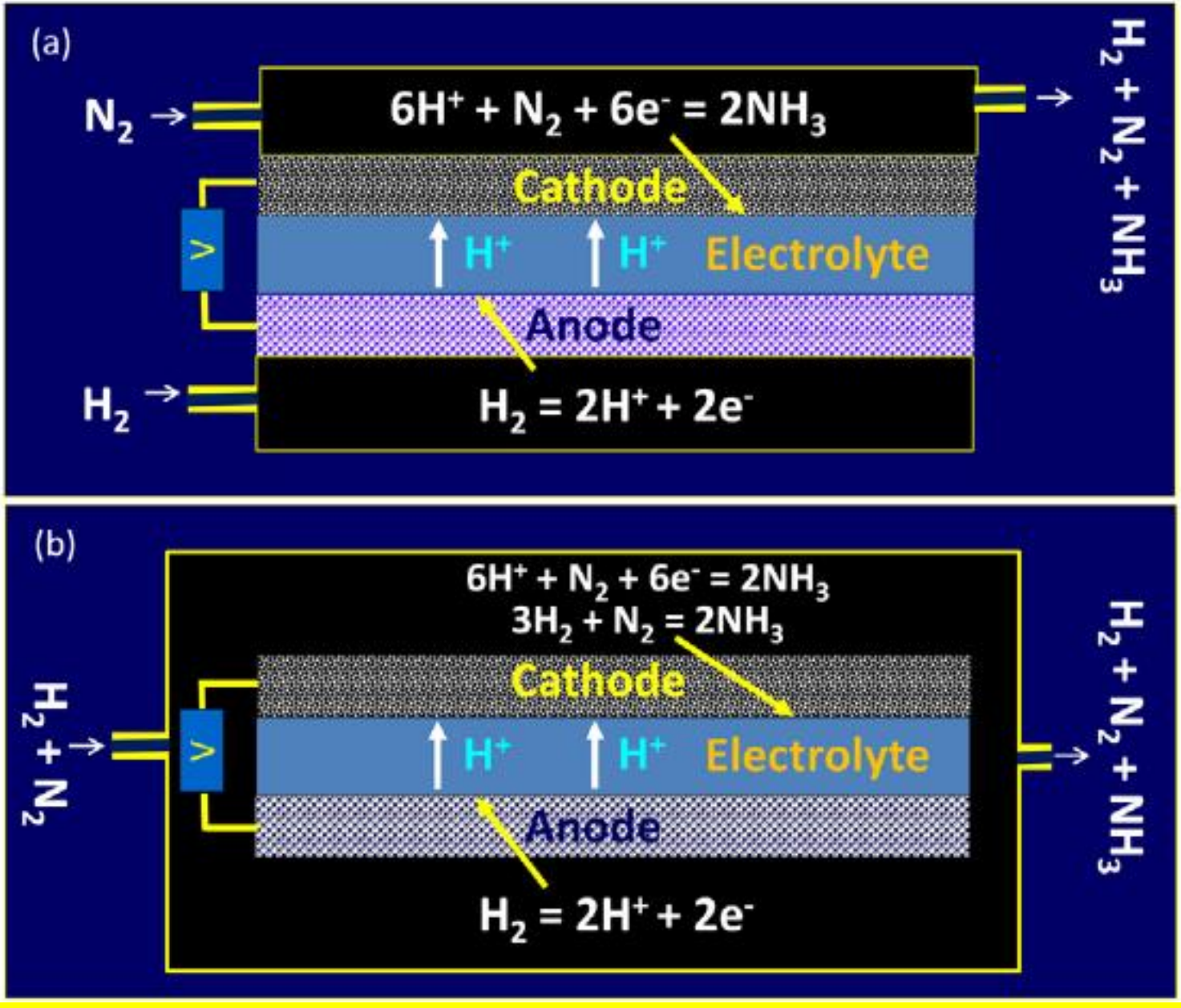
Perovskites



Fluorites

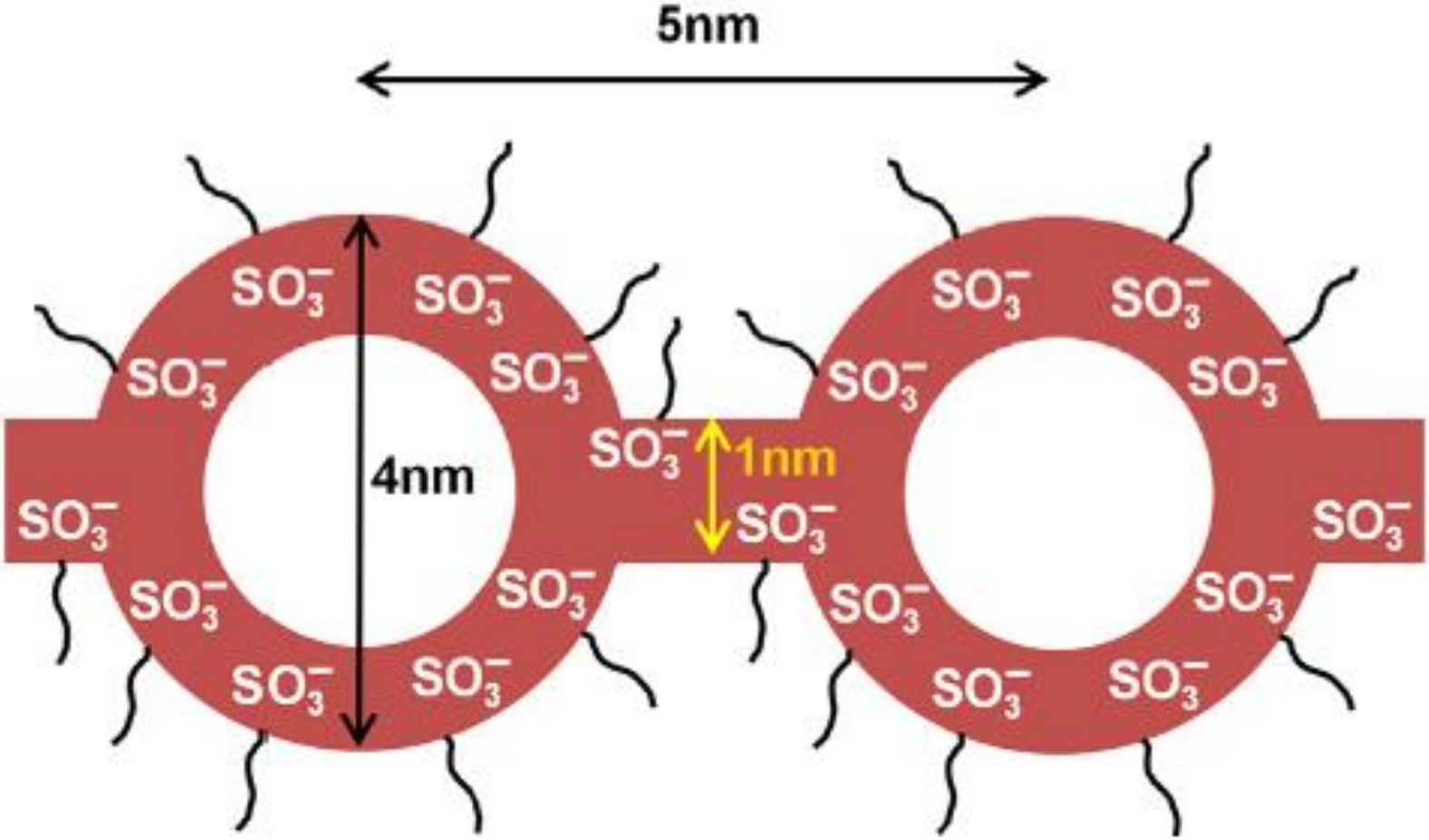


Pyrochlores



Proton Conducting Ceramic Electrolyte Cell

TOP: Double-chamber **BOTTOM: Single-chamber**



Cluster Model of "NAFION" Membrane

~ 10^{-8} mol per cm^2 per second

What is NTP?

- NTP species include: energetic electrons, photons, atoms, and molecules, highly reactive radicals, ozone, etc. Ozone is the most widely used NTP species.
- NTP is generated though electrical discharge in gas (in atmosphere or liquid).

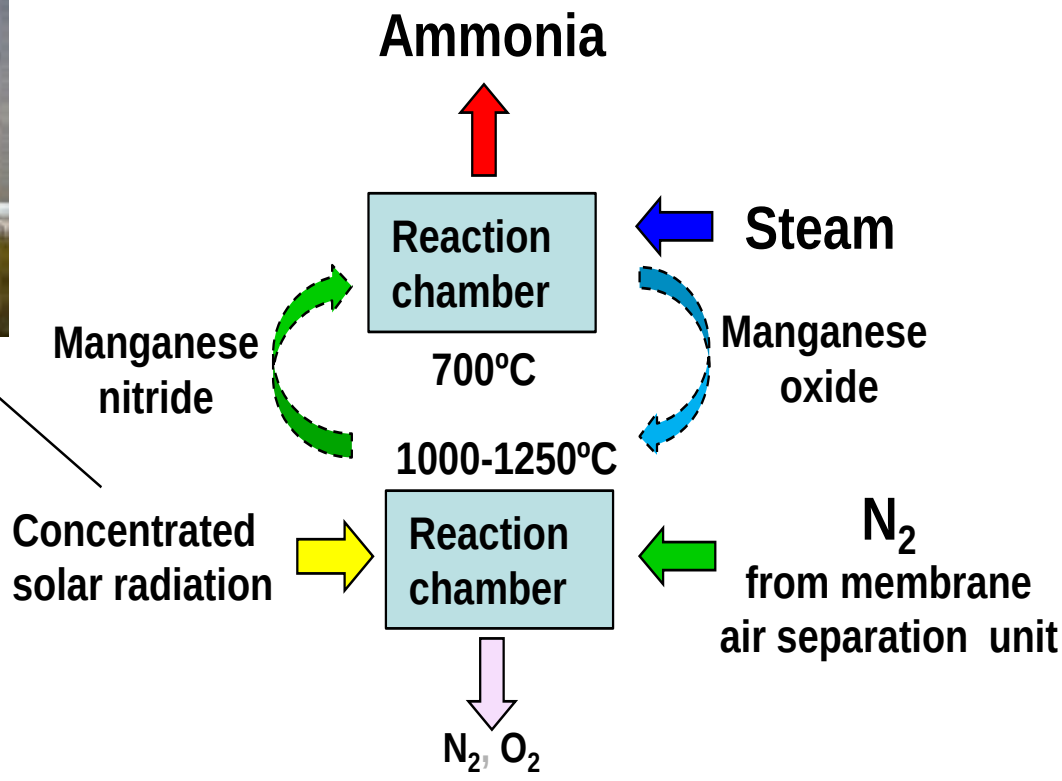
Highest single-pass conversion = 13%

Source: Roger Ruan, University of Minnesota

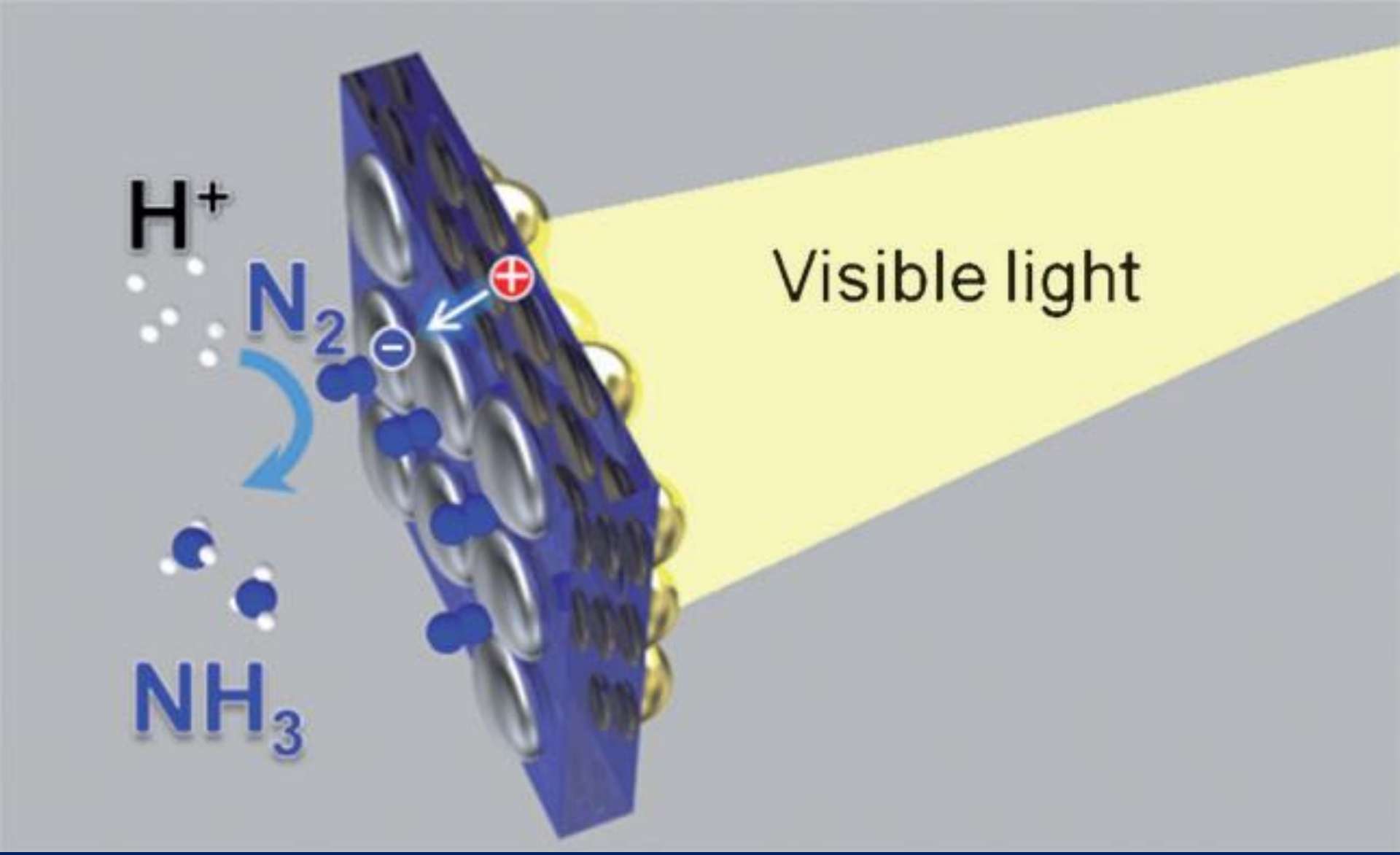
Solar Thermochemical Ammonia

P. Pfromm, R. Michalsky*, Kansas State University

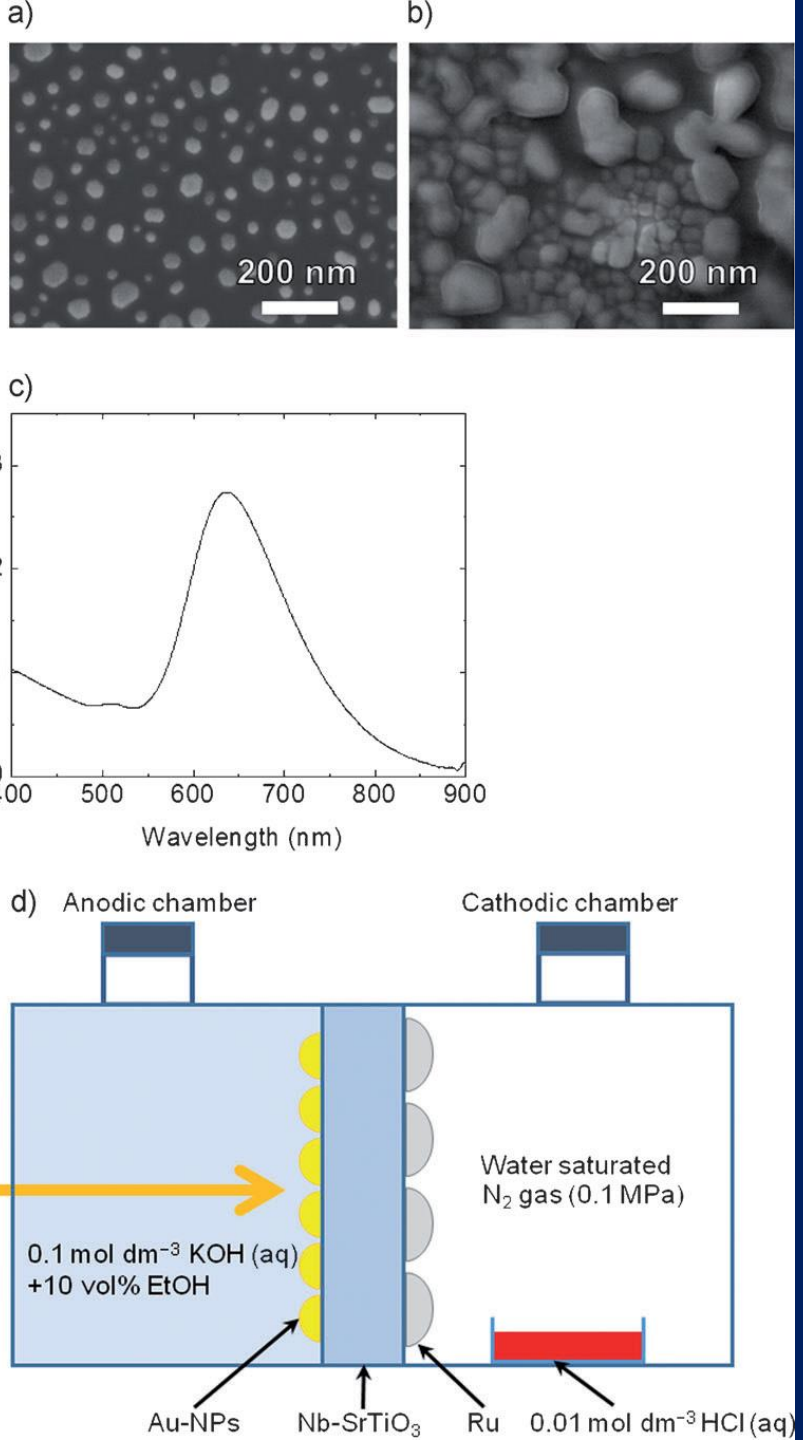
Solar tower with heliostats

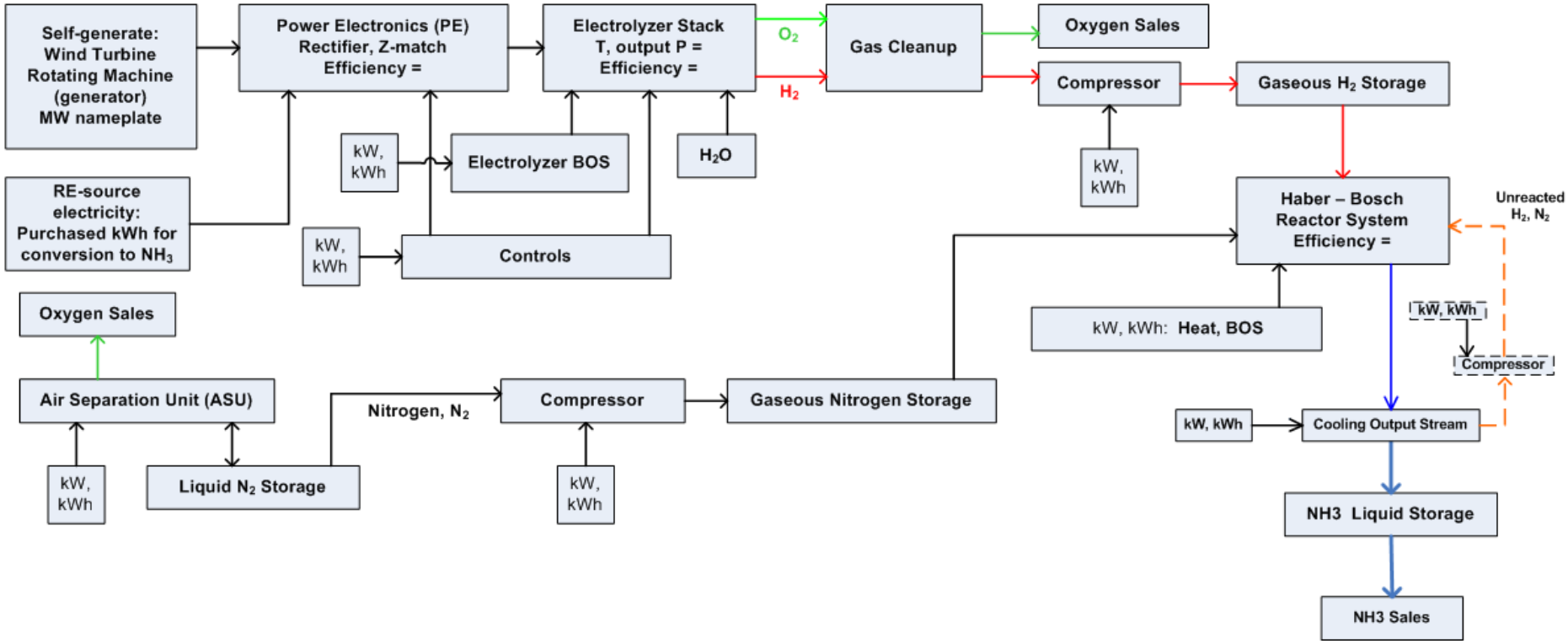


*now ETH, Zurich

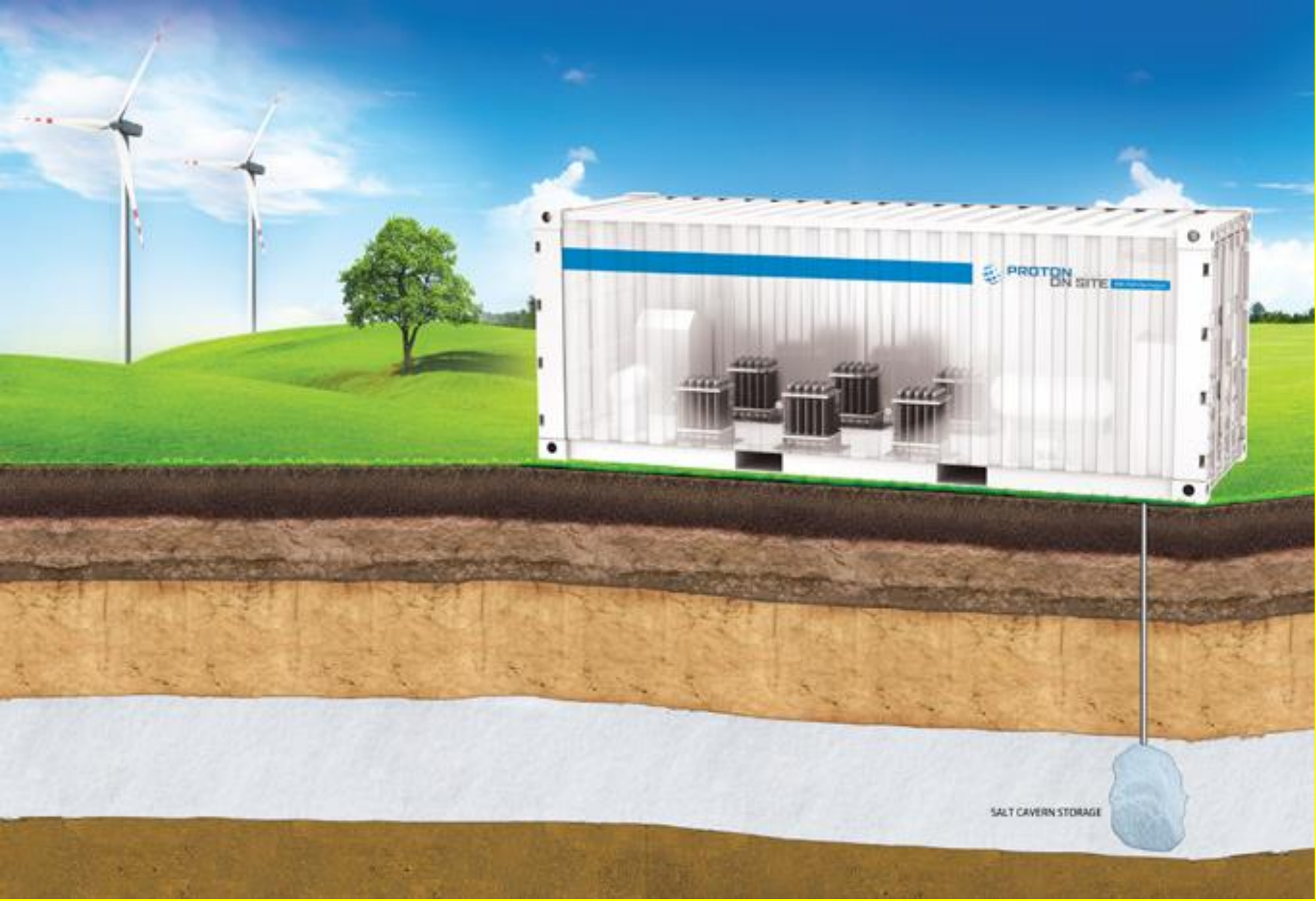


Plasmon-Induced Ammonia Synthesis through Nitrogen Photofixation with Visible Light Irradiation

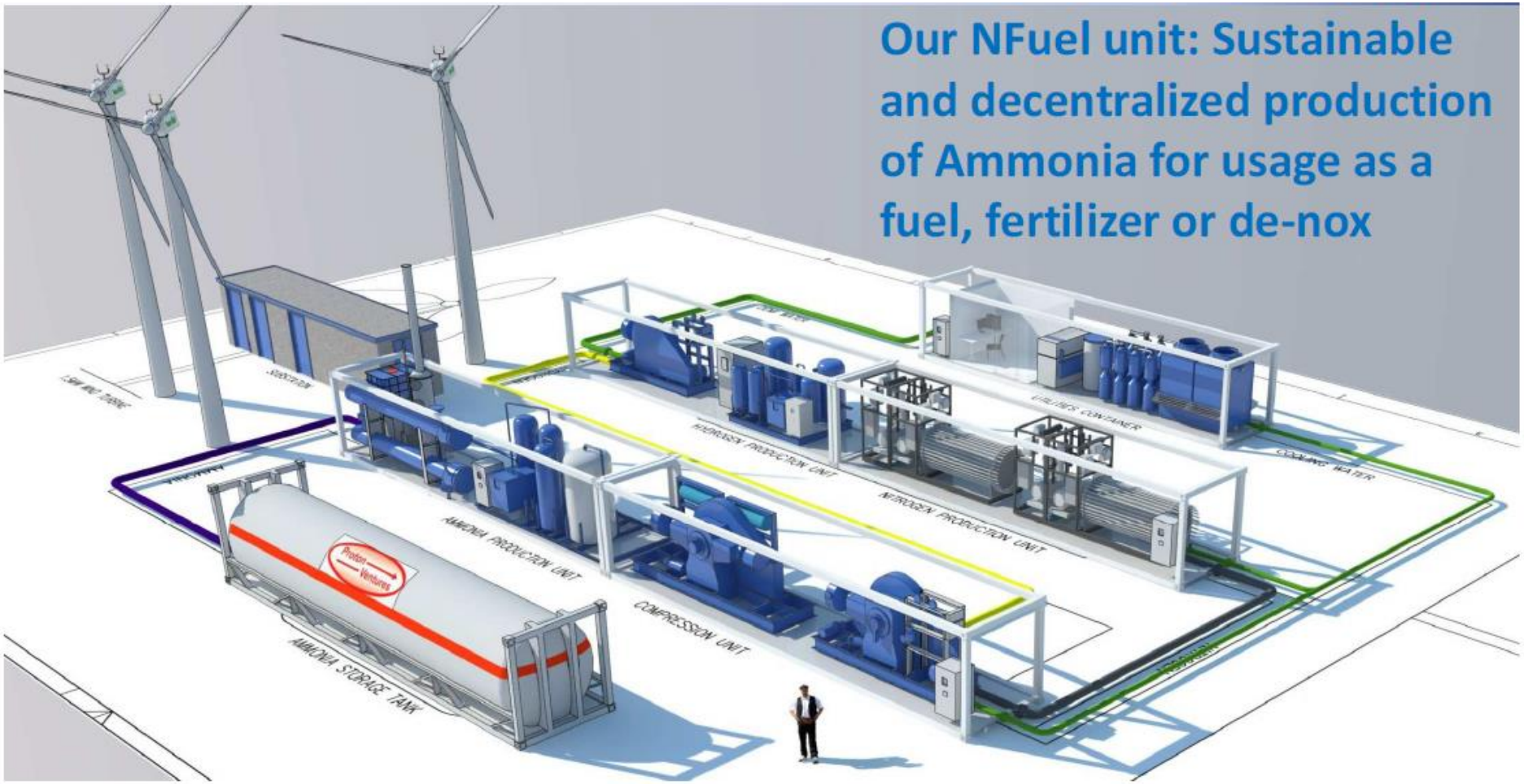

a)
b)
200 nm
200 nm
c)
Extinction
0.0
0.1
0.2
0.3
400
500
600
700
800
900
Wavelength (nm)
d)
Anodic chamber
Cathodic chamber
Xe Lamp
hν (λ=550-800 nm)
0.1 mol dm−3 KOH (aq)
+10 vol% EtOH
Water saturated
N2 gas (0.1 MPa)
Au-NPs
Nb-SrTiO3
Ru
0.01 mol dm−3 HCl (aq)



Ag Ventures Alliance, Mason City, Iowa
Electrolysis + Haber-Bosch (EHB) system
For RE-source Electricity, Water, and Air inputs

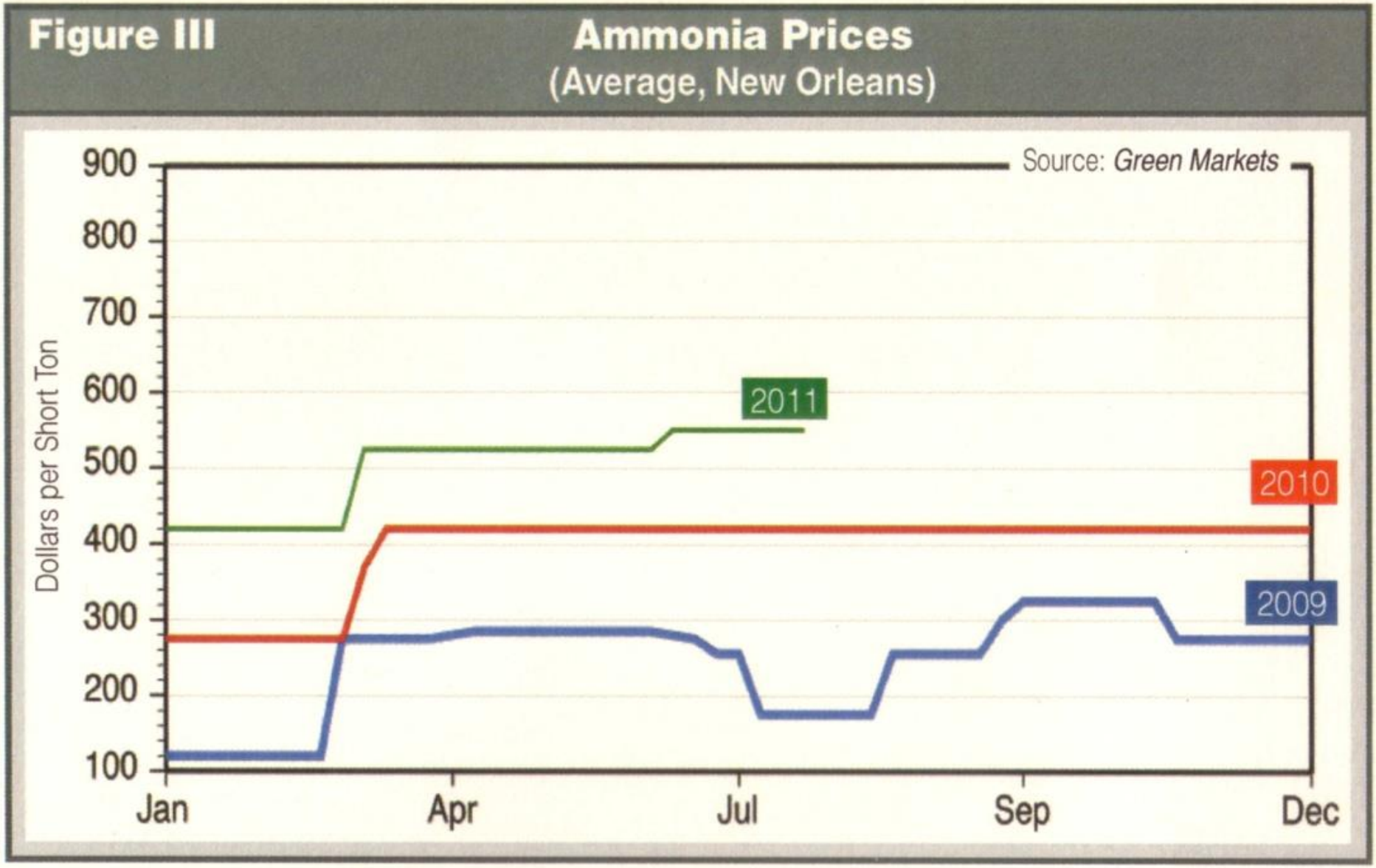


Source: Proton Onsite

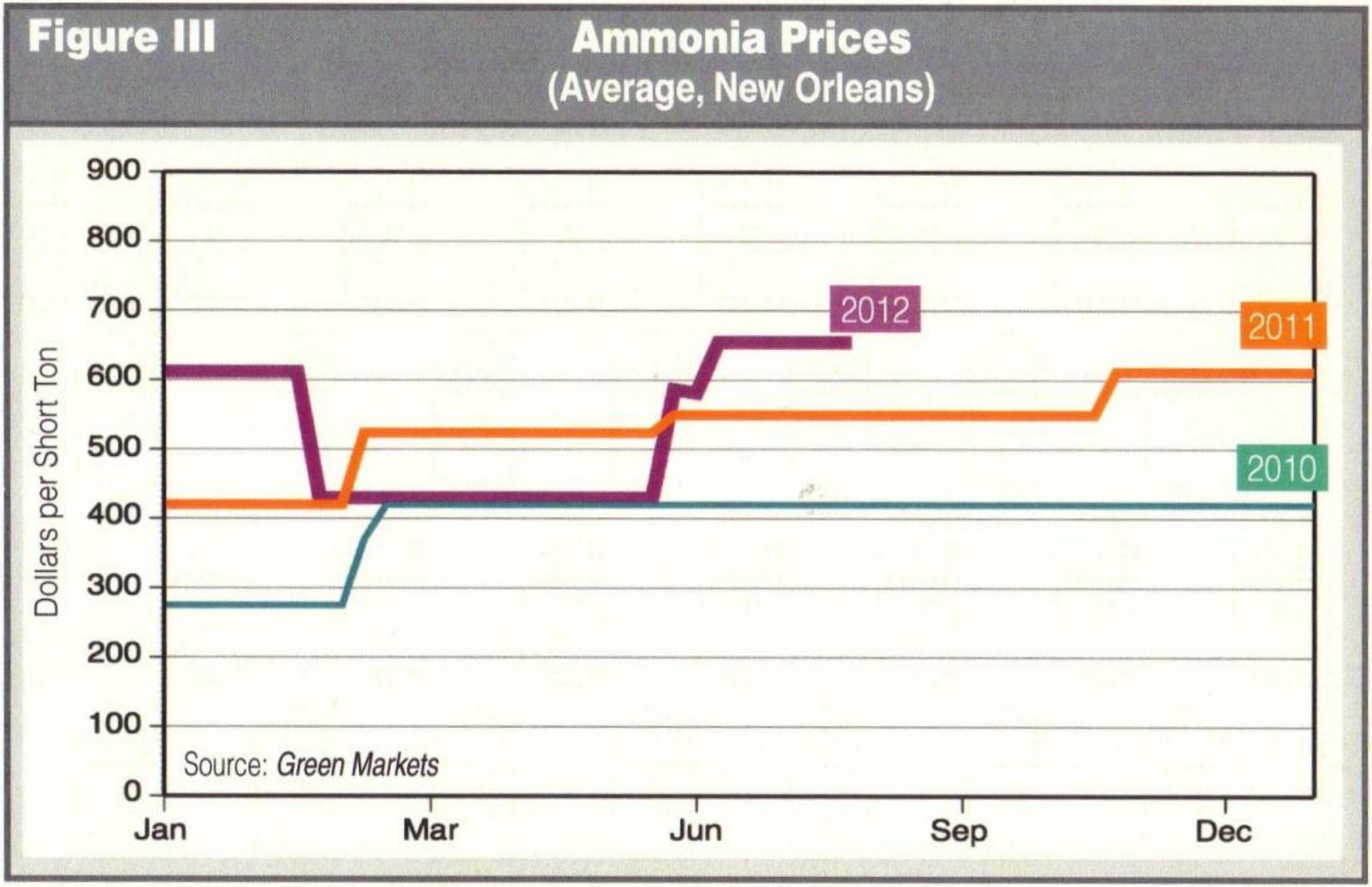


Proton Ventures BV, Netherlands

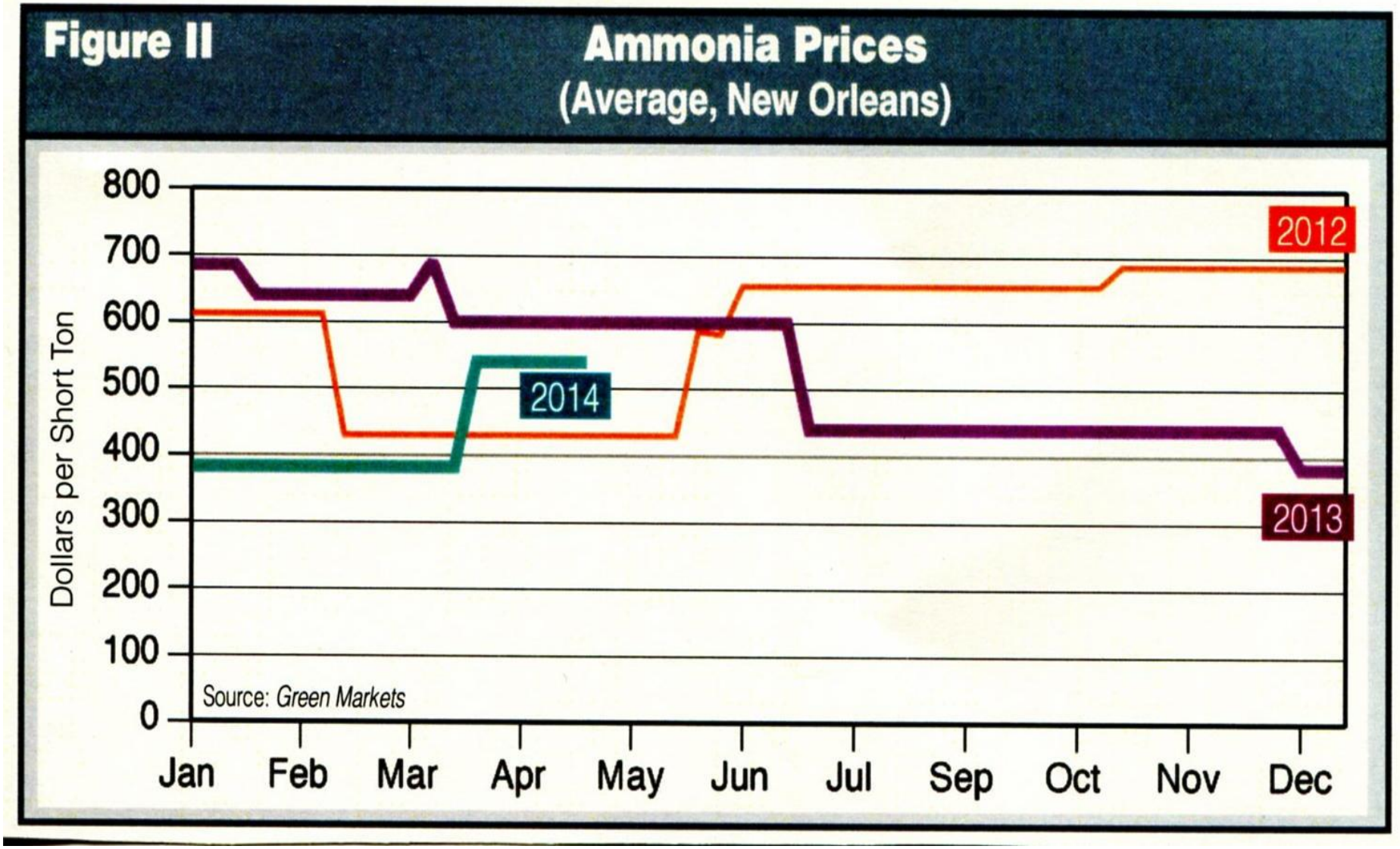
www.protonventures.com



Source: FINDS, Keith Stokes



Source: FINDS, Keith Stokes

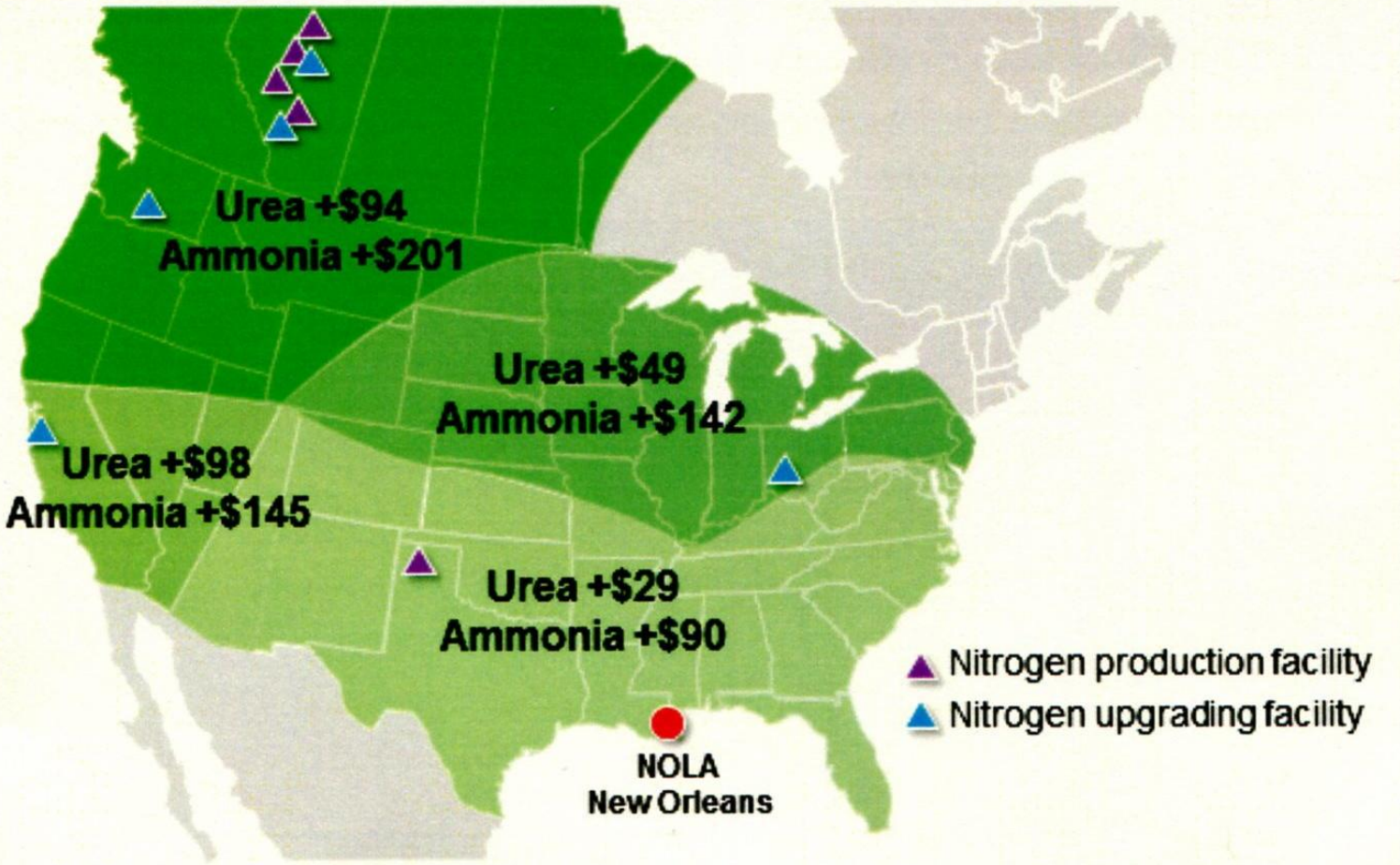


Source: FINDS, Keith Stokes

Figure V

Regional Nitrogen Price Premium Over U.S. Gulf (NOLA) Price

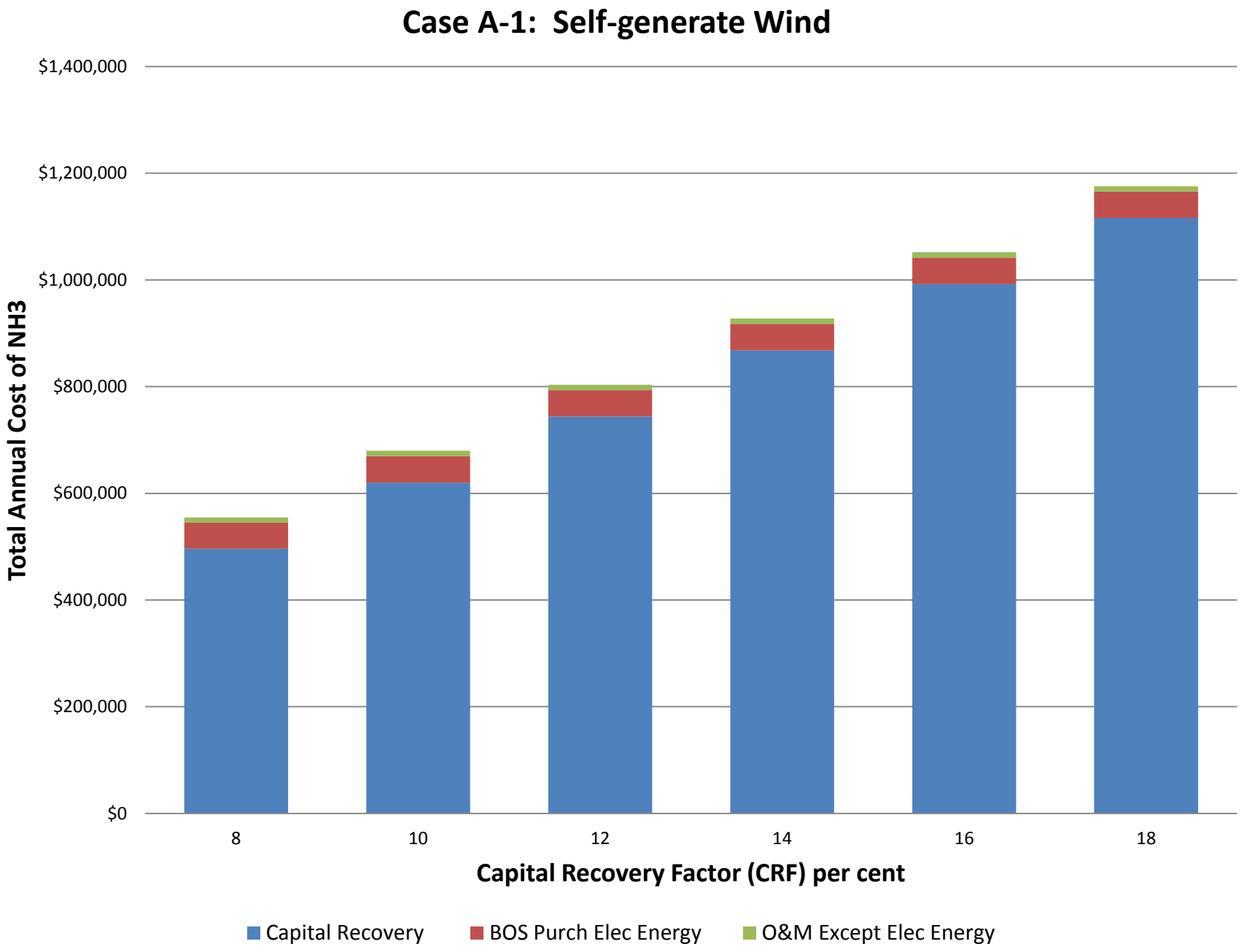
($U.S./metric tonne)



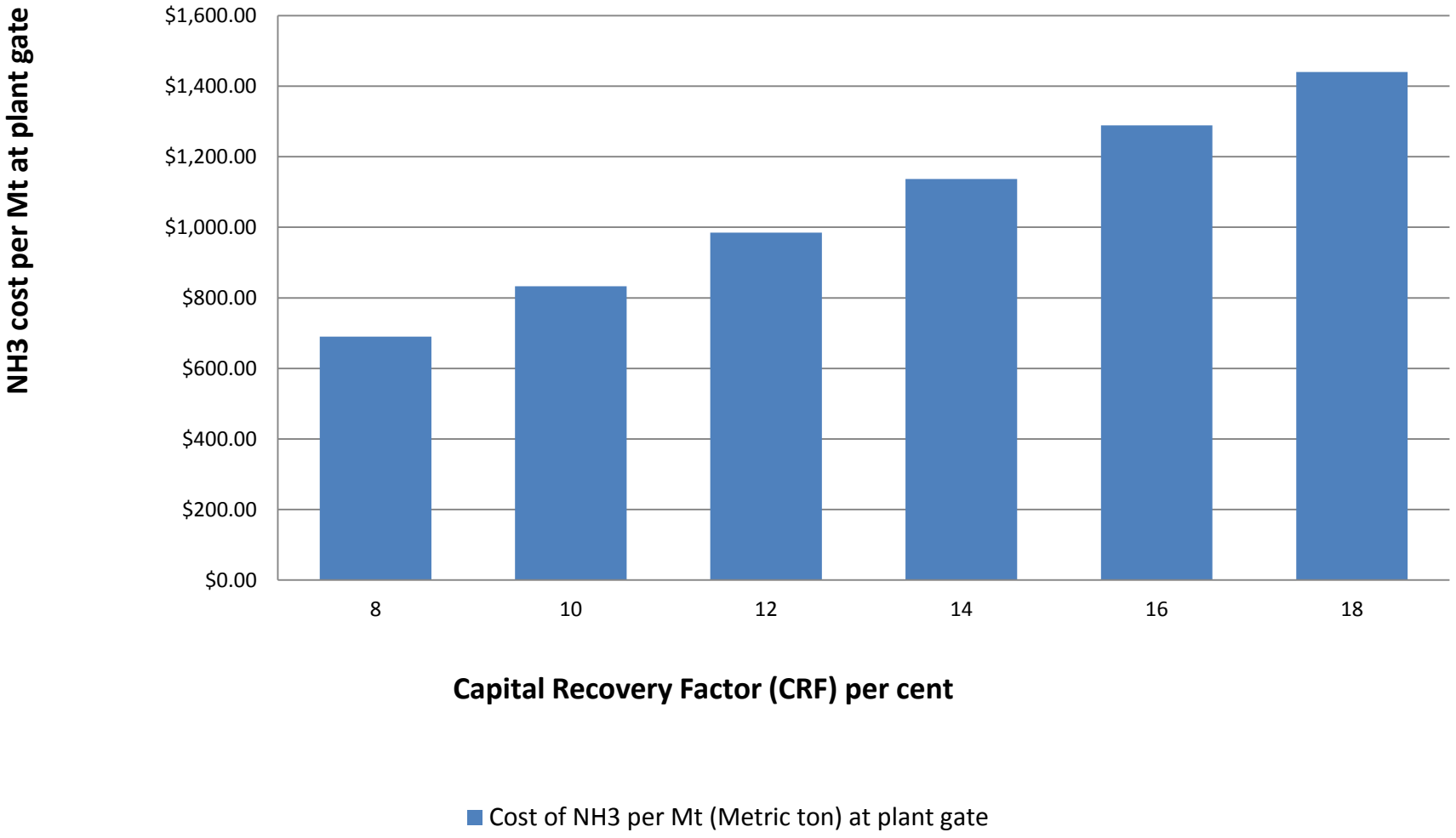
NOTE: Delivered prices adjusted by -$5/t for urea and -$9/t for ammonia to estimate FOB prices. Based on a 10-year average from 2003-2012.

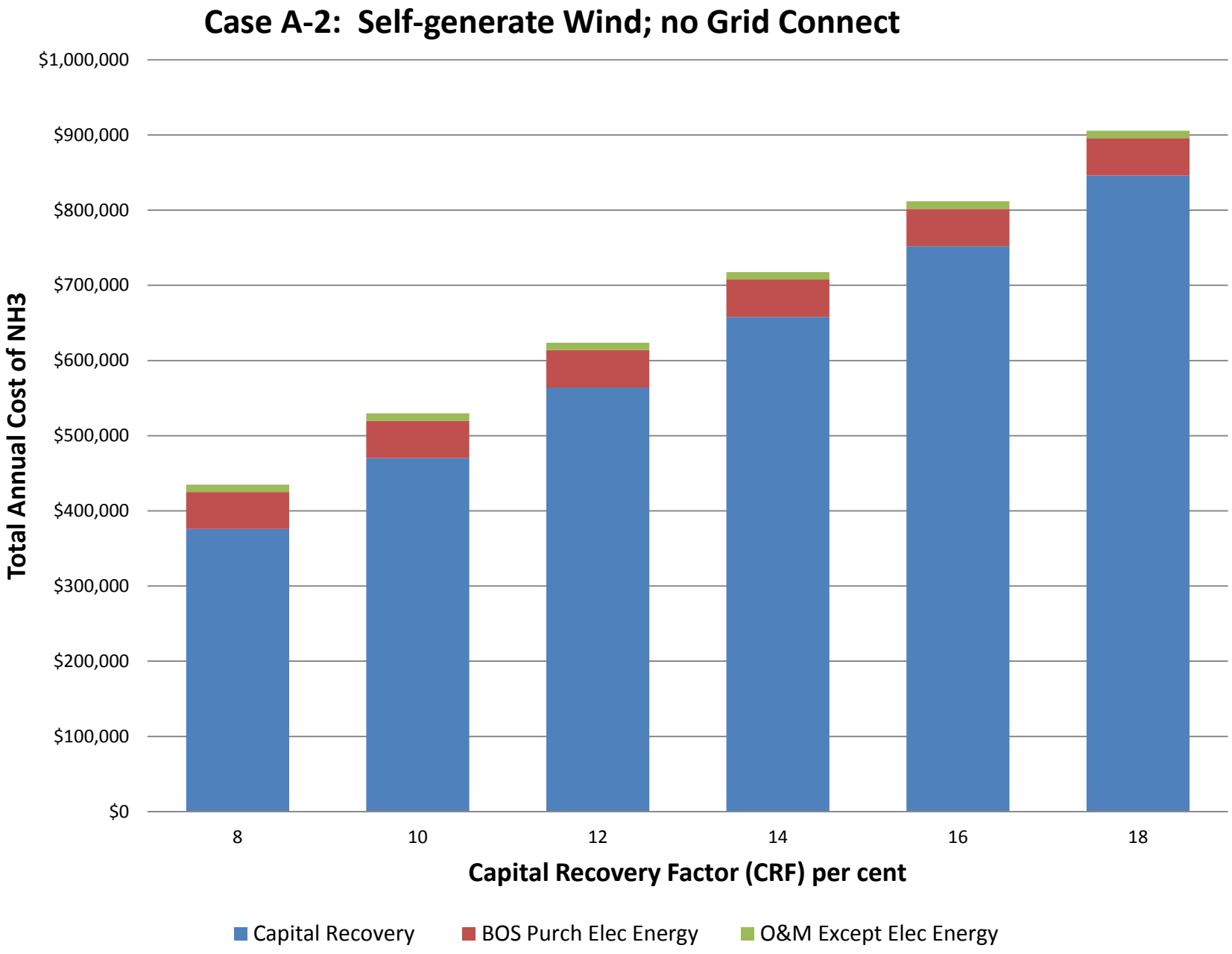
SOURCE: *GreenMarkets*: Spread equals average regional reference price minus NOLA reference price.

Source: FINDS, Keith Stokes

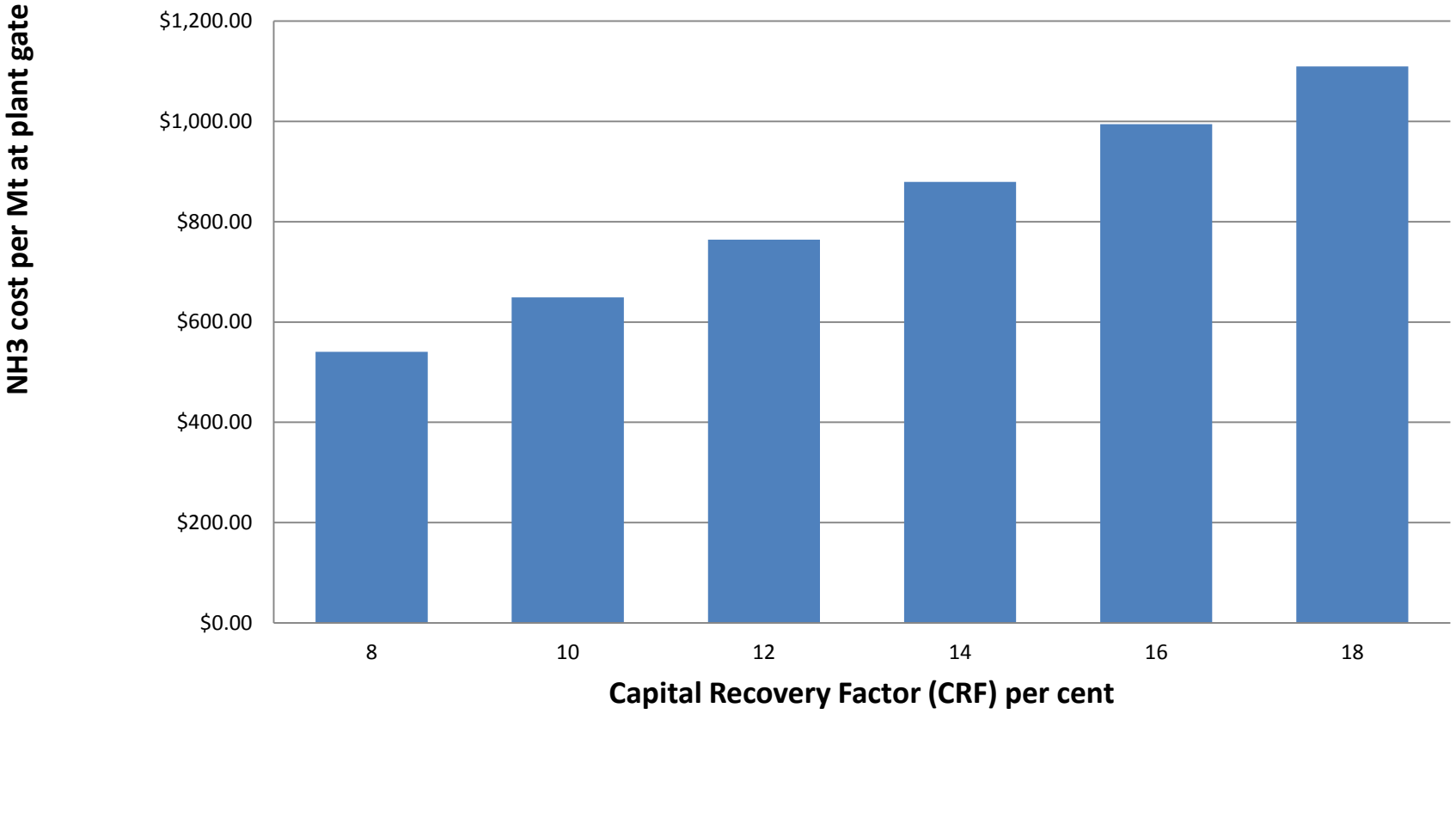

Case A-1: Self-generate Wind
$1,400,000
$1,200,000
$1,000,000
$800,000
$600,000
$400,000
$200,000
$0
Total Annual Cost of NH3
8
10
12
14
16
18
Capital Recovery Factor (CRF) per cent
Capital Recovery
BOS Purch Elec Energy
O&M Except Elec Energy

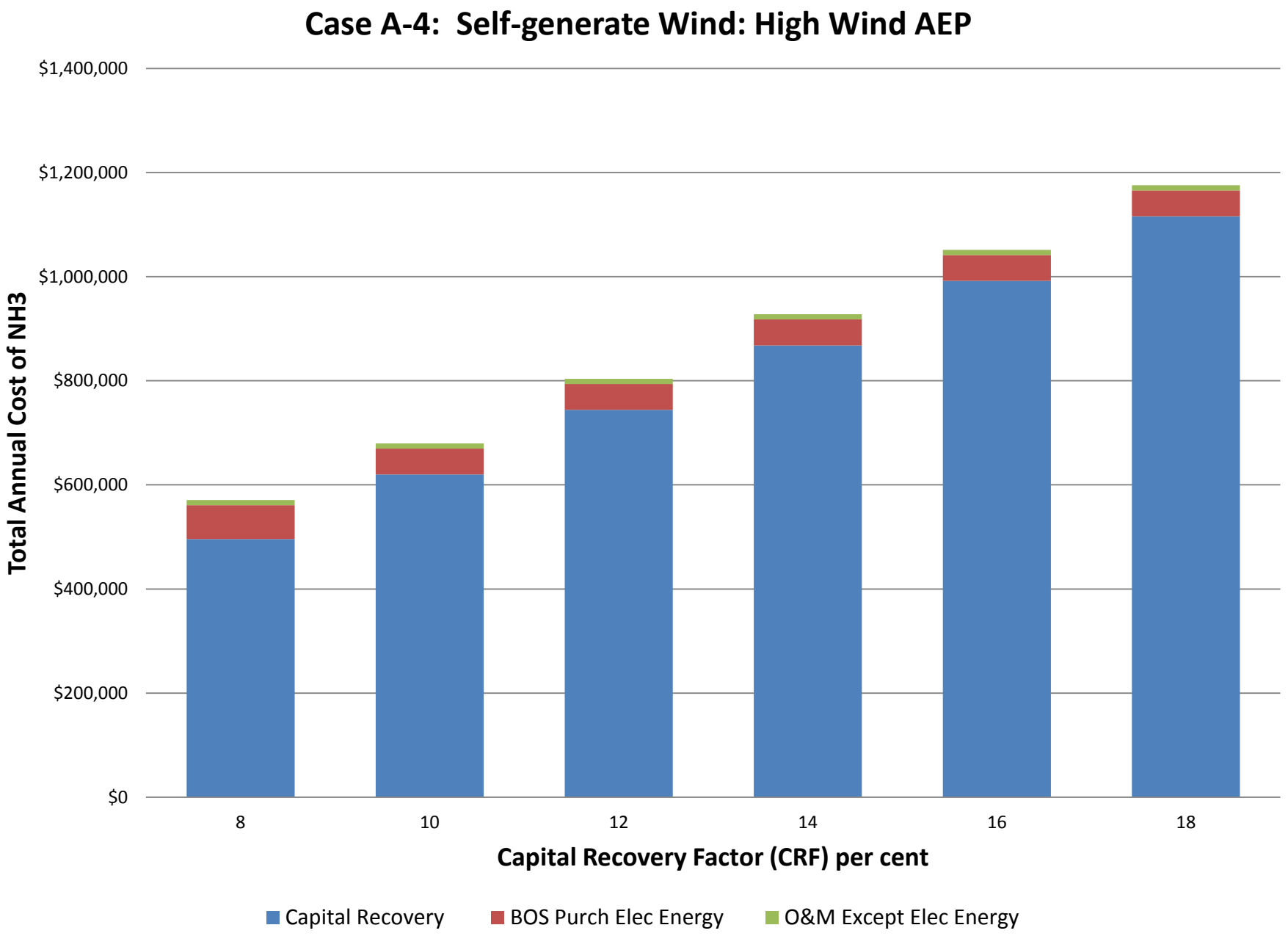
Case A-1: Self-generate Wind



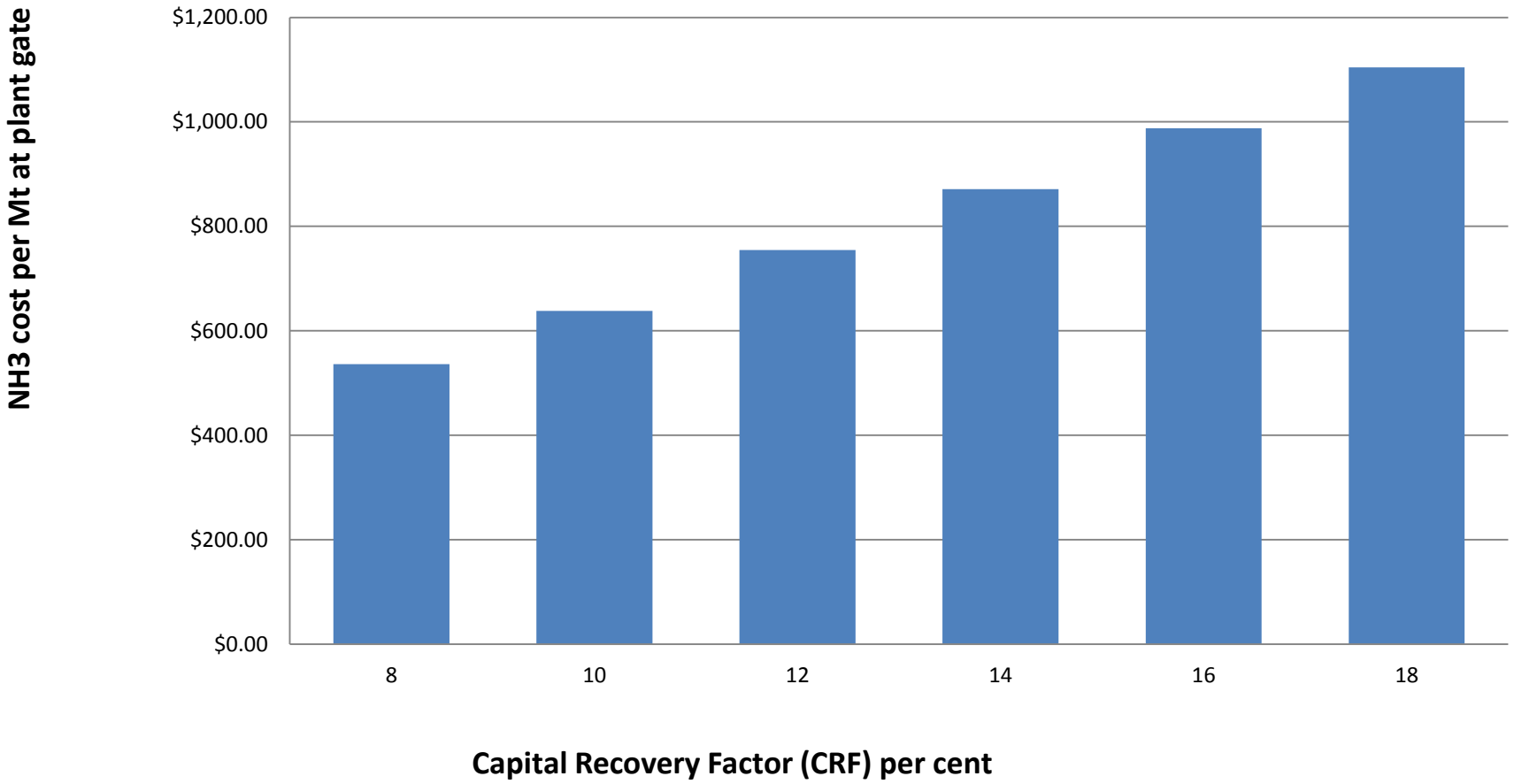

Case A-2: Self-generate Wind; no Grid Connect
$1,000,000
$900,000
$800,000
$700,000
$600,000
$500,000
$400,000
$300,000
$200,000
$100,000
$0
Total Annual Cost of NH3
8
10
12
14
16
18
Capital Recovery Factor (CRF) per cent
Capital Recovery
BOS Purch Elec Energy
O&M Except Elec Energy

Case A-2: Self-generate Wind; no Grid Connect

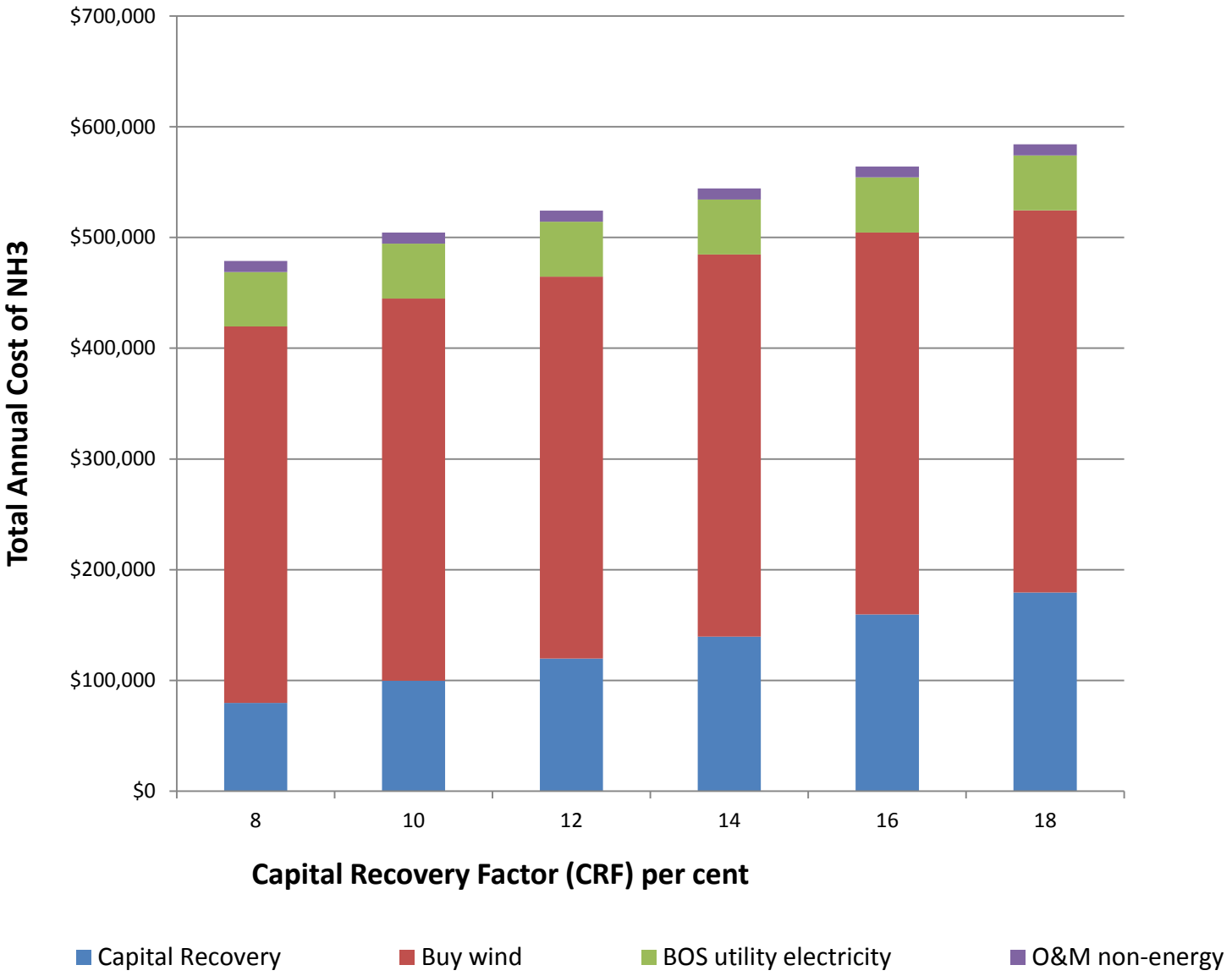


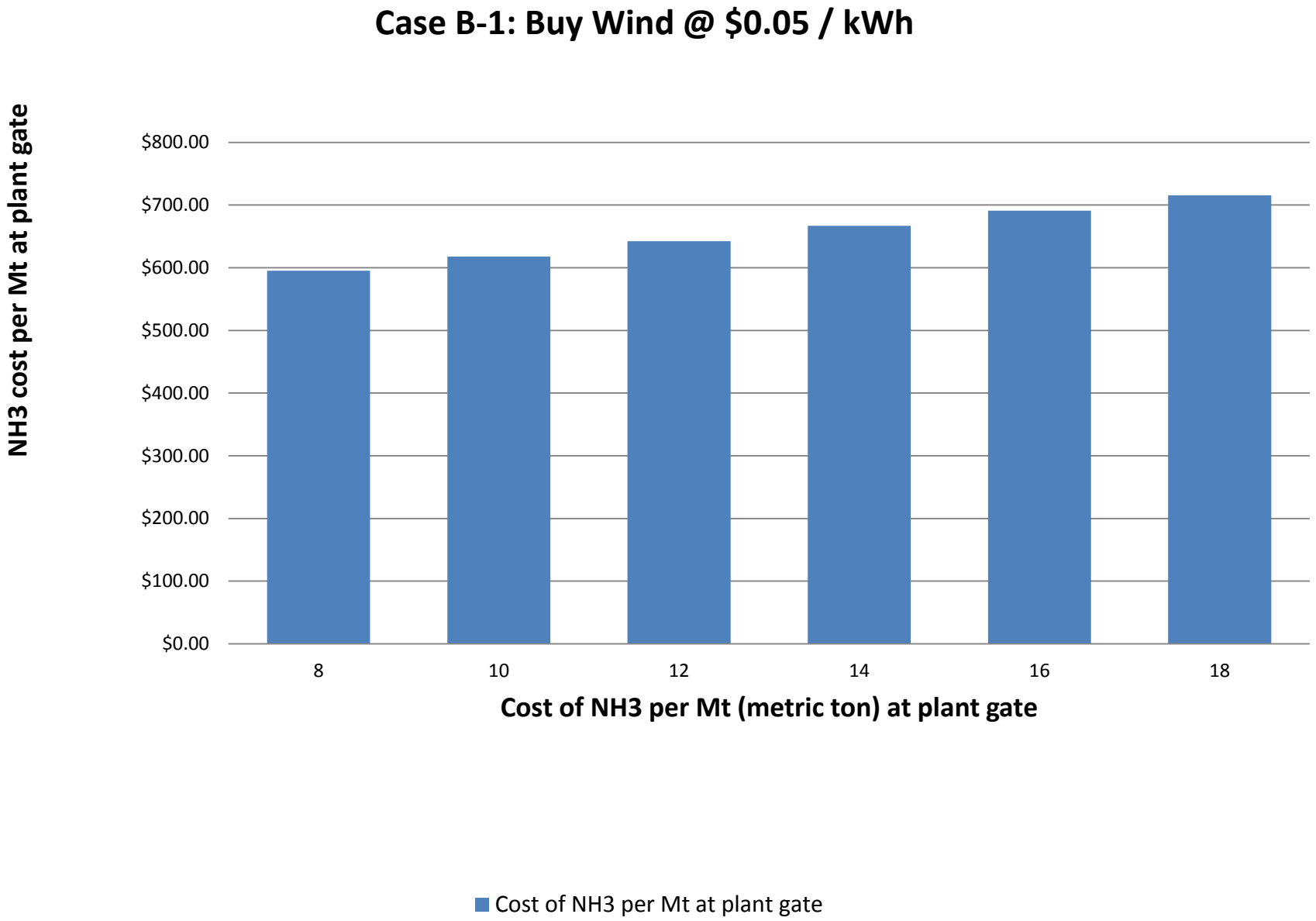

Case A-4: Self-generate Wind: High Wind AEP
$1,400,000
$1,200,000
$1,000,000
$800,000
$600,000
$400,000
$200,000
$0
Total Annual Cost of NH3
8
10
12
14
16
18
Capital Recovery Factor (CRF) per cent
Capital Recovery
BOS Purch Elec Energy
O&M Except Elec Energy

Case A-4: Self-generate Wind: High Wind AEP

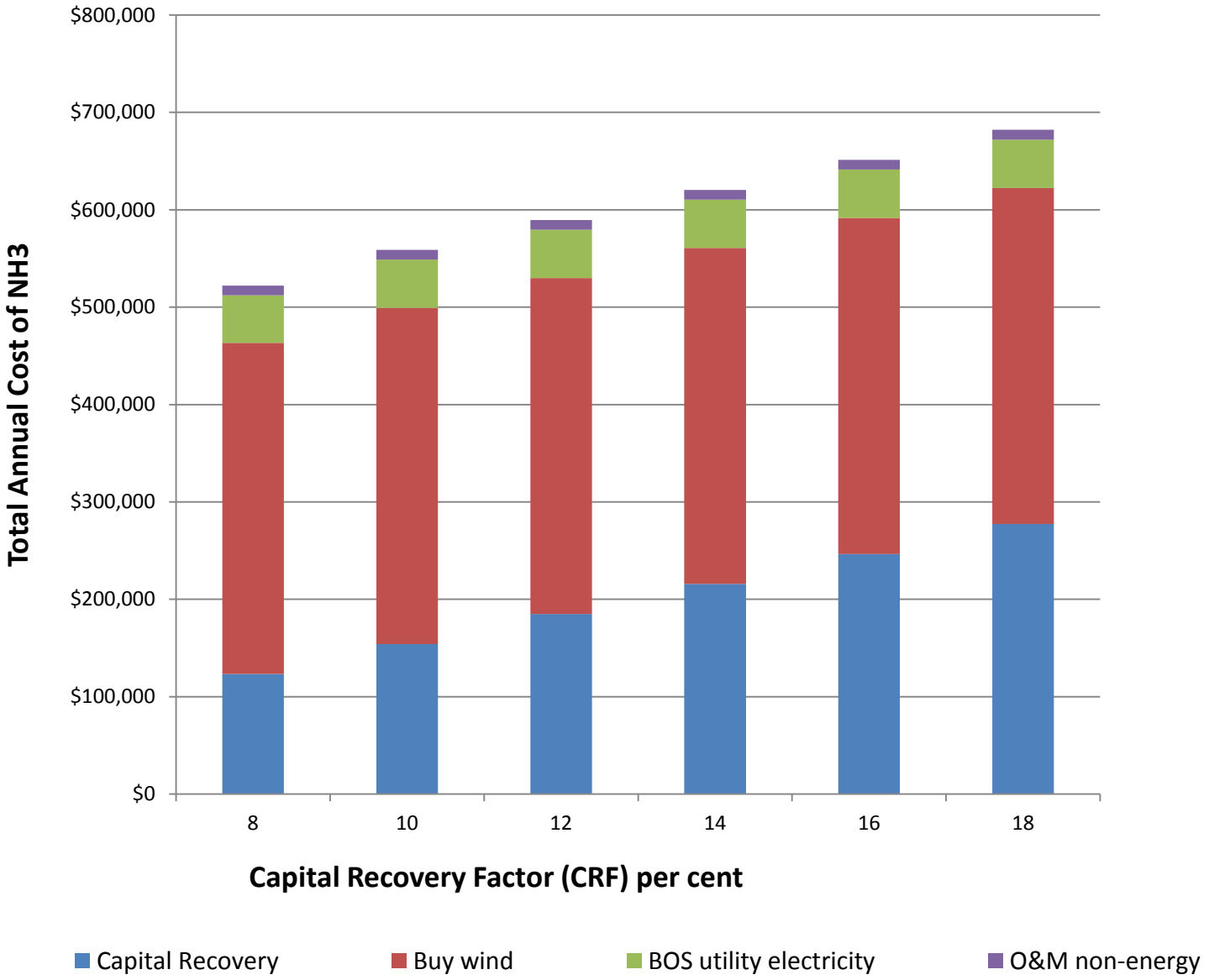


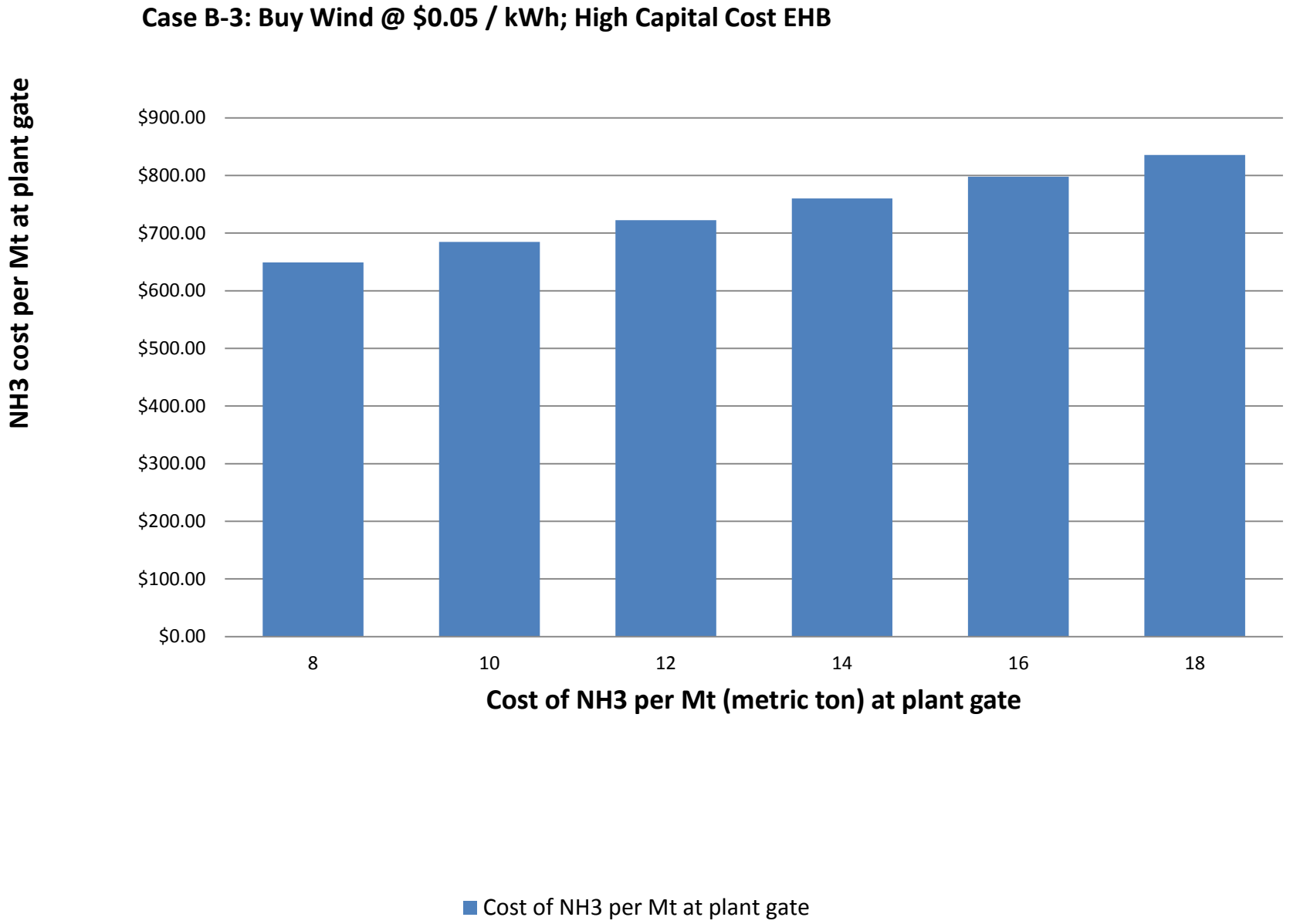
Case B-1: Buy Wind @ $ 0.05 / kWh




Case B-1: Buy Wind @ $0.05 / kWh
NH3 cost per Mt at plant gate
$800.00
$700.00
$600.00
$500.00
$400.00
$300.00
$200.00
$100.00
$0.00
8
10
12
14
16
18
Cost of NH3 per Mt (metric ton) at plant gate
Cost of NH3 per Mt at plant gate

Case B-3: Buy Wind @ $ 0.05 / kWh; High Capital Cost EHB




Case B-3: Buy Wind @ $0.05 / kWh; High Capital Cost EHB
NH3 cost per Mt at plant gate
$900.00
$800.00
$700.00
$600.00
$500.00
$400.00
$300.00
$200.00
$100.00
$0.00
8
10
12
14
16
18
Cost of NH3 per Mt (metric ton) at plant gate
Cost of NH3 per Mt at plant gate

Landscape: RE-source NH3

- Alaska demo project: AASI
- Artificial Photosynthesis: UK, July ‘14
- Ag Ventures, Iowa: Wind → NH3 study
- Synthesis tech survey
  - From H2
  - From electricity
- ICE gensets conversion: demand demo
- Complete RE-source energy systems

Landscape: RE-source NH3 Synthesis

1. **H-B reactor only good candidate**
   - **RE - H2 + N2**
   - **RE electricity → electrolyzer → H2 + O2**
   - **Complex system: Alaska deploy ?**
   - **MWe input scale costs, efficiency unknown**

2. **Beyond Haber-Bosch "BHB" Electrolytic**
   - **Diverse technologies**
   - **TRL 1 – 3**
   - **Less complex system ?**
   - **MWe input scale costs, efficiency unknown**

Landscape: RE-source NH3 Synthesis

- **Electricity source RE:**
  - **H-B reactor only good candidate**
  - **Electrolysis plus Haber-Bosch (EHB)**
- **Hydrogen source RE:**
  - **H-B reactor only good candidate**
  - **Beyond Haber-Bosch "BHB" Electrolytic**
- **Many technology options:**
  - **All TRL 1 – 3**
  - **Years and $ for R&D, Demo, Commercialize**

NH3 from Renewable-source Electricity, Water, and Air: Technology Options and Economics Modeling

DVD's + Handouts

Ammonia Fuel Association
21 – 24 September 2014
Des Moines, Iowa USA

Bill Leighty, Director
The Leighty Foundation
Juneau, AK
wleighty@earthlink.net
907-586-1426 206-719-5554 cell