Innovative Circular Technologies for Harmful Nitrogen Compounds/ To Solve Planetary Boundary Issues

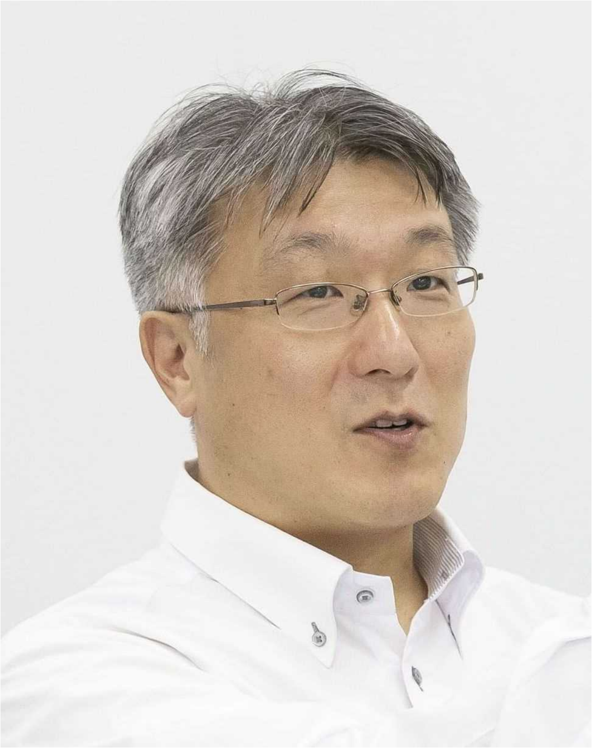
PM : Dr. Tohru KAWAMOTO, Prime Senior Researcher, AIST

Implementing organizations :

AIST, The University of Tokyo, Waseda University,
Tokyo University of Agriculture and Technology, Kobe University,
Osaka University, Yamaguchi University,
Kyowa,Hakko Bio Co., Ltd., ASTOM Corporation, Toyobo Co., Ltd.,
FUSO Corporation, Ube Industries, Ltd,

Subcontracting :

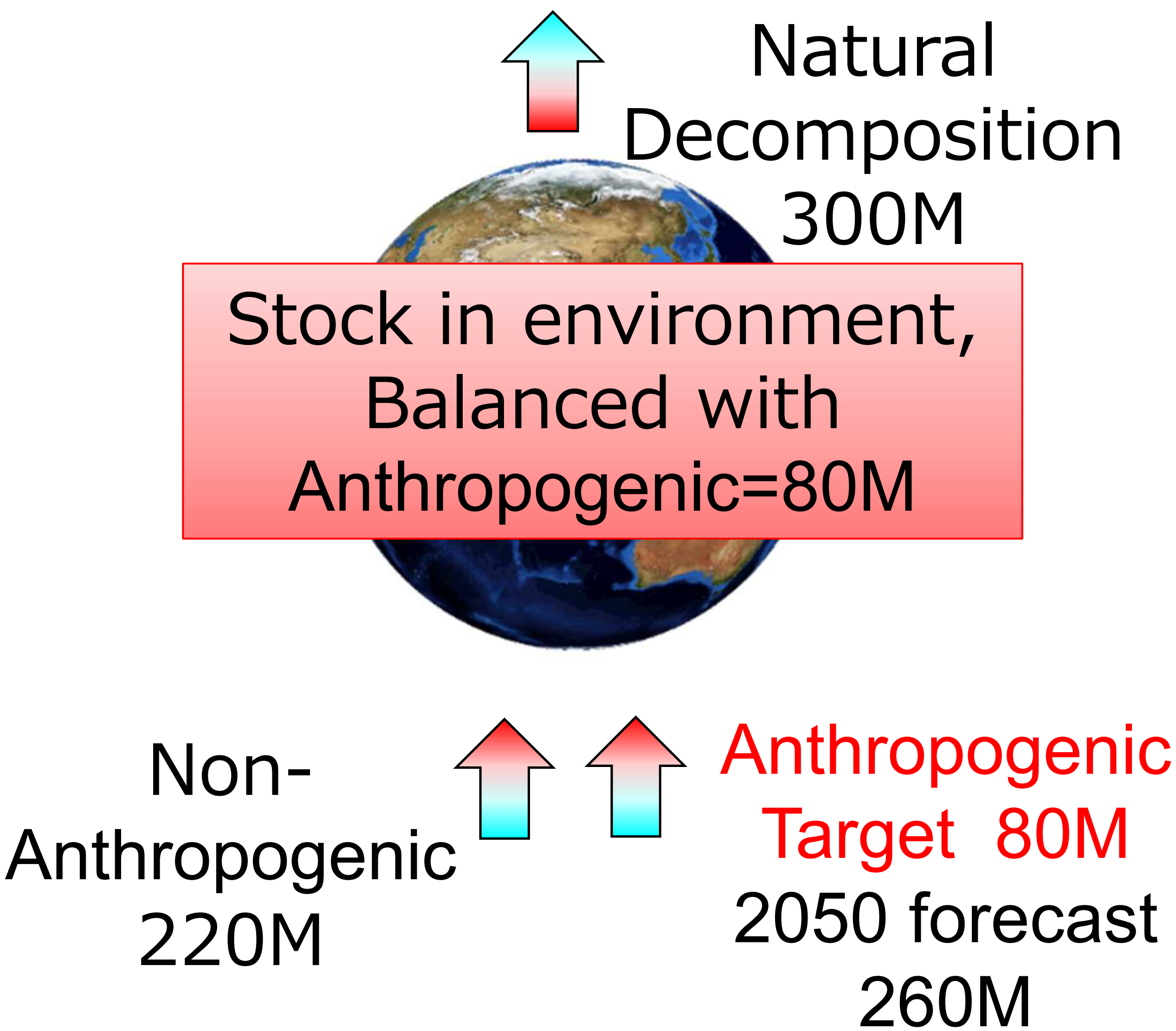
Tokyo Institute of Technology, Kyoto University,
Hiroshima University, Nagoya University, Seibu Giken



Dr. Tohru Kawamoto

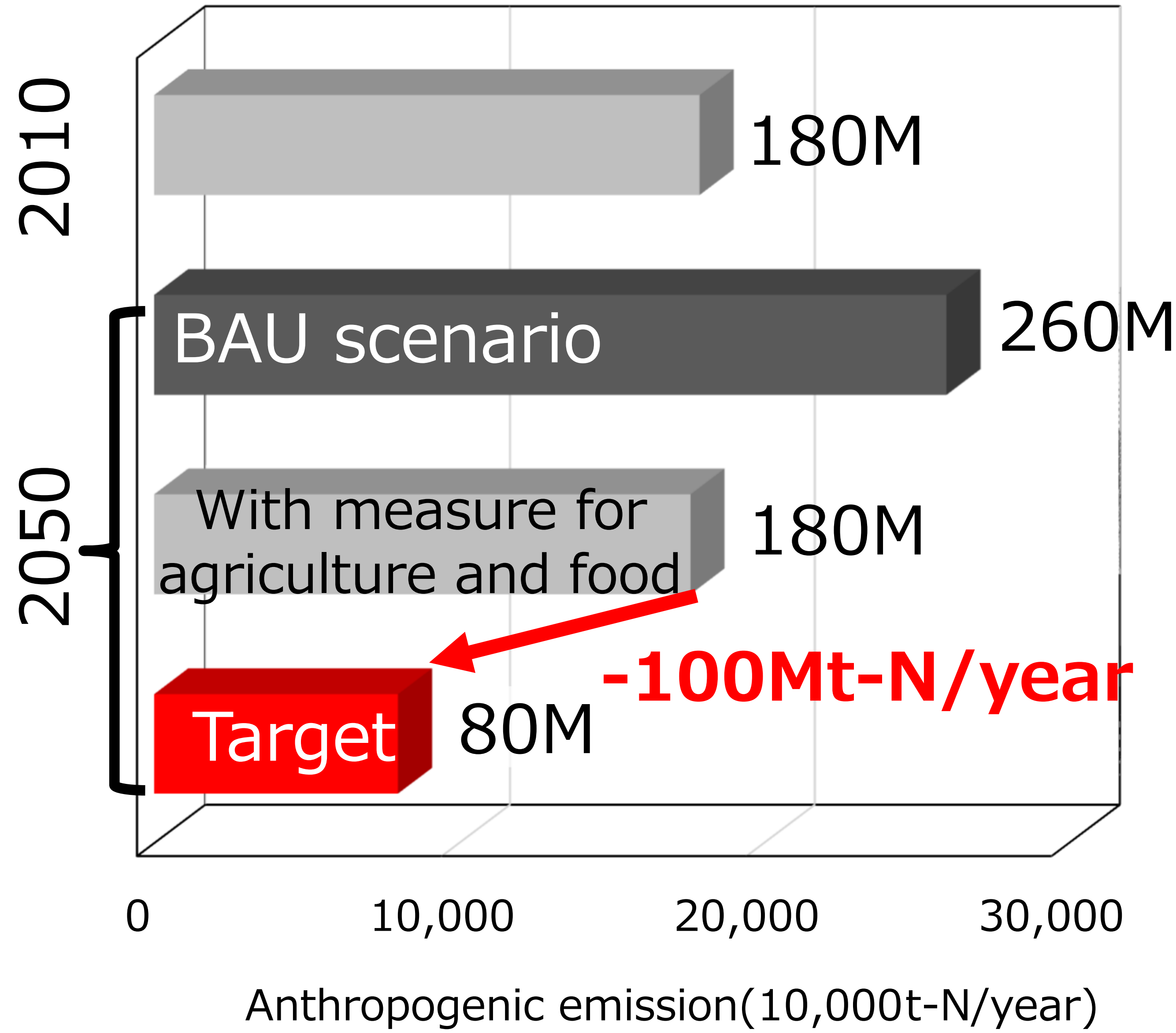
Environmental pollution problems to be solved

(a)Target of Nitrogen compounds emission (t-N/year)



Galloway, Biogeochem. (2004),
Fowler, Philos.Trans. R. Soc. B Biol. Sci. (2013)
de Vries, Curr. Op. Env. Sus. (2013)

(b)Current status and target for anthropogenic nitrogen compound emissions



Tsunemi et al., Sustainability

Target: Establishment of Novel Nitrogen Circulation System

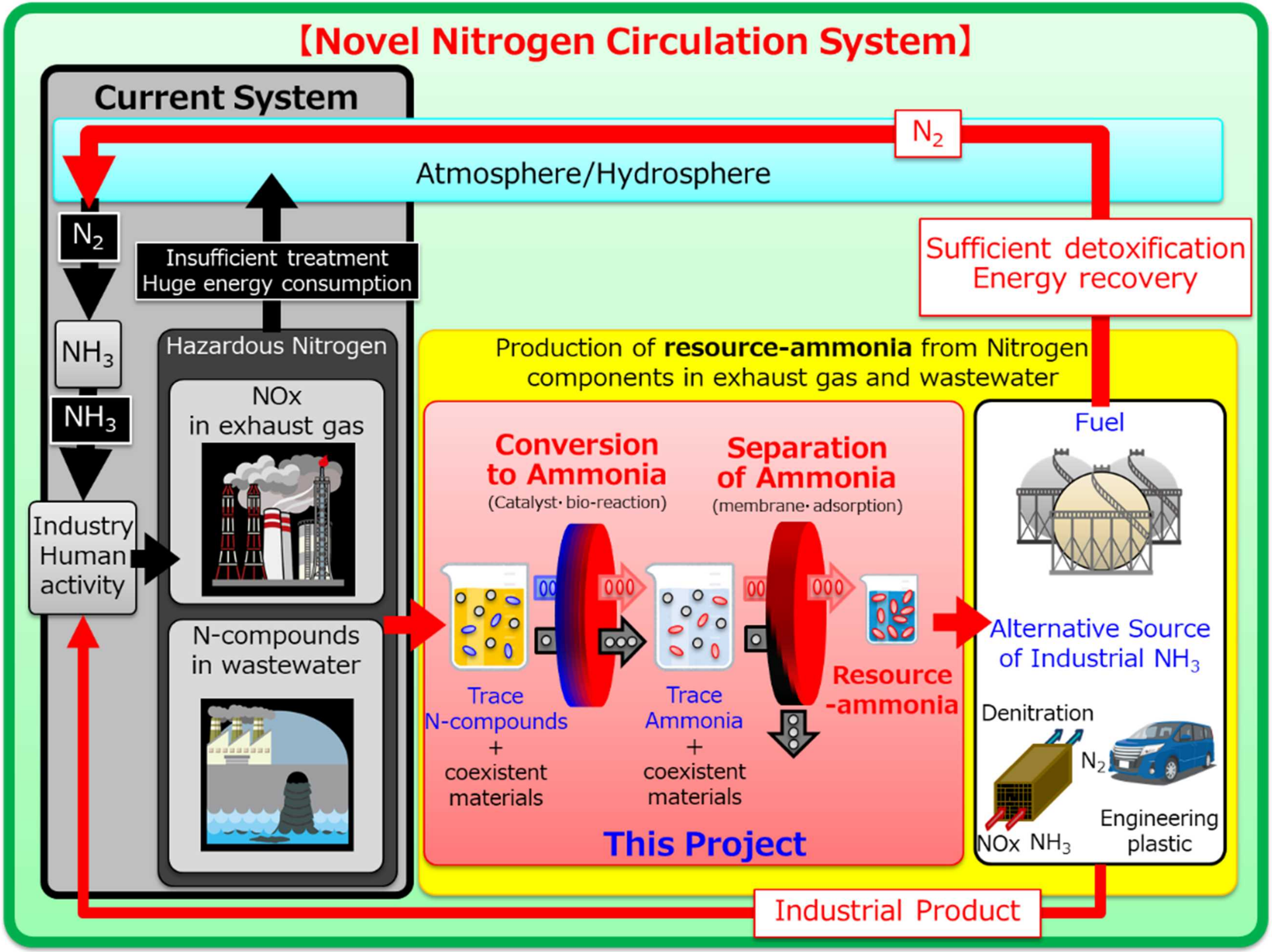
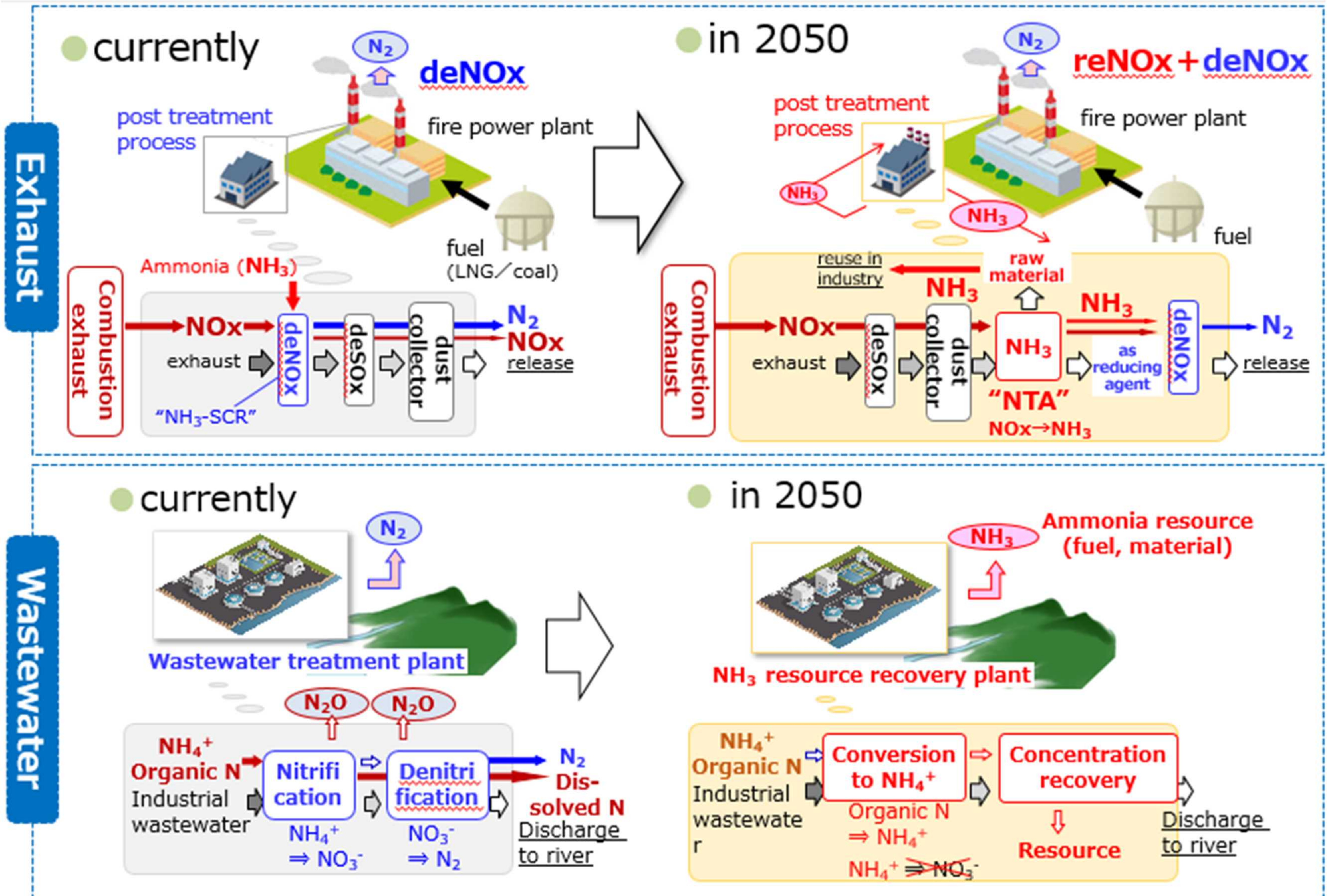


Image of Implementation

NOx in exhaust is converted to NH_3, and utilized as an industrial raw material.
Nitrogen compounds in wastewater are recovered as NH_3, and reused as fuel and raw material.



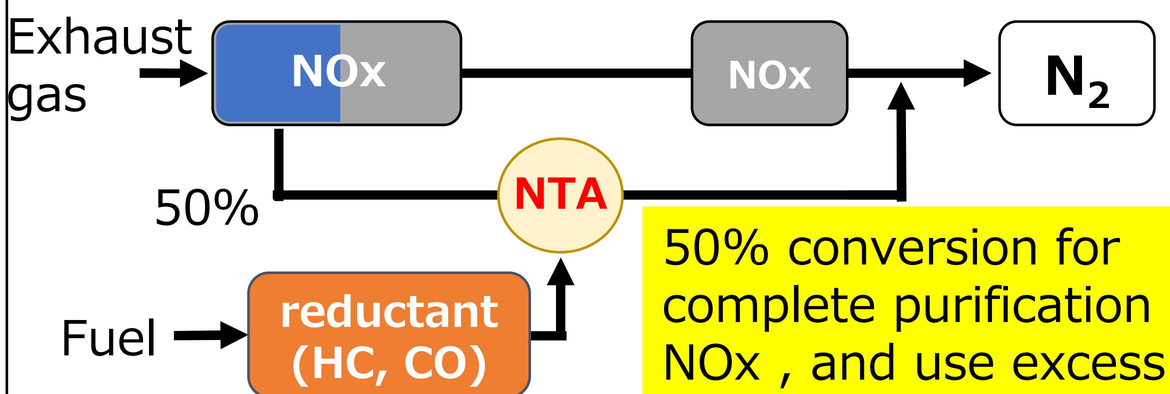
Outline of this project

AIST
Create the Future, Collaborate Together

【1. NOx to ammonia】

Prof. Ogura, Tokyo Univ.

①concentration of NOx·NH_3 in gas phase
②catalyst for NOx→NH_3 at low temperature
③catalyst even with O2 coexistence

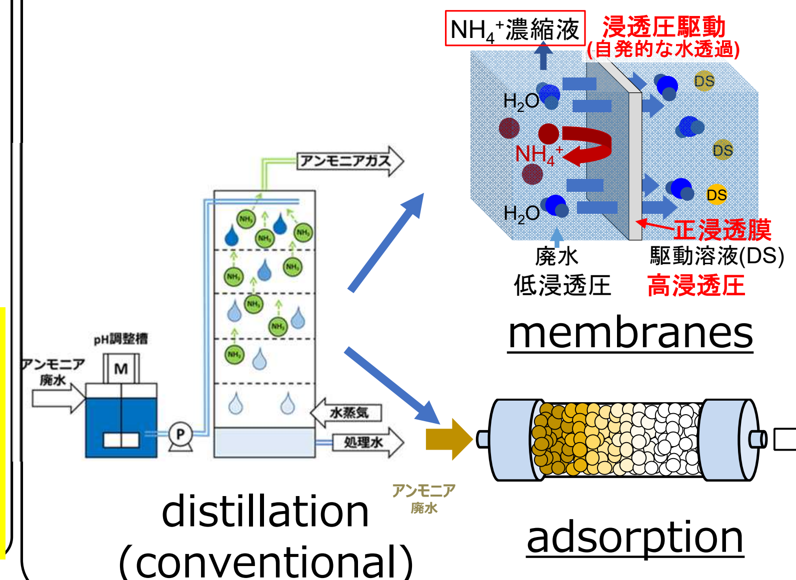


50% conversion for complete purification of NOx , and use excess NH_3 as a resource

【2-2. ammonia recovery in water】

Prof. Matsuyama, Kobe Univ.

(1) membrane/adsorption separation
(2) Construction of ultra energy-saving separation and concentration process



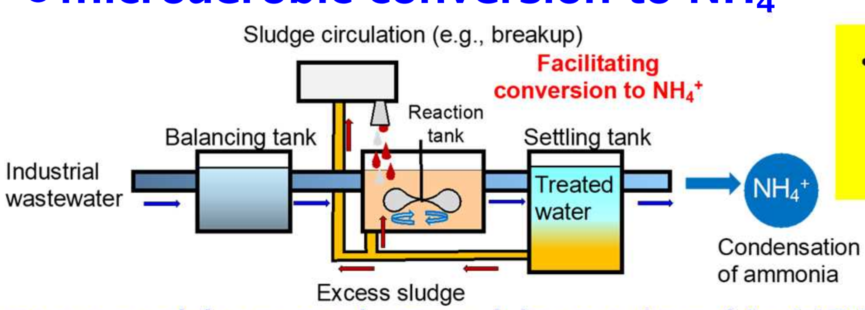
<1/100 of the energy consumption of conventional methods

【2-1. conversion to NH_3 in wastewater】

Dr. Hori AIST

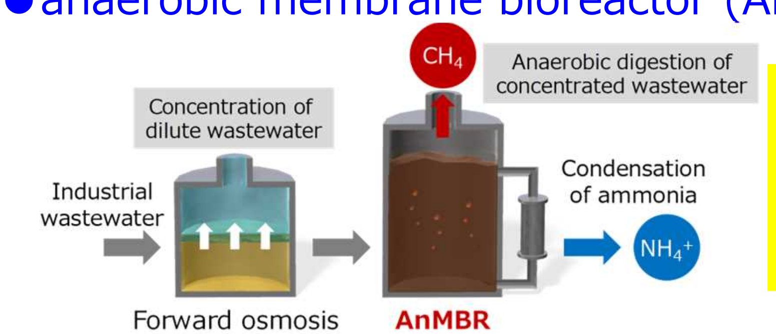
Efficient NH_4^+ conversion bioprocess for various conditions

● **microaerobic conversion to NH_4^+**



・Low NH_4^+ loss
・Use excess sludge as nitrogen source

● anaerobic membrane bioreactor (AnMBR) for high-NH_4^+



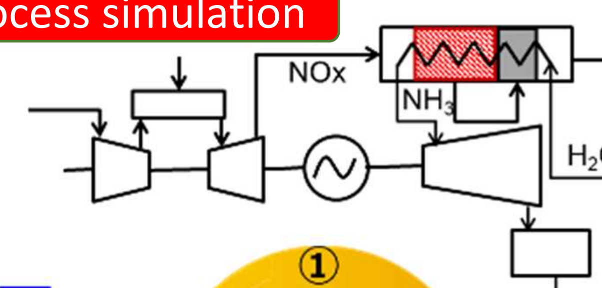
・Work at high NH_4^+ concentration
・High energy efficiency and compact size

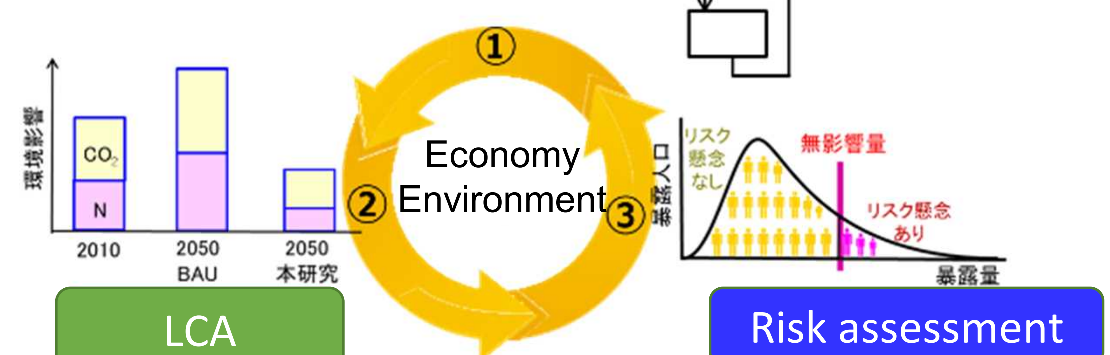
【3. Process and evaluation】

Prof. Matsumoto, Tokyo Inst. Tech.

1)Design of actual equipment and pilot-scale process 2) Techno-economic analysis and environmental impact assessment.

Process simulation





NA

Development schedule

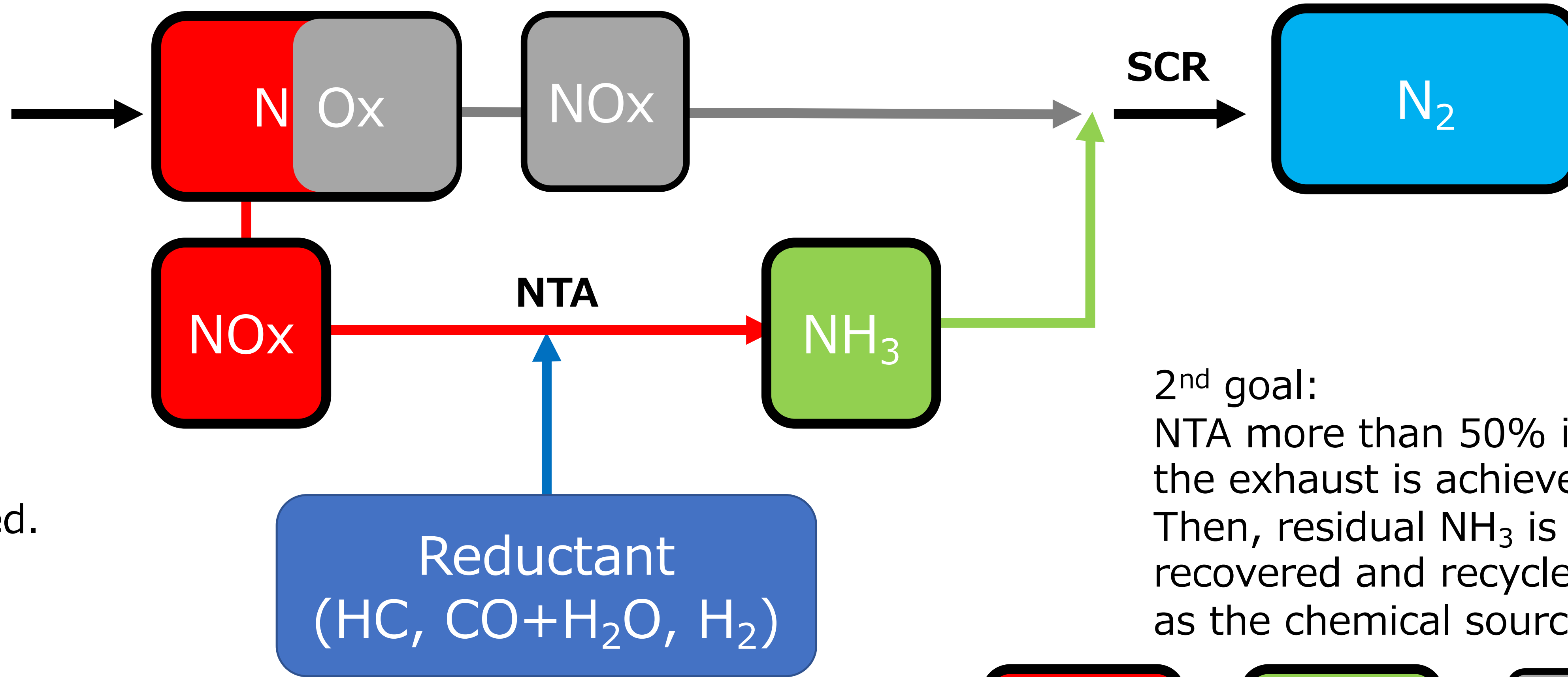
Bench demonstration in 2024, pilot demonstration in 2029

	2020 2021 2022		2023 2024		2025 2026 2027		2028 2029		2039 2050
overall	R&D for Basic technology	Interim evaluation and review	Benchscale	Interim evaluation and review	Establishment of technologies for pilot test	Interim evaluation and review	Pilot-scale	Final evaluation	implementation
NOx to ammonia in gas phase	deNOx ・R&Ds for high performance NTA catalysts and adsorbents		deNOx ・NTA catalyst system design (1step, 2step, strorage)		reNOx ・Evaluation of NTA catalyst and adsorbent using bench scale equipment ・Identification of issues		Pilot demonstration (Hundreds Nm^3/h)		Practical application and prevailing N recycling technologies to solve the Planetary boundaries problems
Nitrogen compound to ammonia in wastewater	Conversion to NH_4^+ ・ Construction of nitrogen converting microbial community		Conversion to NH_4^+ and Ammonium recovery ・Bench-scale demonstration ・Evaluation using real wastewater		Conversion to NH_4^+ ・ Management method and design of pilot-scale system		Pilot-scale demonstration (5-15m^3/d)		
	Ammonium recovery from aqueous phase ・Development of separation membranes and adsorbents				Ammonium recovery from aqueous phase ・Pilot plant development ・Modules preparation				
Establishment of N-circular system	Process design, Environmental impact assessment ・Modeling, Constructing inventory database		Process evaluation ・Energy saving, Risk, LCA		Design of nitrogen circular systems ・Pilot plant performance, Local environmental impact		Design of global nitrogen circular system		

Item 1.deNOx and reNOx - overview

First of all “deNOx” to transform half to NH_3. Local production for local comsumption. Then, ”reNOx”.

Combustion exhaust



1st goal:
NTA 50% in the exhaust is achieved. Then, deNOx is attained.

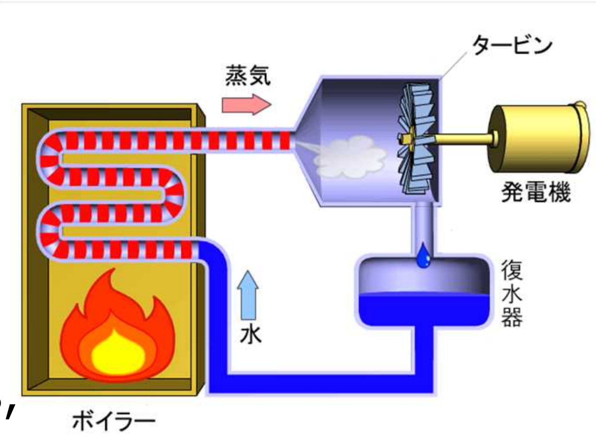
NOx = NOx = NH_3

2nd goal:
NTA more than 50% in the exhaust is achieved. Then, residual NH_3 is recovered and recycled as the chemical source.

NOx = NH_3 > NOx

NTA system implant target

Power plant
Large volume of out gas, ultra low conc. NOx



Dust combustion
High temp exhaust, impurities

Ships posttreatment
Urgently required

ITEM 1: A Single Stage NTA in O_2 and H_2O (Waseda University)

AIST
Create the Future, Collaborate Together

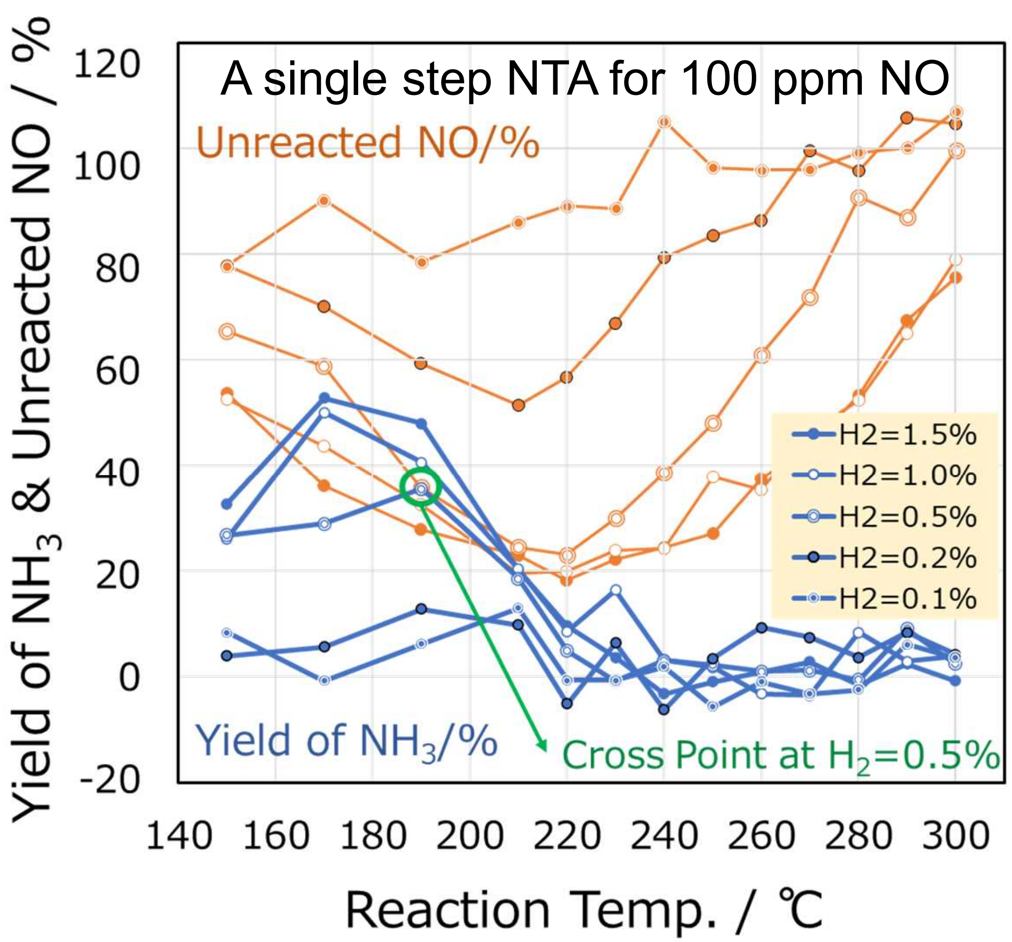
Development of efficient single-stage NTA catalysts to realize ultra-dilute NO detoxification and NH_3-SCR systems without NH_3 supply

1. Development of a single-stage NTA catalyst, WSD-02, applicable to 100 ppm NO, paving the way to realize ultra-dilute NO detoxification

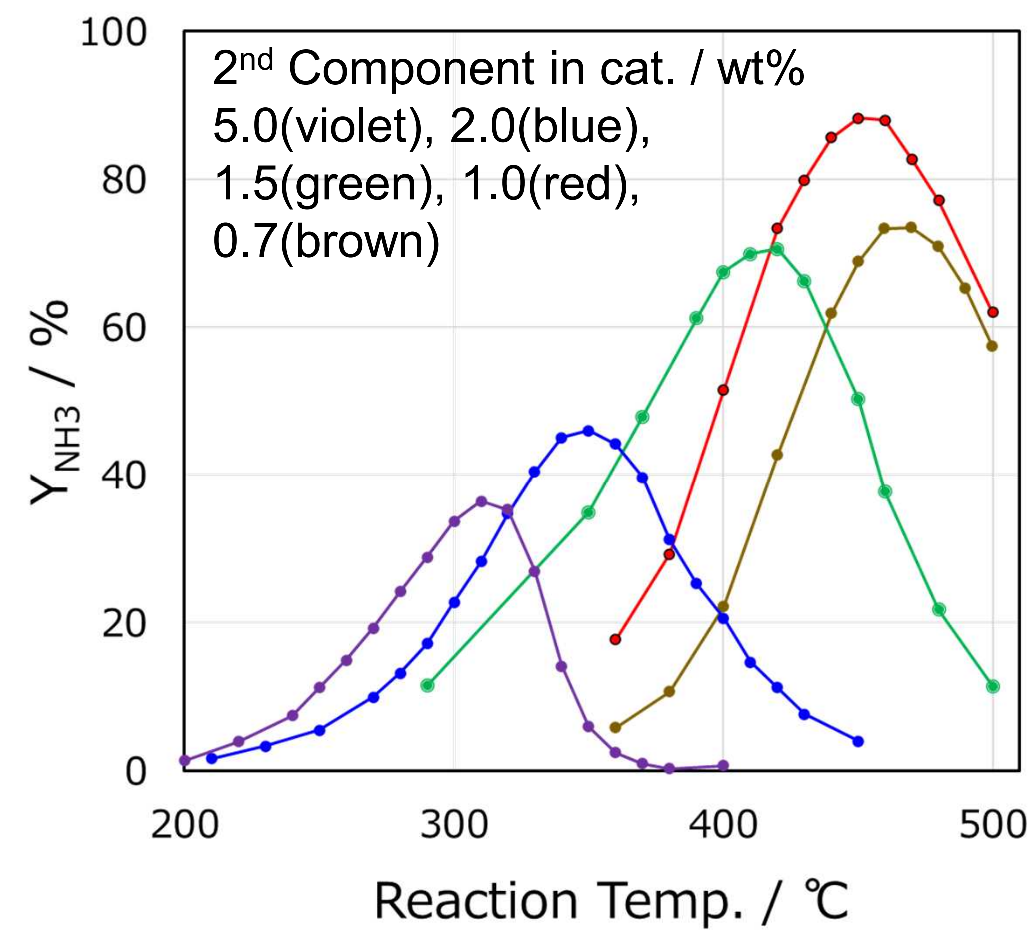
The developed NTA catalyst was effective for the reaction of ultra-dilute NO below the current environmental standards. Promote further improvement of the atmospheric environment.

2. A hydrocarbon-based NTA catalyst, WSD-03, was developed to provide a temporary solution until the realization of a hydrogen society

If a hydrogen supply network is not available, the NTA reaction can be carried out using a hydrocarbon-based reducing agent. Compatible with current internal combustion engines.



Catal. Sci. Technol. (2023), **Front Cover**



Cat. WSD-02, SV 50,000 h^{-1}, **0.01% NO**, 0.1-1.5% H_2, 10% O_2, 10% H_2O, balanced N_2

Cat. WSD-03, SV 10,000 h^{-1}, 0.1% NO, **0.5% C_3H_6**, 10% O_2, 10% H_2O, balanced N_2

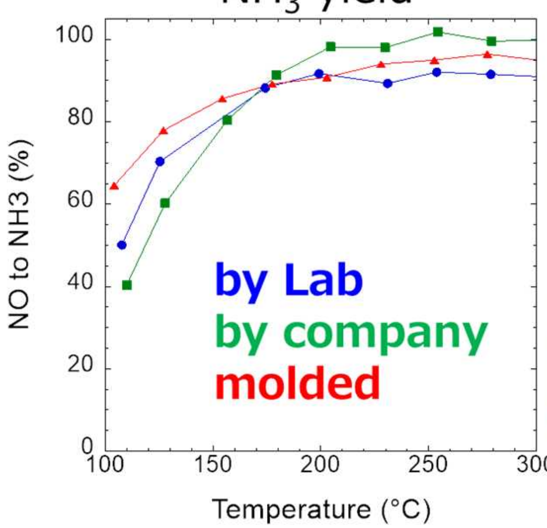
THEME 1.Results of deNOx and reNOx (Univ.Tokyo, AIST)

Seamless continuous reaction of 2step catalytic reactions with far different conditions

2029 model :
1. NOx selective adsorption from combustion exhaust (treatment zone)
2. Supply conc. NOx in O_2-free stream to AIST-NTA catalyst (regeneration zone)

2029 model of 2step NTA catalyst system using honeycomb rotor

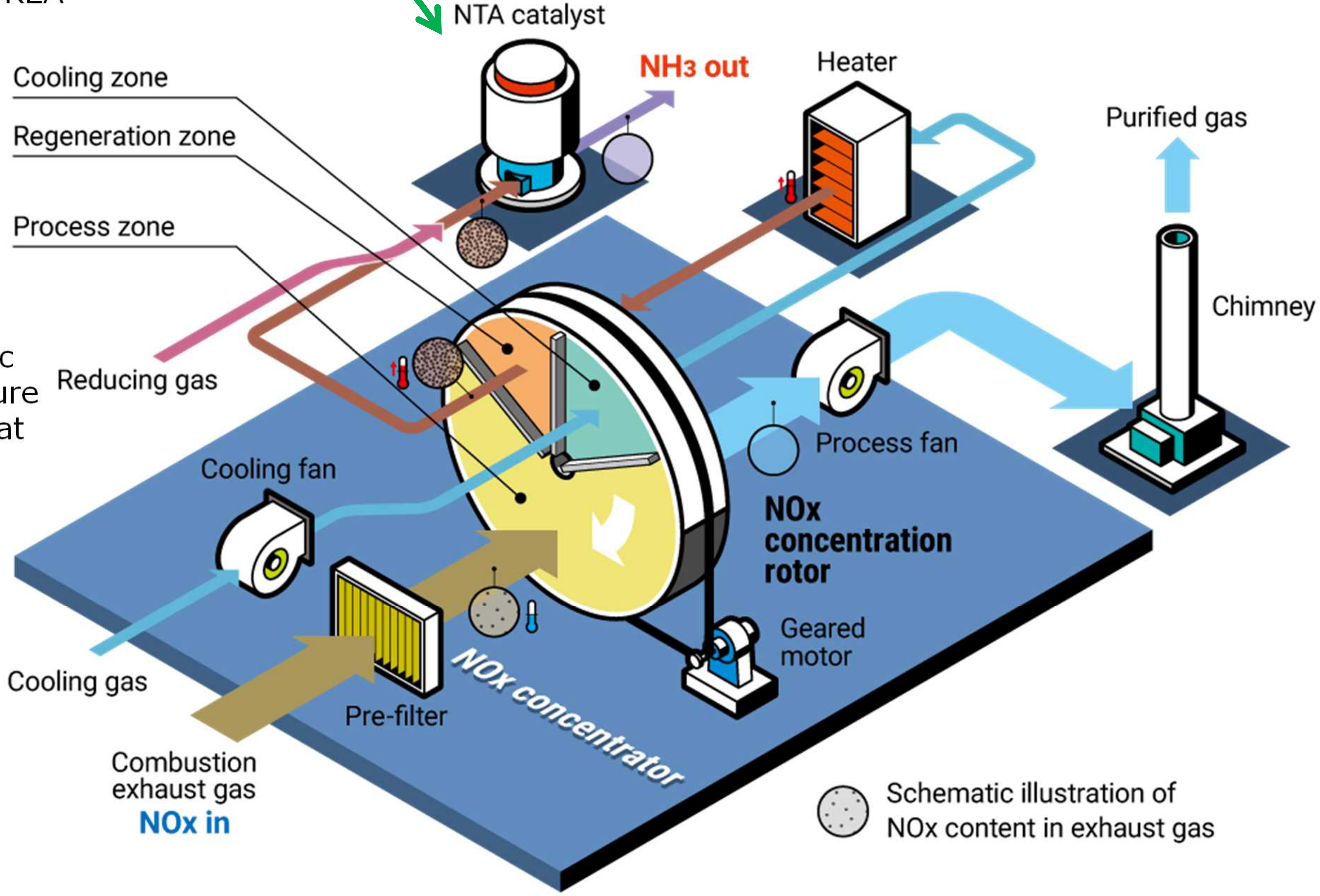
NH_3 yield



Cat.: 0.15g; flow rate: 250 mL/min (SV 40,000 h^{-1}) ; composition: NO 1000ppm, H_2 3000ppm

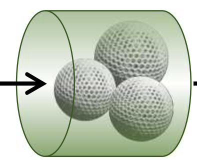
NTA bench reactor@AIST FREA

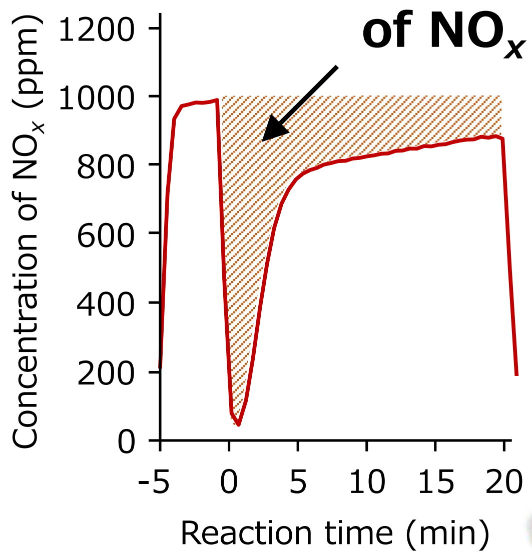
Catalyst bed at most 100 cc
5 ThermoCouples to measure heat of reaction and for heat management



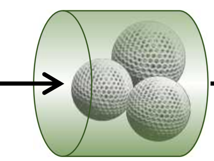
Achieving over 90% selectivity to NH_3 by a gas-switching NO_x storage reduction

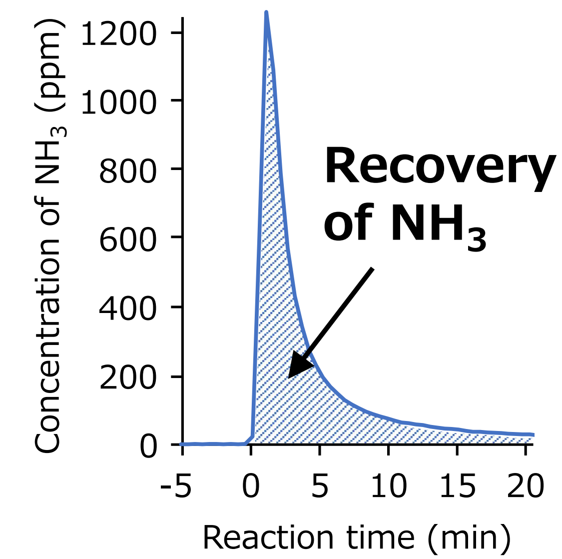
Effective recovery of NO_x

Combustion gas →  →
$NO+O_2$···



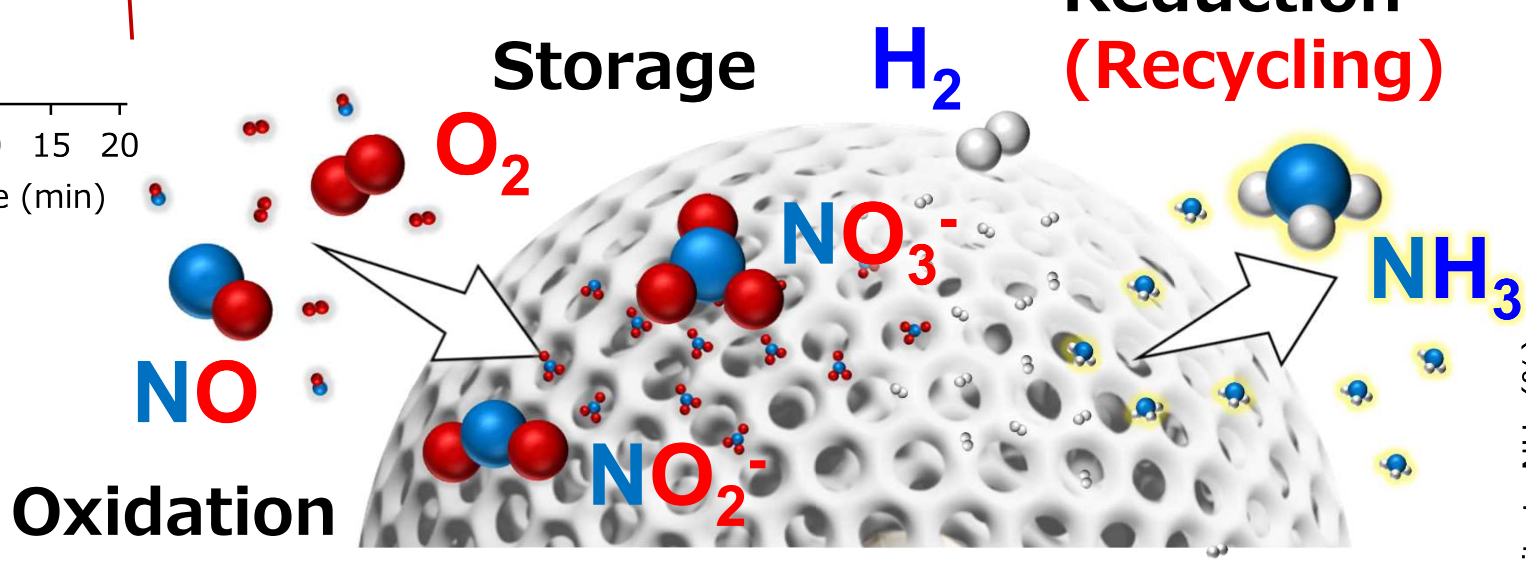
Selective synthesis of NH_3

Reductive gas →  → NH_3
(H_2, etc.)



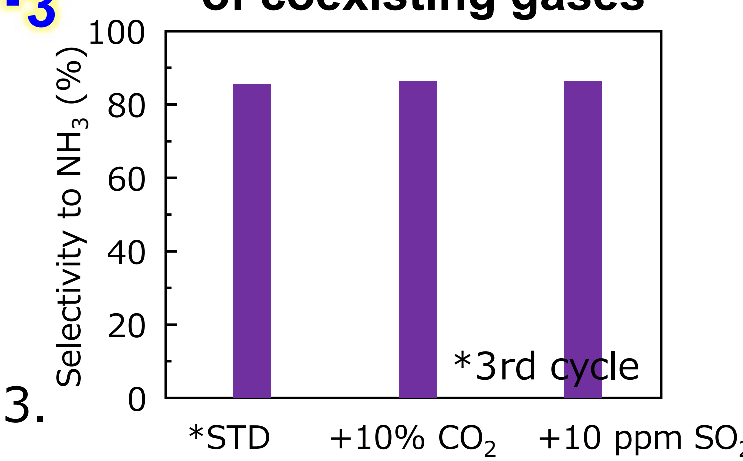
Switching the inlet gas at constant reaction temp.

<Reaction conditions>
1000 ppm NO + 10% O_2 ⇆ 1~5% H_2
100 mL min^{-1}



Nanocomposite NSR catalyst

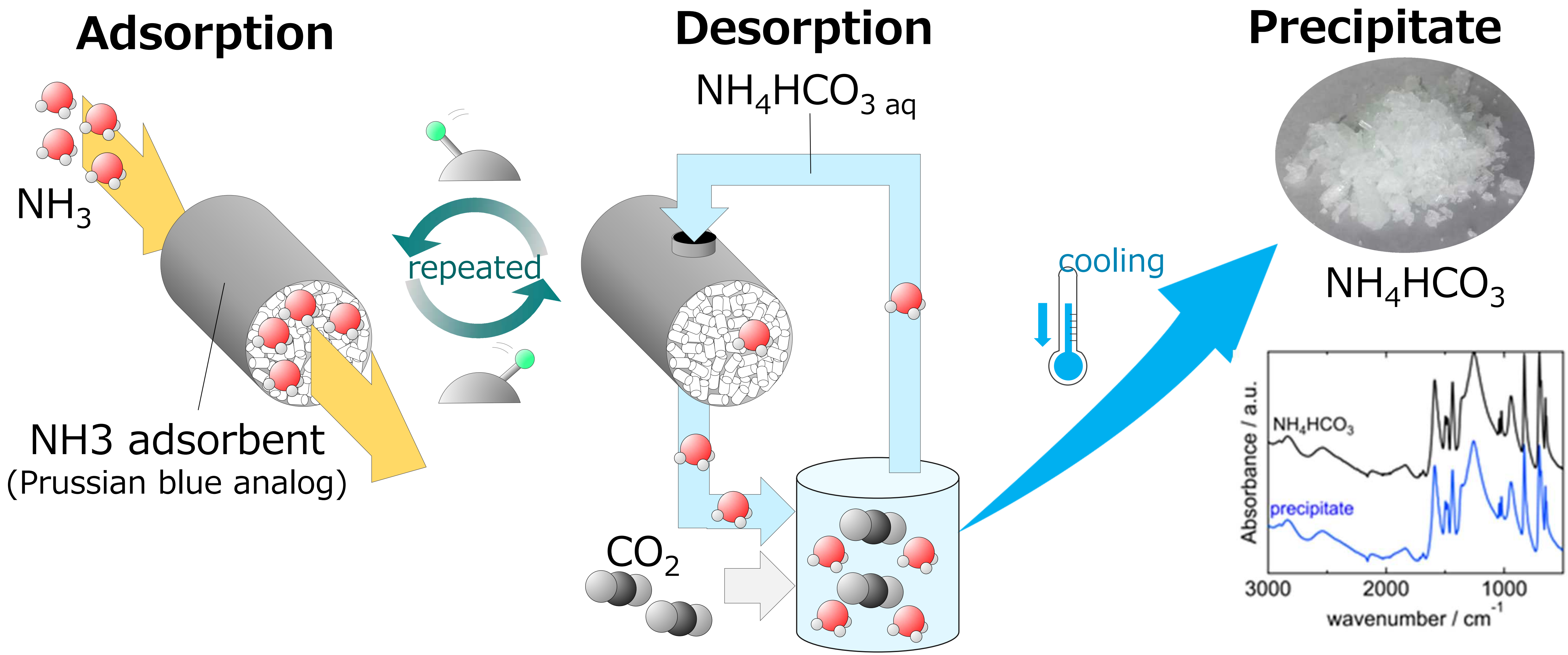
★Influences of coexisting gases



A. Tomita, R. Wakabayashi, T. Kimura*, released on our web site on 31 Jan 2023.
A nanocomposite catalyst for the recycling of NO_x in combustion gas
~ A proposal of a new method to synthesize NH_3 for nitrogen resource circulation ~

A. Tomita, R. Wakabayashi, T. Kimura*, *Catal. Sci. Technol.*, **2023**, *13*, 2927-2936. (Front Cover)

Adsorption and recovery of NH_3 to produce ammonium carbonate solid



- Converts to ammonium bicarbonate solids without heating and with low energy consumption
- Ammonium Bicarbonate is not toxic or deleterious substance. It is also a solid, which is advantageous for storage, etc.
- Ammonium Bicarbonate decomposes at low temperatures (~70°C) and is immediately converted to a gas mixture of NH_3:H_2O:CO_2 = 1:1:1

Usuda, ACS Sustain. Chem. Eng., accepted

AIST
Create the Future, Collaborate Together

Systems connecting "conversion to NH_4^+" and "separation and concentration of NH_4^+"

Ammonia resource (fuel, material)

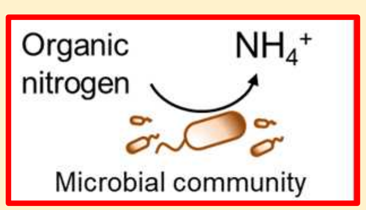
NH_3

Resource recovery plant

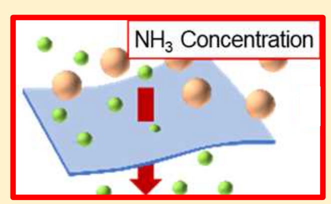
Theme 2－1　Theme 2－2

NH_4^+
Organic N

Industrial wastewater



Effective and fast conversion



Ultra energy saving separation

NH_3 resource

Discharge to river

● **Current state**

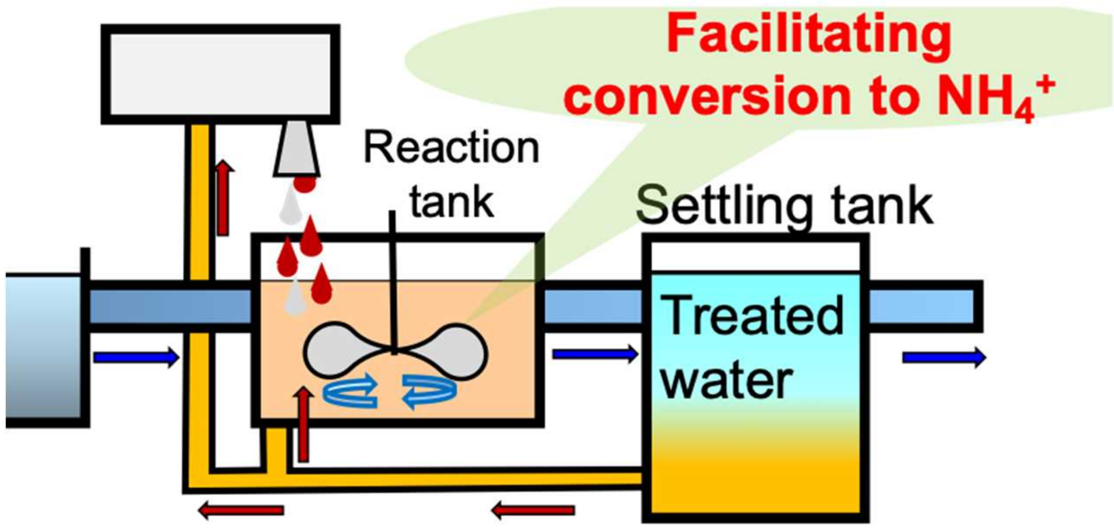
- N compounds in wastewater were converted to N_2 gas, accompanied with N_2O emission
- Required massive energy
- Residual N discharge

● **Future image in 2050**

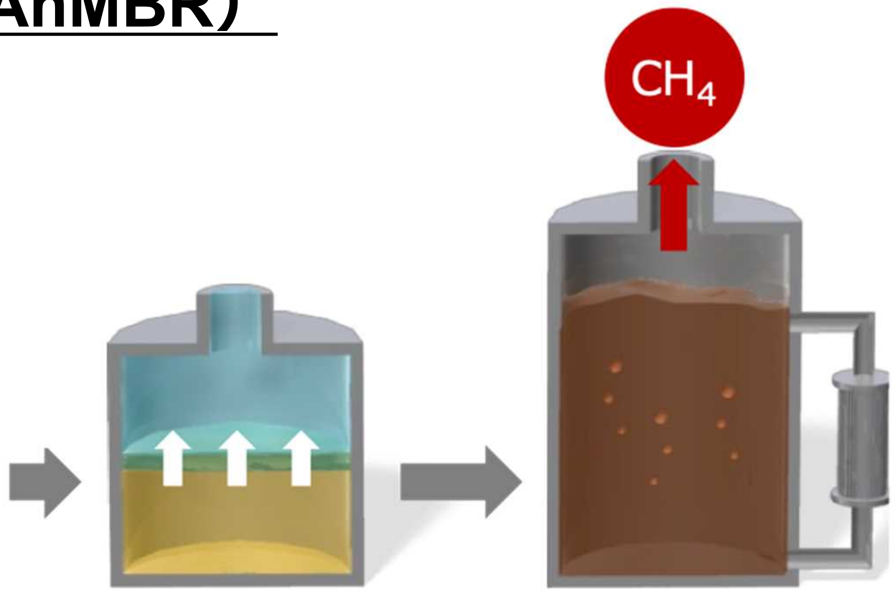
- Conversion to NH_4^+ and subsequent separation and concentration of NH_4^+
  → **Utilization as ammonia resource**

Constructing multi-bioconversion processes for various wastewater types and situations

● Microaerobic conversion process



● Anaerobic membrane bioreactor (AnMBR)

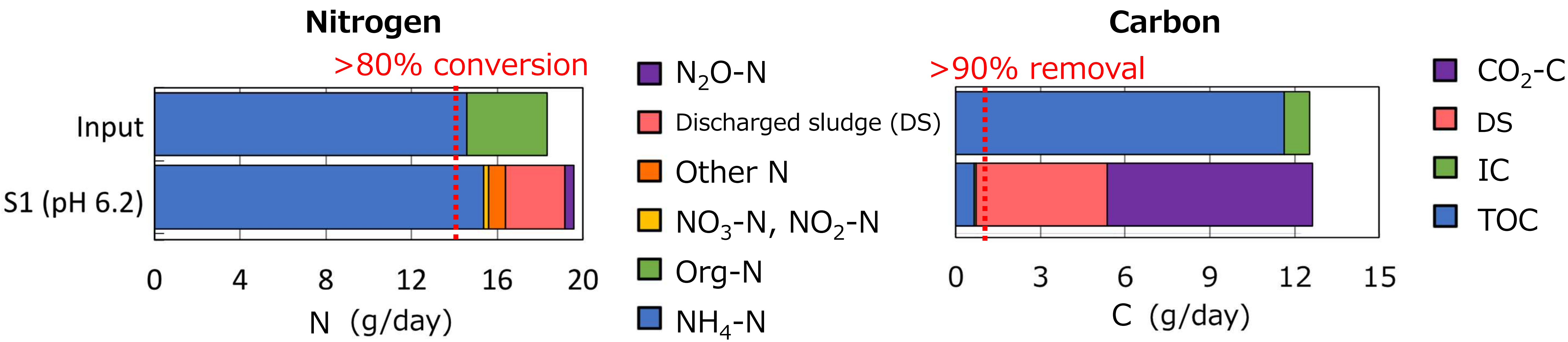


Organic loading	○ Low concentration	○ High concentration
Decomposition ability	○ Organics-C is completely degraded	○ Residual organics-C is <10%
Nitrogen recovery	○ Recovery by nitrification inhibition	○ Complete recovery
Biogas recovery	-	◎ **CH_4 recovery**
Retrofit	◎ **Current infrastructure can be used**	△ **Process renewal is needed**
Target wastewater	**O Low-concentration industrial and municipal wastewater**	**O Low- & high-concentration industrial and municipal wastewater (+ FO membrane)**

AIST
Create the Future, Collaborate Together

Microaerobic process: Optimization using lab-scale reactors towards bench-scale test

● Lab-scale reactor mass balance: >90% of carbon removal and >80% of NH_4^+ recovery

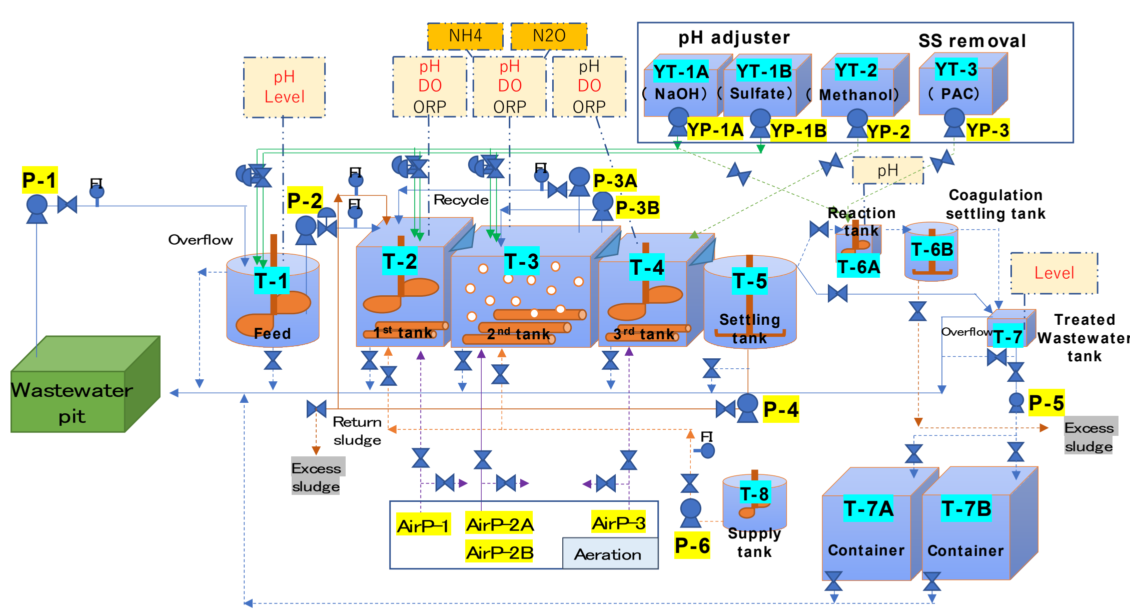


Zhou et al., Water Research, 247, 120780, 2023.

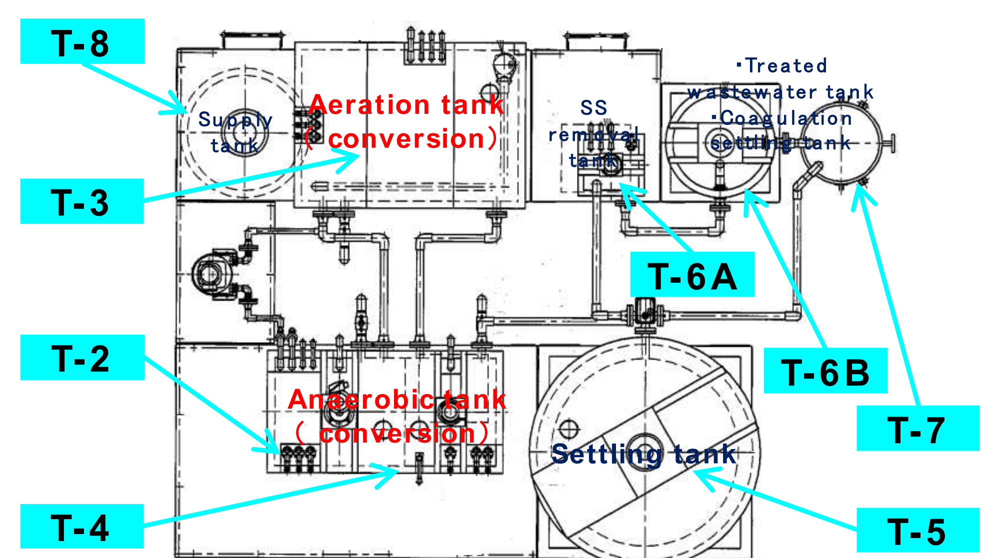
● Preparation for bench-scale demonstration

<Location>

<Material flow>



<Design chart>

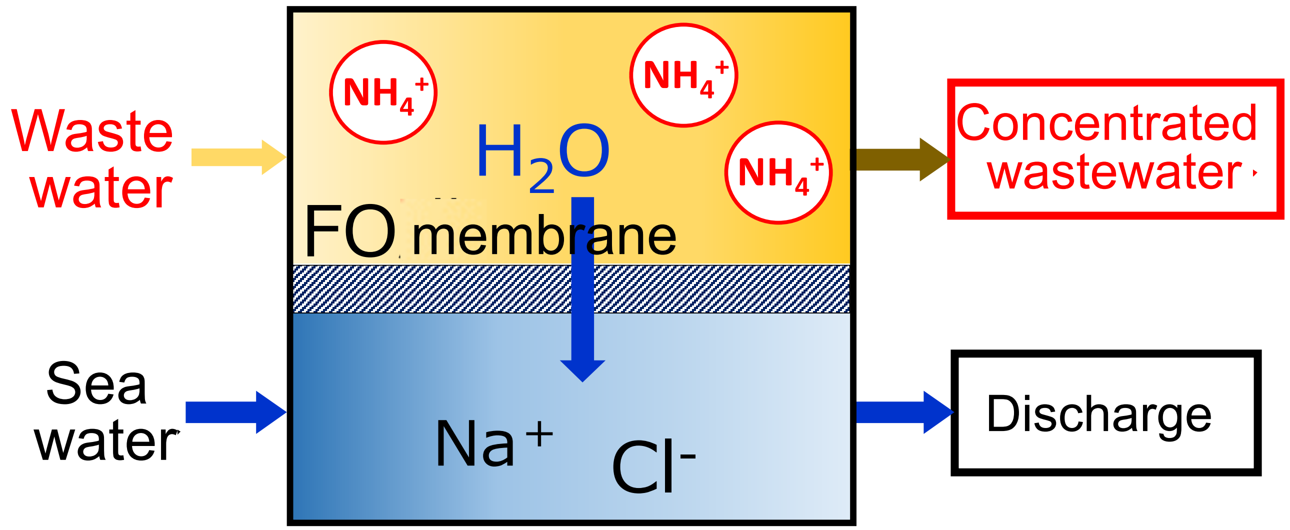


THEME 2-2. Ammonium recovery from aqueous phase (Concentration)

AIST
Create the Future, Collaborate Together

Combining several membrane technologies to treat various wastewater

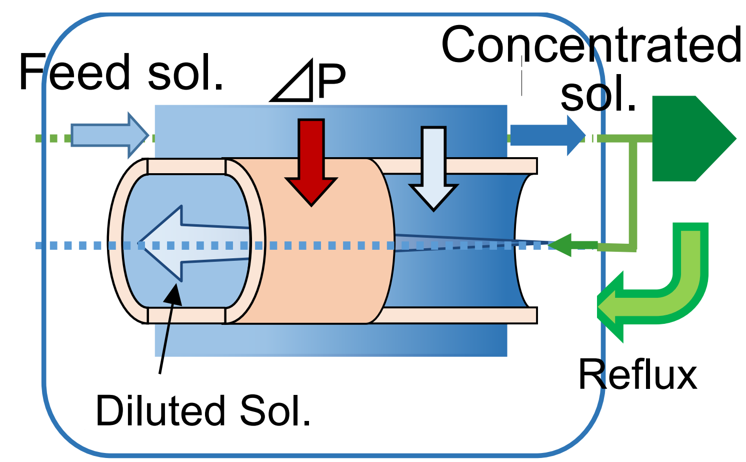
FO membrane: Ultra low-energy, 40~400 mg/L→0.4%



- Diluted seawater generated by FO can be returned to the sea
- Only required energy is pump power

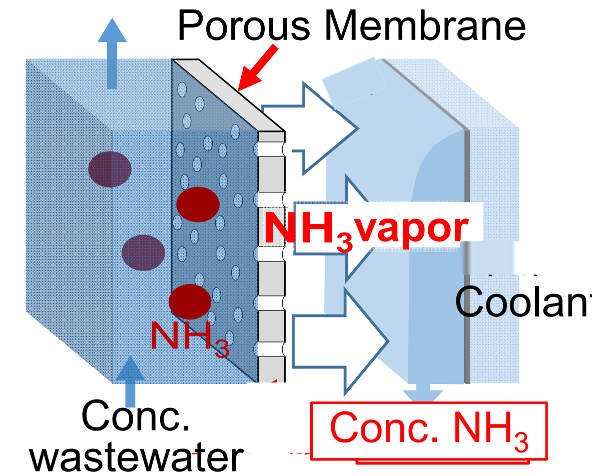
BC & MD : High concentration, 0.4%→ >25%

BC: Brine concentration



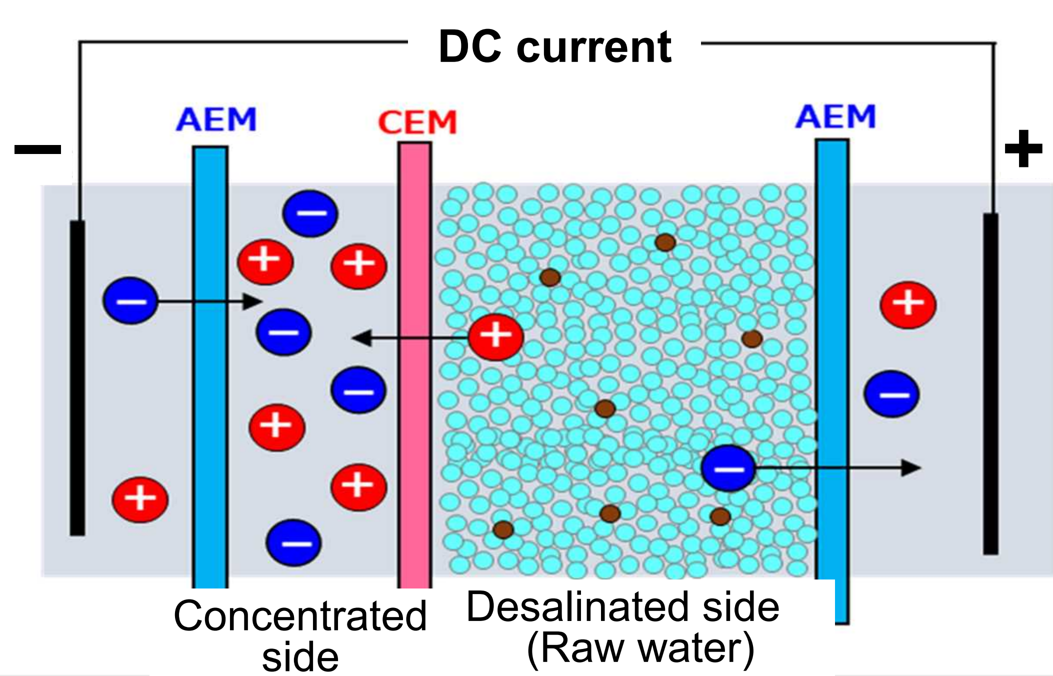
0.4% → 4%

MD: Membrane distraction



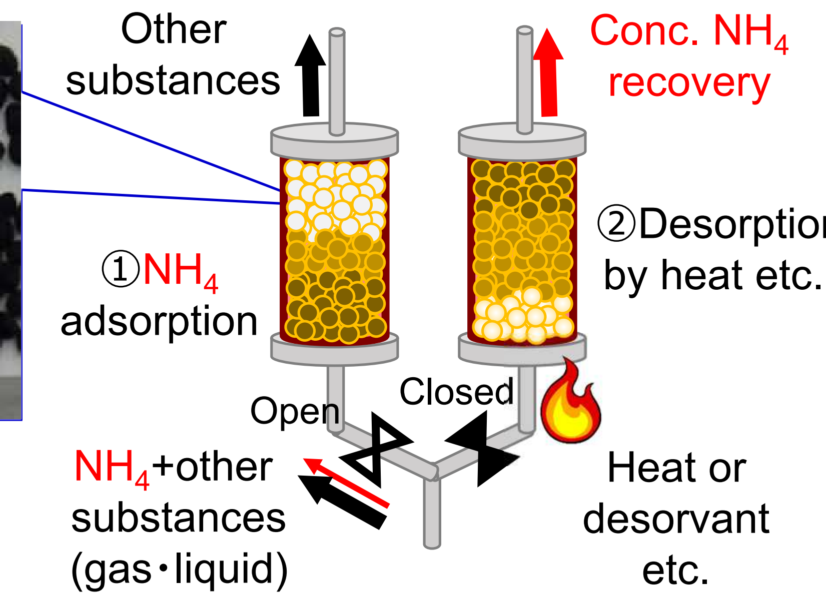
4% → >25%

Ion exchange membrane: Ca removal, <400mg/L→4%



Adsorbent: Na removal, ~1000 mg/L → ~2%

NH_4^+ adsorbent

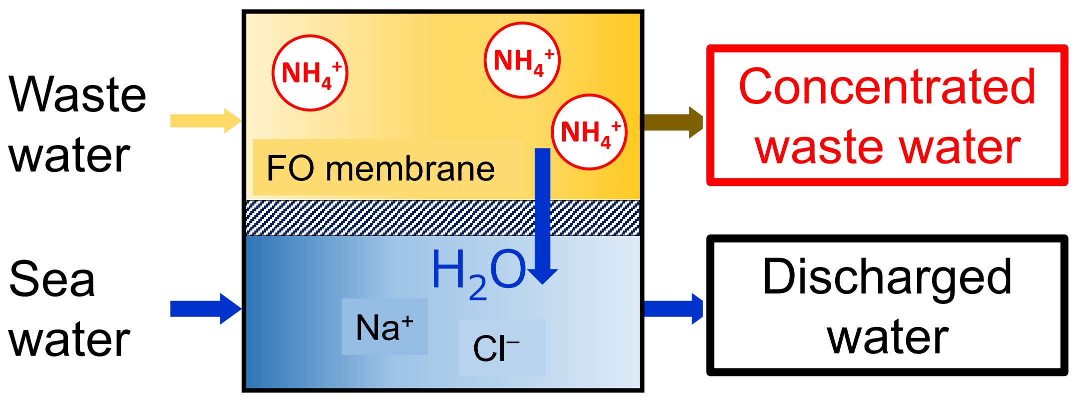


AIST Create the Future, Collaborate Together

FO membrane process to concentrate wastewater with very low energy consumption

Forward osmosis (FO) process

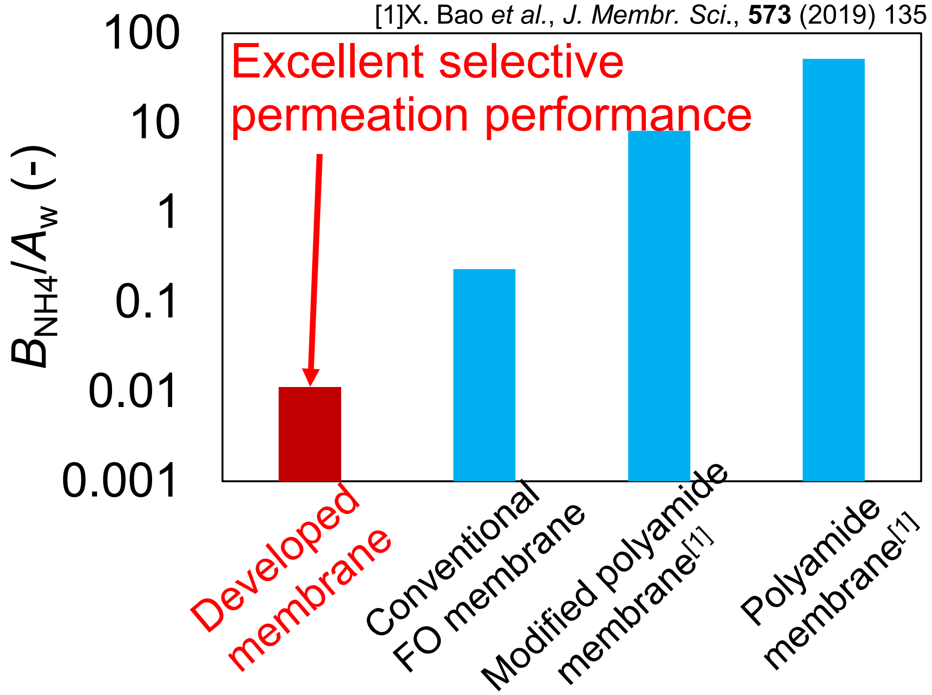
FO process



Using seawater as the draw solution allows to concentrate sewage at a low cost

Development of polymer membrane

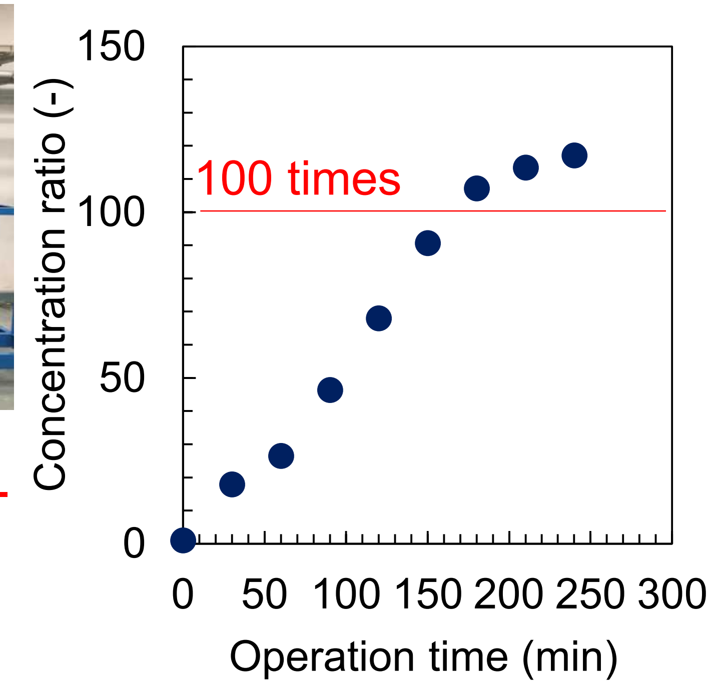
[1]X. Bao *et al.*, *J. Membr. Sci.*, **573** (2019) 135



Succeeded in developing a high-performance FO membrane

Concentration test in bench scale

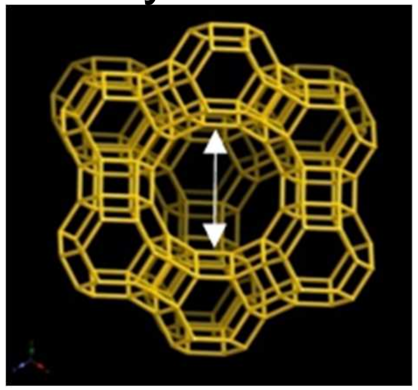
Membrane area : 180 m^3

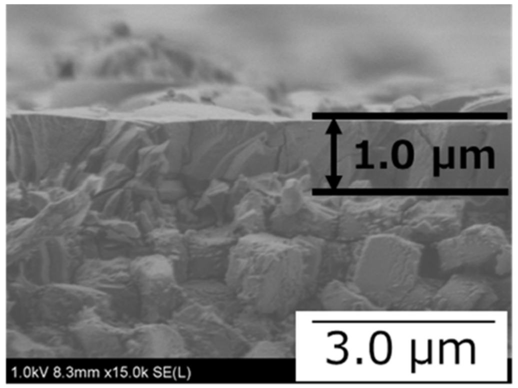


Urban sewage was concentrated more than 100 times by volume at FS flow rate of 2 L/min (=2.88 m^3/day)

Development of zeolite membrane

Zeolite: Crystalline aluminosilicate materials





- Size sieving separation
- High thermal and chemical stability

- Hydrophilic zeolites without cation exchange sites
- Apply positive charge

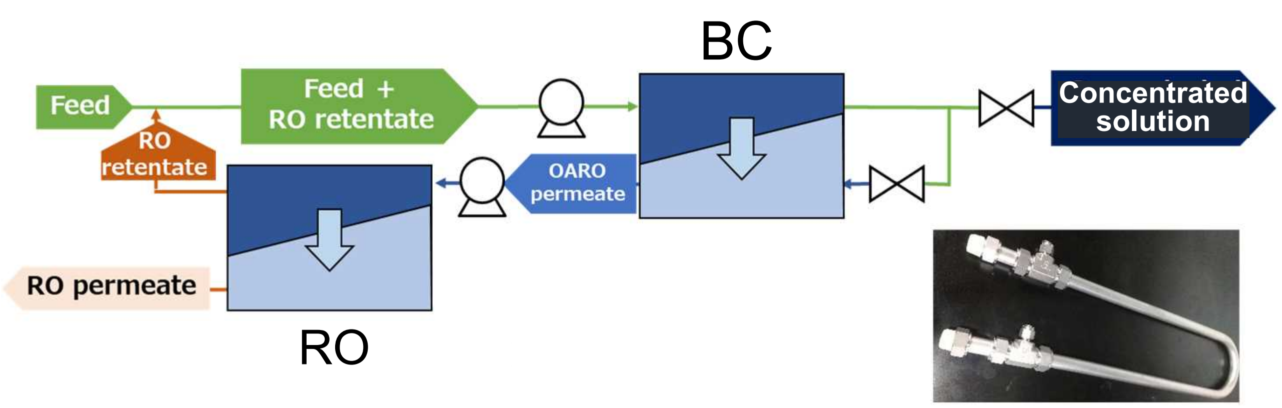
Succeed in developing zeolite membranes to concentrate NH_4^+

THEME 2-2. Ammonium recovery from aqueous phase (Kobe Univ.)

AIST
Create the Future, Collaborate Together

Membrane process to highly concentrate and recover NH_3 as high conc. NH_3 solution

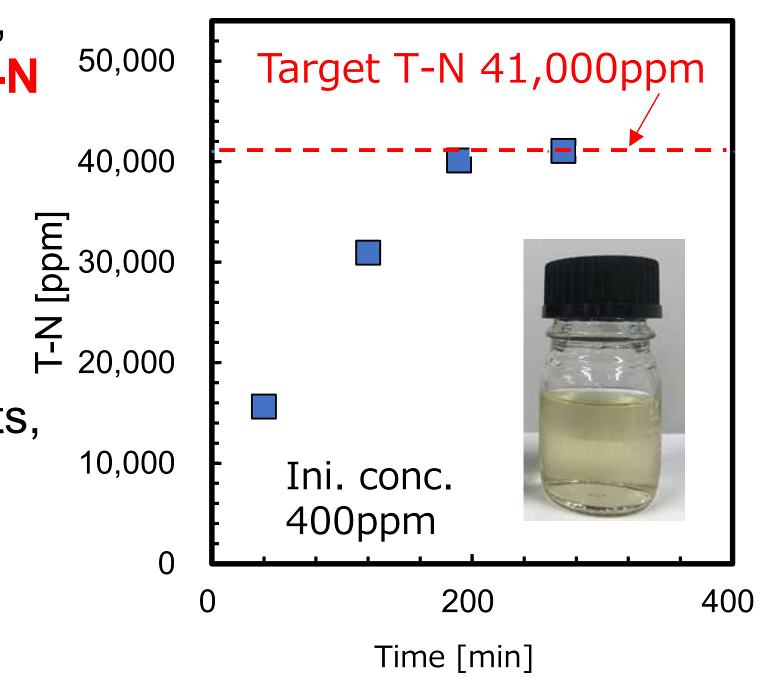
BC + RO membrane process



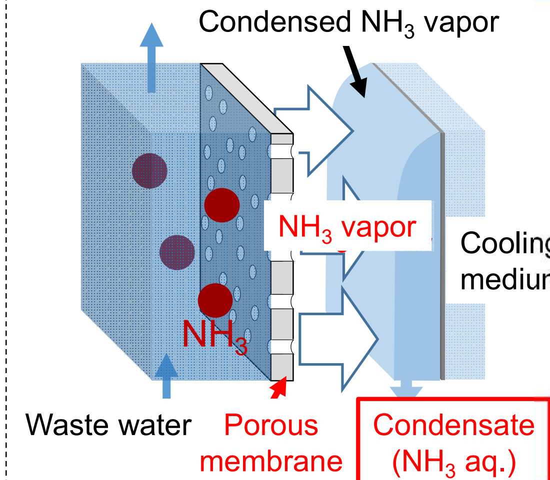
Development of **brine concentration (BC) - reverse osmosis (RO) hybrid process** for simultaneous NH_4^+ high-concentration and water recovery

- BC-RO Hybrid membrane process was established, achieving **41,000 ppm T-N** from FO concentrate of actual wastewater
- Pretreatment process was constructed to remove scale components, and its effectiveness was confirmed with actual wastewater (patent pending).

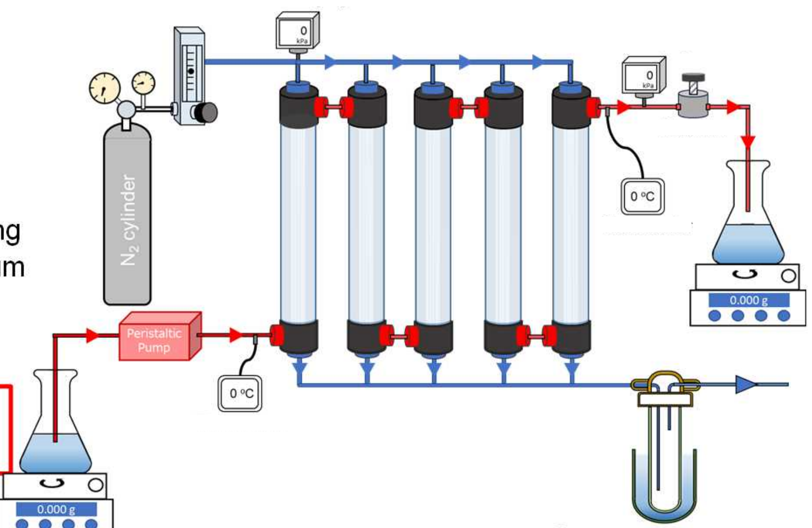
【Real wastewater】



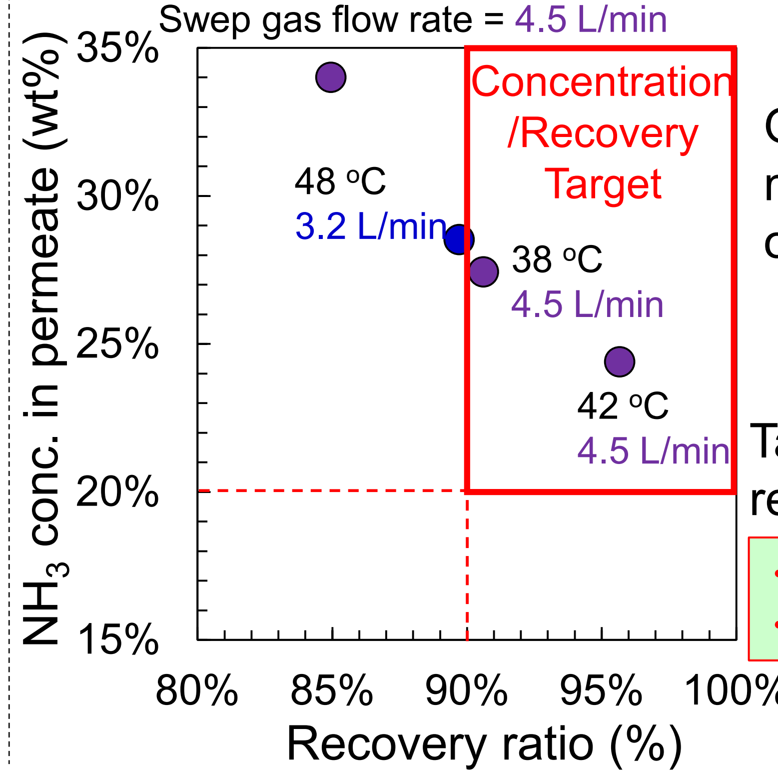
MD membrane process



Membrane Distillation (MD)



One-pass NH_3 recovery system with multiple membrane modules



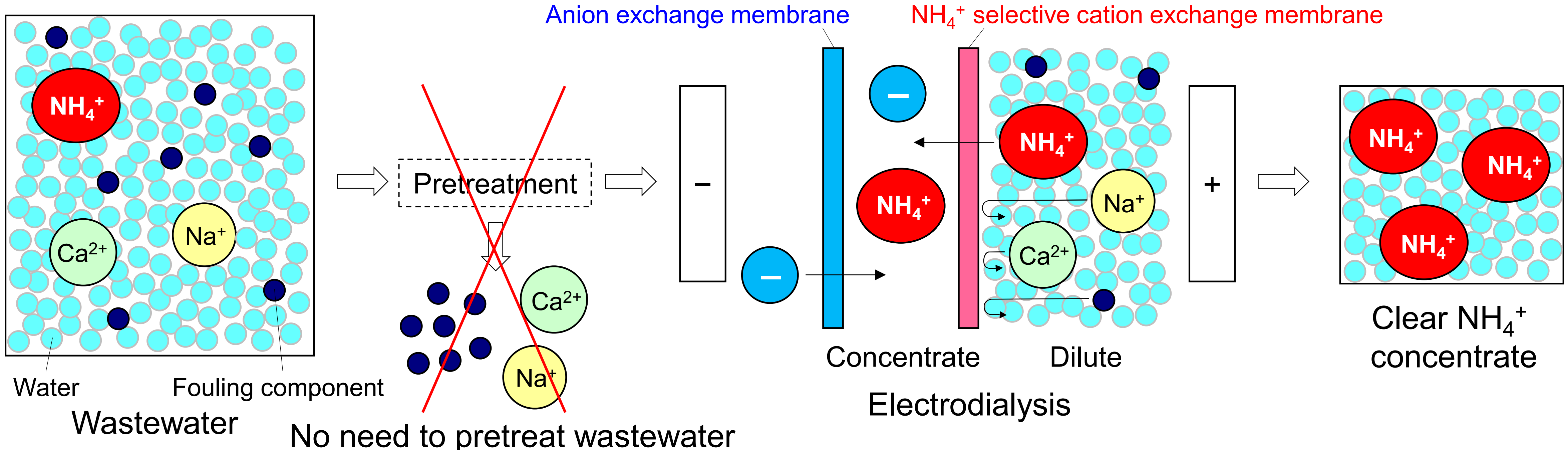
Optimization of membrane module configurations and operating conditions

Target concentration and recovery ratio was achieved.

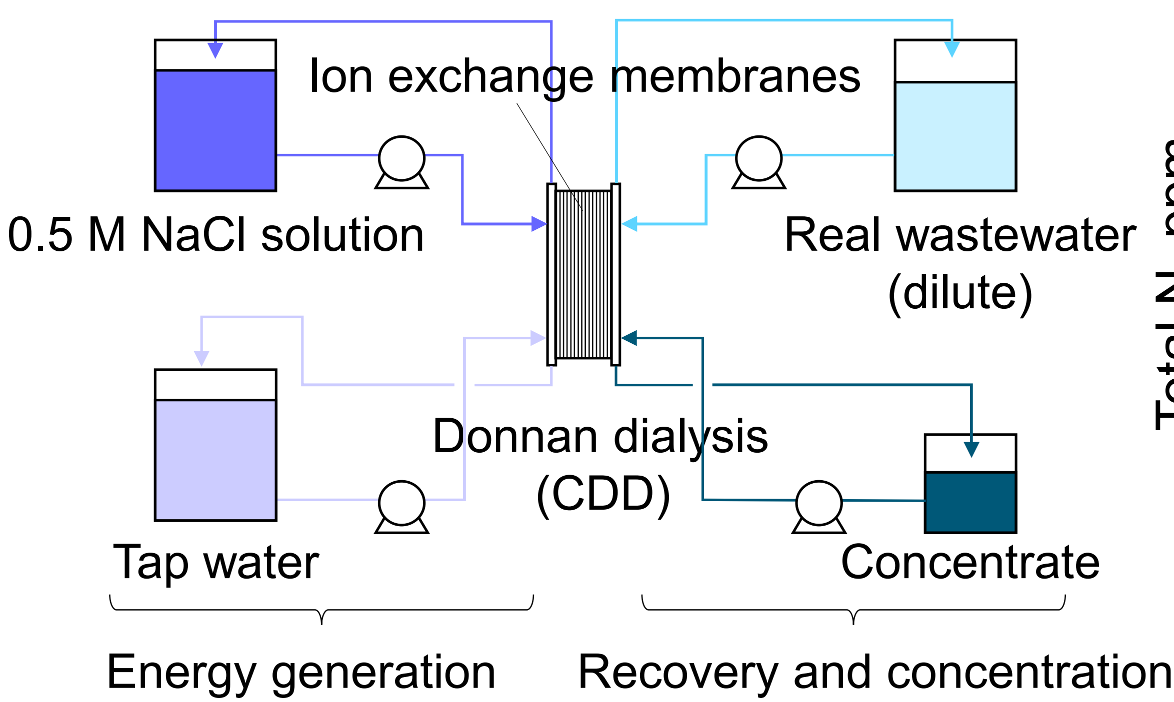
- NH_3 recovery ratio > 90%
- NH_3 concentration > 20 wt%

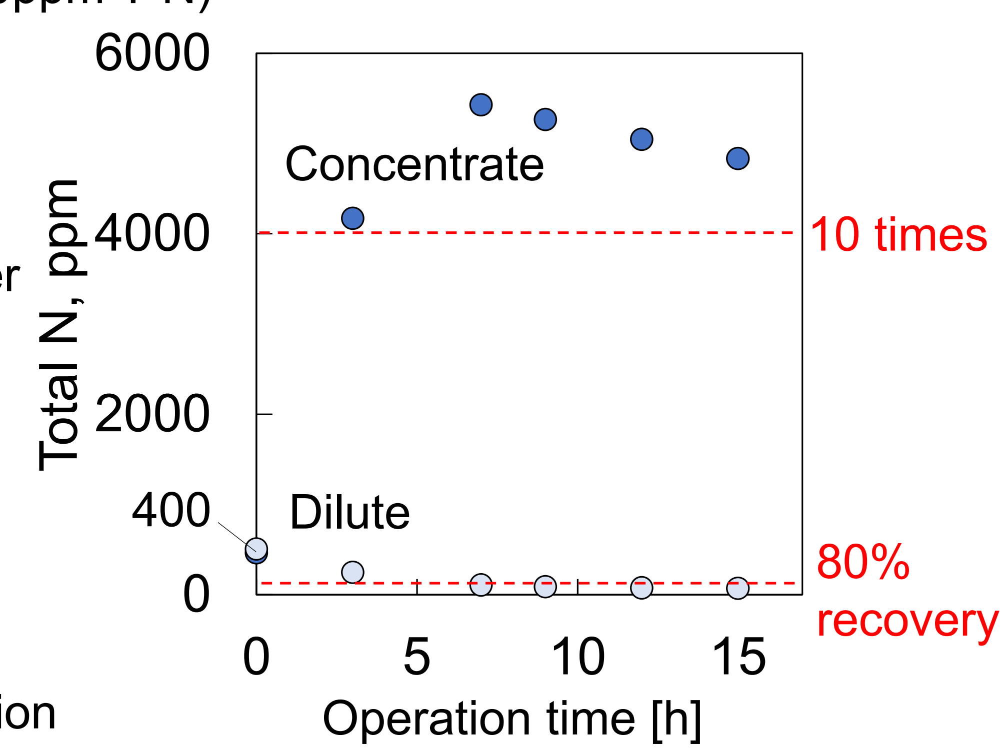
TMEME 2-2. Ammonium recovery from aqueous phase (Yamaguchi Univ., Astom Corp.)

Recovery and concentration of NH_4^+ from wastewater containing fouling components without pretreatment using ion exchange membranes



Real wastewater concentration test (<400ppm→4000ppm T-N)






Real wastewater


Concentrate

THEME 2-2. Ammonium recovery from aqueous phase (AIST, Fuso Corp., Univ. Tokyo)

AIST
Create the Future, Collaborate Together

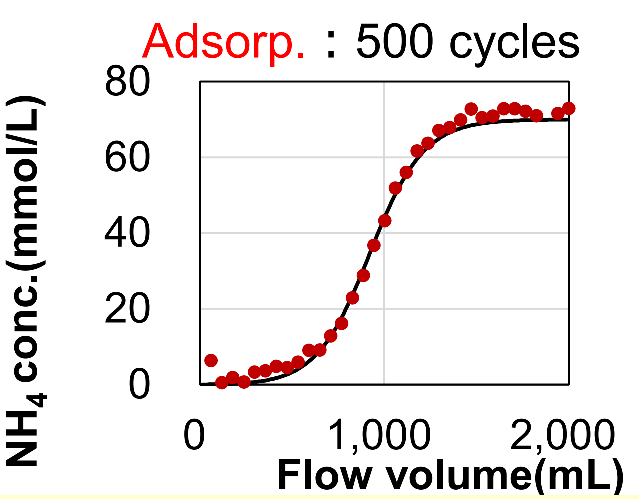
Recovery of NH_4^+ ions in wastewater as NH_4^+ concentrate by optimizing adsorbent and adsorption/desorption process

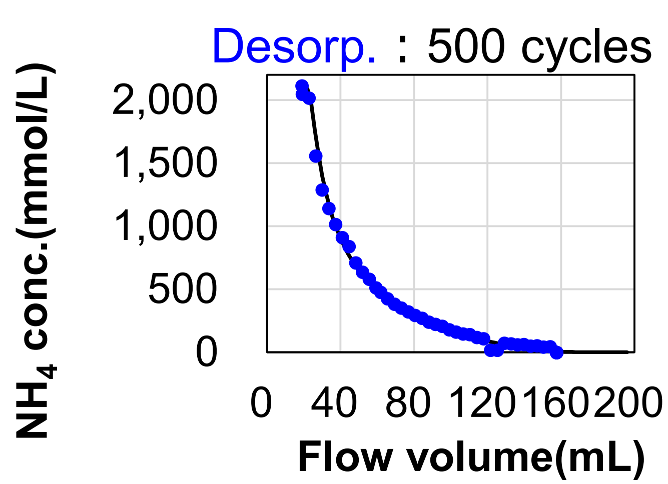
NH_4^+ recovery by adsorbent

KZnHCF granules (made by Fuso Corp.)
($K_2Zn_3[Fe(CN)_6]_2 \cdot 3H_2O$)

KZnHCF granules can be used to adsorb and desorb (concentrate) ammonium ions.

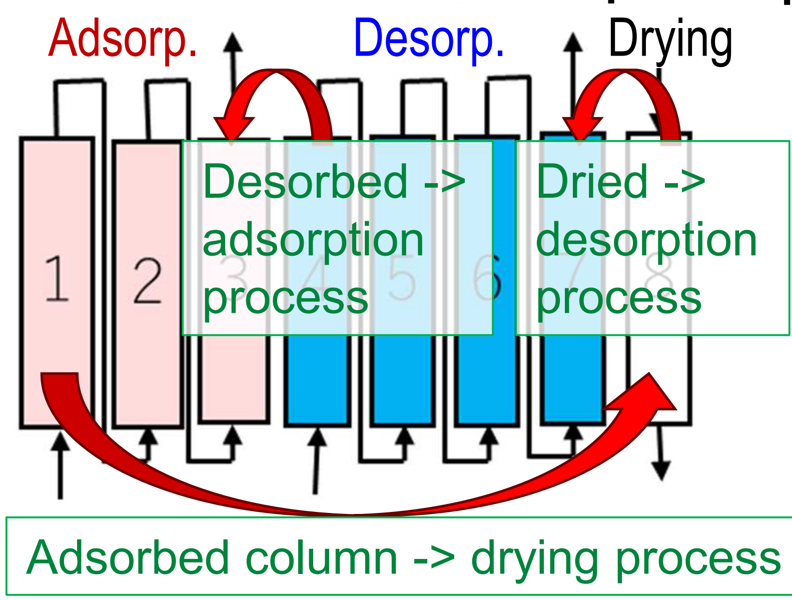
Column adsorp./desor. cycle test (single column)





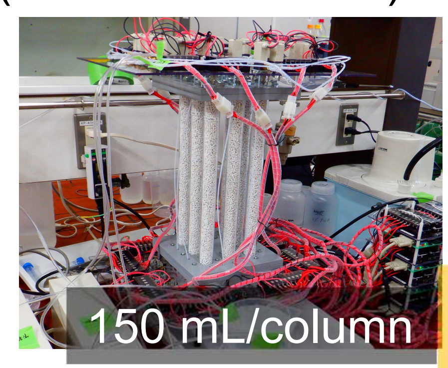
No hinderance of performance is observed until the 500th cycle.

Multi-Column Continuous Adsorp./Desorp. System



NH_4 recovery treatment is continuously performed by operating the adsorption and desorption columns in circulation (by reconnecting the tubes).

Laboratory test equipment (simulated effluent)



Optimization of NH_4 outlet concentration, NH_4 concentration rate, etc. in labo tests

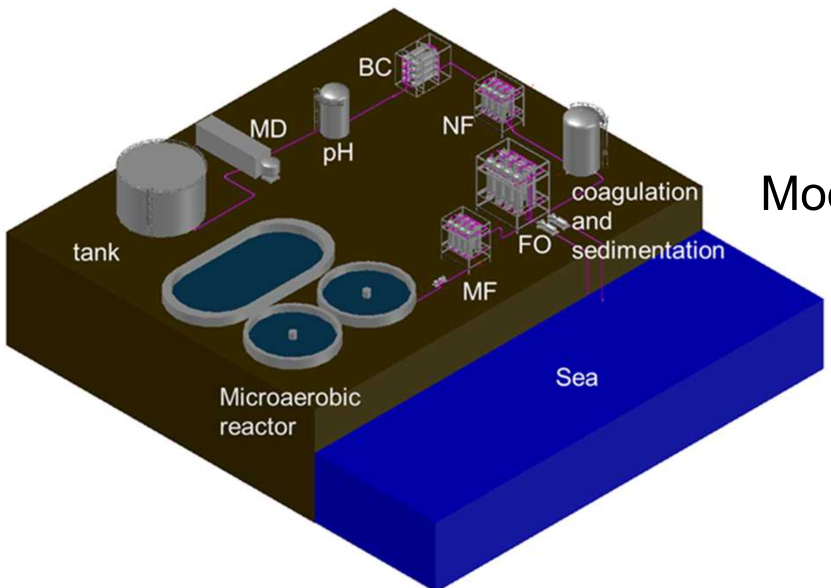
Reflected in on-site test

On-site Test Equipment (actual waste liquid)

Development of electrochemical recovery systems that do not require K^+ for desorption is being accelerated.

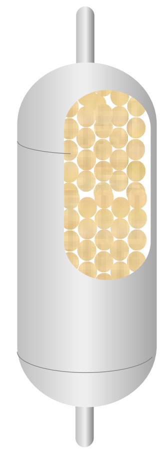
AIST
Create the Future, Collaborate Together

Basic design and multidimensional evaluation of process systems for nitrogen cycle



Basic design of process systems

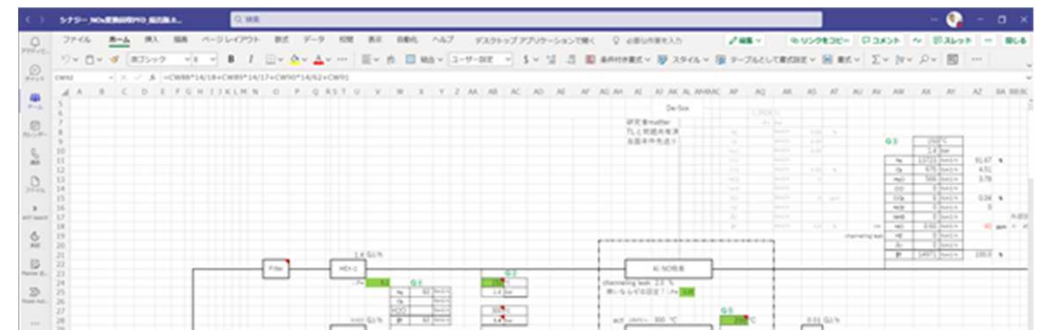
Model / Data



Data

R&D of elementary process technologies

Examining the ideal structure of the nitrogen circular process system



- Calculation of mass balance for NOx in gas and nitrogen compounds in wastewater
- Calculation of energy balance
- Calculation of CO_2 emissions , etc.

■Life cycle assessment of nitrogen circular technologies

Nitrogen inventory data and input-output tables mainly for chemical industrial products

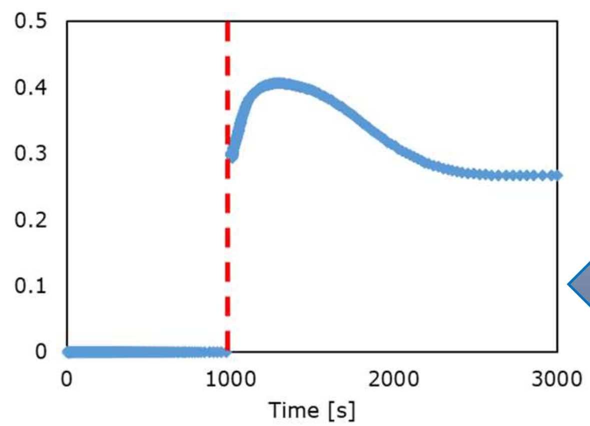
Flow analysis of NH_3, reactive nitrogen and other harmful substances

■Risk assessment of nitrogen compound cycle

Benefits of nitrogen circular technologies to human health and the ecosystems

TMEHE 3. Process and evaluation(Tokyo Inst.Tech)

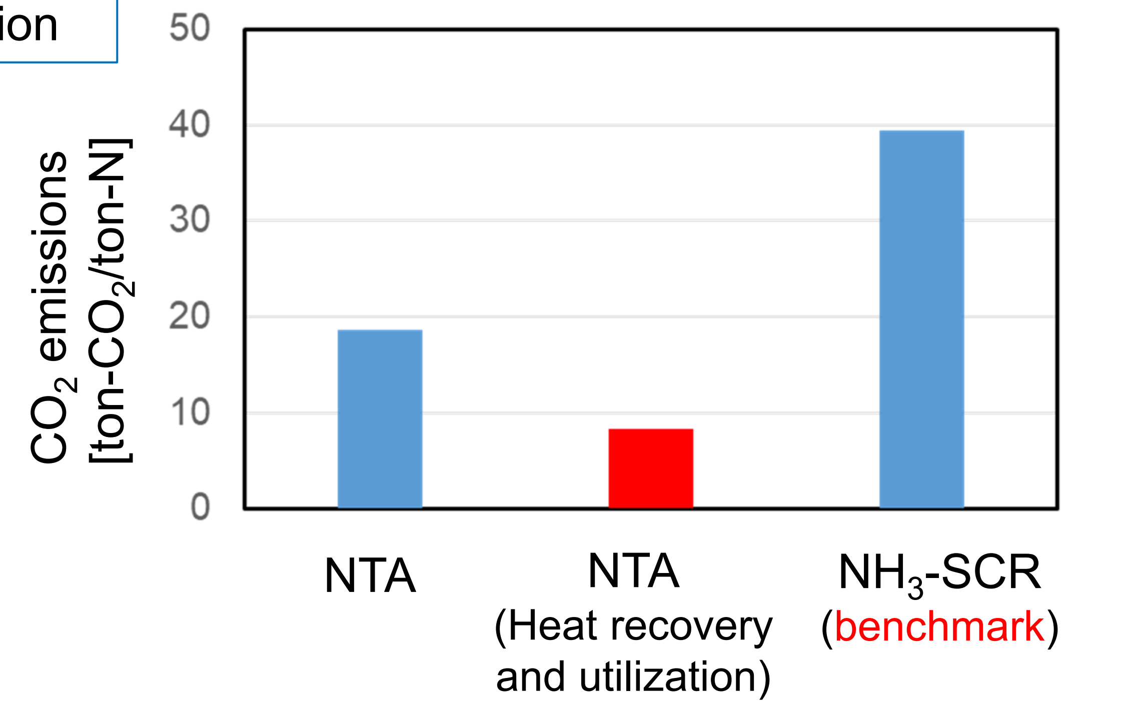
Synthesis, dynamic analysis and evaluation of NTA process systems

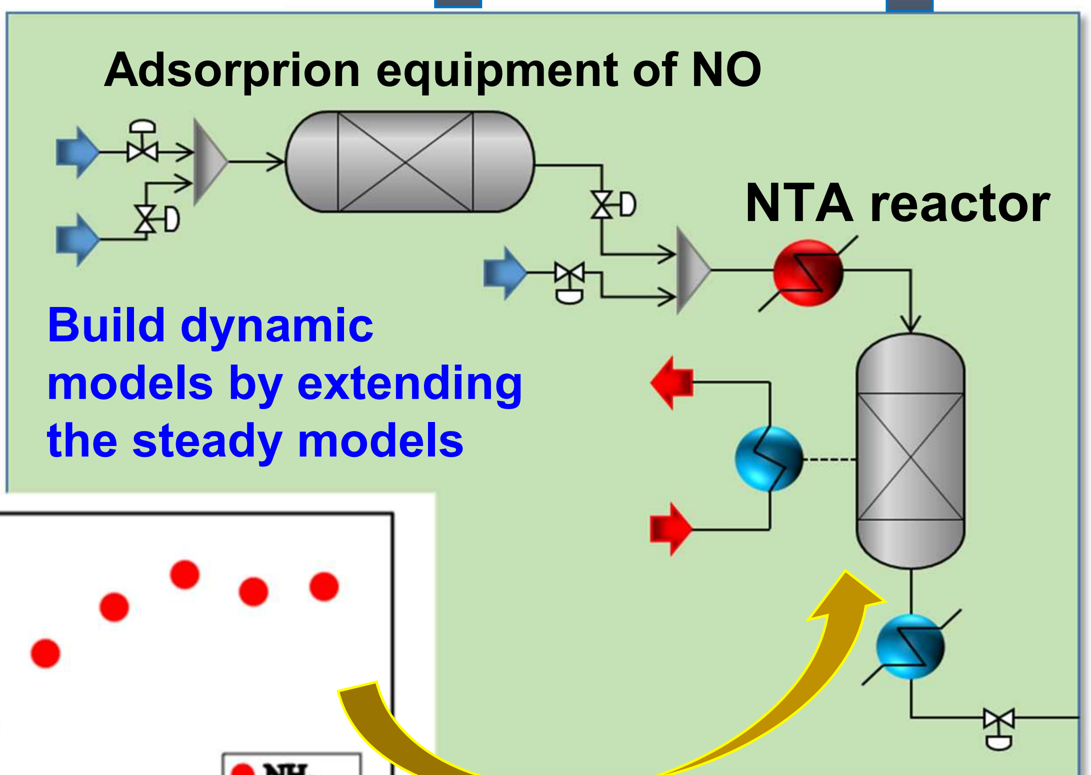


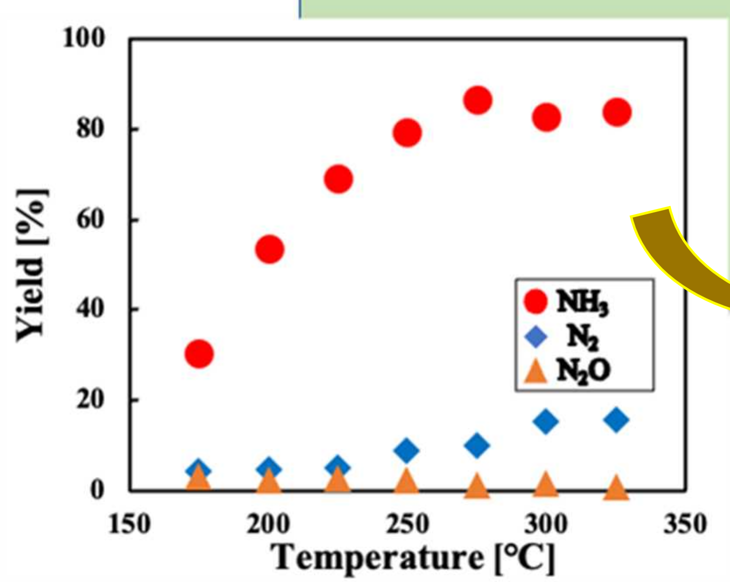
Dynamic analysis of NO desorption process using R&D materials

Calculation of mass and energy balance using steady-state simulation

Comparison of the amount of CO_2 emissions required to achieve zero NOx emissions





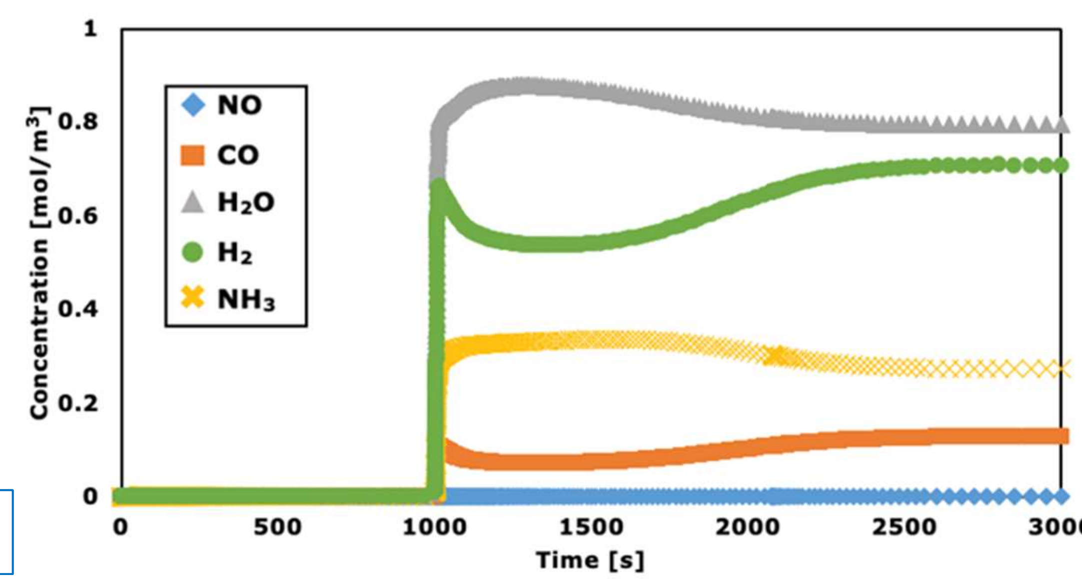


Catalyst activity test data for NTA

Develop reaction rate equation models

Dynamic simulation

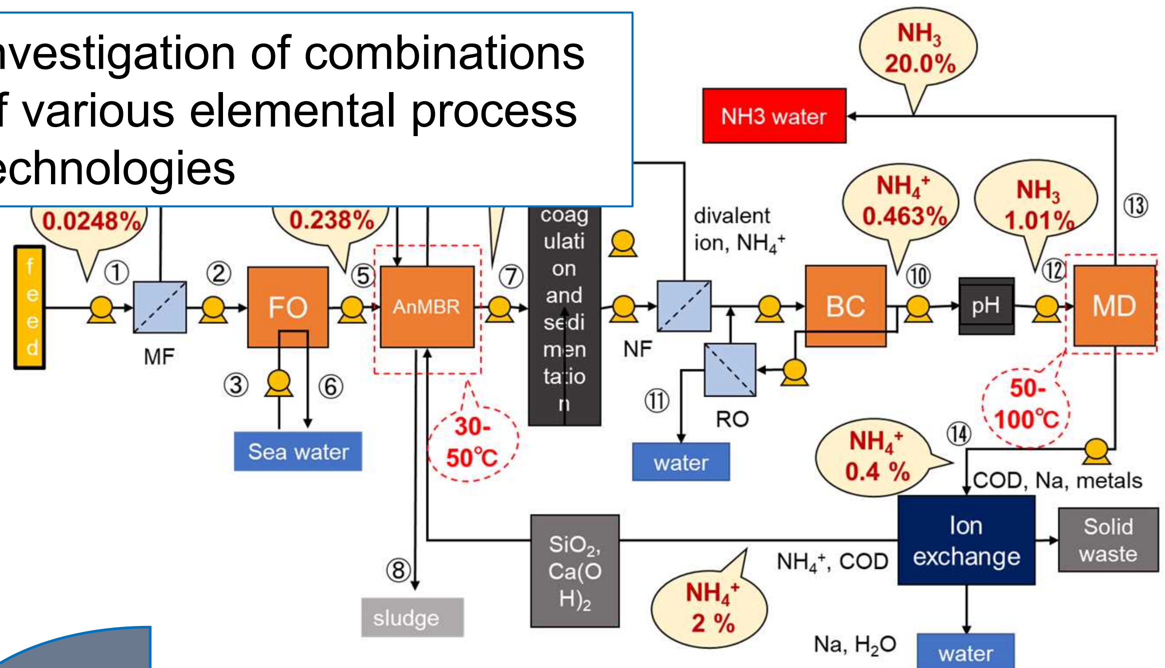
Influence of unsteady operation of NO adsorption process to the behavior of NTA reactor



TMEHE 3. Process and evaluation(Nagoya Univ)

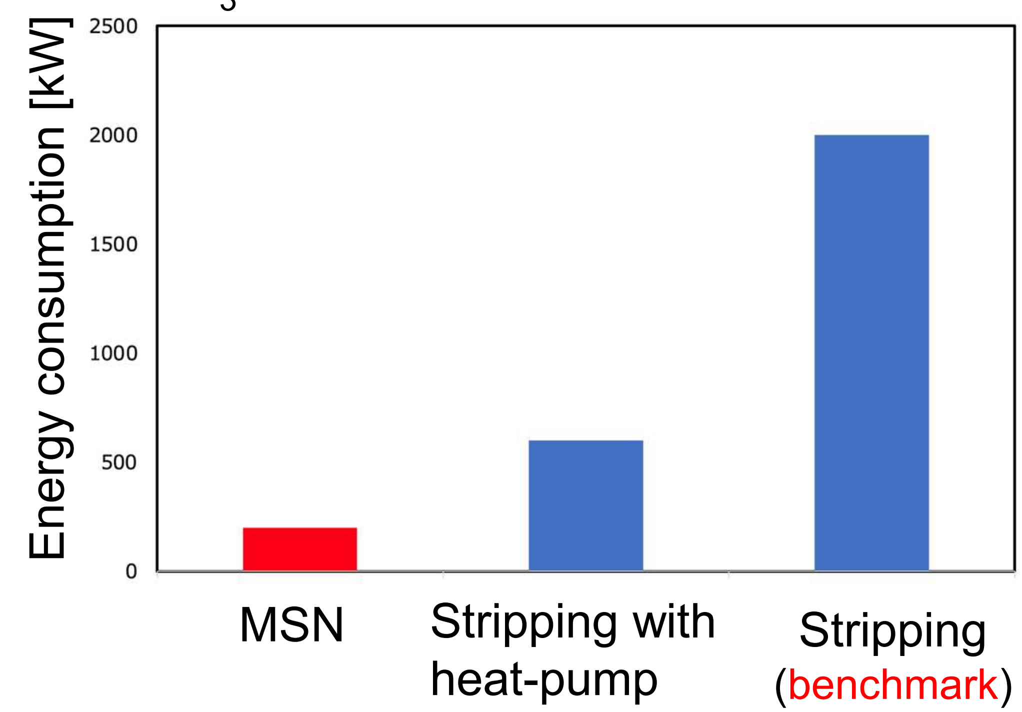
Synthesis, dynamic analysis and evaluation of liquid phase concentration process systems

Investigation of combinations of various elemental process technologies

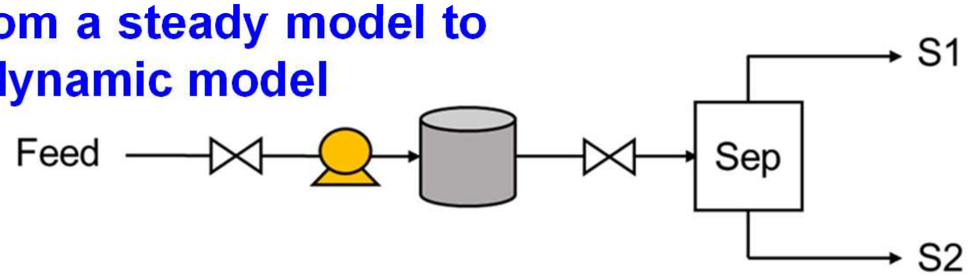


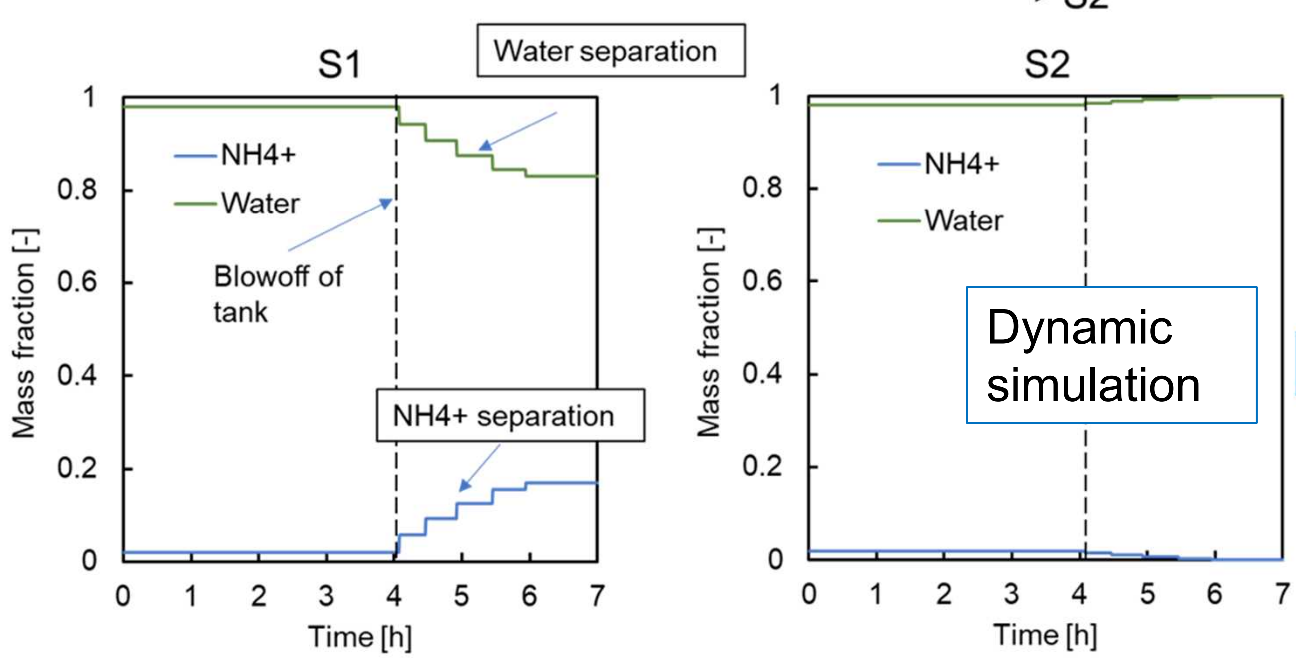
Calculation of mass and energy balance using steady-state simulation

Comparison of energy input required for NH_3 concentration

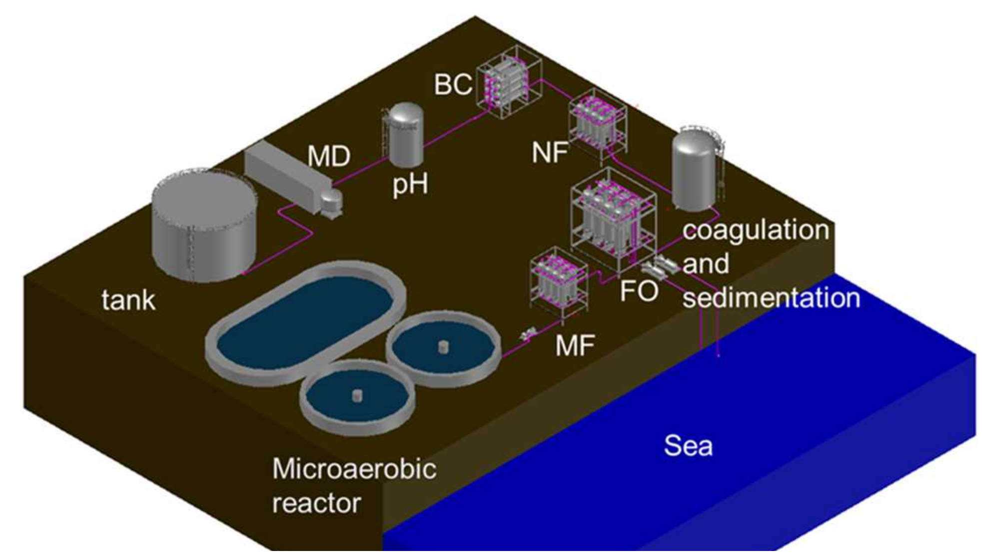


From a steady model to a dynamic model





Dynamic simulation

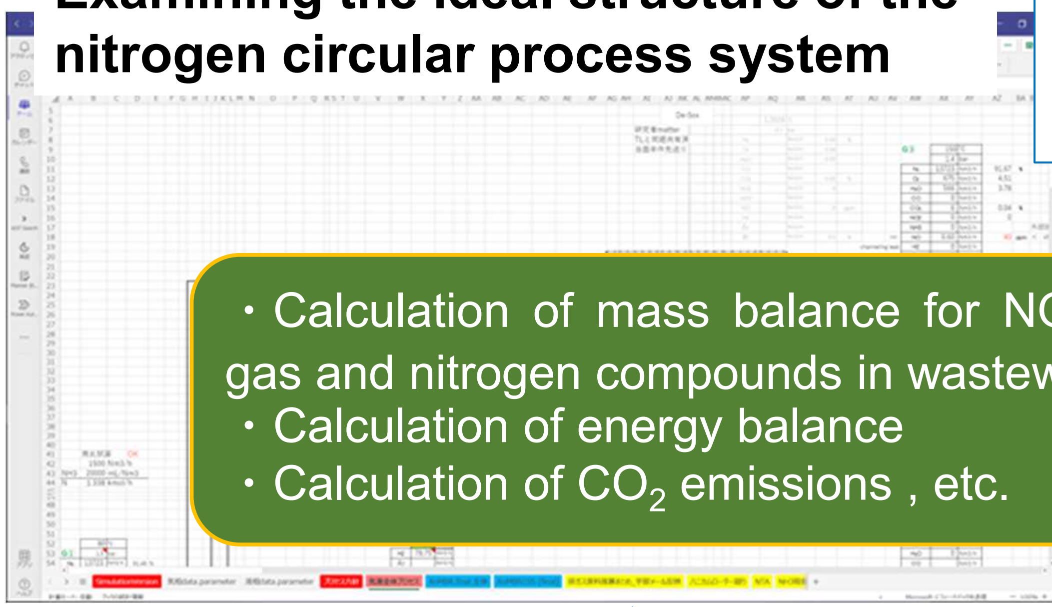


Investigation of interactions among elemental processes with different throughputs, residence times, materials and energies

TMEHE 3. Process and evaluation(AIST)

Environmental impact assessment of introduction of nitrogen circular technologies

Examining the ideal structure of the nitrogen circular process system

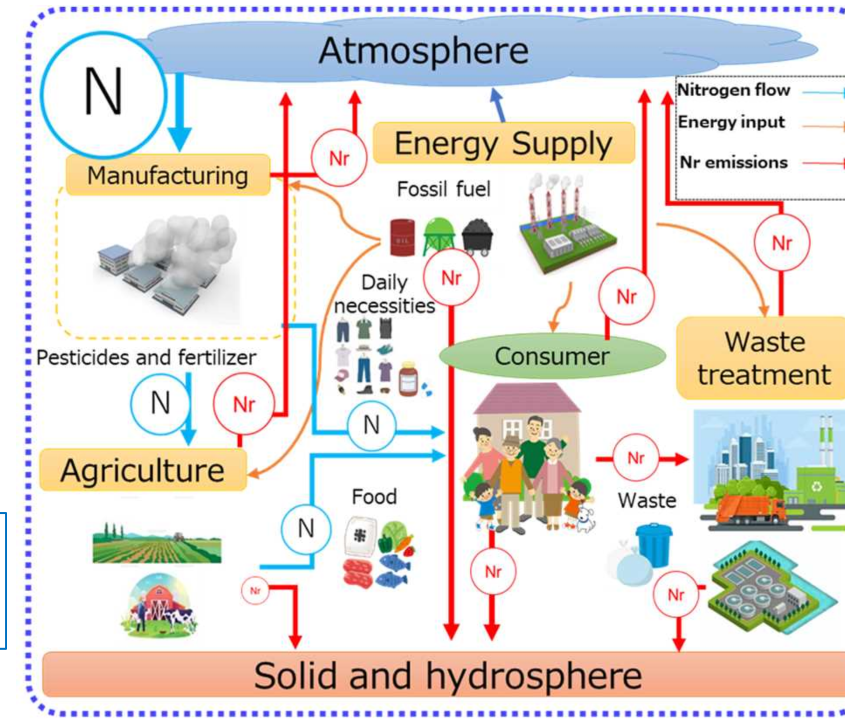


- Calculation of mass balance for NOx in gas and nitrogen compounds in wastewater
- Calculation of energy balance
- Calculation of CO_2 emissions , etc.

Construction of database for assessment of nitrogen circular technologies

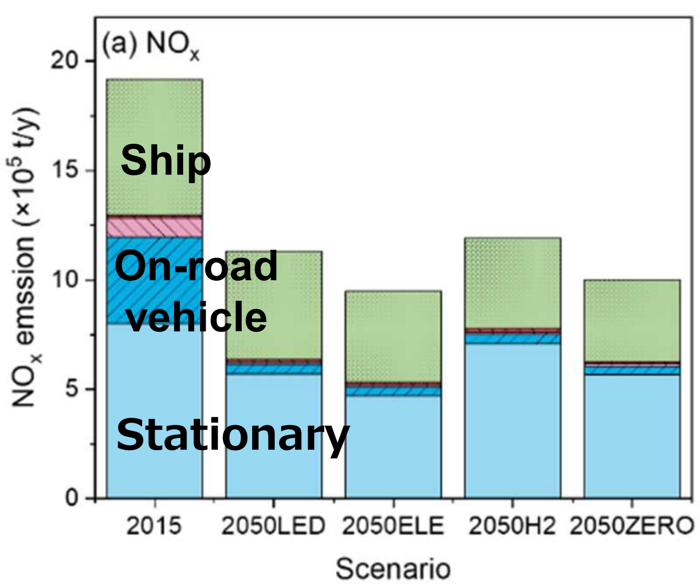
Constructing nitrogen inventory data of approximately 700 products

Visualization of domestic nitrogen flow by adapting annual production based on nitrogen input and output amount of each product



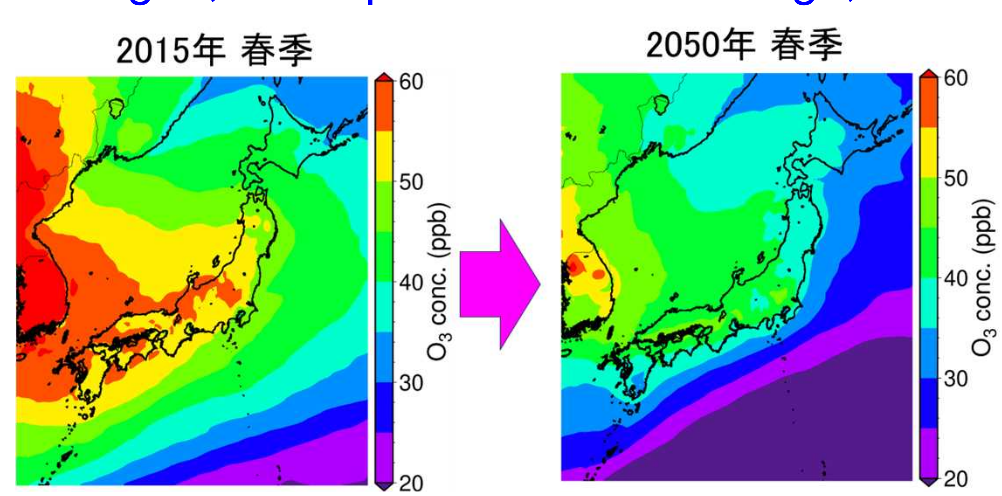
Scope of nitrogen inventory database in IDEA

Development of application methods for simulation based on air quality models



Estimated NOx emissions in 2050

Considering the effect of reducing reactive nitrogen, the impact of climate change, etc.



O_3 concentration in 2015 and 2050

Multidimensional evaluation of effects of nitrogen circular technologies (NRT) through integration with process system design

- ●LCA visualizes energy wellbeing, environmental improvement after installation of NRT.
- ●Suggesting benefits of NRT to human health and the ecosystem.

Summary

◆Background◆

- Environmental release of nitrogen compounds is one of the biggest challenges in the planetary boundary.
- The United Nations Environment Program adopted a resolution recommending significant reduction of nitrogen waste and sharing of national action plans. Ministry of the Environment also started to consider.

◆Research and Development◆

- Conversion of NOx in exhaust gas to ammonia for detoxification and recycling.
- Conversion of nitrogen compounds in wastewater to ammonia for recycling.
- Evaluation of the effectiveness of the developed ammonia recycling technology.

→Shifted to the overall design of the process, and the solution of problems in actual gas and liquid utilization for the social implementation.

◆Summary of Achievements◆

255 external publications, including 39 academic papers and 21 patent applications