No. A-9-1E

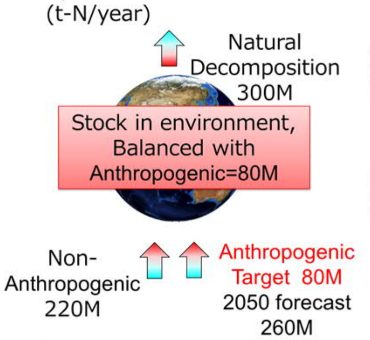
PJ : Innovative Circular Technologies for Harmful Nitrogen Compounds / To Solve Planetary Boundary Issues

Organization: AIST and 16 university / companies

Contact: Dr. Tohru Kawamoto (AIST), tohru.kawamoto@aist.go.jp

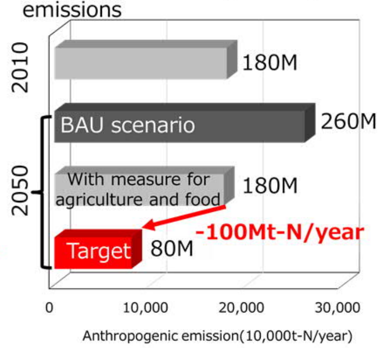
◆Background◆

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



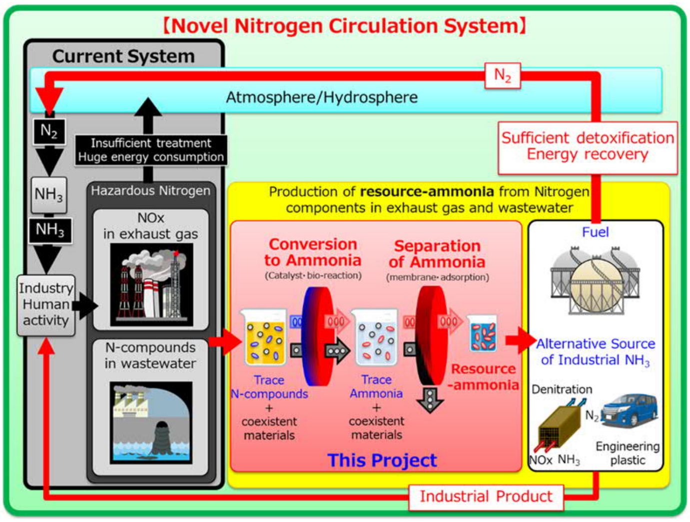
Galloway, Biogeochem. (2004), Fowler, Philos.Trans. R. Soc. B Biol. Sci. (2013) de Vries, Curr. Op. Env. Sus. (2013)

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

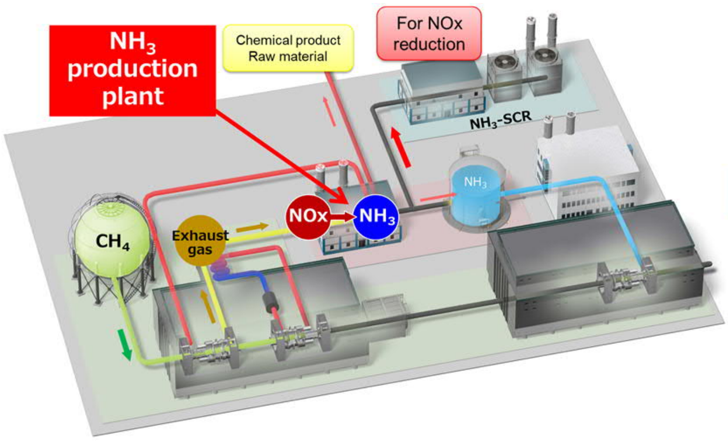


Additional 100Mt-N/year reduction is necessary

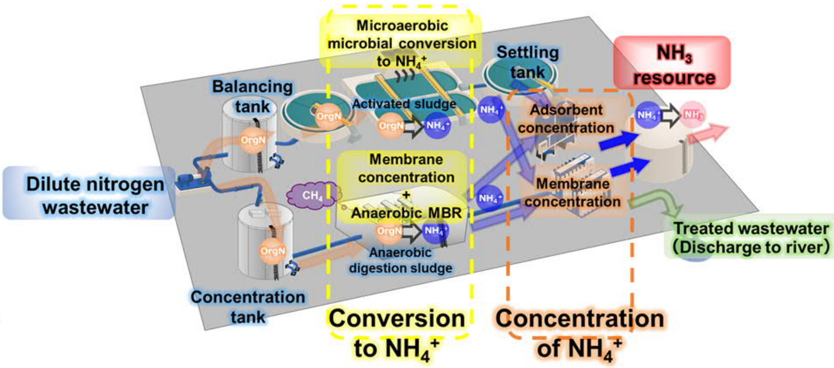
◆Nitrogen circulation systems◆



◆Plant image(NOx to ammonia)◆



◆Plant image(Aqueous N to ammonia)◆



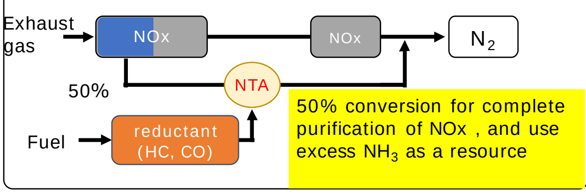
◆Research theme◆

【1. NOx to ammonia】

①concentration of NOx·NH_3 in gas phase

②catalyst for NOx→NH_3 at low temperature

③catalyst even with O2 coexistence

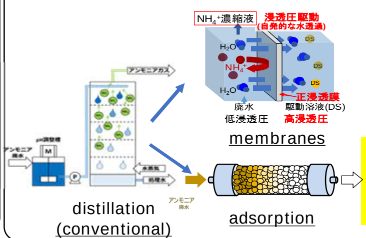


50% conversion for complete purification of NOx , and use excess NH_3 as a resource

【2-2. ammonia recovery in water】

(1) new membrane/adsorption separation

(2) Construction of ultra energy-saving separation and concentration process

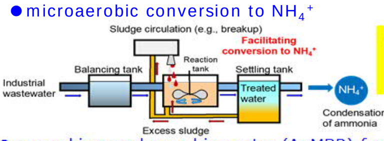


<1/100 of the energy consumption of conventional methods

【2-1. conversion to NH_3 in wastewater】

Efficient NH_4^+ conversion bioprocess for various conditions

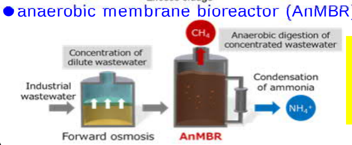
● microaerobic conversion to NH_4^+



・Low NH_4^+ loss

・Use excess sludge as nitrogen source

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

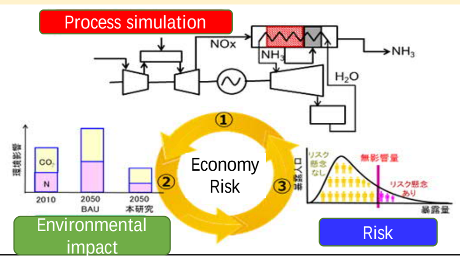


・work at high NH4- concentration

・High energy efficiency and compact size

【Theme 3. Process and evaluation】

1) Process design of actual equipment and pilots 2) economic and environmental impact assessment.



No. A-9-2E

PJ : Innovative circular technologies for harmful nitrogen compounds

Theme: Gas phase NOx recylcle-NOx adsorption, concentration+NTA+application

Organization: The University of Tokyo, AIST, UBE, Seibu Giken
Contact: Prof. Masaru Ogura (UT), oguram@iis.u-tokyo.ac.jp

R&D#1-①,③. 2 step NTA= ①NO concentration & O_2 separation + ③NTA process in O_2-free flow

【Item of this technology】Design of 2 step NTA catalytic system composed of NO separation in coexistence of excess O_2 and H_2O and its successive NTA catalysis in the absence of O_2

【Goal】Removal of more than 90% NO in exhaust stream below 200 °C, Scale-up of NTA catalytic system to a bench reactor

【Future plans】Fabrication and evaluation by use of columnar reactor for the "Honeycomb rotor"

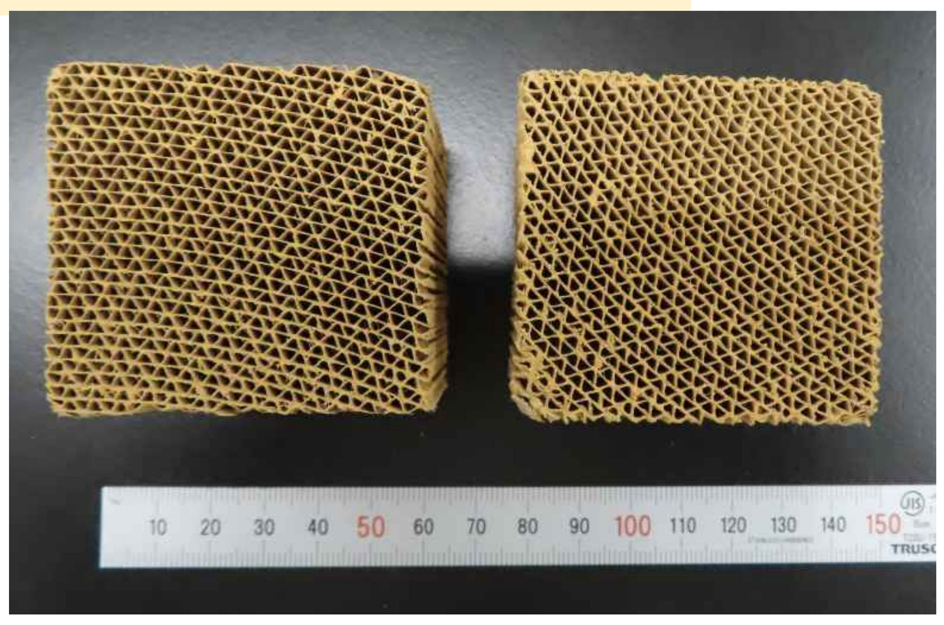
2step NTA catalytic system：

NO→NOad（adsorption and concentration）
NOad+reductant→NH_3（NTA）

the role of the "Honeycomb rotor"：

① NO selective adsorption in exhaust (Separation Zone)
② NO concentrated gas supply to NTA (Desorption and Regeneration Zone)

NTA catalytic reactor follows successively.

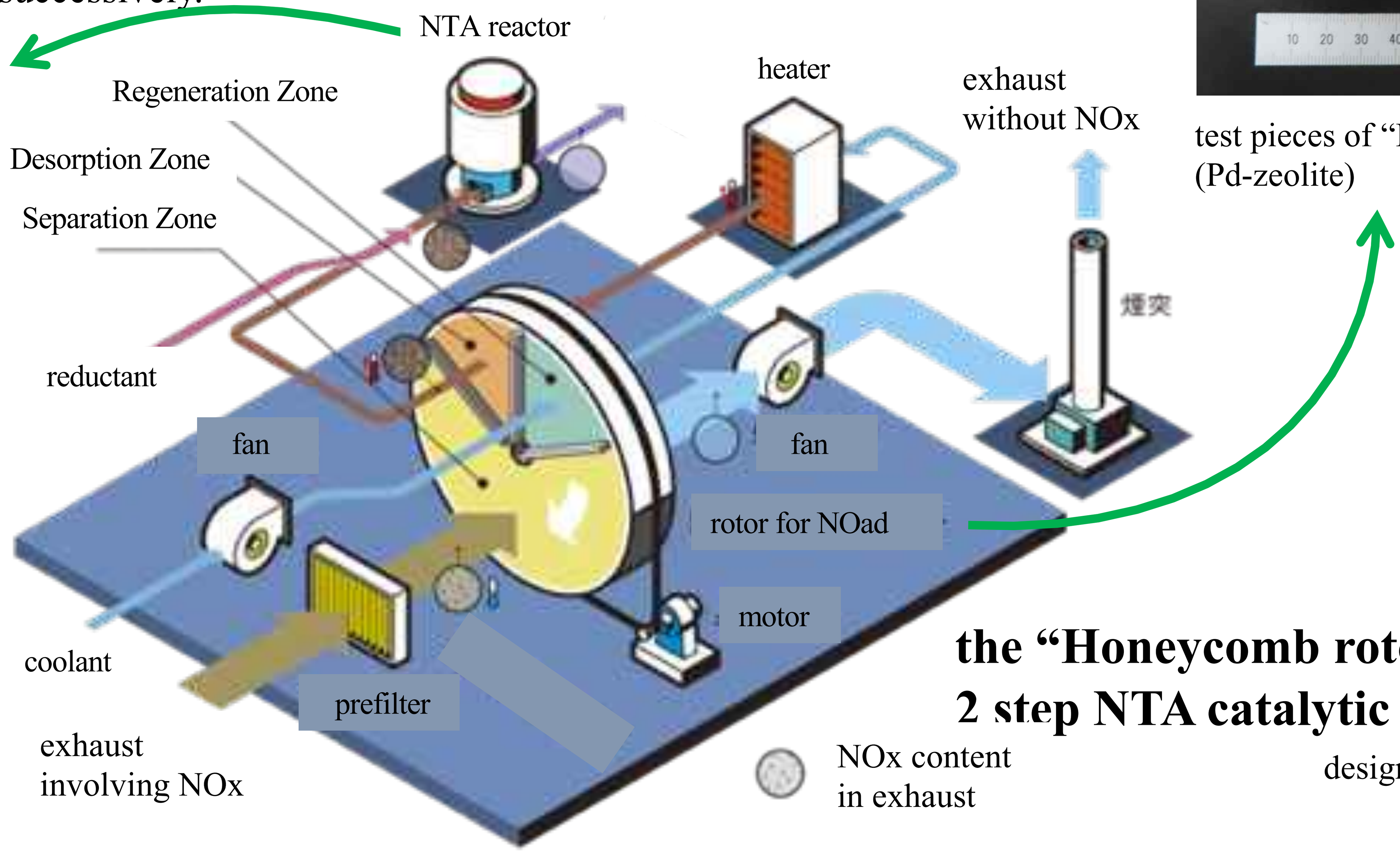


test pieces of "Honeycomb" NO adsorbent (Pd-zeolite)

NO→NOad（ad&conc）

NTA reactor@AIST

+reductant
NOad→→→NH_3（NTA）



valuable source from exhaust!?

this is NTA ＝ NOx To Ammonia

the "Honeycomb rotor" 2 step NTA catalytic system

designed by Seibu Giken

R&D#1-⑦. Feasibility studies for 2 step NTA in real chemical plants

Candidate Site for NTA process：Denitrification Equipment for Lactam Plant

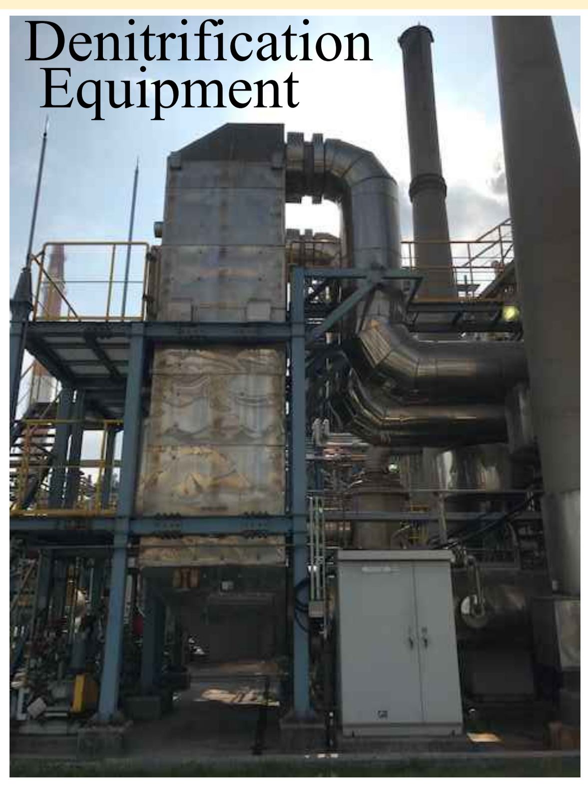
Check requirements and FS survey ⇒ Consideration of feasibility of pilot plant in FY 23

UBE Lactam Plant

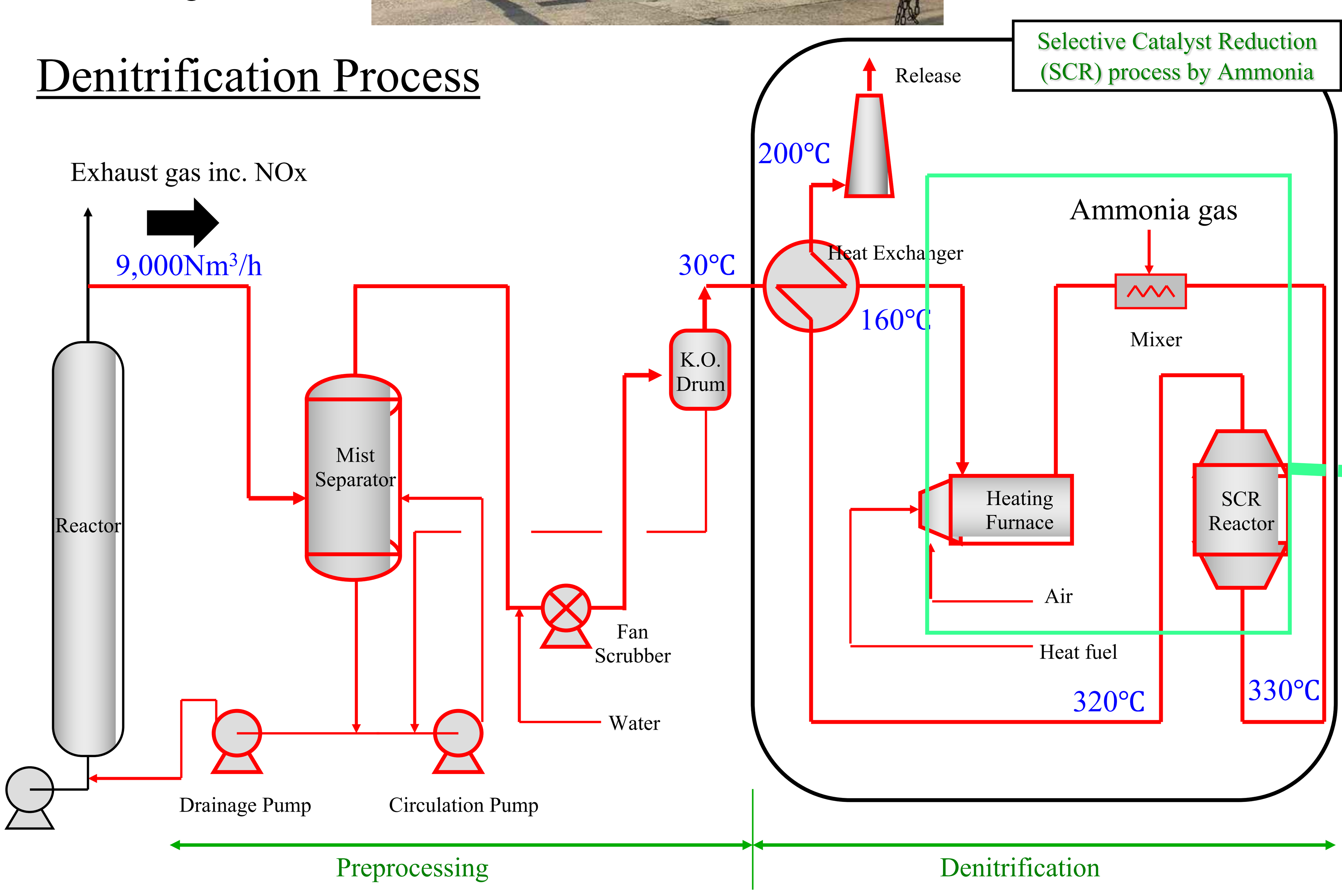
Production Equip.
Denitrification Equip.

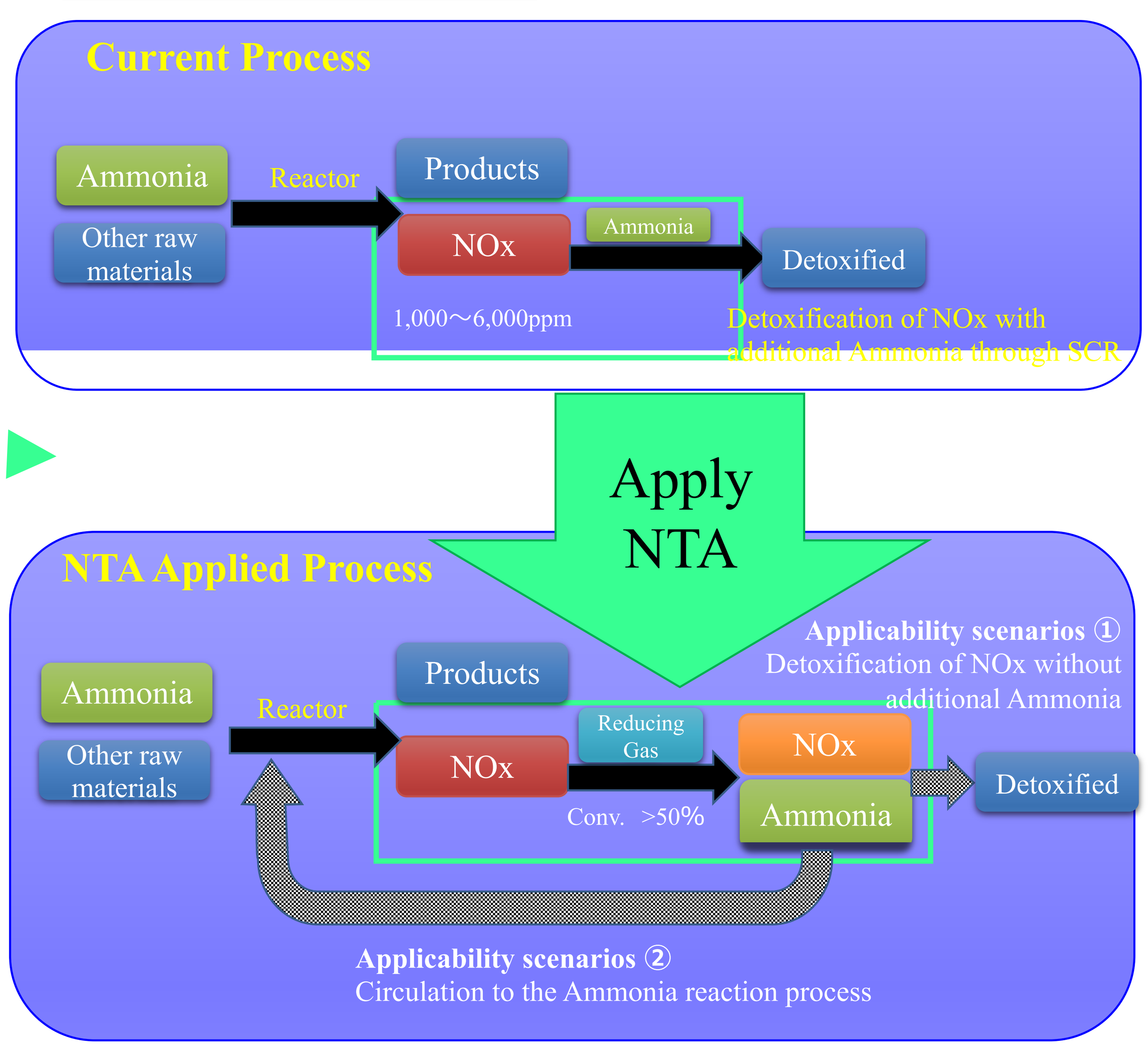
Plant tour on 9-10 August, 2022

Denitrification Equipment



Denitrification Process





No. A-9-3E
PJ : Innovative circular technologies for harmful nitrogen compounds
Theme: Recycling of Gas-phase NOx – NTA in O_2 and concentration of NH_3

Organization: Waseda Univ., AIST

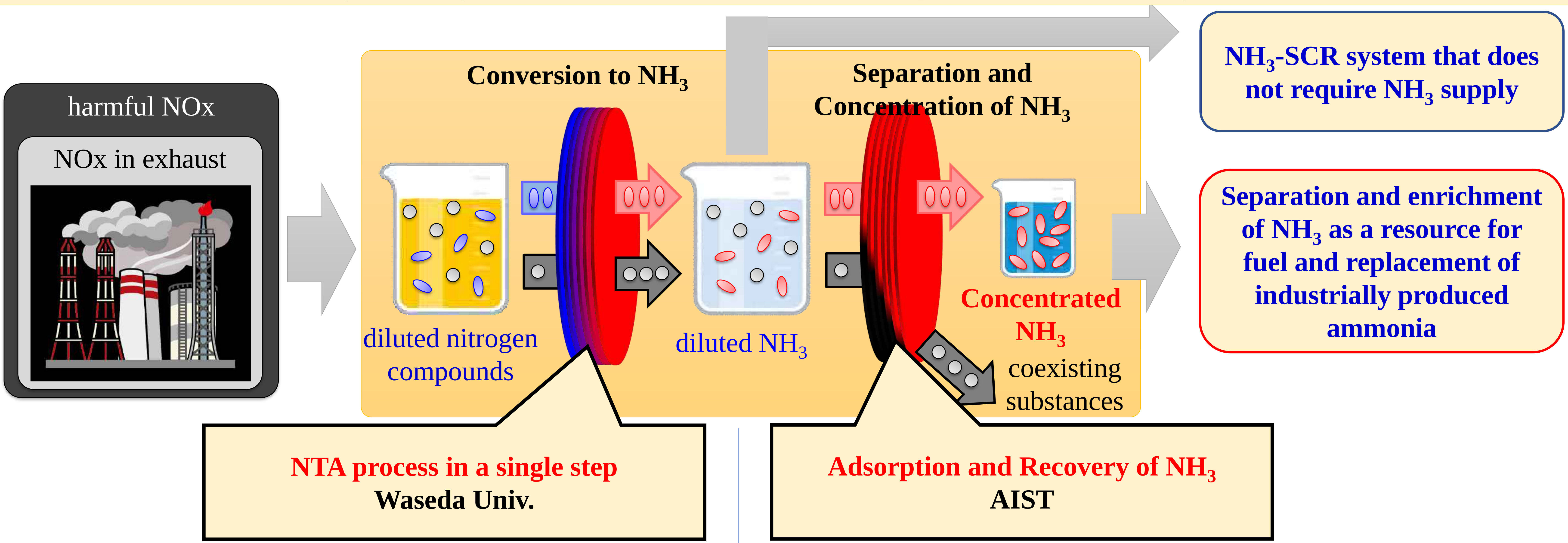
Contact: Dr. M. Iwamoto m.iwamoto3@kurenai.waseda.jp, Dr. K. Minami kimitaka-minami@aist.go.jp

Item 1-(4), (5) Recycling of gas-phase NOx – Conversion of NOx to NH_3 in O_2, concentration and recovery through adsorption

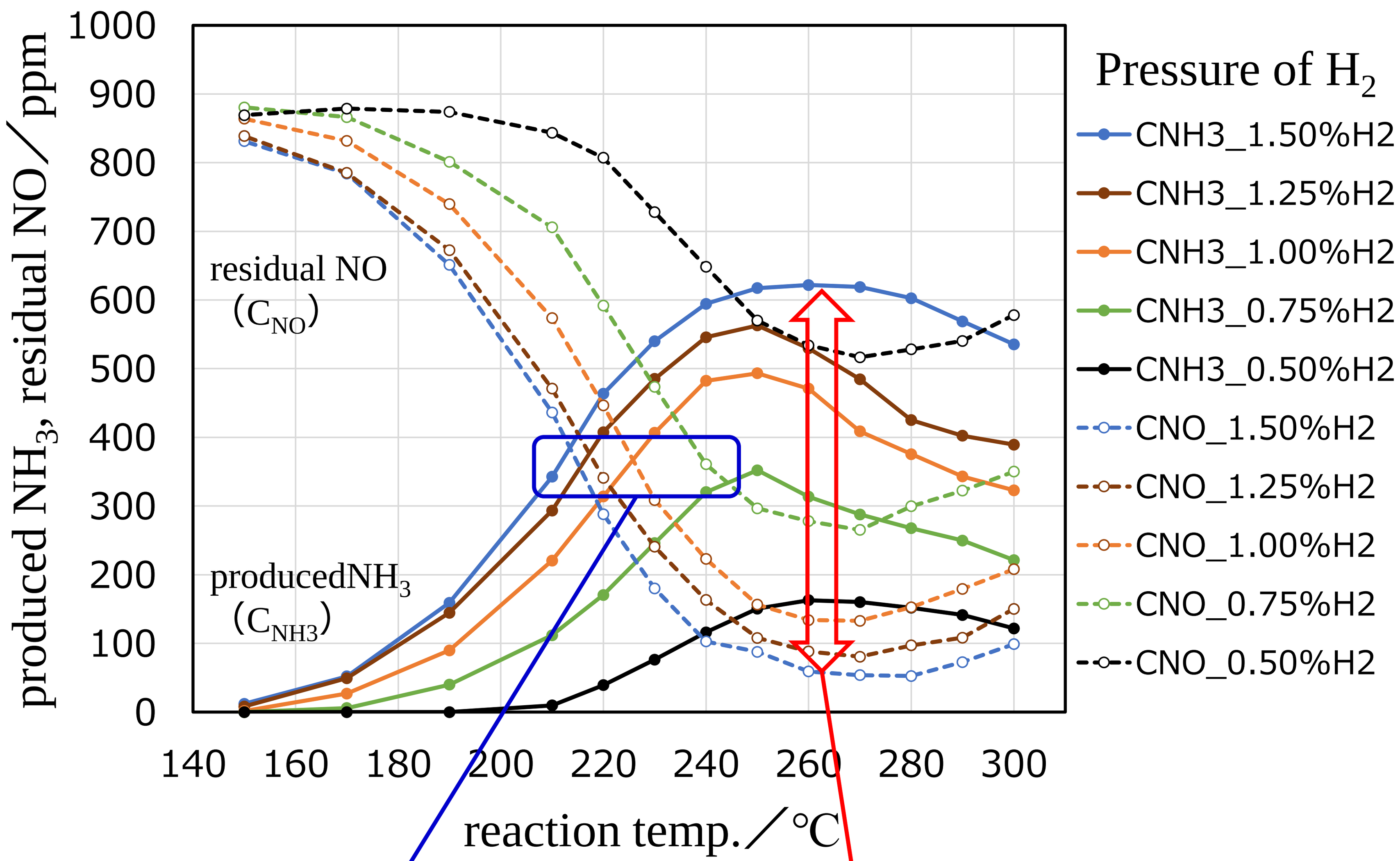
[Outline] NO is directly converted to NH_3 in O_2 and H_2O by H_2 (NTA reaction). The adsorption-desorption of the produced NH_3 leads to its usage as a resource.

[Goal] Realization of NH_3-SCR system that does not require NH_3 supply, and separation and enrichment of NH_3 as a resource for fuel and replacement of industrially produced ammonia.

[Future Plans] Evaluation of catalytic activity on mini-bench-scale and bench-scale separation/concentration systems.



We Developed a one-step NTA catalyst in O_2 and H_2O, suggesting a new NH_3-SCR and recycling of NO.



Realization of NH_3-SCR, that does not require NH_3 supply, at Cross-points $C_{NO} = C_{NH3}$. H_2-NTA + NH_3-SCR can be achieved with only P_{H2}=0.75%.

Connection to the NH_3 adsorption and enrichment system shown in the right figures, when $C_{NH3} \gg C_{NO}$.

Standard reaction conditions (an atmospheric fixed bed flow reactor) : catalyst W02(0.3mL), total gas flow rate 100 mL/min (space velocity SV=30,000 h^{-1}), 0.1% NO, 1.5% H_2, 0% O_2, 10% H_2O, N_2 balance.

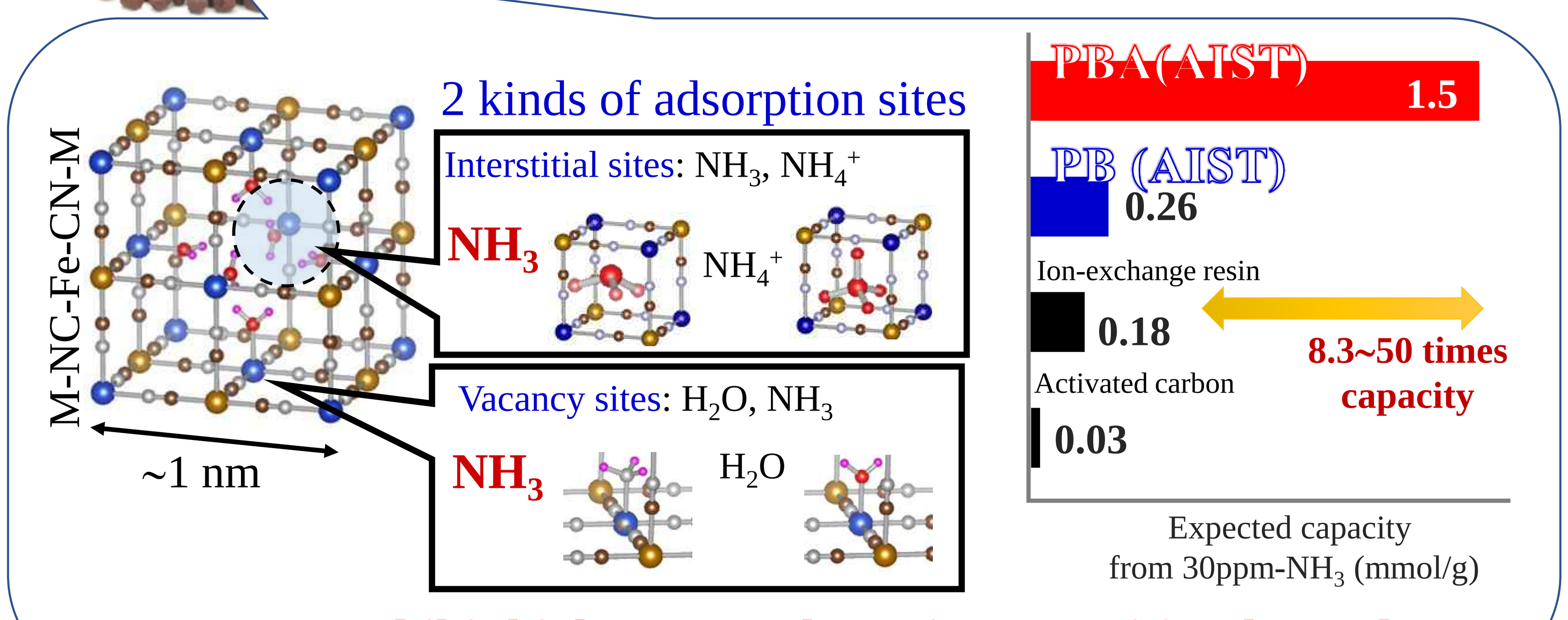
Ammonia concentration System using Prussian blue analogues(PBA)

PBA

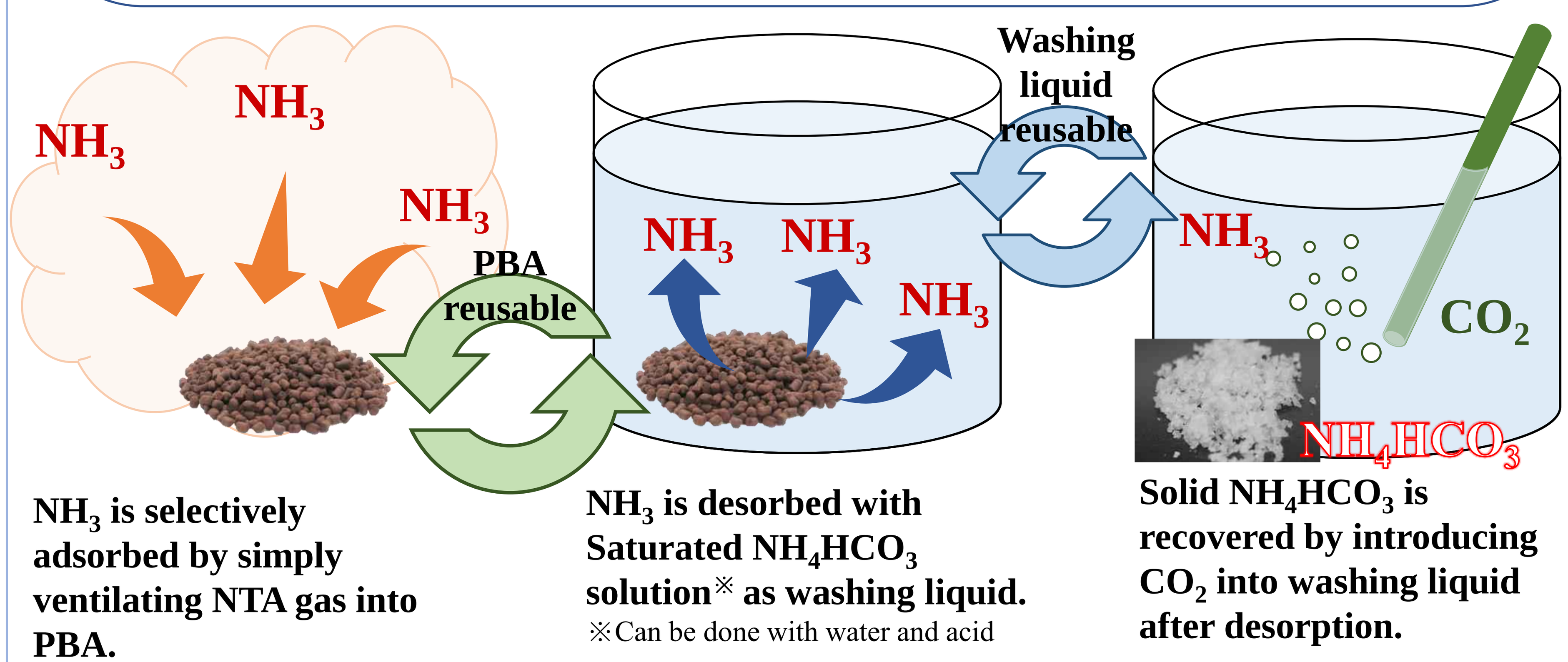
$A_xM_y[M'(CN)_6]\cdot zH_2O$

M=M'=Fe: Prussian blue (PB)

M,M'=Fe, Cu, Zn,Ni, Co···, A=Na,K,NH4··: PBA



PBA exhibit higher NH_3 adsorption capacities than others



H. Usuda *et al.*, *Environ. Pollut.* **288** (2021) 117763.

NTA gas is vented into PBA, and NH_3-removed gas can be exhausted
PBA and washing liquid are reusable.
NH_3 is concentrated and recovered as solid NH_4HCO_3

[Usage and effect] A new circulation system for gas-phase NOx to reduce the amount of N-compounds released into the global environment.

Applicable to small-scale NO sources such as ships, garbage incinerators, etc.

Realization of NH_3-SCR with self-consumption of generated NH_3. Hydrogen source is hydrocarbon or hydrogen. Compact reactor that can be attached to existing NH_3-SCR equipment, eliminating the need for NH_3 storage tanks, lorry transfers, and toxicology supervisors.

Applied to large-scale NO sources such as power plants, oxidation processes, cement kilns, etc.

Separation and concentration of the produced NH_3 into a resource for use as a fuel or as a substitute for ammonia in industrial production. Construction of a medium-scale NH_3 synthesis plant in the area of demand for use as an industrial feedstock or fuel on site, realizing NO-independent operations (improved energy efficiency).

No. A-9-4E
PJ : Innovative circular technologies for harmful nitrogen compounds
Theme: Gas-phase NOx recycling – NOx Storage Reduction（NSR）for NTA

Organization: AIST
Contact: Dr. Tatsuo Kimura（AIST）t-kimura@aist.go.jp

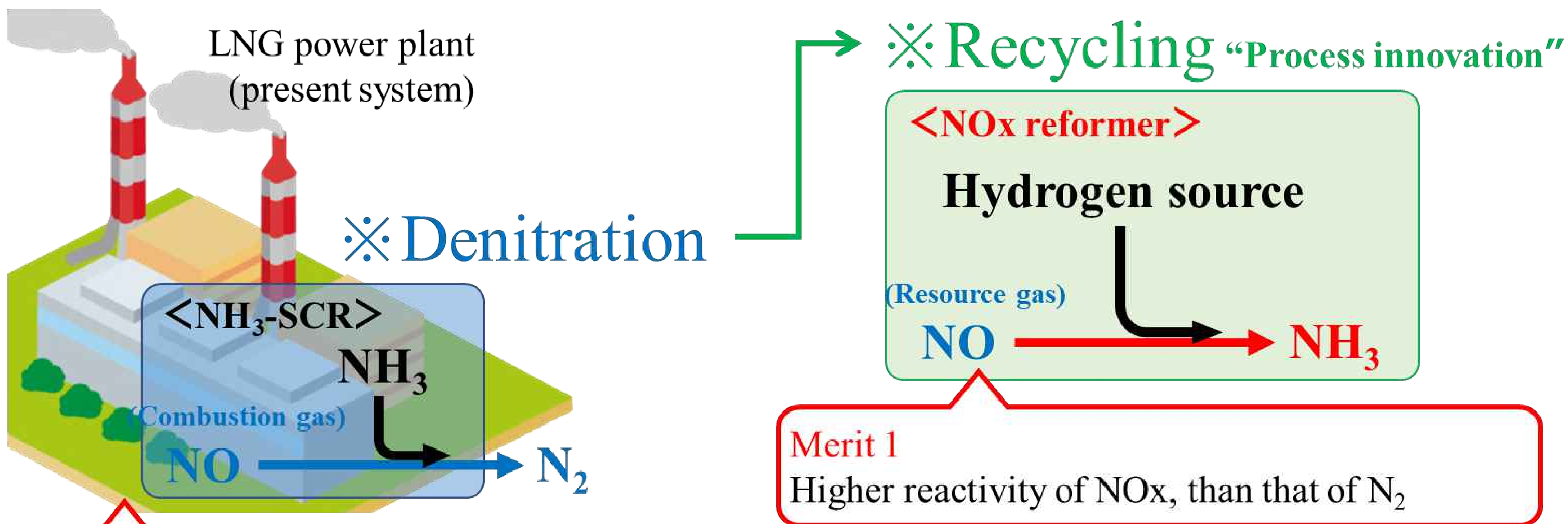
Research theme 1-②. Precise design of nanoporous metal oxides for applying selective NTA reaction after NOx storage (NSR for NTA）

【Overview of our technology】
Design for selective conversion from stored NOx to NH_3 at constant temperature by switching reaction gases for eliminating coexisting gases

【Our research target for the first quarter】
Achieving 50% of NOx recovery rate, enabling the design of complete NH3-SCR process combined with the NTA process

【Our future plan】
Improving NOx storage property and then proposing a guideline for the design of a high-performance catalyst for NRS for NTA

Game change technology for recycling nitrogen resources



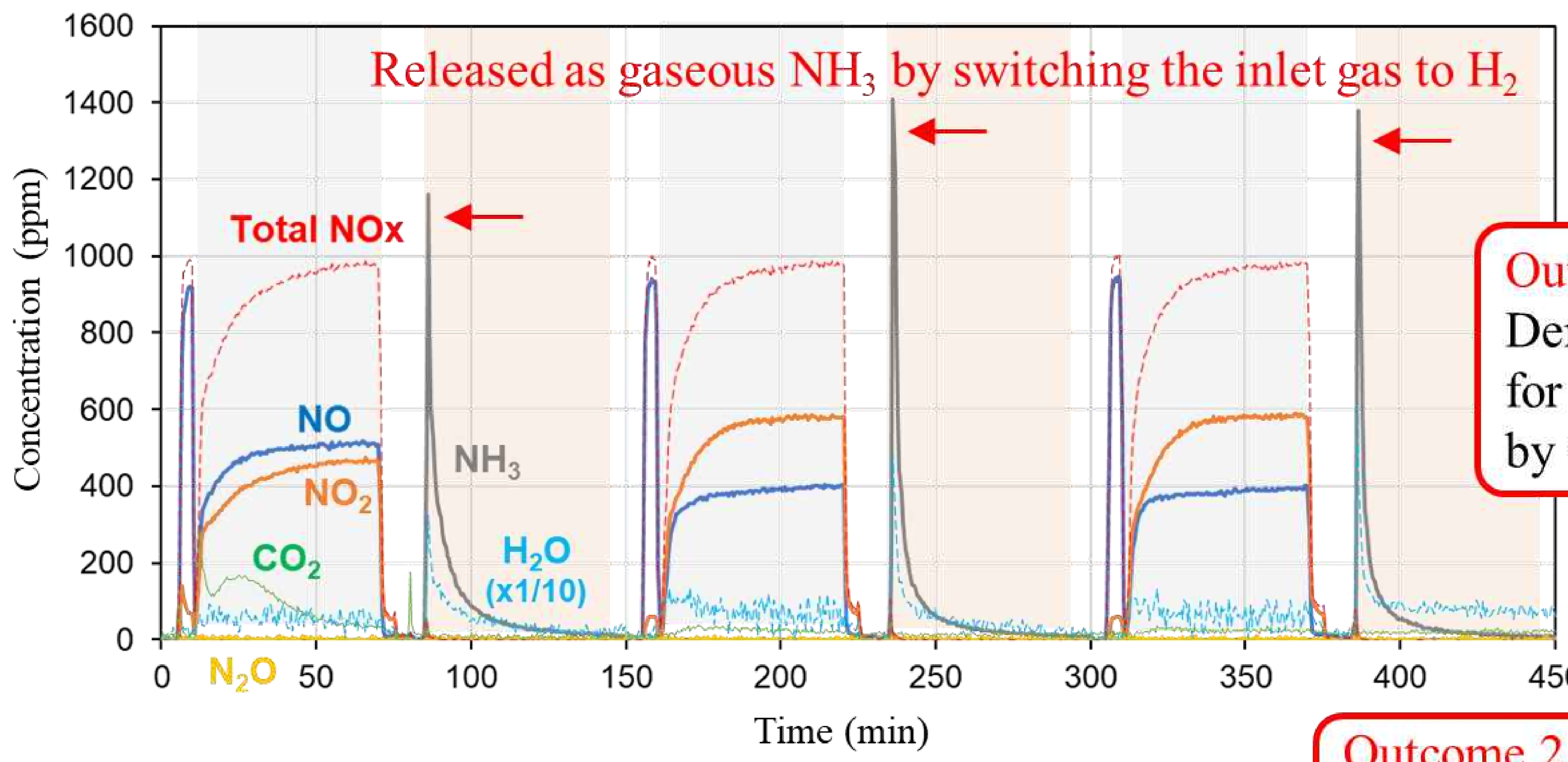
Merit 1
Higher reactivity of NOx, than that of N_2

Merit 2
Sufficient supply, expected
410,000 ton/year (after denitration)

Benefit 1 Onsite procurement of NH_3 for denitration ?
Benefit 2 No more energy than used in the present denitration process ?
Benefit 3 Reduce the amount of NH_3 imported as a reducing agent ?

An example to synthesize ammonia from stored NOx at AIST-Chubu

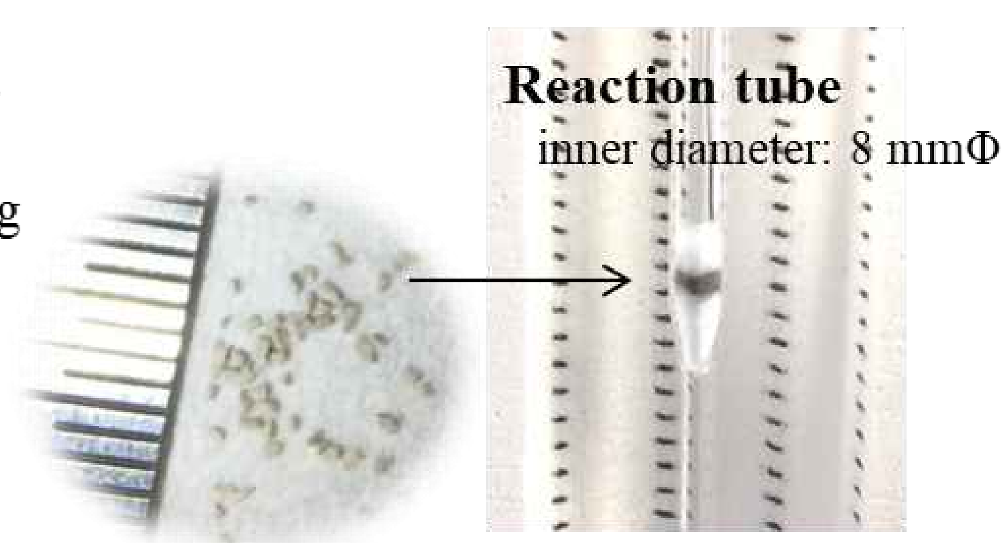
NOx storage → NH_3 synthesis → NOx storage → NH_3 synthesis → NOx storage → NH_3 synthesis → **NSR for NTA**



Outcome 1
Demonstrating our process for selective NH_3 synthesis by switching reaction gas

Outcome 2
Achieving over 90% selectivity to NH_3 by reviewing composition of material and optimizing operation conditions

■ **Catalyst: Ba/Pt@mAl_2O_3**
Granule size: 150~250 µm
Weight (before use): 100 mg
Weight (after use: 85 mg



■ **Space velocity (SV)**
WHSV : 60,000 h^{-1} g_{cat}^{-1}
SV 29,000 h^{-1}（calculated by using the density ca. 2.1 ml/g

■ **Reaction conditions**
Reaction temperature: 300℃
Gas flow rate: 100 mL min^{-1}
NOx storage: 1000 ppm NO + 10% O_2 + N_2
NH_3 synthesis: 1% H_2 + N_2

No. A-9-5J

PJ : Innovative circular technologies for harmful nitrogen compounds

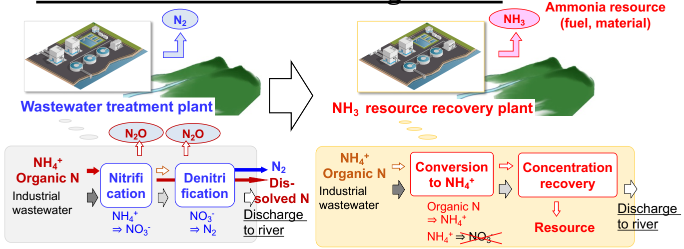
Theme: Wastewater N compounds to NH_4^+– Microaerobic conversion process (1)

Organization: AIST, Kyowa Hakko Bio Co., Ltd. (KHB)
Contact: T Hori (AIST) hori-tomo@aist.go.jp; T Shimizu (KHB) takeshi.shimizu@kyowa-kirin.co.jp

R&D points (bioconversion processes)

- A set of systems connecting "conversion to NH_4^+" and "separation and concentration of NH_4^+"
- Ceasing nitrogen discharge into natural environments and achieving resource and energy recovery
- Constructing aerobic and anaerobic bioconversion processes for various wastewater types and situations

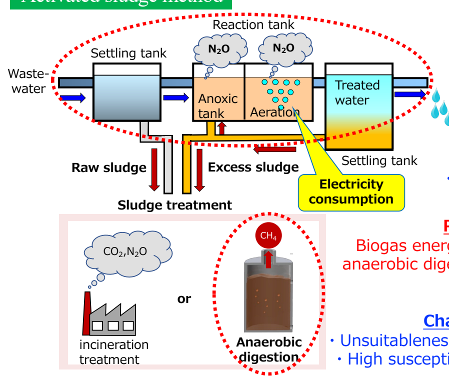
Current state and future image in 2050



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

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

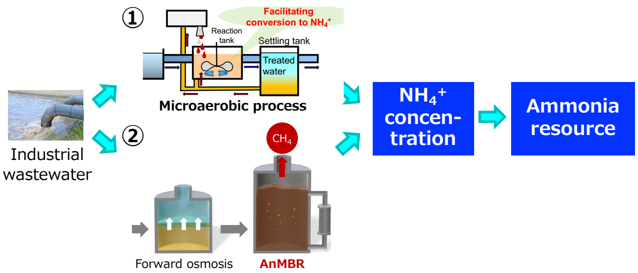
Two important points for bioconversion process



Point ①
Use of the current infrastructure (retrofit technology)
⇕
Challenge ①
- Vast energy requirement
- N_2O and CO_2 emission
- Cost for sludge treatment

Point ②
Biogas energy acquisition from anaerobic digestion of wastewater
⇕
Challenge ②
- Unsuitableness for dilute wastewater
- High susceptibility to contaminants

Objectives：Conversion of nitrogen compounds in wastewater to NH_4^+ using ①Microaerobic system and ②AnMBR

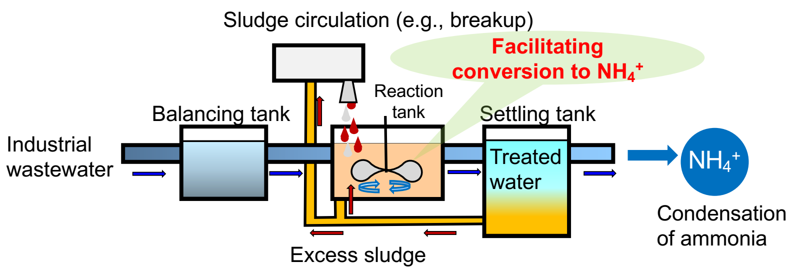


	① Microaerobic conversion process	② AnMBR
Organic loading	○ Low concentration	○ High concentration
Decomposition ability	○ Organics-C is completely degraded	○ Residual organics-C is <10%
Nitrogen recovery	○ Recovery by nitrification inhibition	○ Complete recovery
Biogas recovery	-	◎ CH_4 recovery
Retrofit	◎ Current infrastructure can be used	△ Process renewal is needed
Target wastewater	○ Low-concentration industrial and municipal wastewater	○ Low- & high-concentration industrial and municipal wastewater (+ FO membrane)

R&D points (microaerobic process [1])

- Current infrastructure for activated sludge method can be utilized <Retrofit technology>
- Facilitating conversion to NH_4^+ with removal of organic carbon in wastewater <Resource recovery>
- Energy saving by reduced aeration, N_2O emission mitigation, use of excess sludge as nitrogen source

Microaerobic conversion process



R&D Items and Organization

- Operation management based on microbial community control (AIST)
- Operation management based on nitrogen compound dynamics control (TUAT)
- Energy and material balance evaluation and N_2O emission mitigation strategy development (Kyoto Univ.)
- Construction, operation and maintenance of the bench-scale microaerobic conversion process (KHB)


Dr. Hori (AIST)

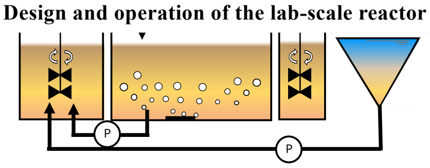

Prof. Terada (TUAT)


Prof. Fujiwara (Kyoto U)


Dr. Shimizu (KHB)

Achievements and future works

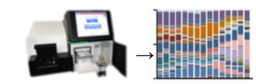
Design and operation of the lab-scale reactor



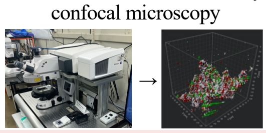
- **Long-term and stable treatment of the fermentation industrial wastewater**
(10- to 20-fold concentrated wastewater)
  - NH_4-N; ca. 5,000 mg-N/L
  - Total nitrogen; ca. 7,000 mg-N/L
  - Total organic carbon; ca. 12,000 mg-C/L
  - pH; ca. 1.5

Microbial communities

Identifying sludge microbes by high-throughput sequencing

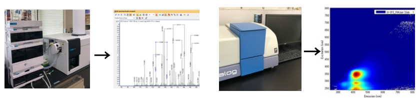


Non-destructive observation by confocal microscopy

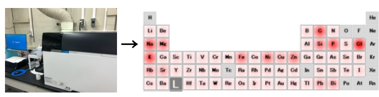


Dissolved chemical compounds

Comprehensive evaluation of organic compounds using LC/CE-TOF-MS and 3D-EEM



Metals profiling using ICP-MS-MS



- **Microaerobic conversion was demonstrated at laboratory scale**
- **>1500-L treated wastewater was provided for the membrane team**
- **Bench reactor to treat 0.5〜5-m³/d wastewater was designed**

No. A-9-6E

PJ : Innovative circular technologies for harmful nitrogen compounds

Theme: : Wastewater N compounds to NH_4^+– Microaerobic conversion process (2)

Organization: Tokyo University of Agriculture and Technology, and Kyoto University

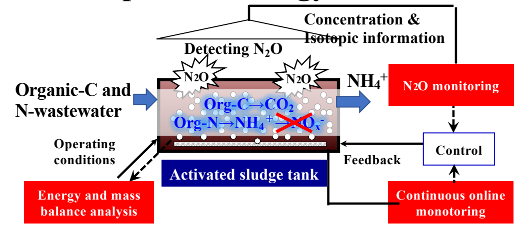
Contact: Prof. Akihiko Terada (Tokyo Univ. Agr.&Technol. (TUAT)), akte@cc.tuat.ac.jp

Prof. Taku Fujiwara (Kyoto Univ.), fujiwara.taku.3v@kyoto-u.ac.jp

R&D points (microaerobic process [2])

- Operating a simplified NH_4^+ conversion process achieves NH_4^+ retention (**efficiency > 80%**) from synthetic medium.
- The stable operation mitigates the emissions of highly potent greenhouse gas N_2O (**< 0.2%** for short-term period)
- The operation suppresses the abundance and activity of nitrifying bacteria that impair NH_4^+ retention.
- The three-tank system, designed for a full-scale implementation, was constructed and the material balance was confirmed. The operating conditions to allow for high NH_4^+ conversion and retention were revealed.

Development strategy



Org-C removal and deterring nitrification

- High-rate Org-C removal
- High-rate NH_4^+conversion
- Preventing nitrification
- N_2O emission mitigation

POC by a simplified NH_4^+ conversion process (TUAT)

For practical application | For stabilization

Extending (Kyoto U.)

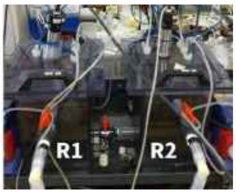
- Mass balance analysis
- Optimum operation
- N_2O emission mechanisms

Retrofitting a process (TUAT)

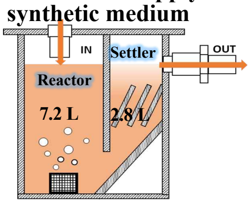
- Feedback technology by N_2O monitoring
- Granulation technology

Scaleup to a bench level

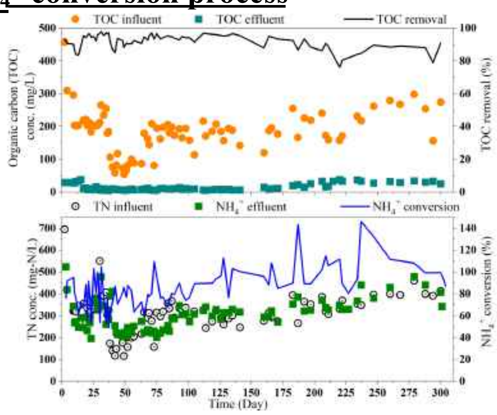
Performances of a simplified NH_4^+ conversion process

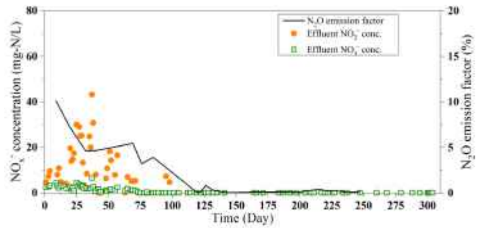


Continuous supply of synthetic medium



Duplicate	Period [day]	HRT [hrs]	SRT [days]	Aeration rate [L/min]
R1	0~300	11.2	5	2.0 (DO conc. 0.1 mg-O₂/L)
R2				

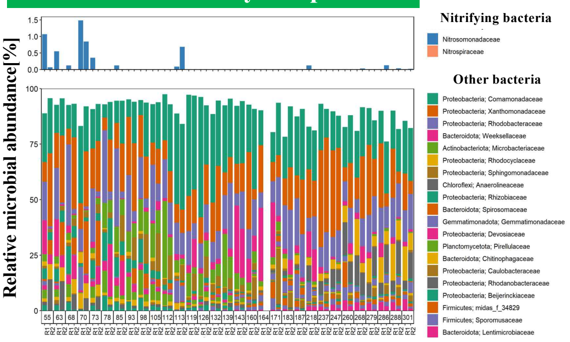




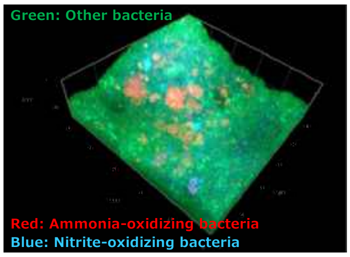
- Aeration control allowed long-term stable performances of NH_4^+ conversion & retention
- High efficiency of Org-C removal
- Mitigations of N_2O emission (Short-term N_2O emission factor < 0.2%)

Microbial community analysis and activities of nitrifying bacteria

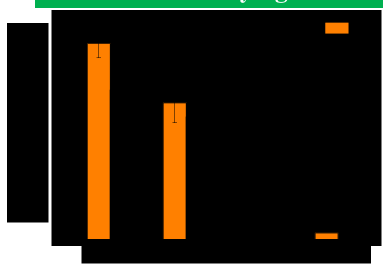
Microbial community compositions



Localization of nitrifying bacteria

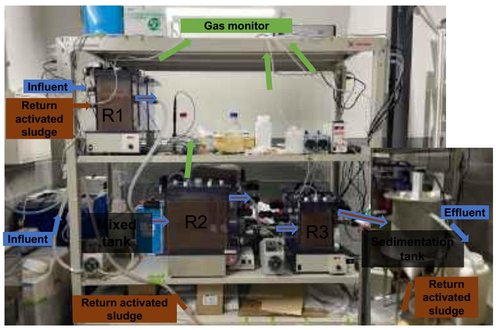


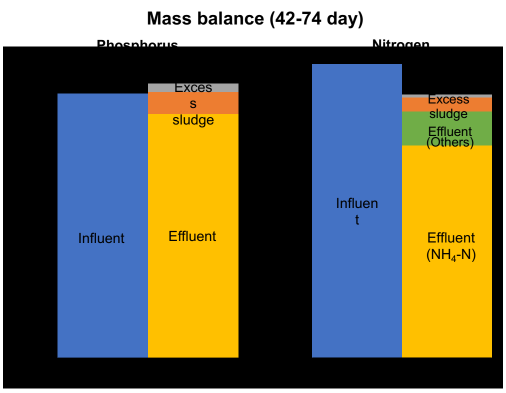
Activities of nitrifying bacteria



- Suppression of nitrifying bacteria (Relative abundance < 1.5%)
- Limited O_2 supply localized nitrifying bacteria in anaerobic zones, deterring their activities

Mass balance analysis





- Startup experiment was implemented (Stable operation: 42-74 day)
- MLSS = ca. 2500 mg/L
- HRT = 30 hrs, SRT = 30 days
- Phosphorus balance was ensured.
- The amount of effluent N was ca. 90% of effluent N (including the internal change)
- Effect of pH on nitrogen balance is now under investigation.
- A power consumption measurement was initiated to assess the energy balance.

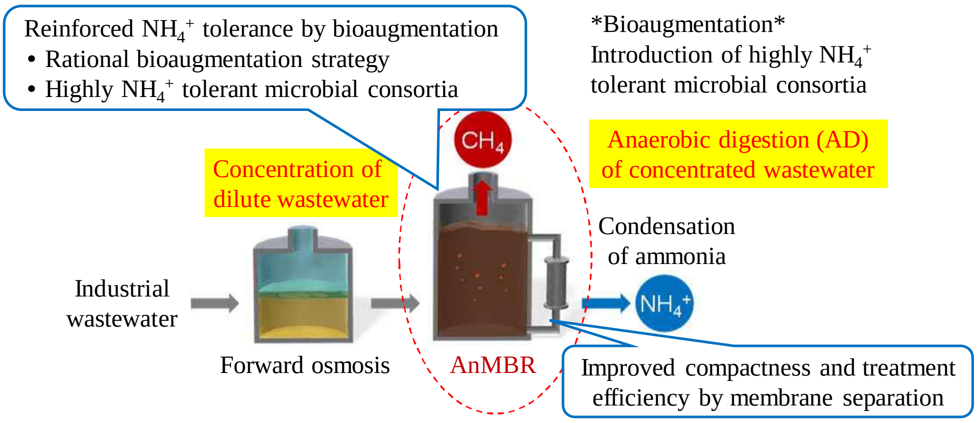
Outlooks

- Identifying N_2O-producing and N_2O-reducing bacteria by an OMICS approach
- Constructing a feedback system based on continuous N_2O monitoring
- Achieving a high-rate NH_4^+ conversion

No. A-9-7E
PJ : Innovative circular technologies for harmful nitrogen compounds
Theme: Wastewater N compounds to NH_4^+-high NH_4^+-tolerant AnMBR system
Organization: Osaka Univ., Hiroshima Univ., Kobe Univ.
Contact: Prof. Michihiko Ike (Osaka U), ike@see.eng.osaka-u.ac.jp

R&D Points
- Concentration of wastewater by forward osmosis to be used in anaerobic digestion (AD) <Energy saving>
- Efficient conversion of organic carbon and nitrogen to CH_4 and NH_4^+, respectively <Resource recovery>
- Applying anaerobic membrane bioreactor (AnMBR) in AD as the compact treatment facility
- Bioaugmentation to mitigate the AD inhibition by high concentrations of NH_4^+ and NaCl in the concentrated wastewater

Anaerobic Membrane Bioreactor (AnMBR)



R&D Items and Organization
- Development of bioaugmentation technology of highly NH_4^+-tolerant microbial consortia (Osaka U)
- Construction of highly NH_4^+-tolerant microbial consortia (Hiroshima U)
- Establishment of efficient AnMBR operating methods (Kobe U)

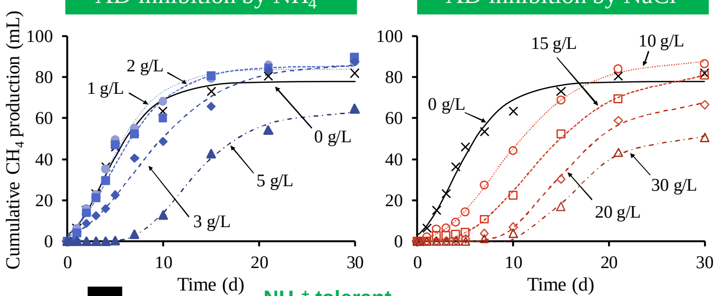

Prof. Ike (Osaka U)

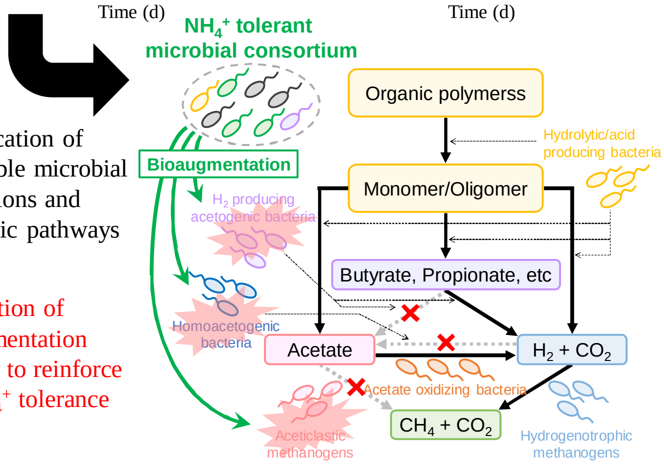

Prof. Tajima (Hiroshima U)


Prof. Ihara (Kobe U)

Major Achievements

Proposal of rational bioaugmentation strategy



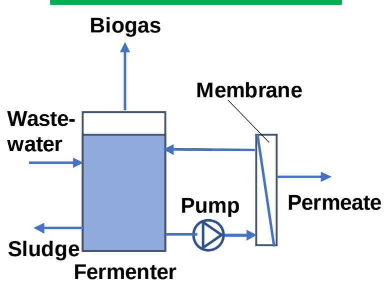


Identification of vulnerable microbial populations and metabolic pathways

Conception of bioaugmentation strategy to reinforce the NH_4^+ tolerance

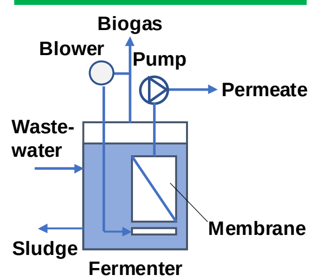
Establishment of efficient AnMBR

Cross-flow type

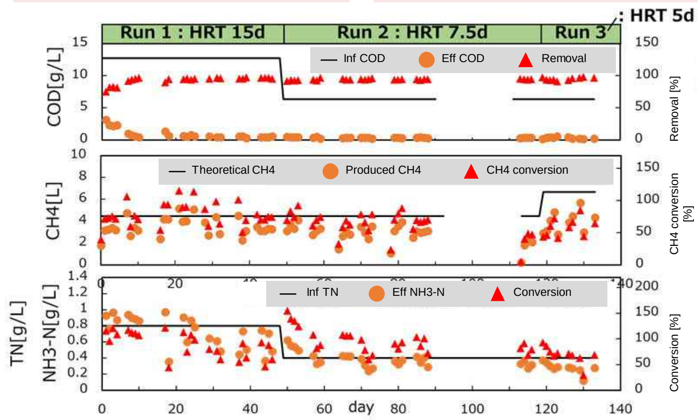


- Cross-flow membrane separation installed outside of fermenter
- Easy membrane washing and replacement

Inner-submerged type

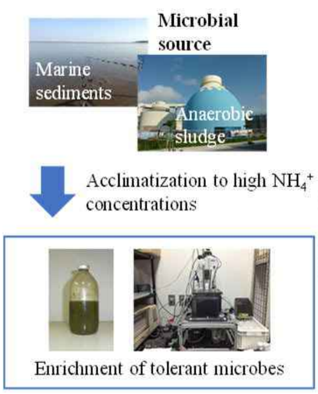


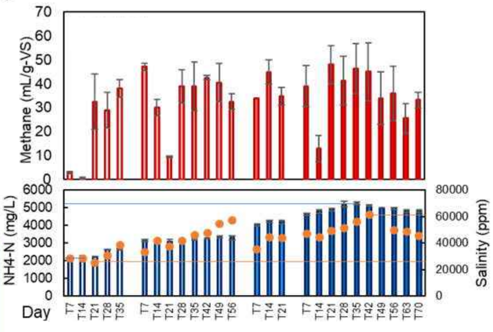
- Simultaneous AD and membrane separation in fermenter
- Power requirement for pumping and membrane washing



An example of lab-scale AnMBR operation (inner-submerged type)
Achievement of high organic removal and CH_4 production at HRT $\geq$ 3 d and recovery of nitrogen compounds as NH_4^+ solution

Construction of highly NH_4^+ tolerant microbial consortia





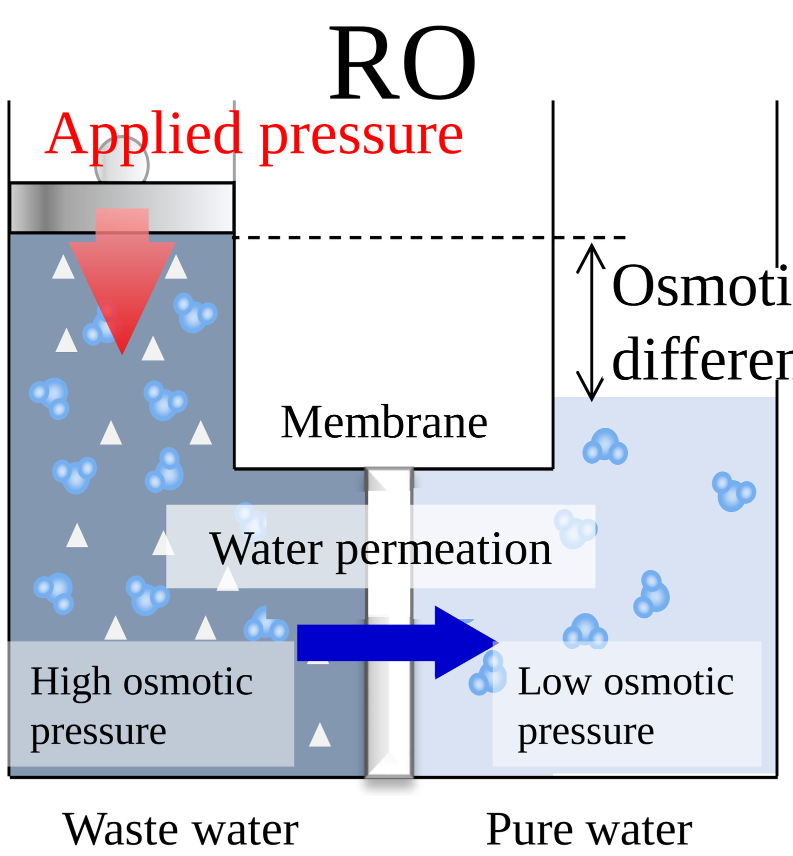
An example of acclimatization of high NH_4^+ and NaCl tolerant AD microbial consortia

Future Works
- To verify the reinforcement of NH_4^+ tolerance by bioaugmentation in AnMBR and establish its effective application methods
- To construct various tolerant microbial consortia, establish their large-scale cultivation methods, and characterize the key microbes
- To demonstrate efficient CH_4 production and NH_4^+ recovery using actual wastewater in bench-scale AnMBR

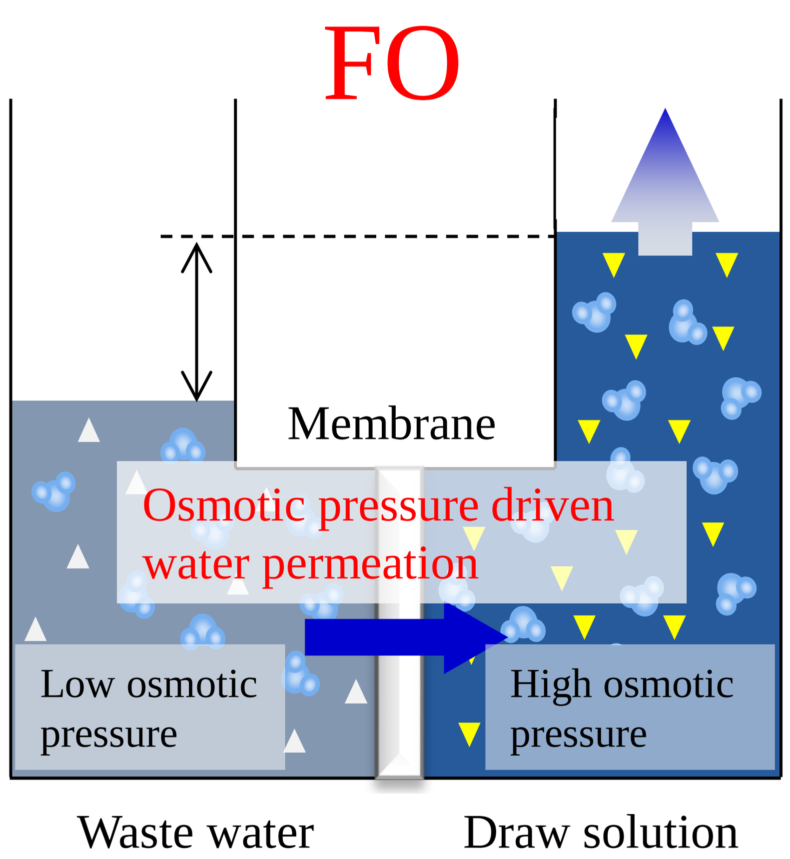
No. A-9-8E
PJ : Innovative circular technologies for harmful nitrogen compounds
Theme: NH_4 separation and concentration – Concentration by forward osmosis

Organization: Kobe Univ., Toyobo Co., Ltd., Waseda Univ.
Contact: Prof. Hideto Matsuyama (Kobe Univ.) , matuyama@kobe-u.ac.jp

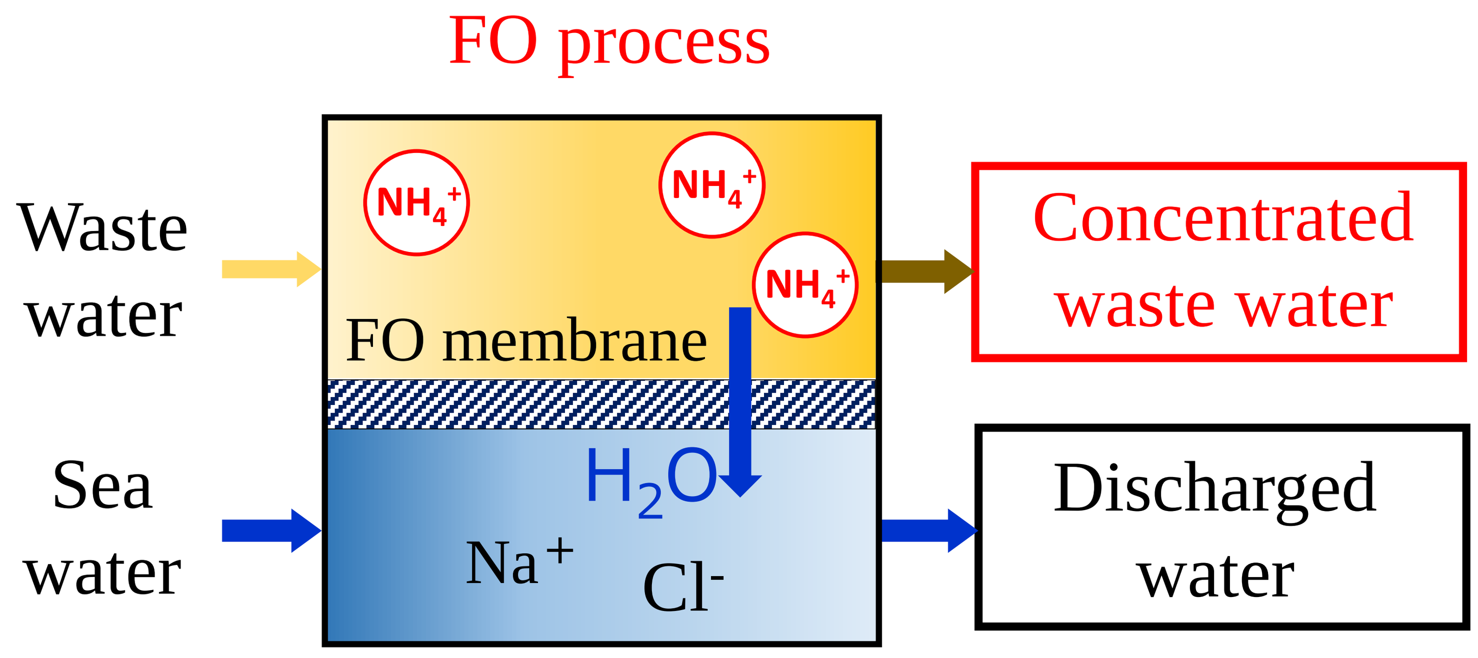
Forward osmosis (FO) Process



Require high pressure for water permeation
→High energy consumption



Spontaneous water permeation based on osmotic pressure
→Low energy consumption

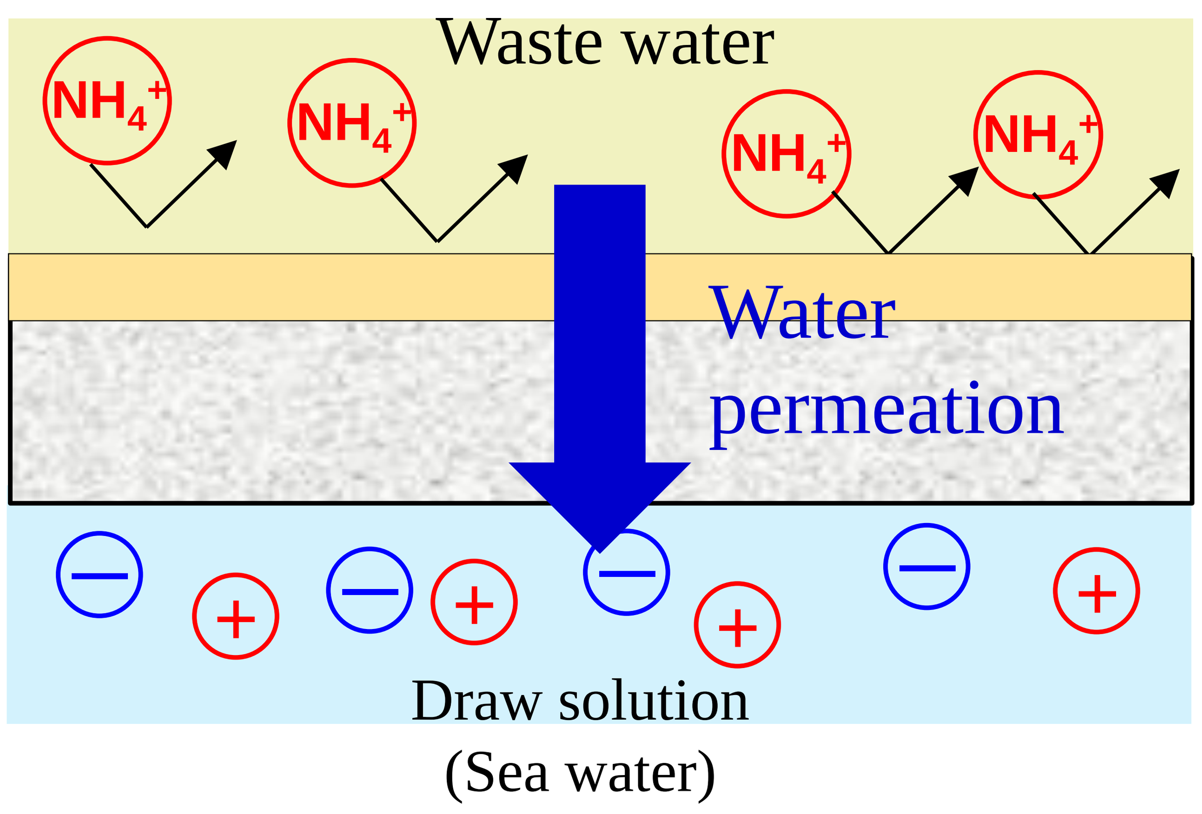


- Diluted seawater after the process can be discharged
- Energy required for concentration is only pump power

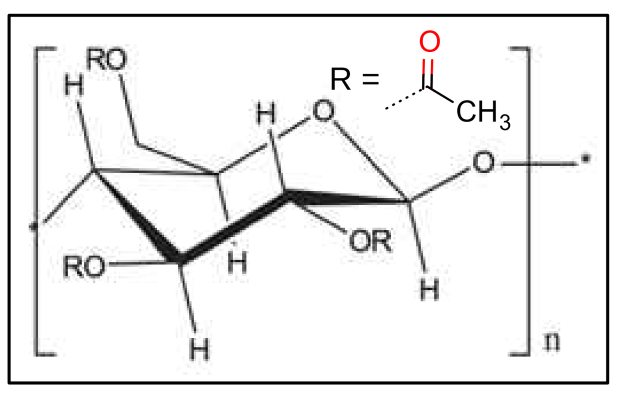
Using seawater as the draw solution allows the waste water concentration at a low cost

Development of FO membrane (Toyobo) and evaluation (Kobe U.)

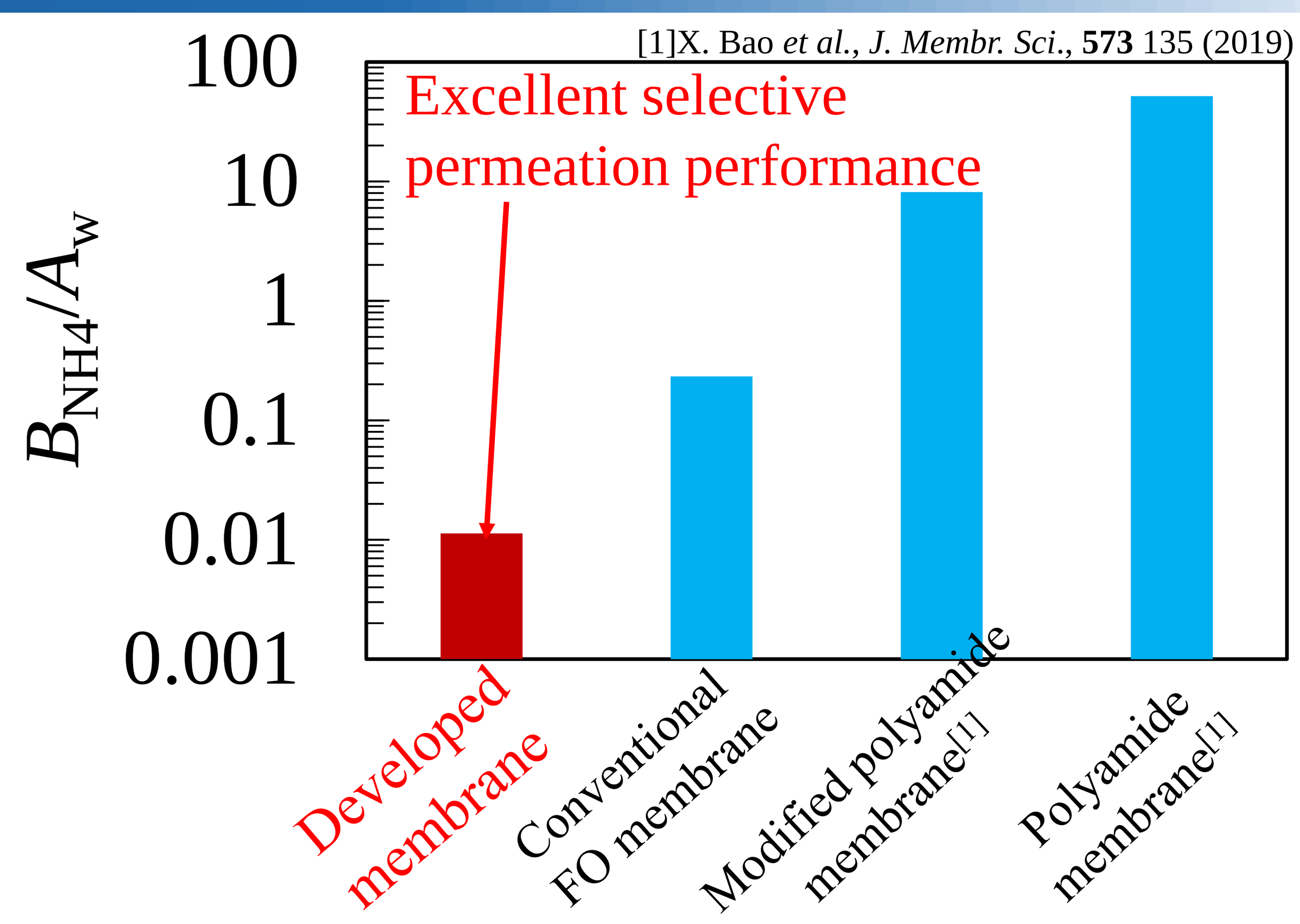
High performance FO membrane with excellent water permeability (A_w) and less leakage of NH_4^+ (B_{NH4}) was developed.



Cellulose triacetate-based FO membrane



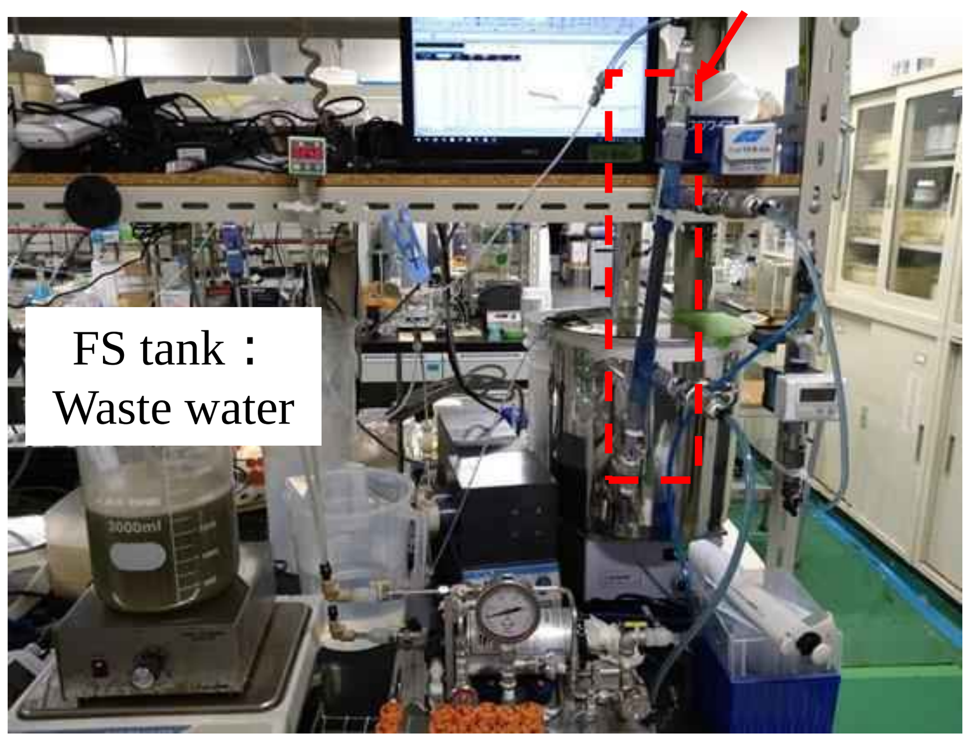
Neutral polymer with high ion blocking ability

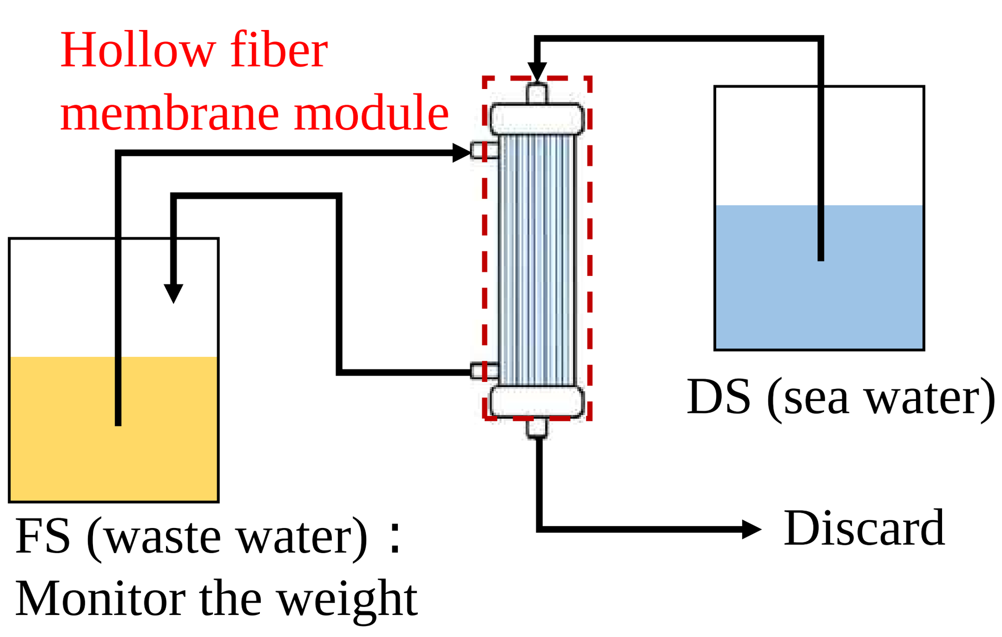


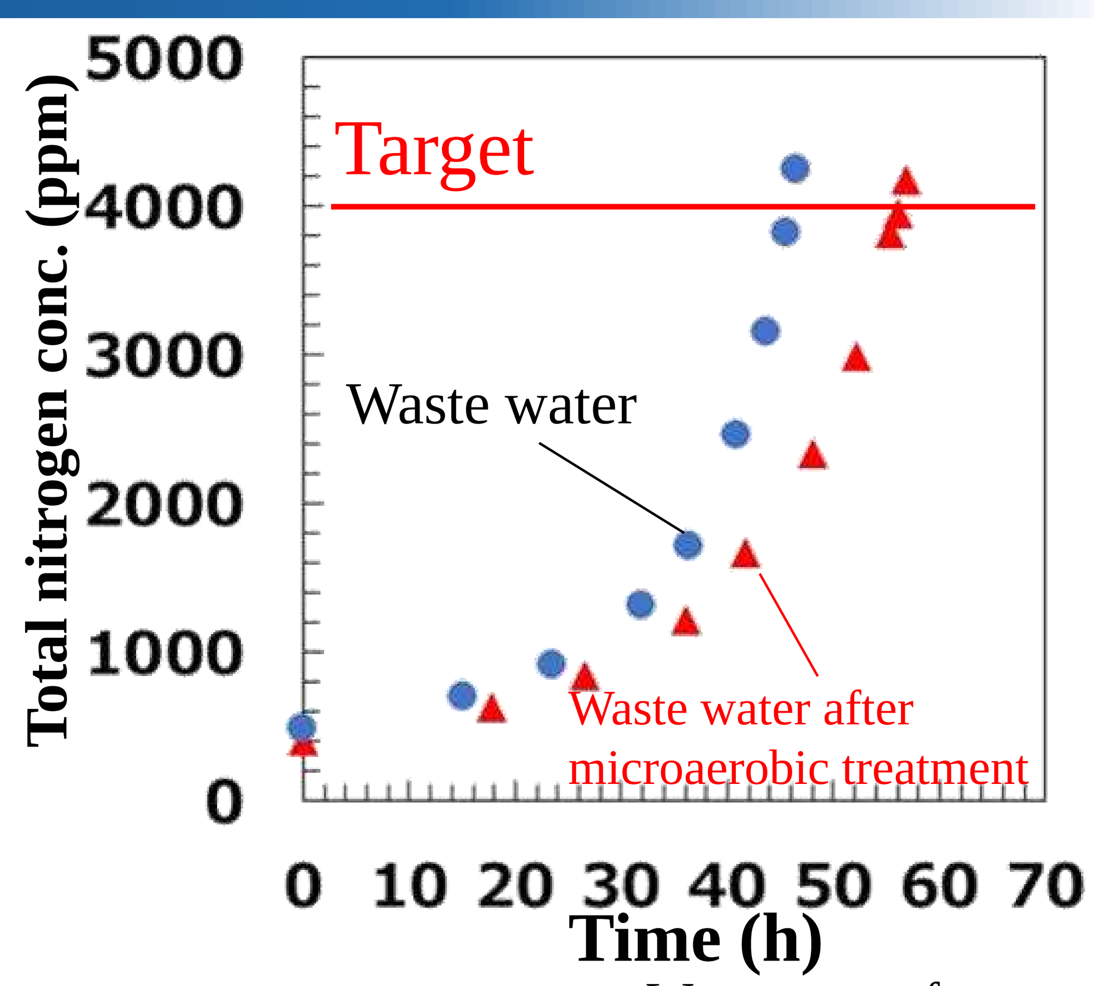
Succeeded in developing a high-performance FO membrane by controlling the membrane structure

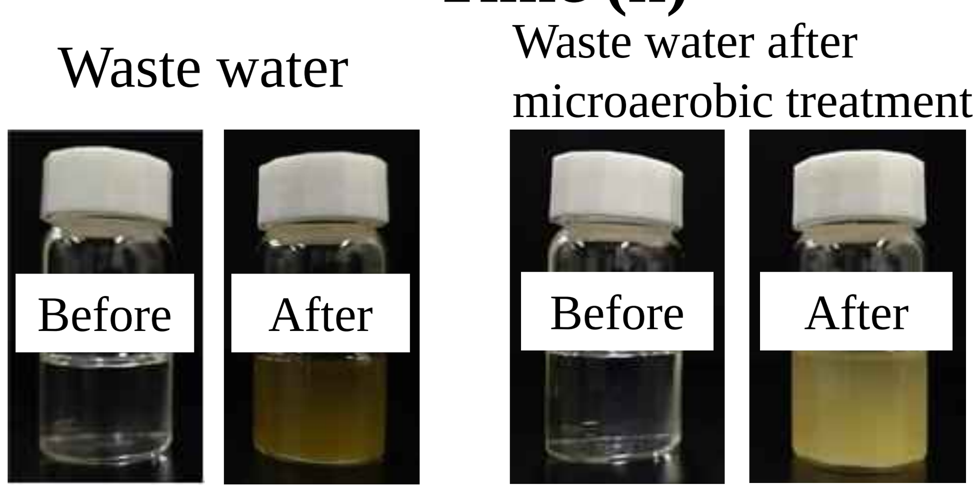
Concentration of wastewater (Kobe U.)

Hollow fiber membrane module





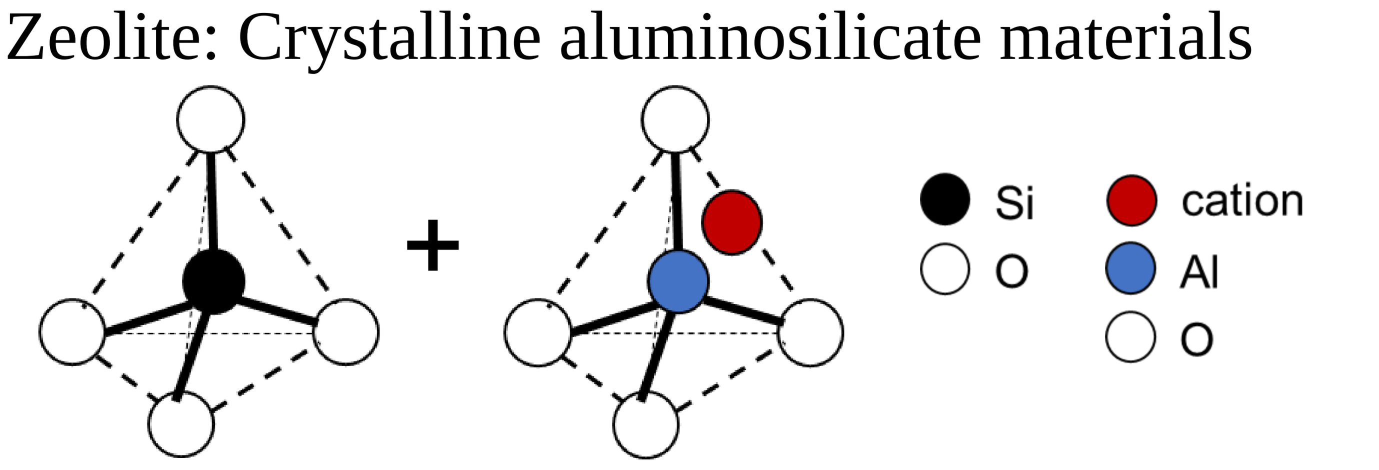


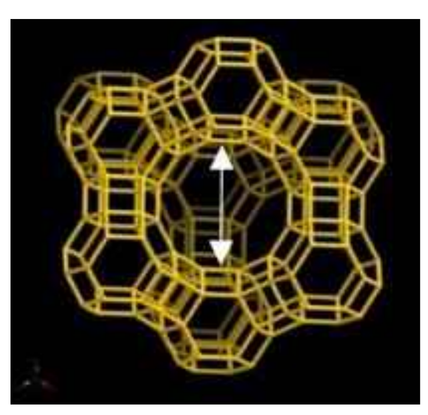


Concentrate to target concentration using seawater

Zeolite membrane (Waseda U.)

Zeolite: Crystalline aluminosilicate materials

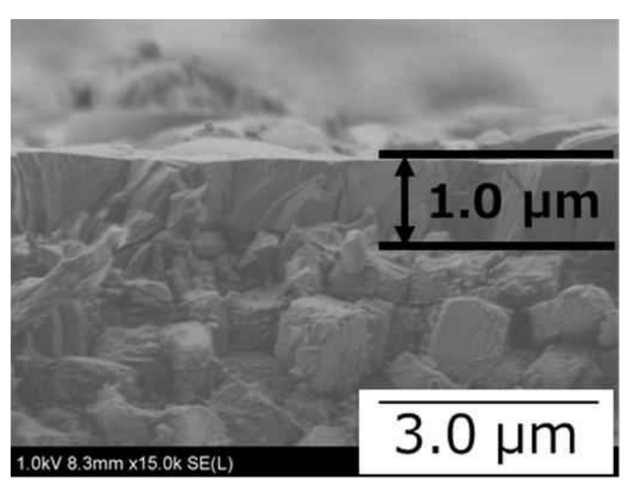




- Size sieving separation by nanopore
- High thermal, chemical stability

Zeolite membranes can be used in high-temperature wastewater

Zeolite membrane preparation



Hydrophilic zeolites without cation exchange sites were developed for NH_4^+ separation membrane
NH_4^+ was successfully concentrated even at high temperatures.

Summary and Publication

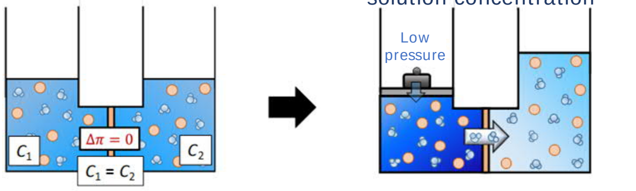
- ✓ By controlling the membrane structure, a high performance FO membrane was developed.
- ✓ NH_4^+ in wastewater was successfully concentrated to 4,000 ppm-N (the target concentration).
- ✓ NH_4^+ was also concentrated at high temperatures by developing a new zeolite membrane.

1. R.R. Gonzales *et al.*, *Sep. Purif. Technol.*, **297**, 121534 (2022)
2. A. Matsuoka *et al.*, *Desalination*, **527**, 115599 (2022)
3. X. Yao *et al.*, *J. Membr. Sci.*, **650**, 120429 (2022)
4. J. Li *et al.*, *Desalination* **541**, 116002 (2022)

No. A-9-9E
PJ : Innovative circular technologies for harmful nitrogen compounds
Theme: NH_4 separation and concentration - Brine concentration process
Organization: Kobe Univ.
Contact: Keizo Nakagawa (Kobe Univ.), k.nakagawa@port.kobe-u.ac.jp

Introduction

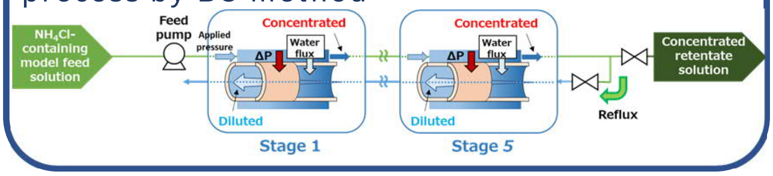
✓ **Brine concentration (BC):**
Concentration method by osmotically assisted reverse osmosis using forward osmosis membrane



➢ BC method enables salt concentration with less than 1/3 the energy consumption of the evaporation method (conventional method).

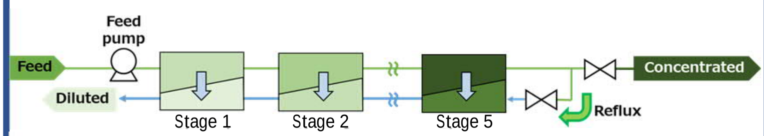
➢ BC method can concentrate three times more than the RO method when using the same amount of energy consumption as the RO method.

Purpose: Establishment of NH4 enrichment process by BC method



Experimental

Schematic of brine concentration process



Split feed configuration
- Feed is delivered onto pressurized side
- Concentrated solution is refluxed back into other side

Hollow fiber module

Module	
Parameter	
Module length	100 cm
Number of hollow fibers	1750
Membrane area	1.1 m^2
Membrane	
Material	Cellulose triacetate
Inner diameter	90 μm
Outer diameter	200 μm
Active layer	Shell side (outer)
Water permeability coefficient (A) *	0.071 L m^{-2} h^{-1}/bar
NaCl permeability coefficient (B_{NaCl}) *	0.0035 L m^{-2} h^{-1}
NH_4Cl permeability coefficient (B_{NH4Cl}) *	0.00013 L m^{-2} h^{-1}
NaCl rejection *	99.2 %
NH_4Cl rejection *	99.7%

Tested operational parameters:
Applied pressure
Feed flow rate
Reflux ratio ($F_{refluxed}/F_{retentate}$)
Initial feed concentration
Presence of other ionic species in feed

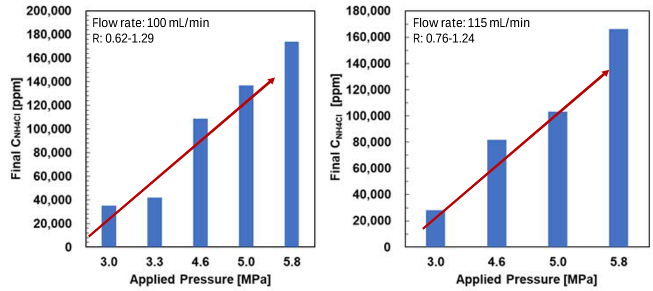
Conclusion

✓ The target concentration of NH_4Cl (more than 10 times) was achieved by adjusting various operating conditions of the BC method.

✓ The operating pressure, feed flow rate, reflux ratio, and initial concentration affected the degree of enrichment. In addition, NH_4Cl was similarly concentrated when NaCl coexisted.

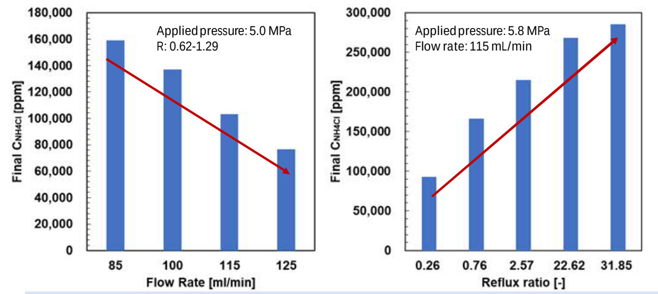
Results

■ Effect of initial applied pressure



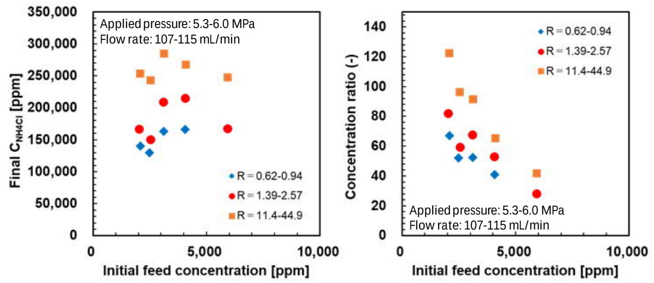
✓ Better concentration performance at higher pressure

■ Effect of flow rate / ■ Effect of reflux ratio



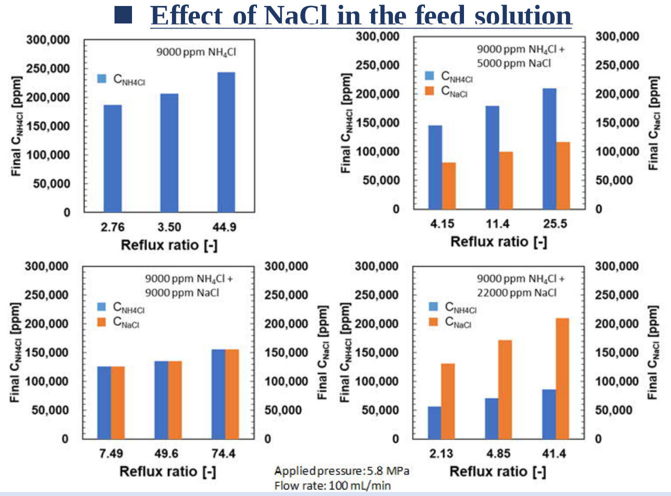
✓ Better concentration performance at lower flow rate and higher reflux ratio

■ Effect of initial NH_4Cl feed solution concentration



✓ For all initial feed solution concentration, higher reflux ratio resulted in more effective concentration
✓ Higher concentration ratio at lower initial concentration

■ Effect of NaCl in the feed solution



✓ Final salt concentrations were influenced by feed composition
✓ Both NH_4Cl and NaCl have similar concentration performance
✓ Both ionic species did not affect other's rejection and diffusivity

R. R. Gonzales et al., J. Membr. Sci, 665, 121122 (2023)

No. A-9-10E

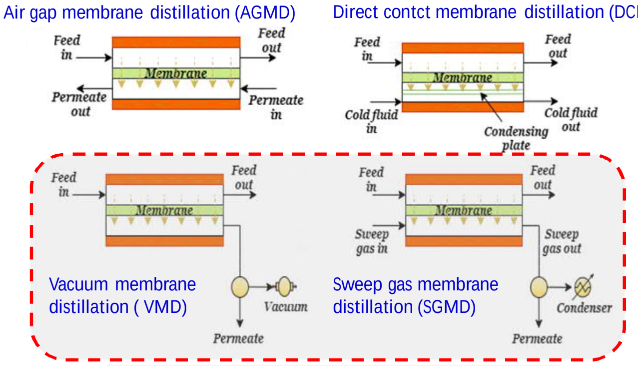
PJ : Innovative circular technologies for harmful nitrogen compounds

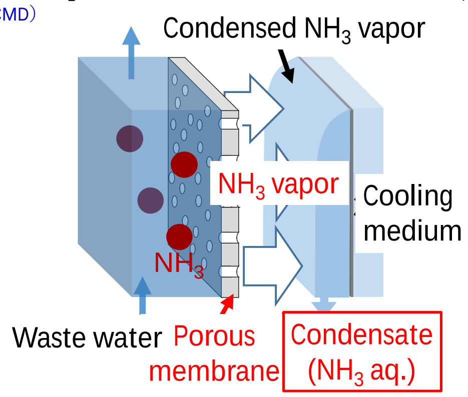
Theme: NH_4 separation and concentration - Membrane distillation

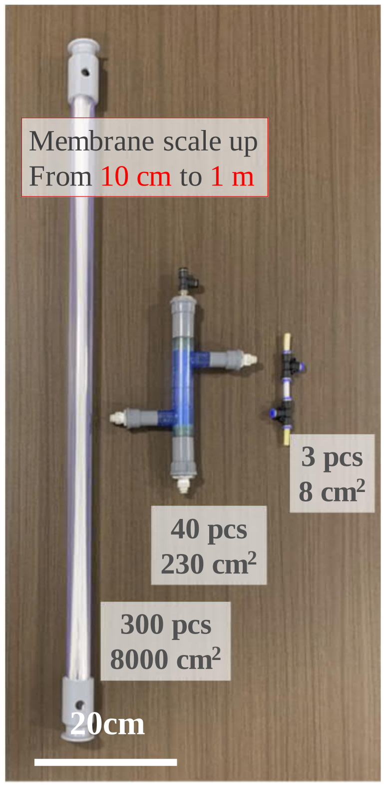
Organization: Kobe Univ., Hiroshima Univ.

Contact: Tomohisa Yoshioka (Kobe Univ.), tom@opal.kobe-u.ac.jp

Experimental study on development of membranes and membrane processes for membrane distillation (MD) of NH_3 aqueous solution (Kobe Univ.)





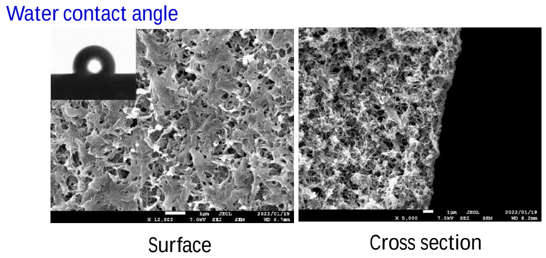


For NH_3 Recovery & Concentration

× DCMD (dilution in permeate side)

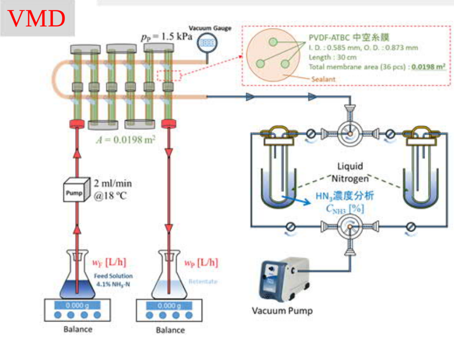
× AGMD (impossible to condense NH_3)

○ VMD and SGMD are feasible process

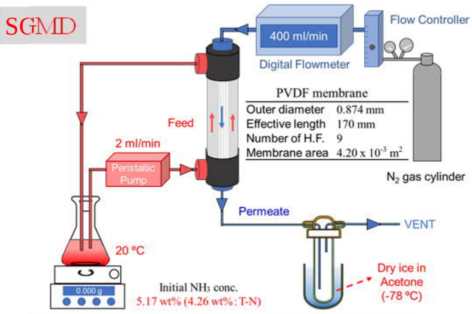


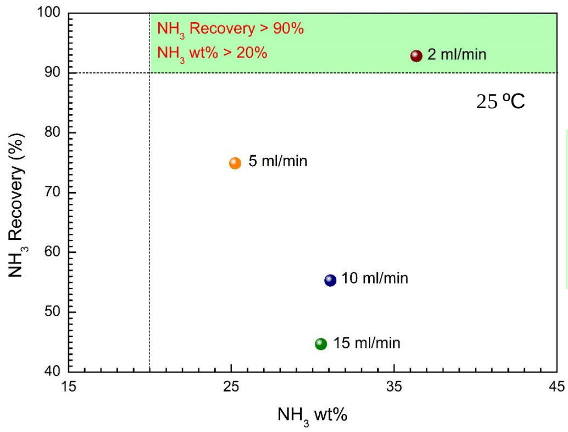
Porous hydrophobic membrane for mmbrane distillation

VMD



SGMD





NH_3 concentration in permeate side and recovery ratio

The NH_3 aqueous solution can be successfully concentrated around 6 times from 5 wt% to 35 wt% via VMD process under room temperature (25 °C) at a constant feed flow rate of 2.0 ml/min.

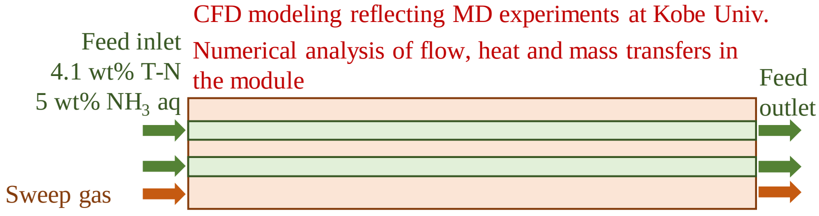
Publications

1. Z. Li, T. Yoshioka *et al.*, Desalination, **536**, 115818 (2022)

Development of a Computational Fluid Dynamics (CFD) model for predicting the performance of MD membrane modules (Hiroshima Univ.)

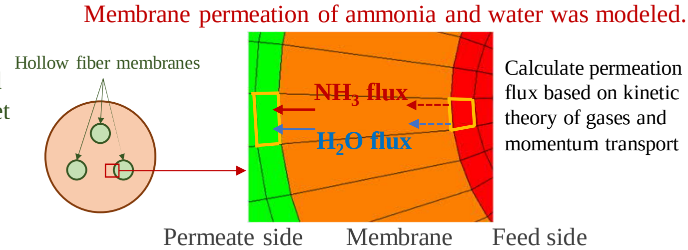
CFD modeling reflecting MD experiments at Kobe Univ.

Numerical analysis of flow, heat and mass transfers in the module



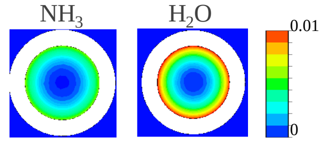
Membrane module model

Membrane permeation of ammonia and water was modeled.

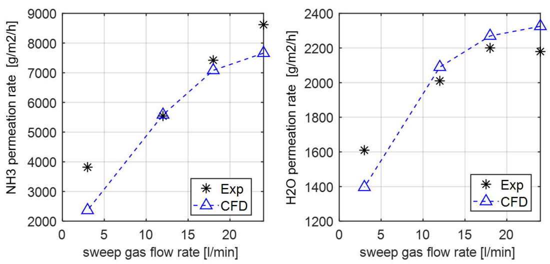


Calculate permeation flux based on kinetic theory of gases and momentum transport

Concentration distribution inside the hollow fiber membrane

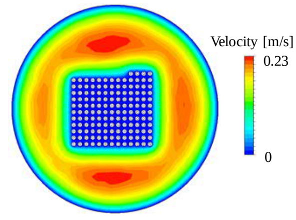


Comparison of simulation and experimental results

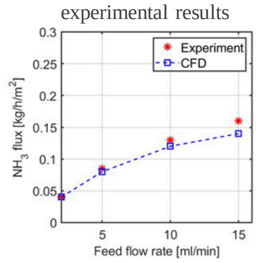


CFD modeling of a large-scale module (147 hollow fiber membranes)

Velocity distribution



Comparison with experimental results



Publications

1. Shirzadi *et al.*, *Ind. Eng. Chem. Res.*, **61**, 7381 (2022)
2. Kawashima *et al.*, *Powder Technol.*, **410**, 117872 (2022)

The CFD model developed in this study can predict the experimental results.

No. A-9-11E

PJ : Innovative circular technologies for harmful nitrogen compounds

Theme: NH_4 separation and concentration – Ion exchange membrane method

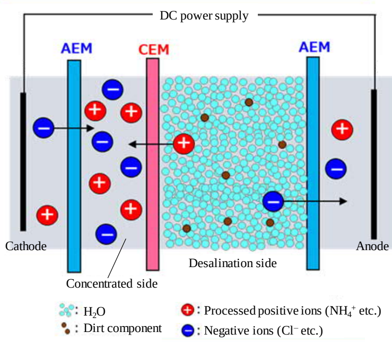
Organization: Yamaguchi University, ASTOM Corporation

Contact: Prf. Mitsuru Higa(Yamaguchi University), mhiga@yamaguchi-u.ac.jp

Overview

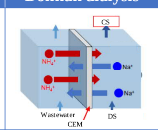
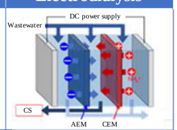
We will develop an ultra energy-saving NH_4^+ separation and concentration system that combines Donnan dialysis (DD) driven by highly concentrated saline solution, and electrodialysis (ED) driven by electric power. Ion exchange membranes (IEMs) and membrane modules for DD and ED are designed, and prototype modules are fabricated and their performance is evaluated. We will also support pilot-scale demonstration of this technology conducted by ASTOM Corporation.

Ion exchange membrane method



Strong point: Highly selective concentration and separation of extremely small amounts of NH_4^+ in a wastewater containing contaminants

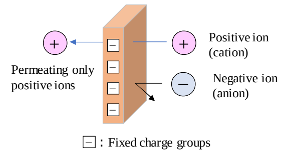
Less impact of substances in real wastewater that interfere with stable operation of the concentration process:
・Ca^{2+} and other divalent ions
・Silica
・Dirty components

	Donnan dialysis	Electrodialysis
Principle		
Driving Force	Highly concentrated saline water	Electric power
Merit	Zero energy	Fast processing speed and suitable for wide range of salt concentrations
Demerit	Slow processing speed	Electric energy is required

Ion exchange membrane

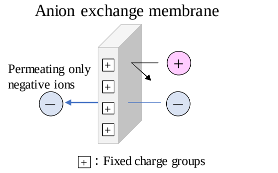
Membranes that selectively permeate counter ions

Cation exchange membrane



Selectively permeating positive ions

Anion exchange membrane

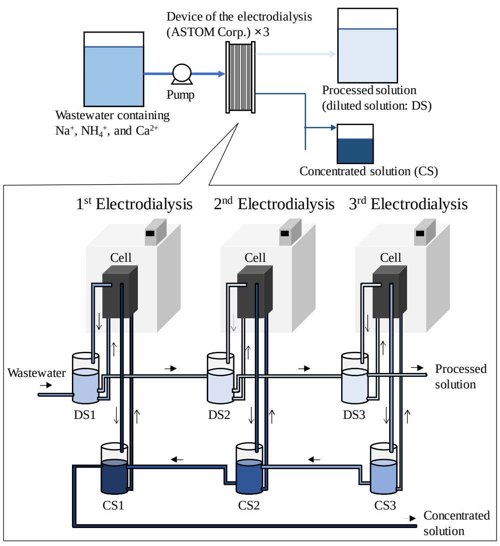


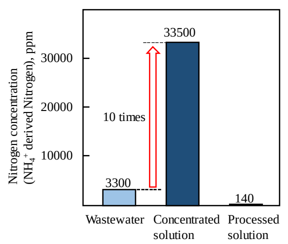
Selectively permeating negative ions

NH_4^+ concentration by triple electrodialysis system

・We have achieved 10 times concentration of NH_4^+ and 96% recovery of NH_4^+ from simulated wastewater

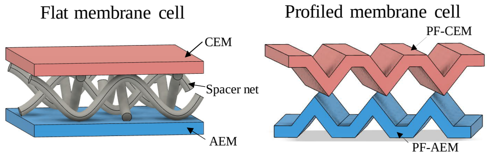
Wastewater concentrating test





Less energy ED by profiled membranes

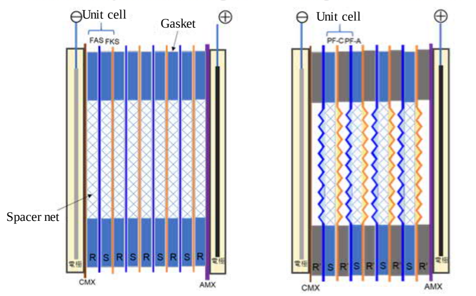
We have developed profiled membrane to achieve power saving ED



Non-conductive spacer nets give
・high electric resistance
・high pressure drop
・high fouling properties

Profiled membranes give
・low electric resistance
・low pressure drop
・low fouling properties

Electrodialysis cells using the flat and profiled membranes

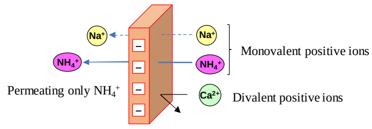


	ED voltage
Flat membrane	2.6 V
Profiled membrane	1.9 V
Energy saving ratio %	25

Development of NH_4^+ selective membranes

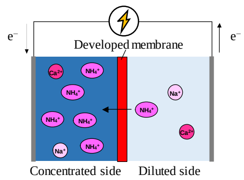
We have achieved highly selective concentration of NH_4^+ using the NH_4^+ selective membrane

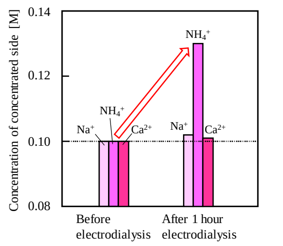
NH_4^+ selective membrane:
Membranes that selectively permeate NH_4^+ relative to other positive ions



In wastewater containing Na^+ and Ca^{2+},
・Decrease in the electrodialysis energy
・Stable, long-term continuous operation without the need for pre-treatment
・Clear concentrated solution.

Membrane performance test by an electrodialysis





Summary

We have successfully developed an ultra energy-saving NH_4^+ separation and concentration system using ion exchange membranes:

・The triple ED system has achieved 10 times concentration of NH_4^+ and 96% recovery of NH_4^+ from wastewater.

・The Profiled membranes saved the power consumption in ED.

・The NH_4^+ selective membrane has achieved the high NH_4^+ permselectivity.

・Application Number (2022)180515, Ion exchange membrane cell and gasket, Mitsuru Higa (Yamaguchi university)
・Application Number (2022)145514, Evaluation and quality control of ion exchange membrane, Mitsuru Higa, Yu Sugimoto (Yamaguchi university), Shoichi Doi (ASTOM Corp.)
・Ion transport properties of hollow fiber cation-exchange membranes prepared from sulfonated polyether sulfone, Shuntaro Ikeda, Yuriko Kakihana, Mitsuru Higa, Materials Research Meeting 2021, Dec. 13th 2021, Yokohama
・Evaluation of Donnan dialysis performance of cation exchange membrane prepared from sulfonated polyether sulfone, Keiko Komuta, Yuriko Kakihana, Mitsuru Higa, Materials Research Meeting 2021, Dec. 13th 2021, Yokohama
・Preparation and characterization of monovalent ion selective hollow fiber cation exchange membranes by plasma graft polymerization, Shuntaro Ikeda, Yuriko Kakihana, Mitsuru Higa, 71th Polymer Science Forum, Sep. 6th 2022, Sapporo
・Donnan dialysis performance of monovalent ion selective hollow fiber cation exchange membranes prepared by plasma graft polymerization, Shuntaro Ikeda, Yuriko Kakihana, Mitsuru Higa, EuroMembrane2022, Nov. 22nd 2022, Sorento
・Concentration of ammonia ions from model wastewater using a triple-flow electrodialysis system, Yuta Yonehara, Yu Sugimoto, Yuriko Kakihana, Mitsuru Higa, 37th Western Honshu Polymer Science Young Research Forum, Dec. 2nd 2022, Kagawa

No. A-9-12E

PJ : Innovative circular technologies for harmful nitrogen compounds

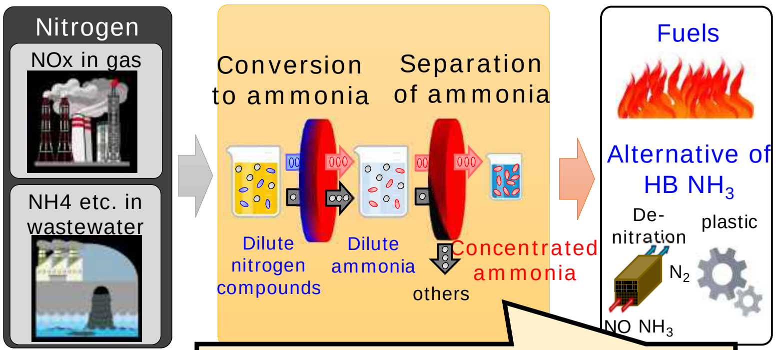
Theme: Recovery from water) – Adsorption technology

Organization: AIST, The Univ. Tokyo, Fuso Ltd.

Contact: Dr. Tohru Kawamoto(AIST), tohru.kawamoto@aist.go.jp

【Background, Concept】

NH_4^+ Separation with adsorption

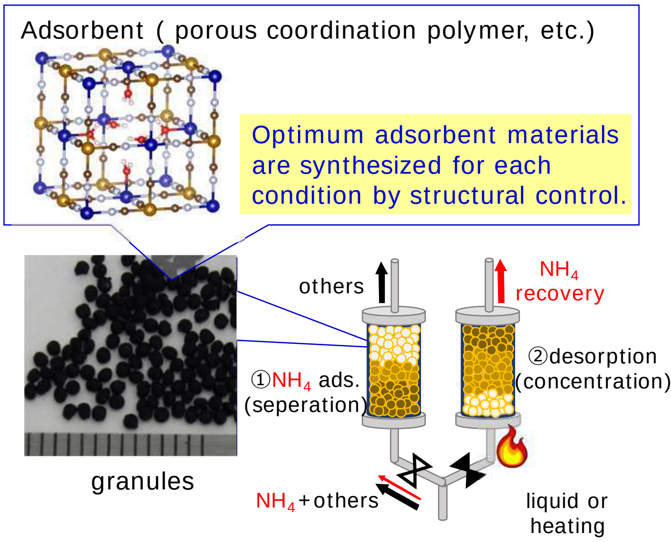


AIST : ion-exchange : selective NH_4^+ recovery

Univ.Tokyo : heat desorption : NH_3 recovery

FUSO inc. : plant engineering

Basic concept

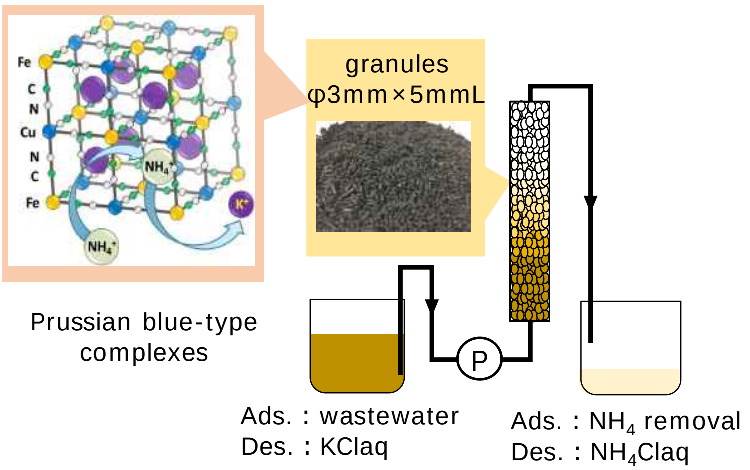


【Ion-exchange technology】

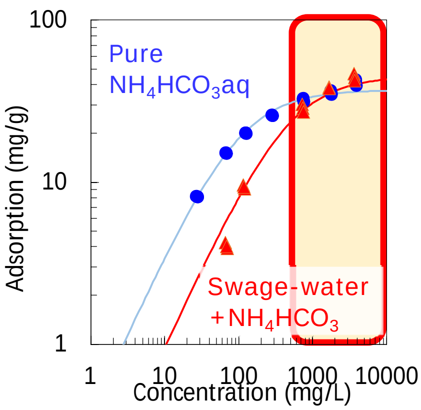
Selective adsorption of NH_4^+,recovery to desorption liquid.

Ads.: $K_xM[Fe(CN)_6]_x + xNH_4^+ \rightarrow (NH_4)_xM[Fe(CN)_6]_x + xK^+$

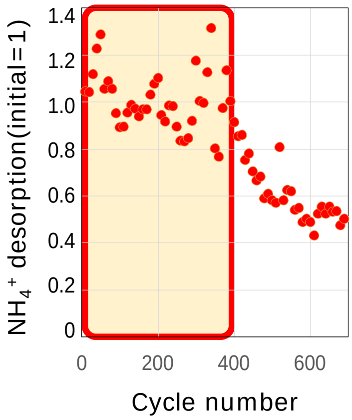
Des.: $(NH_4)_xM[Fe(CN)_6]_x + xK^+ \rightarrow K_xM[Fe(CN)_6]_x + xNH_4^+$



Adsorption isotherms (batch tests)

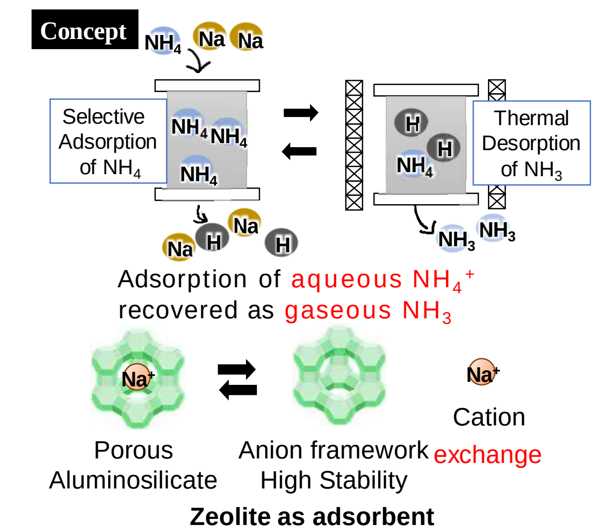


Cycle test for adsorption and desorption (column test).

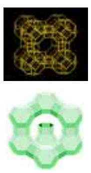


- At the target NH_4^+ concentration, adsorption behavior is kept even in the realistic wastewater
- Little degradation due to cycling for around 400 cycles.

【Thermal desorption technology】



Selection of Zeolite Species

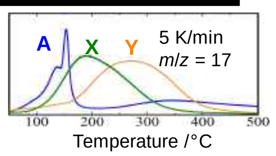


A-type
High Ion-exchange capacity

X-type・Y-type
Various Si/Al ratio

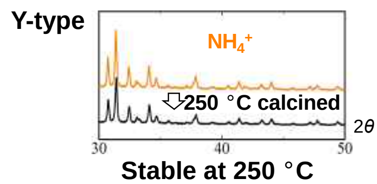
	A	X	Y
Si/Al ratio	Low	⟹	High
Ion capacity	High	⟹	Low

NH_3 Elimination (TG-MS)



	A	X	Y
NH_3 elimination	Low T	⟹	High T

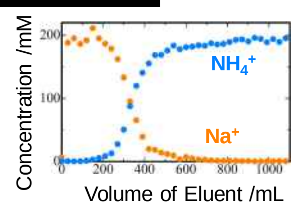
Stability (XRPD)



Stable at 250 °C

	A	X	Y
Thermal stability	Low	⟹	High

Column test



Good ion-exchange ability

No. A-9-13E

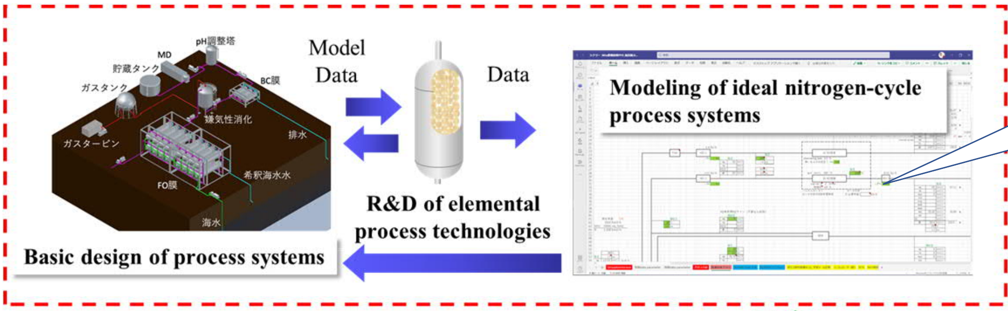
PJ : Innovative circular technologies for harmful nitrogen compounds

Theme: Synthesis and evaluation of process technologies for recycling nitrogen compounds

Organization: AIST, Tokyo Tech, Yamagata U.
Contact: Assoc. Prof. Hideyuki Matsumoto (Tokyo Tech), matsumoto.h.ae@m.titech.ac.jp

【Overview of research and development】

To disseminate the process technologies for NOx in exhaust gas and nitrogen compounds in wastewater developed in this research project by 2050, it is necessary to design an innovative plant system. In this study, our research groups investigate a case study for integration of the elemental process technologies developed in the project.



Creation of calculation model for visualization of flows of chemical substances and energy in Microsoft Excel so that many researchers and engineers can easily use them

- ■ LCA of implementation of new technologies
- ■ Risk assessment of nitrogen compounds emitted from new processes

Life Cycle Impact Assessment: LCIA

Economic viability / Environmental impact

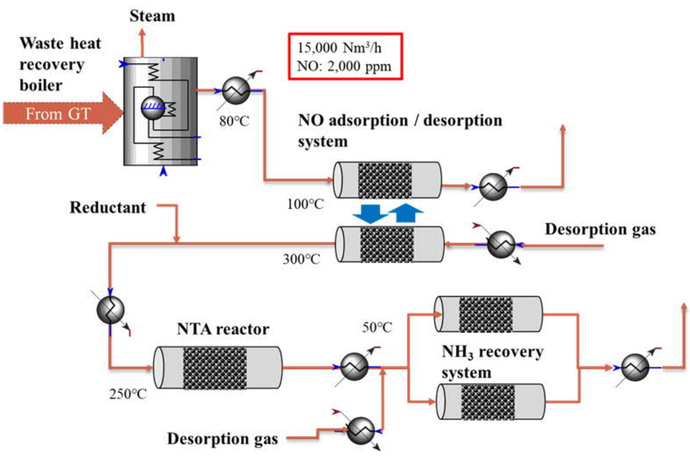
- Calculation of mass balance for NOx in gas and nitrogen compounds in wastewater
- Calculation of energy balance
- Calculation of CO_2 emissions , etc.

【Research and development results】

① Modeling of ideal nitrogen-cycle process systems
Creation of implementation cases of element process technologies to be developed in the project
⇒ Creation of calculation model for visualization of flows of chemical substances and energy

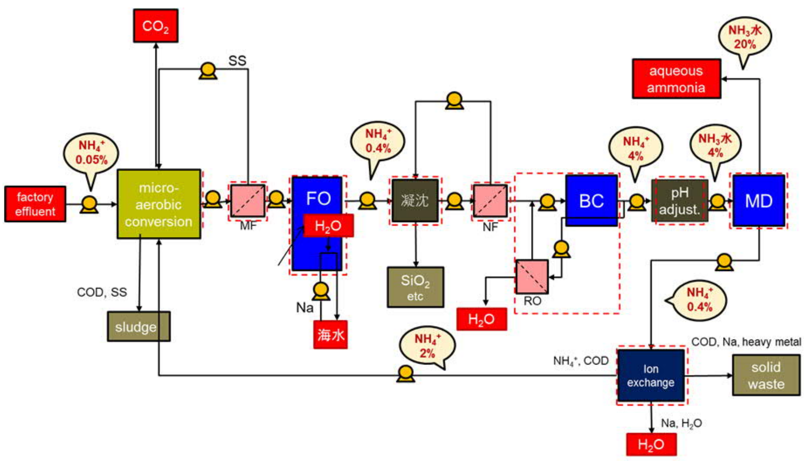
② Synthesis and evaluation of process systems for recycling nitrogen compounds
Investigation on method of introduction to chemical plant, Optimization of network for recovery and utilization of heat, Evaluation of effects on energy saving and reduction of CO_2 emission

Recycling nitrogen compounds in gas phase to ammonia resource



- Estimation of the CO_2 emissions*1): the process system in the above figure is less than 1/4 of the application of the selective catalytic reduction method (SCR)
- Optimization of network for recovery and utilization of heat: approximately 65% energy savings (55% reduction in CO_2 emissions)

Recycling nitrogen compounds in wastewater to ammonia resource



- Synthesis of processes including recycle streams, purging and related equipment to eliminate the effects of impurities
⇒ Synthesize and evaluate 6 or more alternative processes
- Estimation of the CO2 emissions*2): the process system in the above figure is less than 1/20 of the application of the ammonia stripping method

Note 1：Estimated based on input heat energy, not including CO_2 emissions related to production of separators, reactors and N_2
Note 2：Estimated based on input energy, not including CO_2 emissions related to microaerobic conversion

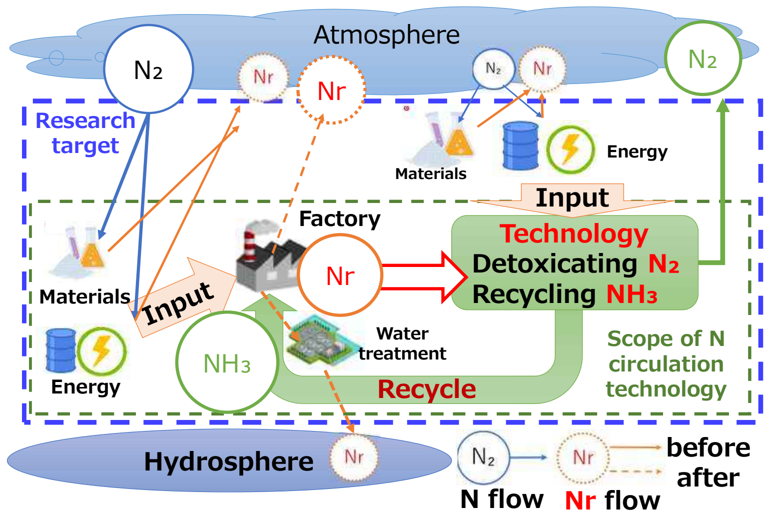
【Future developments】

In order to promote research and developments and implementation of elemental process technologies, it is essential to develop the basic design of the nitrogen-cycle process system and conduct various environmental impact assessments incorporating information of process design. Furthermore, the development of simulation methods that support the basic design / detailed design and environmental impact assessments will be important.

No. A-9-14E
PJ : Innovative circular technologies for harmful nitrogen compounds
Theme: Environmental impact assessment for nitrogen circular technology
Organization: National Institute of Advanced Industrial Science and Technology (AIST)
Contact: Dr. Kiyotaka Tsunemi (AIST), k-tsunemi@aist.go.jp

【Abstract】Constructing nitrogen database for assessment of nitrogen circular technology
【Scope】 Developed of the nitrogen database focusing on the nitrogen input and output balance for each products in the process to assess the nitrogen circular technology
【Future task】Constructing nitrogen database **overall industrial process**

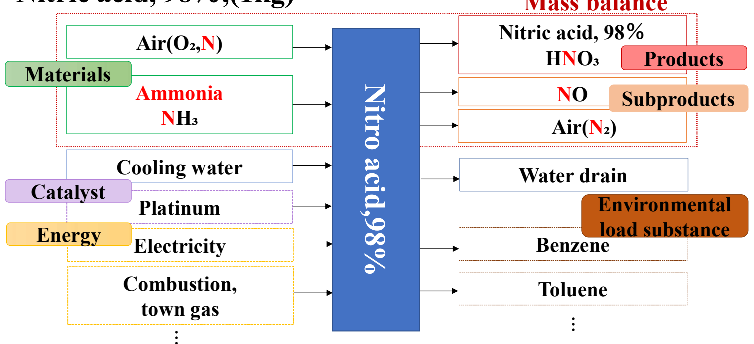
◇Assessment of nitrogen circular technology



Nr: reactive nitrogen (ex N_2O, NOx…) from factory can cause environmental problem. “Nitrogen circular technology” can be transferred to N and recycle to NH_3. Therefore, we developed the **nitrogen database** for each products to assess the new technology.

◇Results of N balance in the process

Nitric acid, 98%,(1kg)



Results of balance check

	Input	Output	Difference	Check
Mass balance	5.443	5.443	0.000	✓
Carbon	0.001	0.001	0.000	✓
Nitrogen	4.302	4.305	-0.002※	✓
Phosphorus	-	-	-	-
Water	10.13	10.13	0.000	✓

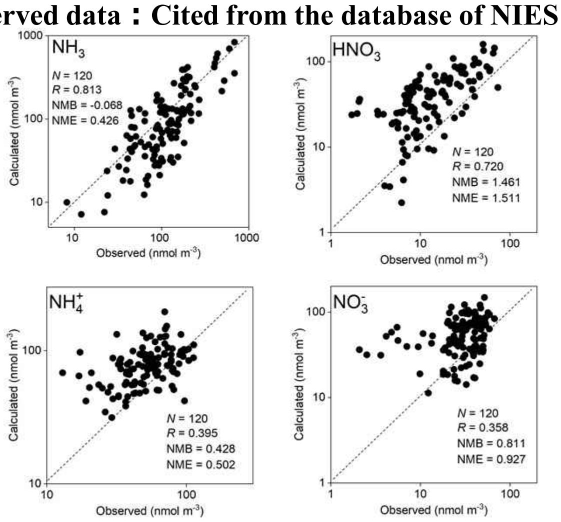
※Excluding chemical substance based on PRTR from place of business in balance check

✓Covering nitrogen amount not only input, but also output
✓Some products are inputting NH_3
→ Recycled NH_3 can be able to reuse in process

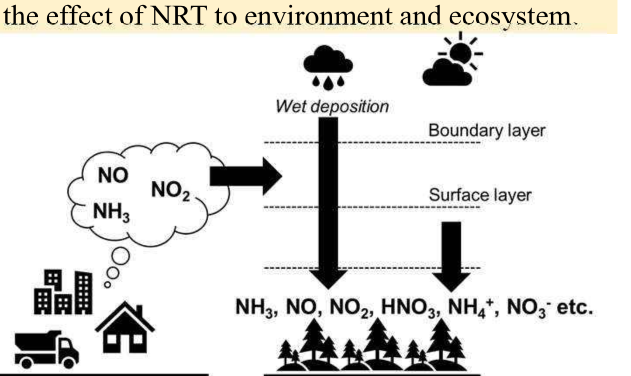
【Abstract】We evaluated model performance of nitrogen deposition and estimated future air quality in 2050 in Japan.
【Scope】Estimation of the contribution of nitrogen recirculation technology (NRT) to atmospheric environment evaluated by the chemical transport model
【Future work】Setting the scenario of the introduction of NRT and estimating the effect of NRT to environment and ecosystem.

◇Evaluation of nitrogen deposition

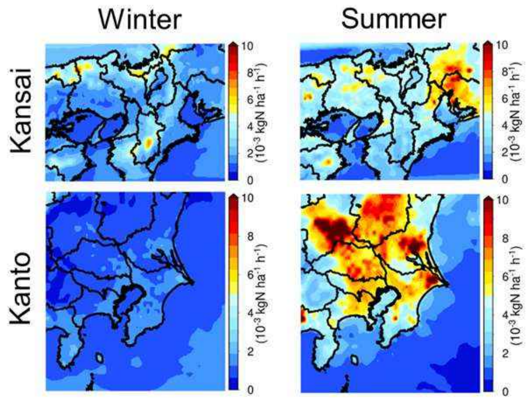
- **Scope 1 : Validating the amount of nitrogen deposition estimated by the chemical transport model**
- **Scope 2 : Estimation of the amount of nitrogen deposition in the urban region of Japan (Kanto and Kansai)**
- **Software : Community Multiscale Air Quality Modeling System (CMAQv5.3.2, USEPA)**
- **Calculation period : Jan. 1 2017～Dec. 31 2017**
- **Observed data : Cited from the database of NIES**



Model performance comparing with observational data
(Hata et al. Atmos. Environ. (2022))



Mechanism of nitrogen deposition to ecosystem



Nitrogen deposition in Kanto and Kansai in 2017

Kanto region shows intense amount of nitrogen deposition