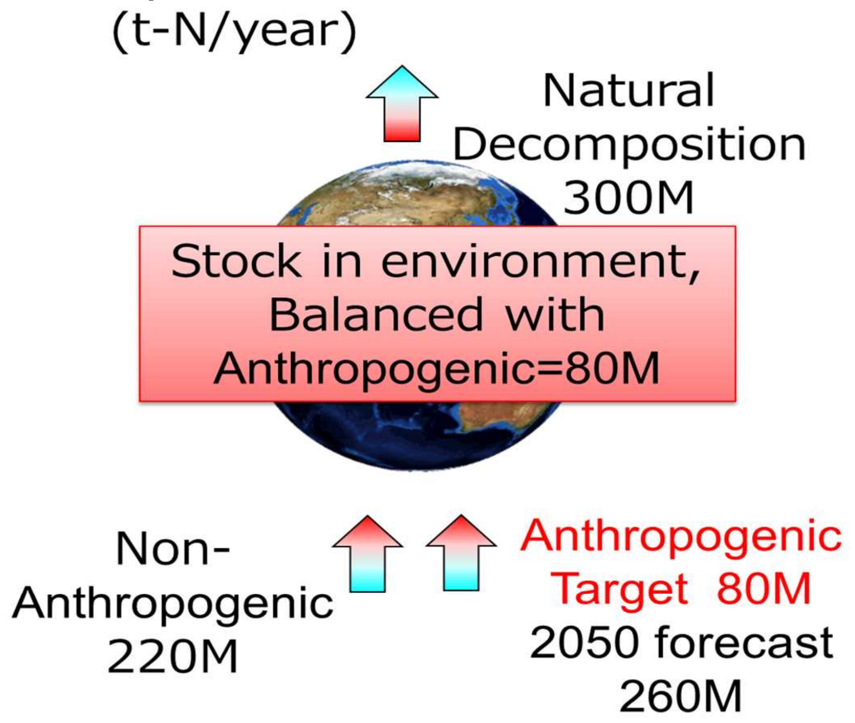
No. A-13-1E
PJ : Innovative Circular Technologies for Harmful Nitrogen Compounds/To Solve Planetary Boundary Issues

Organization: AIST and 16 university/companies
Contact: Dr. Tohru Kawamoto (AIST), tohru.kawamoto@aist.go.jp

<Concept> NOx in exhaust gas and nitrogen compounds in wastewater are converted to ammonia, then separated for recycling. Process design and environmental impact assessment are also available.
<Advantages> High energy efficiency. Enables treatment of exhaust gas and wastewater with less energy than conventional detoxification technologies. Resources are also recovered.

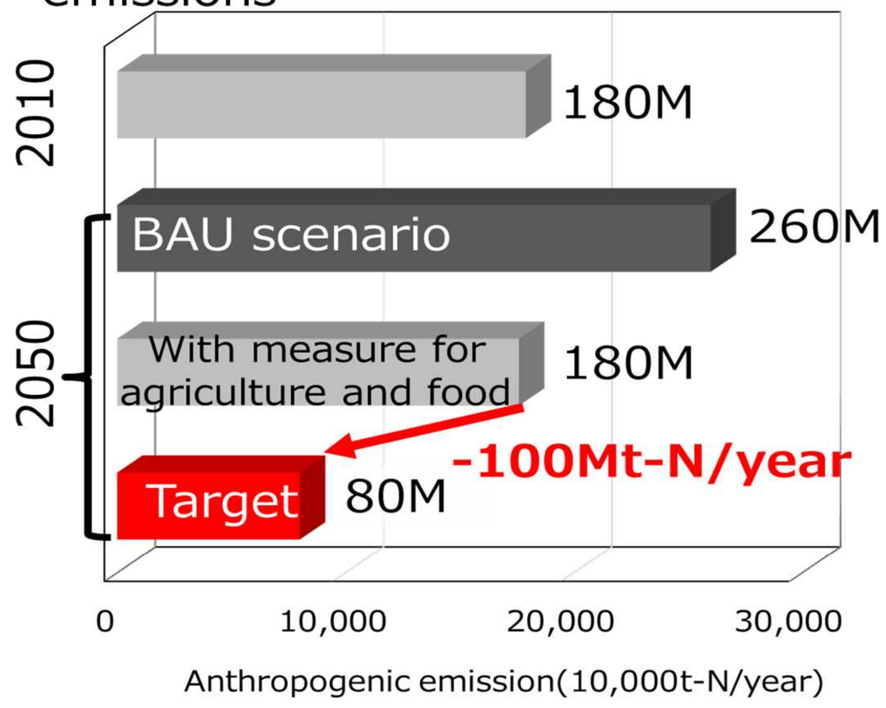
◆Background◆

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



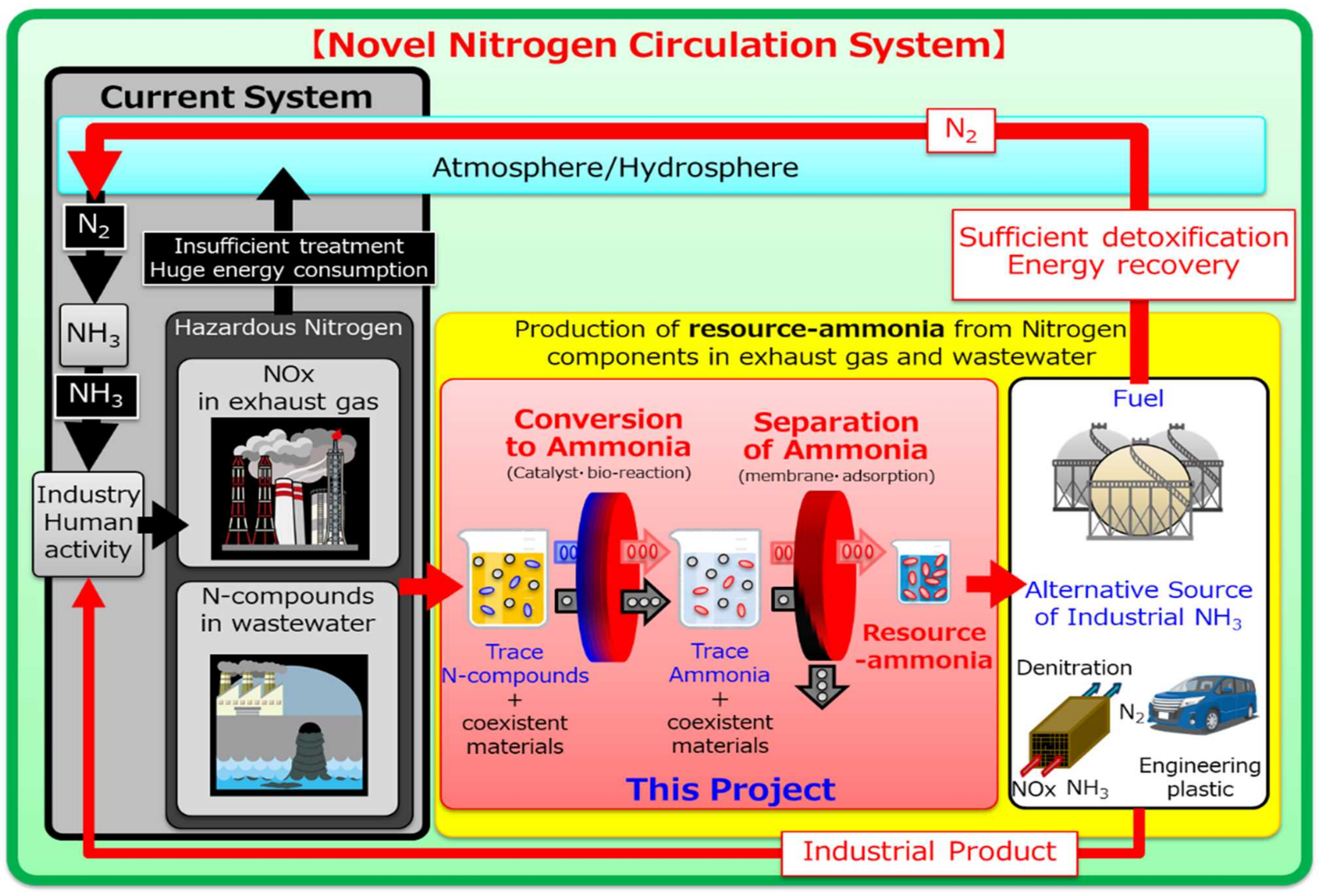
Galloway, Biogeochem. (2004), Fowler, Philos.Trans. R. Soc. B Biol. Sci. (2013) de Vries, Curr. Op. Env. Sus. (2013)

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

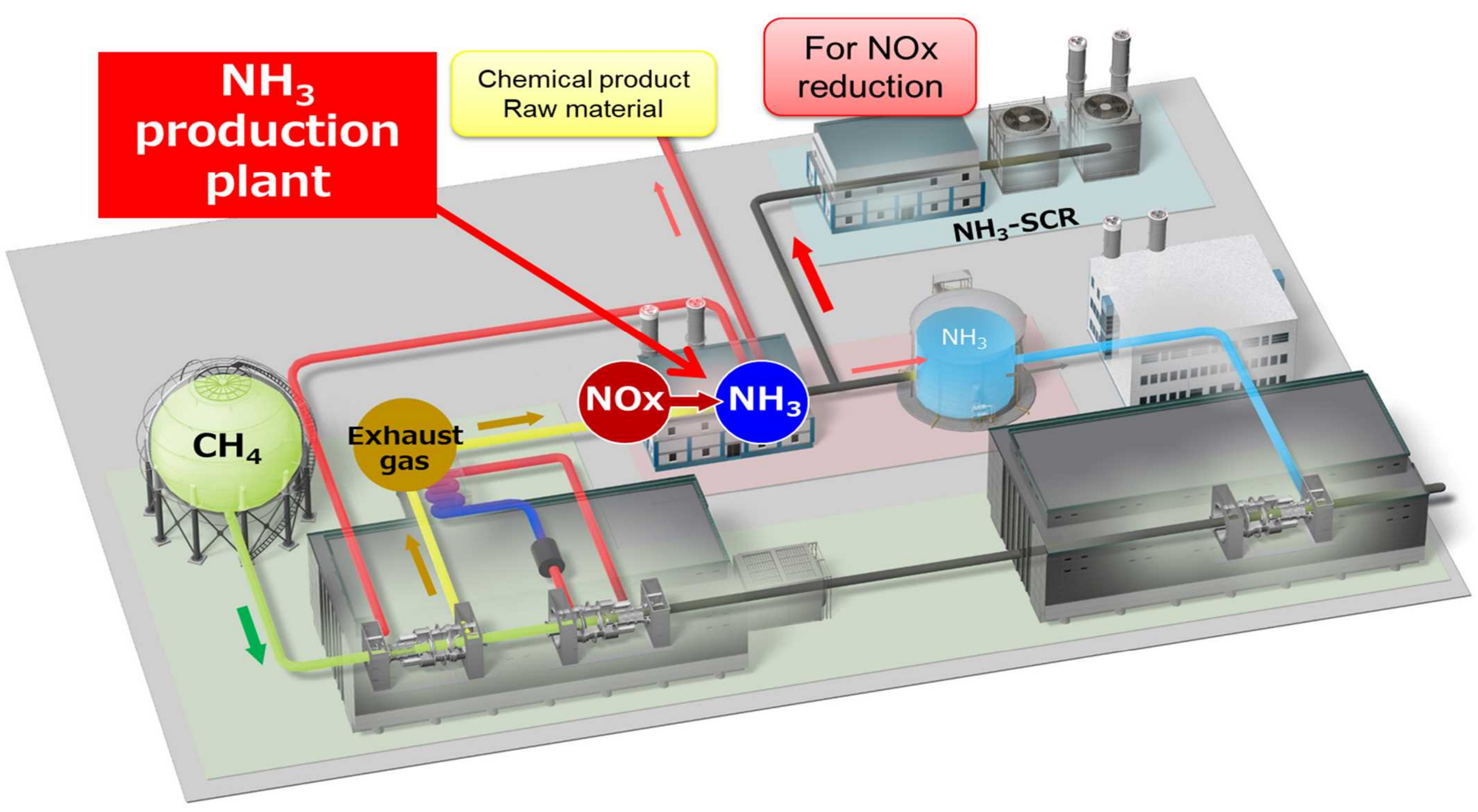


Additional 100Mt-N/year reduction is necessary

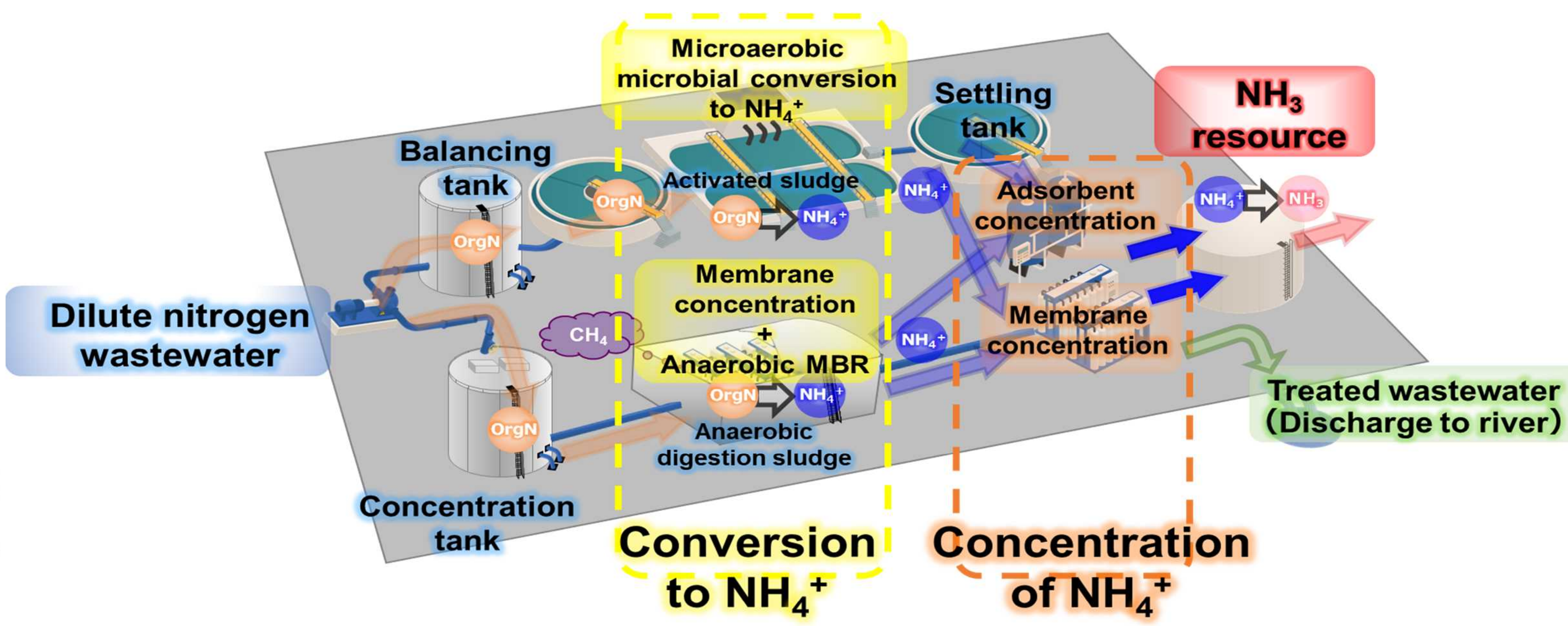
◆Nitrogen circulation systems◆



◆Plant image(NOx to ammonia)◆

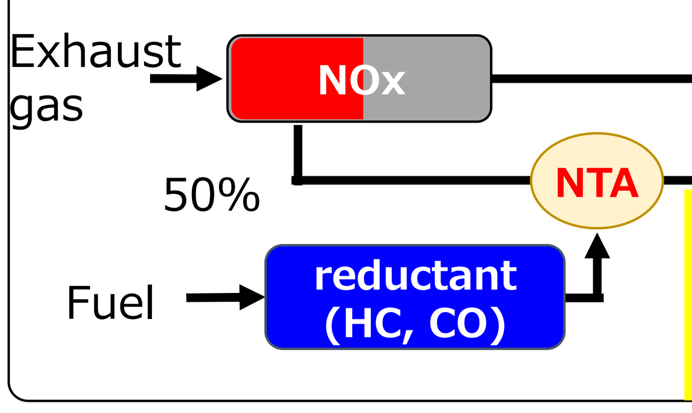


◆Plant image(Aqueous N to ammonia)◆



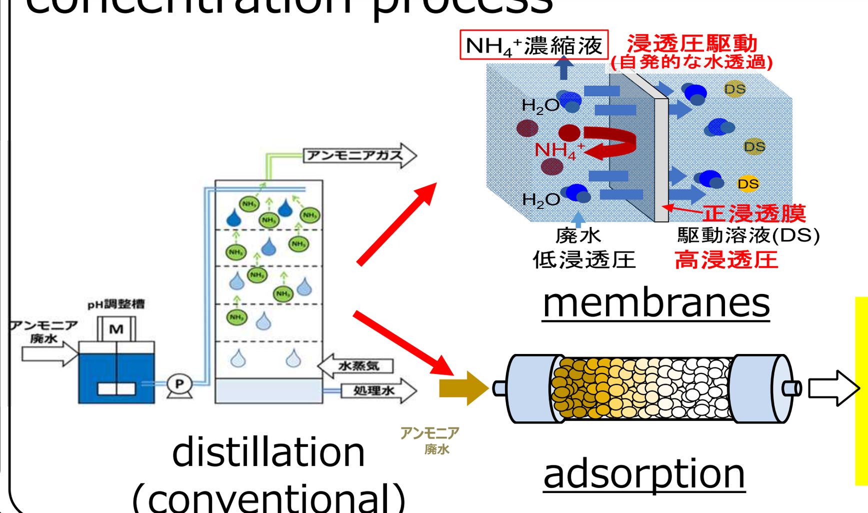
◆Research theme◆

【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

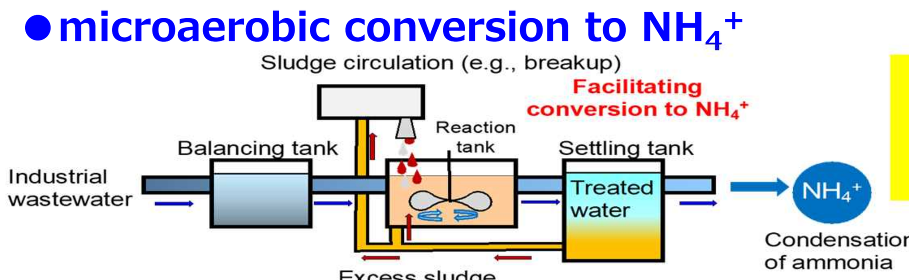
【2-2. ammonia recovery in water】
(1) new membrane/adsorption separation
(2) Construction of ultra energy-saving separation and concentration process



<1/100 of the energy consumption of conventional methods

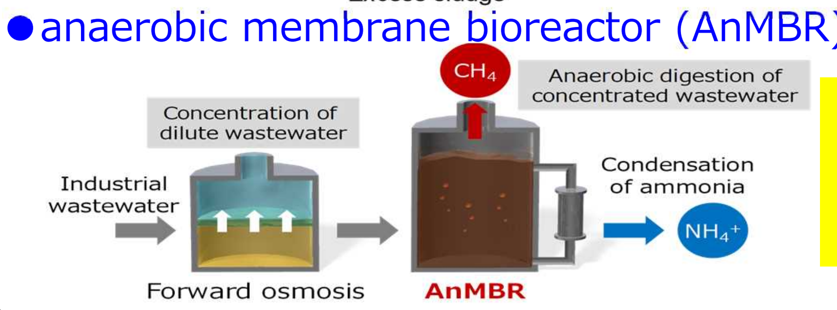
【2-1. conversion to NH_3 in wastewater】
Efficient NH_4^+ conversion bioprocess for various conditions

- microaerobic conversion to NH_4^+



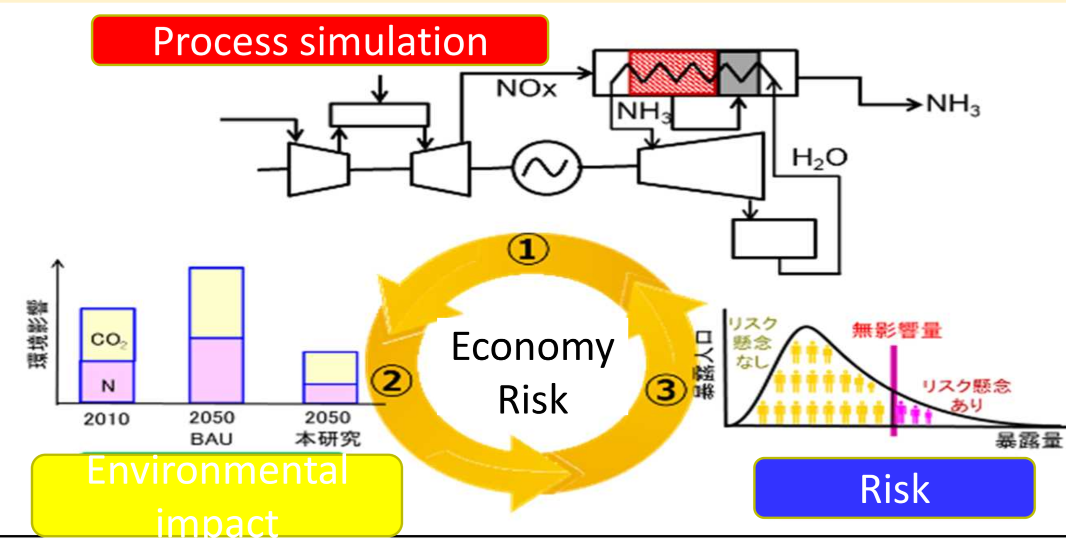
·Low NH_4^+ loss
·Use excess sludge as nitrogen source

- 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-13-2E

PJ : Innovative circular technologies for harmful nitrogen compounds

Theme: Recycling of Gas-phase NOx : A Single Stage NTA in O_2 and H_2O

Organization: Waseda University

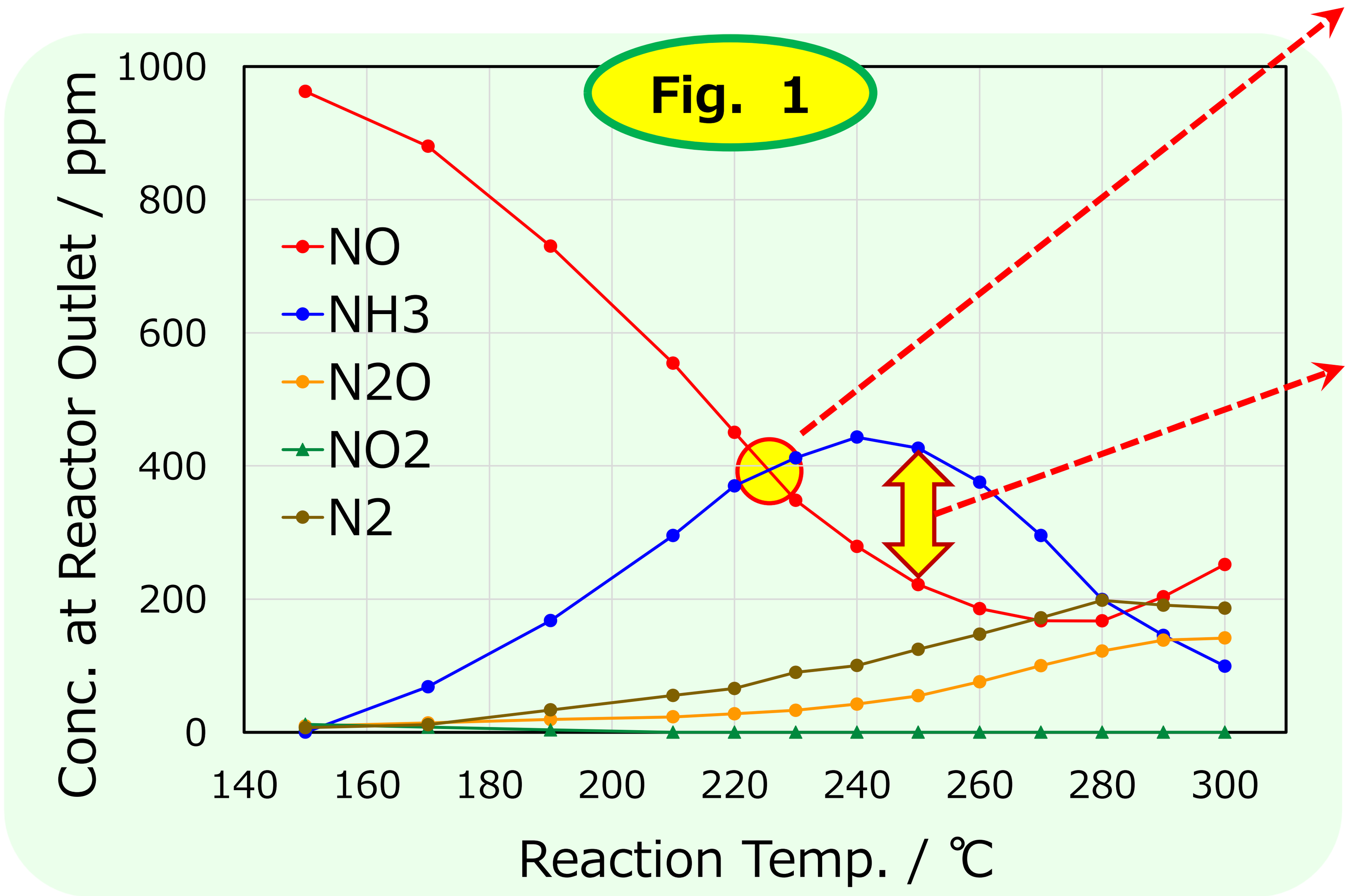
Contact: Masakazu Iwamoto（Waseda University）m.iwamoto3@kurenai.waseda.jp

<Concept> NO is converted to NH_3 (NTA) by H_2 without any concentration or separations (in a single stage). The product NH_3 is fed to the NH_3-SCR or concentrated to the NH_3 utilization industry.
<Advantages> Realization of NH_3-SCR systems without NH_3 supply. Production of industrial NH_3 without the Haber-Bosch process.

1. Development of an efficient single-stage NTA catalyst, WSD-01, and proposed cross-point utilization and industrial NH_3 production (Figure 1).

A single stage NTA without concentration of NO and removal of O_2 and H_2O

$$NO + 5/2H_2 \xrightarrow[\text{Catalyst}]{\text{in } O_2,\ H_2O} NH_3 + H_2O$$



Cat. WSD-01. Reaction Conditions: SV=50,000 h^{-1}, 0.1% NO, 1.5% H_2, 10% O_2, 10% H_2O, balance N_2

Realization of NH_3-SCR w/o NH_3 supply

Crosspoint $C_{NO} = C_{NH3}$

Combination of H_2-NTA and NH_3-SCR realizes a new NH_3-SCR system.

Alternative synthesis of industrially produced NH_3

When C_{NH3} » C_{NO}, produced NH_3 can be separated and concentrated for industrial use.

Produce <u>the required amount</u> of NH_3 <u>on the spot</u> <u>when we need it</u>.

2. Developed a single-stage NTA catalyst, WSD-02, applicable to 100 ppm NO, paving the way to realize ultra-dilute NO detoxification (Figure 2).

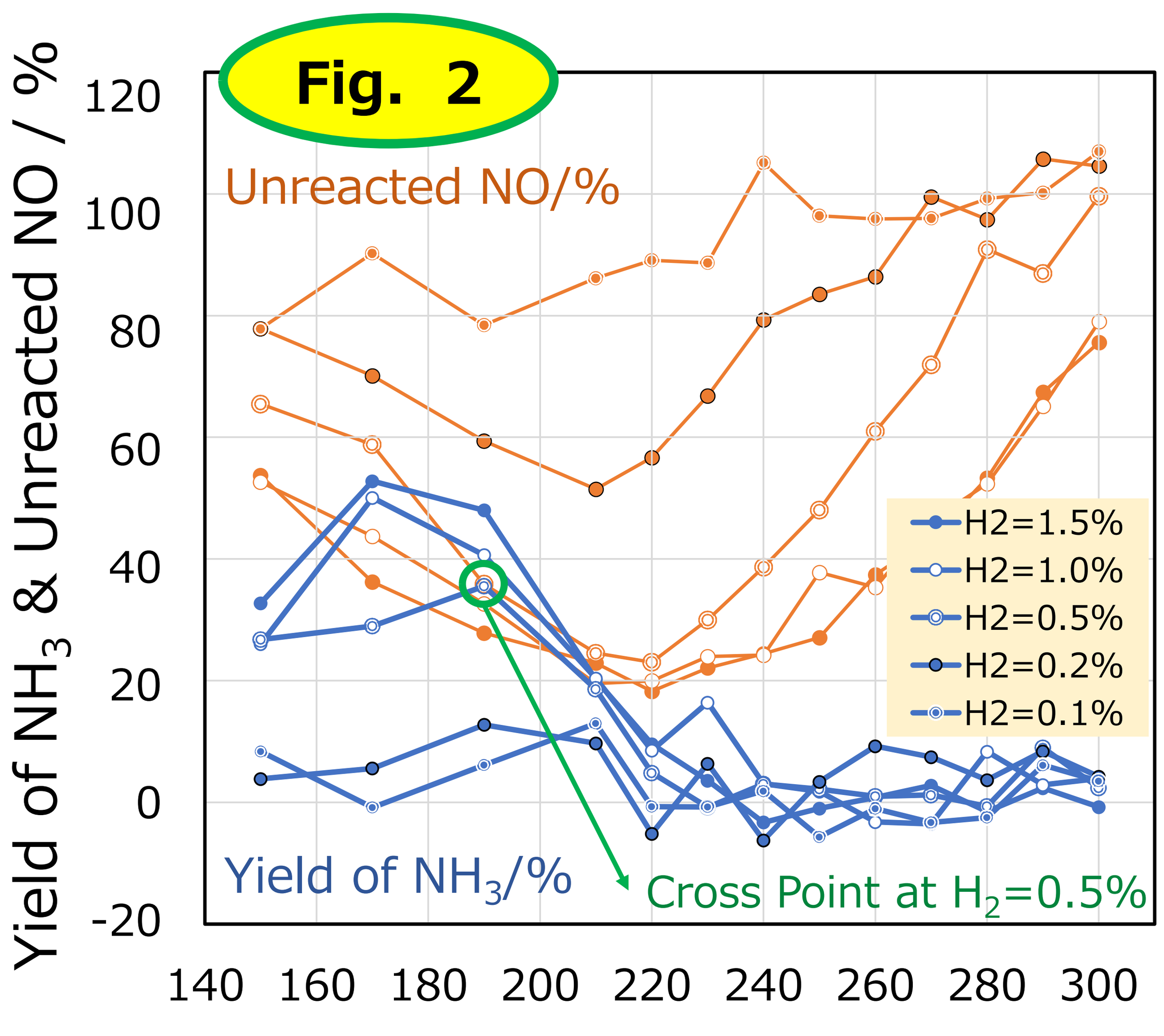
The developed NTA catalyst was effective for the reaction of ultra-dilute NO below the current environmental standards. Promote further improvement of the atmospheric environment.

3. A hydrocarbon-based NTA catalyst, WSD-03, was developed to provide a temporary solution until the realization of a hydrogen society (Figure 3).

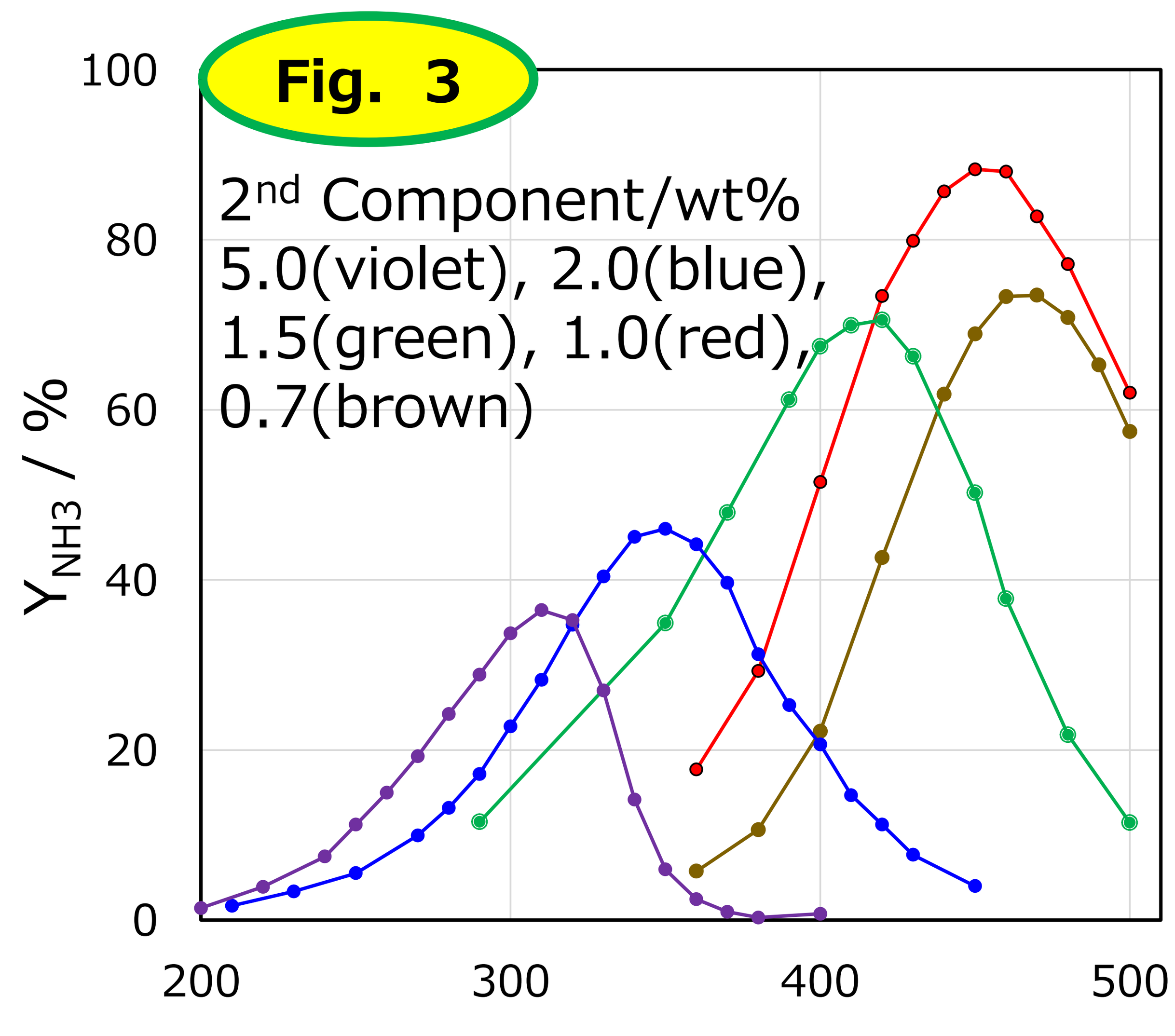
If a hydrogen supply network is not available, the NTA reaction can be carried out using a hydrocarbon-based reducing agent. Compatible with current internal combustion engines.

4. Preparation of pellet catalysts for bench-scale experiments and preliminary tests (Figure 4).

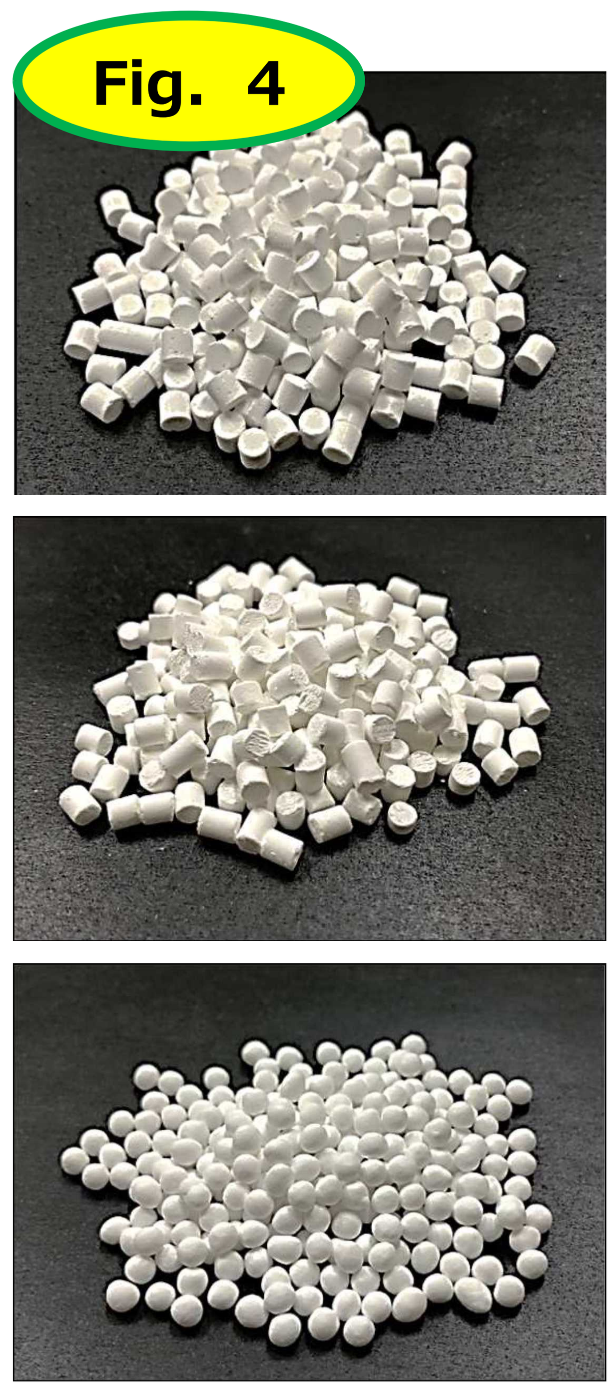
Pellet catalysts were prepared in collaboration with a catalyst manufacturer. Confirmation of crushing strength, specific surface area, and catalytic activity using a microreactor.



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



Compression
2.93mmΦ
3.01mmʰ
Strength 47N
47.6m²/g

Extrusion
2.64mmΦ
3.23mmʰ
Strength 24N
81.3m²/g

Rolling
3.30mmΦ

Strength 27N
60.4m²/g

【Potential Applications and Impacts】

Small NO sources such as ships, garbage incinerators, etc.

Realization of NH_3-SCR with self-consumption of generated NH_3 (no need for NH_3 supply).

Large NO sources such as thermal power plants, oxidation processes, cement kilns, etc.

Separation and concentration of NH_3 to supply industrial NH_3. Localization of NH_3 production.

No. A-13-3E

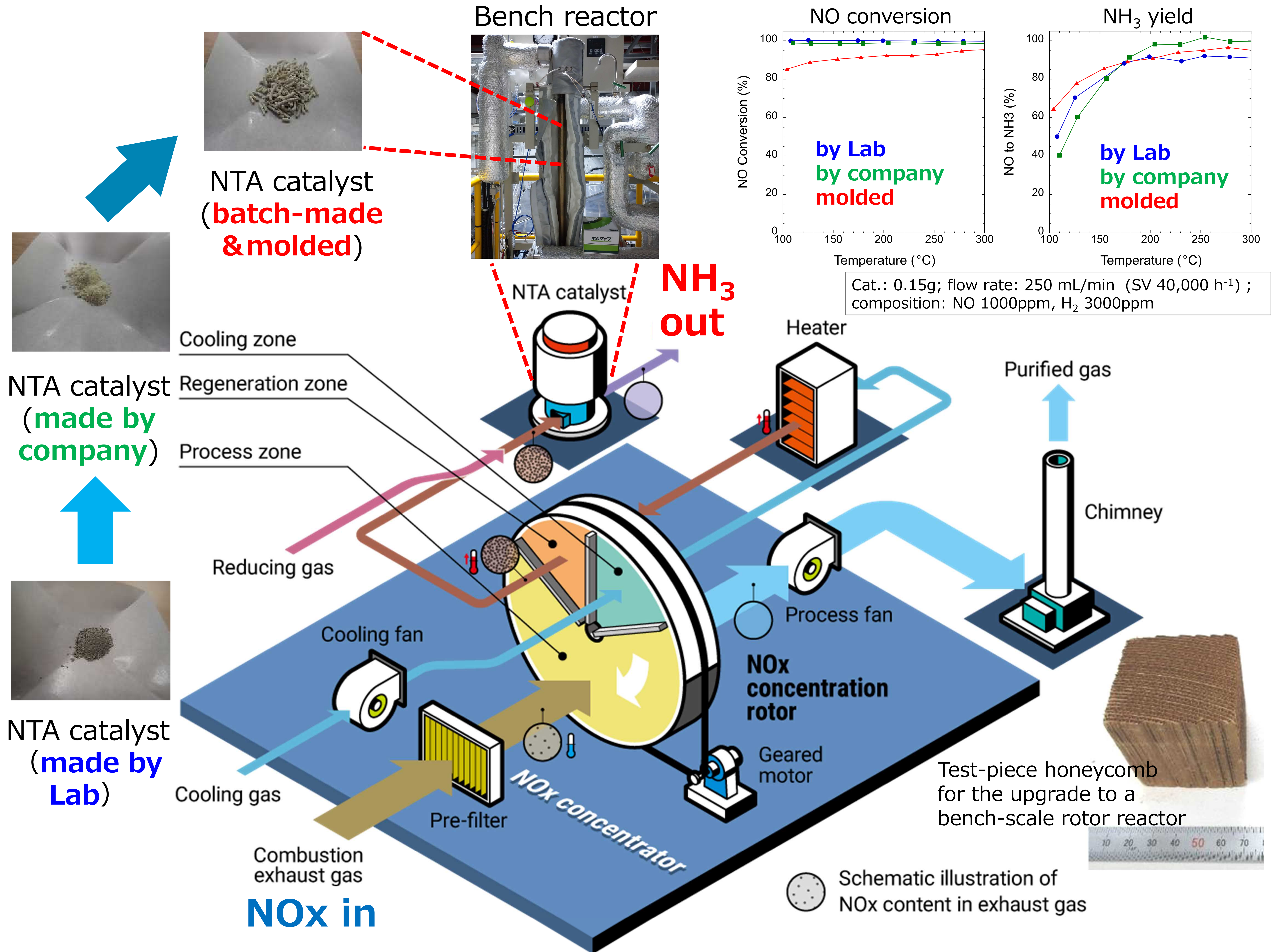
PJ: Innovative circular technologies for harmful nitrogen compounds

Theme: Development of honeycomb rotor-type 2step NTA catalyst system

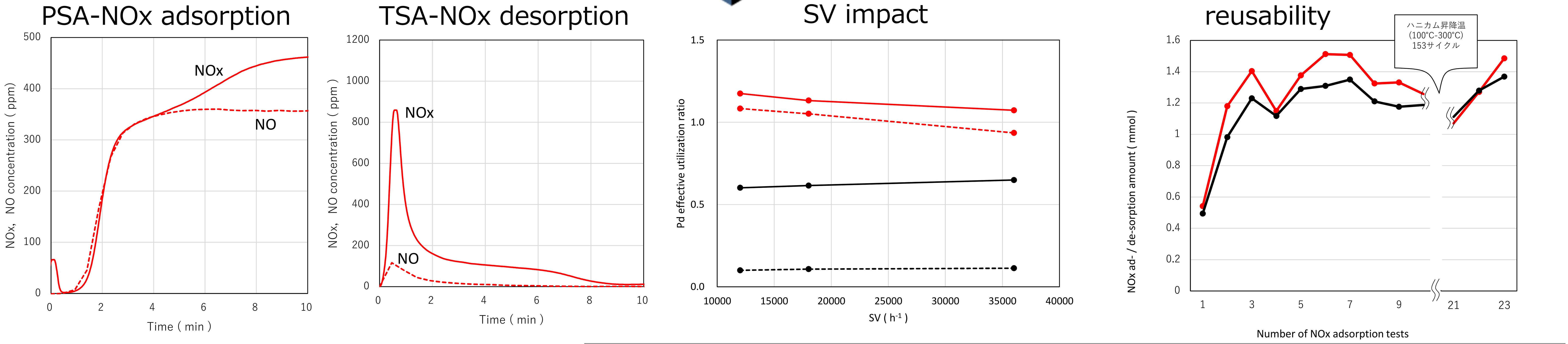
Organization: The Univ. Tokyo, AIST, Tokyo Inst. Tech., Seibu Giken
Contact: Prof. Masaru Ogura (UT), oguram@iis.u-tokyo.ac.jp

<Concept> Design of a **2step NTA catalyst system** that seamlessly connects NOx selective adsorption/concentration in the presence of O_2 and H_2O and NTA reaction under O_2-free conditions.

<Advantages> Capable of deNOx at extremely low conc.; respond to NOx concentration fluctuations; world top-level NOx supplying in the reaction temp.; more than 95% yield of NH_3; closer to recycling



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



500ppm NO/Air (14.7 L/min) at 100°C; N_2 flow(14.7 L/min) 100-300°C temperature ramp (20 K/min)
adsorbent: Pd-beta zeolite with 46wt%·94.1kg/m³ ; honeycomb size : φ25 x 100 mm SV : 18000 h^{-1}

【Potential Applications and effects】

Large-scale, significantly low temperature and concentration NOx sources such as power plants, oxidation processes, cement kilns, etc.

Realization of NH_3-SCR for local production and local consumption of generated NH_3; various utilization routes of hydrogen such as green hydrogen, is envisioned for hydrogen supply source.

No. A-13-4E

PJ : Innovative circular technologies for harmful nitrogen compounds

Theme: Gas-phase NO_x recycling – NO_x Storage Reduction (NSR) for NTA

Organization: AIST

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

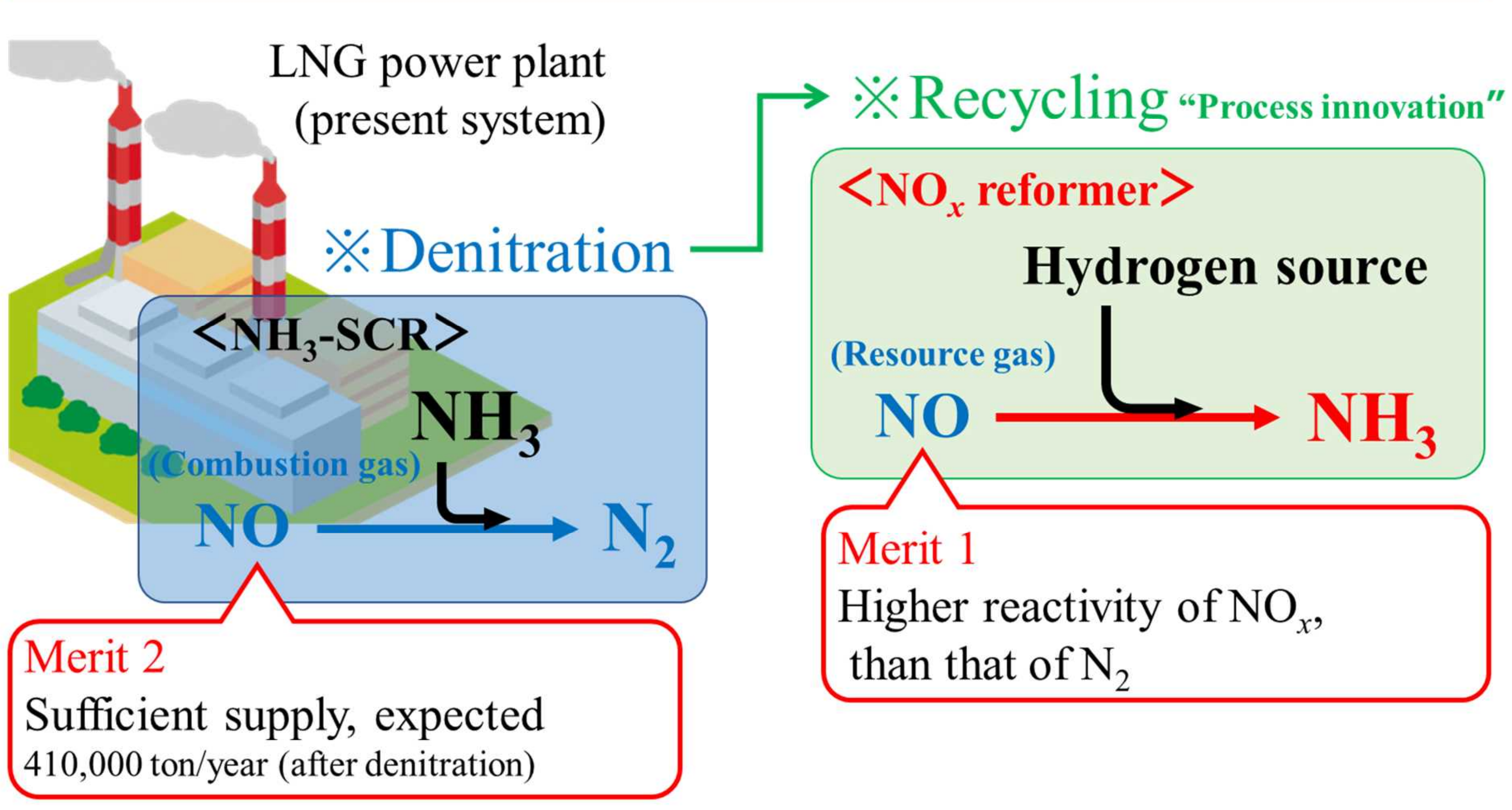
<Concept>

Design for selective conversion from stored NO_x to NH_3 at constant temp. by switching reaction gases for eliminating coexisting gases

<Advantages>

- Performing NO_x storage and NH_3 recovery at constant temp., that thermal management is not required, by considering the possibility to recover NO_x at high temperatures
- Achieving NO_x storage, that can be responded to fluctuated operation conditions, and subsequent NH_3 recovery by using one multi-functional nanocomposite catalyst

Game change technology for recycling nitrogen resources

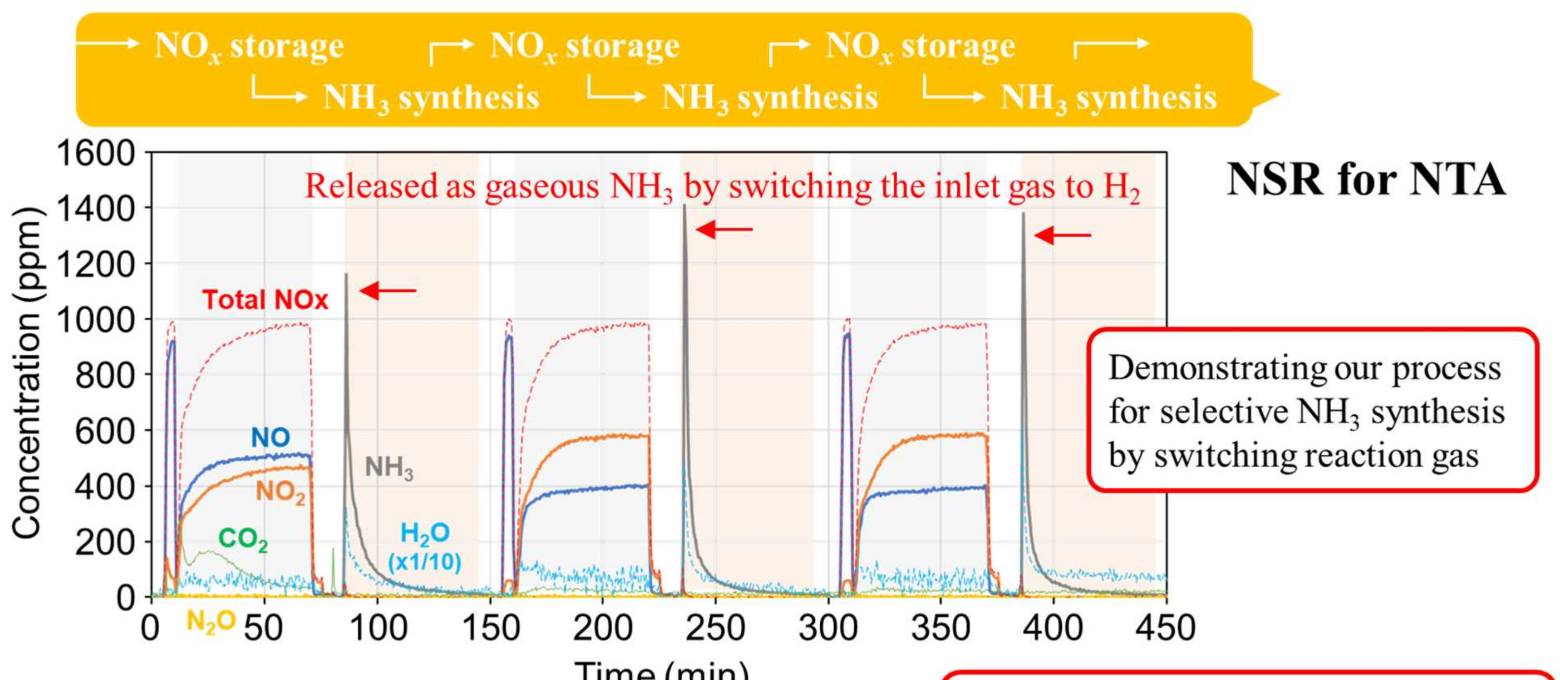


Benefit 1 Onsite procurement of NH_3 for denitration

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 NH_3 from stored NO_x at AIST-Chubu



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

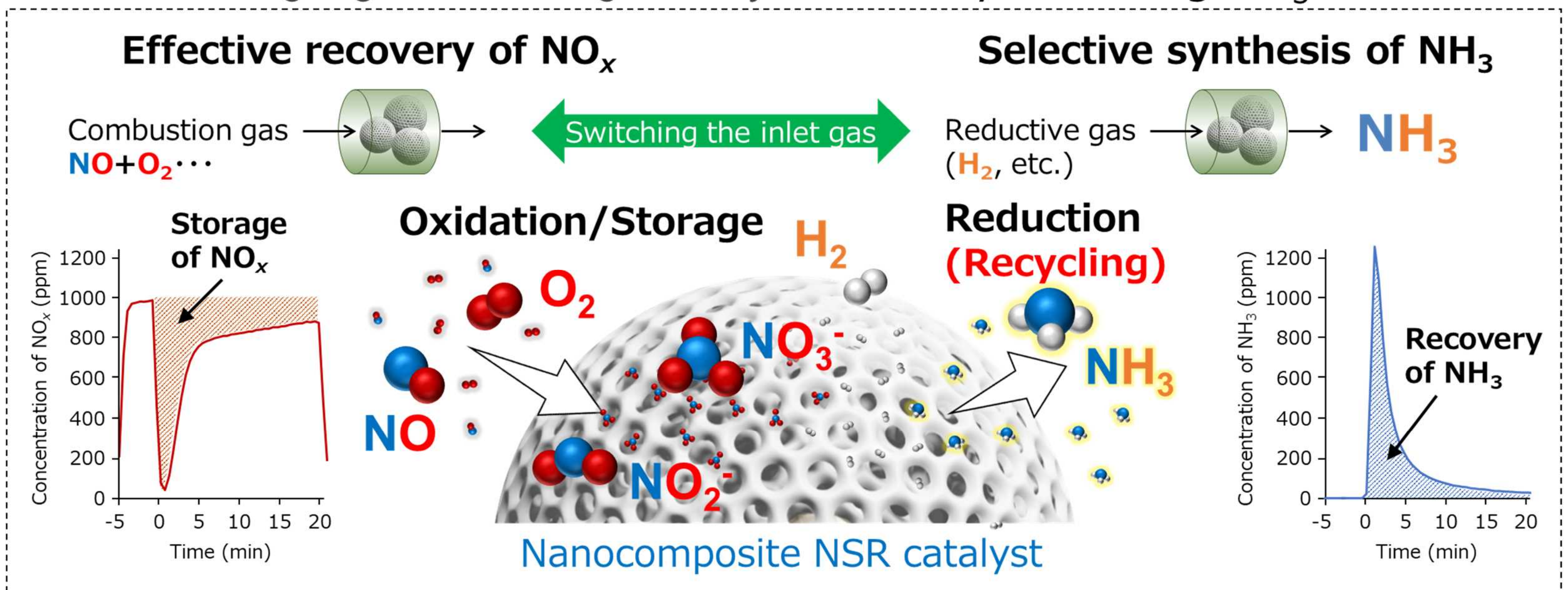
■ Catalyst: $Ba/Pt@mAl_2O_3$
Granule size: 150~250 μm
Weight (before use): 100 mg
Weight (after use: 85 mg

■ 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°C
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

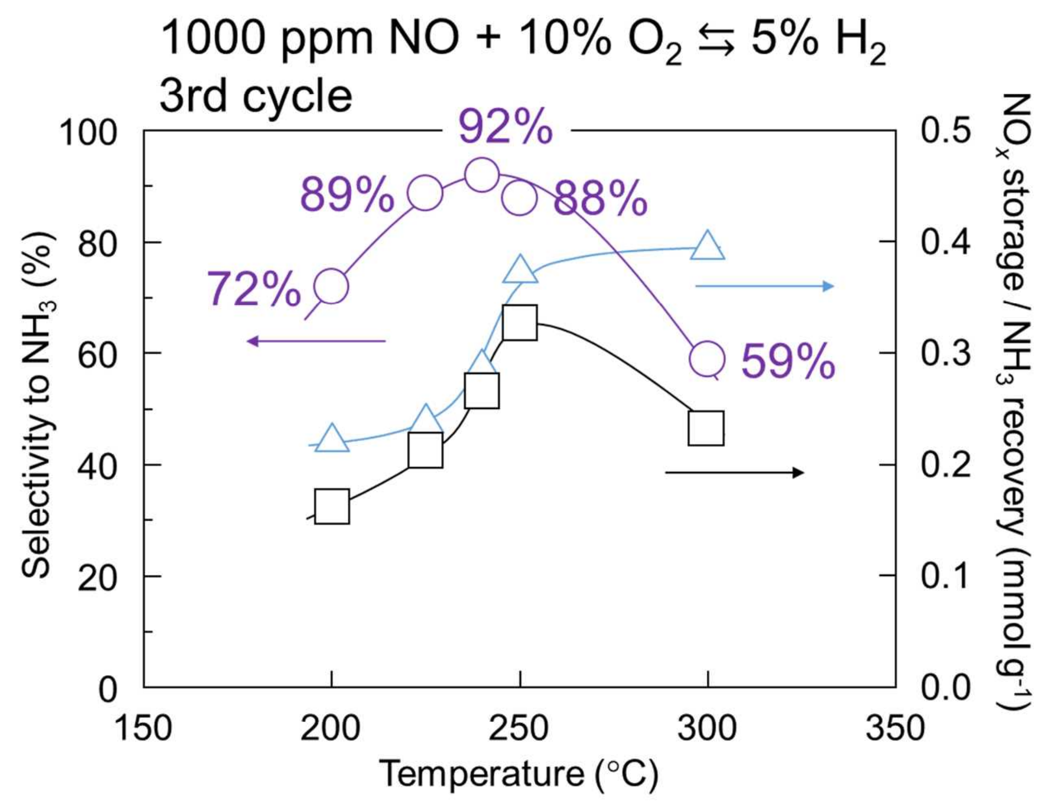
Verifying the influence of reaction conditions and the inhibitory effect of impurities

Demonstrating a gas-switching NSR system for synthesizing NH_3



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)

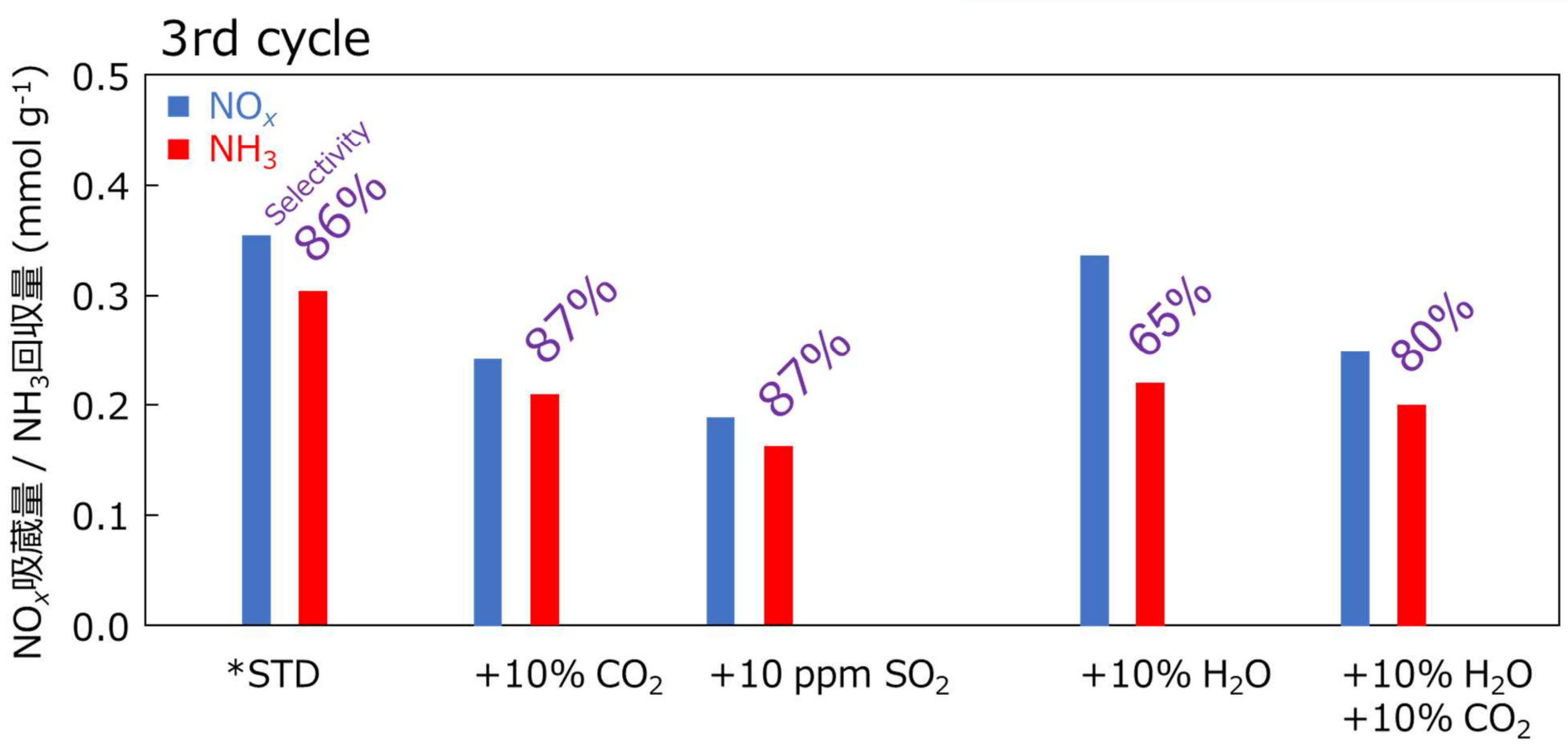
★Influences of reaction temperature



Outcome 1
Clarifying the reaction conditions for the selective conversion to NH_3 more than 90%

★Influences of coexisting gases

■ reaction conditions
Reaction temperature: 250 °C
Gas flow rate: 100 mL min^{-1}
Storage of NO_x: 1000 ppm NO + 10% O_2 + N_2
\+ CO_2 + H_2O + trace-level SO_2
Synthesis of NH_3: 5% H_2 + N_2



Outcome 2
Identifying issues for each gas
Keeping the selectivity to NH_3 by an intentional decrease in the amount of stored NO_x

【Potential Applications and effects】

Small-scale NO_x generation sources such as garbage incinerators

- Designing an onsite NO_x reformer system for supplying as a reducing agent (NH_3-SCR) as well as a mass-production plant of NH_3
- Achieving more than 90% selectivity to NH_3 at the wide range of temp. possibly optimized by the chemical composition of nanocomposite catalysts, being able to effectively working below 200 °C

No. A-13-5E

PJ : Innovative circular technologies for harmful nitrogen compounds

Theme: Ammonia adsorption and concentration recovery and recycling process.

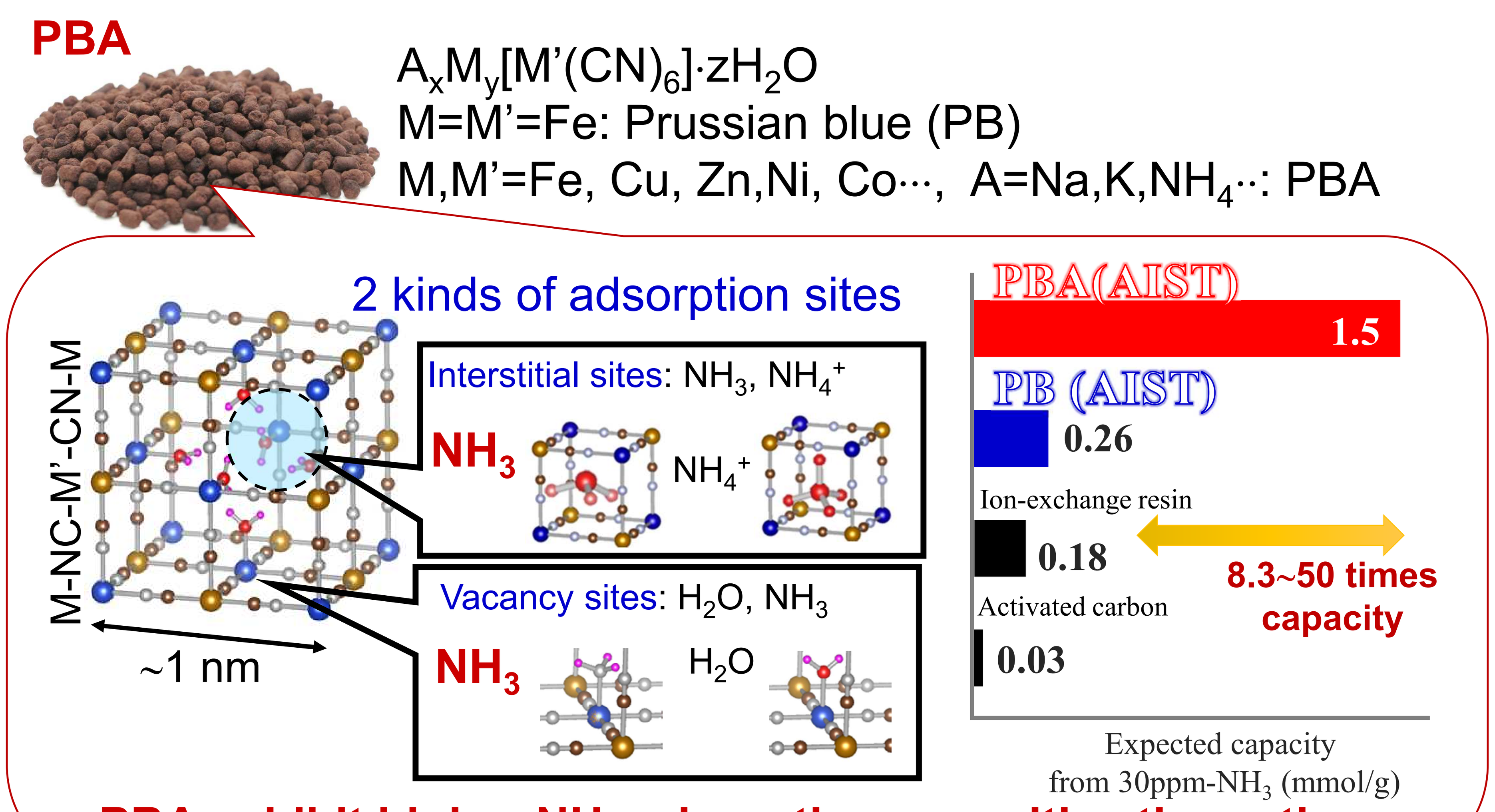
Organization: AIST

Contact: Kimitaka Minami (AIST), Kimitaka-minami@aist.go.jp

<Concept> Technology for the conversion of ammonia into a resource using Prussian blue analogues from NTA gases in which nitrogen oxide is converted into ammonia.

<Advantages> Large capacity and highly selective ammonia adsorbent, even from gases with coexisting H_2O and CO_2. Recovery NH_4HCO_3 (solid) without heating and with low energy consumption.

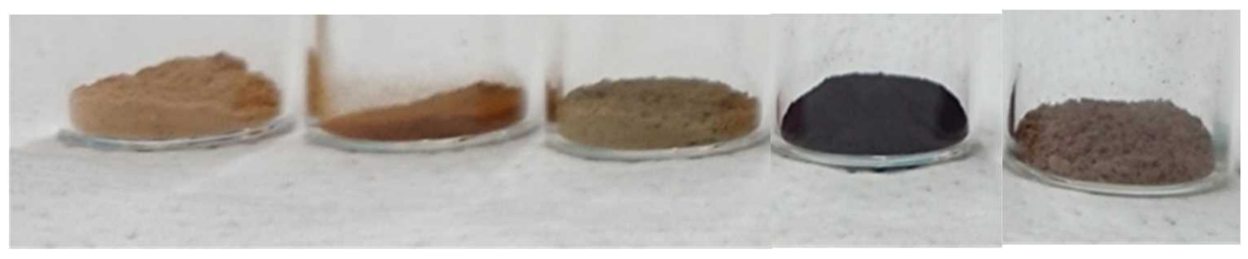
Prussian blue analogues(PBA) for Ammonia adsorbent



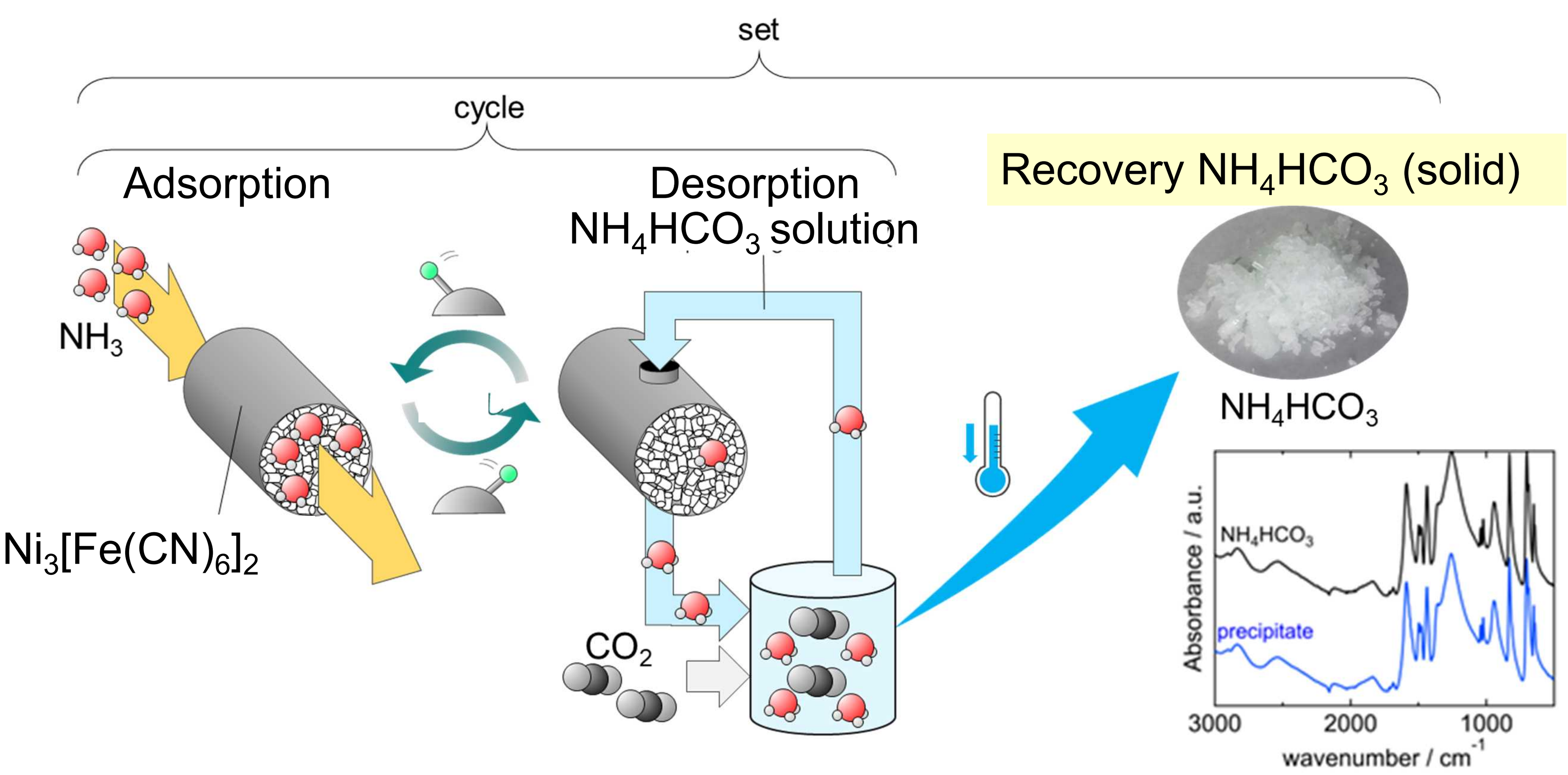
PBA exhibit higher NH_3 adsorption capacities than others

H. Usuda, et al., Molecules 27, 8840 (2022).

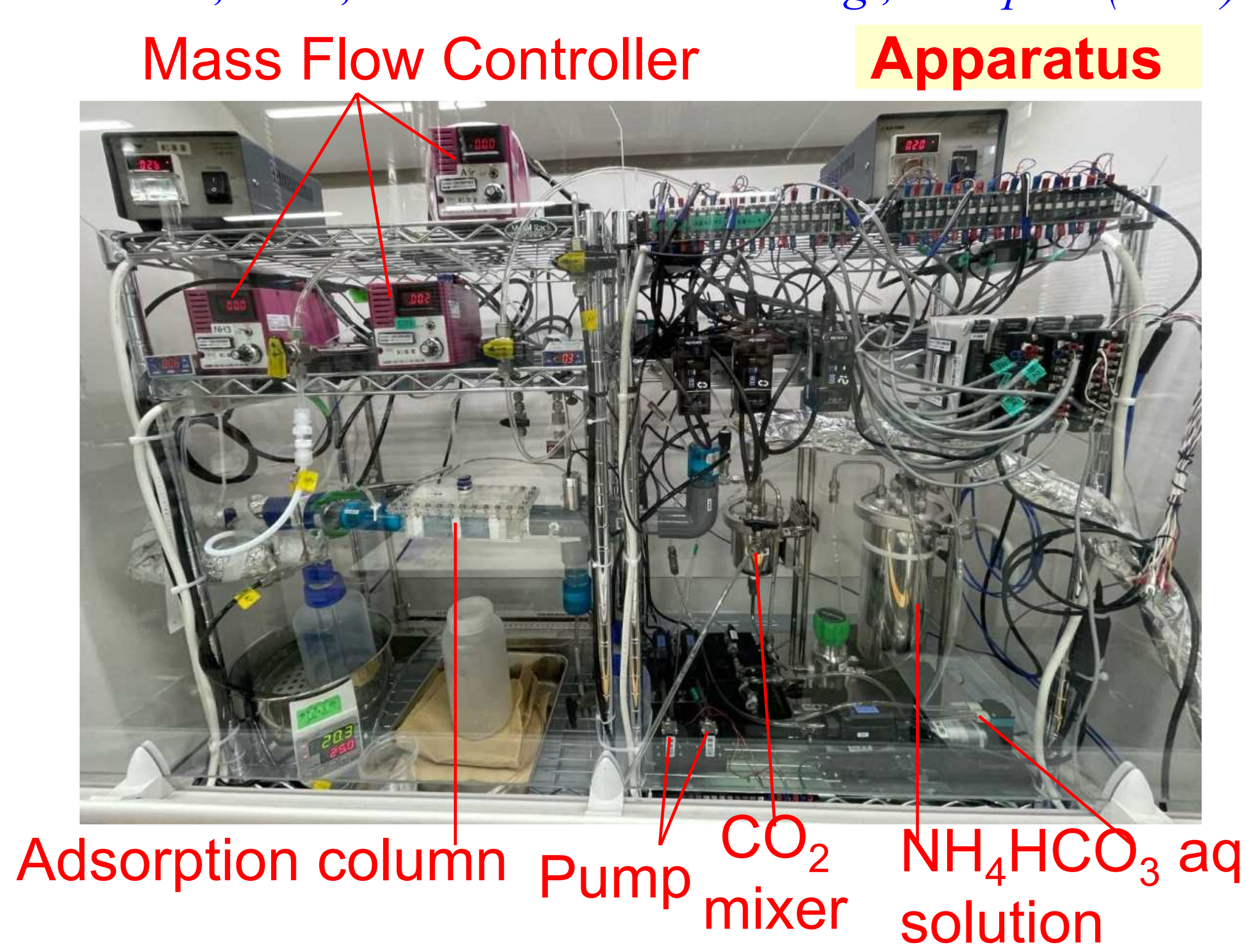
M	Zn^{2+}	Ni^{2+}	Cu^{2+}	Co^{2+}	Mn^{2+}
M'	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}
Ads. [mmol/g]	2.66	5.48	13.2	1.47	4.57
Des. [mmol/g]	0.53	1.49	8.19	0.14	-0.63
Stability (XRD)	×	○	×	○	○



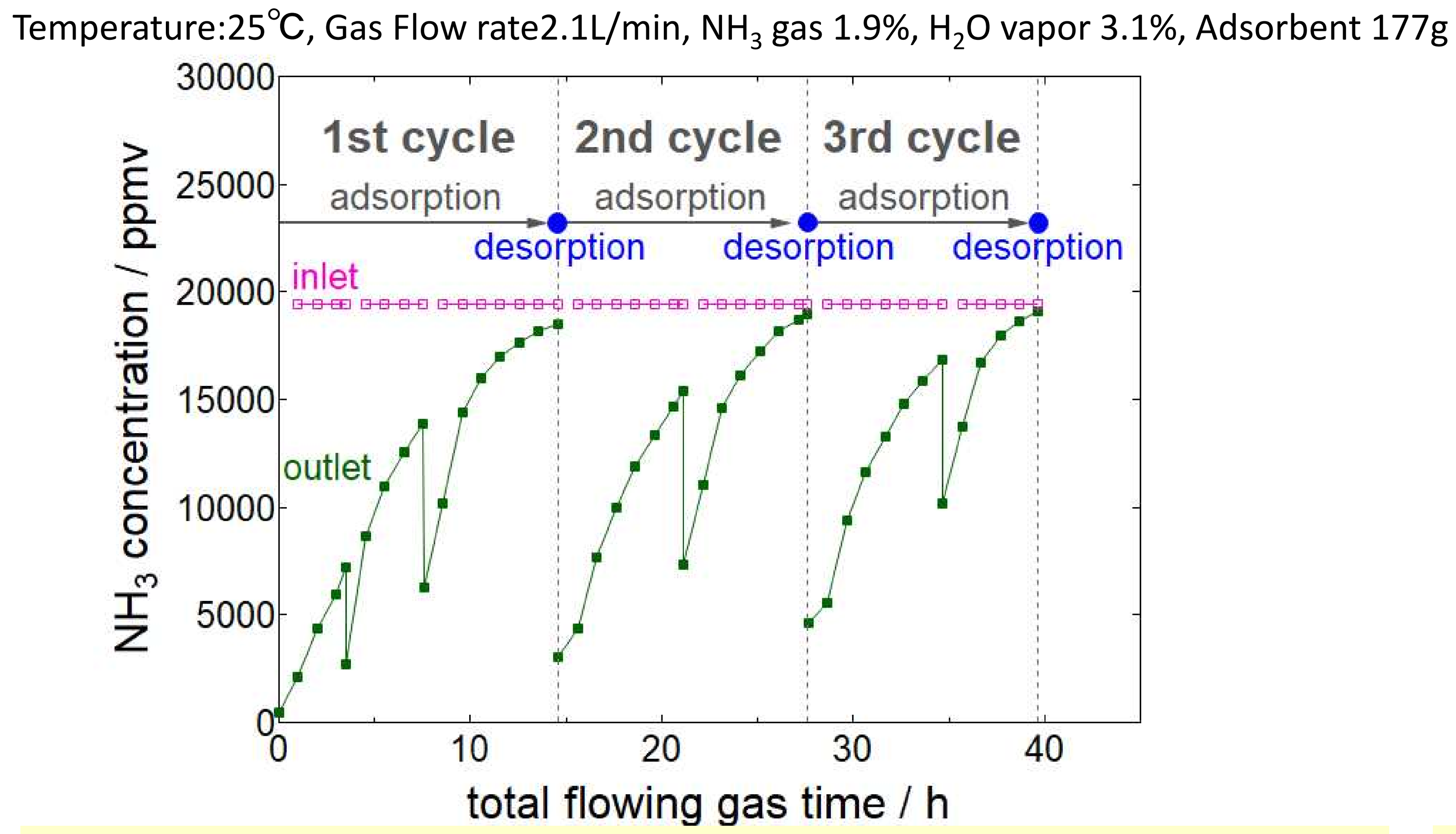
Ammonia concentration System



H. Usuda, et al., ACS Sustain. Chem. Eng., Accepted (2023).

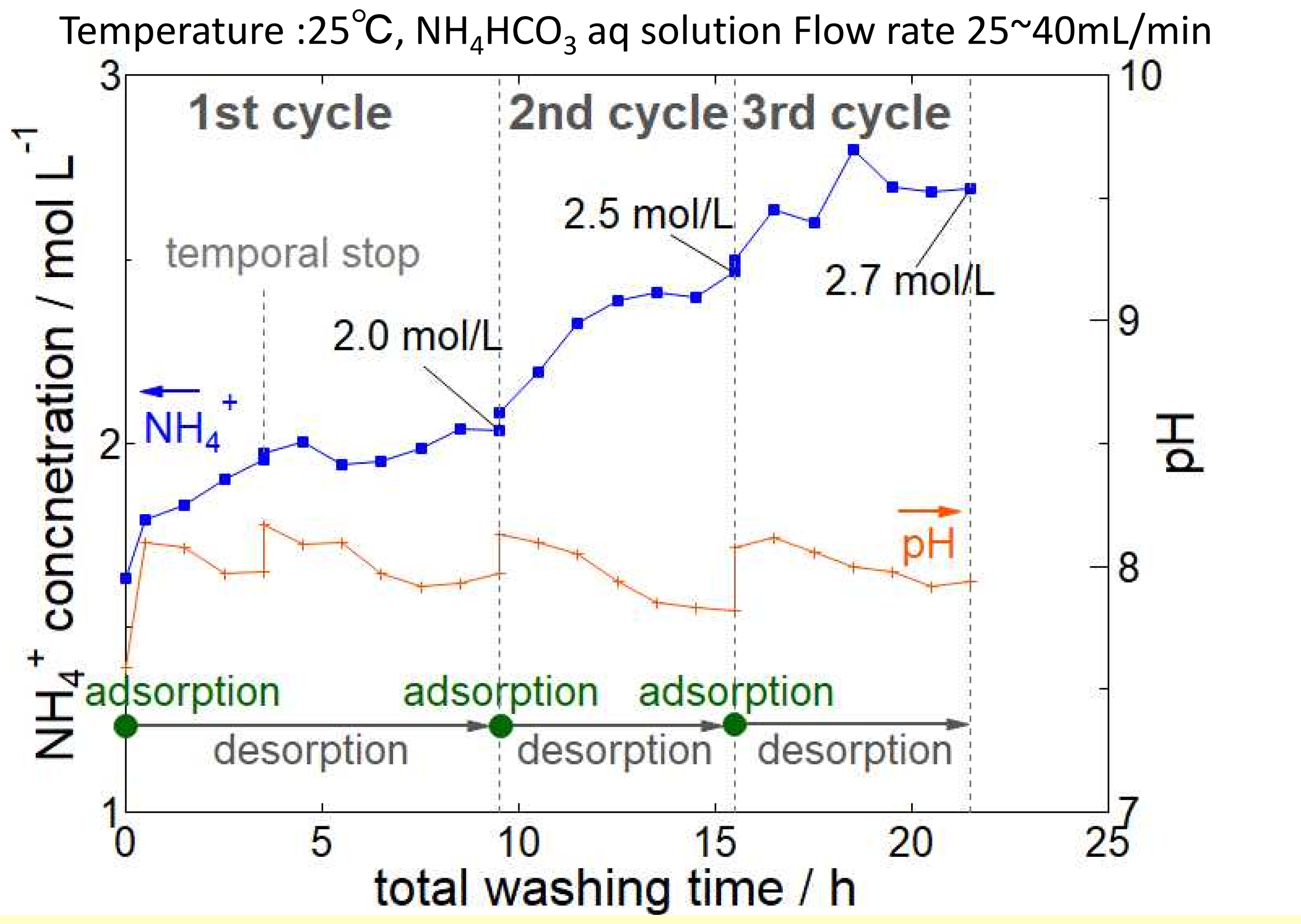


Temperature:25℃, Gas Flow rate2.1L/min, NH_3 gas 1.9%, H_2O vapor 3.1%, Adsorbent 177g



- The NH_3 concentration in OUTLET was more than 95% of INLET in a dozen hours.
- Adsorption recovered after desorption.

Temperature :25℃, NH_4HCO_3 aq solution Flow rate 25~40mL/min



- Desorption increases NH_4 concentration in NH_4HCO_3 solutions.
- Change in pH means that CO_2 dissolves after NH_3 is desorbed.

【Potential Applications and effects】

NO generation sources such as ships, garbage incinerators, thermal power plants, oxidation processes, etc

For separation and concentration of NH_3 from NTA gases.

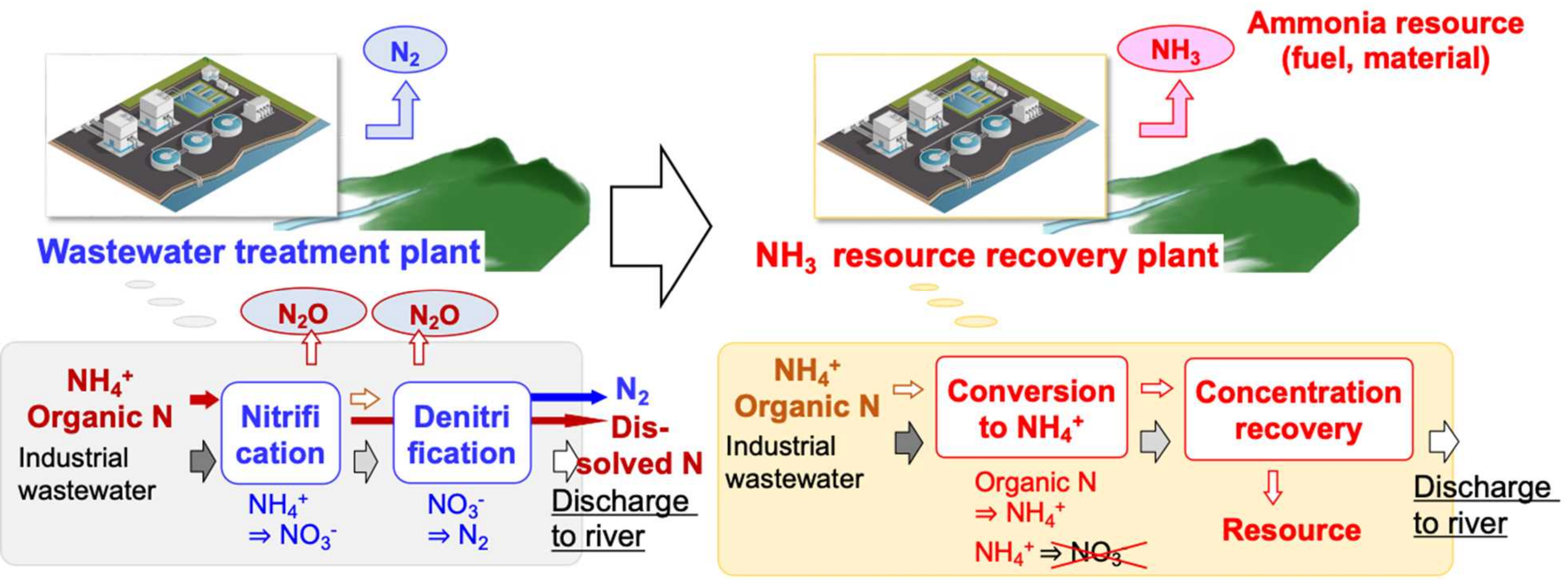
No. A-13-6E
PJ : Innovative circular technologies for harmful nitrogen compounds
Theme: Wastewater N compounds to NH_4^+– Microaerobic conversion process (1)

Organization: AIST, Kirin Holdings Co., Ltd. (KHD)
Contact: T Hori (AIST) hori-tomo@aist.go.jp; T Shimizu (KHD) takeshi.shimizu@kyowa-kirin.co.jp

<Concept> ・A set of systems connecting "conversion to NH_4^+" and "separation and concentration of NH_4^+"
・Ceasing nitrogen discharge to environments and achieving resource and energy recovery

<Advantages> Constructing multi-bioconversion processes for various wastewater types and situations

● Current state and future image in 2050

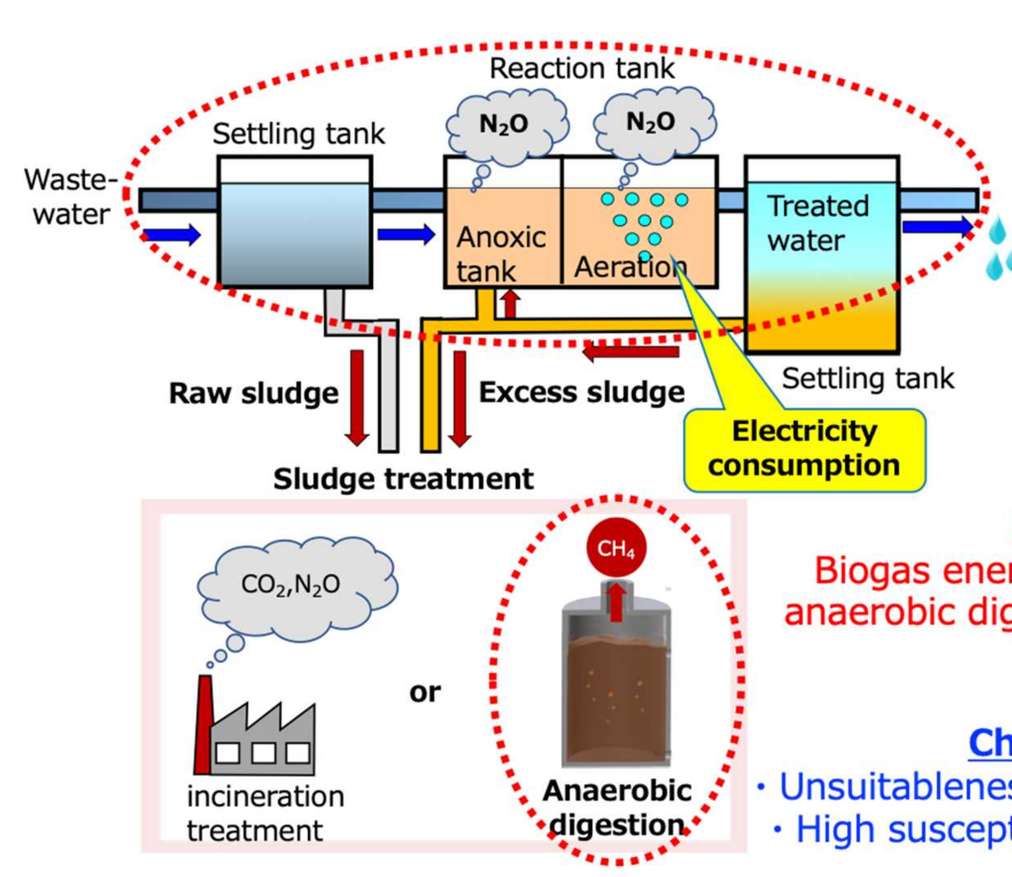


- ☐ N compounds in wastewater were converted to N_2 gas, accompanied with N_2O emission
- ☐ Required massive energy
- ☐ Residual N discharge

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

● Two important points for bioconversion process

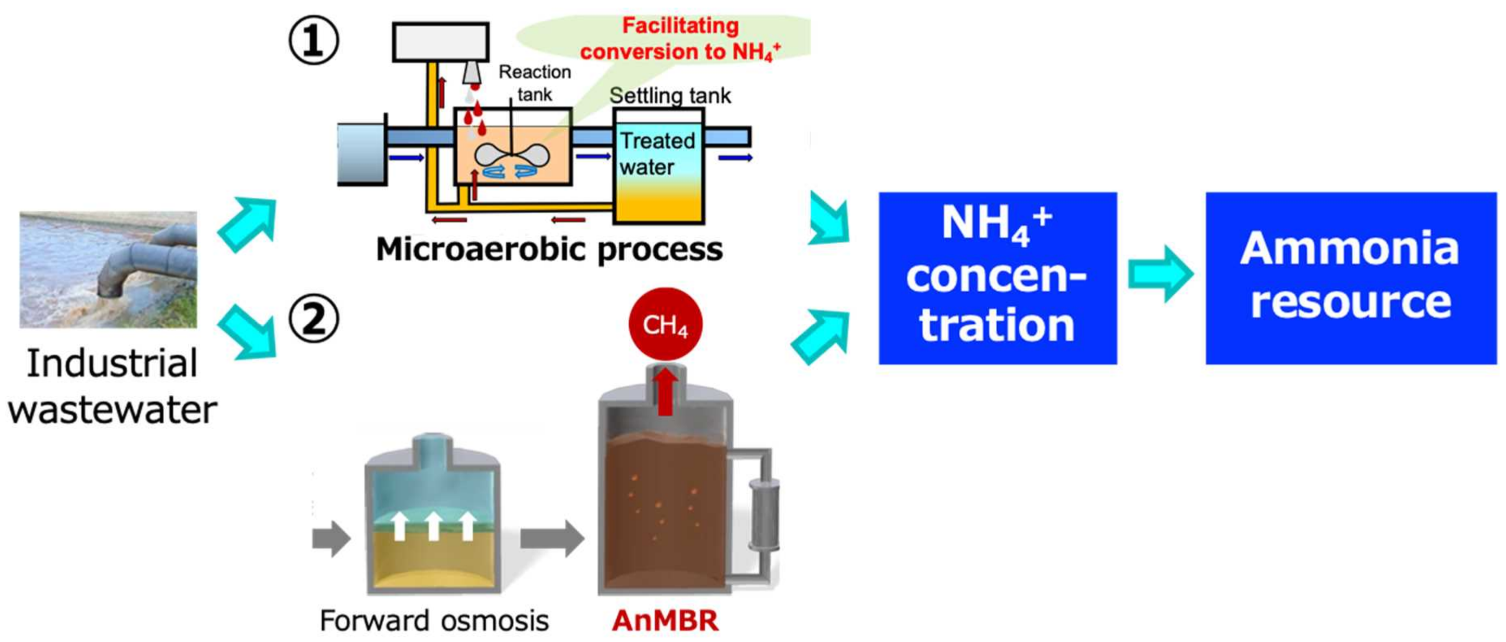
Activated sludge method



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

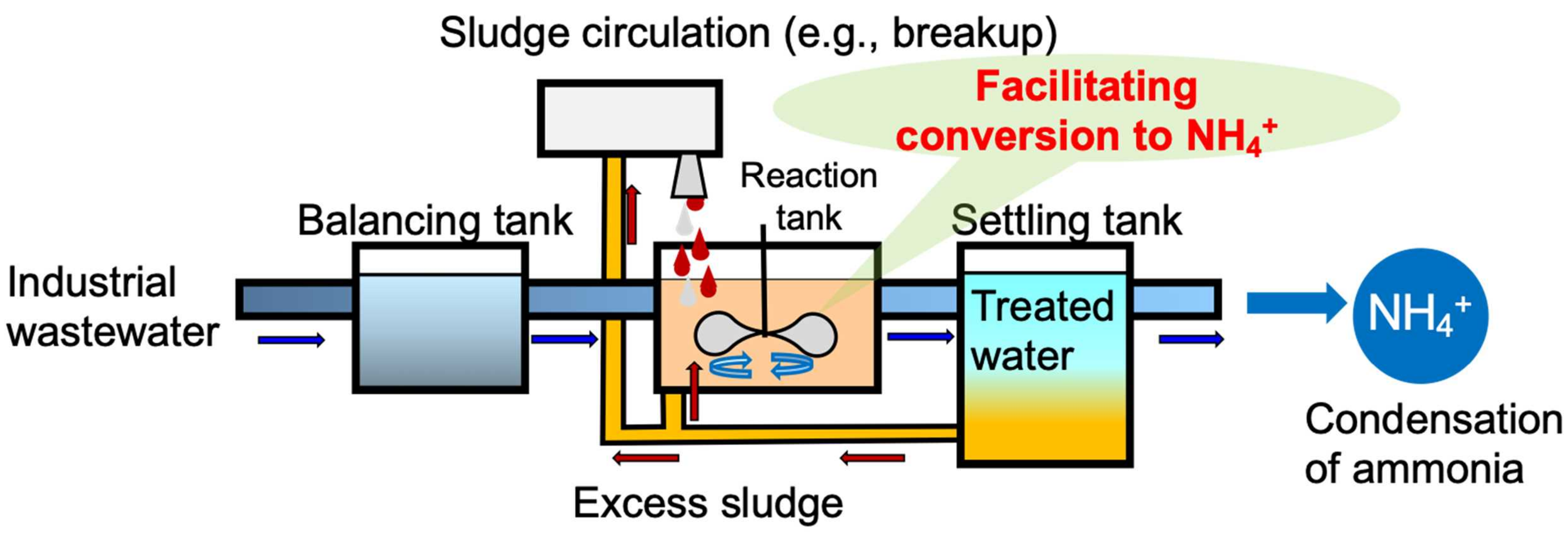
Point ②
Biogas energy acquisition from anaerobic digestion of wastewater
⇳
Challenge ②
- Unsuitableness for dilute wastewater
- High susceptibility to contaminants

● 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)

● 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 (KHD)


Dr. Hori (AIST)


Prof. Terada (TUAT)

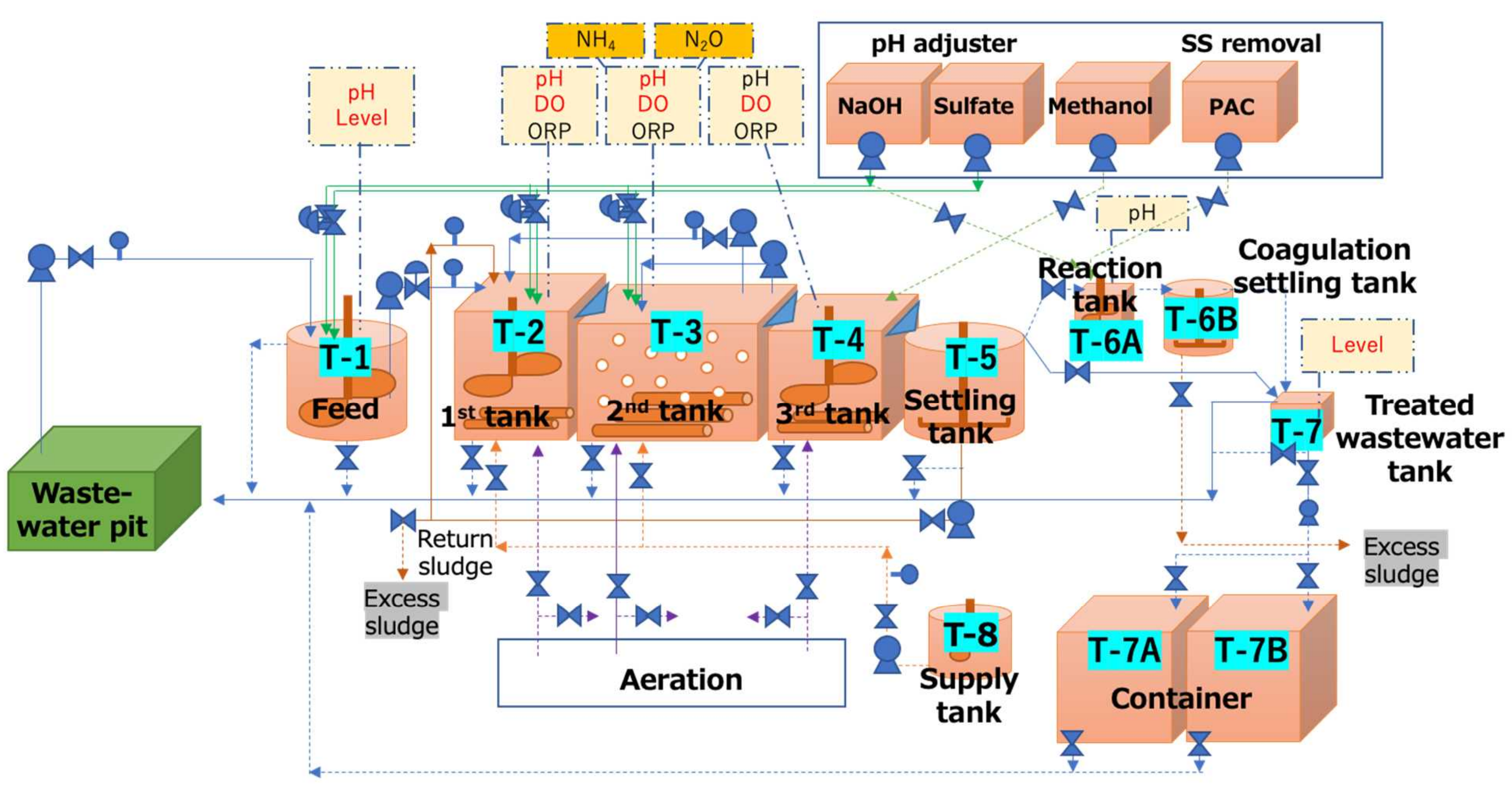

Prof. Fujiwara (Kyoto U)


Dr. Shimizu (KHD)

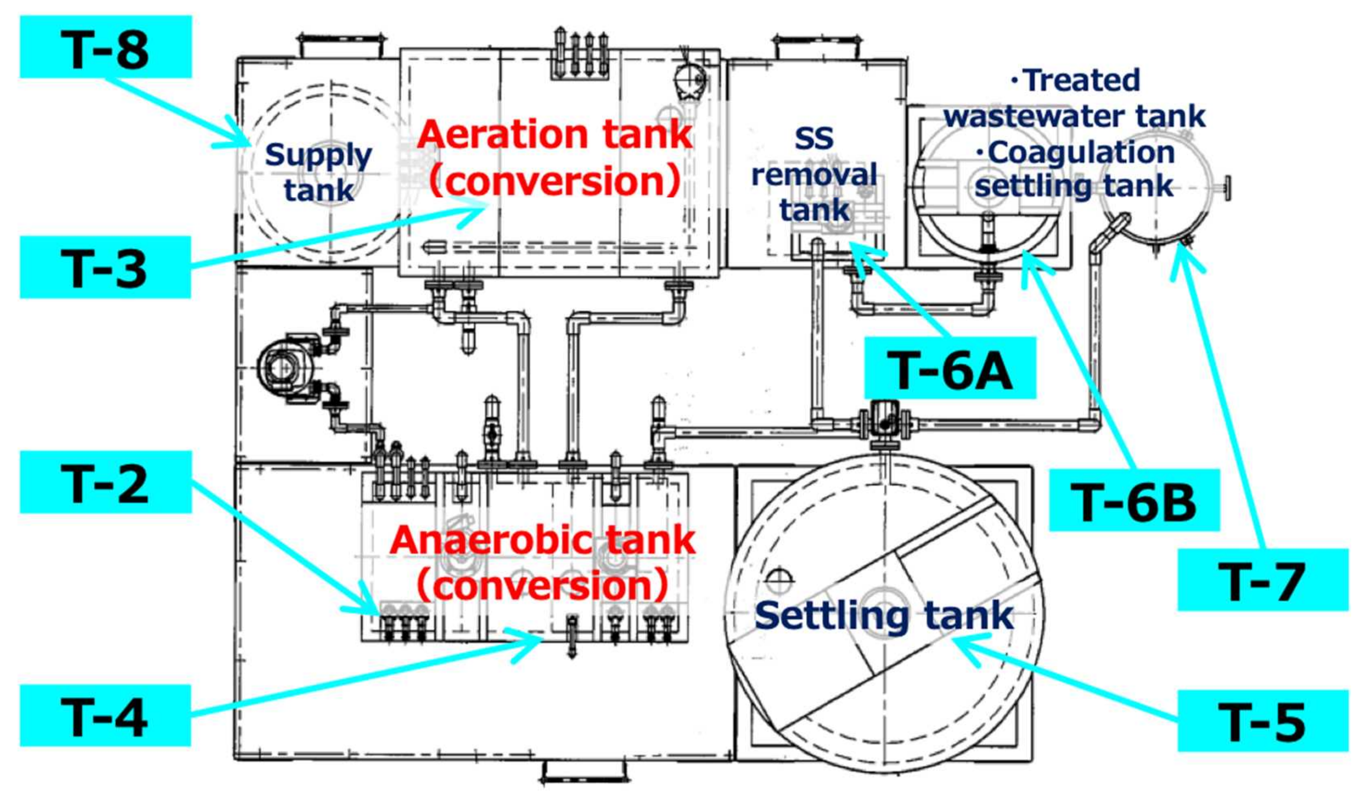
● Preparation for bench-scale demonstration

<Location>

<Material flow>



<Design chart>



<Outlooks> Bench-scale microaerobic conversion from fermentation wastewater N compounds to NH_4^+

● **Retrofit technology: Infrastructure for activated sludge method can be utilized for various wastewater**

No. A-9-7E

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

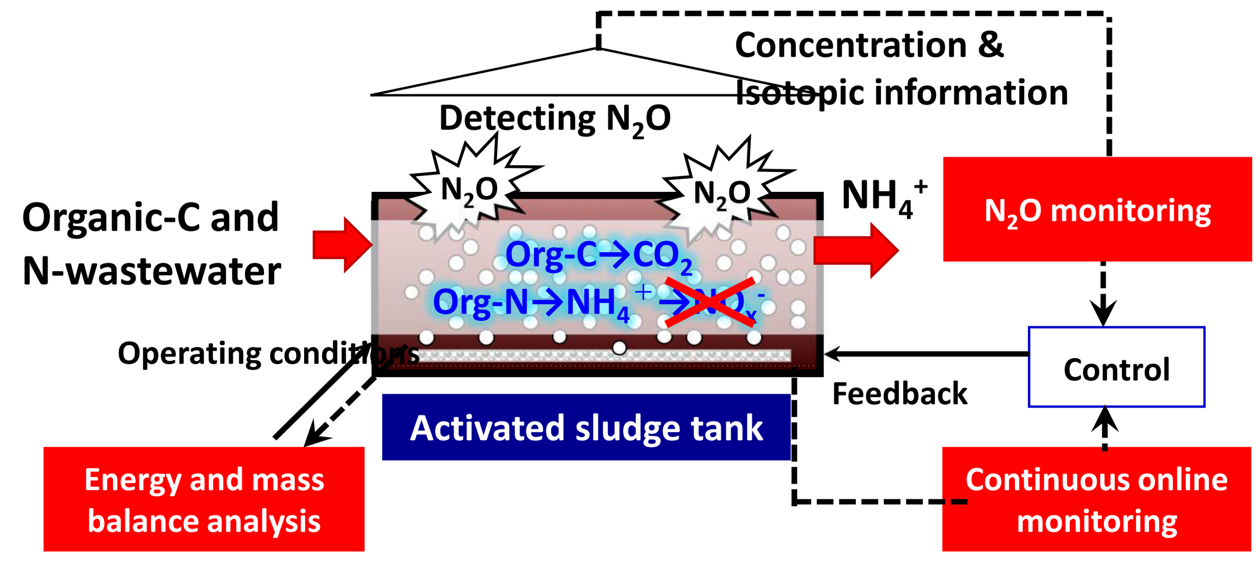
Contact: Prof. Akihiko Terada (Tokyo Univ. Agr.&Technol. (TUAT)), akte@cc.tuat.ac.jp

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

<Concept> By optimizing the operation factors of an activated sludge process, such as dissolved oxygen (DO) and pH, NH_4^+ recovery and sufficient organic carbon removal are expected to be achieved under nitrification inhibition and ammonification conditions. Also, N_2O emissions could be mitigated with nitrification inhibition.

<Advantages> A retrofittable process to adapt to current wastewater treatment plants by adjusting operating conditions.

Development strategy



Org-C removal and deterring nitrification

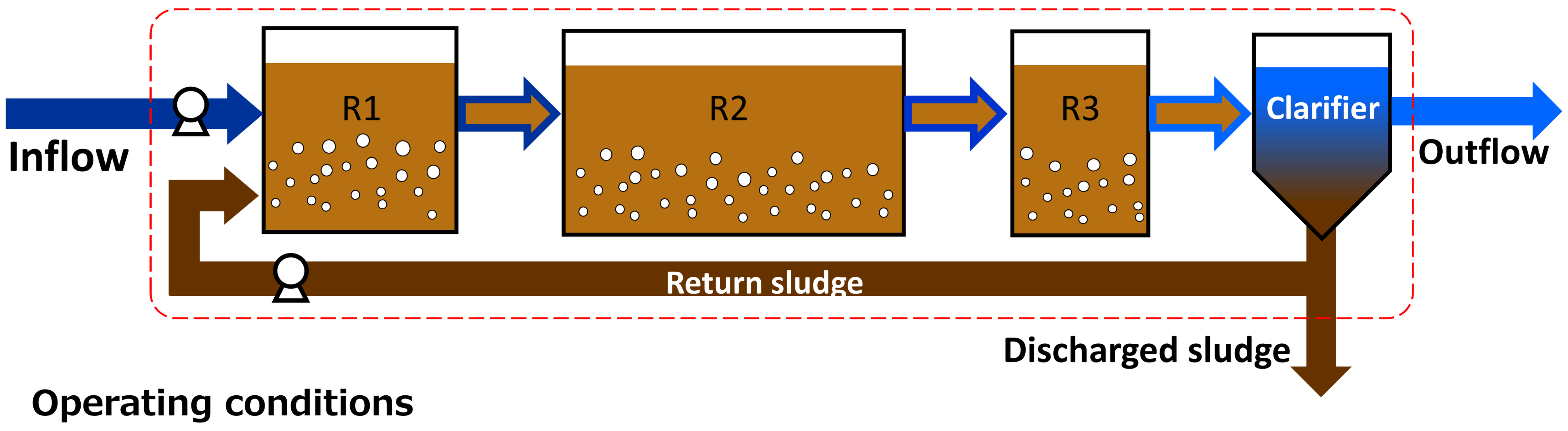
- High-rate Org-C removal
- High-rate NH_4^+conversion
- Preventing nitrification
- N_2O emission mitigation

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

For practical application	For stabilization
Extending (Kyoto U.)	**Retrofitting a process (TUAT)**
☐ Mass balance analysis	☐ Feedback technology by N_2O monitoring
☐ Optimum operation	☐ Granulation technology
☐ N_2O emission mechanisms	

Scaleup to a bench level

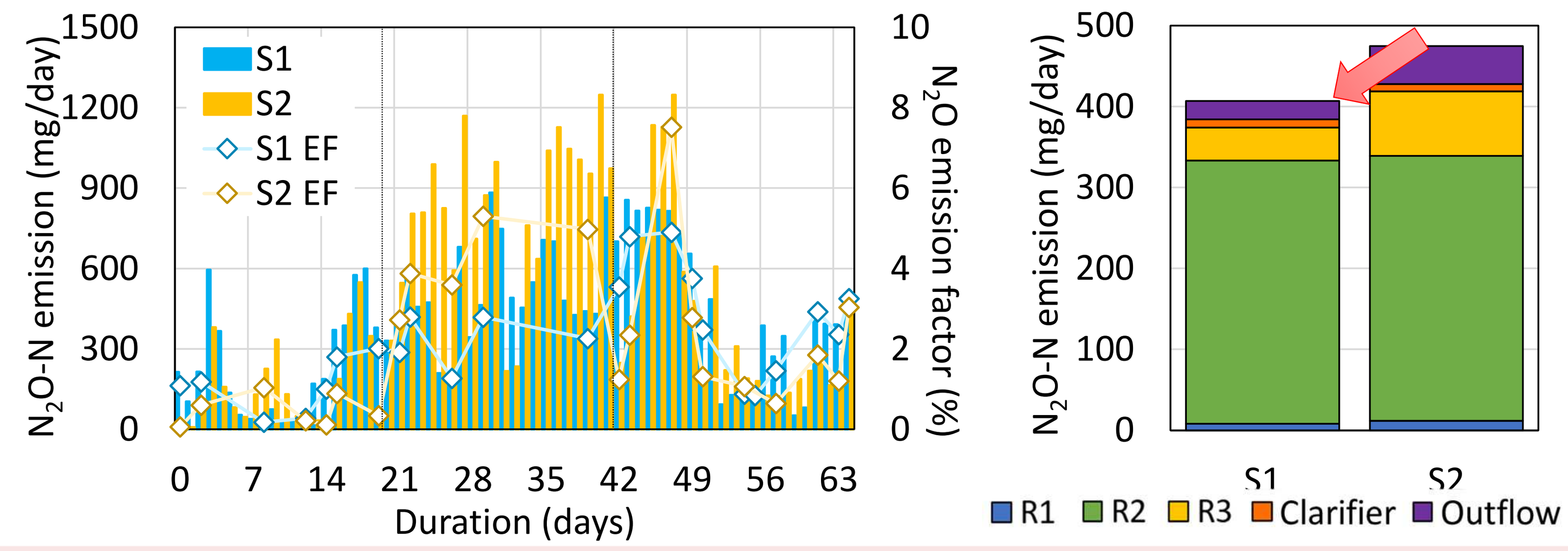
Operation of the 3-reactor system



Operating conditions

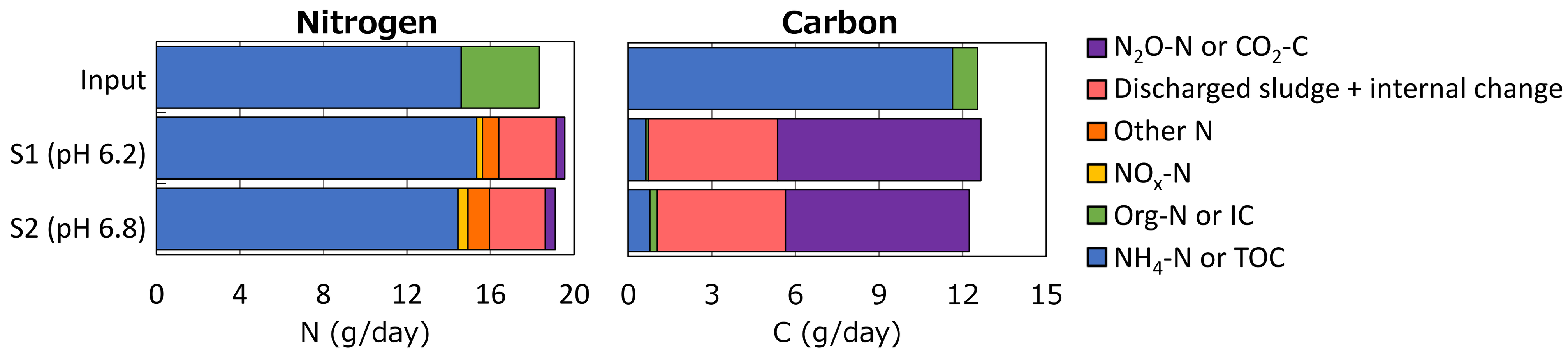
System	Duration (days)	pH control	DO control	SRT (days)	MLSS (mg/L)	HRT (hrs)	Synthesized wastewater
S1	64	R2 = 6.2	R2, R3 < 1 mg/L	10	3036 ± 793	30	TN = 600 mg/L NH_4-N = 480 mg/L TOC = 360 mg/L
S2		R2 = 6.8		9.6	3082 ± 831		

N_2O emissions



- **The N_2O emissions were 15% less in S1 (pH 6.2) than S2 (pH 6.8).** The emission factors were similar to activated sludge processes.
- With the occurrence of nitrification, R2s contributed the most to N_2O emission, followed by R3s.

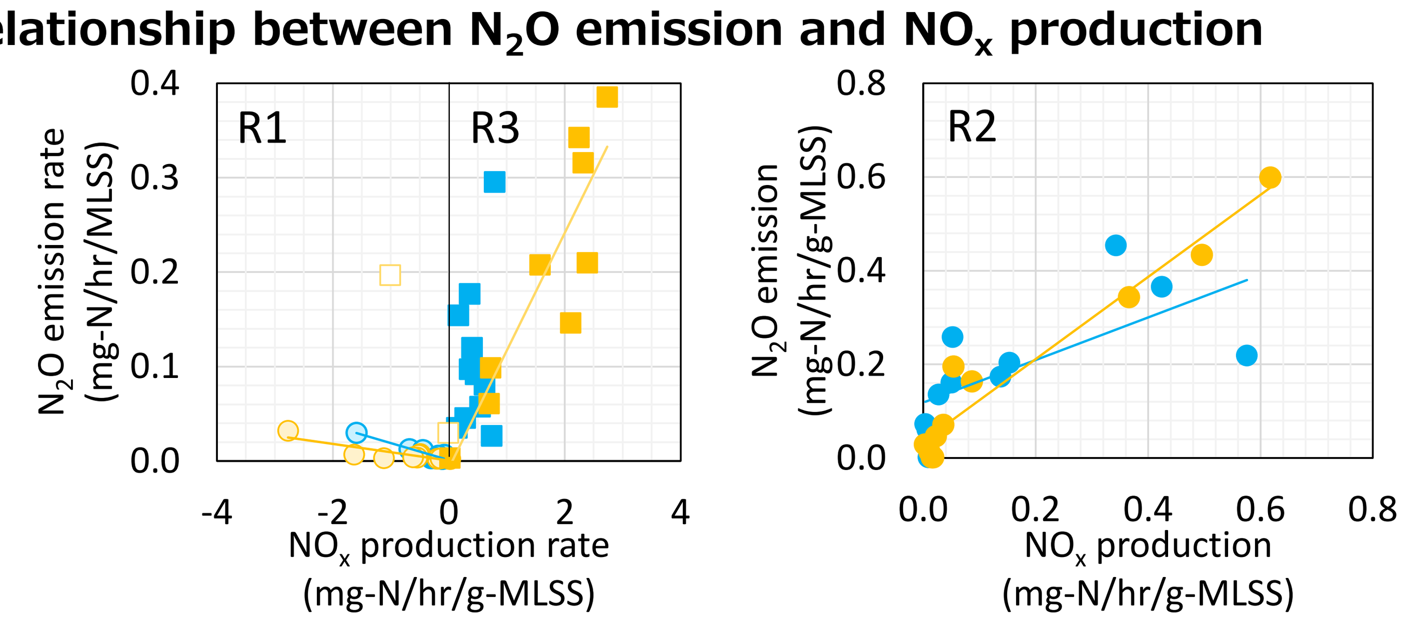
Mass balance



- **Under the microaerobic conditions, over 90% of total organic carbon (TOC) removal and over 80% of NH_4-N recovery were successfully achieved.**
- The main nitrogen loss was caused by discharged sludge in both systems.

Reference: Xinyi Zhou et al., Water Research, 247, 120780, 2023.

Relationship between N_2O emission and NO_x production

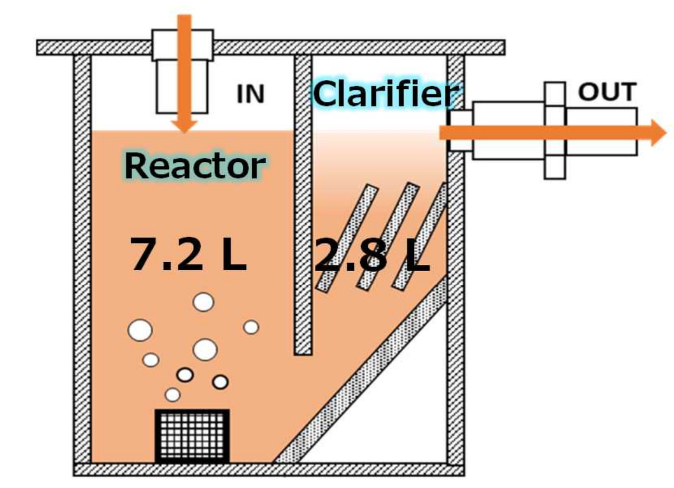


R1: Products of denitrification R3: Byproducts of nitrification

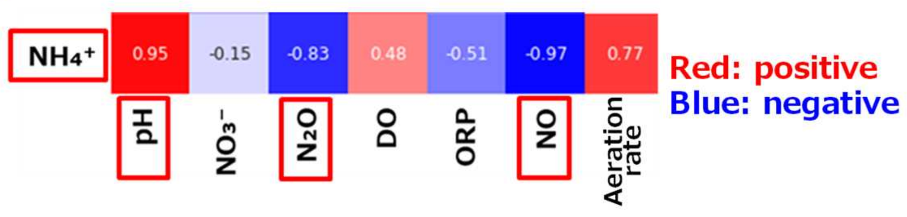
R2: N_2O was emitted through multiple pathways, leading to emission rates similar to NO_x production rates.

Online monitoring for a feedback technology

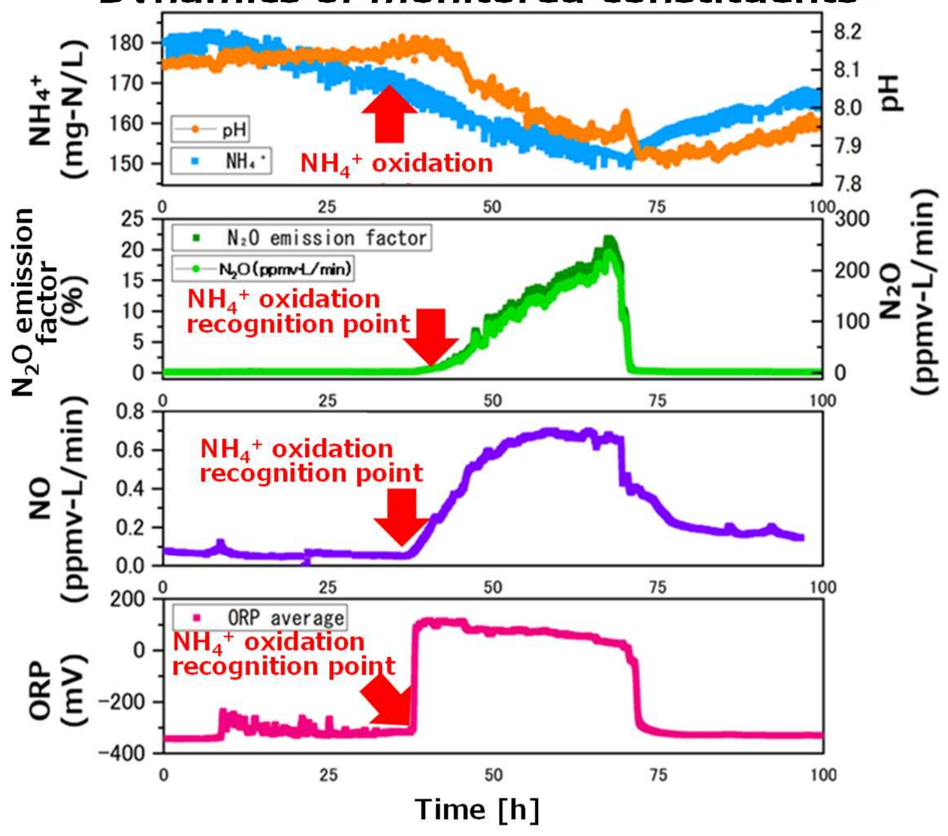
Continuous industrial wastewater supply



Correlation of online monitoring parameters with aeration rate



NH_4^+ suppression → enhancement: Dynamics of monitored constituents

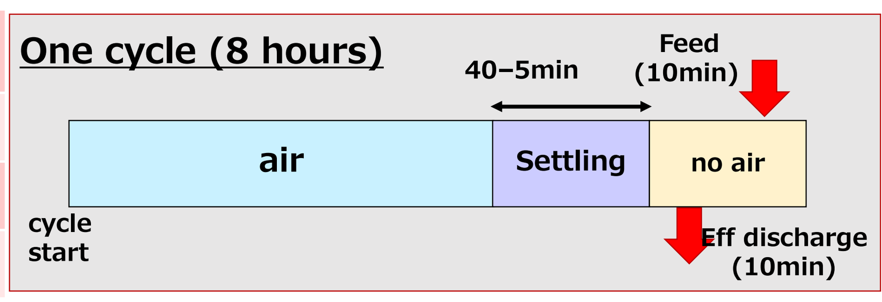


- Online monitoring of NO and N_2O gases can detect the initiation of unwanted NH_4^+ oxidation

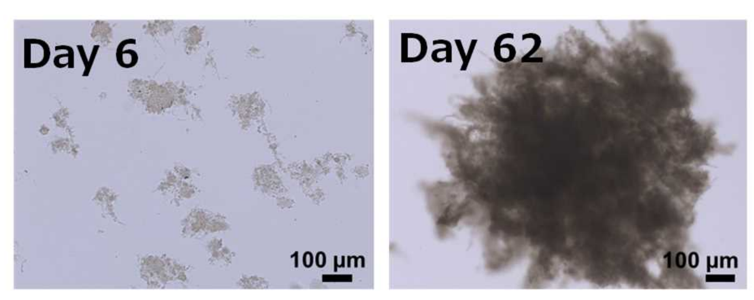
Formation of microbial aggregates (granules)

Formation of granules for improving sludge settleability (Semi-batch operation)

Inf./eff. exchange ratio [%]	50
HRT [day]	0.67
Inf. TOC conc. [mg-C/L]	300
Inf. total-N conc. [mg-N/L]	150

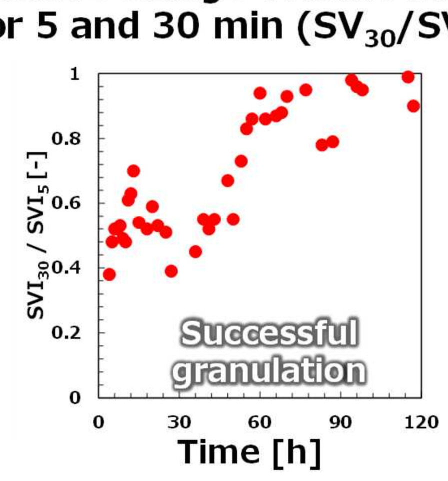


An air-lift reactor intermittently fed with real fermentation industry wastewater

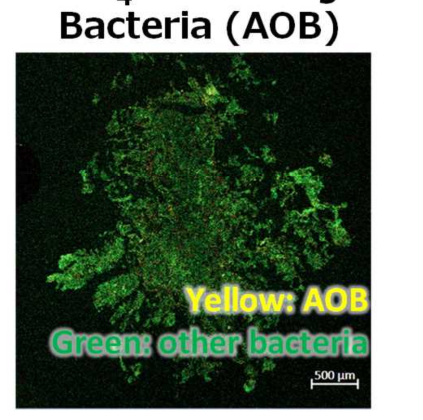


Formation of granules in a month

Relative sludge volume index for 5 and 30 min (SV_{30}/SV_5)



Prevention of NH_4^+-oxidizing Bacteria (AOB)



- Semi-batch wastewater supply allowed granular sludge formation
- Granulation resulted in high settleability and high NH_4^+ retention

<Outlooks> Assistance in a bench-scale reactor operation for NH_4^+ conversion/retention from fermentation wastewater

- Determination of operation conditions for stable TOC removal, NH_4^+ conversion/retention, and N_2O mitigation
- Development of an online monitoring/feedback technology to suppress abrupt unwanted NH_4^+ oxidation
- Formation of granular sludge to suppress discharge of unsettled suspended sludge and to facilitate NH_4^+ conversion/retention
- Application of the developed technologies to other wastewaters

No. A-13-8E

PJ : Innovative circular technologies for harmful nitrogen compounds

Theme: Wastewater N compounds to NH_4^+-high NH_4^+-tolerant AnMBR system

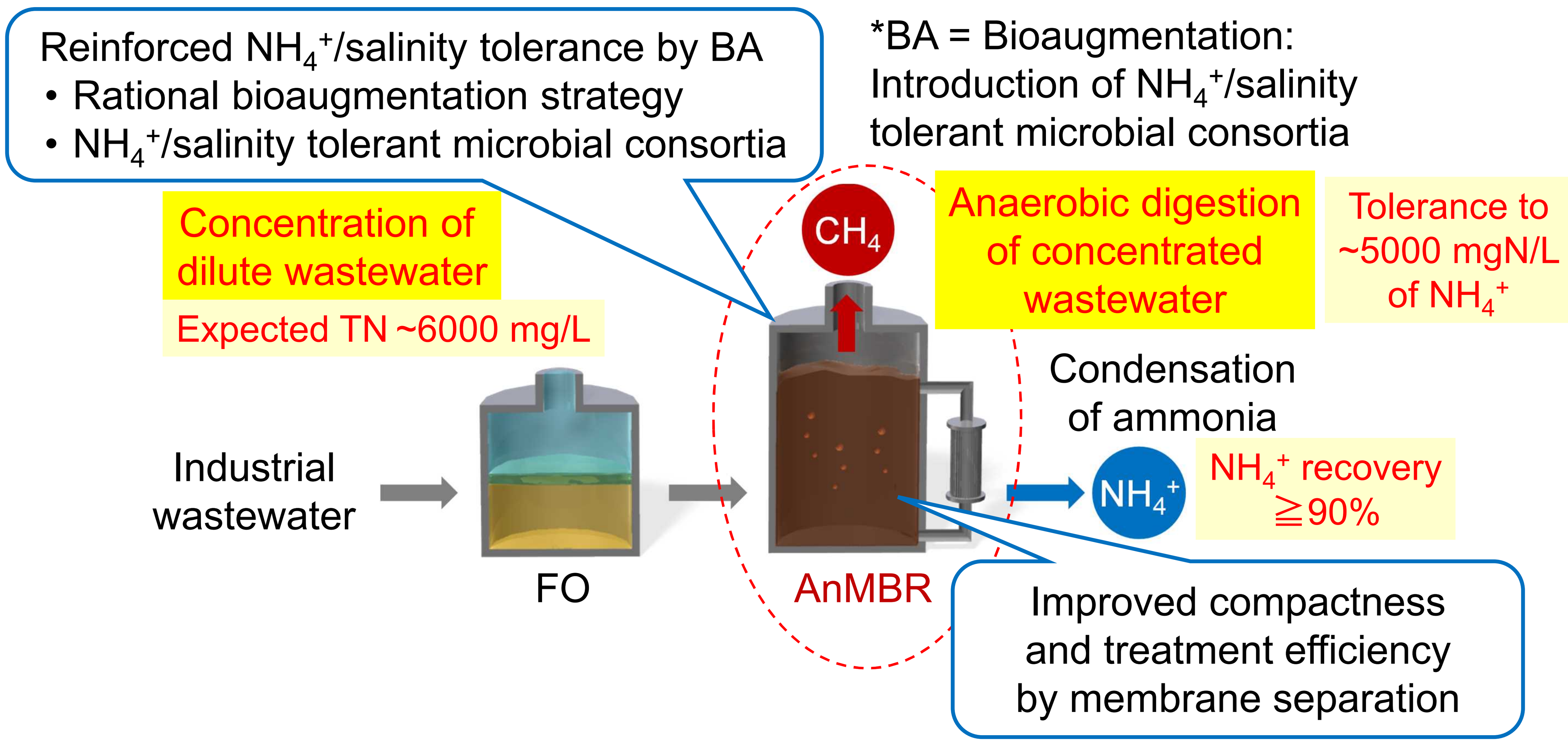
Organization: Osaka Univ., Hiroshima Univ., Kobe Univ.

Contact: Prof. Michihiko Ike (OU), ike@see.eng.osaka-u.ac.jp

<Concept> Efficient conversion of organic carbon and nitrogen in concentrated wastewater by forward osmosis (FO) to CH_4 and NH_4^+, respectively, by anaerobic digestion in anaerobic membrane bioreactor (AnMBR) with the help of bioaugmentation (BA) with highly tolerant microbial consortia

<Advantages> Compactness, simultaneous NH_3 and CH_4 recovery, applicability to harsh conditions

● Anaerobic Membrane Bioreactor (AnMBR)

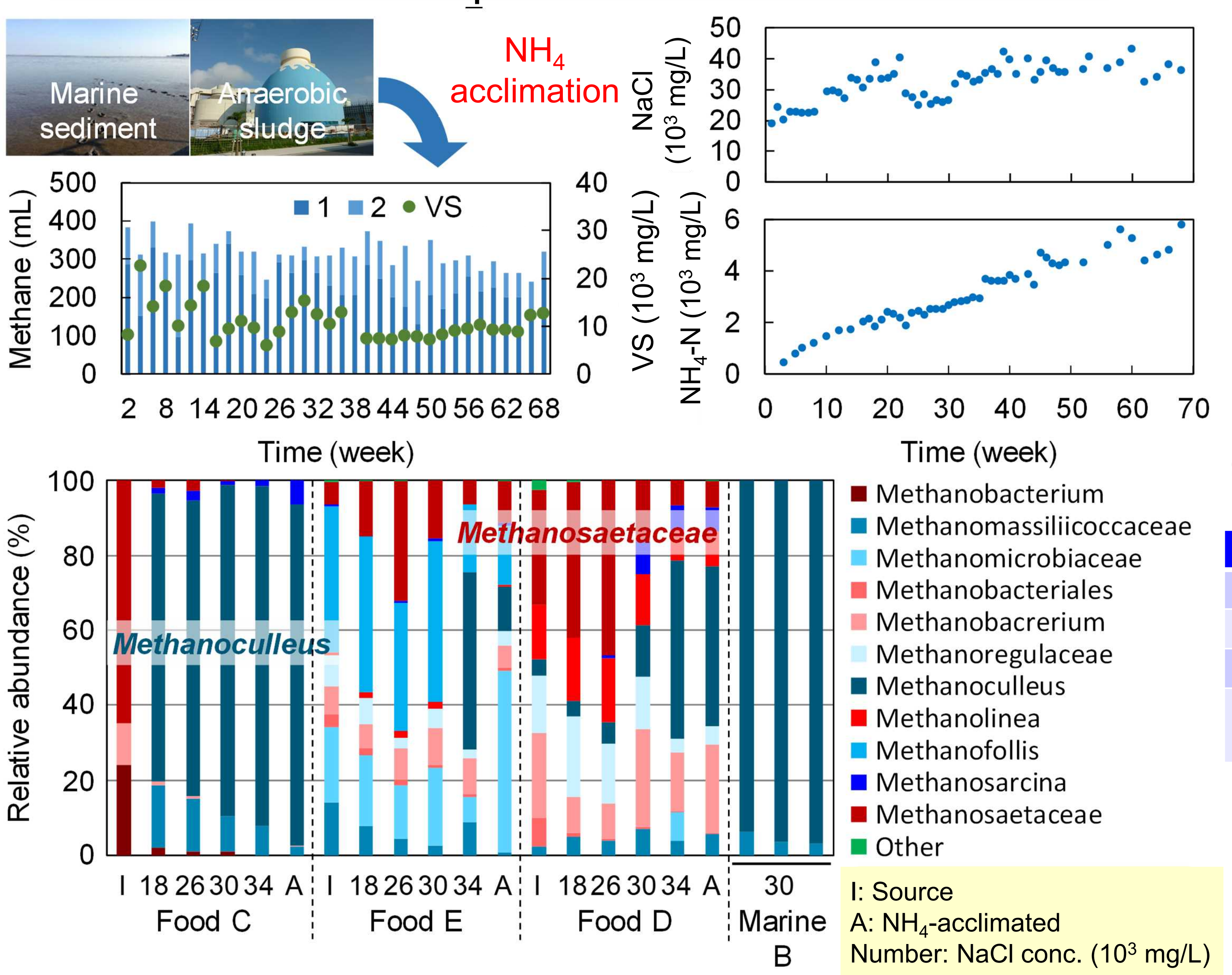


● R&D Items and Organization

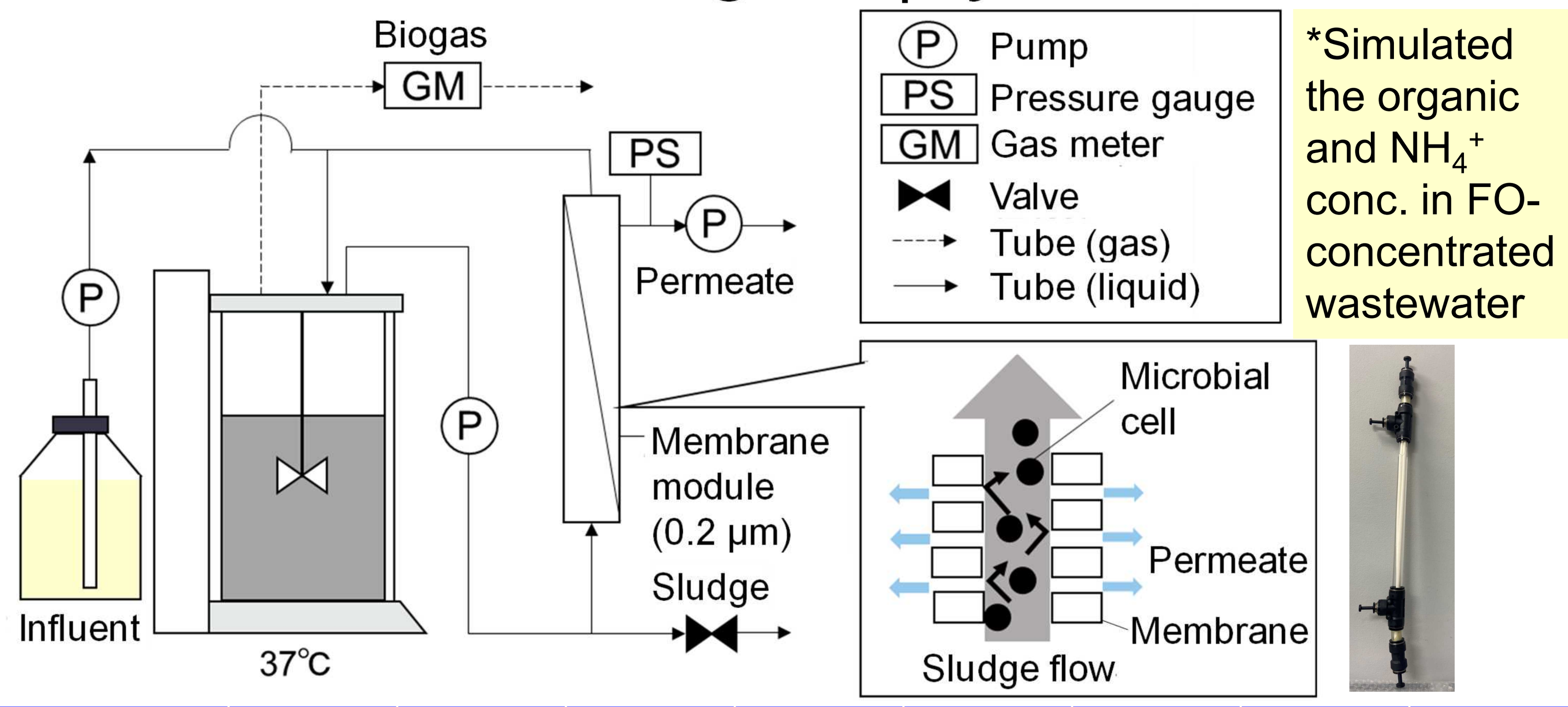
- Development of bioaugmentation technology of highly NH_4^+-tolerant microbial consortia (Osaka U)
- Construction of highly NH_4^+-tolerant microbial consortia (Hiroshima U)
- Establishment of efficient AnMBR operating methods (Kobe U)

Prof. Ike (Osaka U) | Prof. Tajima (Hiroshima U) | Prof. Ihara (Kobe U)

● Construction of NH_4^+ tolerant microbial consortia

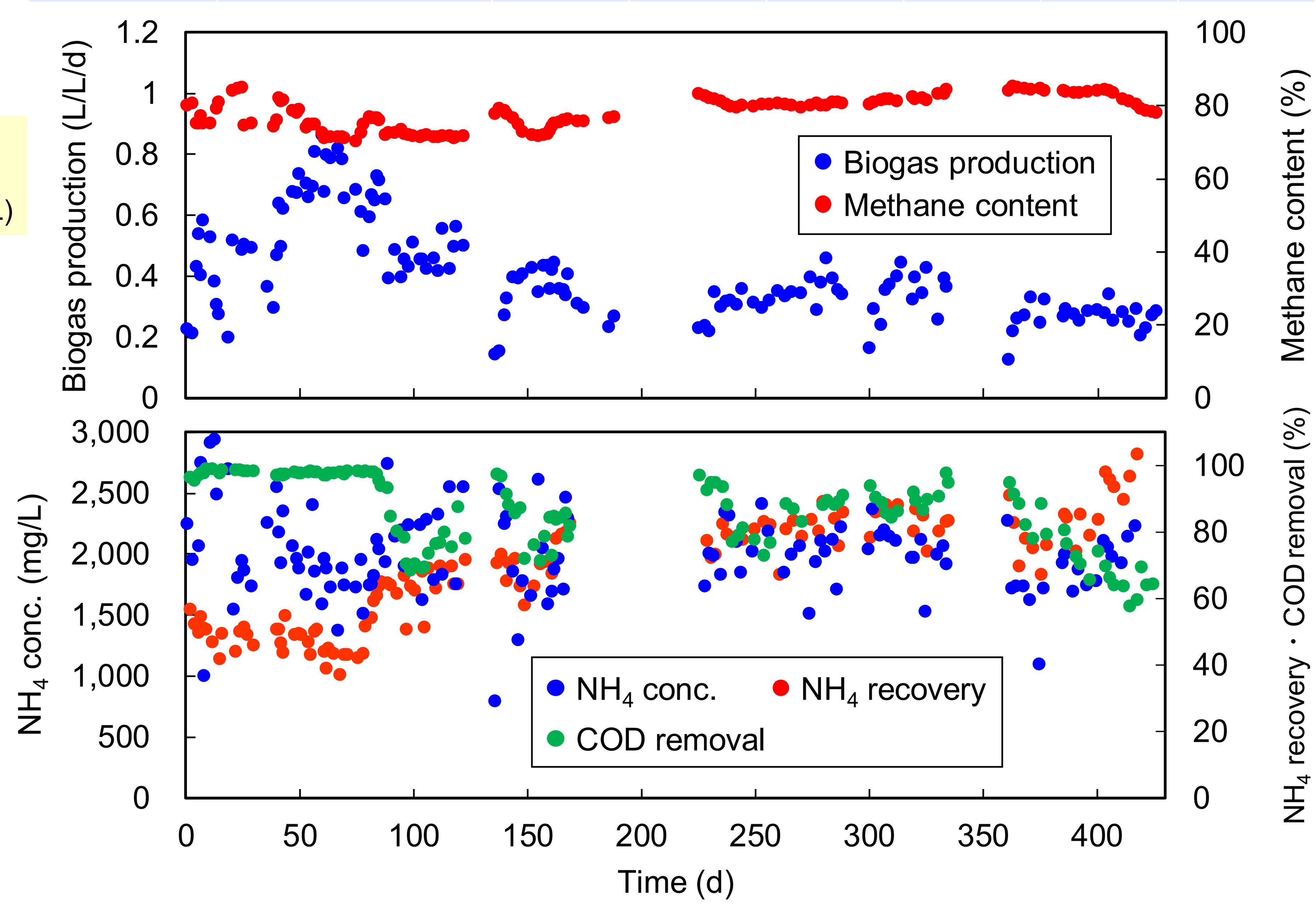


● AnMBR treatment of high NH_4-synthetic wastewater*



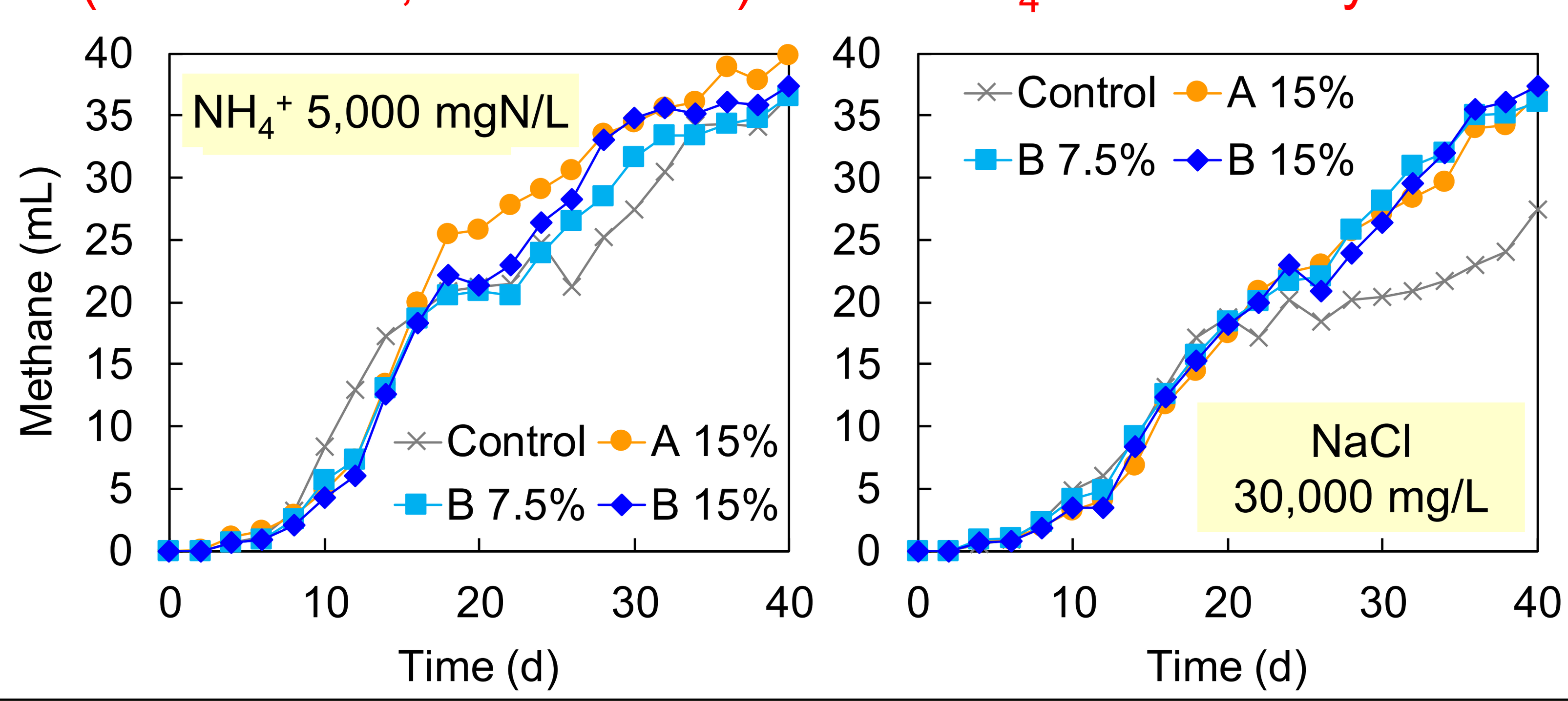
*Simulated the organic and NH_4^+ conc. in FO-concentrated wastewater

	RUN1	RUN2	RUN3	RUN4	–	RUN5	–	RUN6
Time (d)	1-34	35-77	78-159	160-248	249-269	270-371	372-397	398-426
HRT (d)	5	3	3	5	5	5	5	5
COD (mg/L)	6120							
NH_4^+ (mg/L)	1,170		1,800	2,180	2,180-2,400	2,400	2,400-2,800	2,800



● Confirmation bioaugmentation effects

Bioaugmentation with marine sediment-derived tolerant consortia A and B (A: Marine A, B: Marine B) under NH_4^+ and salinity inhibition



【Potential Applications and Effects】

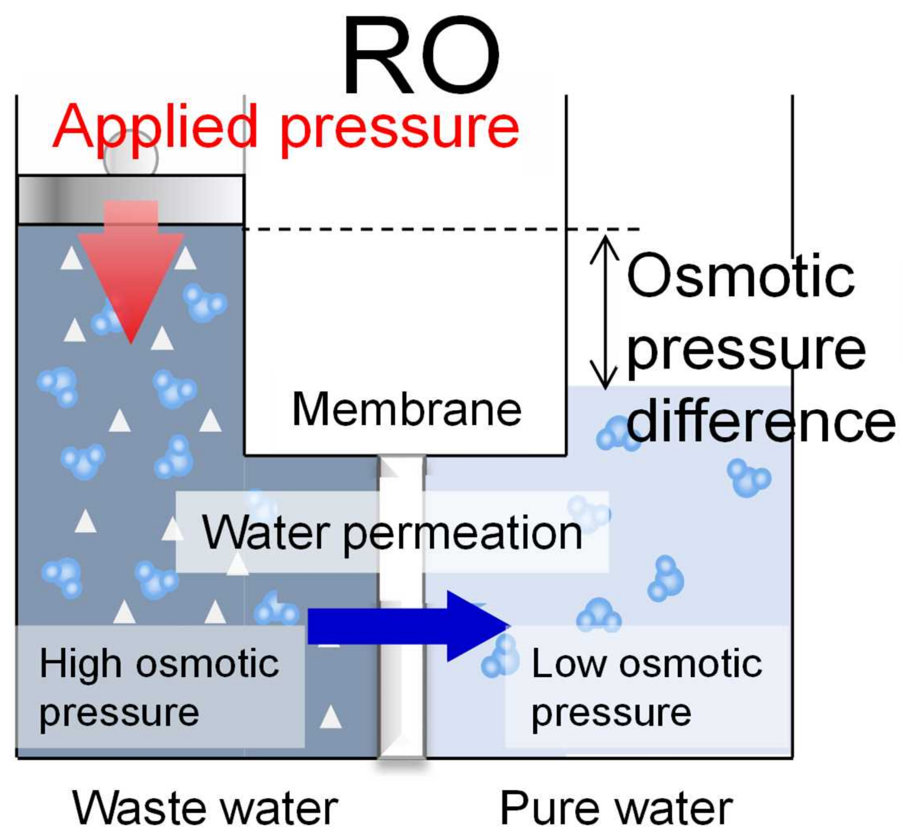
Municipal and industrial wastewater treatment facilities

Realization of highly efficient treatment and simultaneous recovery of NH_3 and CH_4 under inhibitory conditions in a compact facility by combining FO concentration, AnMBR and bioaugmentation.

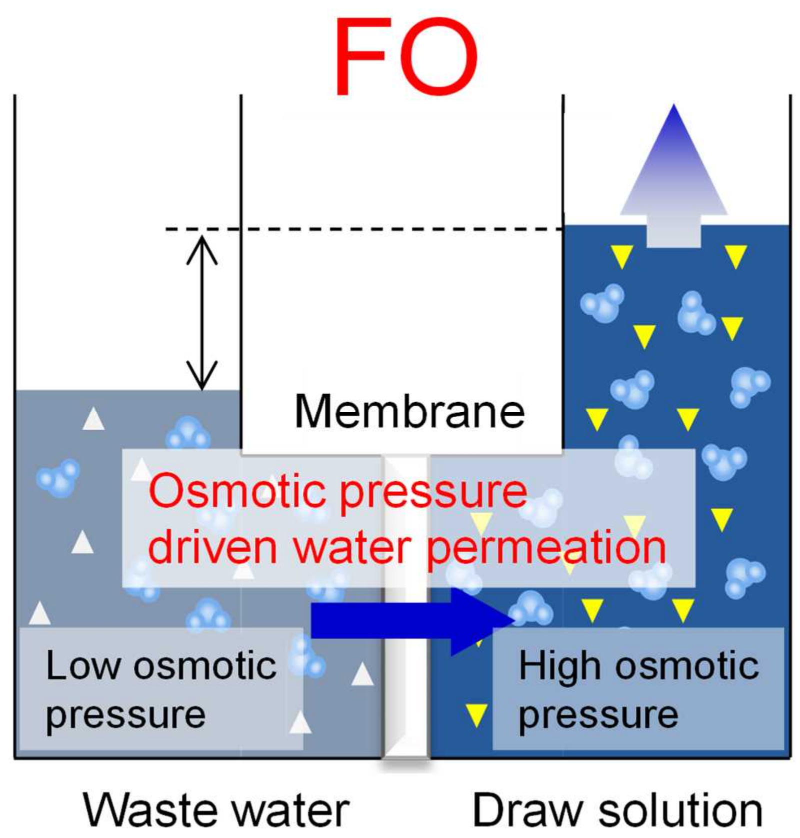
No. A-13-9E
PJ : Innovative circular technologies for harmful nitrogen compounds
Theme: NH_4 separation and concentration – Concentration by forward osmosis
Organization: Kobe Univ., Toyobo MC Corp., Waseda Univ.
Contact: Prof. Hideto Matsuyama (Kobe Univ.) , matuyama@kobe-u.ac.jp

<Concept> Concentrate waste water by a forward osmosis membrane process driven by osmotic pressure differences
<Advantages> Low energy consumption due to the spontaneous water permeation

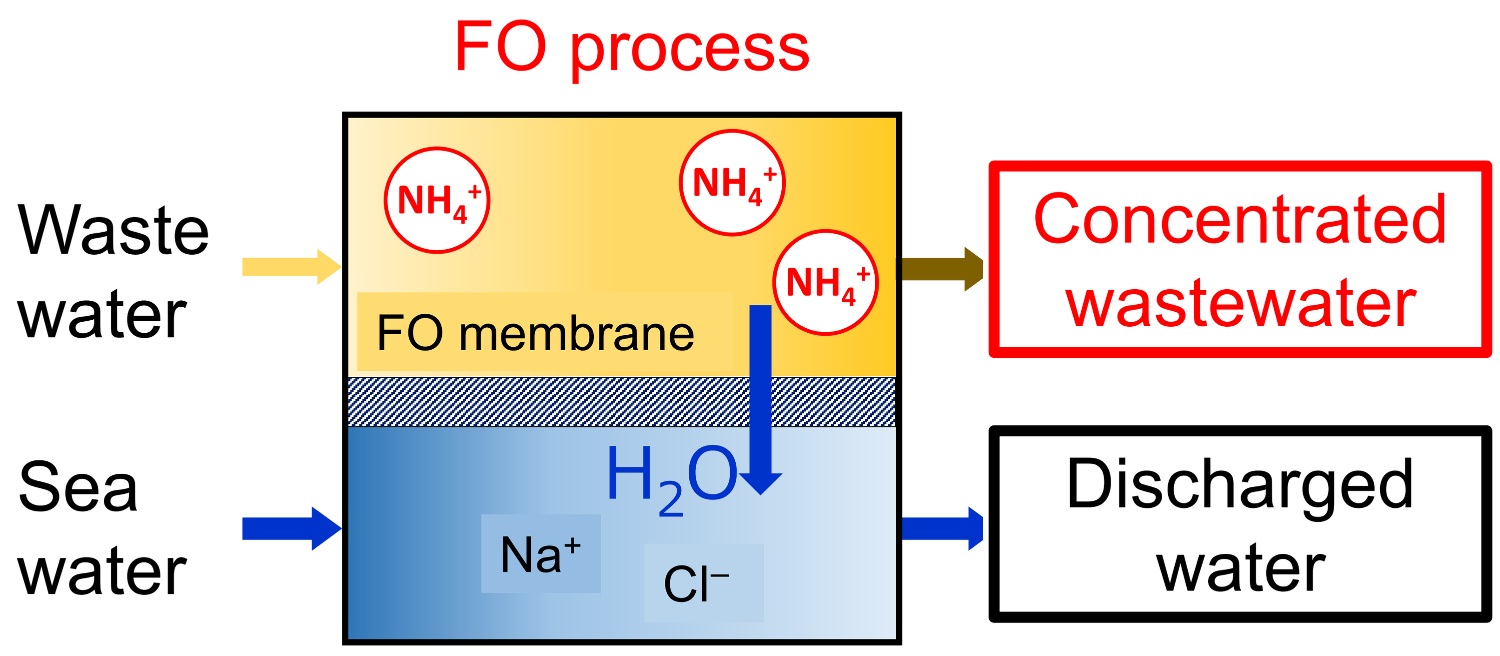
Forward osmosis (FO) Process



Require high pressure for water permeation
→High energy consumption



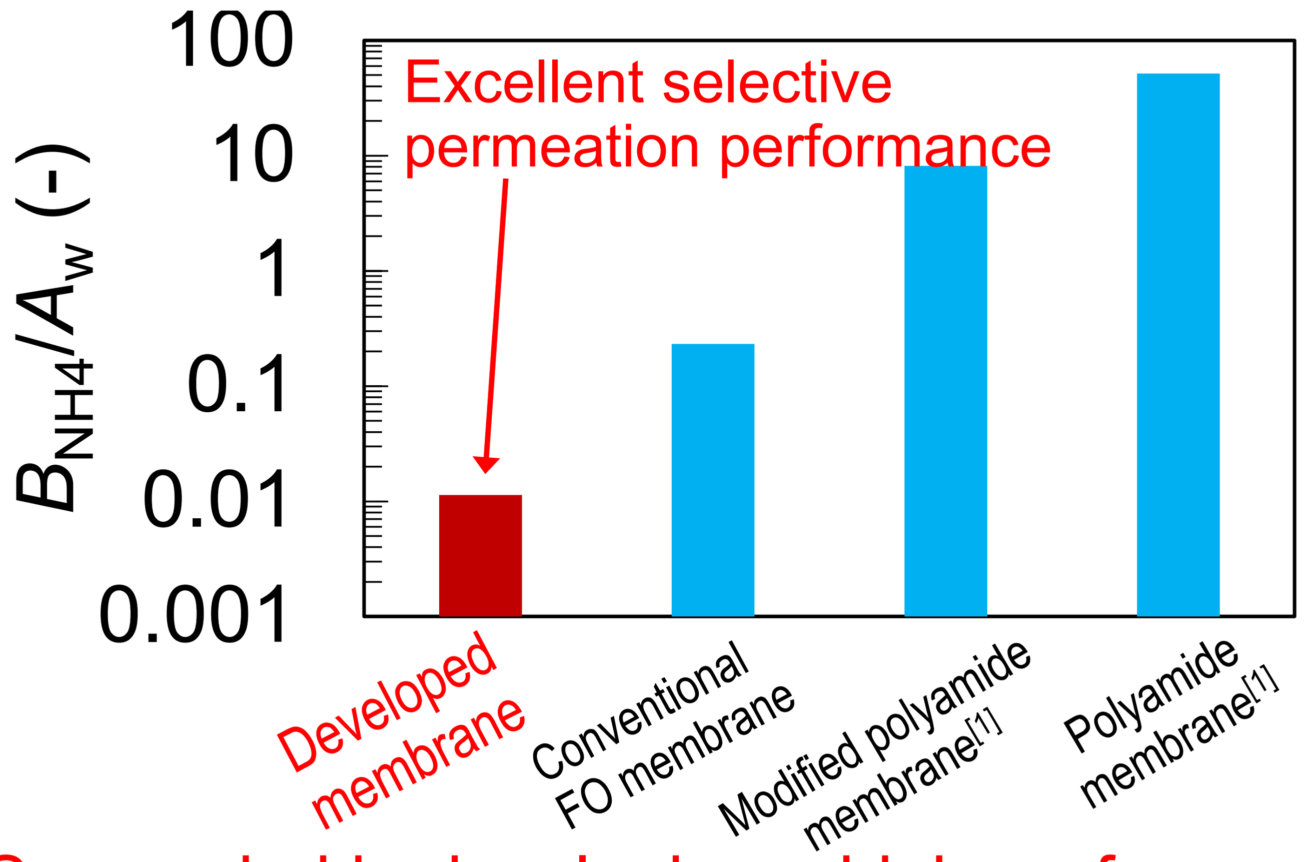
Spontaneous water permeation based on osmotic pressure
→Low energy consumption



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

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

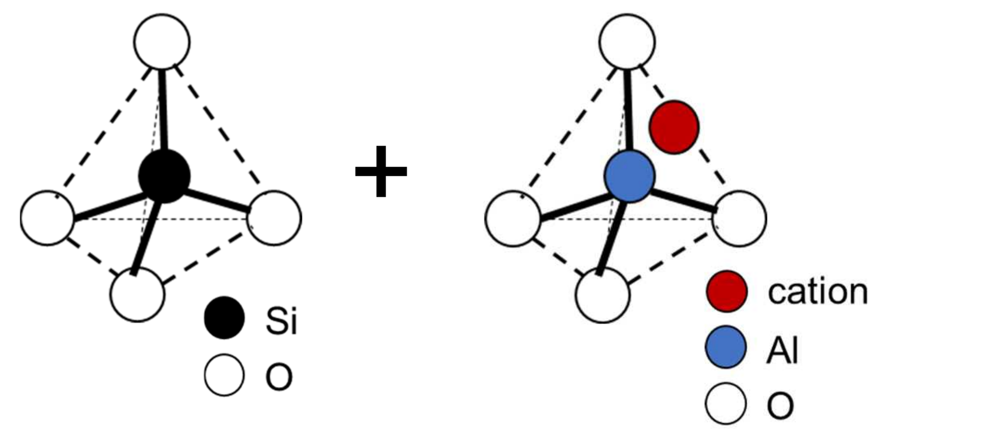
Development of high-performance polymer FO membrane



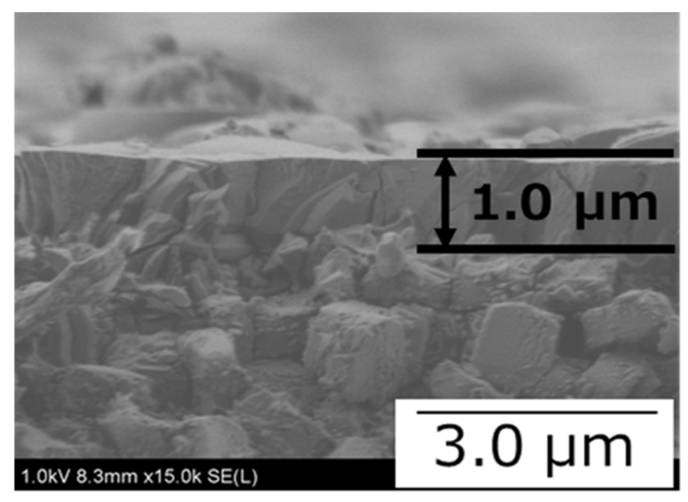
Succeeded in developing a high-performance FO membrane by controlling the membrane structure

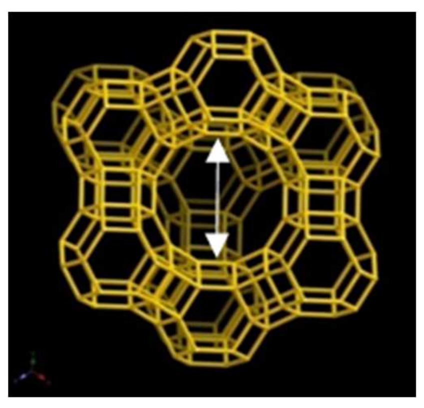
[1]X. Bao *et al.*, *J. Membr. Sci.*, **573** 135 (2019)

Development of Zeolite FO membrane for high-temperature process



Zeolite: Crystalline aluminosilicate materials





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

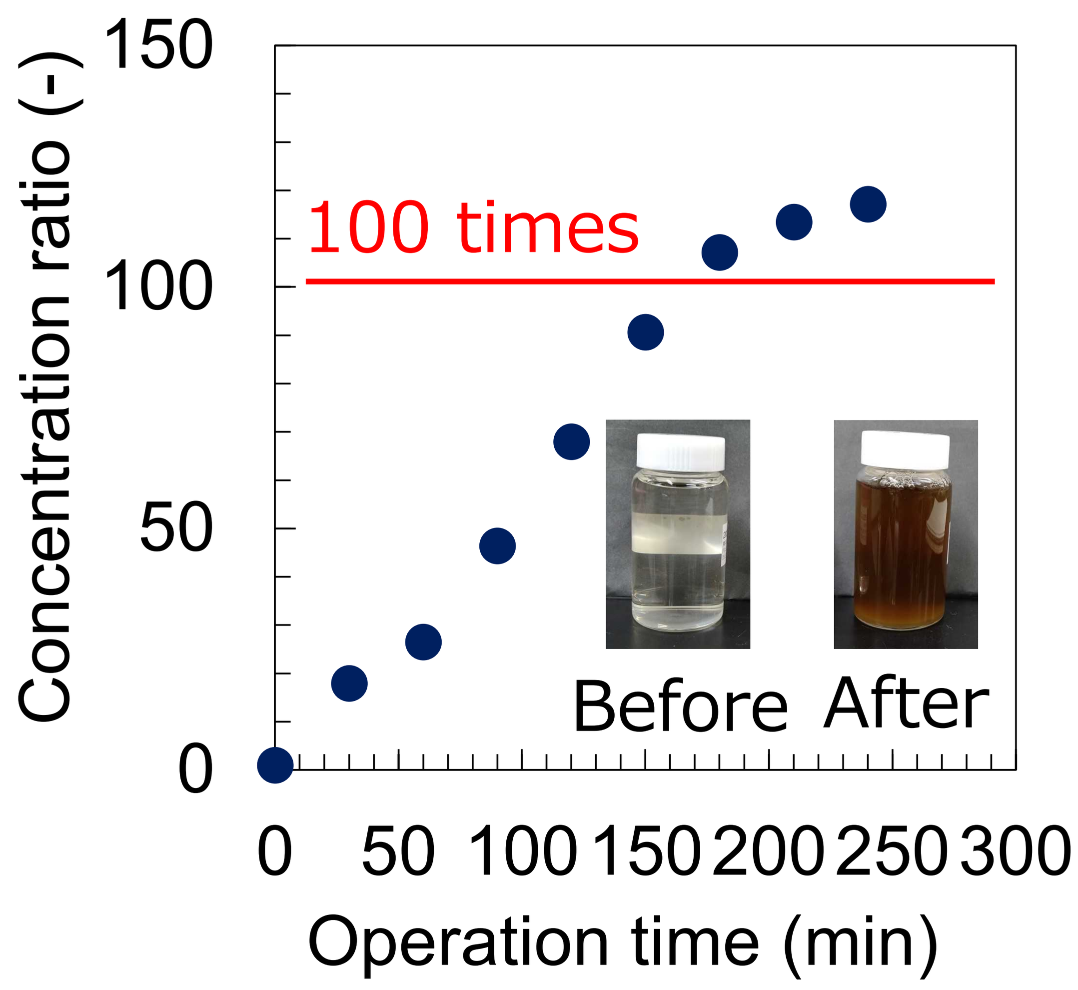
Suit to use for high-temperature wastewater

- ✓ Hydrophilic zeolites without cation exchange sites
- ✓ Surface modification to apply positive charge

Succeed in developing zeolite membrane to concentrate NH_4^+

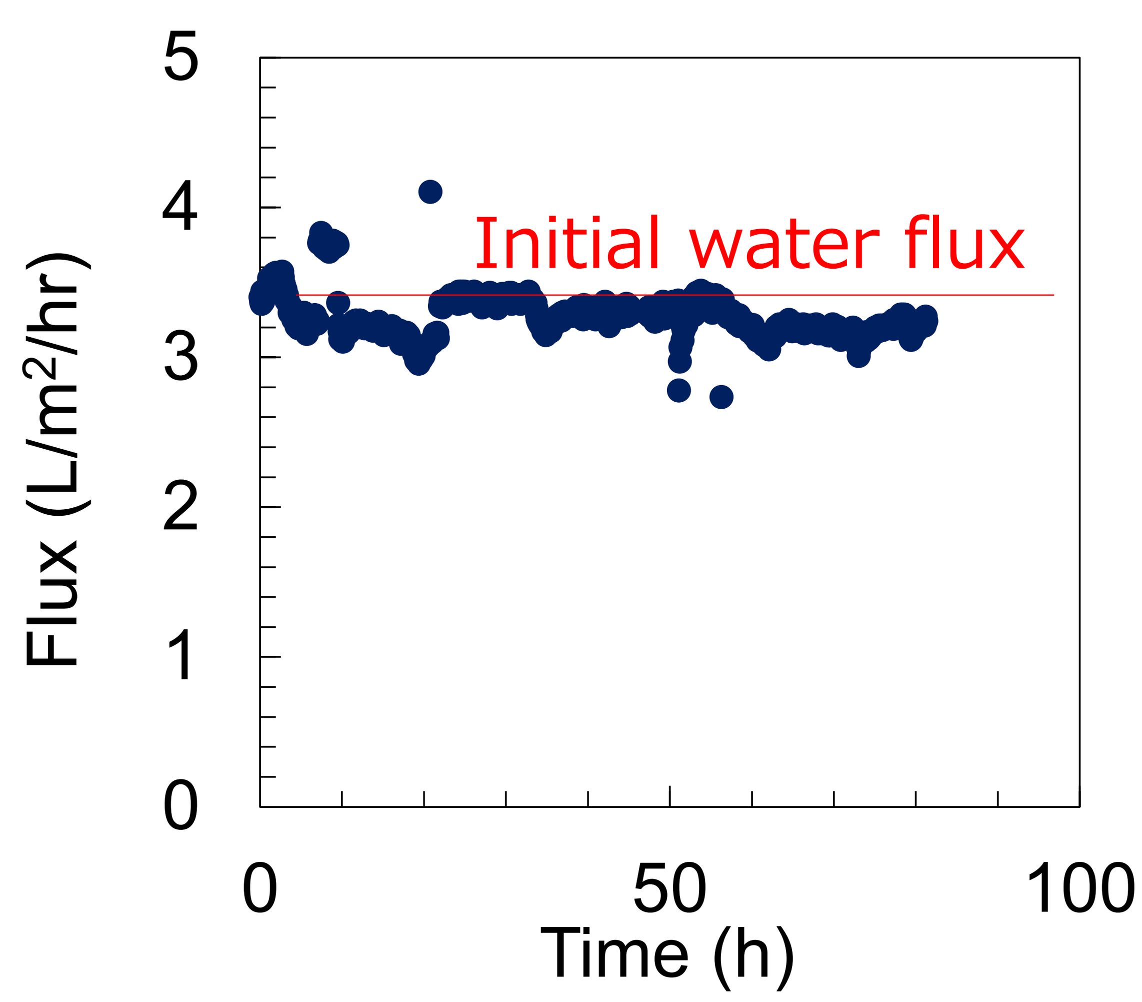
Bench scale FO test using actual wastewater

Equipped with three 5-inch FO modules (each 60 m^2)



Concentrated more than 100 times by volume using bench scale modules at FS inlet flow rate of 2 L/min (=2.88 ton/day)

Anti-fouling performance



No serious membrane fouling was observed for 80 h

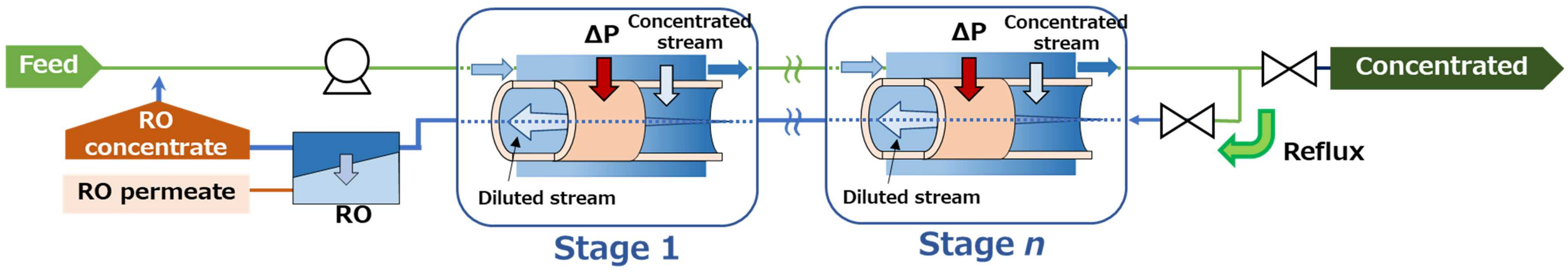
【Potential Applications and effects】
Efficient concentration of NH_4^+ from wastewater such as industrial wastewater and sewage
Large scale, energy-saving, 10-100 times concentration to T-N 4000 ppm from very dilute wastewater

No : A-13-10E
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

<Concept> Hybrid brine concentration (BC) - reverse osmosis (RO) process for simultaneous NH_4^+ concentration and recovery and minimal liquid discharge of wastewater
<Advantages> More efficient NH_4^+ concentration and clean water production

◆Establishment of NH_4-N concentration process by BC method and clean water recovery by RO method

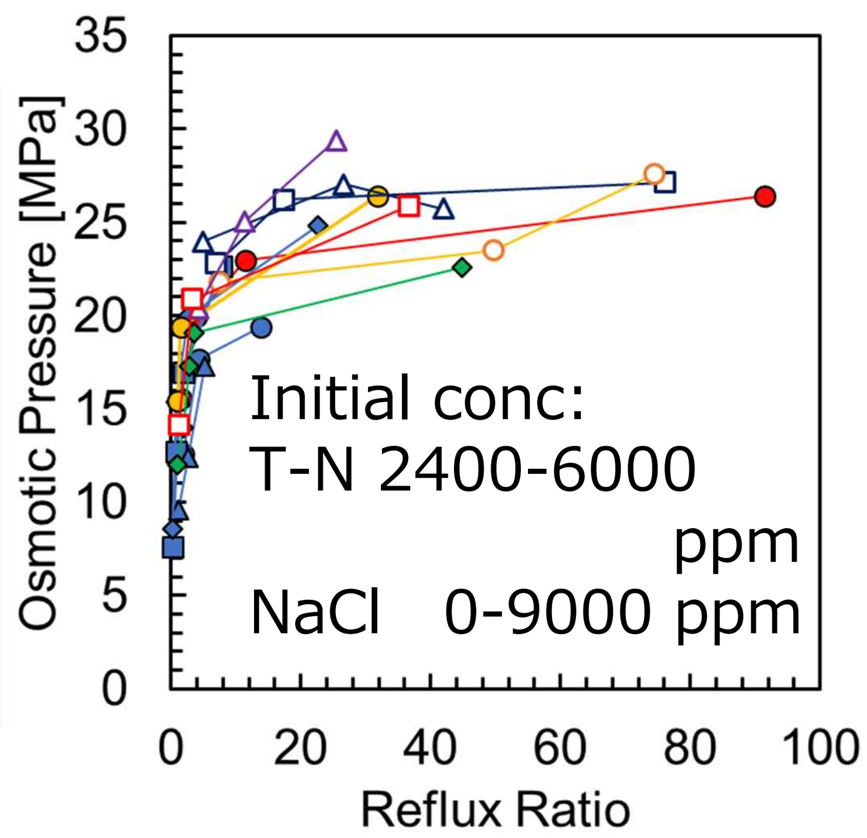


■ Brine concentration (BC)
Concentration method by osmotically assisted reverse osmosis using dense membrane

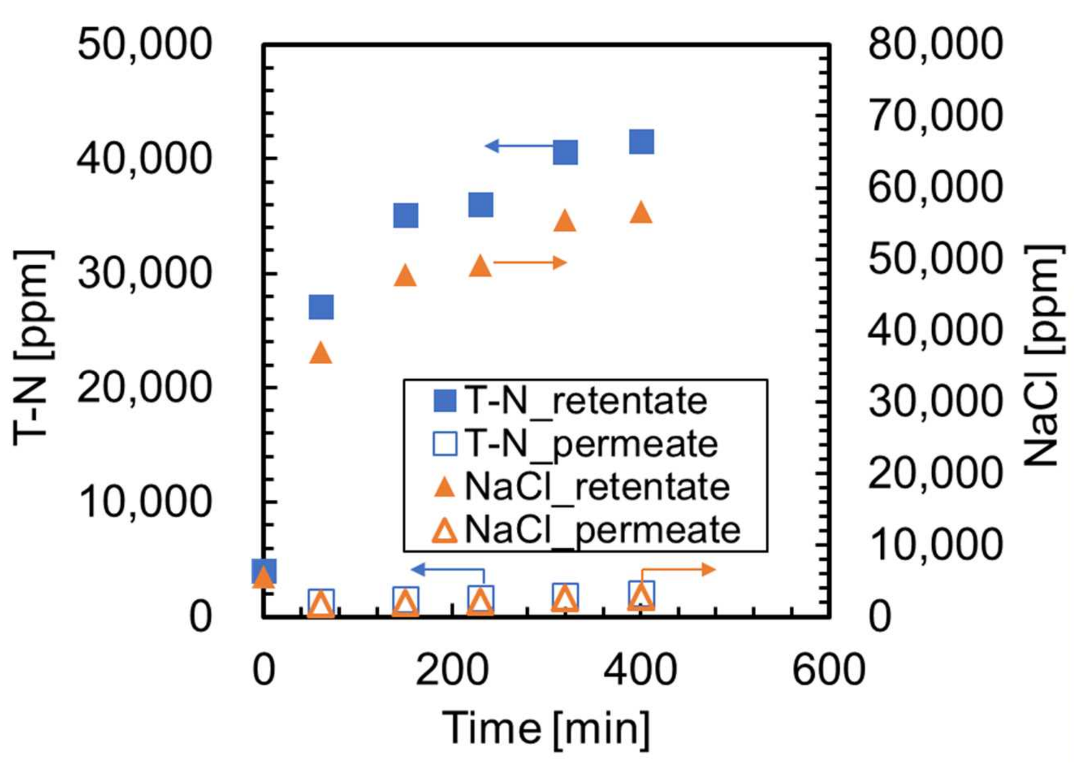
■ Hybrid membrane processes (BC+RO)
Effective method to enhance concentration of nutrient and recovery of water from waste streams and can regulate the amount of environmental discharge

【Model wastewater】

✓**Osmotic pressure (concentration degree) increases with increasing reflux ratio**
✓**Osmotic pressure increases to around 30 MPa (85,000 ppm T-N)**



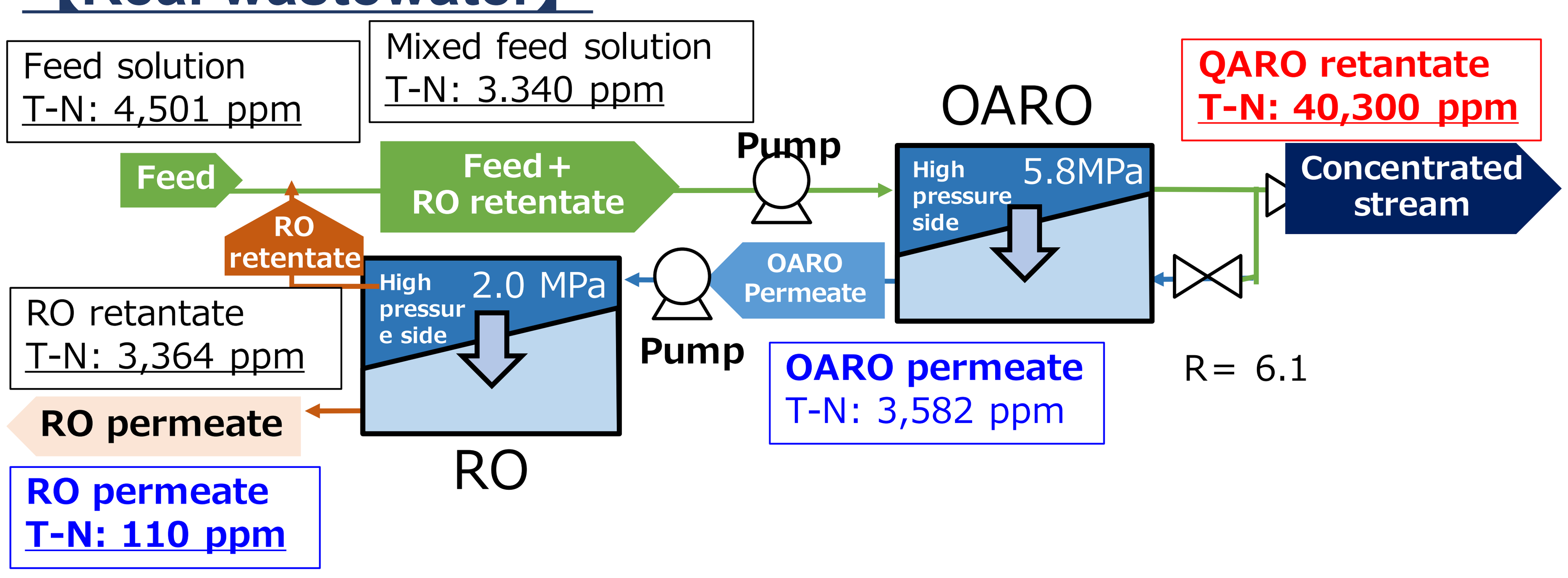
BC-ROハイブリッド膜プロセス

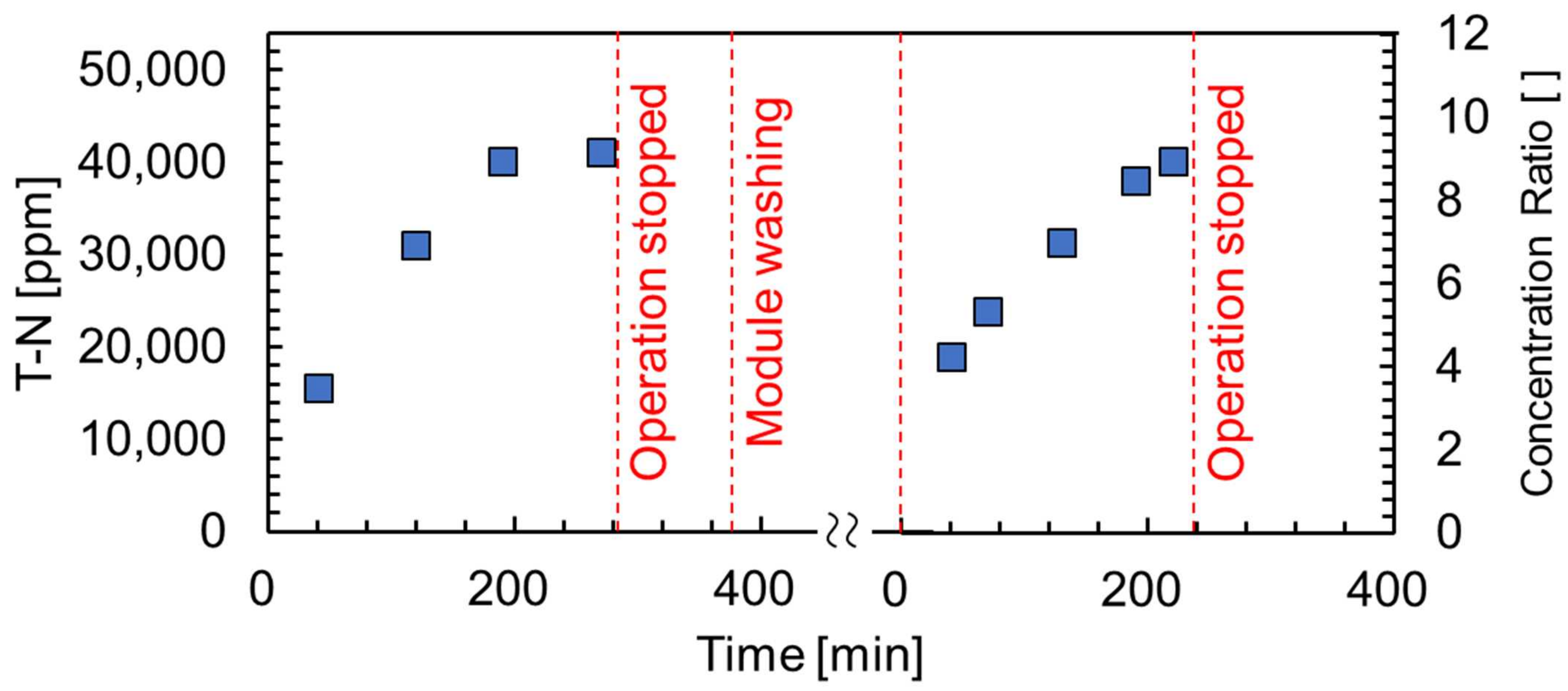


Initial conc : T-N 4,000 ppm, NaCl 5,460 ppm
BC : ΔP_{BC} = 6.5 MPa, R = 1.04
RO : ΔP_{RO} = 2.0 MPa

✓**BC-RO method enables efficient NH_4^+concentration**
✓**NH_4Cl concentration of RO permeate is almost 0**

【Real wastewater】





✓**A hybrid BC-RO method achieves approximately 10-fold enrichment of NH_4^+ and a high NH_4^+ recovery (98%) in real wastewater**

【Achievements】

✓ Hybrid BC-RO process was applied first time for dewatering and NH_4-N concentration of model and real wastewater
✓ Hybrid membrane process enhanced the recovery of NH_4-N and minimized the discharge of NH_4-N-containing waste streams by clean water recovery
✓ A pretreatment process was constructed to remove scale components to prevent scaling during concentration, and its effectiveness was confirmed with actual wastewater (patent pending).

【Potential Applications and Effects】

Efficient concentration of ammonia (NH_4^+) from municipal sewage and industrial wastewater
Ammonia (NH_4^+) concentrated by forward osmosis (FO) method (T-N 0.04% → 0.4%) can be further concentrated at a low energy consumption (T-N 0.4% → 4%).

No. A-13-11E

PJ : Innovative circular technologies for harmful nitrogen compounds

Theme: NH_4 separation and concentration-Membrane distillation

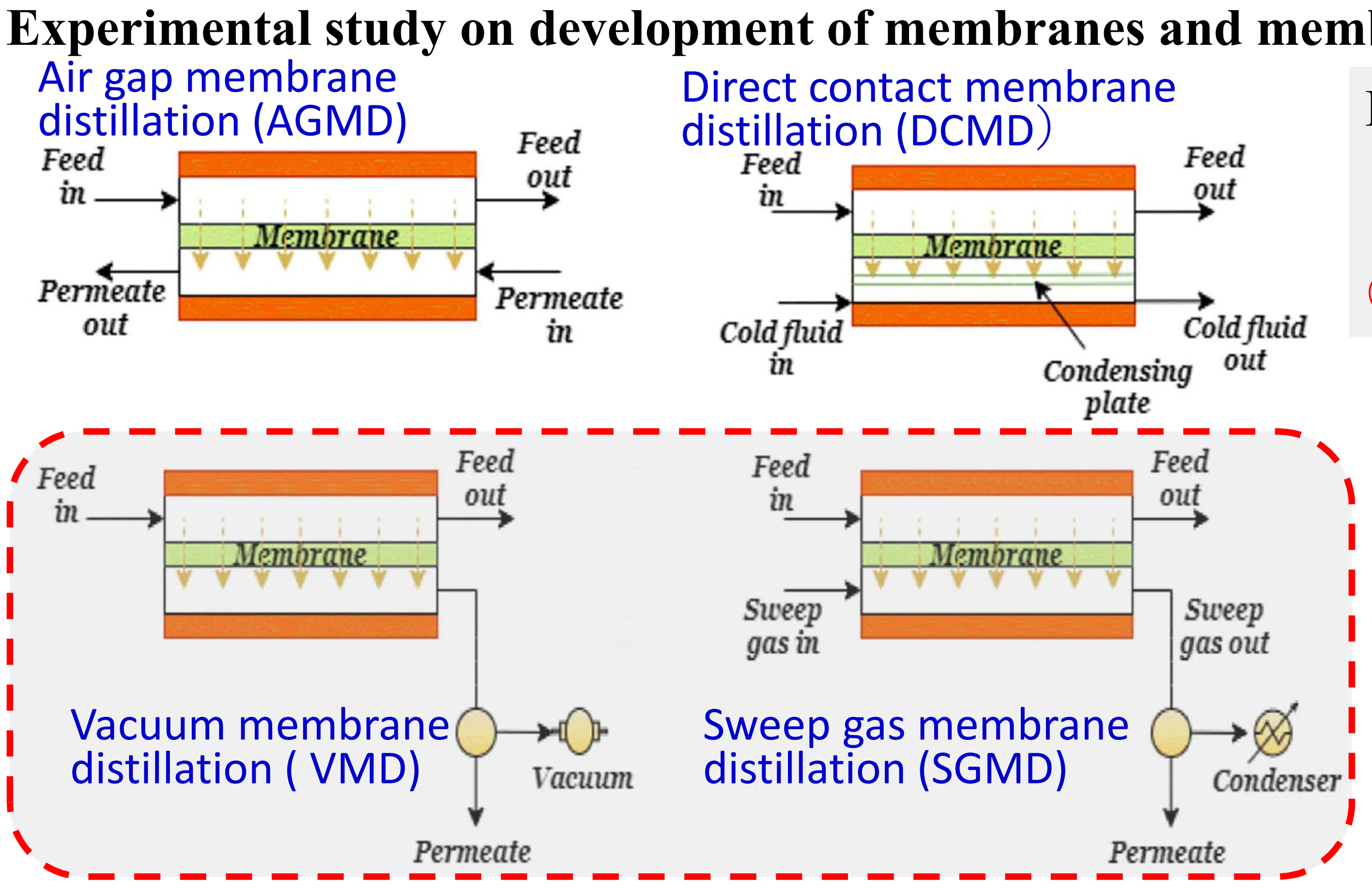
Organization: Kobe Univ., Hiroshima Univ.

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

<Concept> Membrane distillation (MD) method, in which aqueous NH_3 solution is evaporated through a porous membrane to concentrate NH_3

<Advantages> Space-saving and highly efficient purification and concentration of volatile NH_3

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

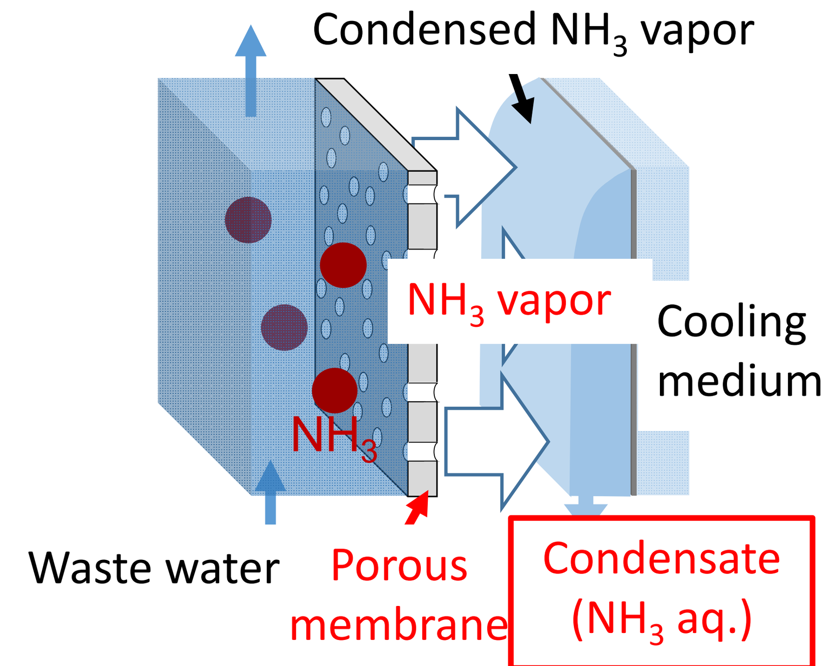


For NH_3 Recovery & Concentration

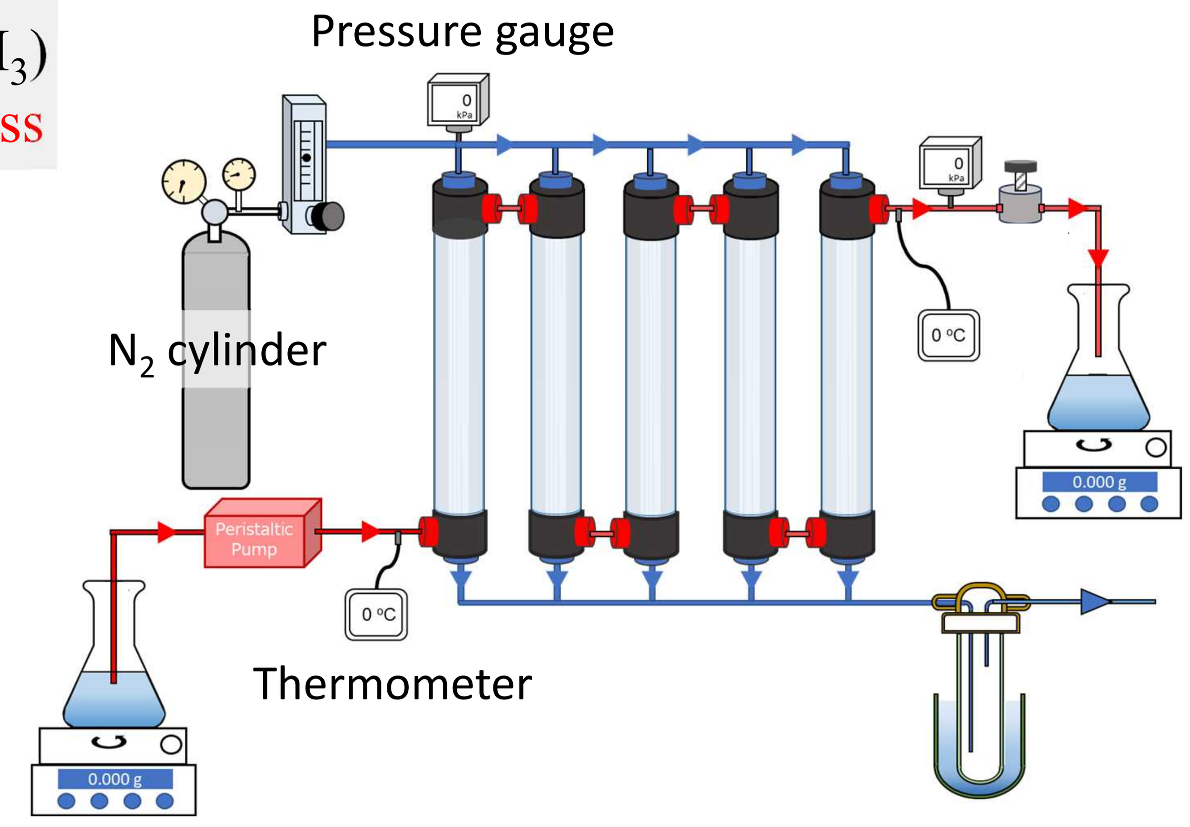
× DCMD (dilution in permeate side)

× AGMD (impossible to condense NH_3)

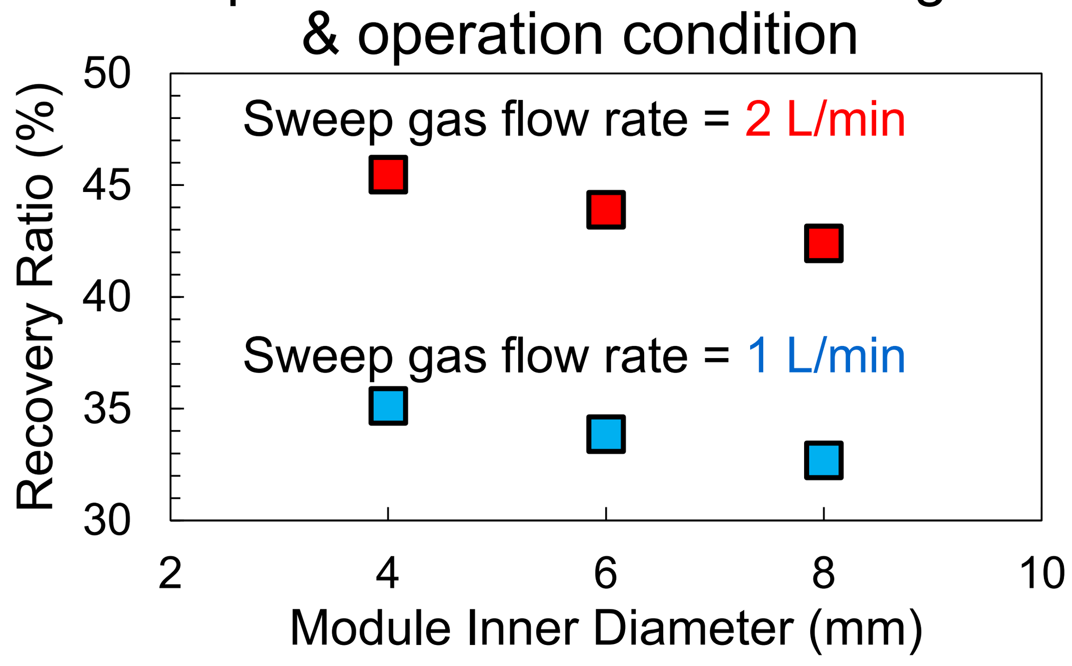
○ VMD and SGMD are feasible process

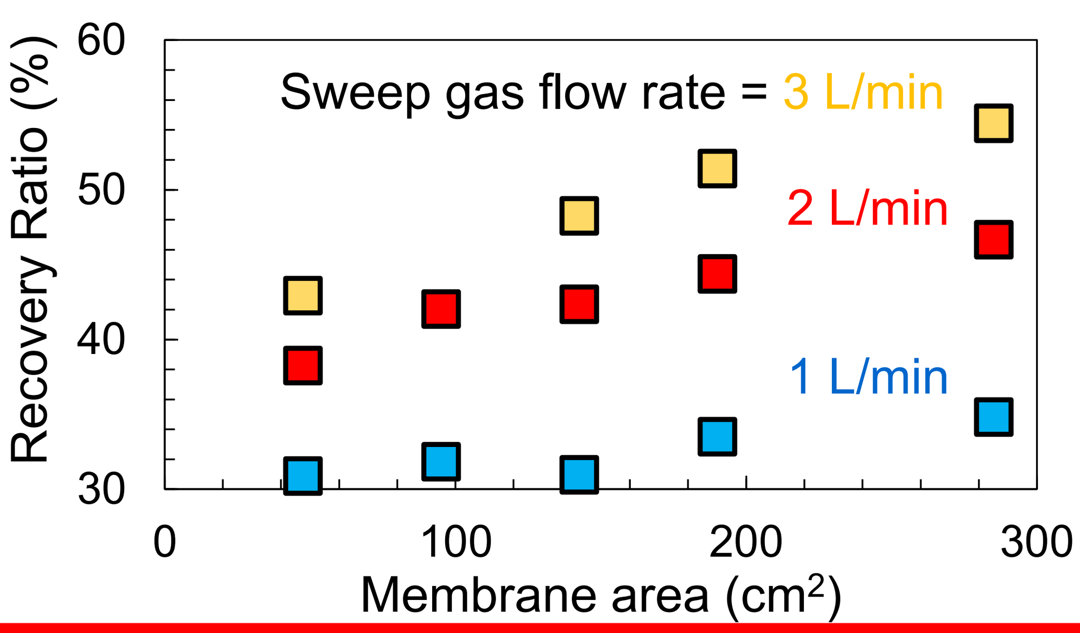


One-pass NH_3 recovery system multiple membrane modules



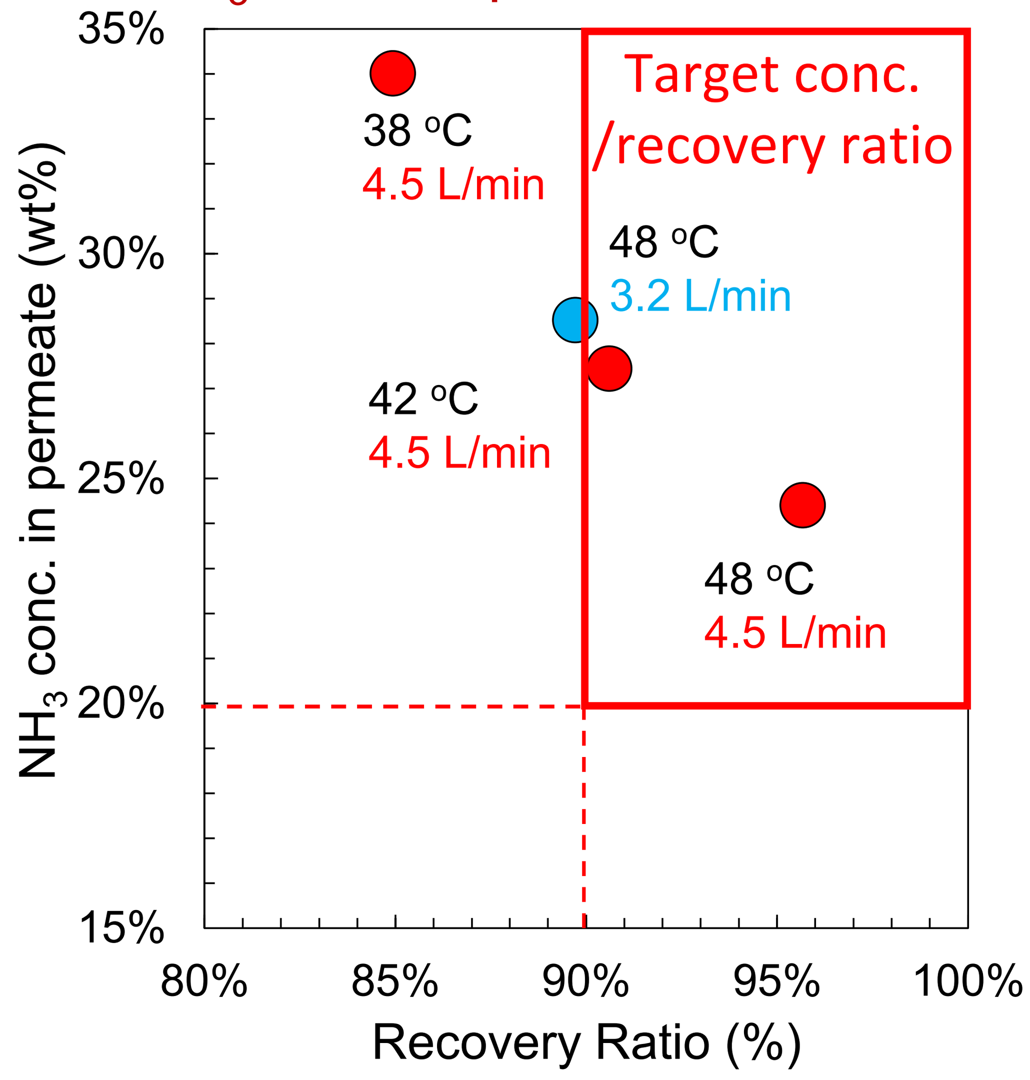
Optimization of module design & operation condition



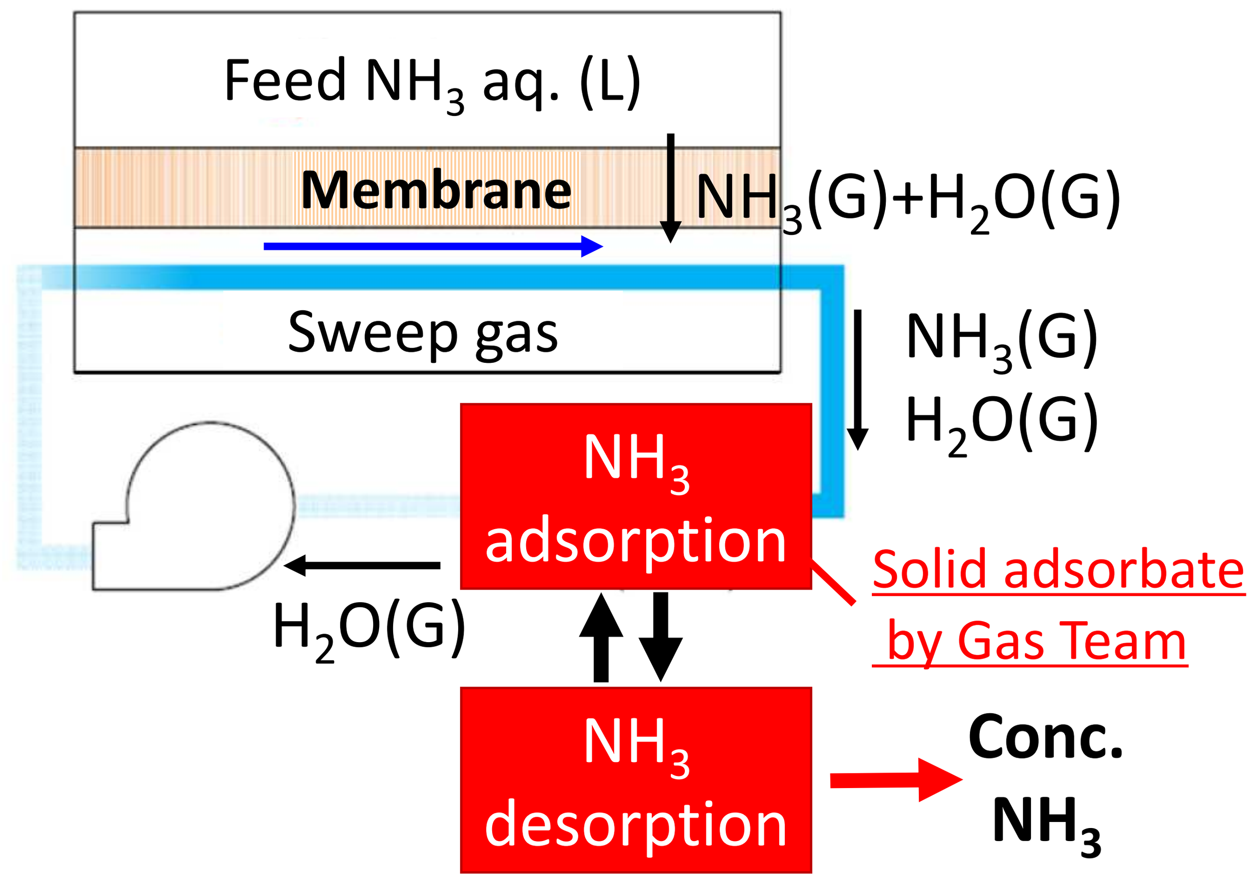


Optimal results achieving

- NH_3 recovery ratio > 90%
- NH_3 conc. in permeate > 20 wt%



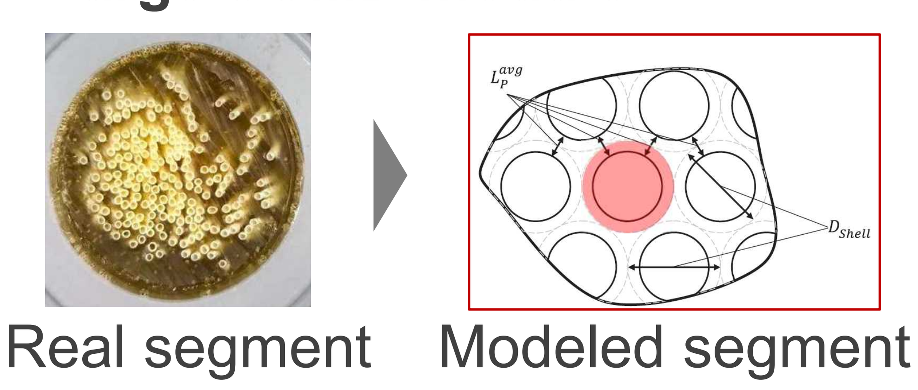
Synergy between gas-phase Team and water-phase Team



Demonstrated using a new adsorbent capable for adsorbing NH_3 with high efficiency and capacity

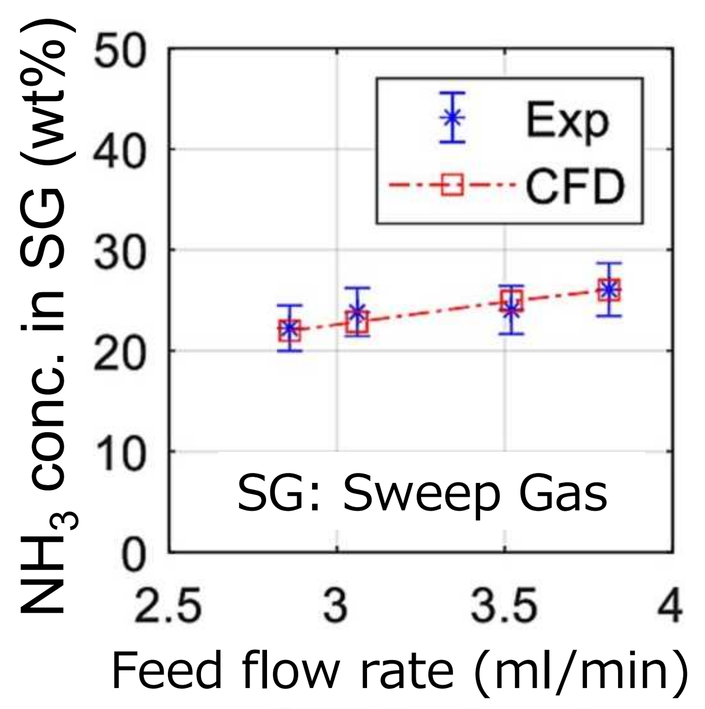
Development of a Computational Fluid Dynamics (CFD) model for predicting the performance of MD membrane modules (Hiroshima Univ.)

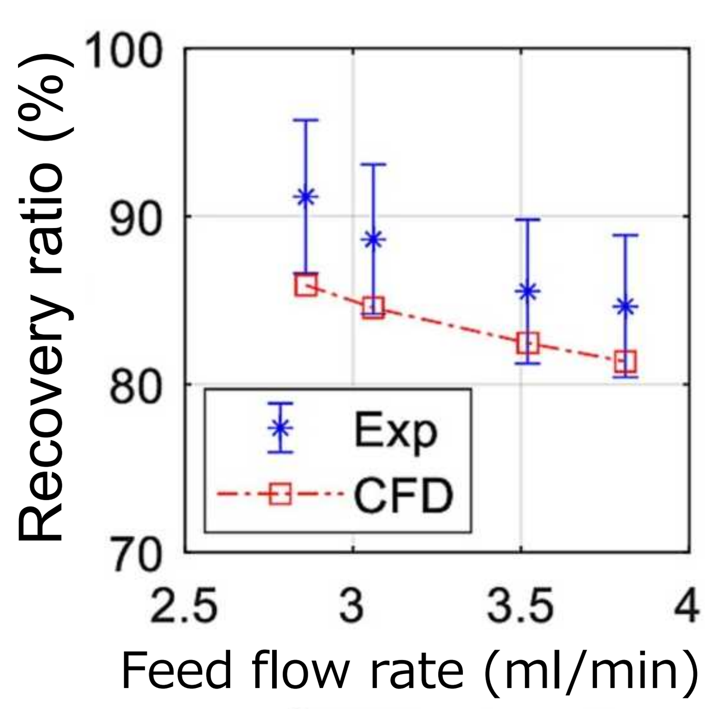
1. Segment model for performance prediction of large SGMD module



Only a modeled segment is simulated.

Performance prediction and Experimental validation

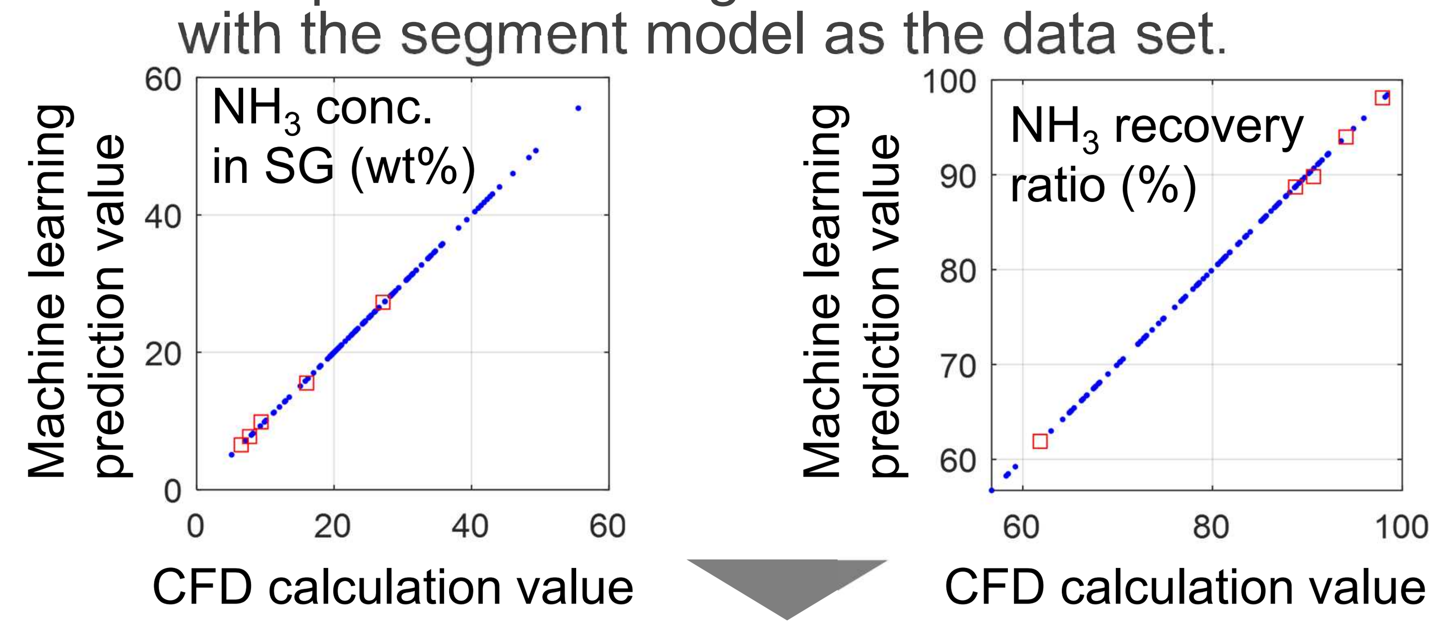




The model predicted well the experimental results of large module.

2. Optimization of SGMD process conditions using machine learning (ML)

ML was performed using the simulation results with the segment model as the data set.



ML was integrated with an optimization solver (genetic algorithm).

	Feed temp.(K)	SG temp. (K)	SG linear velocity (m/s)	Recovery ratio (%)	NH_3 conc. in SG (%)
Optimized	**320.69**	**298.15**	**2.5**	**93.04**	**32.91**
Exp.	297.65	297.68	7.47	88	40.49

Process conditions for large module were successfully optimized.

【Potential Applications and effects】

Recovery of ammonia from municipal sewage and industrial wastewater

Purification and recovery of NH_4^+ preconcentrated by forward osmosis (FO) (T-N 0.04% to 0.4%) and brine concentration (BC) (T-N 0.4% to 4%) technologies, as a highly concentrated NH_3 aqueous solution (4% to 20-25%) with energy-saving without using high temperatures

No. A-13-12E

PJ : Innovative circular technologies for harmful nitrogen compounds

Theme: NH_4^+ separation and concentration – Ion exchange membrane method

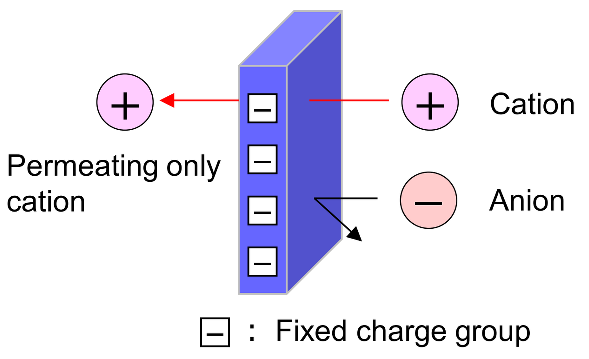
Organization: Yamaguchi University, ASTOM Corporation
Contact: Prof. Mitsuru Higa (Yamaguchi University), mhiga@yamaguchi-u.ac.jp

【Concept】 Selective recovery and concentration of NH_4^+ using ion exchange membranes: energy-saving concentration by Donnan dialysis for the primary concentration (<400 ppm to 4,000 ppm T-N) and fast and stable concentration by electrodialysis for the secondary concentration (4,000 ppm to 40,000 ppm T-N).

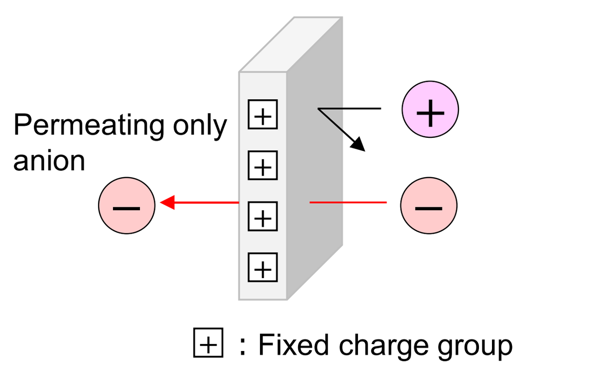
【Advantages】 Continuous treatment of wastewater containing fouling components.

Background

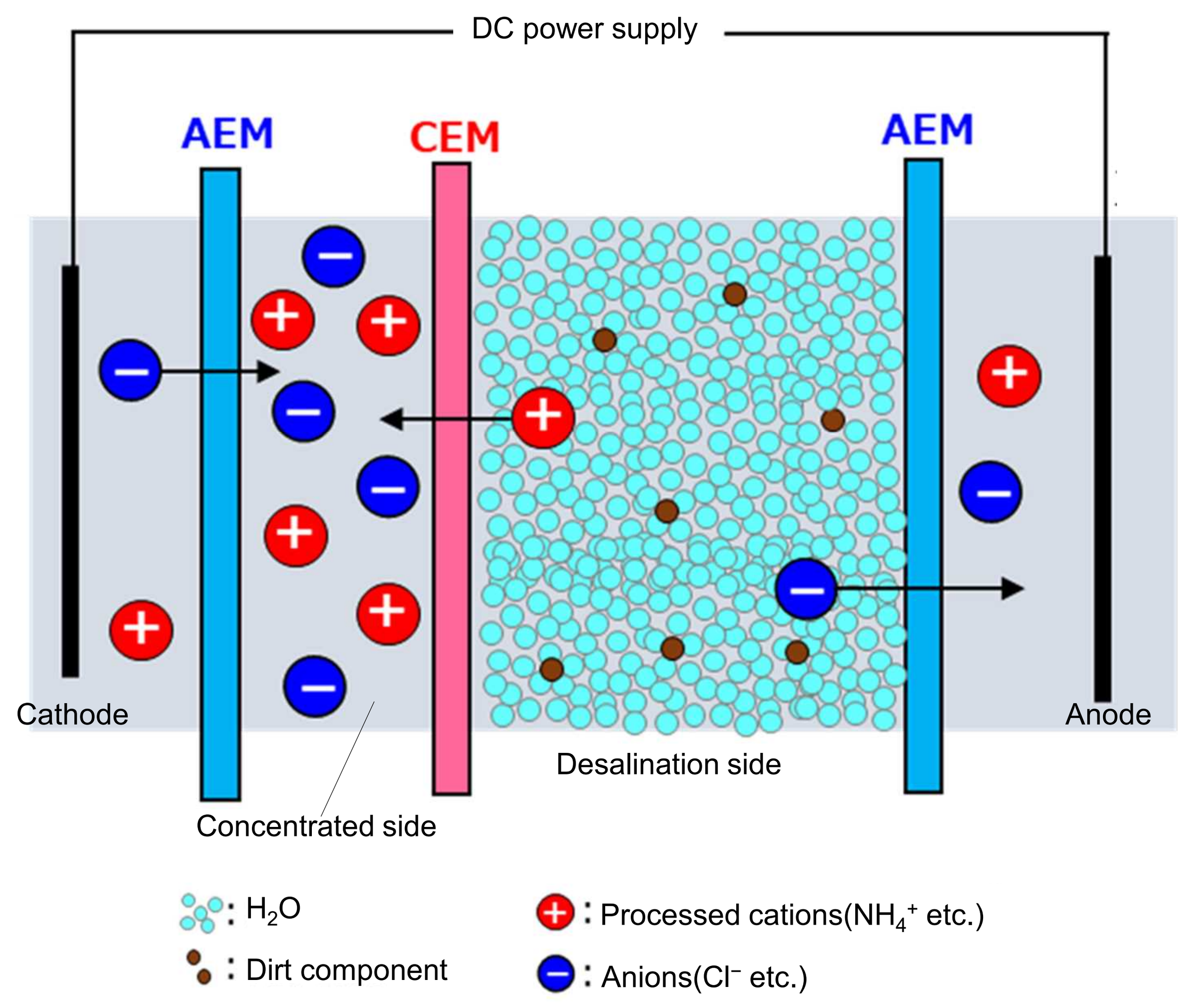
Cation exchange membrane (CEM)



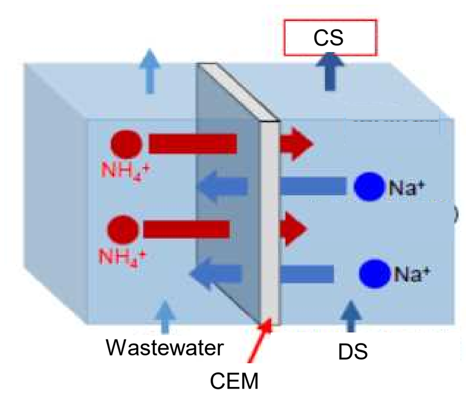
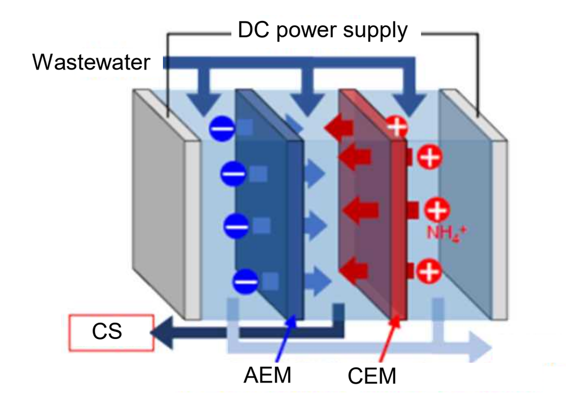
Anion exchange membrane (AEM)



Membranes that selectively permeate counter ions



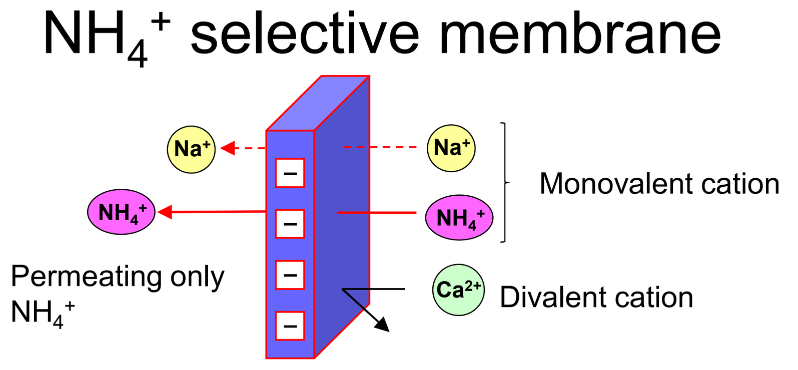
Strong point: Selective recovery and concentration of small amounts of NH_4^+ in a wastewater containing contaminants

	Donnan dialysis	Electrodialysis
Principle		
Driving force	Concentrated saline water	Electrical energy
Merit	Zero energy	Fast processing speed and suitable for wide range of salt concentrations
Demerit	Slow processing speed	Electrical energy is required
Applicable area	400ppm→ 4,000ppm T-N	4,000ppm→ 40,000ppm T-N

Development of NH_4^+ selective membranes

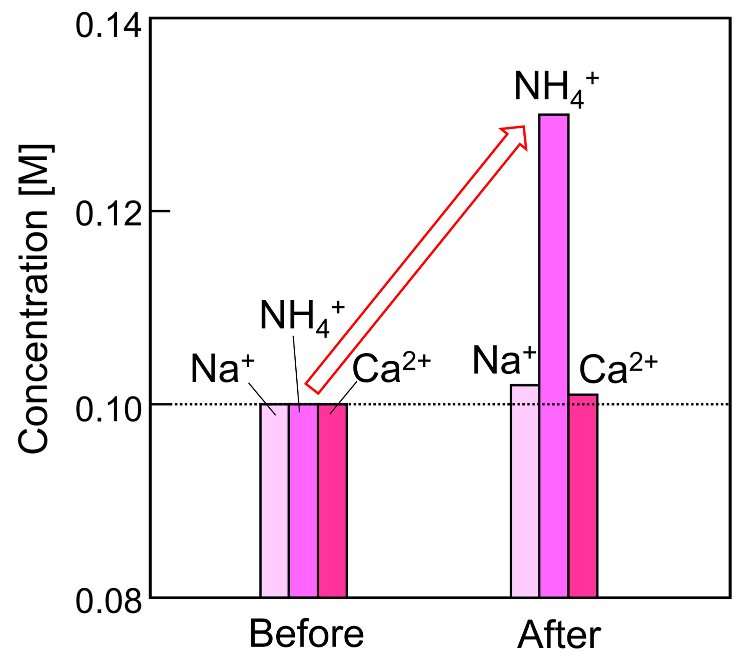
We have achieved highly selective concentration of NH_4^+ using the NH_4^+ selective membrane

NH_4^+ selective membrane



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

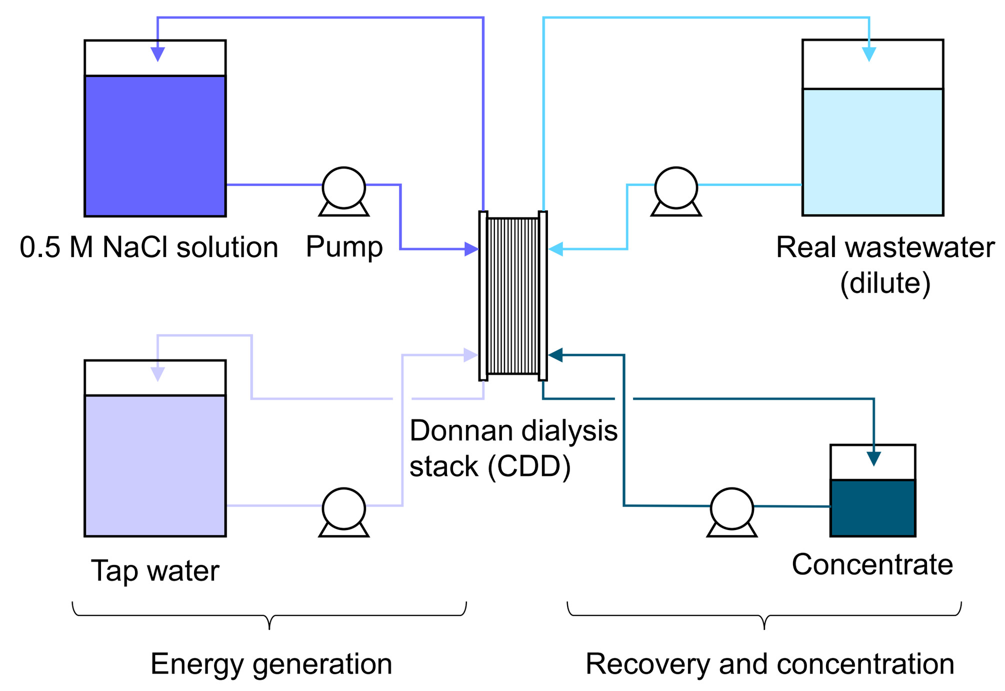
Electrodialysis test using NH_4^+ selective membrane

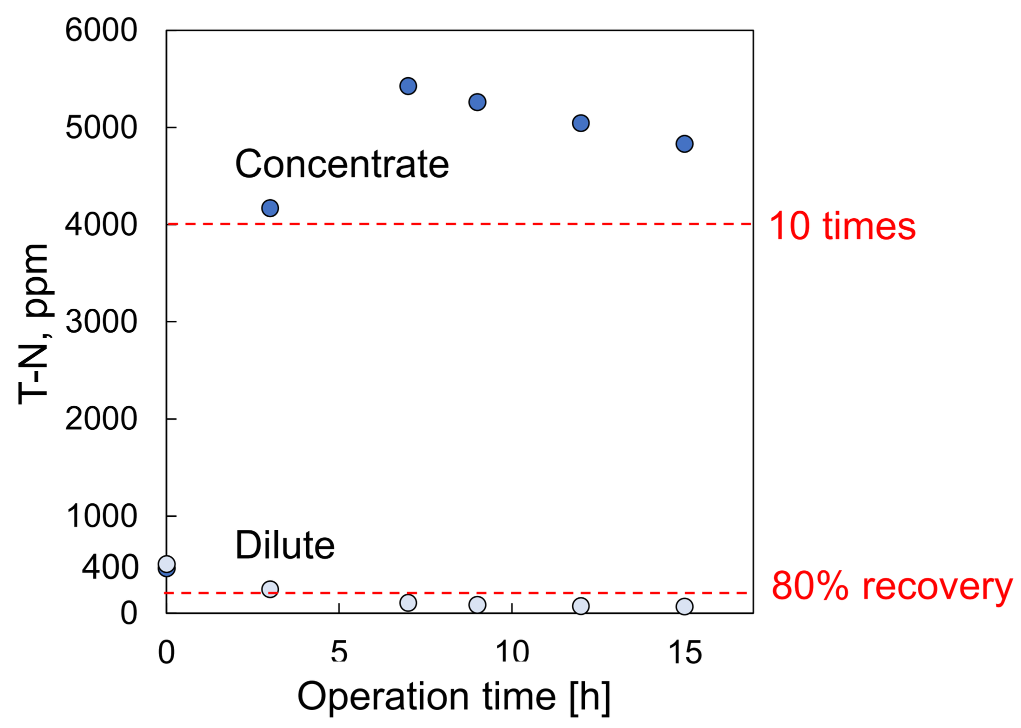


NH_4^+ concentration by Donnan dialysis system

We have achieved 10 times concentration of NH_4^+ and 80% recovery of NH_4^+ from real wastewater

Real wastewater concentration test

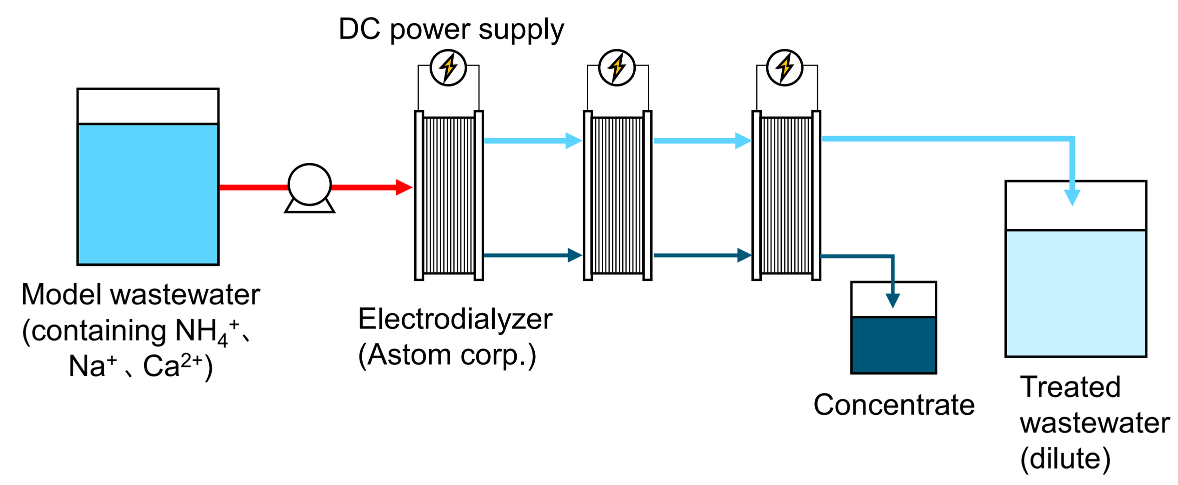




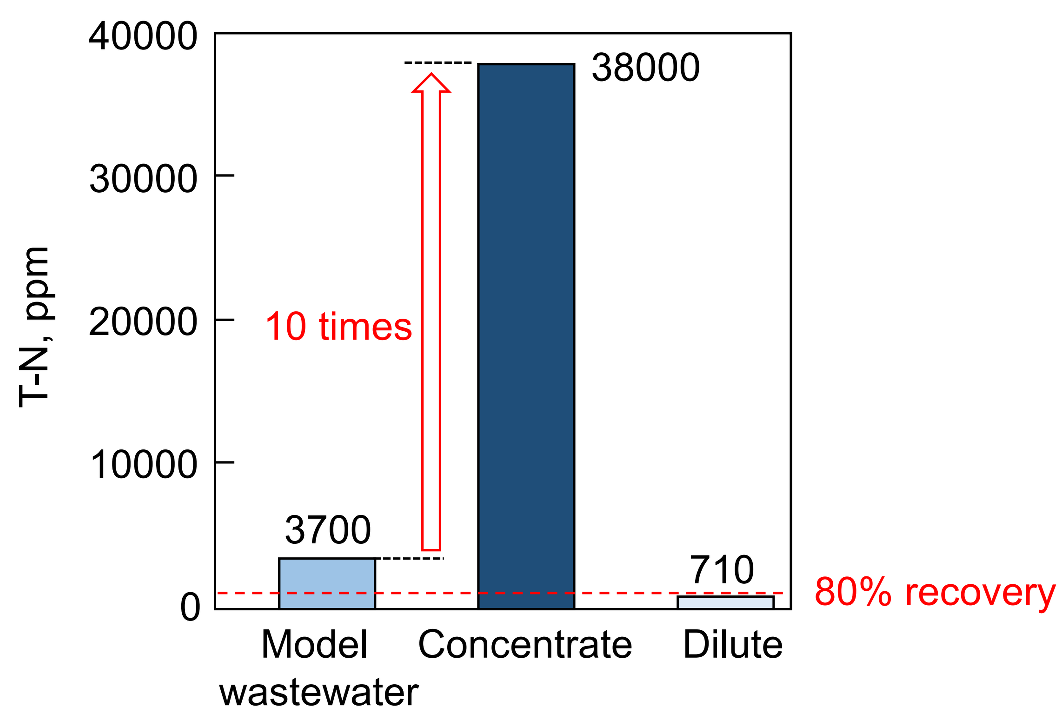
NH_4^+ concentration by triple electrodialysis system

We have achieved 10 times concentration of NH_4^+ and 80% recovery of NH_4^+ from model wastewater

Model wastewater concentration test



	Model wastewater, ppm	Concentrate, ppm	Concentration factor
Na^+	440	2700	6.2
Ca^{2+}	2100	4800	2.2



【Potential Applications and effects】

Recovery and concentration of NH_4^+ from wastewater containing fouling components that is difficult to concentrate by membrane filtration

Capable of continuous concentration of low purity NH_4^+ solution from less than 400 ppm to about 40,000 ppm (T-N) without using chemicals or heat

No. A-13-13E

PJ : Innovative circular technologies for harmful nitrogen compounds

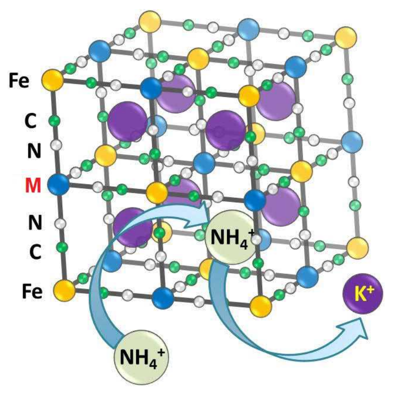
Theme: NH_4^+ recovery from water with adsorbent

Organization: AIST, The Univ. Tokyo, Fuso Corp.
Contact: Hisashi TANAKA (AIST), hisashi.tanaka@aist.go.jp

【**Overview**】 We aim to concentrate and recycle NH_4^+ by selectively separating and recovering the NH_4^+ ion in wastewater using an adsorbent and desorbing and recovering them.
【**Advantage**】 Separation & recovery of NH_4^+ from waters with co-ions in higher concentration.

NH_4^+ recovery by ion exchange method

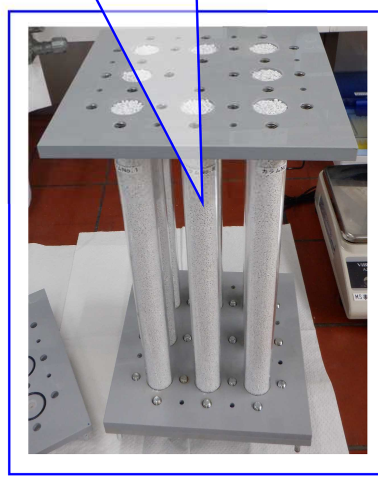
Material：Prussian blue analogs ($KMHCF$、$KMFe(CN)_6 \cdot nH_2O$)
(M =Fe, Ni, Cu, Co, Zn, etc)



NH_4^+ and K^+ ion exchange of KMHCF
(The crystal structure of KZnHCF differs from that of Cubic.)

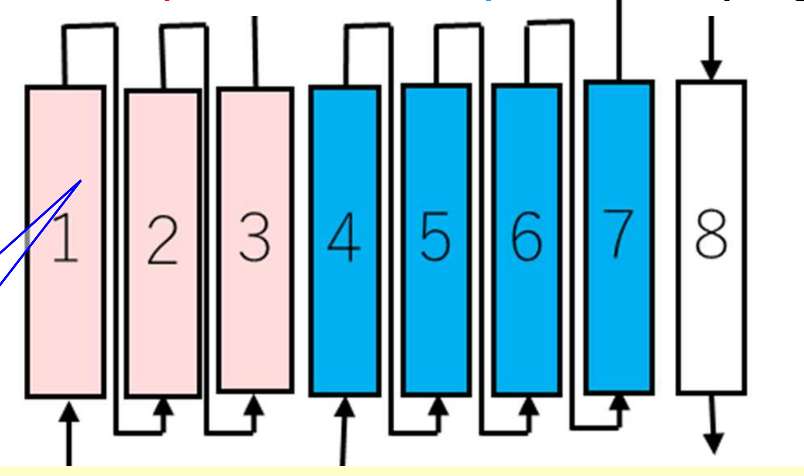
Adsorption：NH_4^+ ion in; K^+ ion out
Desorption：K^+ ion in; NH_4^+ ion out

KZnHCF Granules
($K_2Zn_3[Fe(CN)_6]_2 \cdot 3H_2O$)



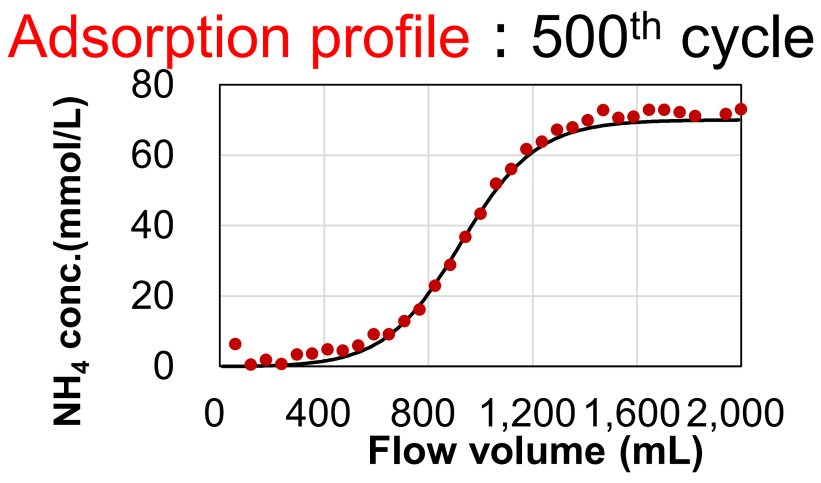
KZnHCF Column

Multiple column adsorption-desorption system

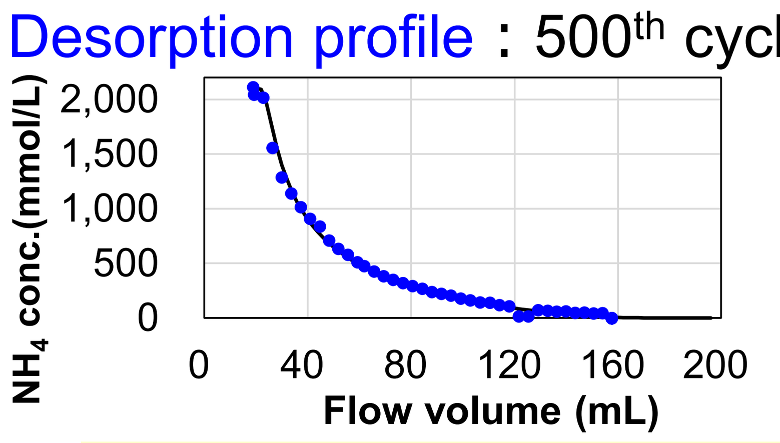


By operating in a merry-go-round style, adsorption and desorption is carried out continuously. It is possible to set and optimize
1) NH_4 outlet concentration,
2) NH_4 concentration rate, etc. as per the requirement of each waste liquid treatment site.

Adsorption profile：500th cycle



Desorption profile：500th cycle

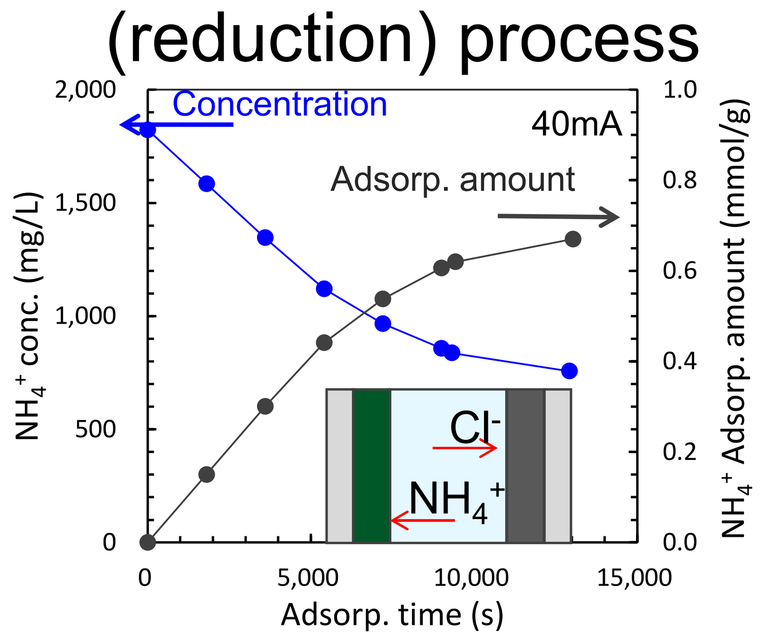


No hinderance in the adsorption – desorption performance is observed until the 500th cycle.

Applied to On-site test

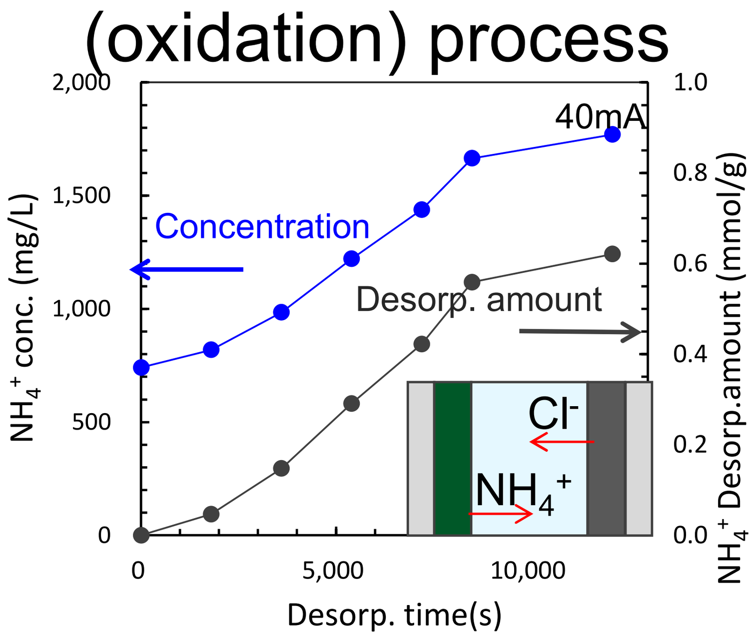
Electrochemical NH_4^+ recovery

Adsorption (reduction) process



$Cu[Fe^{III}(CN)_6]_x + x(NH_4^+ + e^-) \rightarrow (NH_4)_xCu[Fe^{II}(CN)_6]_x$

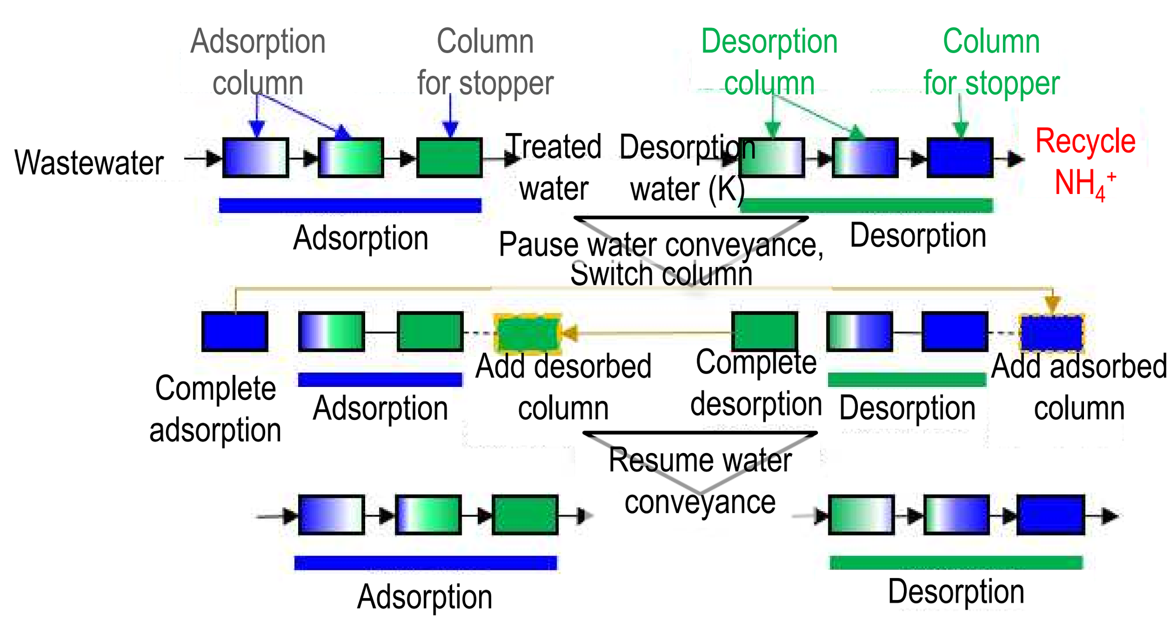
Desorption (oxidation) process



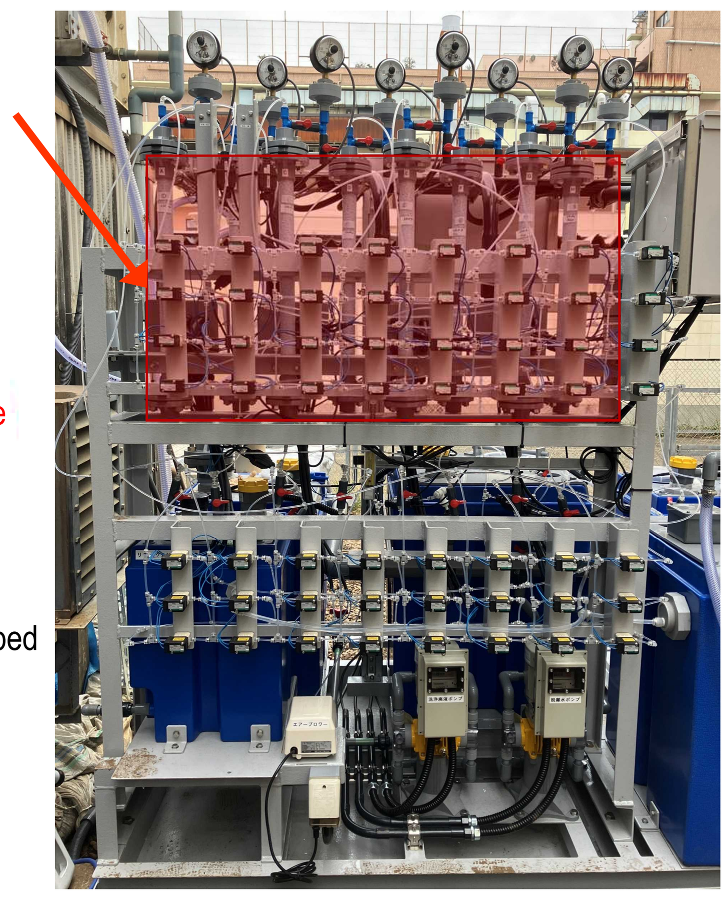
$(NH_4)_xCu[Fe^{II}(CN)_6]_x \rightarrow Cu[Fe^{III}(CN)_6]_x + x(NH_4^+ + e^-)$

Field bench test

Adsorption column for NH_4^+

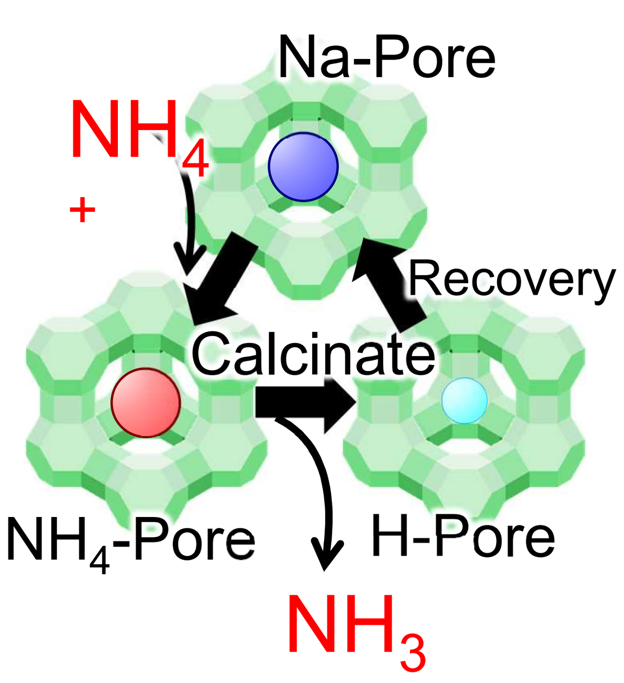


Flow of ammonia recycling



On-site test equipment

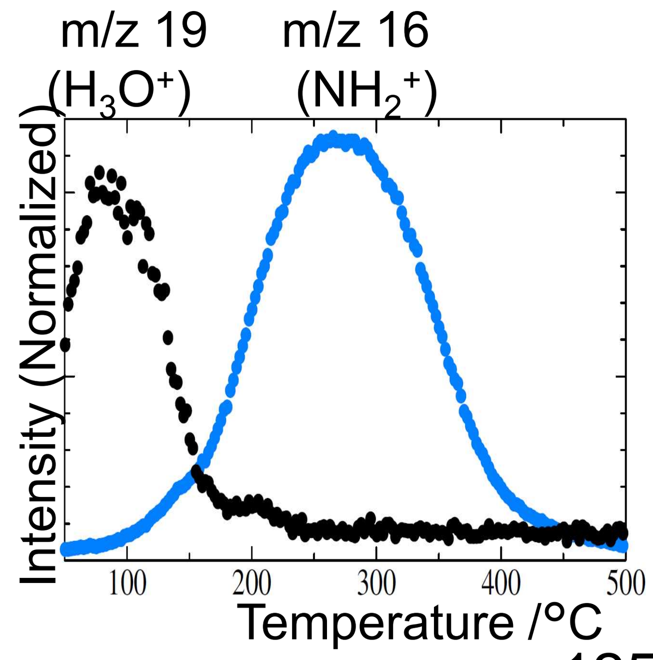
Ion-exchange & thermal elimination



NH_4 capture in water
Gas. NH_3 by heat
Recovery of adsorbate

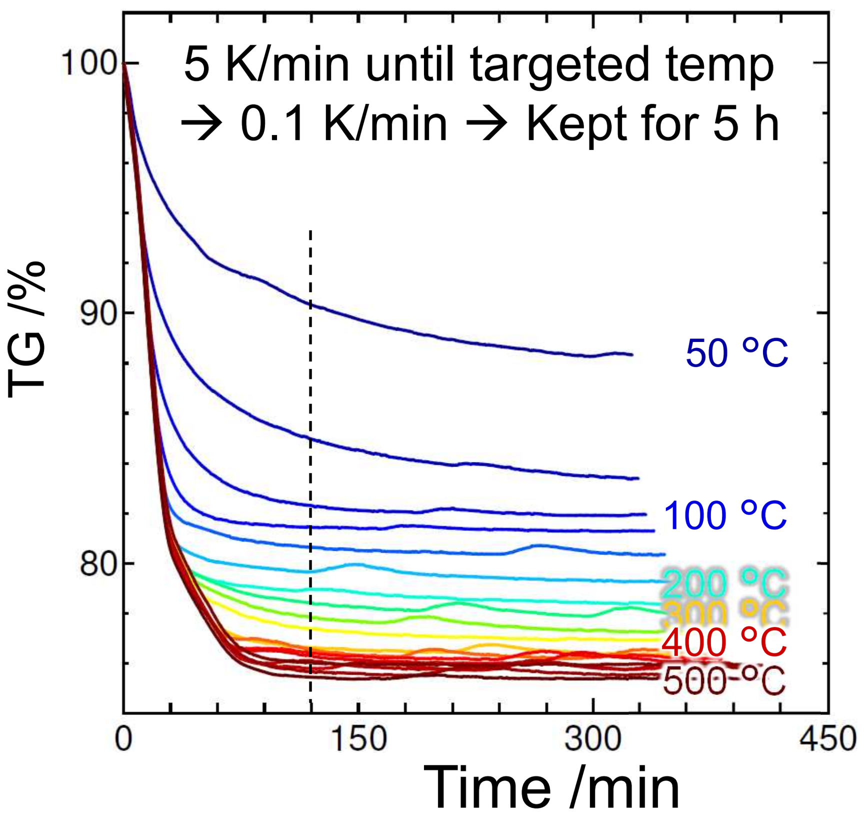
Thermal elimination of NH_3 and H_2O

TG-MS Chromatogram

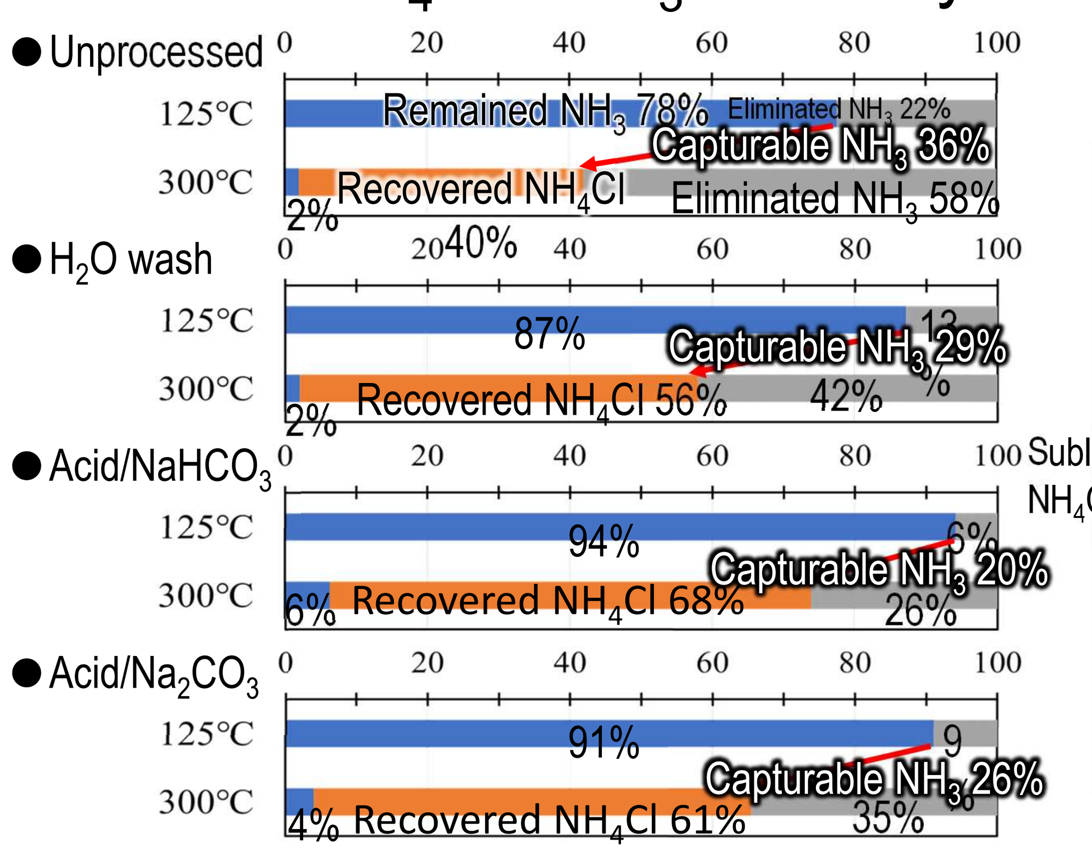


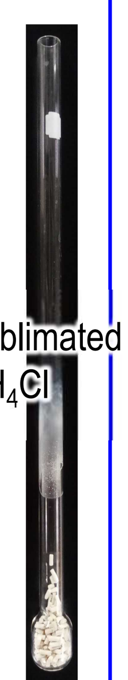
～125 ℃：Mainly H_2O
Afterwards：NH_3 gradually eliminated

TG curves of NH_4-Pore



Pretreatment of pellets and NH_4Cl / NH_3 recovery





85% recovery of NH_4^+ ion as NH_3 gas and solid NH_4Cl

【Potential Applications/Effects】

Recovery and recycling of NH_4^+ from various industrial wastewater.

- Recover and recycle NH_4^+ from various industrial wastewater and wastewater from agriculture, fisheries, etc. with little energy. Especially applicable to low~high concentration NH_4^+ solution containing high concentrations of Na ions, coexisting ions, and SS.
- In the future, we aim to purify and treat sewage water that requires mass treatment and environmental water that requires NH_4^+ treatment at lower concentrations.

No. A-13-14E

PJ : Innovative circular technologies for harmful nitrogen compounds

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

Organization: AIST, Tokyo Tech, Nagoya U.

Contact: Assoc. Prof. H. Matsumoto (Tokyo Tech), matsumoto.h.ae@m.titech.ac.jp

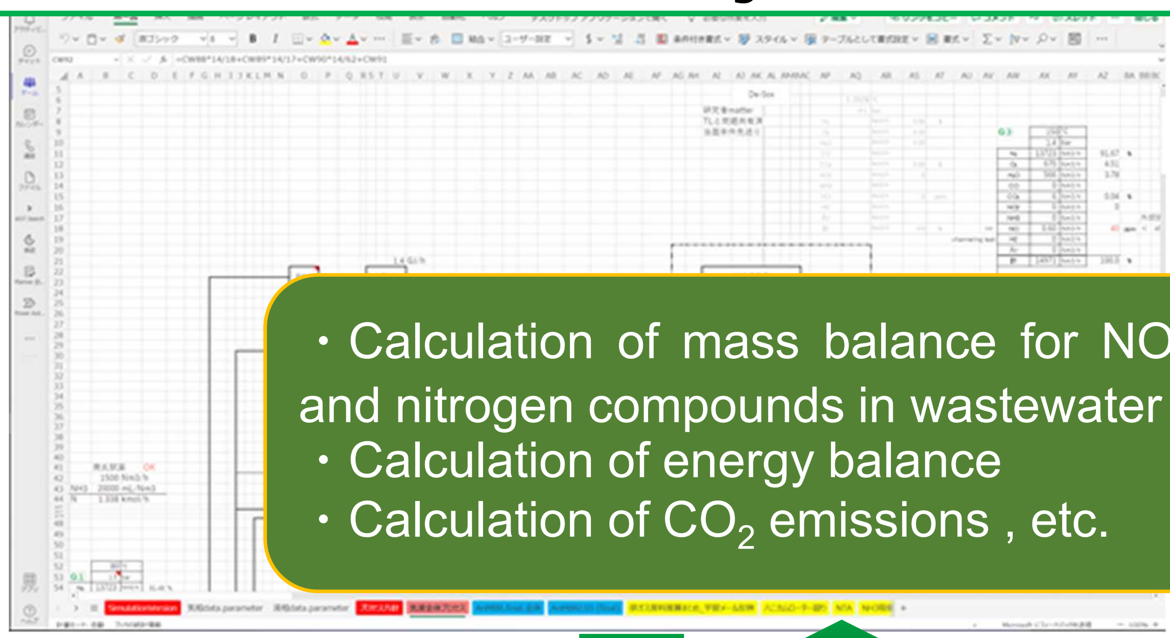
<Concept> Development of rate-based process models, Synthesis and evaluation of the gas phase NTA process systems & the liquid phase concentration process systems for nitrogen compounds

<Advantages> Efficient analysis of test data from bench/pilot scale processes

【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.

Examining the ideal structure of the nitrogen circular process system based on a calculation and visualization model of mass and heat flow using Microsoft Excel



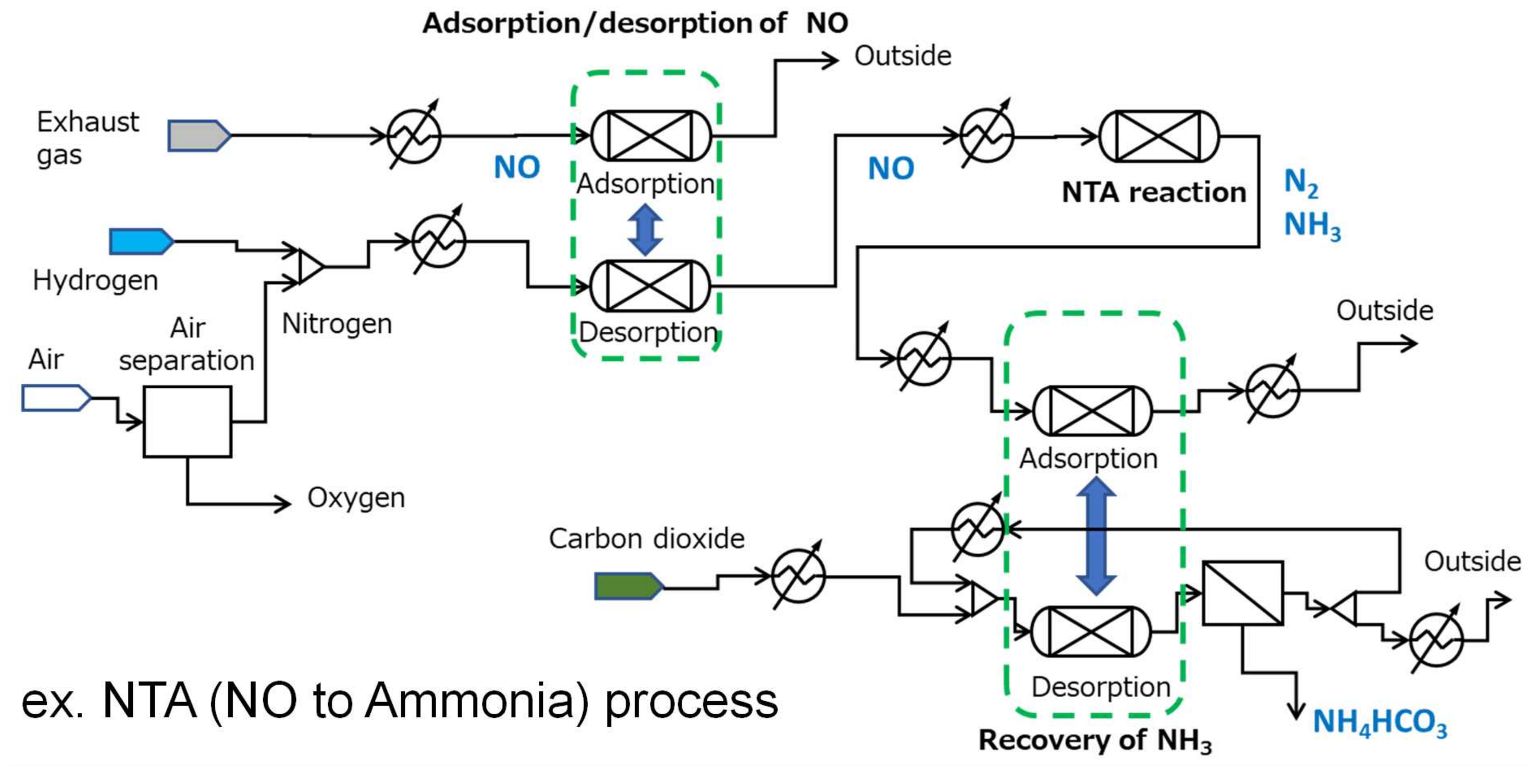
・Calculation of mass balance for NOx in gas and nitrogen compounds in wastewater
・Calculation of energy balance
・Calculation of CO_2 emissions , etc.

Flow analysis of NH_3, reactive nitrogen and other harmful substances

- Life cycle assessment of nitrogen circular technologies
- Risk assessment of nitrogen compound cycle

Poster No. A-13-15E

Conceptual design of elemental processes and evaluation of the overall system based on steady-state model



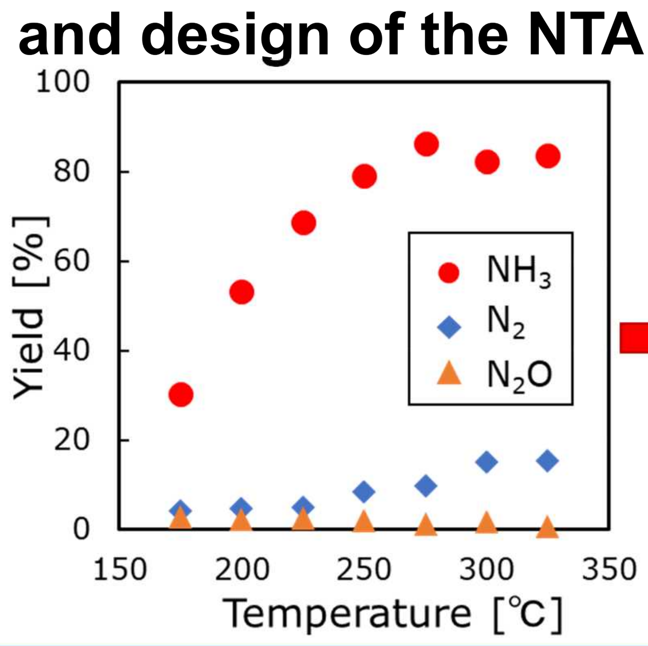
ex. NTA (NO to Ammonia) process

- Estimation of the CO_2 emissions: 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)

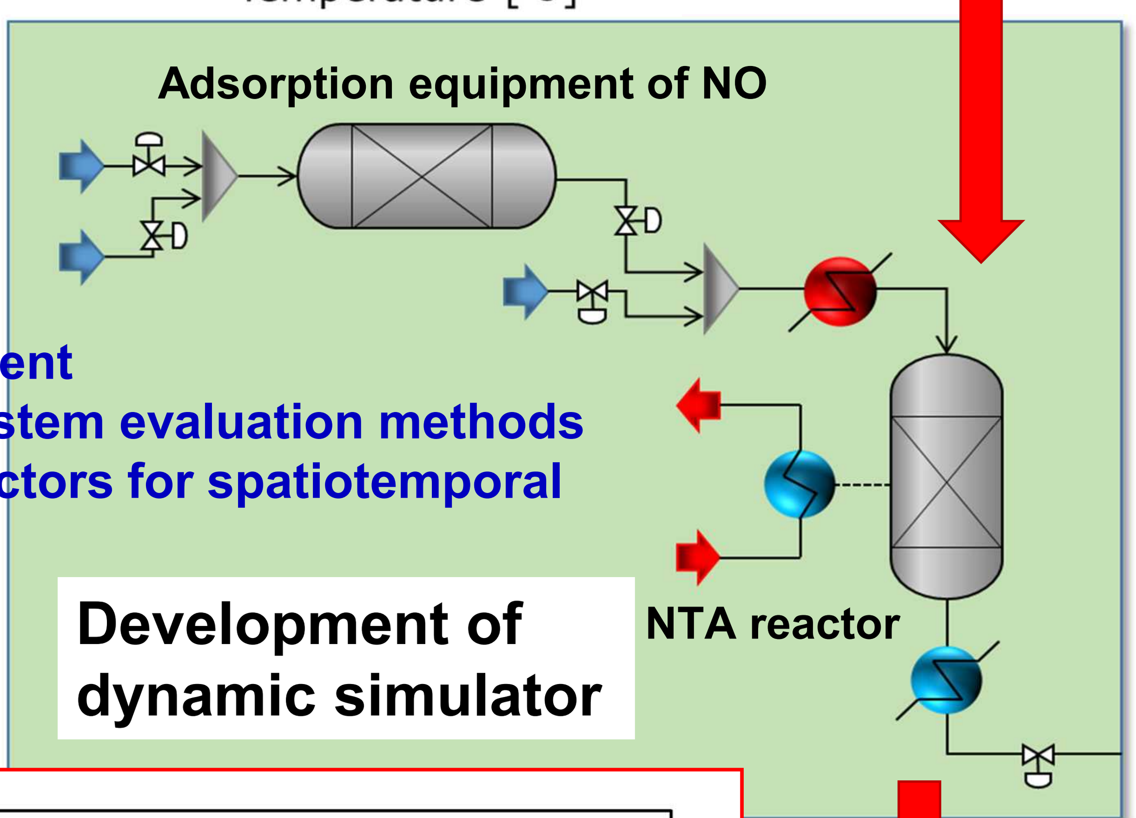
Simulation of Bench/Pilot Scale Process and Dynamic Analysis

① Synthesis and design of the NTA process systems

Collection of catalyst activity test data using lab-scale experiments

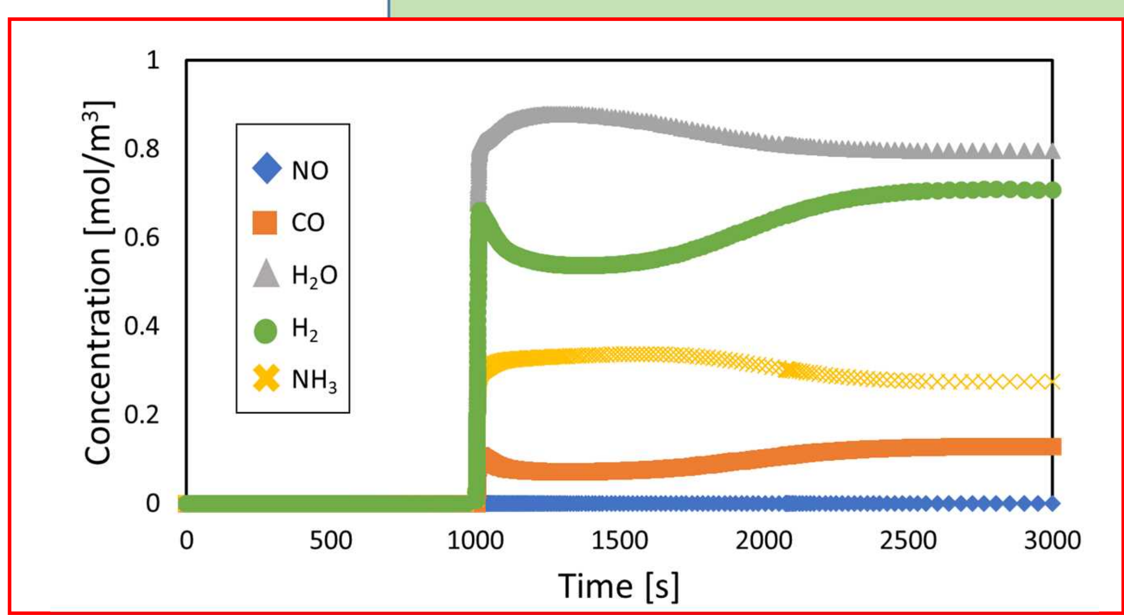


Develop reaction rate equation model



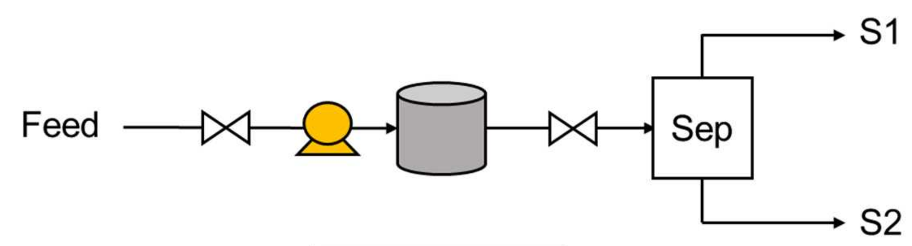
Development of dynamic simulator

・Sizing of equipment
・Organizing of system evaluation methods
・Organizing of factors for spatiotemporal variation

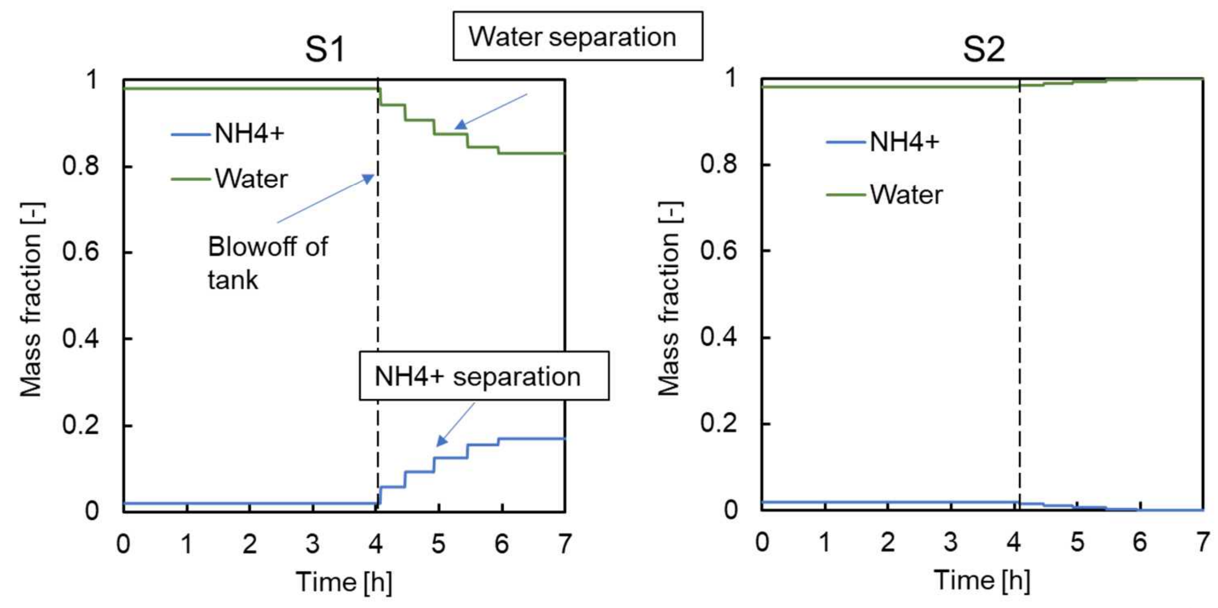


Influence analysis of unsteady operations

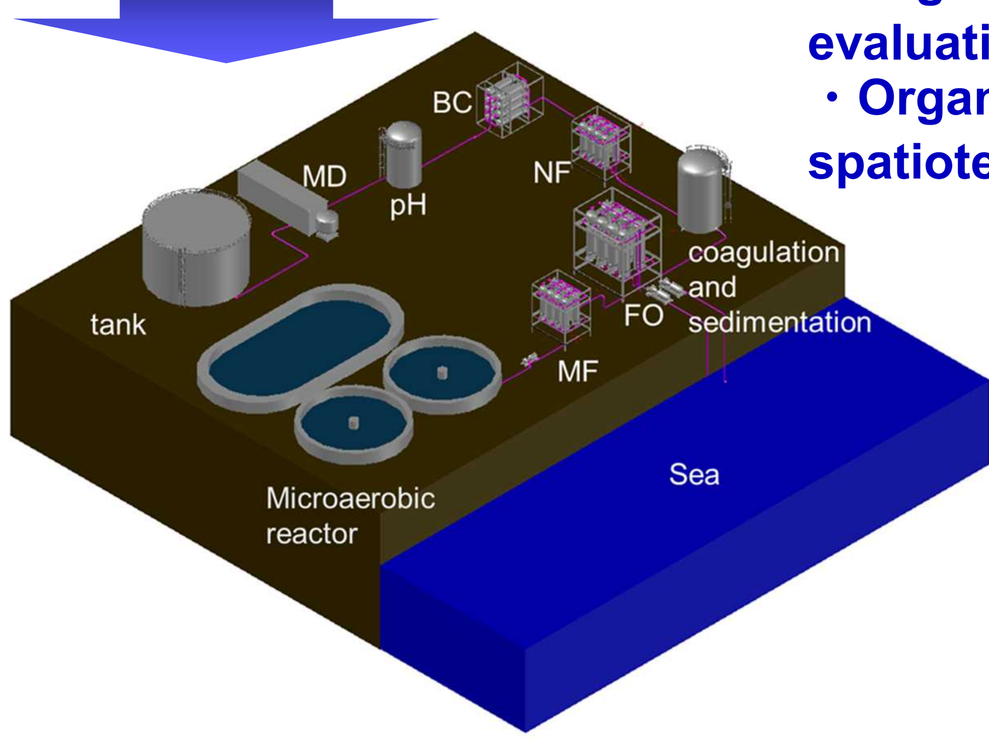
② Synthesis and design of the liquid phase concentration process systems for nitrogen compounds



Build dynamic models by extending the steady models



Dynamic analysis using unsteady process simulation



・Organizing of system evaluation methods
・Organizing of factors for spatiotemporal variation

[Common issues for ① and ②] Synthesis and design of the entire system that establishes the operation of each process in time and space, since each elemental process has a different throughput, residence time, material and energy

【Potential Applications and effects】

Shorten lead times for R&D by feeding back information on process design and evaluation that takes operability and controllability into consideration to R&D for elemental technologies

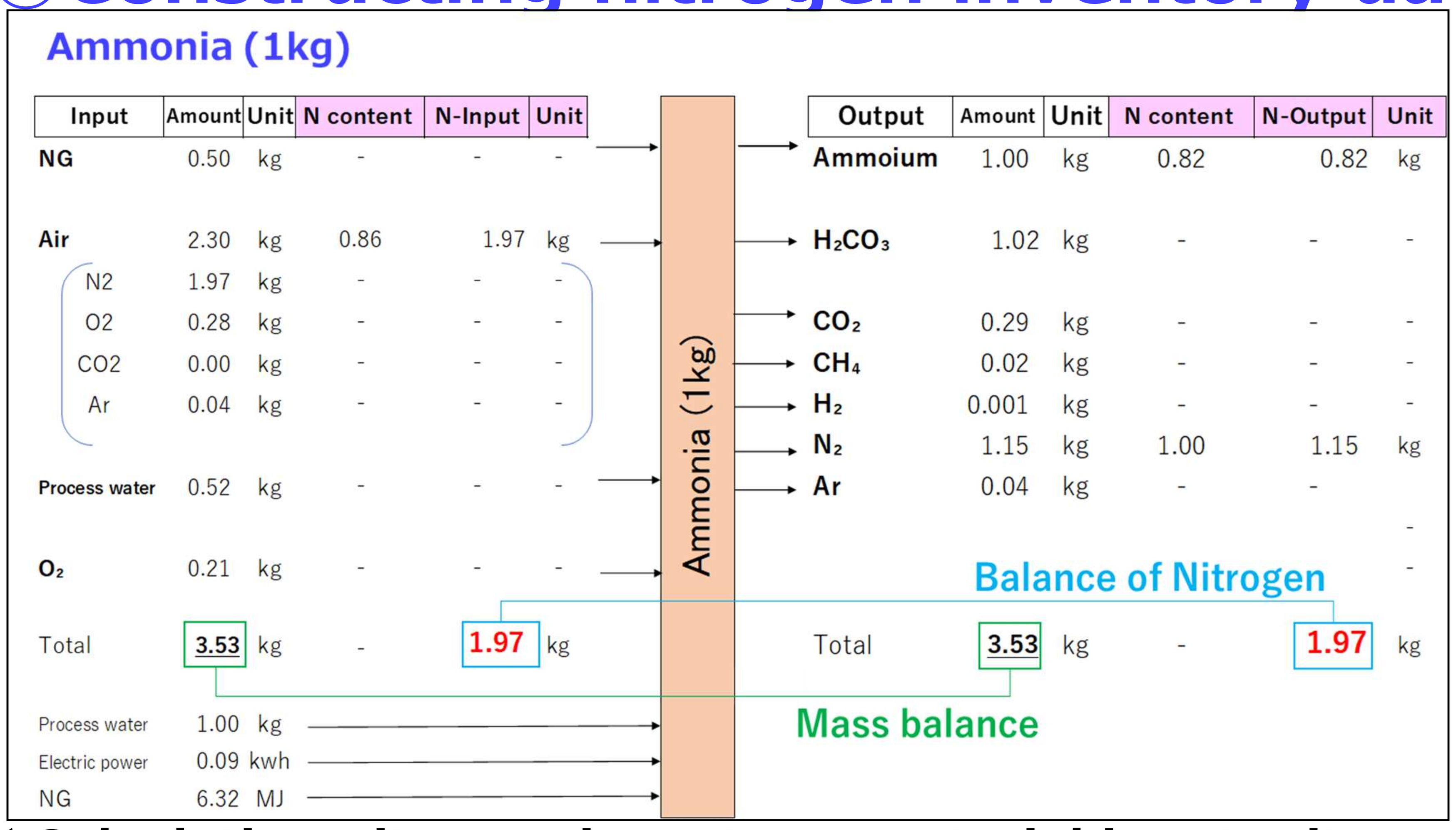
No. A-13-15E

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. Kazuya Inoue (AIST), kazuya-inoue@aist.go.jp

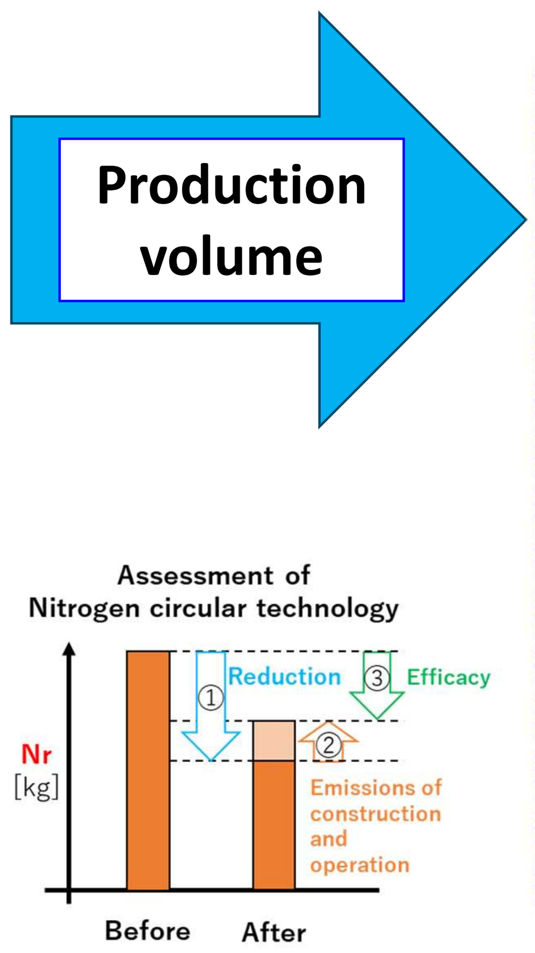
<Concept> Constructing nitrogen database for assessment of nitrogen circular technologies
<Advantage> Existing database has been developed output nitrogen as reactive nitrogen. In contrast, we developed IDEA database not only output nitrogen, but also nitrogen input. We have been finished constructing nitrogen inventory data of approximately 700 products.

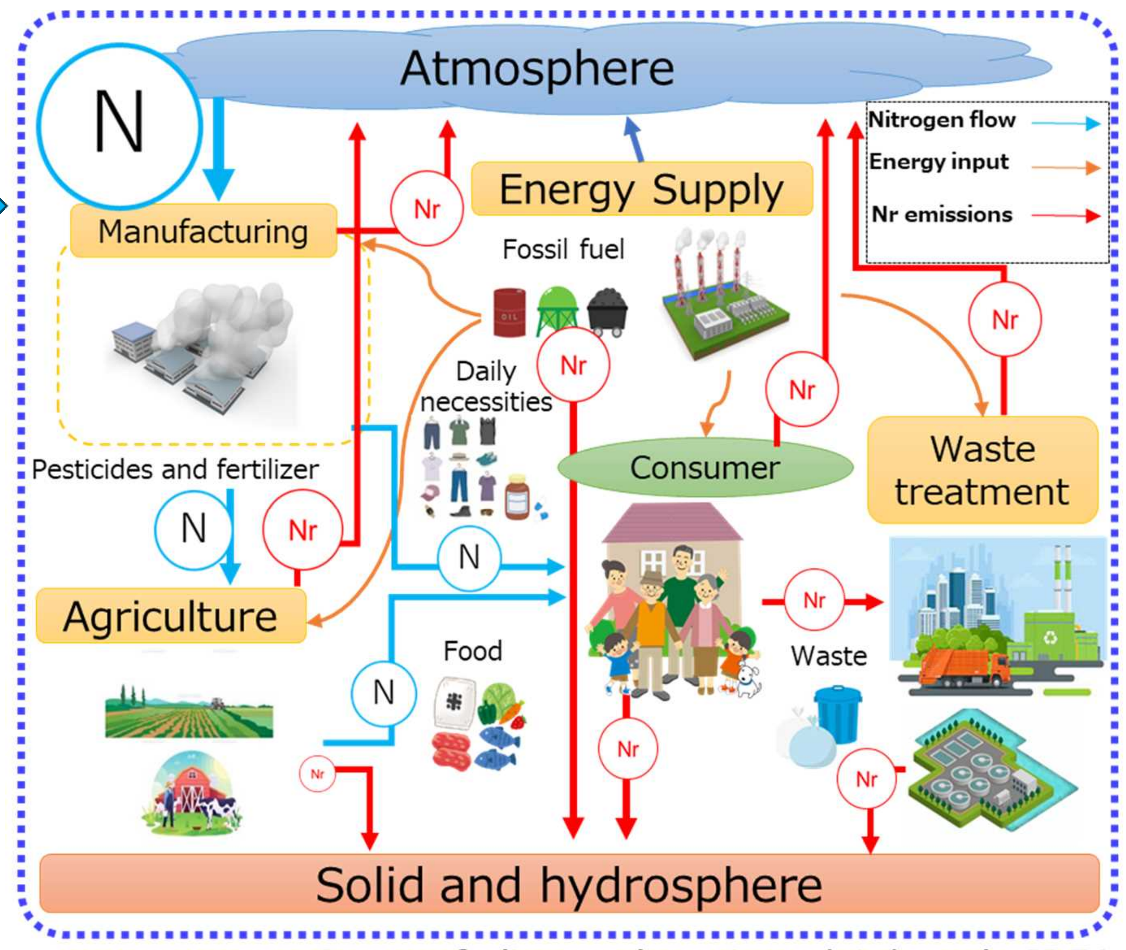
①Constructing nitrogen inventory database



✓ Calculating nitrogen inventory; material input, nitrogen content in products and Nr emissions to environment
✓ Constructing nitrogen inventory data of approximately 700 products

②Domestic nitrogen flow





Scope of nitrogen inventory database in IDEA

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

<Concept> Estimated the inventory of anthropogenic reactive nitrogen emissions (Nrs) in 2050 and evaluated the effect to secondary generated pollutants such as ozone (O_3).
<Advantage> Preparation of future inventories which could be applied to the evaluation of air quality assessment after introducing nitrogen recirculation technology (NRT).

- **Aim① : Estimation of the inventory of anthropogenic Nrs emissions (NO_x, NH_3, ⋯) in 2050**
- **Aim② : Evaluation of the effect of Nrs reductions to atmospheric O_3 and $PM_{2.5}$ in 2050**
- **Software : Community Multiscale Air Quality Modeling system (CMAQv5.3.3)**
- **Meteorology in 2050 : Medium global warming (RCP4.5)* of global climate model (CCSM4)**
- **Future scenarios : LED=Adaption, ELE=Electrification, H2=Hydrogen society, ZERO=Net-zero**

*RCP4.5: The climate scenario which corresponds to 1.1~2.6℃ increase of global temp. in 2100.

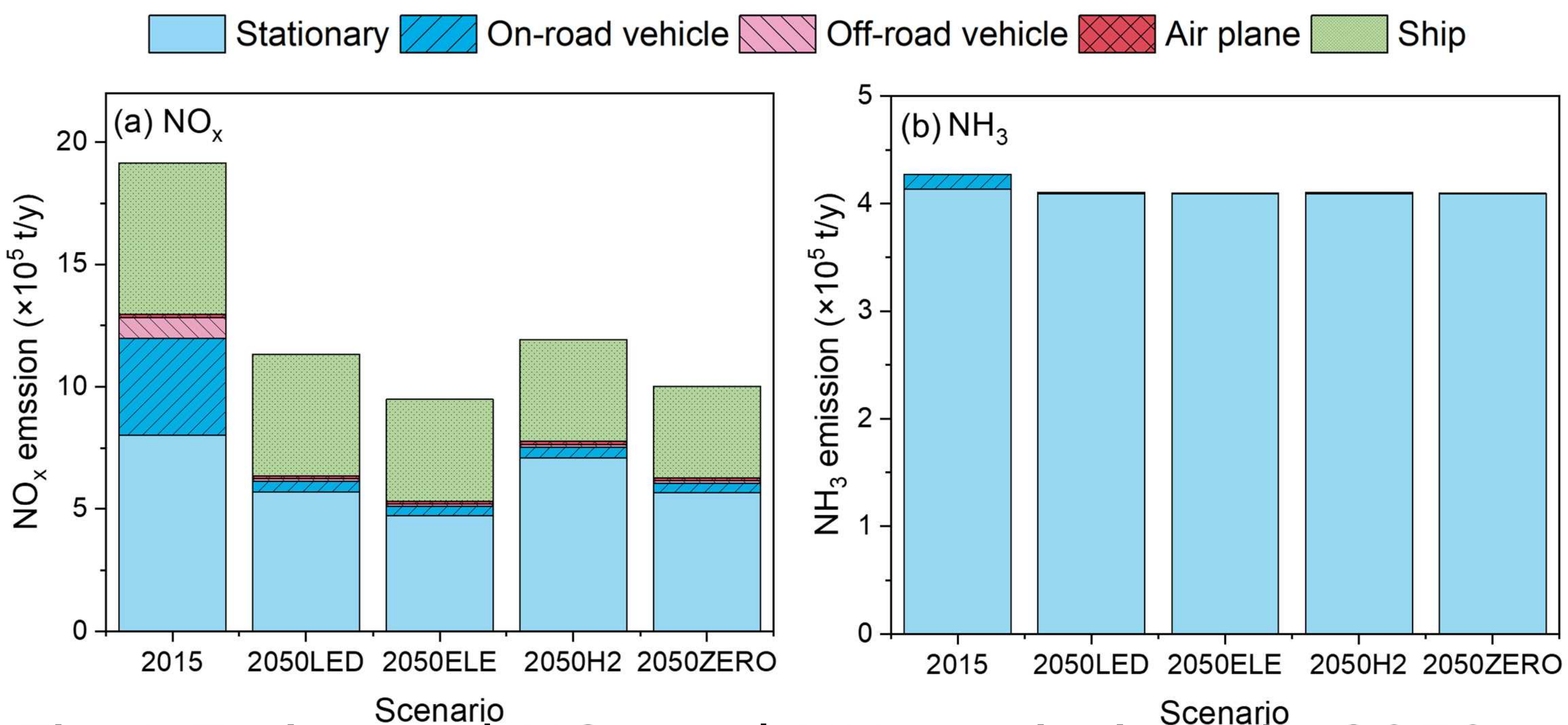


Fig.1 Estimated NO_x and NH_3 emissions in 2050.

- **While NO_x emissions are decreased for vehicles, those from stationaries, ships, and NH_3 emissions will remain.**
- **10ppb decrease of O_3 due to the decrease of Nrs in 2050.**
- **Intensified shortwave radiation due to climate change increases $PM_{2.5}$.**
- **Similar analysis targeting on global-scale air quality is now under proceeding.**

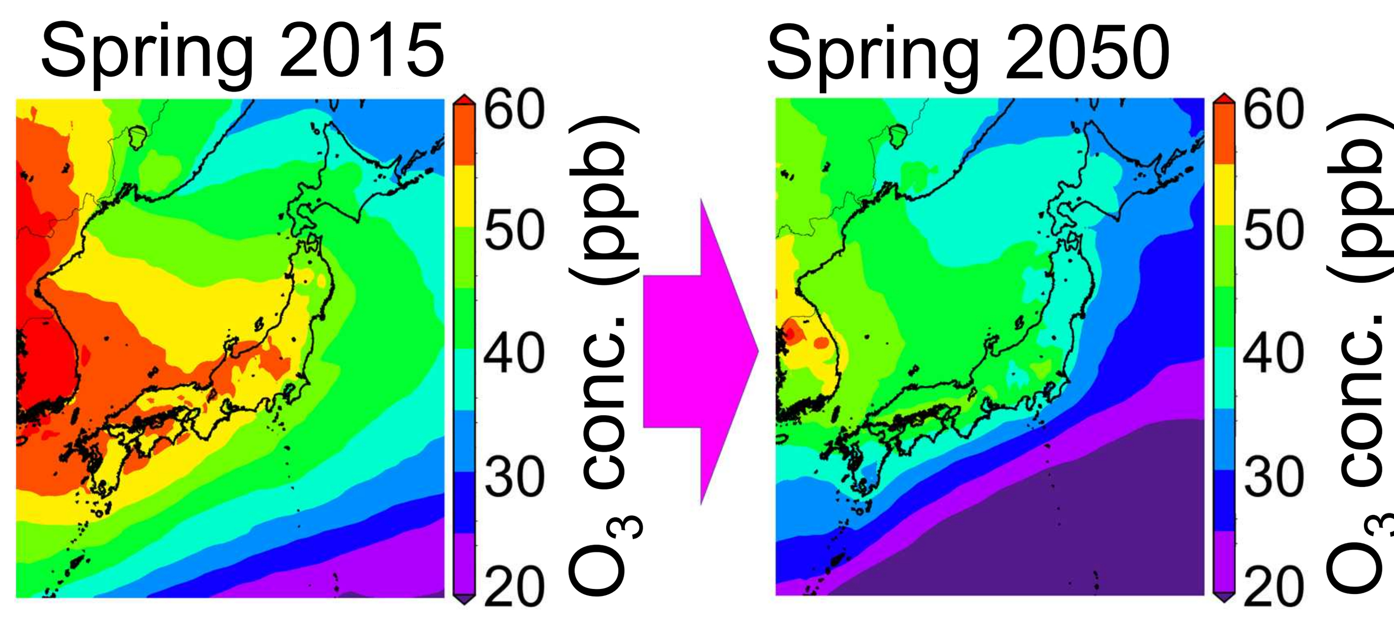


Fig.2 O_3 conc. in 2015 and 2050.

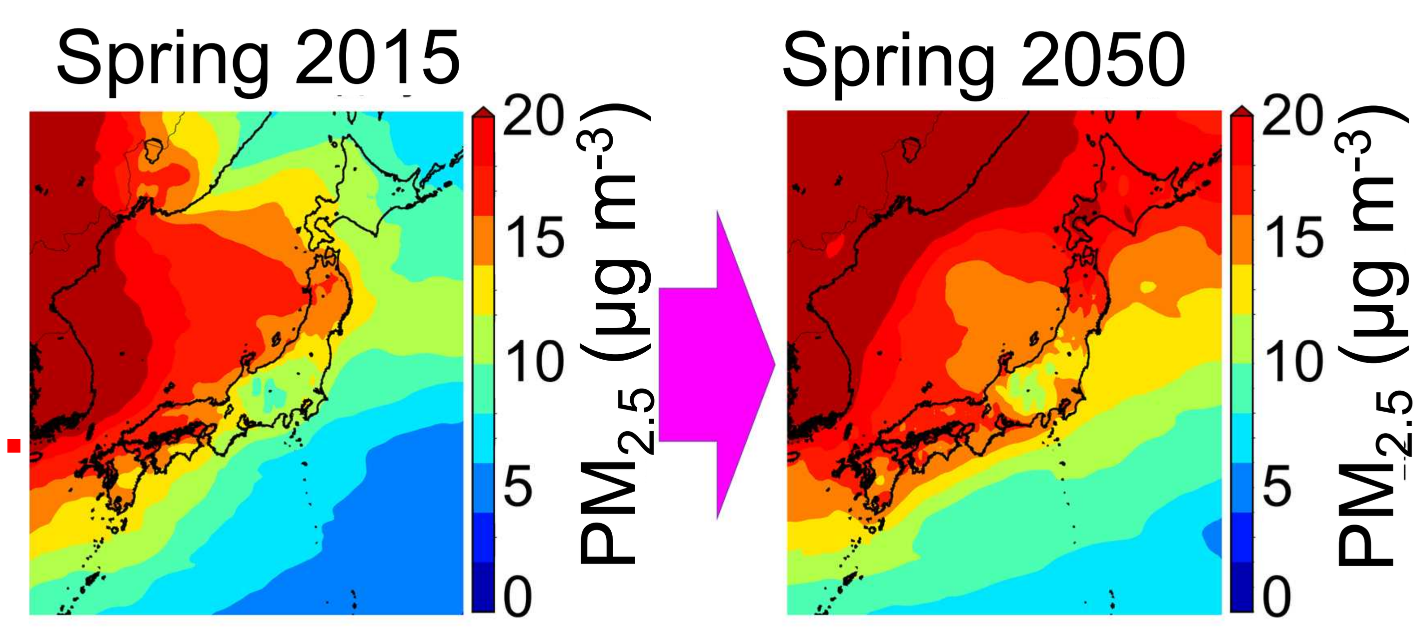


Fig.3 $PM_{2.5}$ conc. in 2015 and 2050.

(Ref. : Hata et al. *Sci. Total Environ.* (2023))

< Potential applications and effects >

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