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

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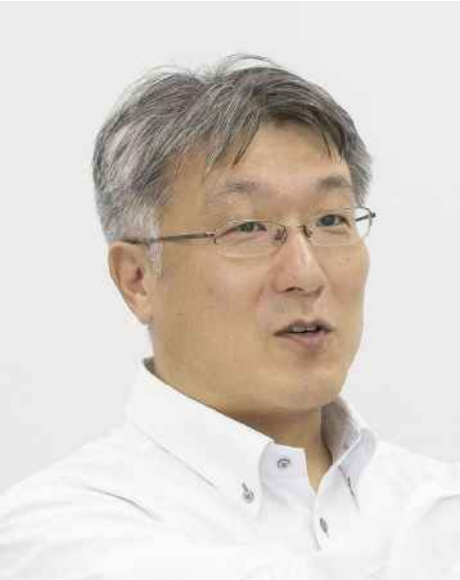
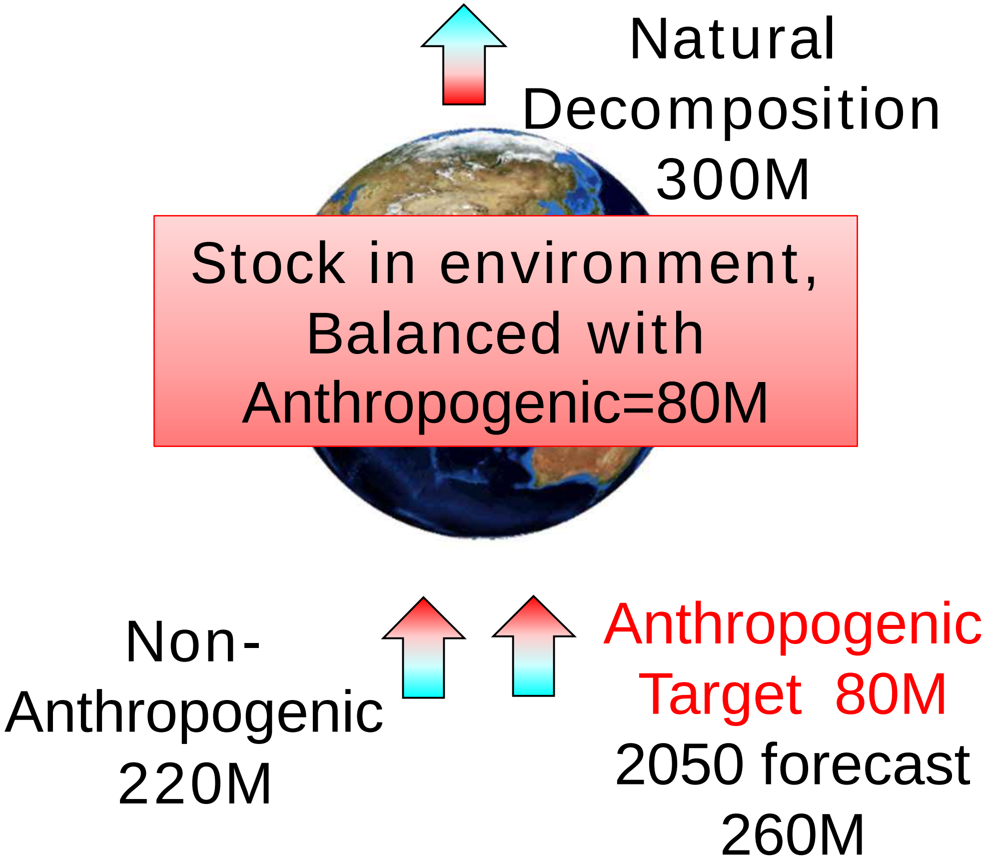
Implementing organizations :
AIST, The University of Tokyo, Waseda University,
Tokyo University of Agriculture and Technology, Kobe University,
Osaka University, Yamaguchi University,
Kyowa,Hakko Bio Co., Ltd., ASTOM Corporation, Toyobo Co., Ltd.,
FUSO Corporation, Ube Industries, Ltd,



Dr. Tohru Kawamoto

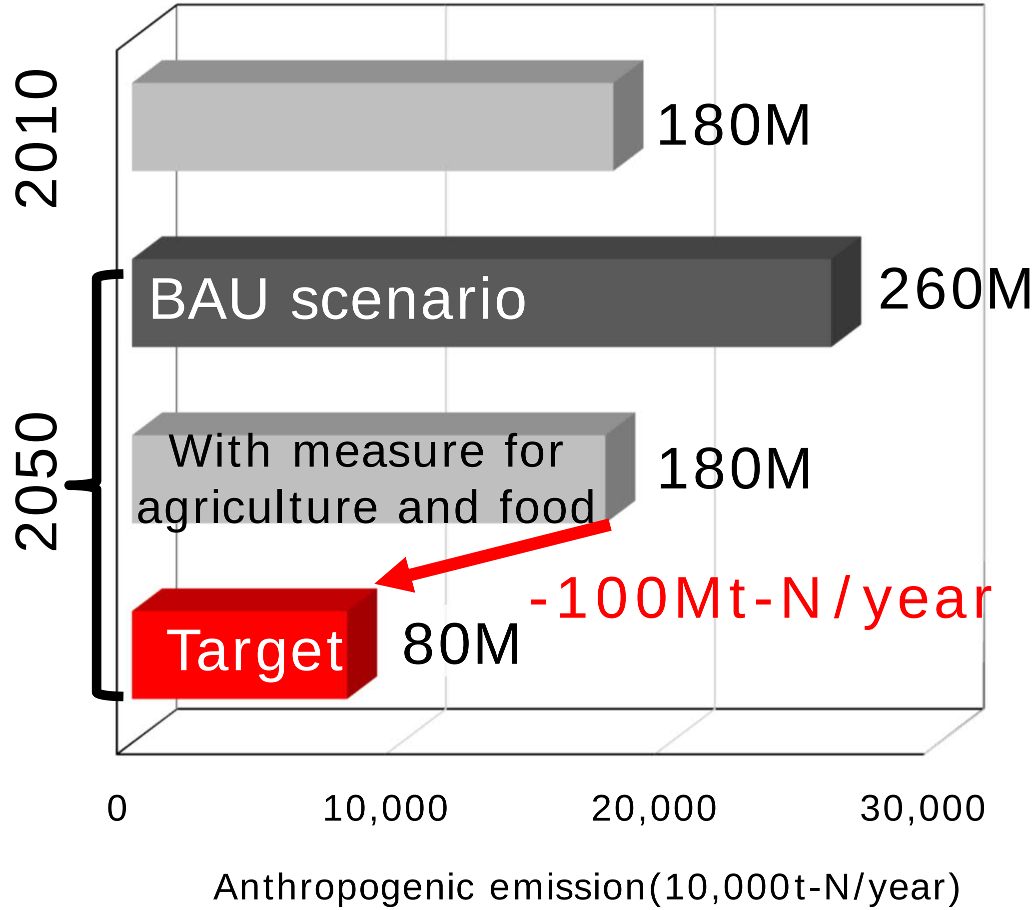
Background of the project

(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)

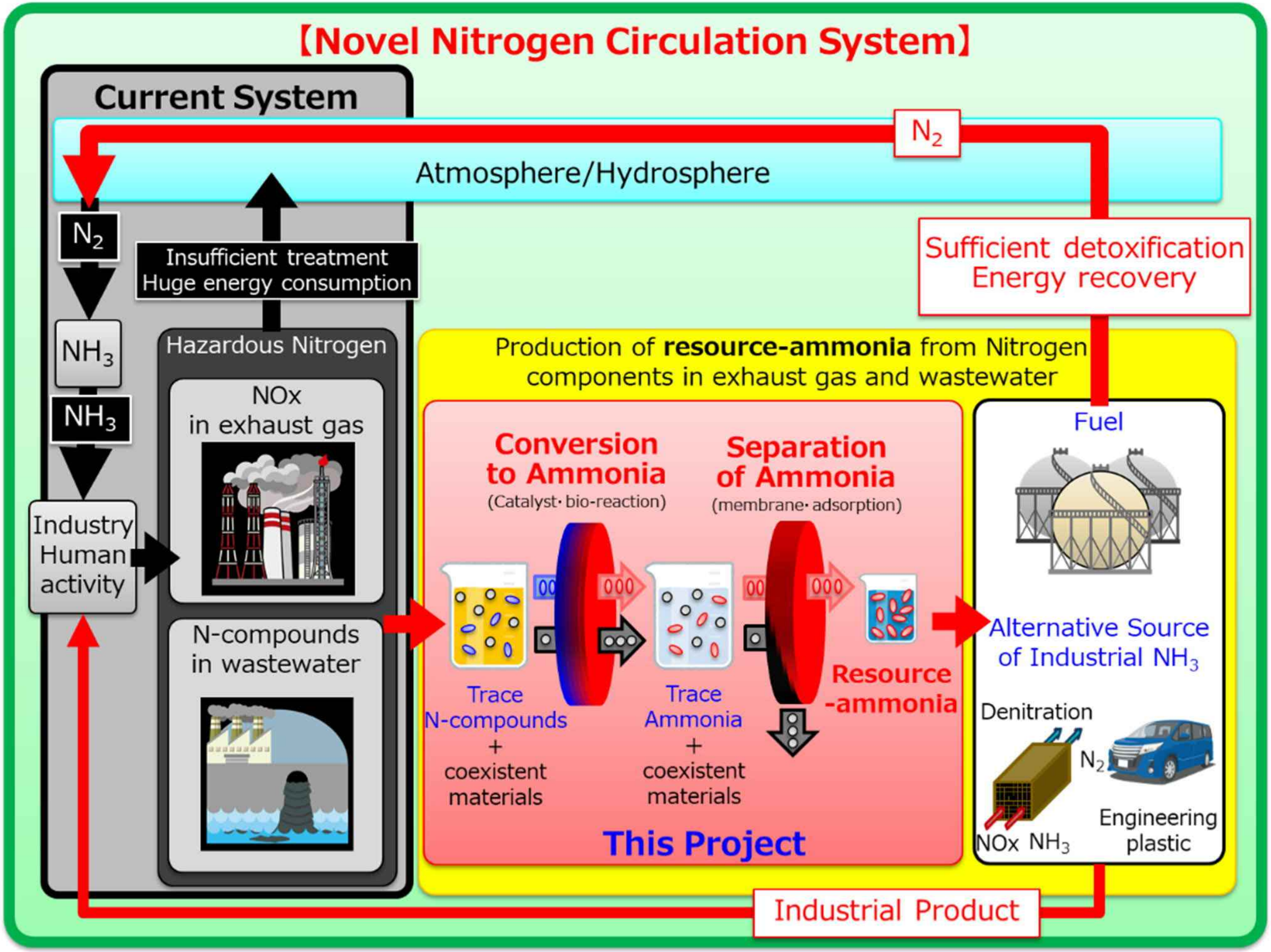
(b)Current status and target for anthropogenic nitrogen compound emissions



Additional 100Mt-N/year reduction is necessary

Tsunemi et al., submitted

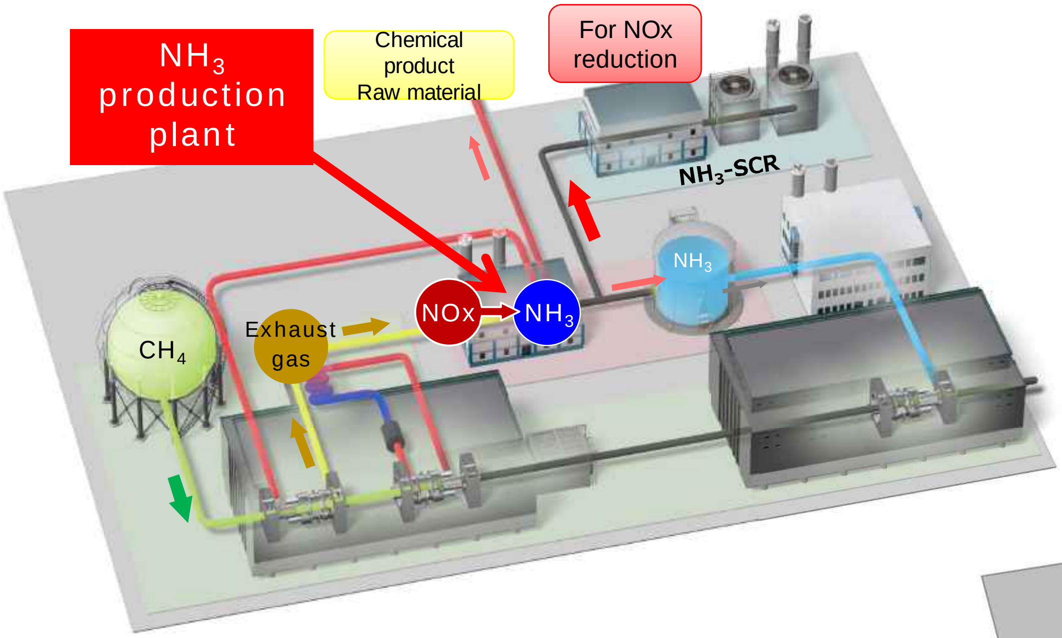
Outline of the project



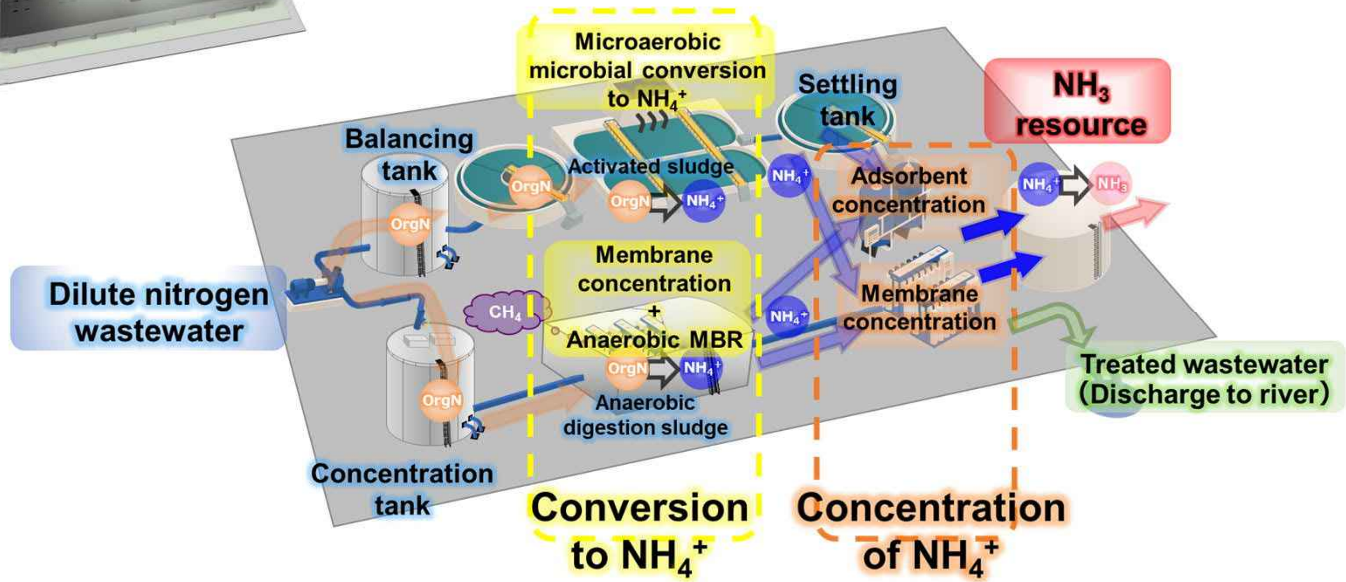
Practical application forecast

NOx in exhaust gas is converted to NH_3, which is used as denitration material and industrial raw material. Nitrogen compounds in wastewater are recovered as ammonia resources and used as fuel and raw materials.

NOx to Ammonia resources

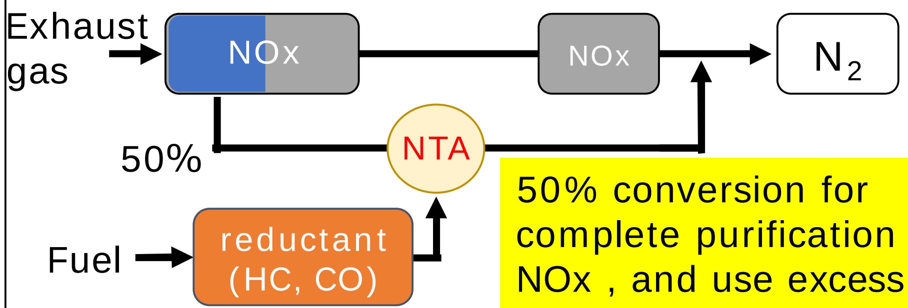


Aqueous nitrogen compounds to Ammonia resources



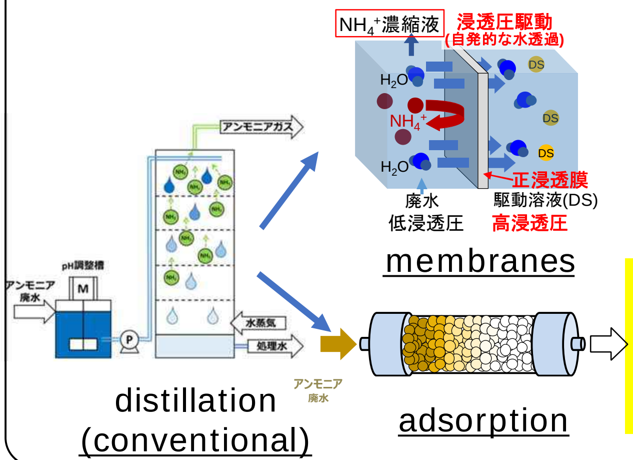
R&D Items

【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

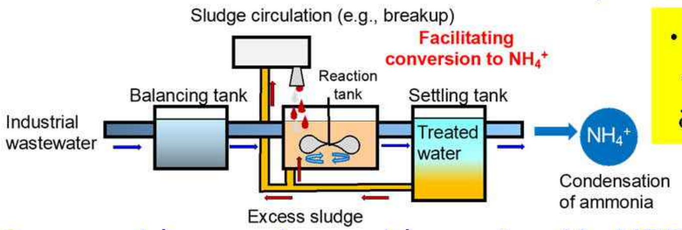
【2-2. ammonia recovery in water】
(1) new membrane/adsorption separation
(2) Construction of ultra energy-saving separation and concentration process



<1/100 of the energy consumption of conventional methods

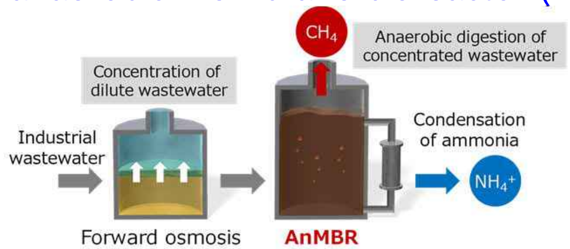
【2-1. conversion to NH_3 in wastewater】
Efficient NH_4^+ conversion bioprocess for various conditions

● microaerobic conversion to NH_4^+



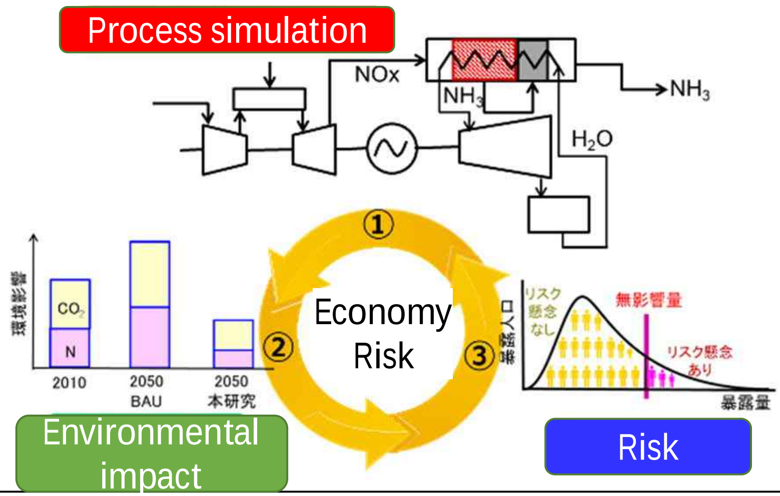
・Low NH_4^+ loss
・Use excess sludge as nitrogen source

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



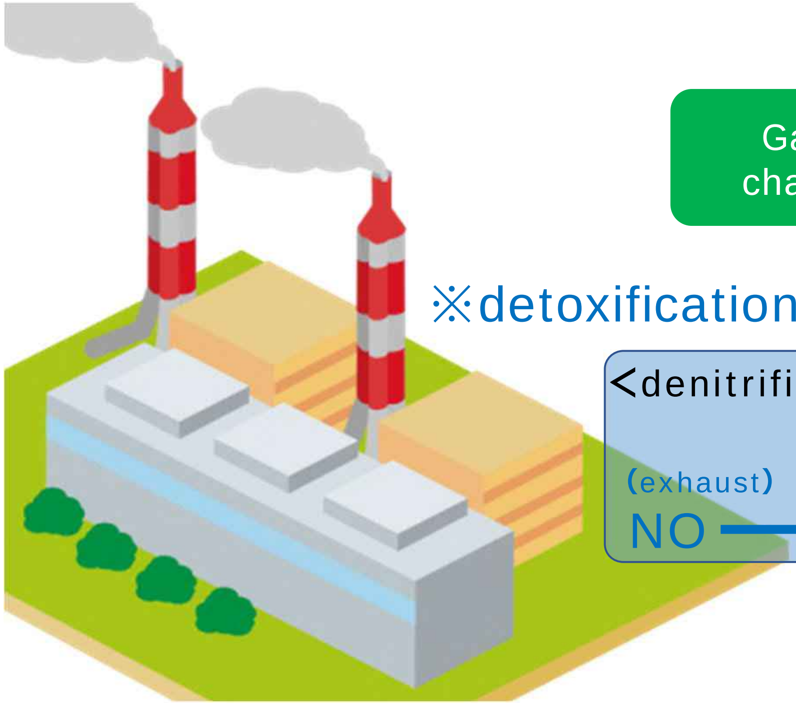
・work at high NH4- concentration
・High energy efficiency and compact size

【Theme 3. Process and evaluation】
1) Process design of actual equipment and pilots 2) economic and environmental impact assessment.



NOx to Ammonia(NTA) catalyst

LNG thermal power generation facility



Game changer

※detoxification

<denitrification>

(exhaust) NO → NH_3 → N_2

※resource recycling "process innovation"

<NOx reforming>

Hydrogen source (CH_4, etc)

(resource) NO → NH_3

Merit①
Eliminate needs for reductant

Merit②
No need to invest more energy

Avoiding HB process

Merit③
Reduction of NH_3 imported

$$NO + NH_3 \rightarrow N_2$$

$$NO + (H) \rightarrow NH_3$$

De-NOx utilises NH_3 as it is. Concentration technology for the obtained NH_3 is also developed for other applications.

2Step-NTA system

- NO→NOad (adsorption &concentration)
- NOad +reducttant→NH_3

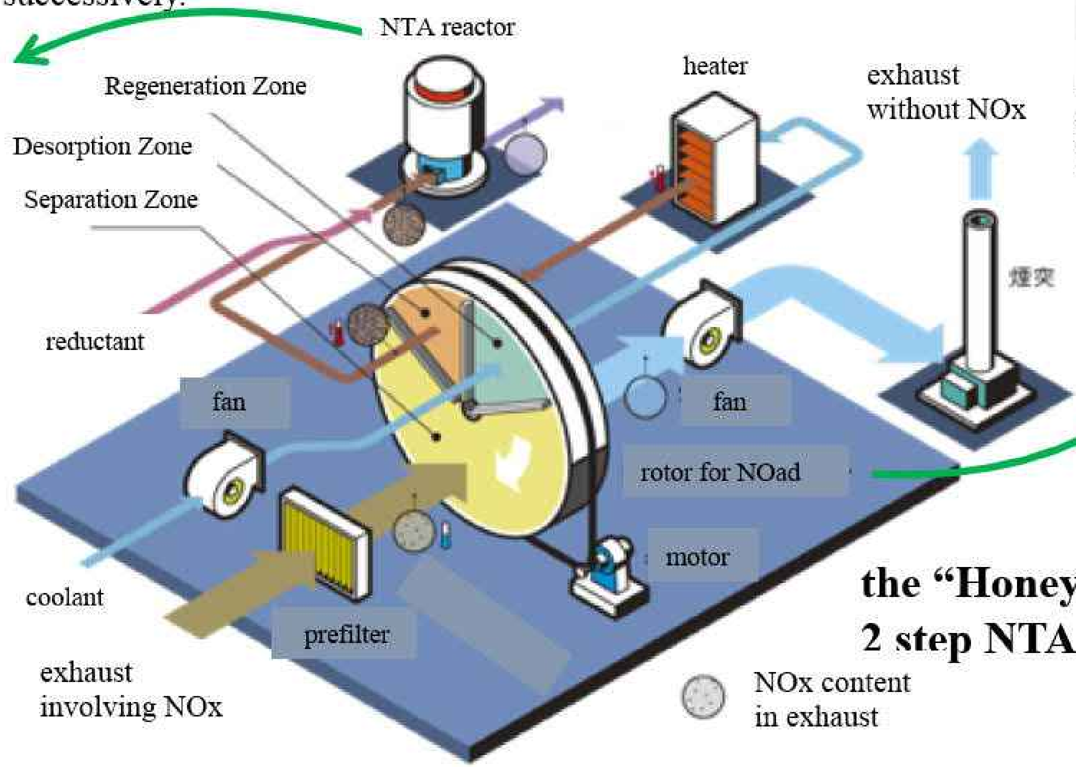
2step NTA catalytic system：

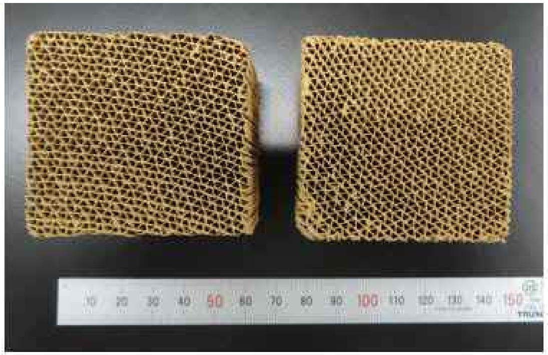
NO→NOad（adsorption and concentration）
NOad+reductant→NH_3（NTA）

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.

NTA reactor@AIST

+reductant
NOad→→→NH_3（NTA）





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

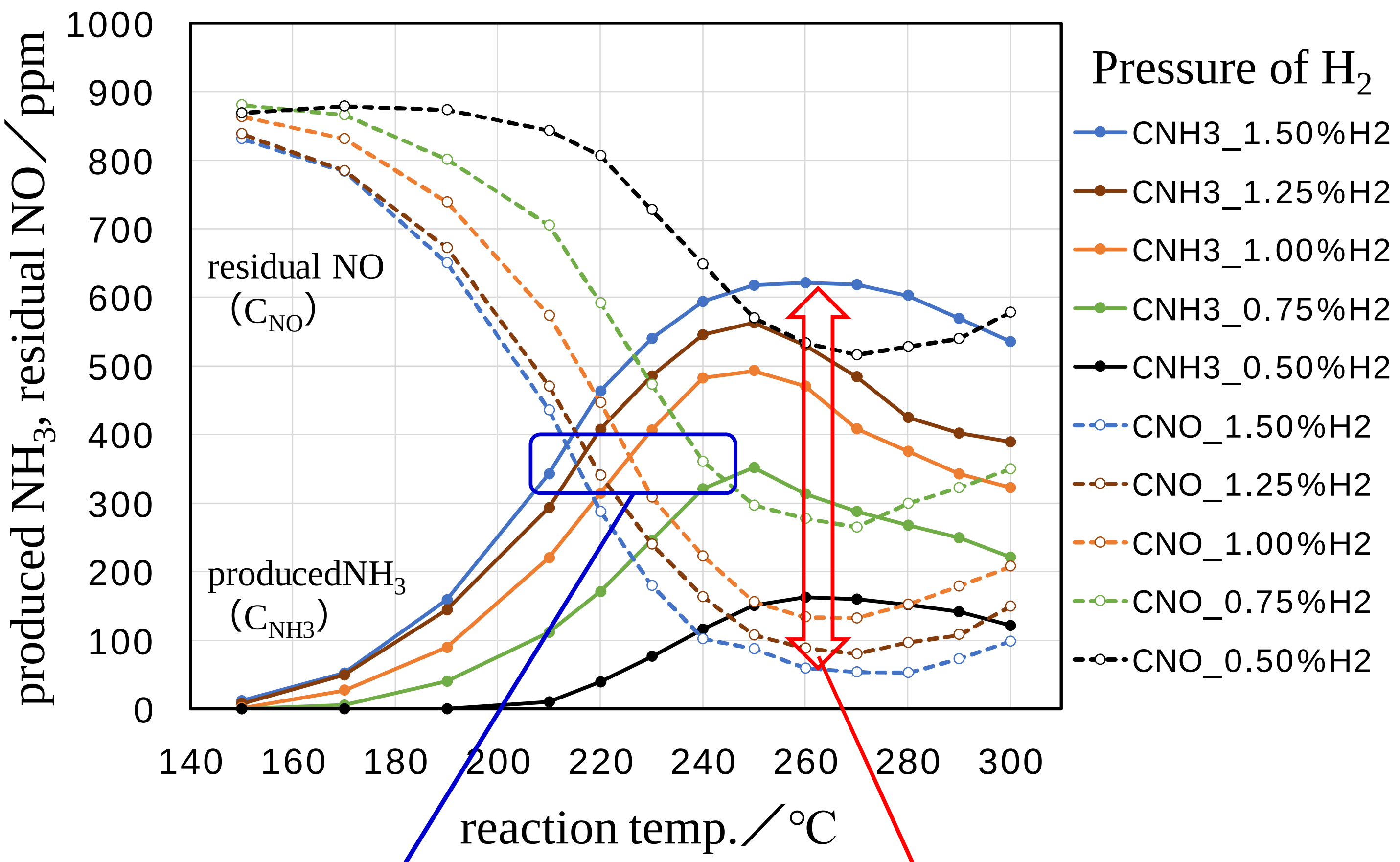
NO→NOad（ad&conc）

valuable source from exhaust!?
this is NTA＝ NOx To Ammonia

the "Honeycomb rotor"
2 step NTA catalytic system
designed by Seibu Giken

早稲田大学 WASEDA University

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

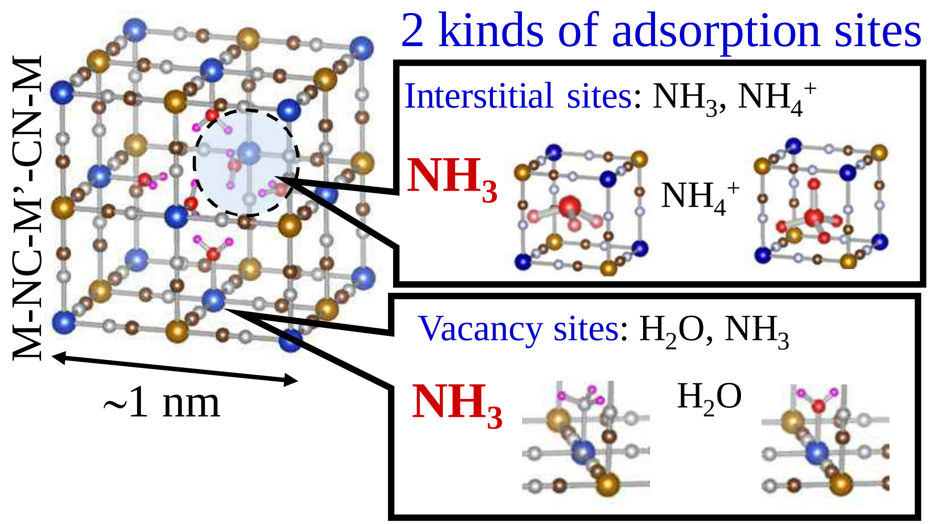


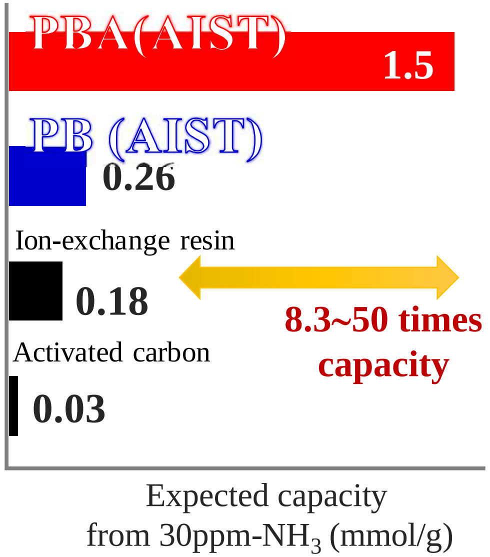
Realization of NH_3-SCR, that does not require NH_3 supply, at Cross-points $C_{NO} = C_{NH3}$. H_2-NTA + NH_3-SCR can be achieved with only P_{H2}=0.75%.

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

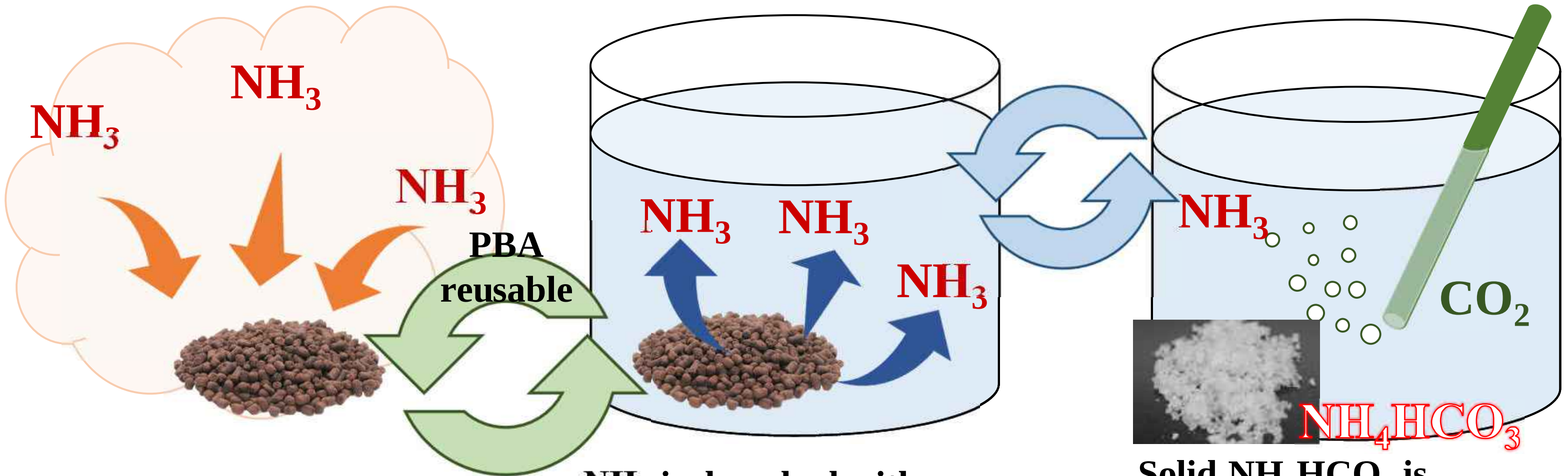
Standard reaction conditions (an atmospheric fixed bed flow reactor) : catalyst W02(0.3mL), total gas flow rate 100 mL/min (space velocity SV=30,000 h^{-1}), 0.1% NO, 1.5% H_2, 0% O_2, 10% H_2O, N_2 balance.

PBA exhibit higher NH_3 adsorption capacities than others





NH_3 is concentrated and recovered as solid NH_4HCO_3



NH_3 is selectively adsorbed by simply ventilating NTA gas into PBA.

NH_3 is desorbed with Saturated NH_4HCO_3 solution※ as washing liquid.

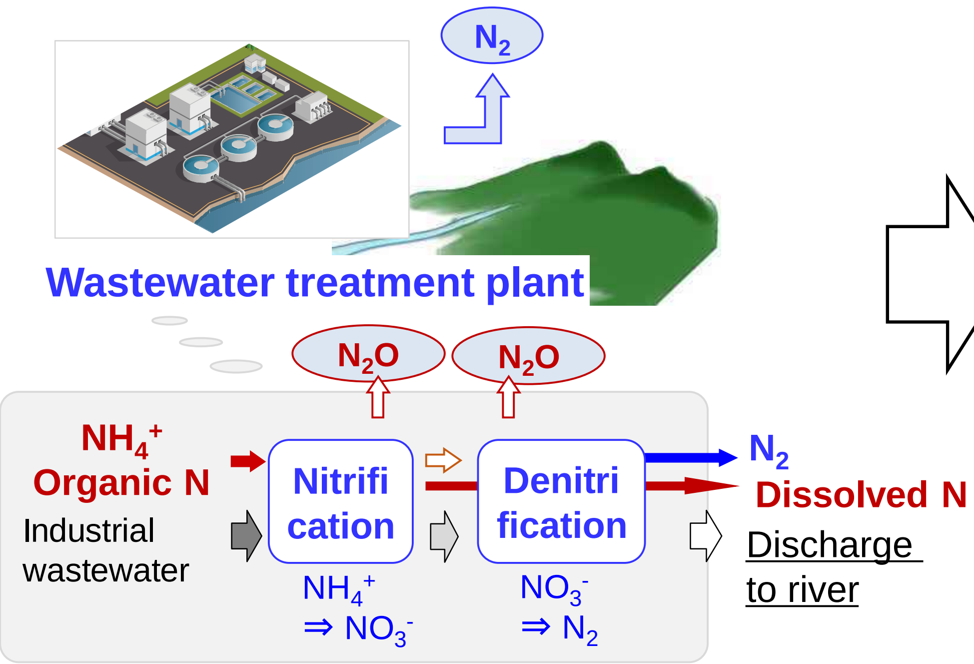
※Can be done with water and acid

Solid NH_4HCO_3 is recovered by introducing CO_2 into washing liquid after desorption.

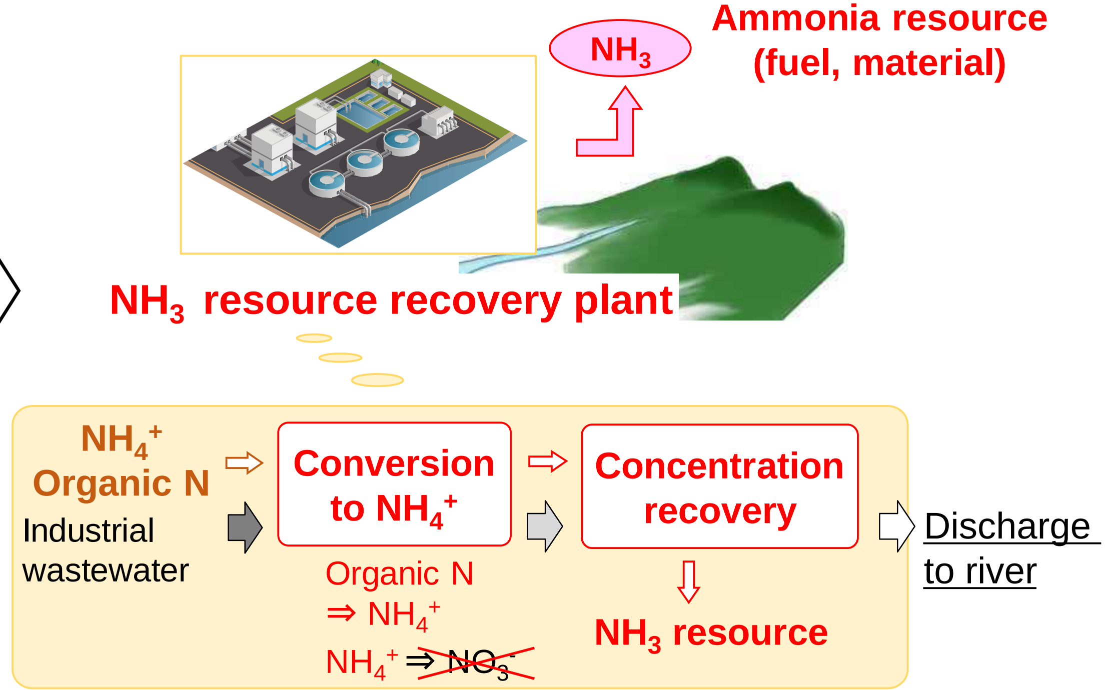
H. Usuda *et al.*, *Environ. Pollut.* **288** (2021) 117763.

Theme 2: Aqueous phase nitrogen compounds to ammonia resources.

Current state



Future image in 2050



Industrial wastewater

Theme 2 – 1

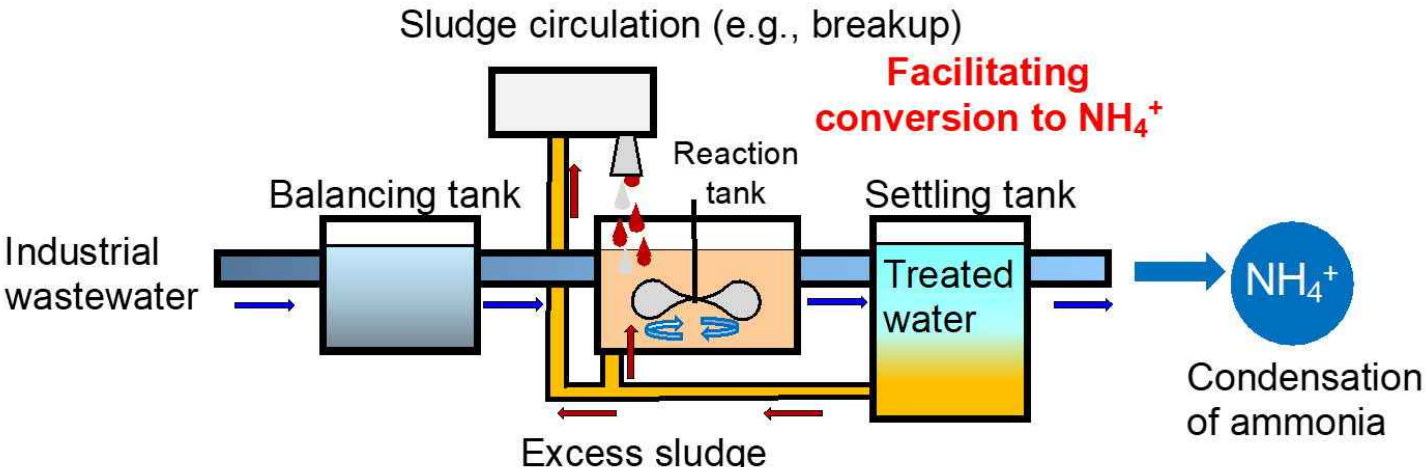
Conversion of nitrogen compounds to NH_4^+

Theme 2 – 2

Separation and concentration of NH_4^+

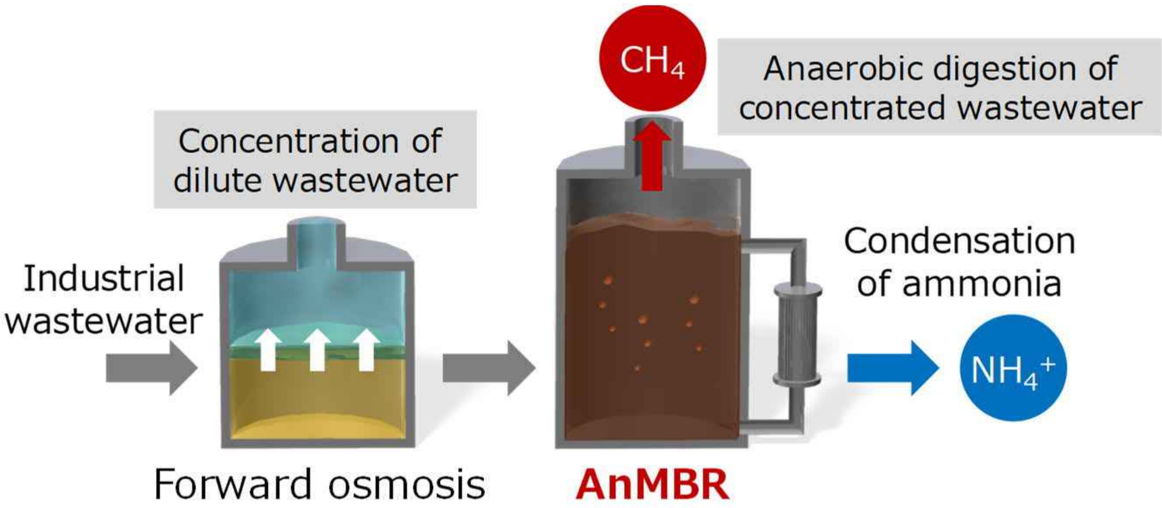
Ammonia resource

Microaerobic conversion process from nitrogen compounds to NH_4^+



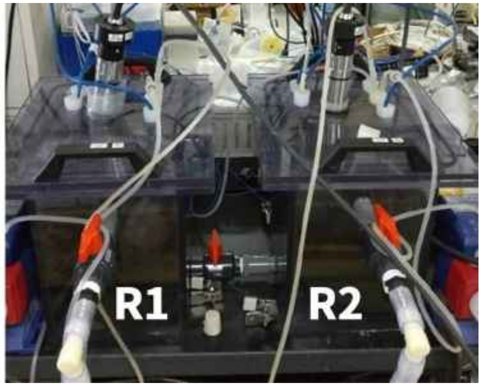
- **Inhibition of NH_4^+ degradation**
- **Recycle of excess sludge as NH_4^+ source**

AnMBR capable of efficient treatment under high ammonium concentrations

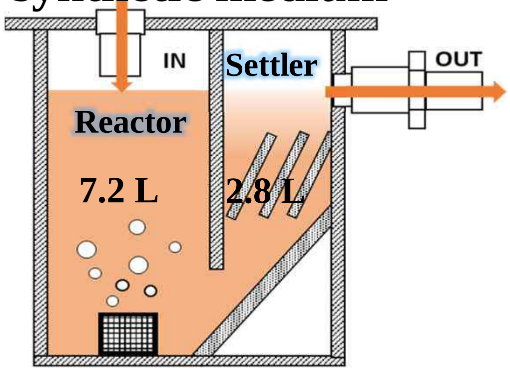


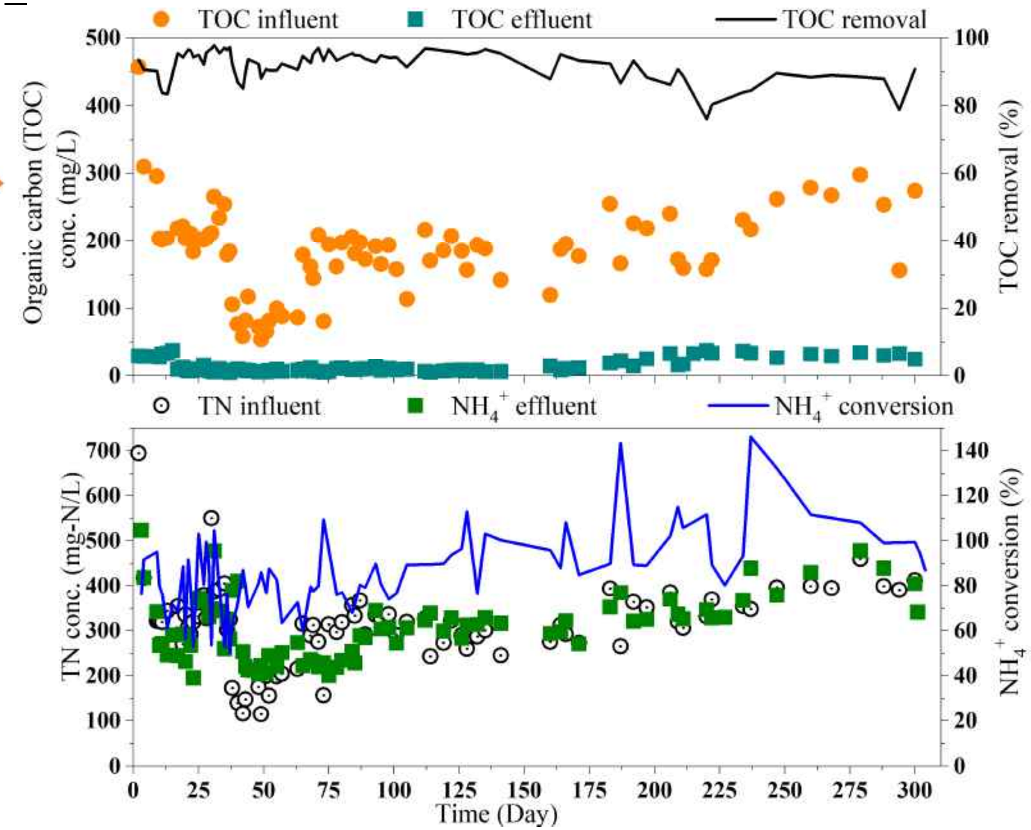
- **Reinforced NH_4^+ tolerance**
- **Improvement of compactness and treatment efficiency**

Performances of a simplified NH_4^+ conversion process



Continuous supply of synthetic medium





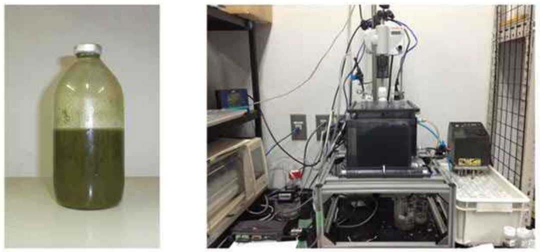
Duplicate	Period [day]	HRT [hrs]	SRT [days]	Aeration rate [L/min]
R1	0~300	11.2	5	2.0 (DO conc. 0.1 mg-O_2/L)
R2				

- 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%)

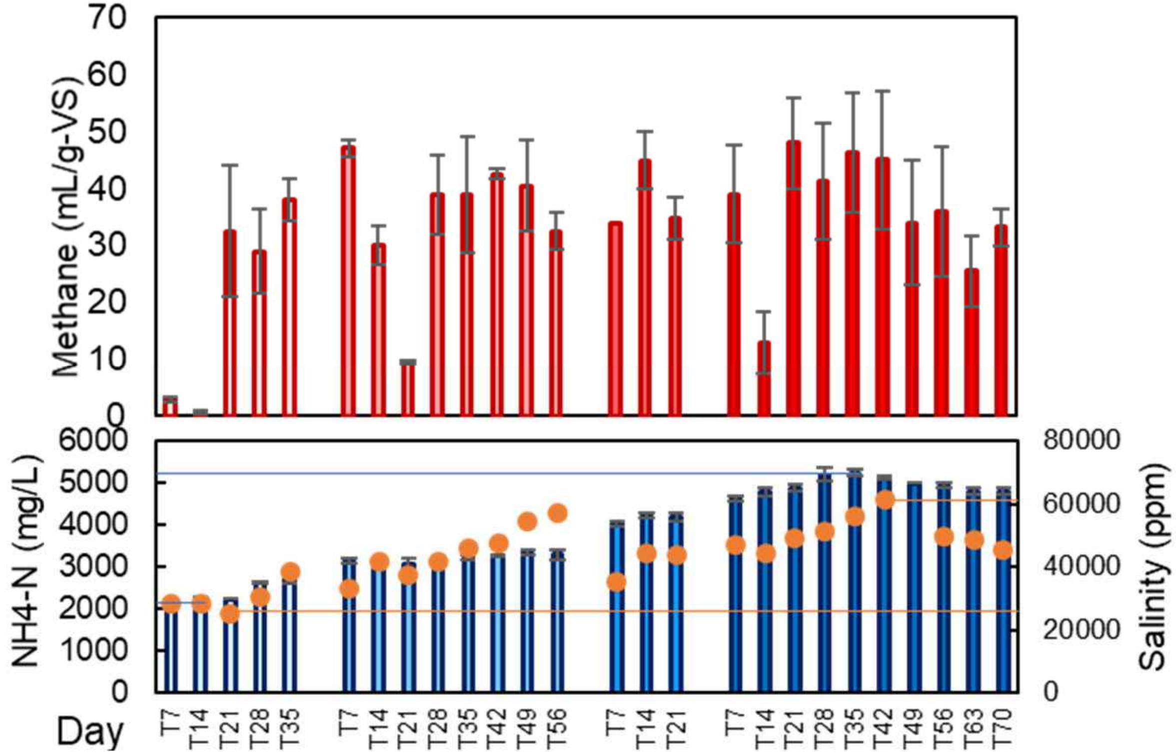
➢ Construction of highly NH_4^+ tolerant microbial consortia

Microbial source

Acclimatization to high NH_4^+ concentrations



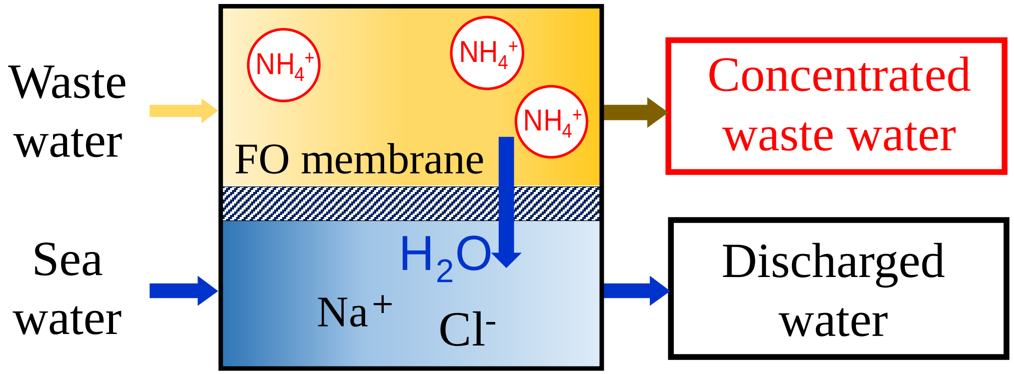
Enrichment of tolerant microbes



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

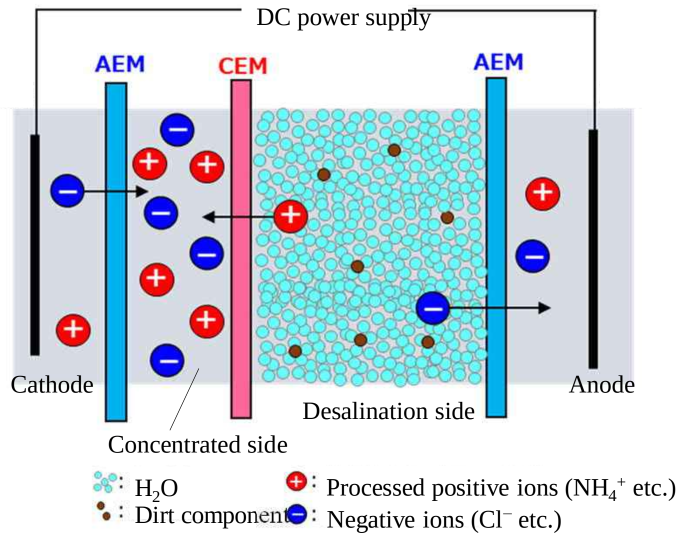
Theme 2-2: Processes for the concentration and recycling of dilute ammonia.

Forward osmosis (FO) Process

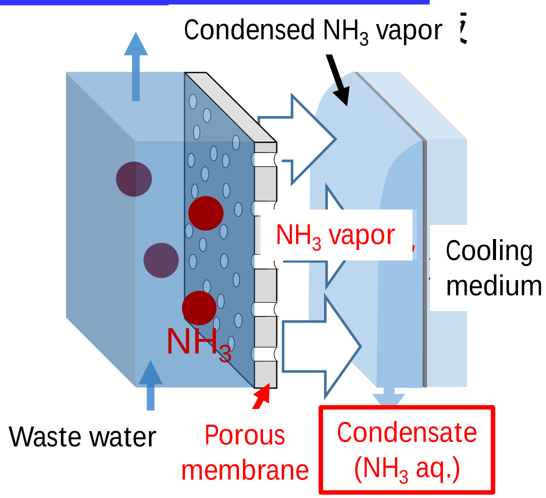


- Diluted seawater after the process can be discharged
- Energy required for concentration is only pump power

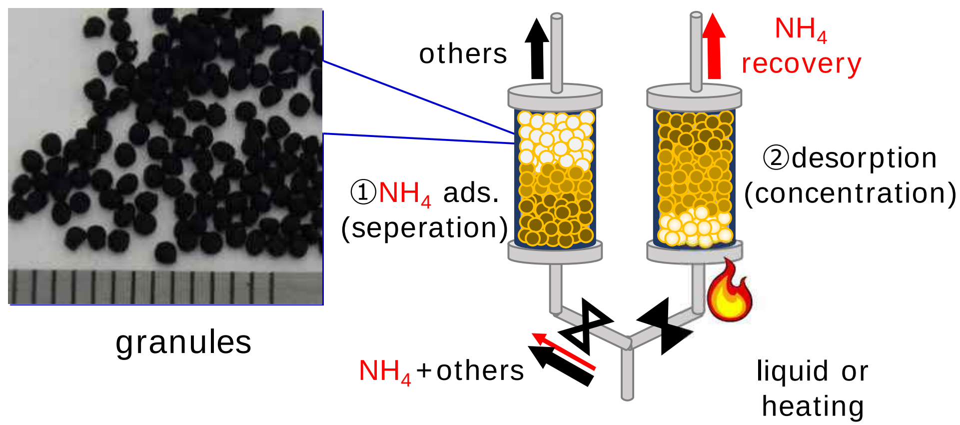
Ion exchange membrane method



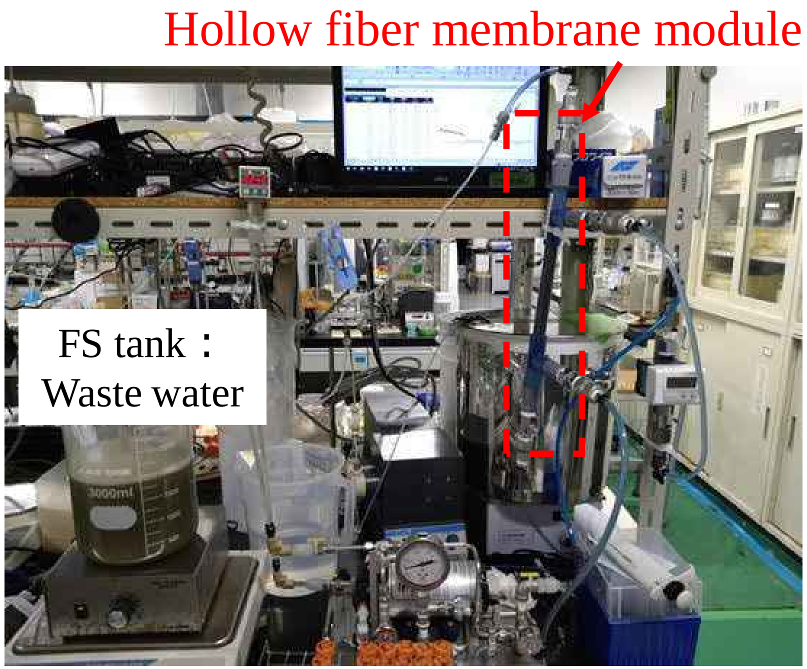
membrane distillation

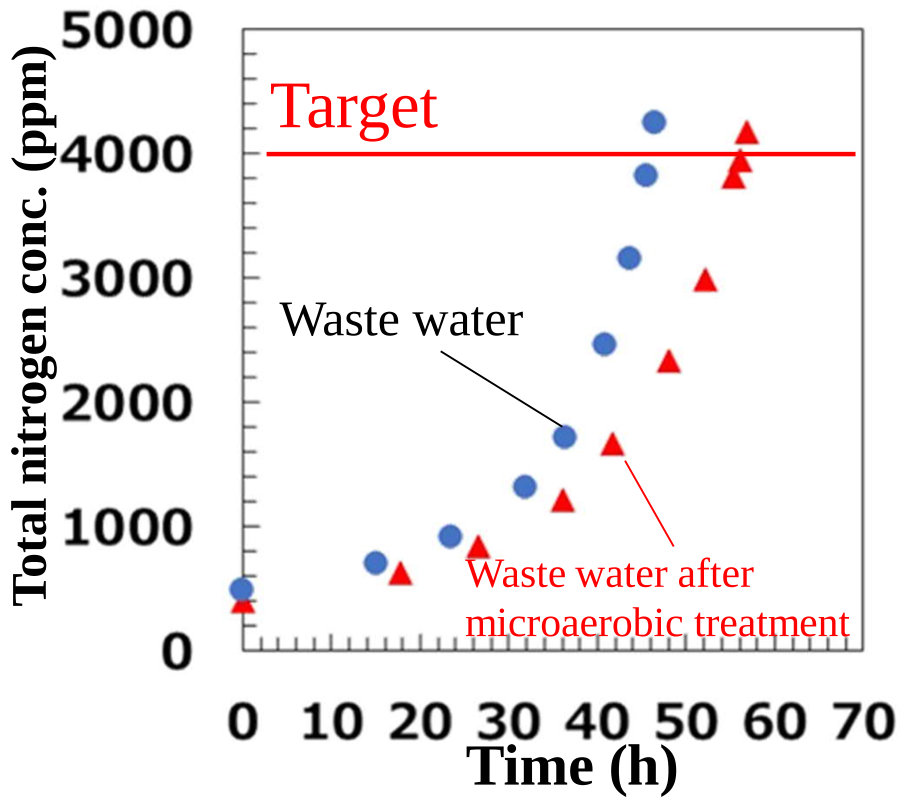


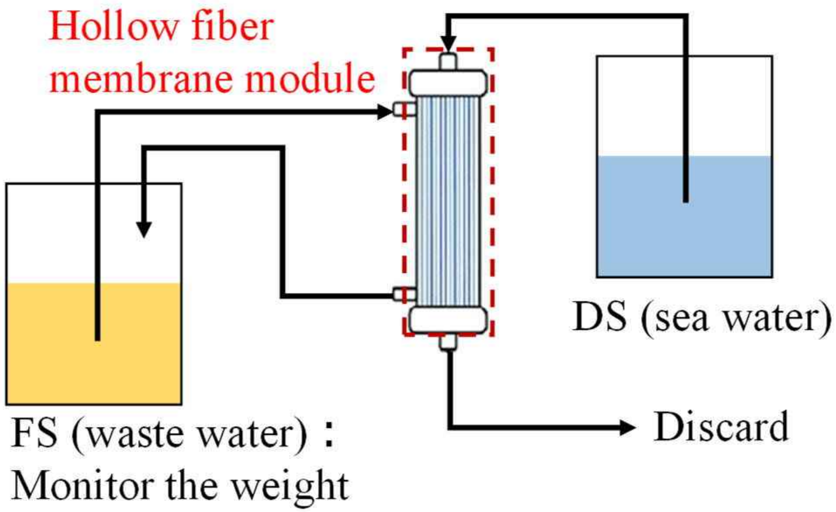
Adsorption separation



Theme 2-2:Concentration by FO membranes



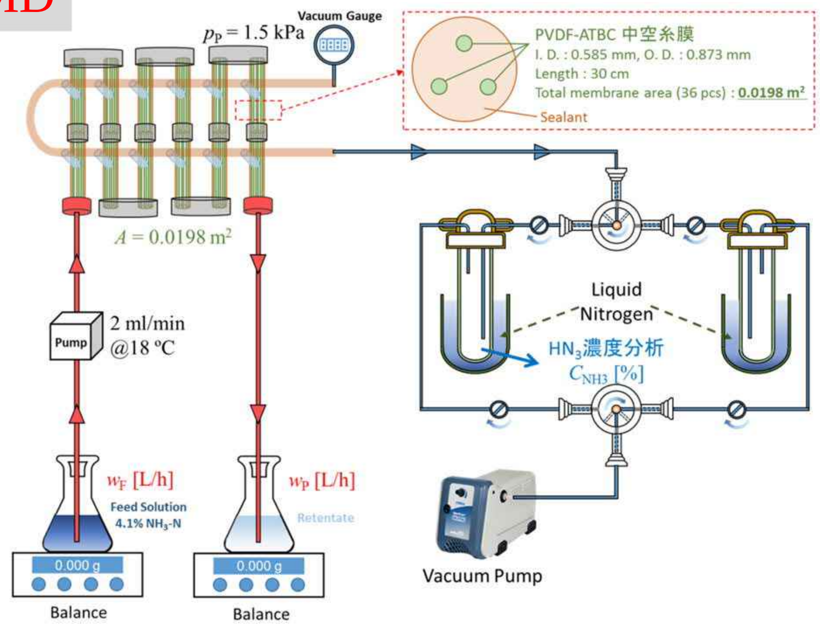




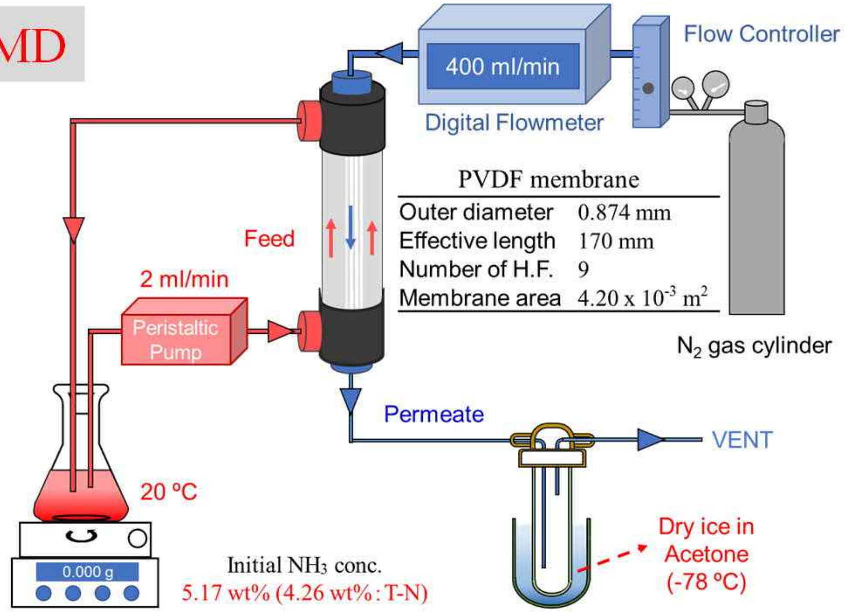
Concentrate to target concentration using seawater

To achieve a 5% to 35% concentration.

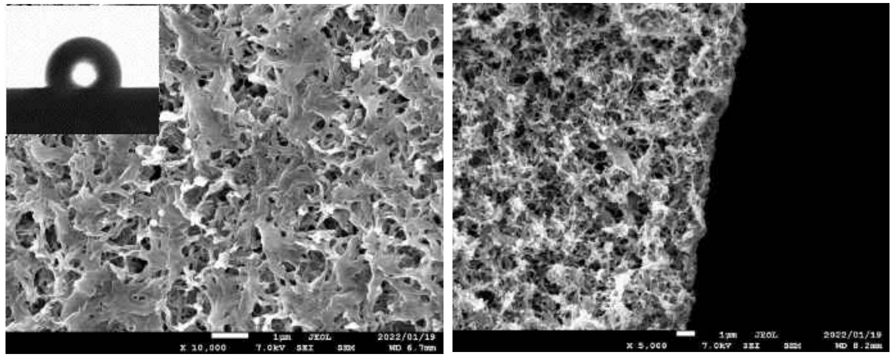
VMD



SGMD

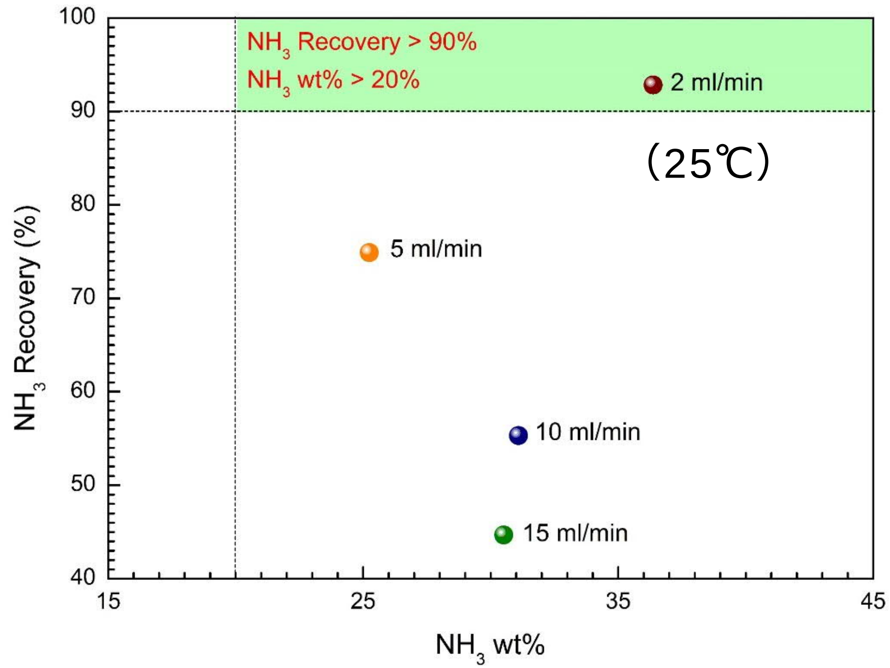


Water contact angle



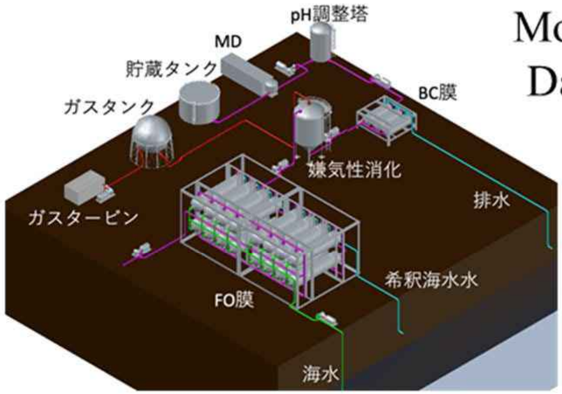
Surface | Cross section

Porous hydrophobic membrane for membrane distillation



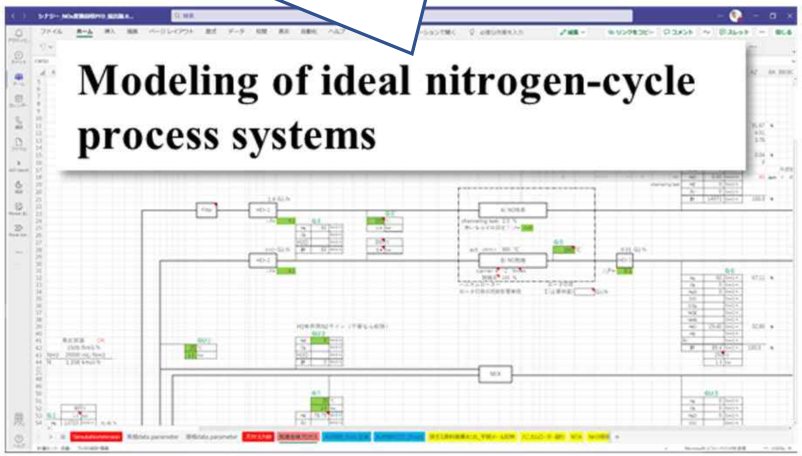
NH_3 concentration in permeate side and recovery ratio

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



Model Data

Data



Modeling of ideal nitrogen-cycle process systems

R&D of elemental process technologies

Basic design of process systems

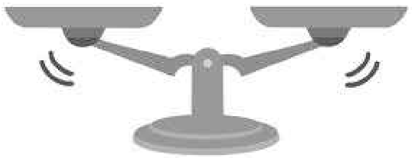
■ LCA of implementation of new technologies

■ Risk assessment of nitrogen compounds emitted from new processes

Life Cycle Impact Assessment: LCIA

Economic viability

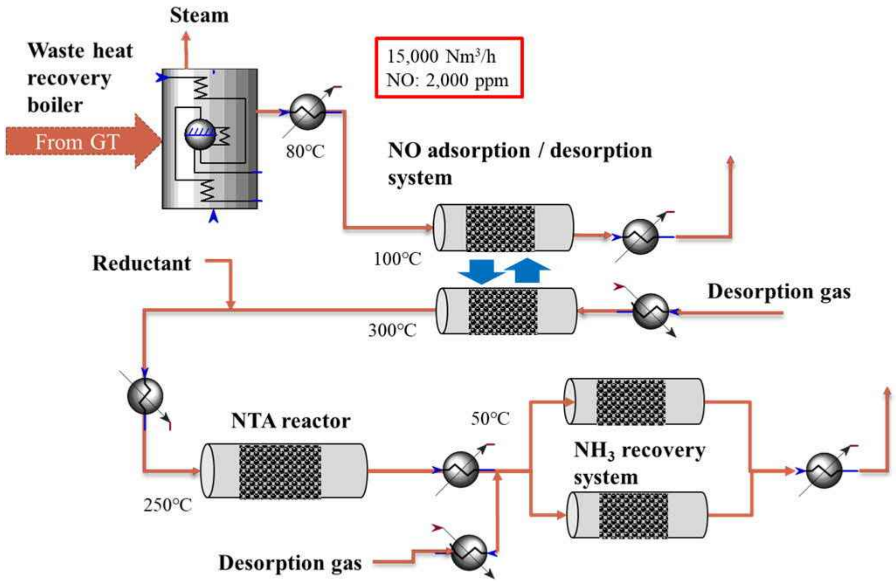
Environmental impact



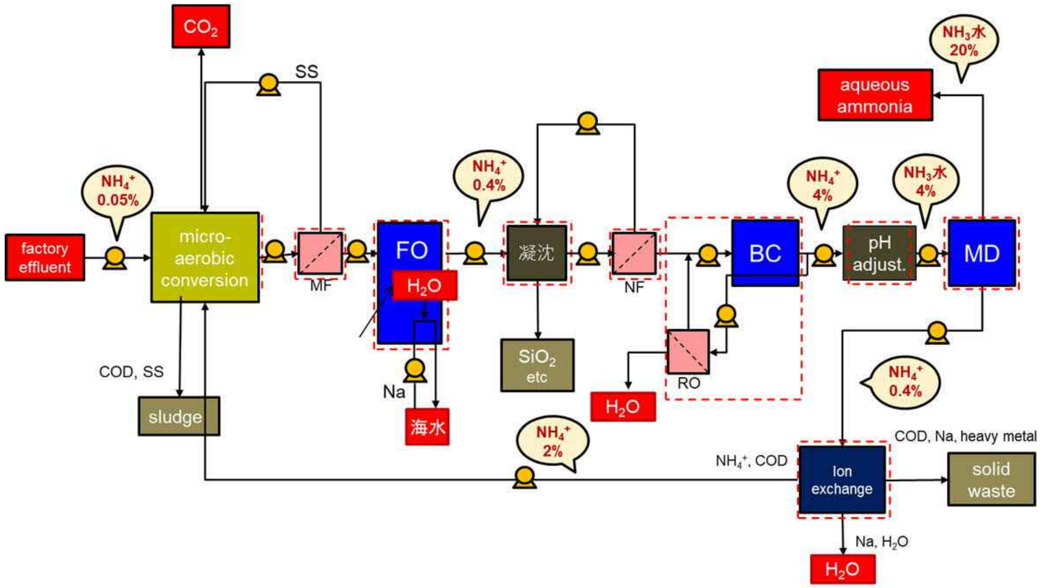
- Calculation of energy &mass balance for NOx in gas and nitrogen compounds in wastewater
- Calculation of CO_2 emissions , etc.

Theme 3: Estimated CO_2 emissions for each process.

Recycling nitrogen compounds in gas phase to ammonia resource



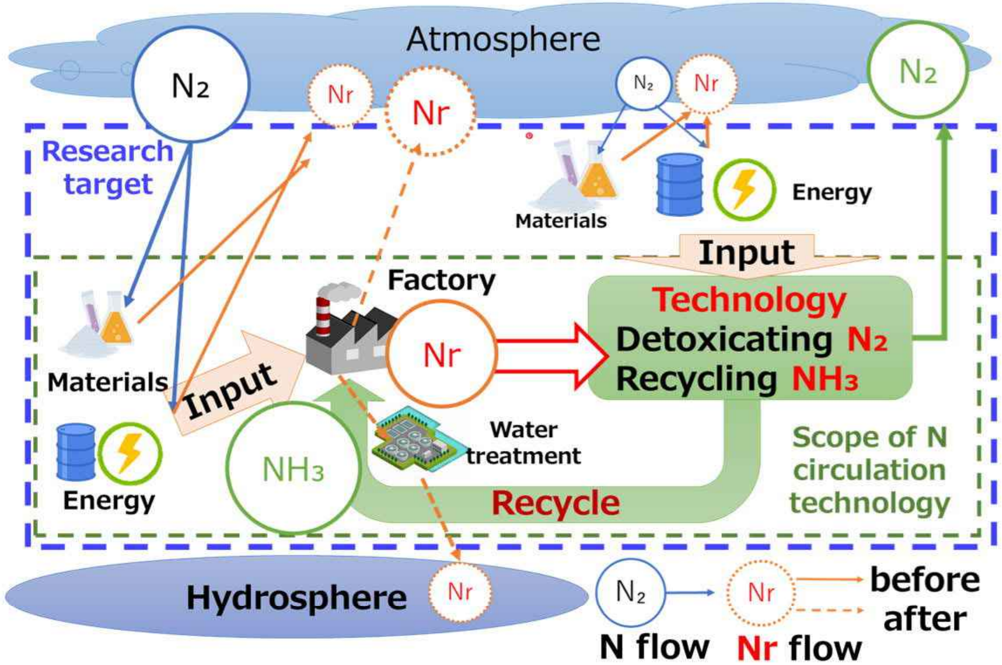
Recycling nitrogen compounds in wastewater to ammonia resource



- 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)

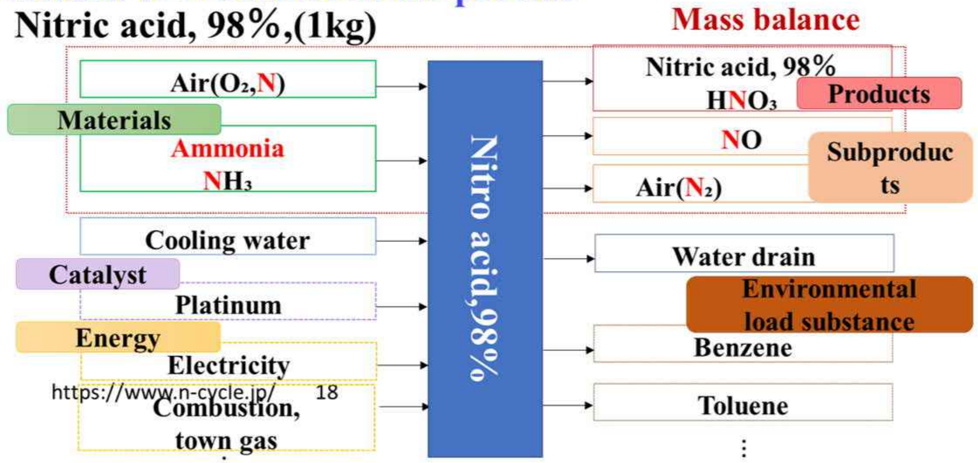
- Estimation of the CO2 emissions: the process system in the above figure is less than 1/20 of the application of the ammonia stripping method

◇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



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