Improving Fe oxidizing/removal process by limestone addition to rice husk bed on large scale passive treatment test for AMD in Japan

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Japan Organization for Metals and Energy Security

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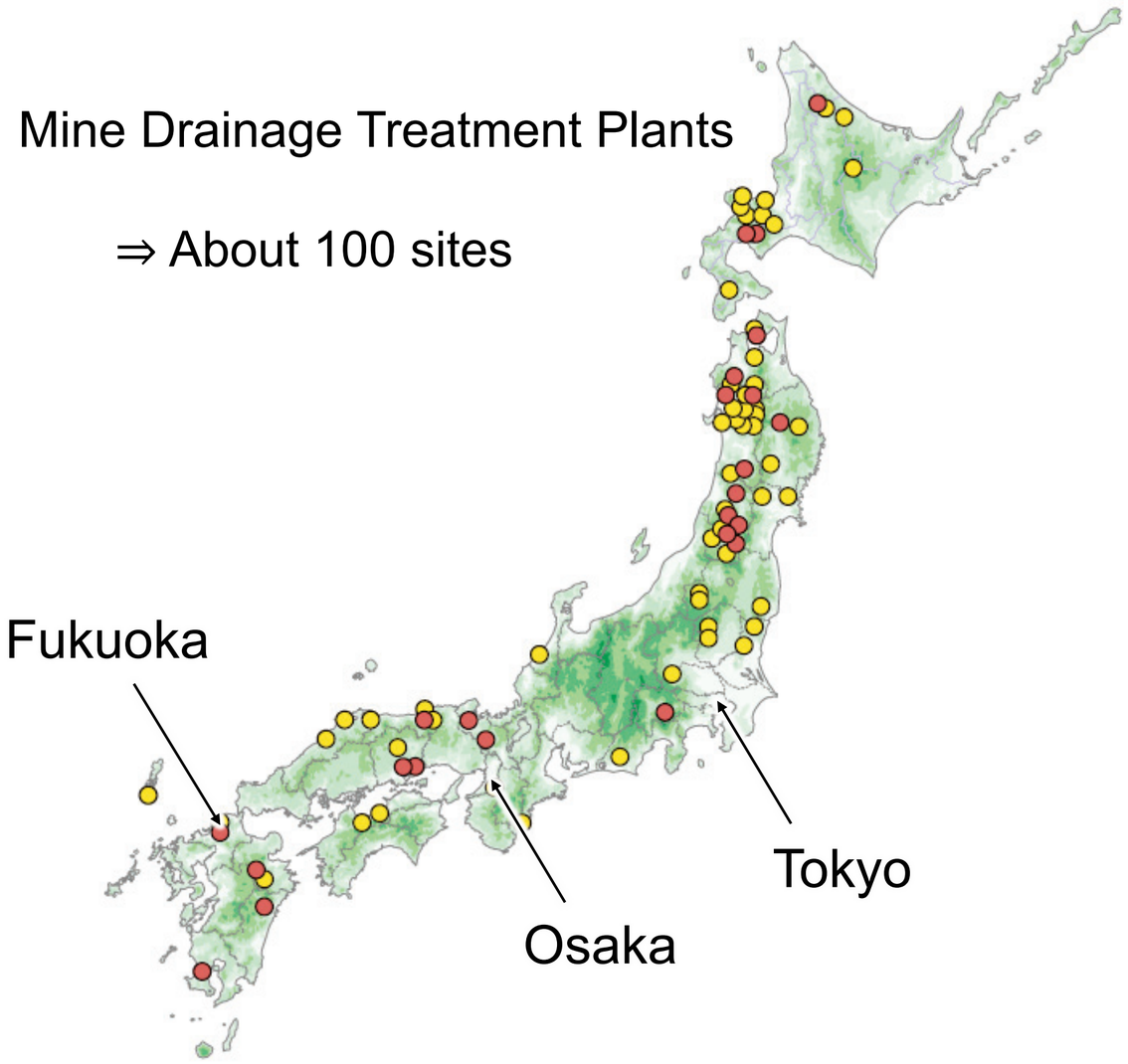
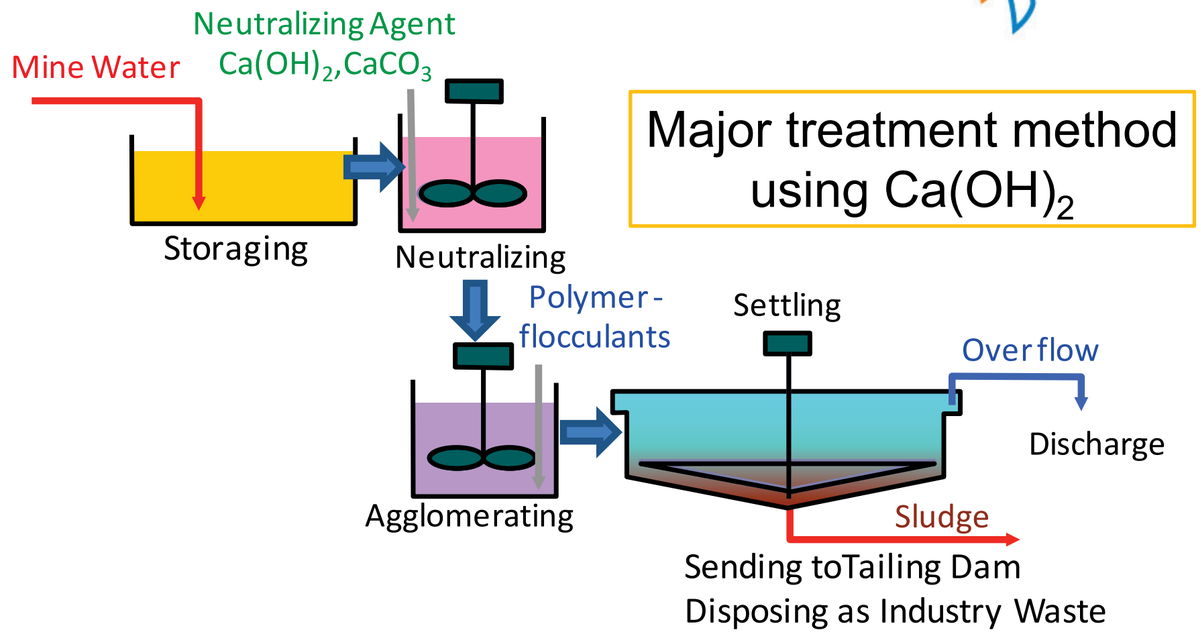
Active Mine Drainage Treatment in Japan

Mine Drainage Treatment Plants

⇒ About 100 sites



Ministry of Economy, Trade and Industry (2022) Central Mine Safety Committee in Japan.



Major treatment method using $Ca(OH)_2$

A large amount of cost

Cost reduction
by Passive treatment techniques

The Test Site

Photo by JOGMEC

The Test Site

Photo by JOGMEC

Acid Mine Drainage at the Test Site

	Temp. (°C)	Fe (mg/L)	pH (-)	Zn (mg/L)	Cu (mg/L)	Cd (mg/L)	SO_4^{2-} (mg/L)
Range	10-18	**32-49**	**3.2-4.0**	**13-20**	1-**10**	**0.04-0.08**	250-340
	Fe Oxidation& Precipitation using Fe-oxidizing bacteria		**Anaerobic sulfate-reducing biochemical (SRB) process with limestone**				
Japan's discharge standard	-	10	5.8-8.6	2	3	0.03	None

AMD flow rate at the site: 160 – 400 L/min

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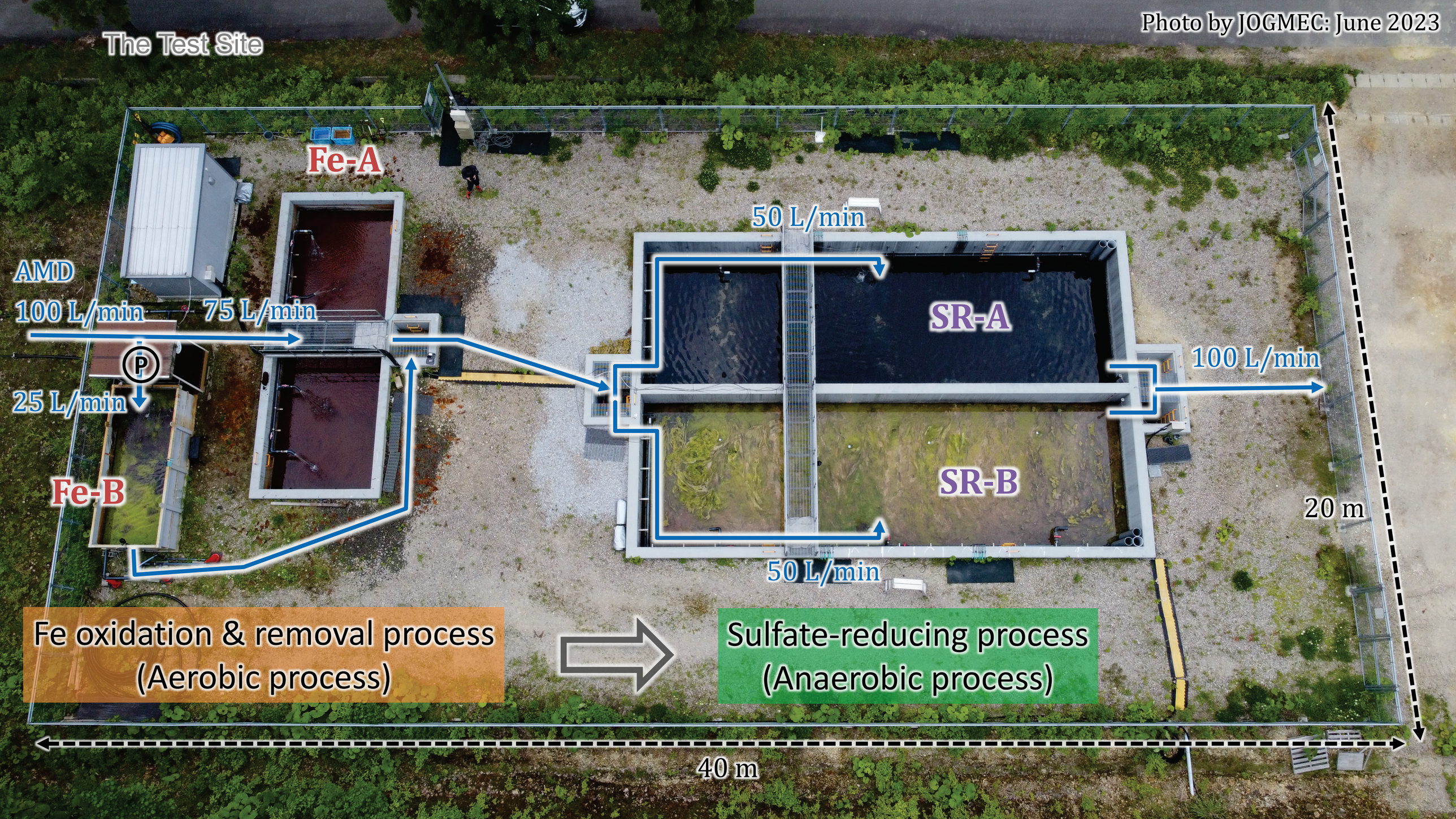
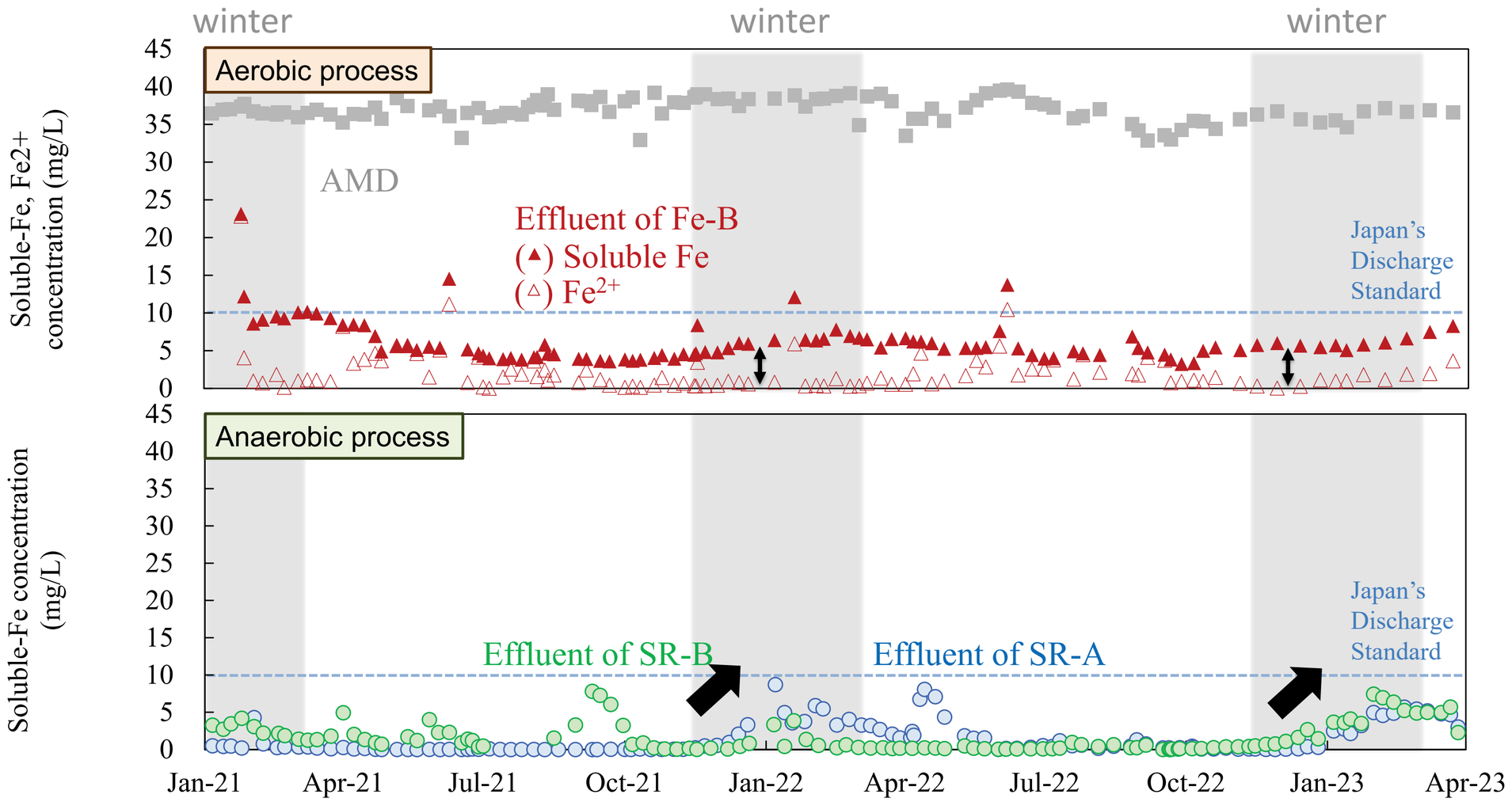

The Test Site
Photo by JOGMEC: June 2023
Fe-A
AMD
100 L/min
75 L/min
P
25 L/min
Fe-B
50 L/min
SR-A
SR-B
100 L/min
50 L/min
20 m
40 m
Fe oxidation & removal process
(Aerobic process)
Sulfate-reducing process
(Anaerobic process)

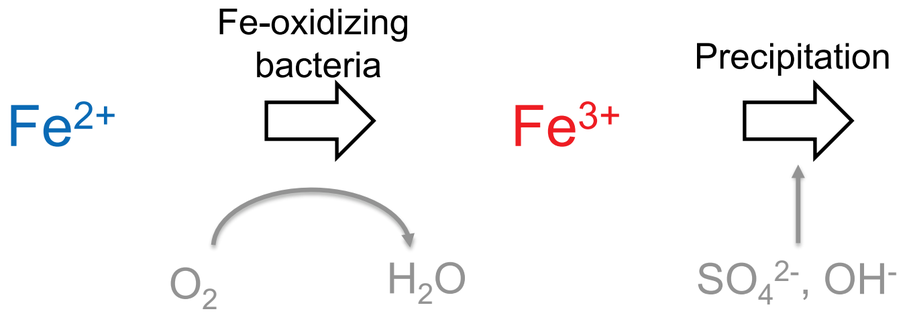
Past Fe Removal Performance



【Problem】✓ Increasing Soluble-Fe concentration of treated water in winter

Chemical Reaction of Multi-step Passive Treatment System

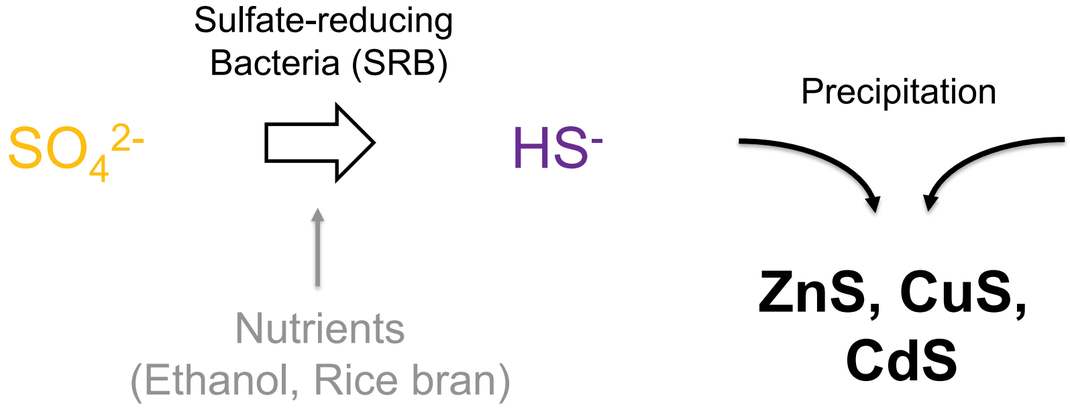
Aerobic process for Fe removal



$Fe_{16}O_{16}(OH)_{9.6}(SO_4)_{3.2}\cdot 10H_2O$

(Mainly as) Schwertmannite

Anaerobic process for Zn/Cu/Cd removal



Zn^{2+}, Cu^{2+}, Cd^{2+}

JOGMEC

Aerobic process

Fe^{3+} precipitates insufficient

Fe^{2+} —(Oxidizing; O_2 → H_2O)→ Fe^{3+} —(Precipitation; Decreasing)→ $Fe_{16}O_{16}(OH)_{9.6}(SO_4)_{3.2}\cdot 10H_2O$

(Mainly as) Schwertmannite

Anaerobic process

Fe ion scarcely precipitate

SO_4^{2-} —(Sulfate-reducing Bacteria (SRB); Decreasing)→ HS^-

$Fe^{2+} \rightarrow Fe^{2+}$

$FeS \rightarrow Fe^{2+}$

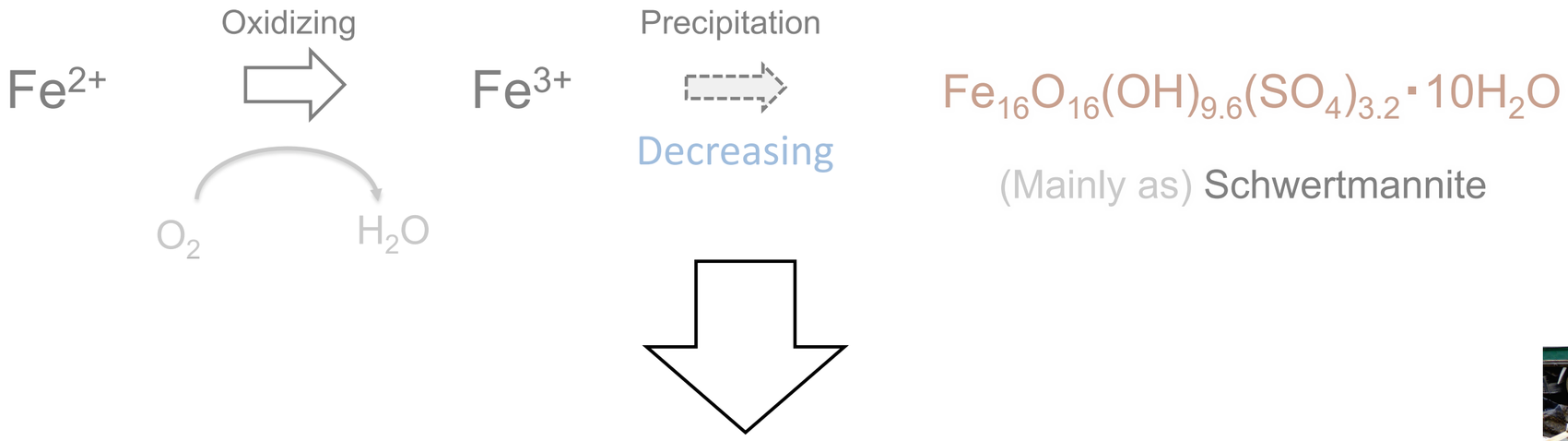
Zn^{2+} (Ion-exchange) → ZnS

→ Discharge

Chemical Reaction in Winter Season

Aerobic process

Fe^{3+} precipitates insufficient



Need to improve Fe precipitation in Fe oxidation/removal reactor by pH increasing using neutralizing material (limestone)

【Objective】

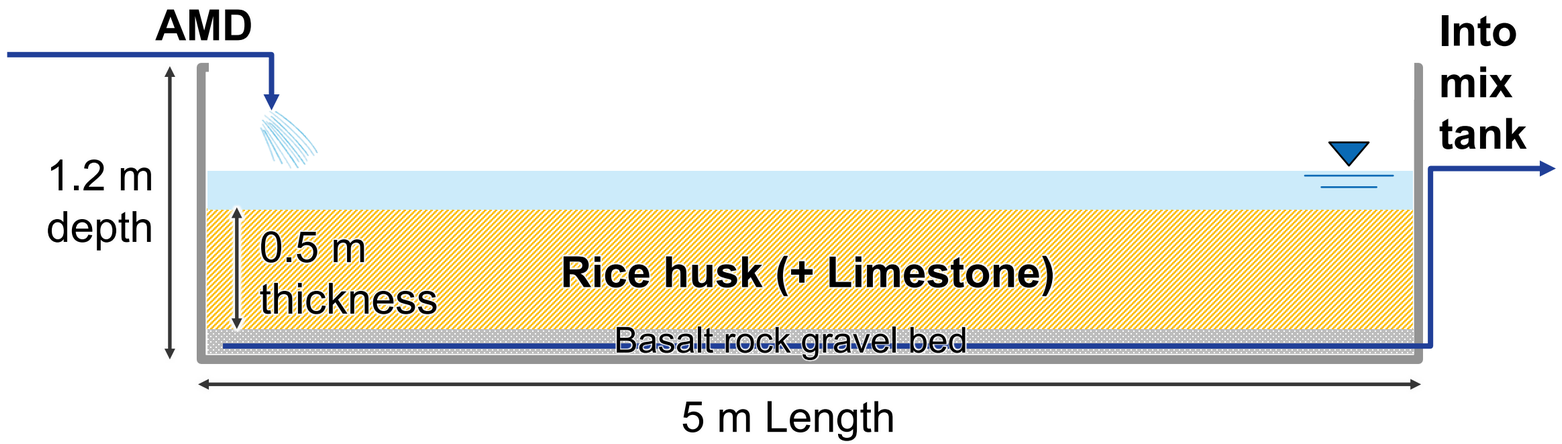
- ✓ **Investigation of Fe removal performance improvement via limestone addition**

Aerobic Bio-chemical Reactor Design

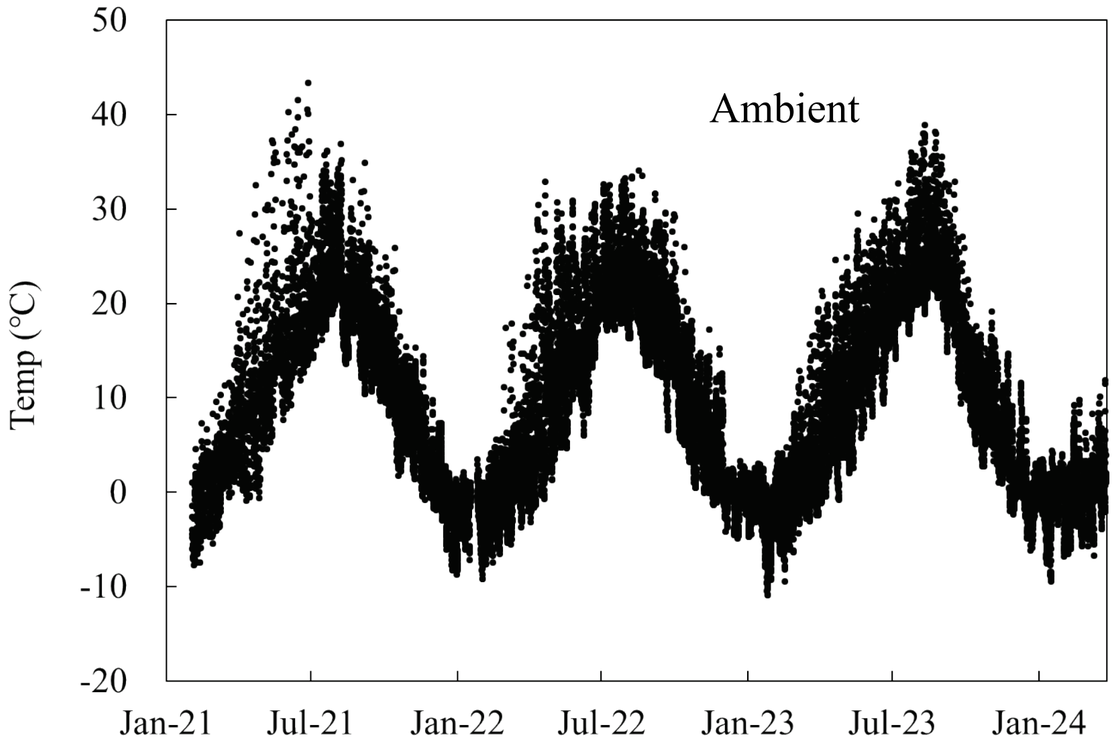
Media	Rice husk	Mixture of Rice husk and Limestone
Period	January 2021–March 2023	April 2023–
Total media volume (m^3)	5	5
Weight of Rice husk (t)	0.6	0.56
Weight of Limestone (t)	0	2.2
HRT (h)	2.0	1.8
Flow rate (L/min)	25	25

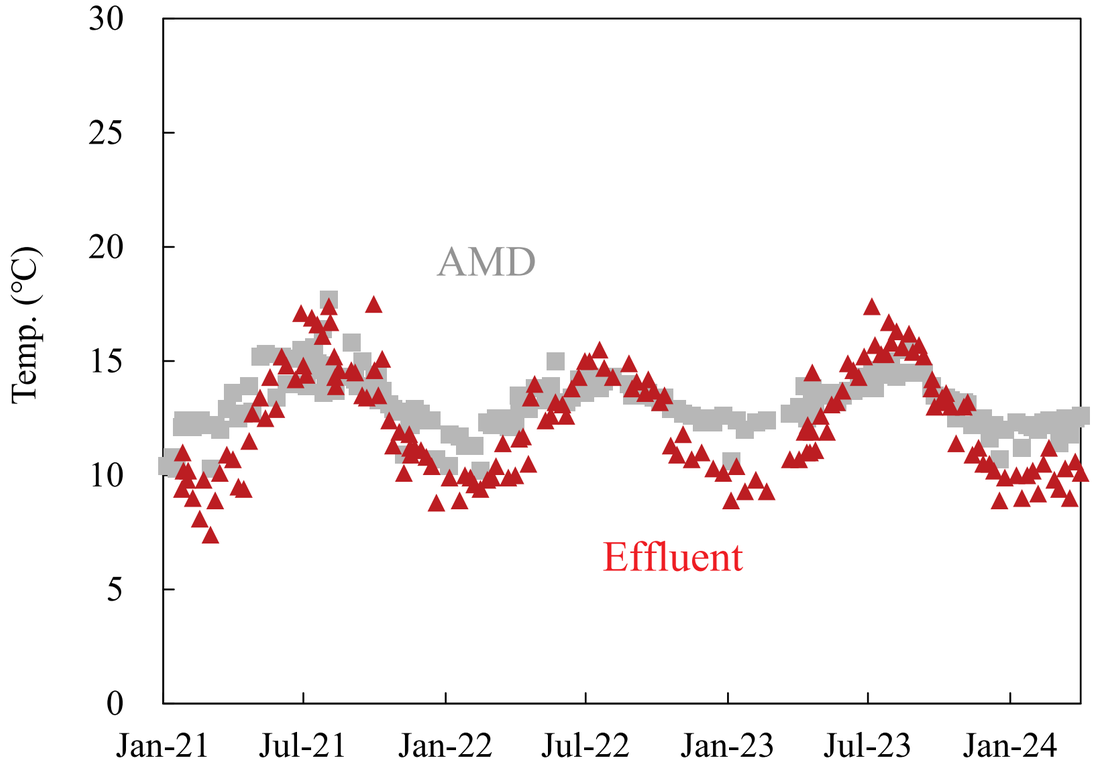
⇐ Weight ratio 1:4

<Cross-section structure of Fe-B>



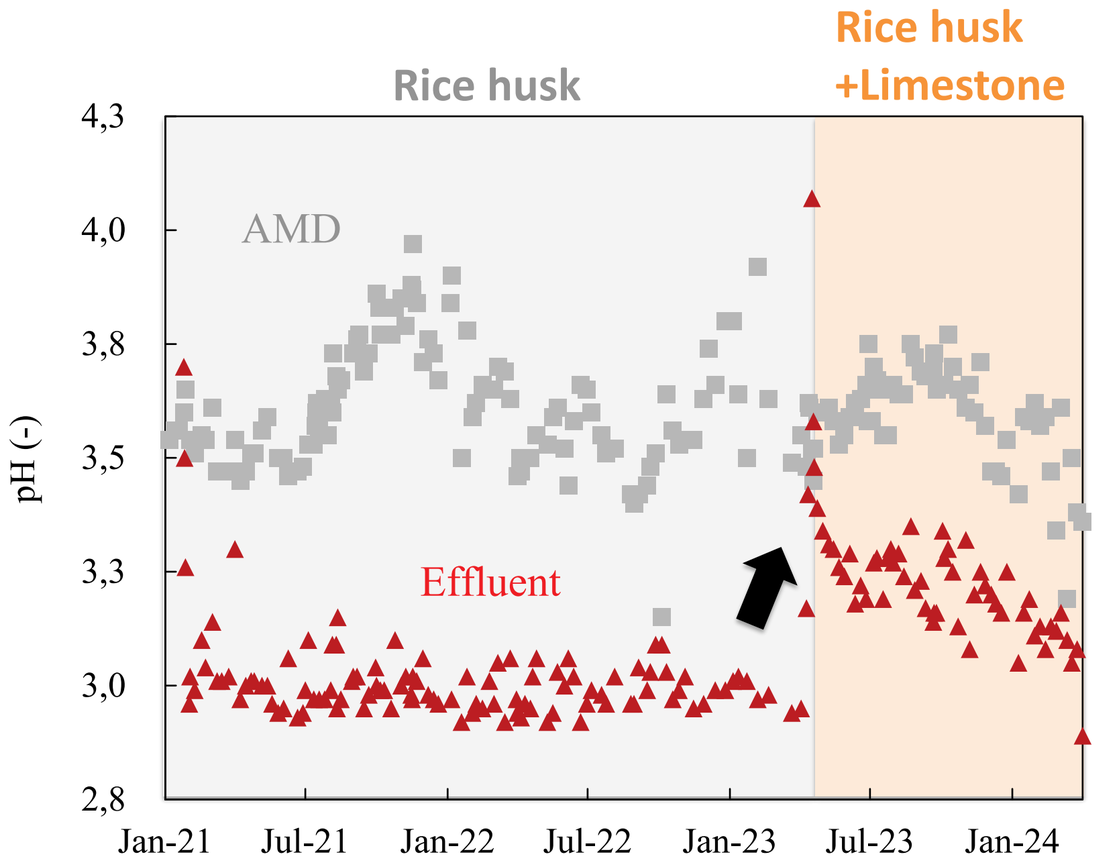
Result: Ambient Temperature and Water Temperature in Fe-B



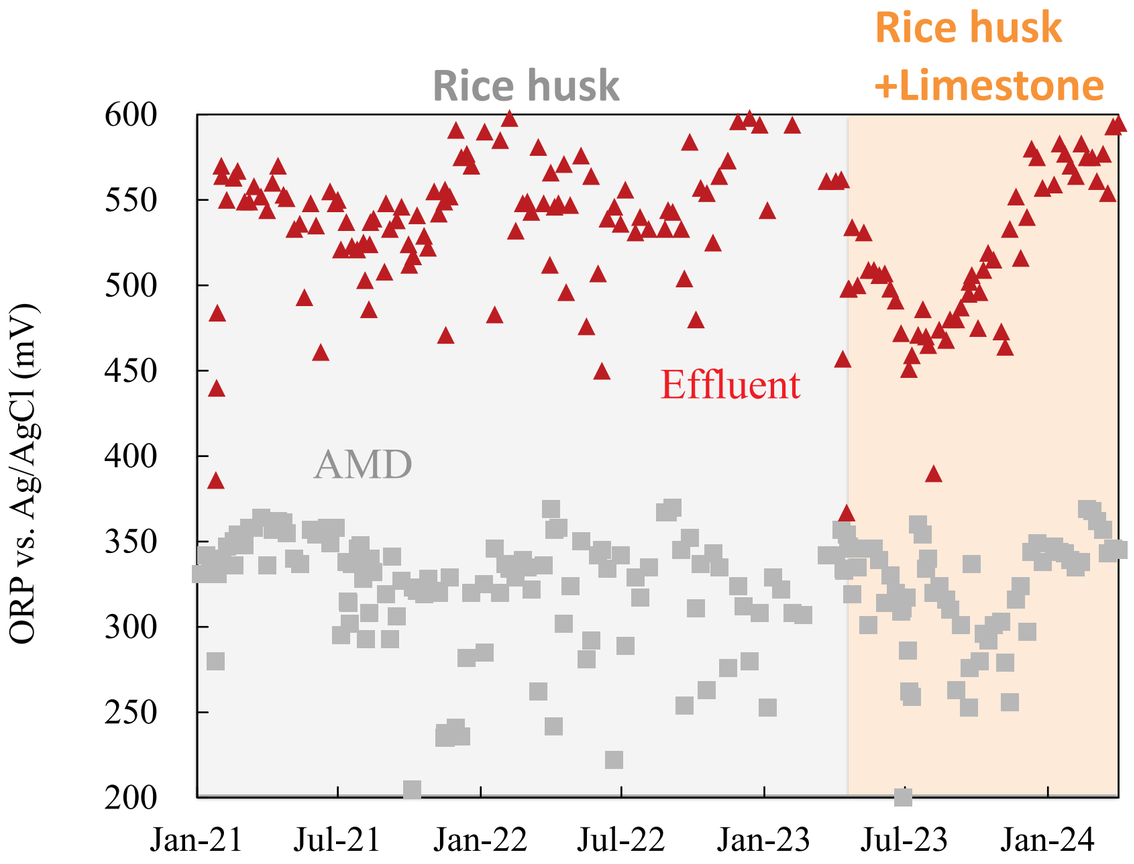


- Ambient temperature was ranging -10 to 40 degree.
- Water temperature of AMD and effluent of Fe-B were 10 to 18 and 7 to 18 degree, respectively.

Result: pH and ORP in Fe-B

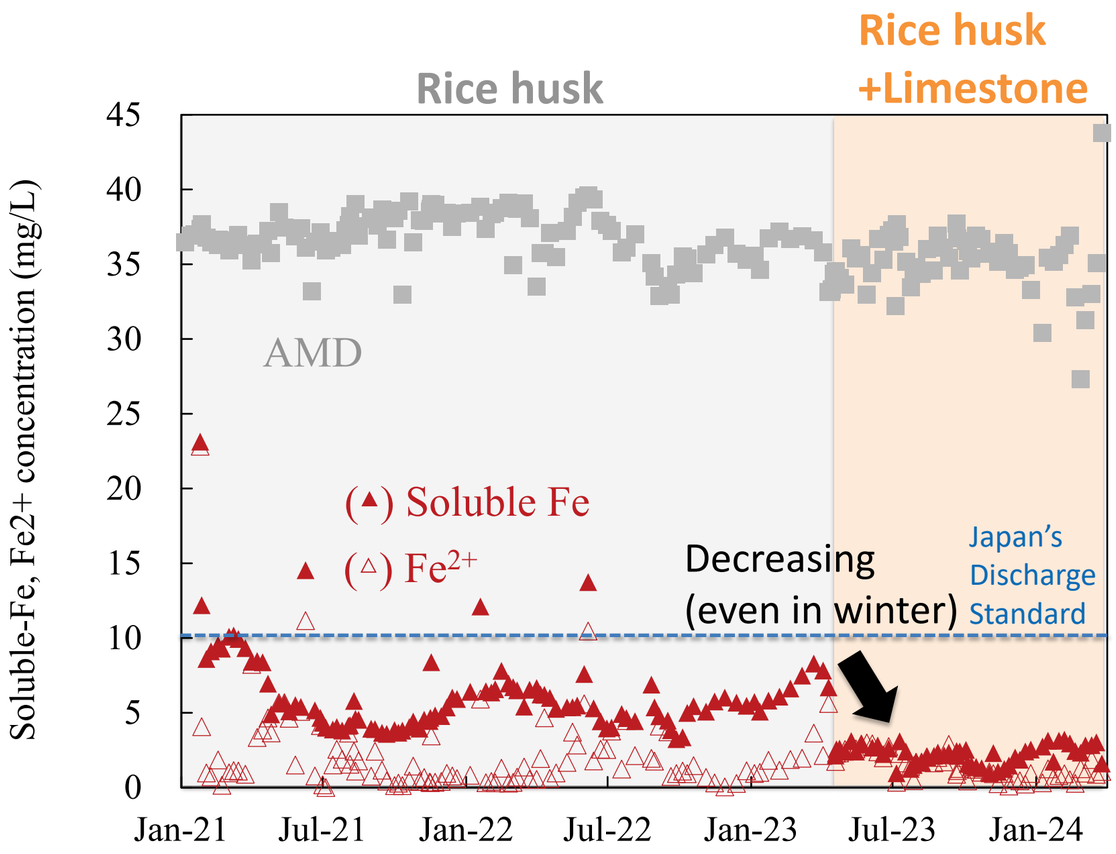


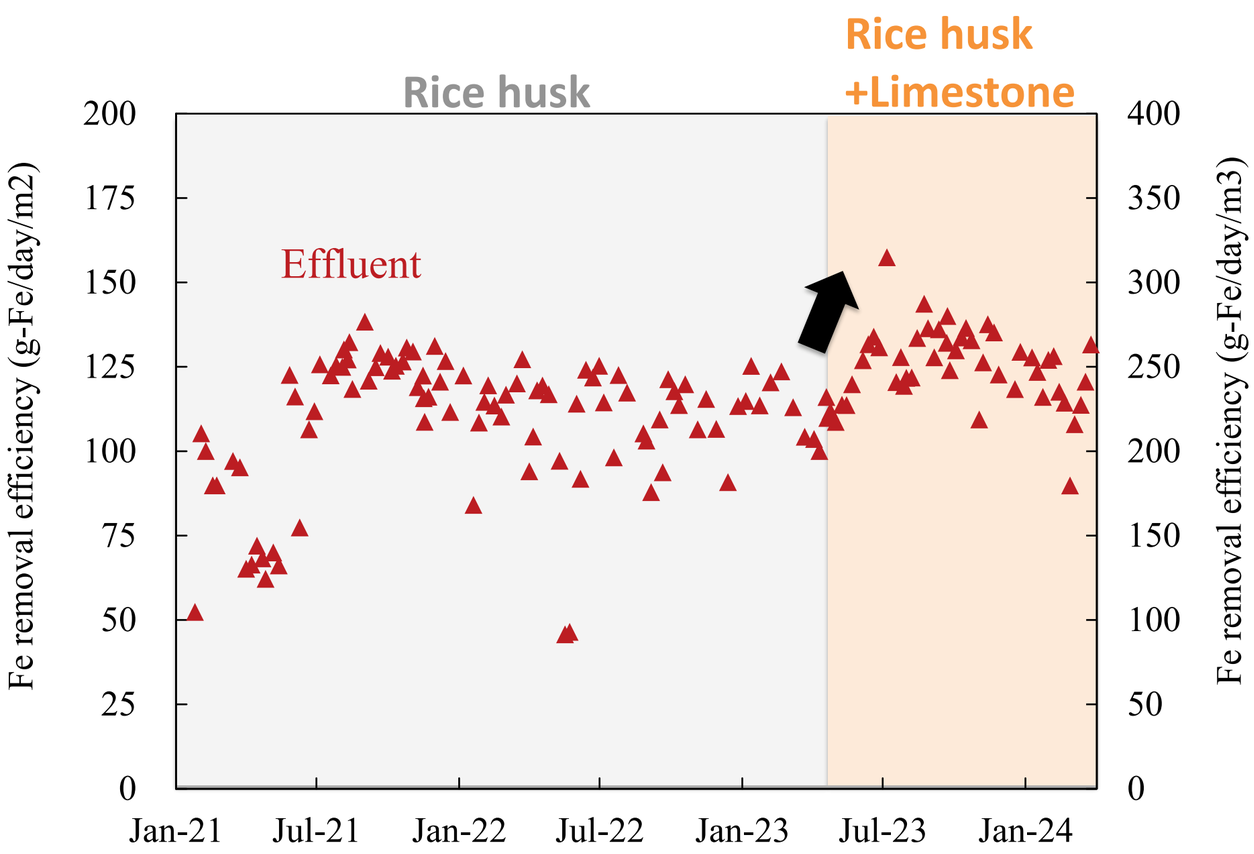
- The average effluent pH was increased: 3.0 → 3.2
- Recently, pH has been gradually decreasing



- AMD→Effluent
  ORP (vs. Ag/AgCl) was increased by Fe oxidation
- Rice husk→Rice husk + Limestone
  The average effluent ORP was decreased: 545 → 490 mV

Result: Concentration of Fe^{2+}, Soluble-Fe and Fe Removal Efficiency in Fe-B

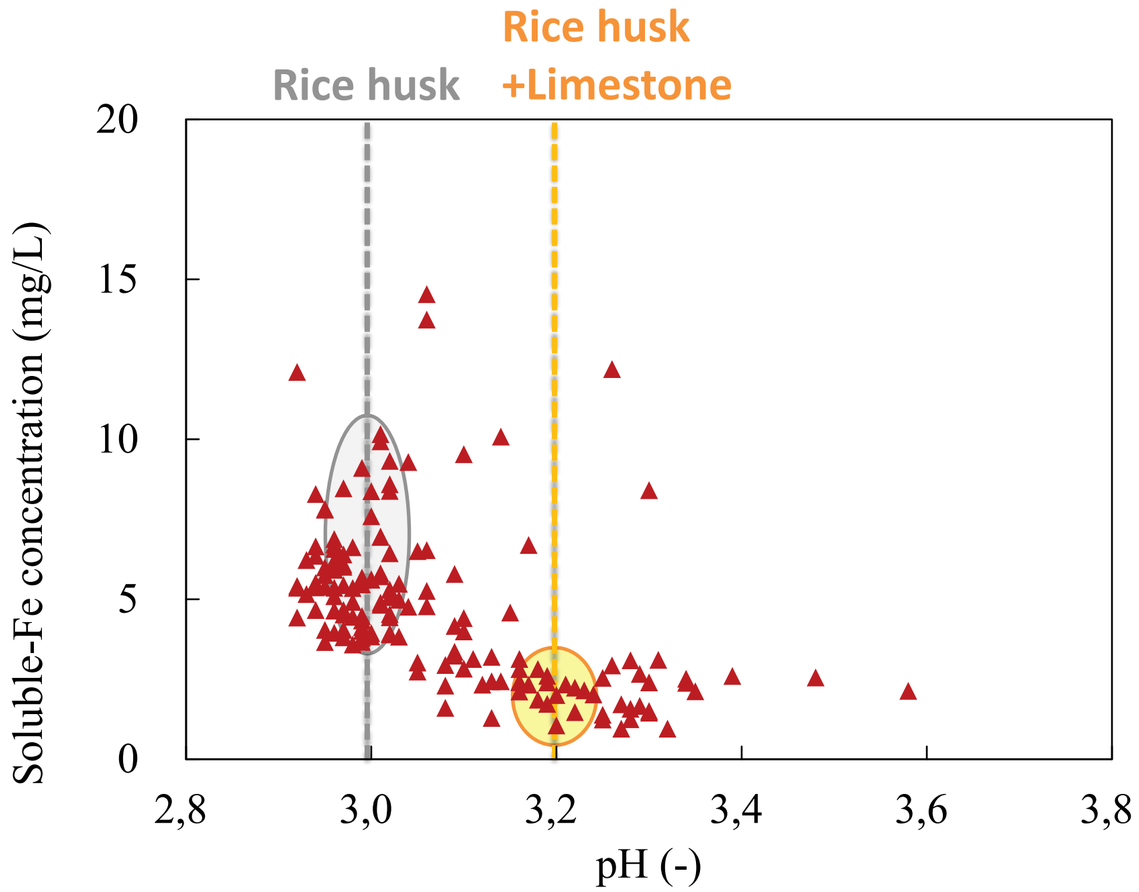




- The average effluent Soluble-Fe concentration was decreased: 6.1 →2.4 mg/L
- Fe^{2+} conc. was not much changed: 2.0 → 1.6 mg/L

- The average effluent Fe removal efficiency was increased: 218 → 253 g Fe/day/m^3

Result: Correlation between pH and soluble-Fe Concentration in Fe-B



- pH was correlated to soluble-Fe concentration.
- Only less than 3 mg/L soluble-Fe remained when pH was higher than 3.2.

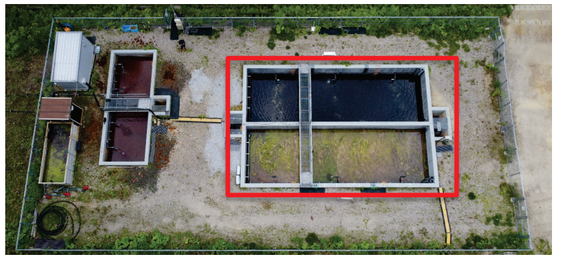
Summary of treatment performances of Fe-B in winter period

Media		Rice husk	Mixture of Rice husk and Limestone
Period		January 2021–March 2023	April 2023–
Average water quality in Fe-B effluent (in winter: October-March)	pH	3.0	**3.2**
	ORP (mV)*	543	545
	Soluble-Fe (mg/L)	7.3	**2.2**
	Fe^{2+} (mg/L)	1.6	0.9

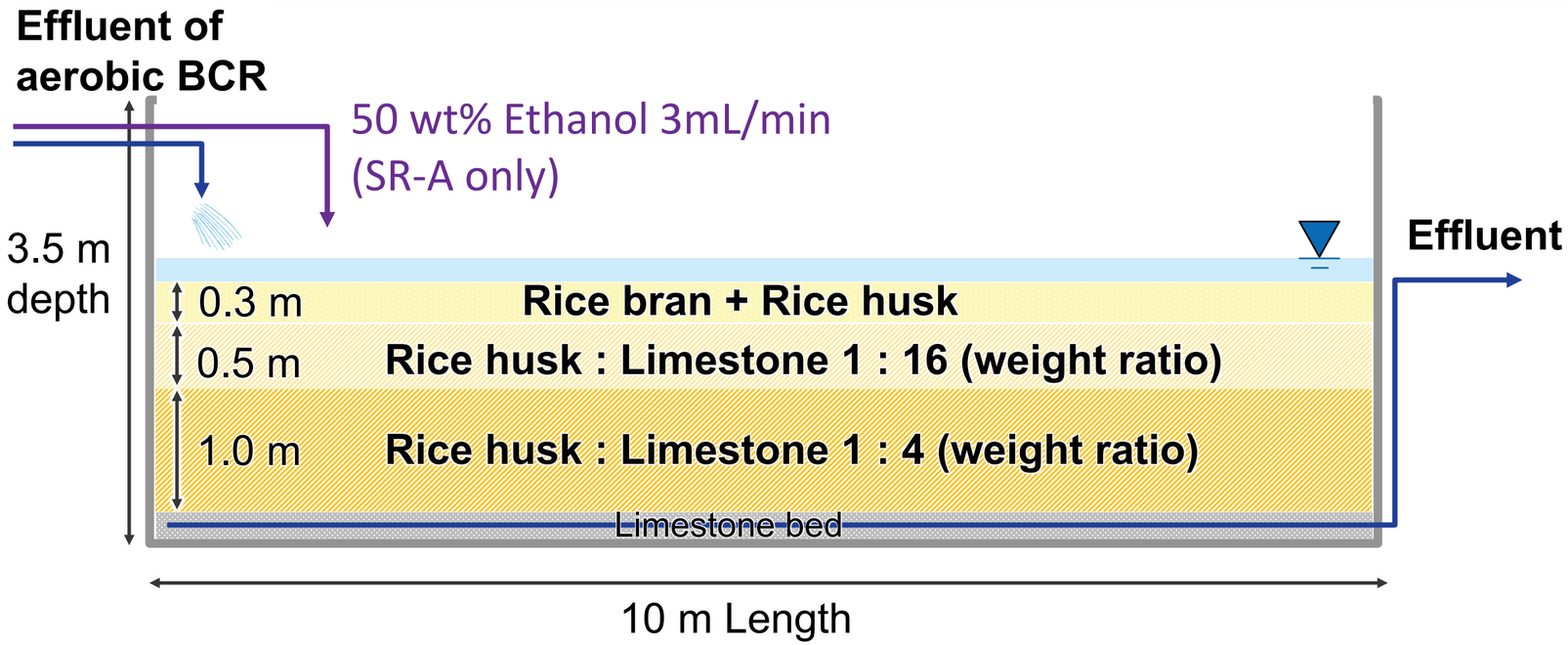
*ORP: mV (vs. Ag/AgCl)

✓ Efficiency of Fe removal was improved by pH increasing caused by limestone adding

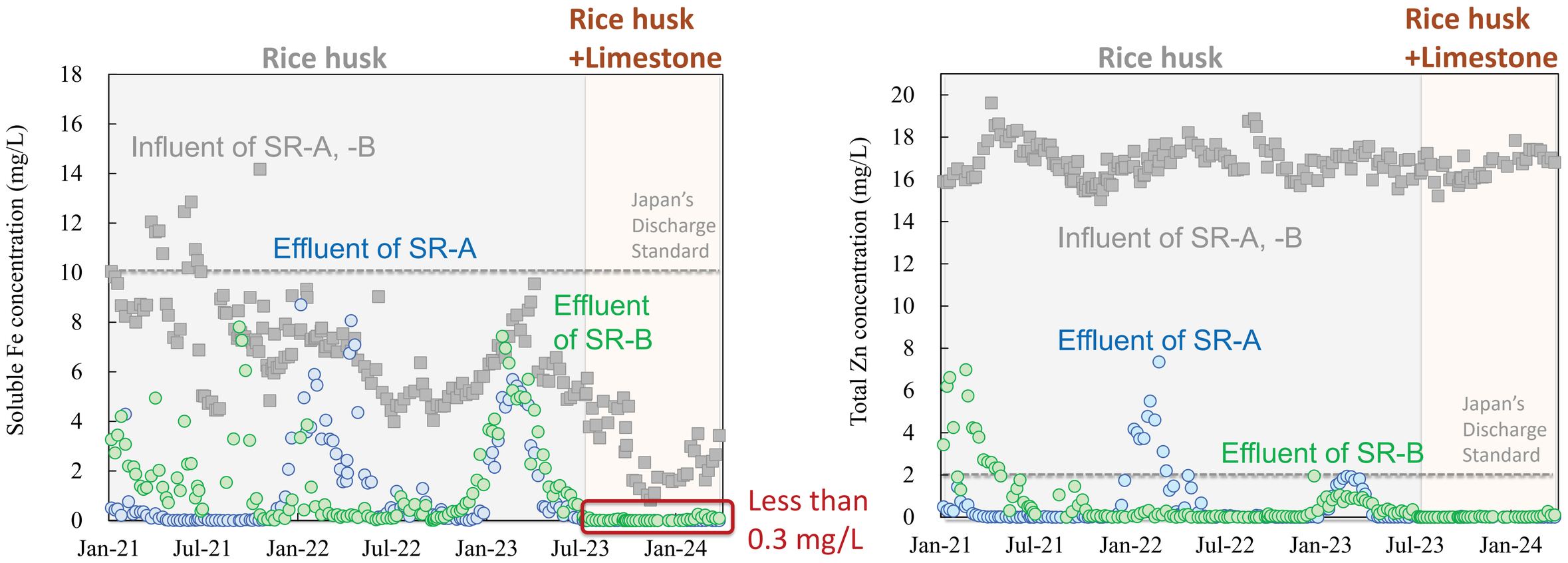
Anaerobic Bio-chemical Reactor Design



Latest condition	SR-A	SR-B
Period	September 2023–	September 2023–
Nutrition condition	Ethanol + Rice Bran (Hybrid)	Rice Bran
Ethanol addition (mL/min)	3.0	0
Weight of Rice bran (t)	1.0	2.0
HRT (h)	22.5	22.5
Flow rate (L/min)	50	50

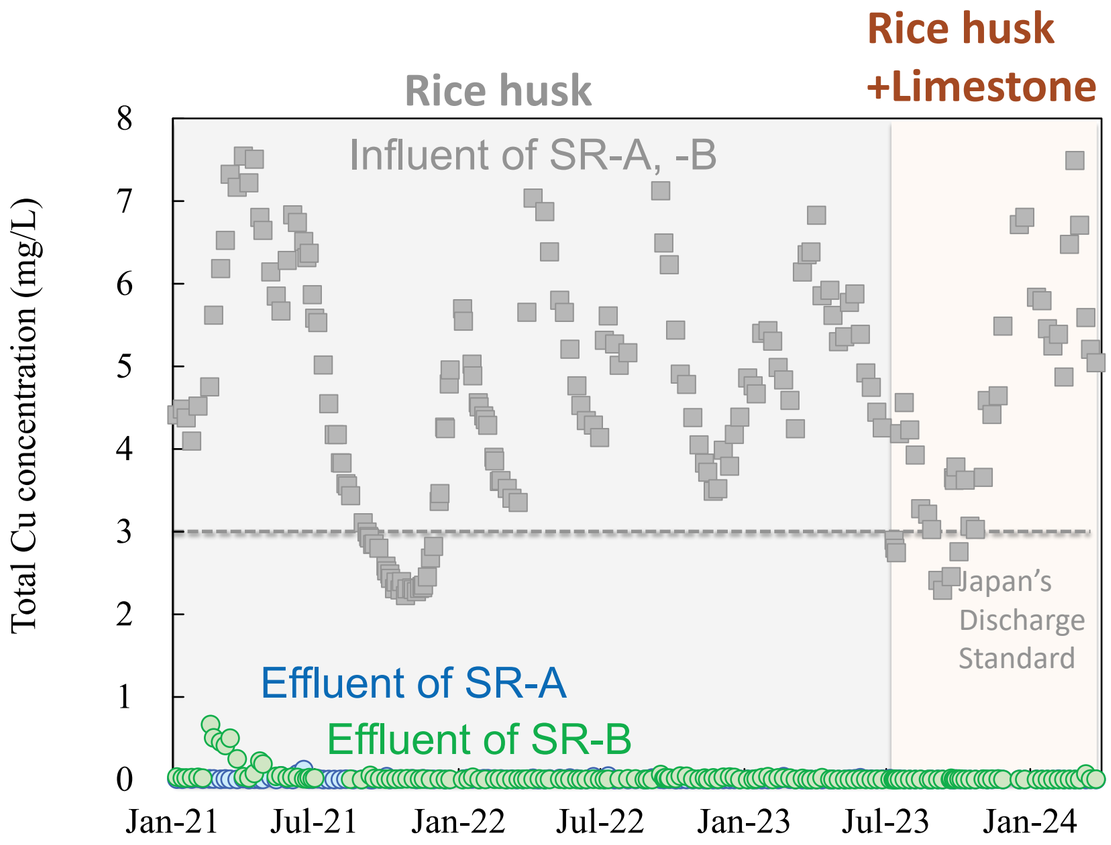


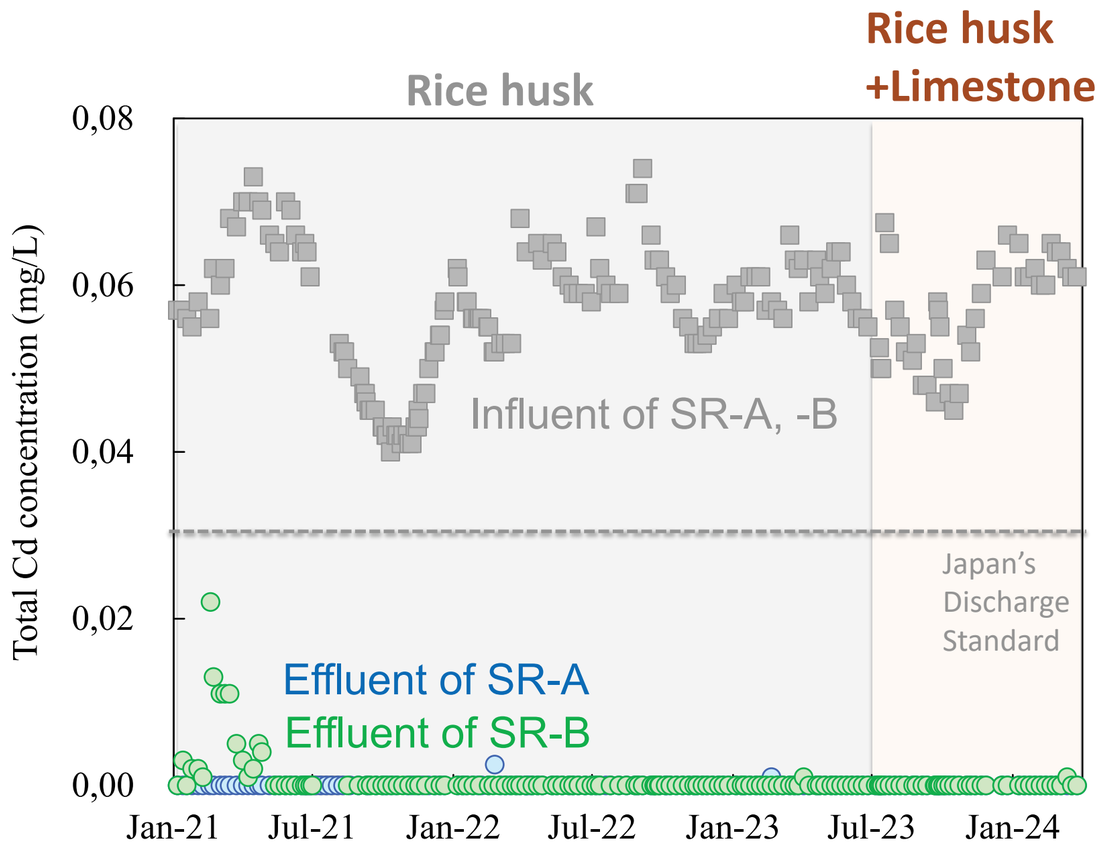
Result: Soluble-Fe and Total Zn Removal in Anaerobic Reactor



- Soluble-Fe concentration in the effluent of SR-A, B → Less than 0.3 mg/L
- Total-Zn concentration also less than 0.3 mg/L (mainly depend on SR nutrition condition)

Result: Total Cu and Total Cd Removal in Anaerobic Reactor





- Total-Cu and Cd concentration in the effluent of SR-A, B were well below the Japan's discharge standard.

Conclusions

- ✓ **Limestone addition** to the media of Fe oxidation/removal reactor **improved Fe removal**
- ✓ The average pH in the Fe-B effluent increased from 3.0 to 3.2 and the concentration of **soluble-Fe decreased from 6.1 to 2.4 mg/L** (Removal rate increased 10%)
- ✓ Fe and other metals (Zn, Cu, Cd) were also stably treated in anaerobic process

【Future prospects】

- ✓ Duration of pH increase effect by limestone (Frequency of limestone addition)
- ✓ Frequency of clogging (maintenance)