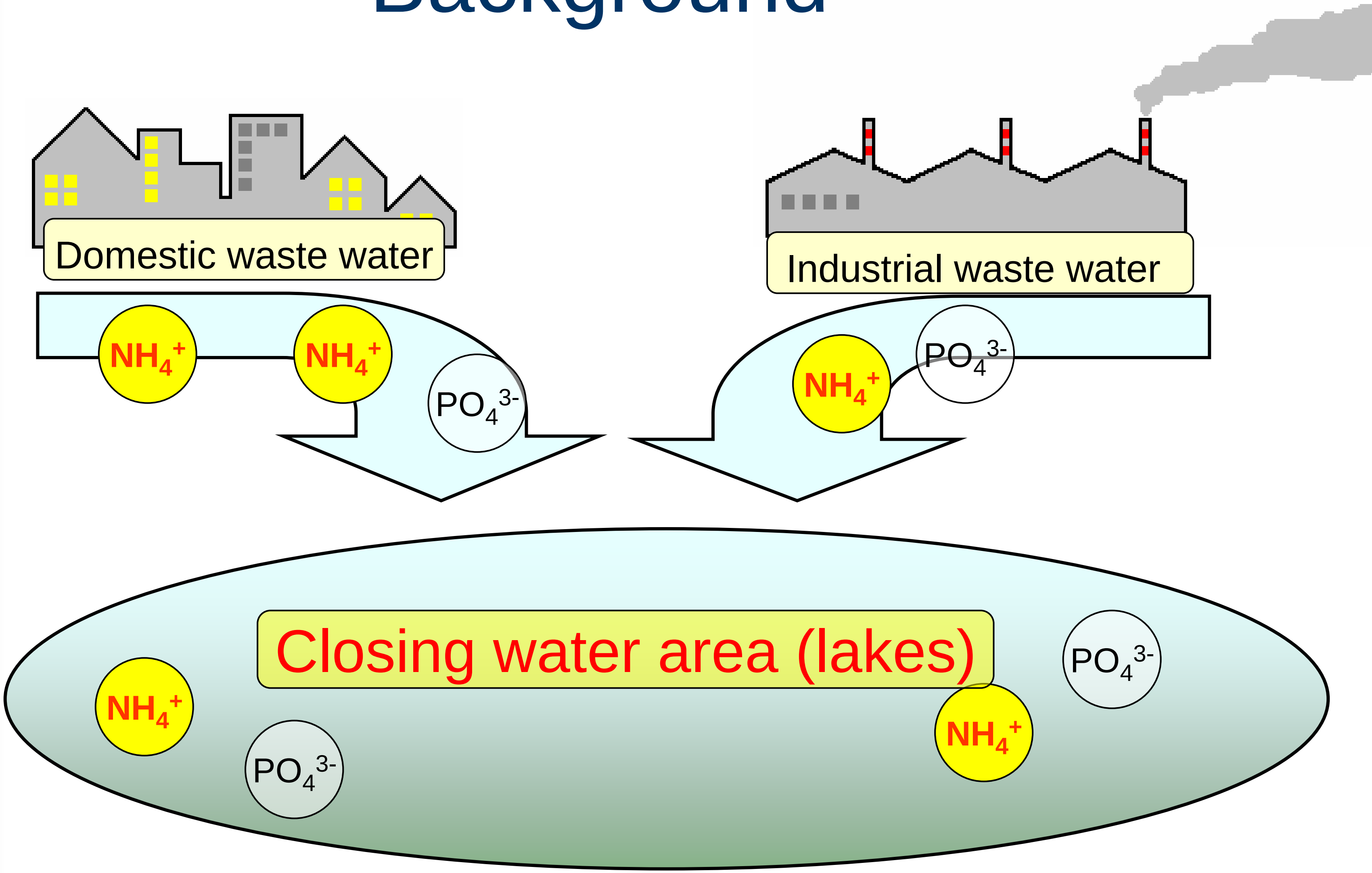
Ion exchange behavior of ammonium ions on various zeolites

Masanori Goto [1], Yujiro Watanabe [1], Hisao Kokusen [1] ,
Hirohisa Yamada [2], Junzo Tanaka [2], and
Yu Komatsu [1],
[1] Faculty of Engineering, Kanazawa Institute of Technology,
7-1 Ohgigaoka, Nonoichi, Ishikawa, 921-8501, Japan.
[2]National Institute for Materials Science,
1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

Background



Eutrophication

Purpose

Ammonia nitrogen (NH_4^+) is one of main factors of eutrophication in lakes.

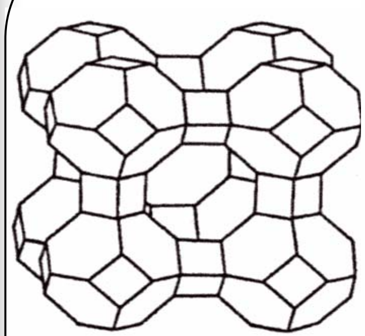
Zeolites have been proposed as material for removal of the ammonium ion.

The behavior of NH_4^+ in ion exchange reaction on different kinds of zeolites, was investigated. In particular the effects of the pH, the reaction time and the concentration of NH_4^+ in aqueous solutions were examined after those reactions reached to the equilibrium values.

Materials: Zeolites

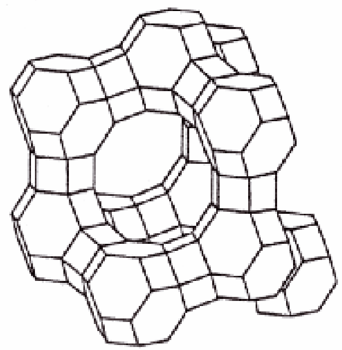
Framework structures

Synthetic zeolites



LTA

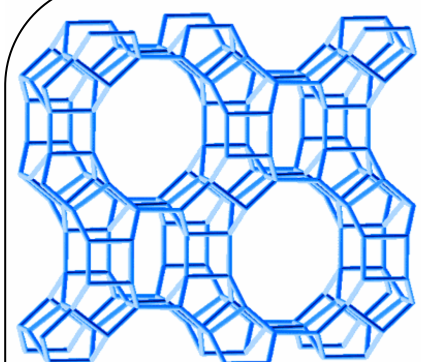
($Na_{12}Al_{12}Si_{48}$ $\cdot 27H_2O$)



FAU

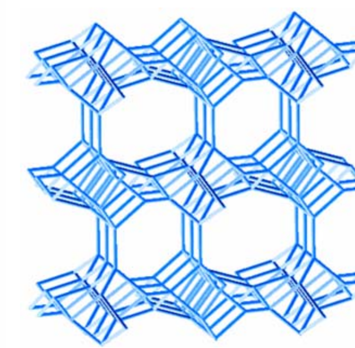
($Na_{12}Al_{12}Si_{48}$ $\cdot 27H_2O$)

Natural zeolites



Mordenite

($Na_8(Al_8Si_{40}O_{96})$ $\cdot 24H_2O$)



Clinoptilolite

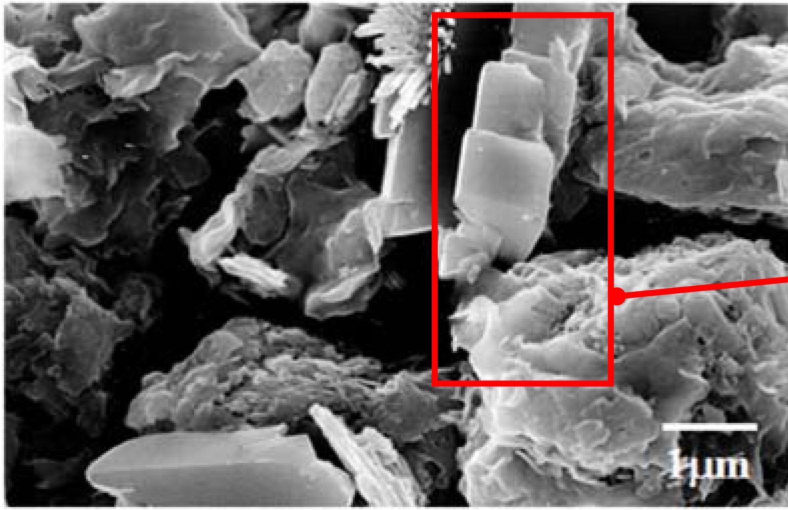
($Na_6Al_6Si_{10}O_{32}$ $\cdot 12H_2O$)

Characteristics

・High cation-exchange capacity (High ammonium ion-selectivity)

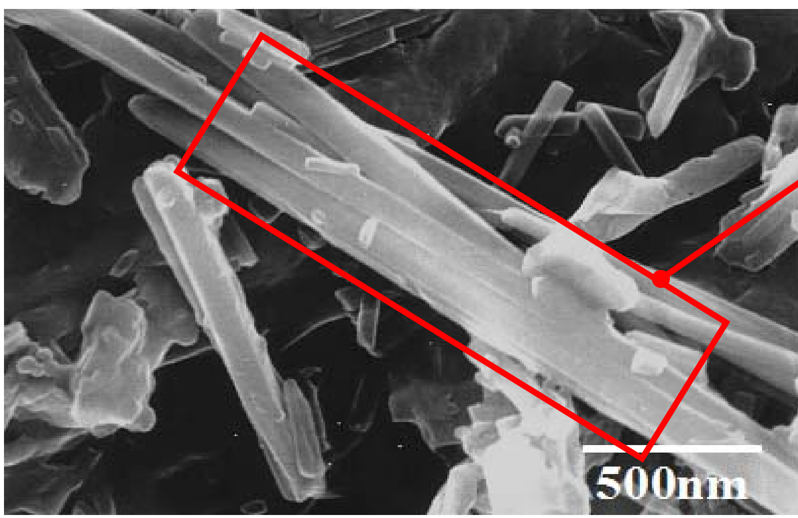
・Ion adsorption

Observation for Zeolites by SEM (1)



Natural zeolites
(Shimane prefecture, Japan)

Clinoptilolite is coffin-shape crystals and submicron in size.

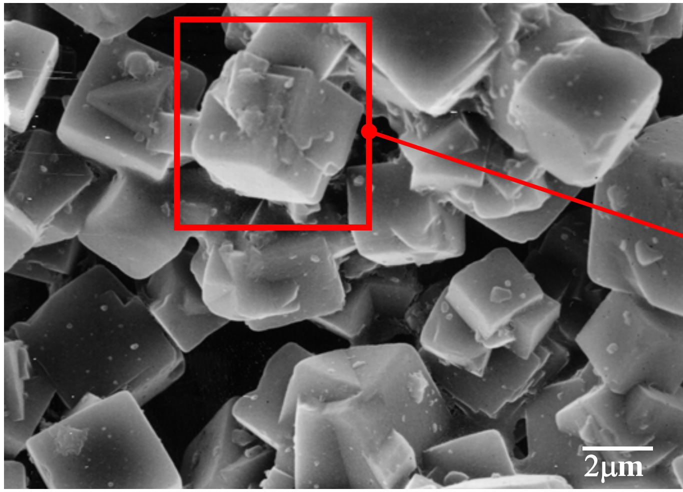


Mordenite is fibrous and ranged from 0.05 to 0.1 mm in diameter and from 1 to 5 mm in length.

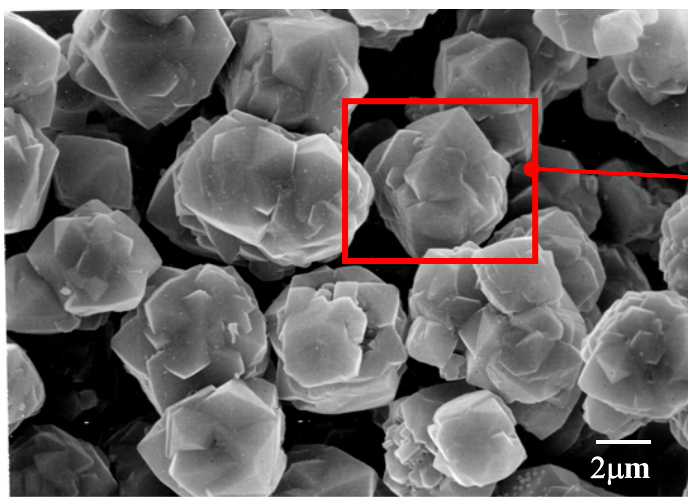
Fig. SEM images of clinoptilolite and mordenite in natural zeolite from Shimane, Japan. ***Y.Watanabe et al. Sep.Sci.Tech.(2003).***

Observation for Zeolites by SEM (2)

Synthetic zeolites (LTA, FAU)



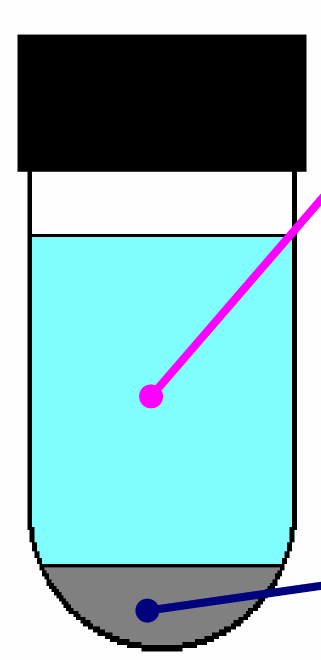
LTA is intergrowth of typical cubic crystallites of micron size in diameter



FAU is aggregate or intergrowth of fine octahedral crystallites of submicron size in diameter

Fig. SEM images of LTA and FAU. ***Y.Watanabe et al. Sep.Sci.Tech.(2003).***

Experimental procedure



Ammonium chloride solution: 30cm^3(1.0×10^{-3}mol dm^{-3})

Time dependence: Reaction time:1～168hrs, pH: 2.0～2.3

pH dependence: pH:1～6(Hydrochloric acid)

Reaction time:24hrs, 168hrs

Dependence of Ammonium ion concentration:

Concentration: 1.0×10^{-4} ～ 3.0×10^{-3}mol dm^{-3}

Synthetic zeolites :LTA(3A)、FAU(13X)

Natural zeolites:Indonesia A 、Indonesia B、

Shimane 、Australia

: 0.1g (200～250mesh)

centrifugation（1500rpm)

filtration（0.45μm)

Liquid phase:FIA (flow injection analyzer)、ICP-AES

Solid phase: SEM

Calculation of the amount of ammonium-ion capture in percent

$$\text{The amount of ammonium-ion capture (\%)} = \frac{C_0 - C_1}{C_0} \times 100$$

C_0 : Initial concentration (mmol dm^{-3})

C_1 : Equilibrium concentration (mmol dm^{-3})

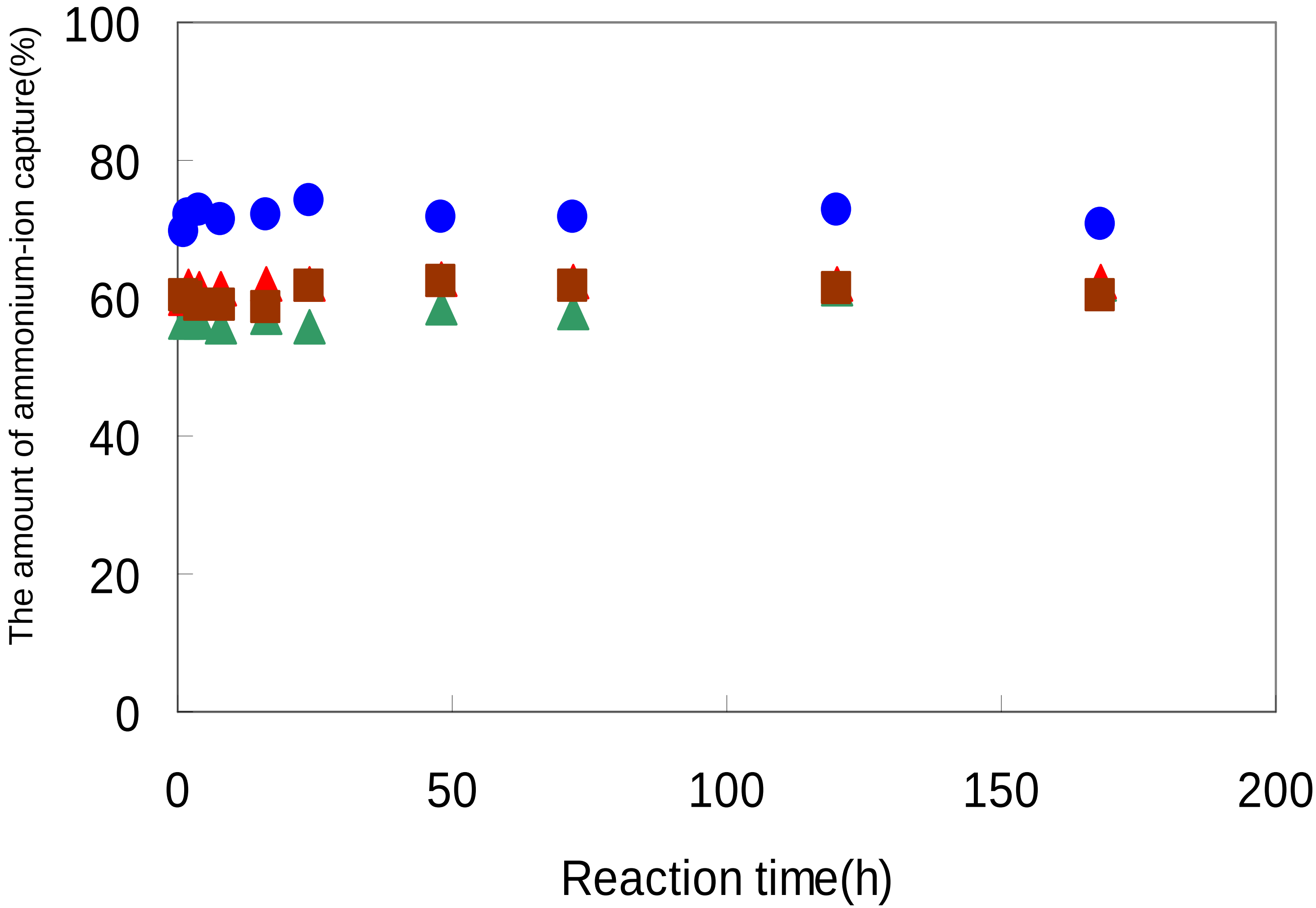


Fig. Relationship between the amount of ammonium-ion capture and the reaction time

● ：FAU（X） ▲ ：LTA ■ ：Shimane ▲ ：Indonesia B

Reaction time：1～168hrs

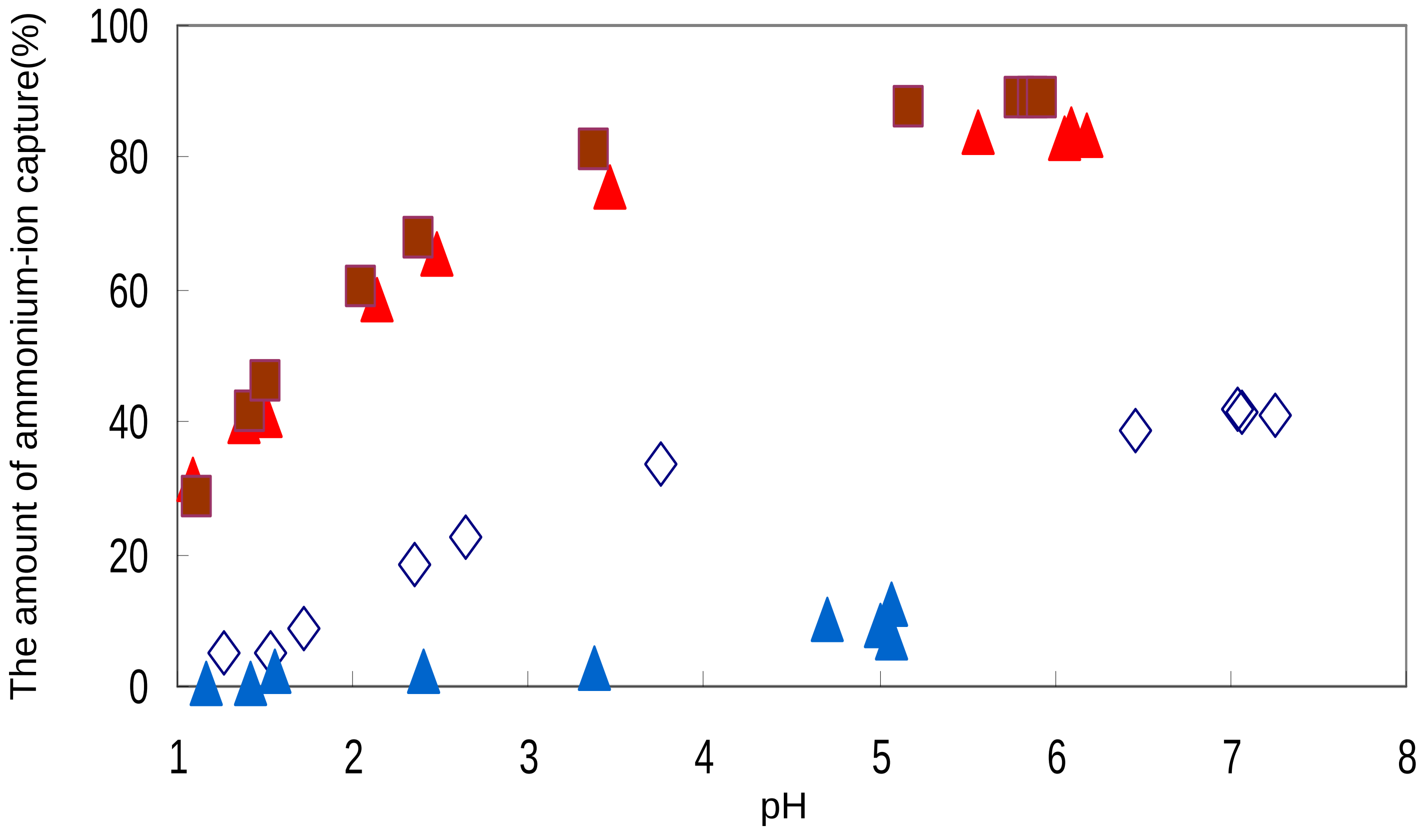


Fig. Relationship between the amount of ammonium-ion capture in percent and the pH in the aqueous solution after reaction.

◇ : Australia ▲ : Indonesia A

▲ : Indonesia B ■ : Shimane

Reaction time : 24hrs

Results and Discussion

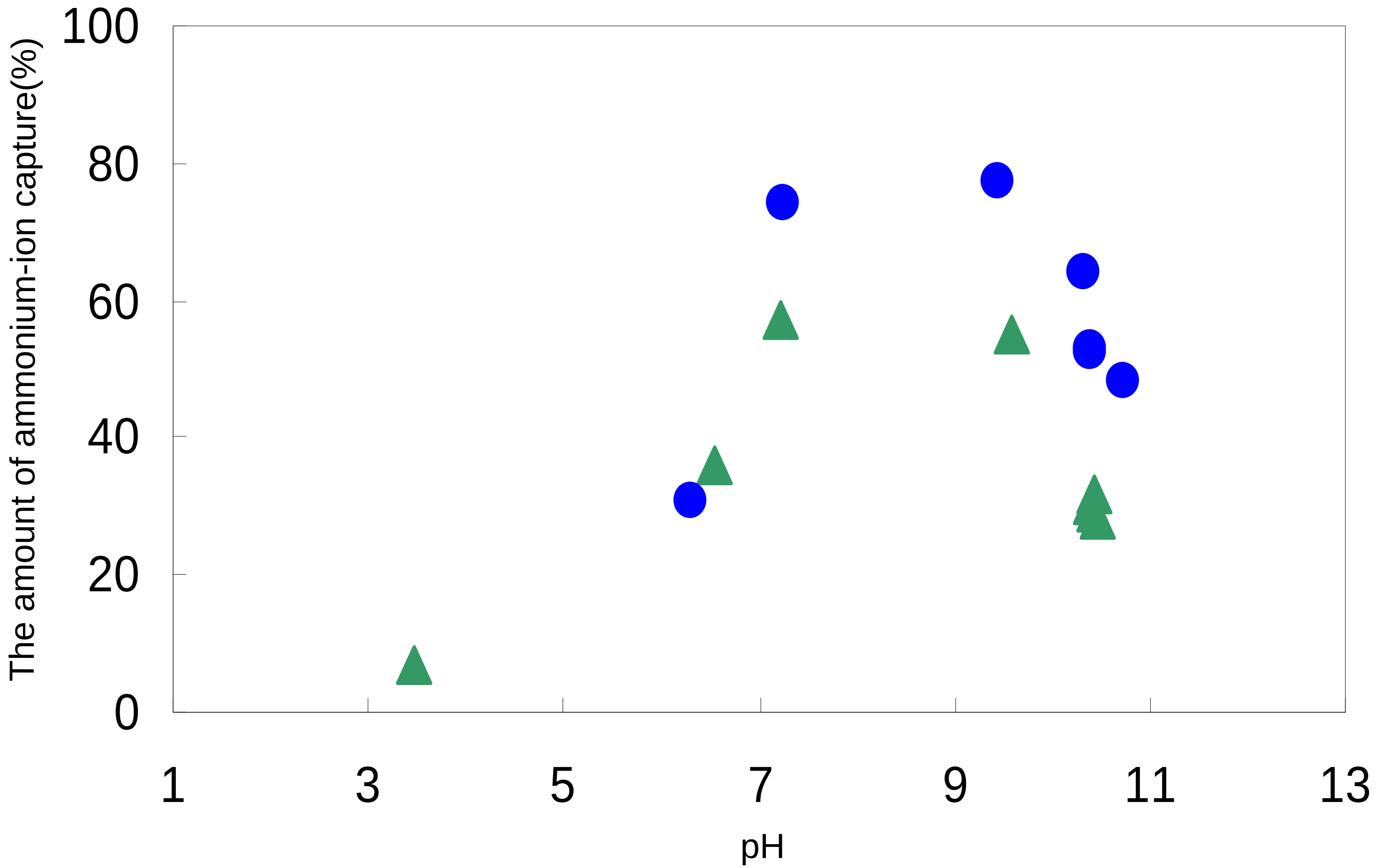


Fig. Relationship between the pH and the amount of ammonium-ion capture on synthetic zeolites.

● :FAU (X), ▲ : LTA .

Reaction time : 24hrs.

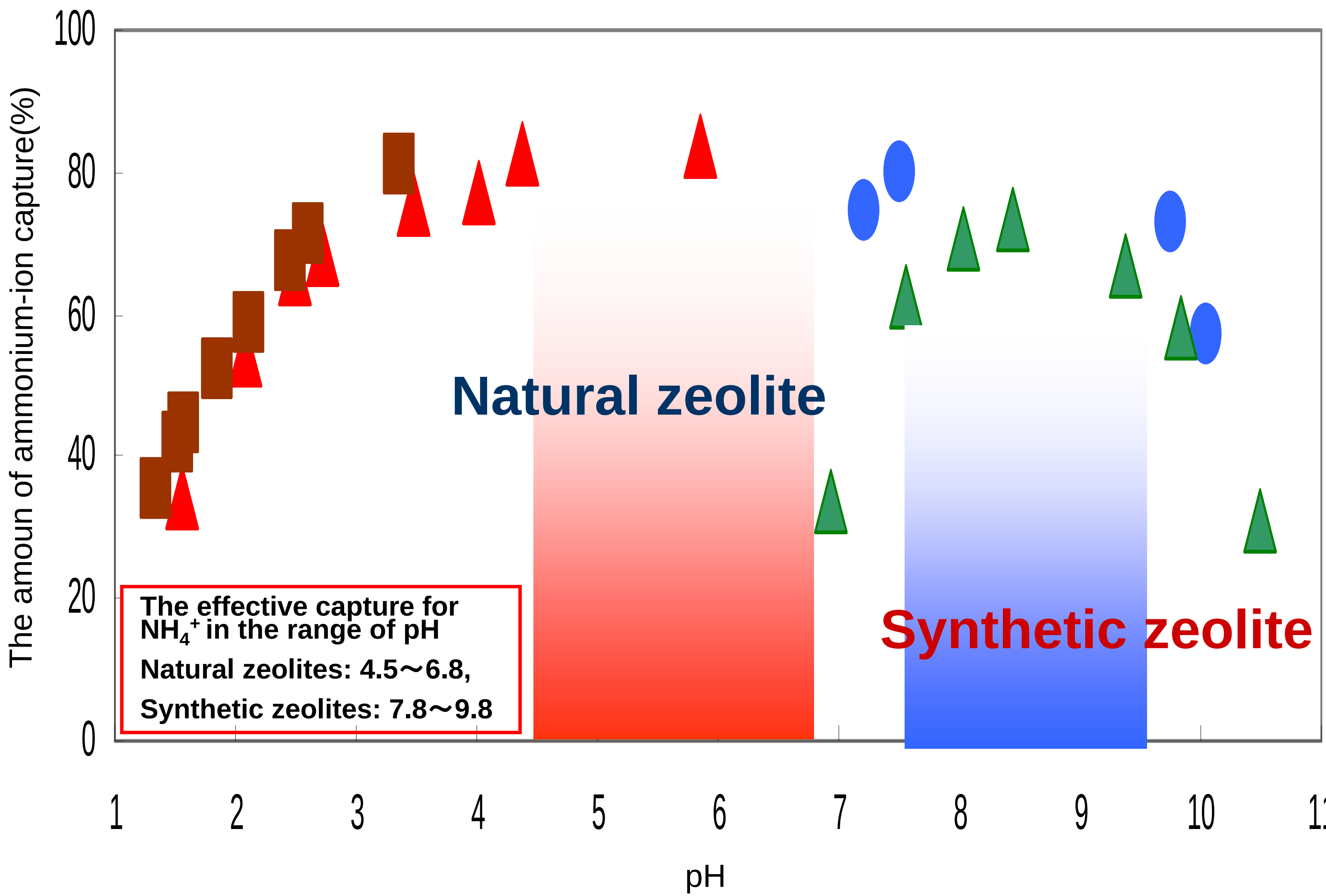


Fig.Relationship between the amount of ammonium-ion capture and the pH.

FAU : ● LTA : ▲ Shimane : ■ Indonesia B : ▲ Reaction time : 168hrs

Ammonium ion exchange behavior

Table. Ammonium ion exchange behavior of zeolite

	C_0 (NH_4^+)	pH_0	pH_{eq}	SiO_2	Al_2O_3	Na^+	K^+	Ca^{2+}	Mg^{2+}	C_1(NH_4^+cal)	C_2(NH_4^+exp)
MOR	3.0	5.42	5.59	0.017	0.000	1.340	0.143	0.086	0.063	0.514	0.568
	1.0	5.30	6.02	0.018	0.000	0.700	0.050	0.021	0.022	0.231	0.270
	0.3	5.52	6.17	0.024	0.001	0.210	0.018	0.004	0.002	0.051	0.084
	0.1	5.70	6.43	0.023	0.001	0.130	0.014	0.009	0.003	0.029	0.027

MOR : mordenite zeolite

C_0 (NH_4^+) : initial concentration (mmol dm^{-3}), pH_0 : initial pH,
pHeq : equilibrium pH,

C_1(NH_4^+cal) : The theoretical values for ammonium ion exchange quantity （mmol/g）

$[NH_4^+\text{cal (mmol dm}^{-3})] = [Na^+ \text{ (mmol dm}^{-3})] + [K^+ \text{ (mmol dm}^{-3})] + 1/2[Mg^{2+} \text{ (mmol dm}^{-3})] + 1/2[Ca^{2+} \text{ (mmol dm}^{-3})]$

C_2(NH_4^+exp) : The experimental values for ammonium ion exchange quantity

C_1(NH_4^+cal) ≒ C_2(NH_4^+exp)

↓

$MZ + NH_4^+ \Leftrightarrow NH_4Z + M^+$ (M : zeolite)

Summary

・The natural zeolites which we used are available to catch the high concentration of NH_4^+ ions in the range of pH 4.5～6.8, because the average values in the lake are pH 4.5～5.5 in Japan,.

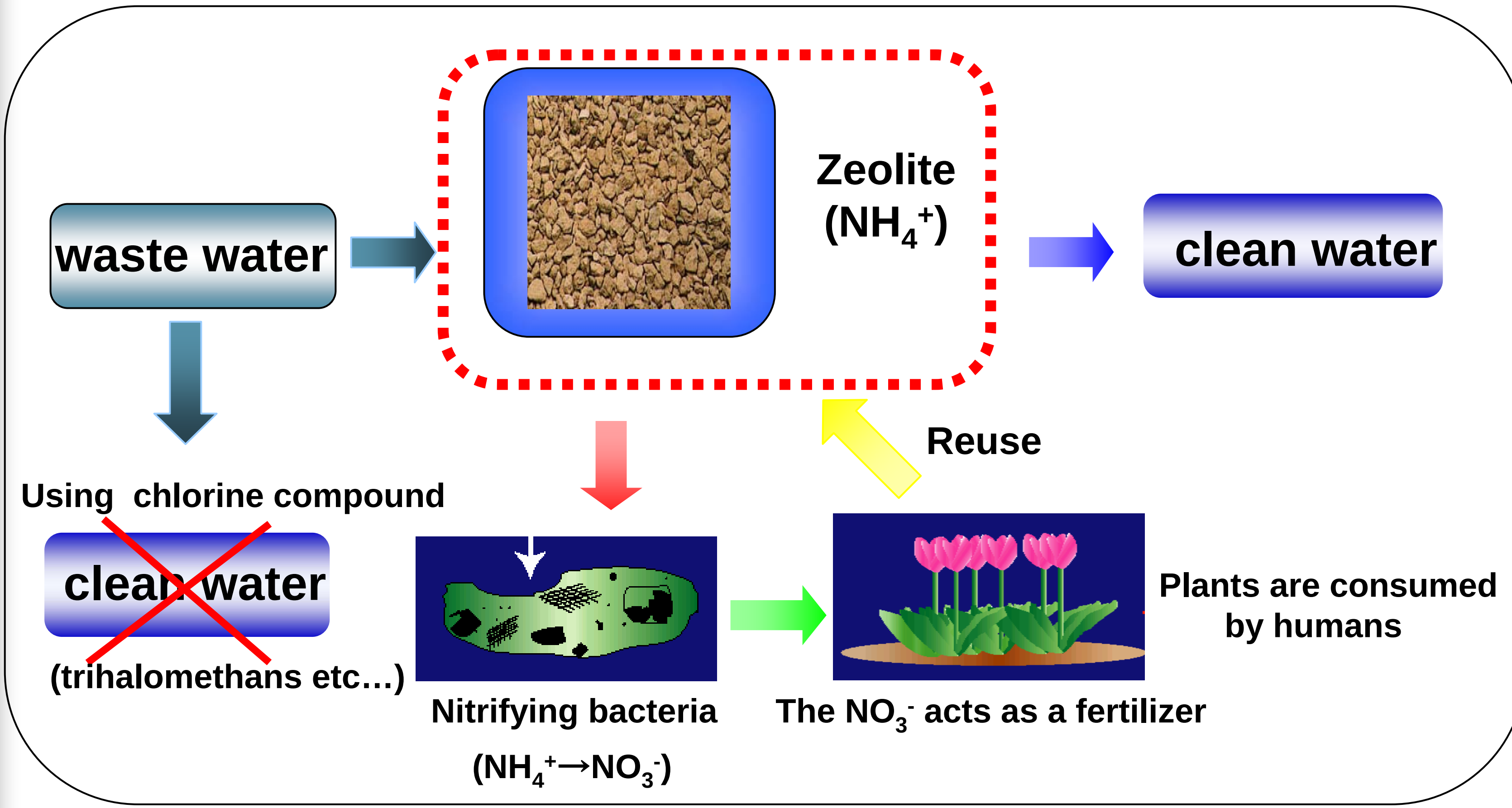
・ The reaction for NH_4^+ capture on natural zeolites reached to equilibrium within 10 min. These fast reaction is very useful for a clean water system.

・The experimental values (C_2:NH_4^+exp) are closed to theoretical values (C_1:NH_4^+cal).

・These reactions can be written in the following equation;

$$MZ+NH_4^+ \Leftrightarrow NH_4Z+M^+ \quad (M:zeolite)$$

Application



To use zeolite for ammonium ion removal from waste water system