

# EQUILIBRIUM ADSORPTION OF HEAVY METAL IONS IN ACID MINE DRAINAGE USING ZEOLITE

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## 1. Introduction

Although mining resources are essential in modern industry and economics, operation and development of mining occasionally cause serious effect to environment and habitat. Especially wastewater called acid mine drainage (AMD) discharged from abandoned mines became problem. AMD is the acidic wastewater containing heavy metals (Fe, Cu, Zn and Mn). It should pollute soil, rivers and ground water when it was untreated[1]. It occurred even after the mine was closed. Thus continuous treatment was required even after the operation was stopped. Table 1 shows the conditions of AMD in Indonesian coal mines[2]. Treatment of AMD often neglected in developing country because wastewater treatment is unproductive.

The common method used in wastewater treatment was neutralization which remove most of the heavy metals in wastewater. However large volume of precipitate were generated continuously, so a place to reclaim is indispensable. Due to these facts, improvement of fundamental processes in treatment of AMD was required. As an alternative method, treatment of AMD using adsorption of natural zeolite was paying attention.

Zeolite is a mineral which has an ability of ion exchange, catalyst and adsorption. Adsorption of heavy metal by natural zeolite has been studied recently. In previous studies, many alkaline impurities in the natural zeolite affected the adsorption of heavy metal ions which made adsorption equilibrium unclear. In order to apply natural zeolite to AMD treatment, clarifying the adsorption mechanism of zeolite was essential[3]. The synthetic zeolite, which was considered as pure zeolite, was used to neglect the effect of impurities to adsorption.

The purpose of this study is to clarify the adsorption of zeolite in AMD. Equilibrium adsorption of model wastewater containing heavy metals was carried out using synthetic zeolite.

Table 1 Condition of AMD in Indonesian coal mine

	Fe <sup>3+</sup> [mg/L]	Mn <sup>2+</sup> [mg/L]	Cu <sup>2+</sup> [mg/L]	Zn <sup>2+</sup> [mg/L]	pH
AMD sample 1	34.11	3.87	0.04	0.53	2.72
AMD sample 2	28.45	3.7	0.13	1.14	2.66

## 2. Experimental

### 2.1. Characterization of zeolite

Na type mordenite (NaMOR) purchased from Fujifilm Wako pure chemical was used in this study. The properties of NaMOR are shown in Table 2. In order to remove moisture in NaMOR, samples were dried in oven at 373K for 24hrs and cooled in the desiccator as a pretreatment.

Cation exchange capacity (CEC) of NaMOR was measured by US-EPA method[4]. Quantitative analysis of

the exchangeable cations in NaMOR was carried out using ammonium acetate. NH<sub>4</sub><sup>+</sup> was exchanged with the cations in NaMOR. 4 g of zeolite sample was contacted with 1 zmol/L ammonium acetate for 10 minutes. The mixture was separated to solid phase and liquid phase was using centrifuge. The new 1 mol/L of ammonium acetate was added to solid phase. The operation was repeated 5 times. The liquid phase obtained from the operation was analyzed to measure the concentrations of exchangeable cations. The liquid phases were analyzed by pH meter (Horiba, F-74) and ICP-AES (SII, SPS7800) to determine the pH of the solutions and metal concentrations in the solutions at equilibrium.

Table 2 Properties of NaMOR

	NaMOR
Si/Al	9
Surface area[m <sup>2</sup> /g]	360
Particle size[μm]	5-7

### 2.2 Batch equilibrium adsorption

Batch equilibrium adsorption was carried out in the experimental condition shown in Table 3. Single metal solutions and binary metal solutions (Mn-Zn) were used as model AMD. The concentrations of Mn and Zn in the solution were adjusted by dissolving MnSO<sub>4</sub> · 5H<sub>2</sub>O and ZnSO<sub>4</sub> · 7H<sub>2</sub>O to ionized water. In the case of binary metal solution, ratio of mass concentration of metals was 1. Initial pH of the solution was adjusted using sulfuric acid. The model AMD 50 ml was fed into Erlenmeyer flask with 2.5 g of NaMOR and this was shaken in a constant temperature bath for 240 h at 300 K. The liquid phase and solid phase was separated by filtration and liquid phase was analyzed using pH meter and ICP-AES.

Table 3 Experimental conditions for batch equilibrium adsorption

Initial concentration of metals	[kmol/m <sup>3</sup> ]	3.0×10 <sup>-3</sup> -2.0×10 <sup>-2</sup>
Initial pH of feed solution		2 - 5
Volume of feed	[m <sup>3</sup> ]	50 × 10 <sup>-6</sup>
Mass of zeolite	[kg]	2.5 × 10 <sup>-3</sup>
Contacting time	[h]	240
Temperature	[K]	300

## 3. Result and Discussion

### 3.1. Characterization of zeolite

CEC of the NaMOR was 1.9×10<sup>-3</sup> keq/kg-zeo. The chemical formula of mordenite is Na<sub>2</sub>Al<sub>2</sub>Si<sub>10</sub>O<sub>24</sub> · 7H<sub>2</sub>O. Assume that all of the Na in this formula is present as exchangeable ions, the CEC will correspond to the number of aluminum ions[5]. The CEC calculated from this assumption is 2.2×10<sup>-3</sup> keq/kg-zeo which was comparable to the CEC of NaMOR[5].

Table 4 shows the result of quantitative analysis of

exchangeable cations. Exchangeable cations in NaMOR were  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .  $\text{Na}^+$  was the main exchangeable cation.  $\text{Na}^+$  had much higher concentration than other cations.

Table 4 Exchangeable cation in NaMOR

Exchangeable cations [kmol/kg-zeo]			
$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$
$1.4 \times 10^{-3}$	$4.5 \times 10^{-5}$	$2.1 \times 10^{-5}$	$7.6 \times 10^{-6}$

### 3.2. Batch adsorption equilibrium

Material balance of heavy metal for batch adsorption is shown as,

$$C_{i,0} V_0 + q_{i,0} S_0 = C_{i,\text{eq}} V + q_{i,\text{eq}} S_{\text{eq}} \quad (1)$$

$C_{i,0}$ ,  $V_0$ ,  $S_0$  and  $q_{\text{Mn},0}$  are the concentration of component  $i$ , volume of the solution, mass of zeolite and adsorbed amount of component  $i$  per unit mass of zeolite at equilibrium. The subscript 0 and eq stand for the initial and equilibrium conditions. It was assumed that there was no change in volume of the solution and mass of zeolite before and after the experiment; i.e.  $V_0 = V_{\text{eq}}$  and  $S_0 = S_{\text{eq}}$ , and  $q_{i,\text{eq}}$  was calculated by Eq. (1) and with measured  $C_{i,\text{eq}}$  and  $C_{i,0}$ . Langmuir model was expressed as

$$q_i = q^* K_{L,i} C_{i,\text{eq}} / (1 + K_{L,i} C_{i,\text{eq}}) \quad (2)$$

where  $q^*$  and  $K_{L,i}$  stands for saturated adsorption amount and Langmuir constant of component  $i$ . Extended Langmuir model was expressed as

$$q_{L,i} = \frac{q^* K_{L,i} C_i^{1/n_i}}{1 + \sum_k K_{L,k} C_k^{1/n_k}} \quad (3)$$

where  $q^*$ ,  $n$  and  $K_{L,i}$  stand for saturated adsorption amount, valence of the ion, and Langmuir constant of component  $i$ [6].

Figures 1 and 2 show the change of  $p\text{H}$  in liquid phase between initial and equilibrium. Diagonal represent the equal  $p\text{H}$  at initial and equilibrium. For both  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$ , the equilibrium  $p\text{H}$  became higher than initial  $p\text{H}$ . The  $p\text{H}$  increased due to the adsorption of hydrogen ion by NaMOR. In the previous research, the impurities in natural Indonesian zeolite increased  $p\text{H}$  around 7-8 at equilibrium in same experimental conditions[3]. From this result, the  $p\text{H}$  value is more affected by impurities in the natural zeolite than adsorption of hydrogen ion.

Figures 3 and 4 shows relationship between the desorbed cations from NaMOR and the concentration of heavy metal in liquid phase at equilibrium in batch adsorption.  $\text{Na}^+$  was the most desorbed cation in NaMOR. As the heavy metal concentration at equilibrium increased, the amount of sodium desorbed was increased. Compared with the concentration of other ions, the concentration of  $\text{Na}^+$  was extremely high at equilibrium. Therefore, it was necessary to consider the concentrations of exchangeable cations in the zeolite in adsorption equilibrium of heavy metals.

Figures 5 and 6 show the adsorption isotherms of Mn and Zn. The adsorption amount increased with the rise of the concentration of metals at equilibrium. The adsorption amount decreased with the decrease of the  $p\text{H}$  at equilibrium. The result of  $p\text{H}_0=3$  and  $p\text{H}_0=5$  were almost

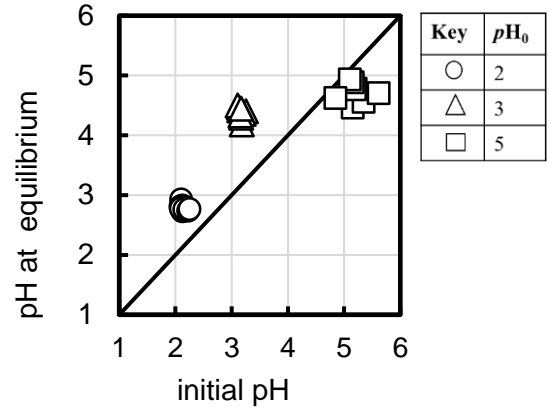


Fig. 1 Change of  $p\text{H}$  in Mn solution

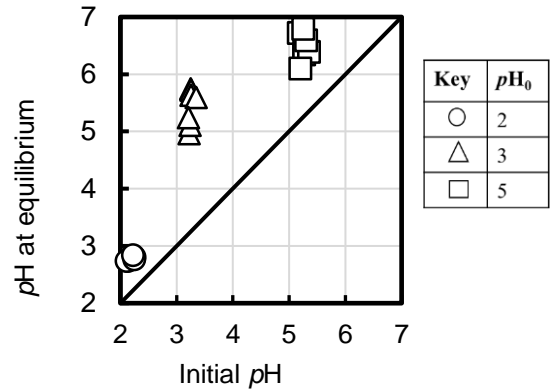


Fig. 2 Change of  $p\text{H}$  in Zn solution

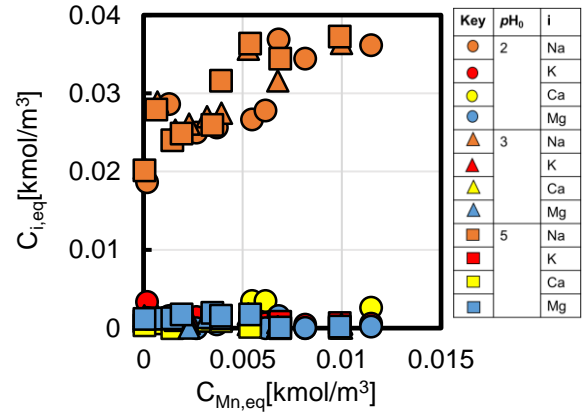


Fig. 3 Concentration of cations at equilibrium in Mn solution

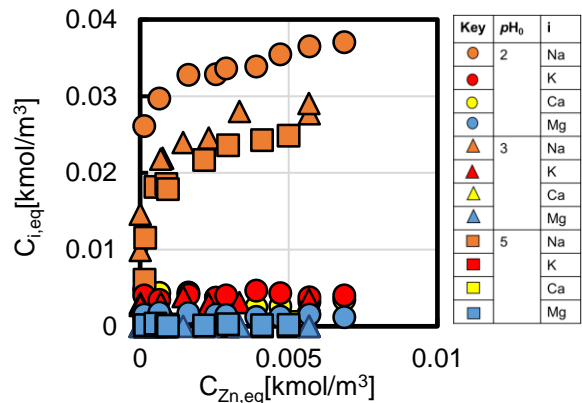


Fig. 4 Concentration of cations at equilibrium in Zn solution

same in both Mn and Zn solution. When  $pH$  at equilibrium was higher than 4, the effect of hydrogen ion became small. The experimental data were fitted by Langmuir model. Solid line and dashed line represent the adsorption isotherm of  $pH_0=2$  and  $pH_0=3, 5$ . Table 5 shows the Langmuir parameters obtained from experimental data. Saturated adsorption amounts of  $Mn^{2+}$  and  $Zn^{2+}$  showed almost the same value. Regarding the values of  $K_{L,i}$ :  $K_{L,Zn}$  was greater than  $K_{L,Mn}$ .  $q^*$  and  $K_{L,i}$  at  $pH_0=3, 5$  was greater than the values of  $q^*$  and  $K_{L,i}$  at  $pH_0=2$ . In the case of  $pH_0=2$ , the adsorbed amount of hydrogen ion by NaMOR was larger than the adsorbed amount of hydrogen ion at  $pH_0=3, 5$ . Therefore the values of  $q^*$  and  $K_{L,i}$  became small at  $pH_0=2$ .

Table 5 Langmuir parameters

Metal	$pH_0$	$K_L$ [ $m^3/kmol$ ]	$q^*$ [ $kmol/kg\text{-zeo}$ ]
Mn	2	567	$2.9 \times 10^{-4}$
	3	598	$3.6 \times 10^{-4}$
	5		
Zn	2	812	$2.9 \times 10^{-4}$
	3	2043	$3.6 \times 10^{-4}$
	5		

As mentioned earlier, it was necessary to consider the effect of exchangeable ions on the adsorption equilibrium. Therefore, the effect of present cations should be taken into account using extended Langmuir model. Three assumptions were made to determine the parameters. ①Na concentration in the zeolite at the initial condition was  $1.4 \times 10^{-3} kmol/kg\text{-zeo}$  (Table 4). ②The effect of hydrogen ion was neglected when  $pH_0=3, 5$ . ③ $q^*_{Na}$  was decided as  $1.9 \times 10^{-3} keq/kg\text{-zeo}$  (CEC, Table 3). With these assumptions,  $q^*_{Mn}$ ,  $q^*_{Zn}$ , and  $K_{L,i}$  that meet the experimental results were fitted to obtained.

Figure 7 shows the comparison between experimental data of adsorption amount and calculated adsorption amount. Diagonal represent  $q_{L,i}=q_{i,eq}$ . Extended Langmuir model could roughly predicted the adsorption amount of Na and heavy metals. Table 6 shows the determined parameters of extended Langmuir model.

Table 6 Parameters of extended Langmuir model

$i$	Mn	Zn	Na
$q^*_{L,i}$ [kmol/kg-zeo]	$1.2 \times 10^{-3}$	$1.2 \times 10^{-3}$	$1.9 \times 10^{-3}$
$K_{L,i}$ [ $m^3/kmol$ ]	1600	1800	15000

Figure 8 shows the change of  $pH$  in binary solution of Mn and Zn. Diagonal represent the equal  $pH$  at initial and equilibrium. The equilibrium  $pH$  became higher than the initial  $pH$  as in the case of single metal solution. NaMOR also adsorbed hydrogen ion in binary solution of Mn and Zn.

Figure 9 shows desorbed cations from NaMOR in adsorption experiment with binary metal solution.  $Na^+$  was the main cation exchanged with heavy metals as in the case of single metal solution. The concentration of  $Na^+$  desorbed was extremely high compared with concentrations of other ions. Therefore, it was necessary to consider the effect of the three ions ( $Mn^{2+}$ ,  $Zn^{2+}$  and

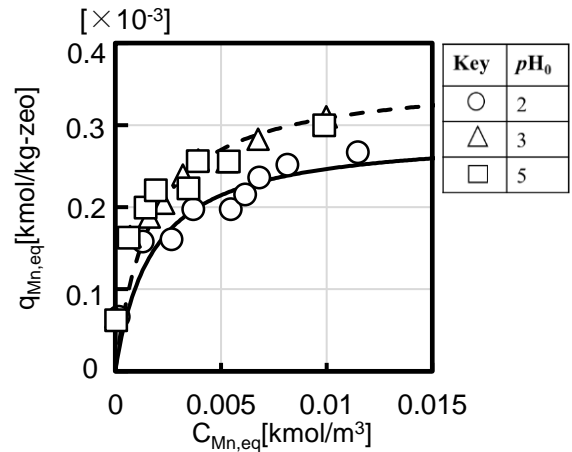


Fig. 5 Adsorption isotherm of Mn

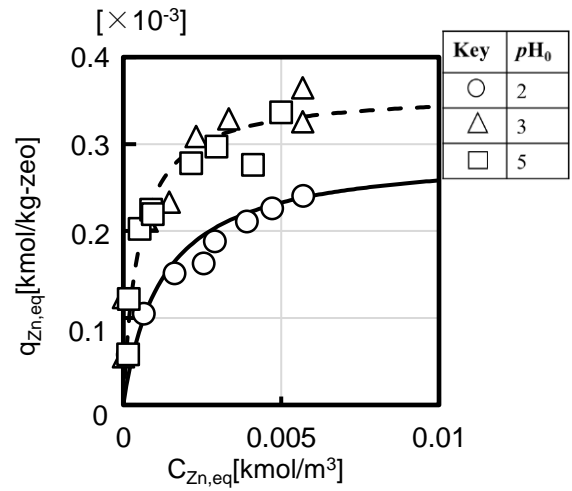


Fig. 6 Adsorption isotherm of Zn

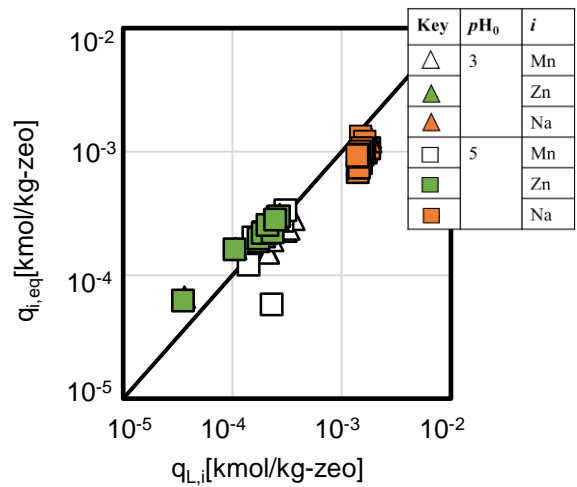


Fig. 7 Comparison of calculated adsorbed amount and experimental data.

Na<sup>+</sup>) in the adsorption equilibrium of binary metal solution.

Figure 10 shows the adsorption isotherm in binary solution of Mn and Zn. As in the case of the single metal solution, the adsorption amount of heavy metals increased as the concentration of heavy metals at equilibrium increased. The adsorbed amount of heavy metals was decreased as the equilibrium pH decreased.

Figure 11 shows the comparison of calculated adsorption amount and experimental adsorption amount. Diagonal represent  $q_{L,i}=q_{i,eq}$ . Parameters in Table 6 were used to calculate the adsorption amount from extended Langmuir model. The model could roughly predicted the adsorption amount considering the effect of three metal ions (Mn<sup>2+</sup>, Zn<sup>2+</sup> and Na<sup>+</sup>) in liquid phase at equilibrium.

#### 4. Conclusion

The CEC of NaMOR was  $1.9 \times 10^{-3}$  keq / kg-zeo. The value was comparable to the CEC of ideal mordenite. The exchangeable cations contained Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>, and the most exchangeable cation Na<sup>+</sup> was  $1.4 \times 10^{-3}$  kmol / kg-zeo.

NaMOR was able to adsorb and remove heavy metals in batch adsorption equilibrium with model acid mine wastewater containing heavy metals. The equilibrium pH in the liquid phase was higher than the initial pH in the liquid phase. The adsorption amount of metals was decreased when pH value of liquid phase at equilibrium was decreased. Extended Langmuir model roughly predicted the adsorption behavior considering the effect of exchangeable cations in liquid phase.

#### Nomenclature

C: concentration in liquid phase	[kmol/m <sup>3</sup> ]
V: volume of liquid phase	[m <sup>3</sup> ]
q: concentration in solid phase	[kmol/kg-zeo]
q*: saturated adsorbed amount	[kmol/kg-zeo]
q <sub>L</sub> : calculated adsorbed amount	[kmol/kg-zeo]
S: mass of zeolite	[kg]
K <sub>L</sub> : Langmuir constant	[m <sup>3</sup> /kmol]

#### Subscript

i: component i
eq: at equilibrium
0: at initial state

#### Reference

- [1] JOGMEC 酸性炭鉱廃水問題の対処動向について
- [2] Fernando, Master thesis 2015 Tokyo Tech, Egashira Lab
- [3] Hasegawa, Master thesis 2018 Tokyo Tech, Egashira Lab
- [4] Chapman HD (1965) Cation-exchange capacity, in 'Methods of soil analysis, part 2.
- [5] N.Hara and H. Takahashi, 1975 ゼオライト基礎と応用
- [6] E. C. Markham and Arthur F. Benton, Journal of the American Chemical Society 1931 53 (2), 497-507

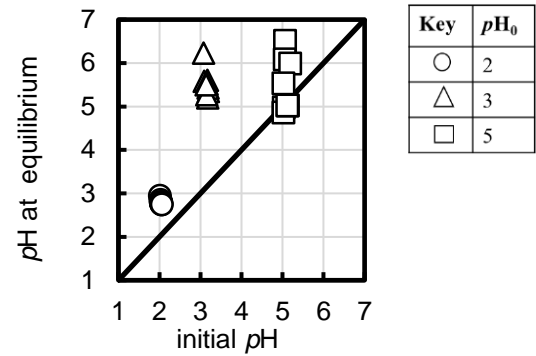


Fig. 8 Change of pH in binary metal solution of Mn and Zn

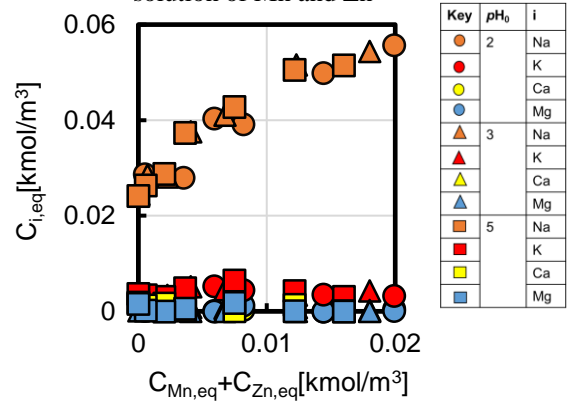


Fig. 9 Desorbed cations from NaMOR in binary metal solution of Mn and Zn

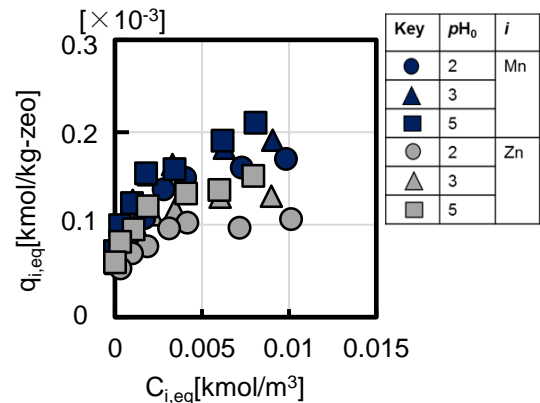


Fig. 10 Adsorption isotherm in binary metal solution of Mn and Zn

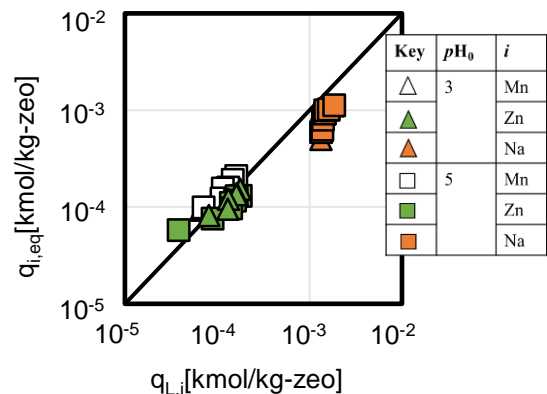


Fig. 11 Comparison of calculated adsorbed amount and experimental data in binary metal solution of Mn and Zn.