Adsorption Equilibrium of Metal Cations of Acid Mine Drainage Treatment using Indonesian Natural Zeolite

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インドネシア産天然ゼオライトによる酸性炭鉱廃水の処理における 金属陽イオンの吸着平衡

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インドネシア・ボゴール産の天然ゼオライトを用いて，モデル酸性廃水中の重金属イオン(Mn, Zn, Cu, Fe)の吸着平衡を実測した。ゼオライトおよびモデル酸性廃水を接触させることによりNa，Mg，K，Caイオンが溶出した。初期pH(2〜5)は，平衡時において7〜8に上昇した。pHの上昇により金属水酸化物が析出したと考えられ，Zn，Cu，Feの水溶液中濃度は大きく減少した。Mnは主としてゼオライトによる吸着により濃度が減少した。拡張Langmuir式は実験結果を良好に推算することができた。

1. Introduction

Indonesia is a country that has large quantity of mineral resources, especially huge reserves of coal, and this country has been a great exporter of coal. Thus mining industry in Indonesia is expected to further develop in the future[1]. On the other hand, Indonesia has been suffered from acid mine drainage (AMD) caused by mining activities. The AMD is acidic wastewater containing heavy metals sulfate, generated through the oxidization of metal sulfide at the surface of mineral deposit with water or air, and polluting the ecological systems[2]. The AMD is mostly drained from abandoned mining sites where no one has duty to treat AMD, and therefore economical and simple treatment to mitigate the high acidity and remove the heavy metal ions is required[2].

For treatment of AMD, neutralization method is most commonly used. Although the method is effective to remove the heavy metal ions in the AMD, large amount of sledges should be generated and the treatment of the sledges also is necessary. On the other hand, the deposits of Indonesian natural zeolite were found abundantly in West Java Province and the utilization of the natural zeolite for the treatment of AMD has been studied. The base components of the zeolites are mainly clinoptilolite and mordenite. Although the previous studies of our research group reported that the natural zeolite from Bogor deposit was effective for removal of heavy metals from real AMD of coal mine and mitigation of acidity in the solution[3], the effects of precipitation of heavy metals and other cations in the solution on the mechanism of heavy metal removal were still necessary to study.

In this dissertation, the characterization of the zeolite samples and batch treatment of the model AMD solutions containing single and binary heavy metal using Indonesian natural zeolite were carried out to study the effects of pH and concentration of metal cations on the adsorption equilibrium in order to clarify the mechanisms of the AMD treatment.

2. Experimental
2.1 Materials

Natural zeolite sample was obtained from Bogor deposit, Indonesia. According to XRD result of previous study[3], the major components of the zeolite were clinoptilolite-Ca and mordenite. In addition, the sample contained albite, cristobalite, and calcite as non-zeolitic material. Before the experiment, the zeolite sample was crushed (Wonder Blender, WB-1, Osaka Chemical Co., Ltd.), and screened (Testing Sieve, aperture 150x10^{-6} m, wire diameter 100x10^{-6} m, Tokyo Screen Co., Ltd.) Then obtained powder was washed with deionized water and dried to remove water.

In the cases of adsorption equilibrium measurements, four kinds of heavy metal ions, such as Mn^{2+}, Zn^{2+}, Cu^{2+} and Fe^{3+}, were selected as the model heavy metal ions contained in AMD, and $MnSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, and $Fe_2(SO_4)_3 \cdot nH_2O$ were used as source of heavy metal ions to prepare the model AMD. The pH of the feed solution was adjusted using H_2SO_4. All reagents used here were in analytical grade and purchased from Wako Pure Chemical Ind., Ltd.

2.2 Characterization of the zeolite sample

The cation exchange capacity (CEC) of the natural zeolite sample also was measured with Method-9081 by the US Environmental Protection Agency. In order to quantify exchangeable cations in the zeolite, leaching of the zeolite using ammonium acetate (NH_4OAc) solution were also carried out. The 4g of natural zeolite sample was contacted with 30mL of 1 mol/L aqueous NH_4OAc solution and shaken for 5 minutes. After phase separation using centrifuge, fresh 30mL NH_4OAc solution was added to the solid and this operation was repeated 10 times. The liquid phase obtained from each operation was analysed to determine metal concentrations.

2.3 Batch AMD treatment

The experimental conditions of batch adsorption are summarized in **Table1**. Single metal solutions and 3 types of binary metal solutions (Mn-Zn, Zn-Fe, and Mn-Fe) were used as feed solutions. The initial metal

concentrations were varied from 1.0×10^{-3} to 1.9×10^{-2} mol/L. In the cases of binary metal solutions, summation of initial metal concentrations of both metal ions were varied from 1.0×10^{-3} to 1.9×10^{-2} mol/L and mass concentration ratio of both metals was set as unity. All experiments were carried out as follows. The specified volume of feed solution V_0, and amount of natural zeolite sample S_0 were put in a 100mL volume plastic bottles with screw cap and shaken at 300K for 240 hours to be equilibrated. After reaching equilibrium the mixture was filtrated with paper filter. The feed solution and the obtained liquid phases were analysed to determine metal concentrations and pH values.

2.4 Analysis

The liquid phases were analysed to determine metal concentrations in the solutions by ICP-AES (SPS7800, SII Nano Technology). The pH values of the solutions were measured by digital pH meter (F-51, HORIBA).

Table1 Experimental conditions of batch adsorption

Solute		MnSO$_4$ 5H$_2$O, ZnSO$_4$ 7H$_2$O, CuSO$_4$ 5H$_2$O, Fe$_2$(SO$_4$)$_3$ nH$_2$O
Adsorbent		Natural zeolite sample from Bogor deposit
Volume of solution, V_0	[m^3]	50×10^{-6}
Initial metal concentration, $C_{i,0}$	[kmol m^{-3}]	1×10^{-3}-1.9×10^{-2}
Initial pH of solution, pH$_0$	[-]	2, 3, 5(Mn, Zn, Cu) 2 (Fe, binary metals)
Mass of zeolite, S_0	[kg]	2.5×10^{-3}

3 Results and discussion

3.1 Characterization of the zeolite sample

Based on the method-9081, the CEC of the zeolite sample was determined as 8.42 x 10^{-4} eq/g. This value was lower than the theoretical CECs of pure Clinoptilolite-Ca (2.44 x 10^{-3} eq/g) and Mordenite (2.24 x 10^{-3} eq/g)[4]. Total equivalent of metal ion i leached from unit mass of the zeolite sample until the k time contacts, $E_{i,k}$, was defined as follows,

$$E_{i,k} = \sum_j^k m_i C_{i,j} V_j / S_0 \qquad (1)$$

where $C_{i,k}$ and V_k ($10 \geqq k \geqq 1$) represent the concentration of metal ion i at the k-th contact and added volume of solution at the k-th contact, respectively.

Figure 1 shows the plots of $E_{i,k}$ against the total volume of NH$_4$OAc contacted with the zeolite samples, and the CEC of the zeolite sample measured above was shown as the dashed line. The metal ions of Ca, Na, Mg, and K dissolved into the NH$_4$OAc solution, and $E_{i,k}$ of Ca was the largest, followed by those of Na, K, and Mg. The $E_{i,k}$ of Na, Mg, and K increased until $k=2$ and kept almost constant in the range of $k>2$. On the other hand, $E_{i,k}$ of Ca kept increasing until 10 time contacts and $E_{i,k}$ of Ca at $k=10$ was almost twice as much as the CEC. According to the previous study, the zeolite sample contained CaCO$_3$ [3] and most of Ca ions in the solution should be derived not from the ion exchange sites of the zeolite, but from CaCO$_3$. Although the amount of

CaCO$_3$ leaching were larger, the effects of the leaching on the CEC measurement should be negligible. The concentration of Ca ion at each shaking steps were much lower than the concentration of Na in the sodium acetate solutions which were used for the CEC measurement. Then, the obtained CEC was considered to be reasonable.
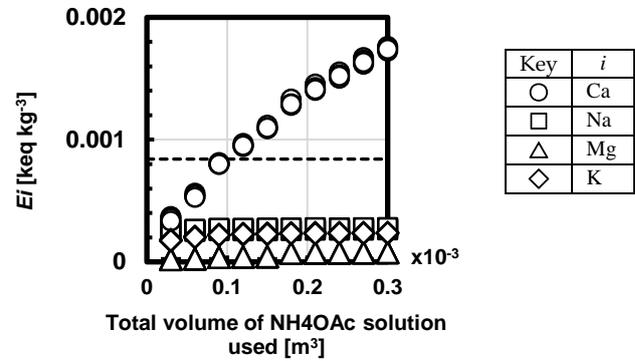

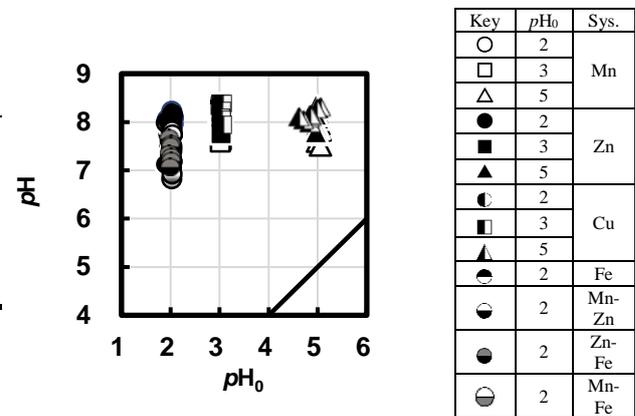**Fig.1** Accumulated equivalent of leached cations in the NH4OAc solution(equivalent based)

Fig.2 pH changes in the equilibrium solution
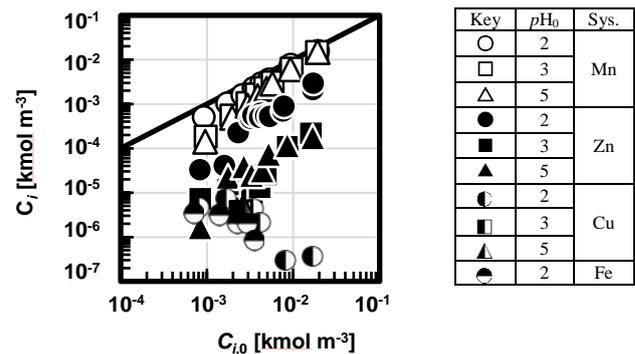

Fig.3 Concentration changes of heavy metals in equilibrium solution

3.2 Batch AMD treatment

Figure 2 shows pH changes of the single and binary heavy metal solution between initial and equilibrium. The pHs in all model AMD solutions at equilibrium increased from the initial ones and settled from 7 to 8, in spite that their initial pHs were varied from 2 to 5. The pH increased as the initial concentration of the metal ion decreased. Although this increment of pH might be caused by adsorption of hydrogen by the zeolite,

dissolution of $CaCO_3$, from the zeolite, and so on, the substantial contributions of these reasons to the pH increment were unclear.

Figure 3 shows the comparison of initial and equilibrium concentrations of heavy metals in the model AMD with the single heavy metal systems. All metal concentrations in the solution were lowered by contacting with the natural zeolite. Especially the equilibrium concentrations of Zn(pH$_0$=3, 5), Cu, and Fe in the single heavy metal systems. In the cases of binary metal systems, the concentrations of all metals also decreased and that of were almost zero.

Figure 4 shows the relationship of the metal cation concentrations and pH in the equilibrium solution in the cases of the single heavy metal systems. The concentrations of leached cations and heavy metal ions increased as pH decreased. The cation most leached from the zeolite sample was Ca and its concentration at equilibrium increased as the initial heavy metal concentrations increased in all cases. In the binary heavy metal systems, Ca was most leached and its concentrations increased with the increment of initial heavy metal concentrations, as same as in the single heavy metal systems.

Figure 5 shows the relationship between the equilibrium pH and concentrations of the metal ions at equilibrium, in which the solubility curves of respective metal hydroxides estimated from their solubility products also were indicated as solid lines. The curves represent solubilities of their metal ions at corresponding pH, and the solubility products were cited from the previous studies [3] and used as the reference solubilities. In all conditions, the concentrations of Mn^{2+} at equilibrium were smaller than the solubility, and the concentrations of the other metal ions were close to or larger than the estimated solubility curves. Since concentration of Mn^{2+} was larger than estimated solubility curve, Mn^{2+} was removed by adsorption onto zeolite. The concentrations of Zn^{2+} were close to the estimated solubility of $Zn(OH)_2$ and some part of Zn^{2+} might be precipitated to be removed from the solution. The concentrations of Cu^{2+} and Fe^{3+} at equilibrium were larger than solubility of $Cu(OH)_2$ or $Fe(OH)_3$ estimated at each equilibrium pH. The concentrations were low enough to be negligible compared to other heavy metal. Thus most of Cu and Fe might be removed by precipitation of hydroxide form in all conditions. The concentration of Ca was the largest among metal ions dissolved from the zeolite sample and the concentration at equilibrium increased as initial heavy metals concentrations increased.

Key	i	Sys.
○	Ca	
□	Na	Mn
△	Mg	
◇	K	
●	Ca	
■	Na	Zn
▲	Mg	
◆	K	
◐	Ca	
◼	Na	Cu
◮	Mg	
◆	K	
◓	Ca	
⬓	Na	Fe
◮	Mg	
◈	K	
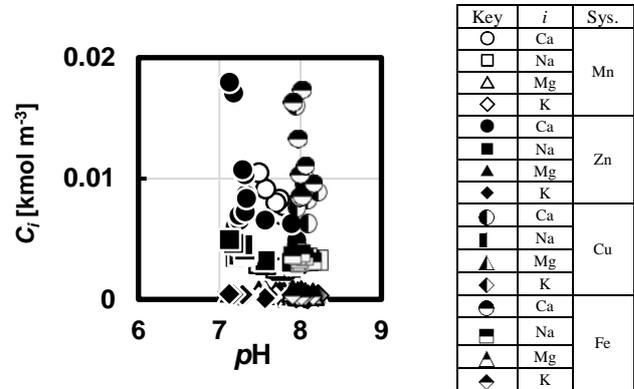
Fig.4 Equilibrium concentrations of eluted cations form the zeolite into the solution at pH$_0$=2

Finally, we tried to predict adsorption isotherm of heavy metals by Langmuir model. The adsorbed amount of heavy metal cation i was calculated from material balance equation and was expressed as,

$$q_i = (C_i - C_{i,0})V_0/S_0 \qquad (2)$$

In this experiment we assumed that initial heavy metal concentrations in solid phase were zero ($q_{i,0}$=0) and volume of the solution and mass of the zeolite were same before and after equilibrium (V_0=V and S_0=S). The extended Langmuir equation was expressed as,

$$q_i = q^*K_iC_i/(1 + K_{Ca}C_{Ca} + K_{Mg}C_{Mg} + K_iC_i) \qquad (3)$$

where q_i^* and K_i were the saturated amount of metal ion i on the zeolite and the Langmuir parameter of metal ion i, respectively. Then it was assumed that only divalent cations were adsorbed; adsorption of Ca^{2+}, Mg^{2+} and Mn^{2+} or Zn^{2+} were considered, and the saturated amount of adsorption, q_i^*, was decided based on the CEC measured here as 4.21×10^{-4} mol/g, and Ks of Ca and Mg were same as that of Mn^{2+}which had no precipitation of hydroxides.

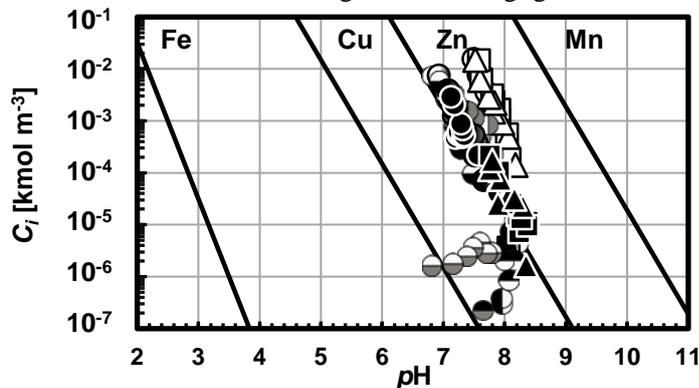| Key	pH$_0$	i	Sys.	Key	pH$_0$	i	Sys.
○	2			◑	2	Mn	Mn-
□	3	Mn	Mn	◓		Zn	Zn
△	5			◐	2	Zn	Zn-
●	2			◓		Fe	Fe
■	3	Zn	Zn	◐	2	Mn	Mn-
▲	5			◒		Fe	Fe
◖	2						
⬓	3	Cu	Cu				
◮	5						
◓	2	Fe	Fe				

Fig.5 Estimated solubility curves of the metal hydroxides and the relations between the metal concentrations and pH values at equilibrium

Figure 6 shows the adsorption isotherms of various kinds of metal ions in the single heavy metal solutions. The natural zeolite could remove most of Zn at $pH_0=3$ or 5, Cu and Fe, and their concentrations in the solutions were almost zero. These ions should be removed as the forms of their hydroxides by elevation of pH. The obtained parameters were shown in **Table 2** and the estimation results by Eq. (3) were shown in **Fig.6** as lines. The K of Mn under the condition of $pH_0=2$ was lower than those of $pH_0=3$ or 5. The K of Zn was much larger than those of Mn adsorption because q_i included the effects of precipitation.

The adsorption isotherms of heavy metal ions in the binary heavy metal solutions are shown in **Figure 7**. The concentrations of Fe were almost zero and the q_{Zn}s in binary metal systems were lower than those in single Zn system at same equilibrium concentrations of Zn. Since the divalent cations were major among all cations in the solutions at equilibrium, the effects of divalent cations on the removal of heavy metals were considered. Then, the extended Langmuir model was used to predict the adsorption isotherm of the metal ions in the binary system as same as the single system, and prediction results are shown in **Fig. 7** by lines. The Ks determined here are listed in **Table 3**, where Ks of divalent cations, Ca and Mg, were set as same as that of Mn. The Ks of Mn were the same as those measured in single Mn system. Whereas K of Zn was higher than that of Mn in the binary metal ion system, it was much smaller than K obtained in the single metal ion system. The amount of precipitated $Zn(OH)_2$ in the binary system might be smaller than those in the single system because the concentration of Zn^{2+} in the binary system lied in wider range than that in the single system.
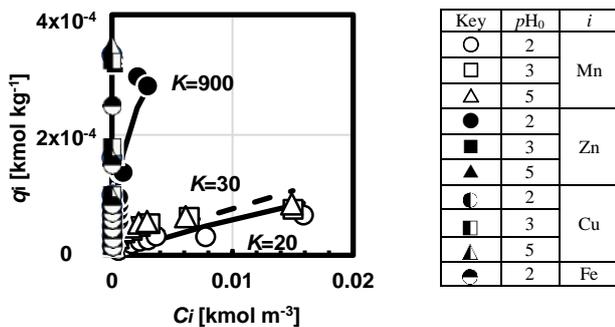
Table 2 Determined Langmuir parameters of Mn and Zn in adsorption experiment

System	Metal	pH_0	K_i [m^3 $kmol^{-1}$]	q^* [$kmol$ kg^{-1}]
Mn	Mn	2	20	4.21×10^{-4}
		3	30	
		5	30	
Zn	Zn	2	900	

Table 3 Determined Langmuir parameters of Mn and Zn in adsorption experiment

System	Metal	pH_0	K_i [m^3 $kmol^{-1}$]	q^* [$kmol$ kg^{-1}]
Mn -Zn	Mn	2	20	4.21×10^{-4}
	Zn	2	20	
Zn -Fe	Zn	2	60	
Mn -Fe	Mn	2	20	

4. Conclusions

The natural zeolite sample from Bogor deposit was used as an adsorbent to study the treatment of the model AMD. CEC of the zeolite sample was determined to 8.42×10^{-4} mol/g by US-EPA method 9081. Part of eluted Ca ions were not derived from exchangeable sites.

The zeolite sample could increase pH of the model AMD solutions to appropriate level ($pH=7-8$). In addition, the natural zeolite could remove heavy metal Mn^{2+}, Zn^{2+}, Cu^{2+}, and Fe^{2+} in model AMD. Zn^{2+}, Cu^{2+}, and Fe^{2+} were removed not only by the adsorption with the zeolite, but also by precipitation to form metal hydroxides. The Mn^{2+} was mainly removed by adsorption onto the zeolite samples. The extended Langmuir model was used to organize the adsorption of Mn and Zn considering the effects of other metal ions dissolved from the zeolite sample, and favorably predicted the adsorption behavior
.

Nomenclature

C	-concentration in liquid phase	[$kmol$ m^{-3}]
q	-concentration in solid phase	[$kmol$ kg^{-1}]
q^*	-saturated amount of adsorption	[$kmol$ kg^{-1}]
V	-volume of liquid phase	[m^3]
S	-mass of zeolite	[kg]
E	-total equivalent of metal leached	[keq kg^{-1}]
K	-Langmuir constant	[m^3 $kmol^{-1}$]
m	-valency of ion	[-]

Subscript

0	-at initial state
i	-component i
k	-at k-th contact

Fig.6 Adsorption isotherm of heavy metals onto zeolite in single heavy metal solutions
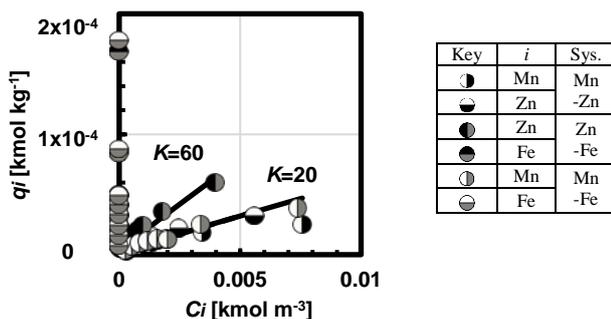
Fig.7 Adsorption isotherm of heavy metals onto zeolite in binary heavy metal solutions

Reference
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