1. Introduction
The contamination of the acid mine drainage solution by heavy metals has been regarded as a serious issue to cause the water or soil pollution. Natural zeolites have been studied as a potency to remove the heavy metals from the solutions\cite{1,2}. The natural zeolite generally contains some kinds of cations, which might influence the removal efficiency of the heavy metals from the solution. In this study the natural zeolite from Mongol was used as adsorbent, and the effects of the cations in the zeolite on removal of the model heavy metals were studied.

2. Experimental
2.1. Zeolite source
The sample of natural zeolite used was obtained from Tsagaan Tsav deposit in Dornogovi province of Mongolia, which was rich in clinoptilolite and the same zeolite sample as used in the previous studies \cite{1, 2}. The zeolites were crushed, ground and passed through 150×150 µm sieves. Then it was preserved in the desiccators with a saturated aqueous solution of ammonium chloride at the room temperature, defined as the zeolite1. To identify the species of the cations in the zeolite1, 1 g of the zeolite1 was contacted with the 1M ammonium acetate solution of 20×10^{-6} m^3 at 298 K for 10 days, and the obtained solution was analyzed. The zeolite1 of 1 g was treated by contacting with 1M sodium acetate solution of 20×10^{-6} m^3 at 298 K for 10 days, and washed by pure water several times, filtered from water and dried for 1 day, defined as the zeolite2.

2.2. Batch adsorption run
Batch adsorption runs were conducted by mixing 1 g of the zeolite1 or zeolite2 with 20×10^{-6} m^3 of synthetic solutions containing the specified concentrations of heavy metal ions. The conditions of adsorption run are shown in Table 1. Copper (Cu), zinc (Zn), and manganese (Mn) were selected as model heavy metals. After equilibration, the obtained solutions were measured to determine the concentrations of the metals in the solutions, which were not only the mentioned heavy metals but also the cations dissolved from the zeolites. The analytical grade reagents of sulfide salts, such as CuSO_4·5H_2O, ZnSO_4·7H_2O and MnSO_4·5H_2O (Wako Pure Chemical Industries, Ltd.), were used as the sources of the metals since the mine wastewater generally contains sulfate ions. The aqueous phases were analyzed by ICP-AES (SPS 7800 Series, Seiko Instruments Inc.) to determine the concentrations of the metals.

Table 1 Experimental conditions of adsorption run

| Mass of initial solution, L_0 [m^3] | 20×10^{-6} |
| Initial concentration of metals, C_0 [kmol/m^3] | 1.5×10^{-3}-1.1×10^{-4} |
| Mass of initial zeolite, S_0 [g] | 1 |
| Contacting time, t [h] | 240 |
| Temperature, T [K] | 303 |

3. Result and Discussion
3.1. Cations dissolved from zeolite
In the solution obtained by contacting the zeolite1 and ammonium acetate solution, the species and amounts of metals dissolved from the zeolite1 were listed in Table 2. Sodium (Na) calcium (Ca), potassium (K), magnesium (Mg) and strontium (Sr) were detected and the concentration of Na was the largest, followed by Ca, K, Mg and Sr. In the solutions at adsorption equilibrium with the zeolite1, the model heavy metal of Cu, Zn or Mn, and 5 cations of Na, K, Ca, Mg and Sr were detected. When the zeolite2 was used, the same kinds of metals were detected as well.

Table 2 Species and concentrations of cations dissolved from zeolite1 [kmol/kg-zeolite]

<table>
<thead>
<tr>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6×10^{-4}</td>
<td>9.6×10^{-5}</td>
<td>2.3×10^{-4}</td>
<td>8.8×10^{-5}</td>
<td>1.6×10^{-5}</td>
</tr>
</tbody>
</table>

Figure 1 shows the effects of the concentration of the heavy metal in the solution on the concentrations of Na for both zeolites, in which the results of Zn were presented as an example. The concentrations of Na increased with the Zn concentration and showed the constant values in the range of C_{Zn}>0.002kmol/m^3. The concentration of Na was larger with the zeolite2 than that with the zeolite1. The operation to contact the zeolite1 with the solution of sodium acetate might be able to exchange some cations in the zeolite1 with Na. This tendency was observed in the cases of Mg and Cu.

3.2. pH change
Figure 2 shows the effects of the metal concentrations on the pH at equilibrium. The equilibrium pH was always higher than the initial pH, and decreased with an increment of the metal concentrations. The pH range

![Figure 1](image1.png)

![Figure 2](image2.png)
increased in the order of the results with Cu, Mn and Zn. The zeolites should adsorb the proton ion to enhance pH and the increment was larger with smaller metal concentration. The pH was higher with the zeolite2 than that with the zeolite1.

### 3.3. Numerical relationships

The material balance of metal $i$ is represented by,

$$L_0C_{i,0} + S_0q_{i,0} = L_0C_i + S_q_i$$  (1)

where $L_0$, $C_{i,0}$, $S_0$, $q_{i,0}$, $L$, $C_i$, $S$ and $q_i$ are the volume of the initial solution, initial molar concentration of metal $i$, initial mass of zeolite, mole of metal $i$ per unit mass of zeolite, volume of the solution at equilibrium, molar concentration of metal $i$ at equilibrium, mass of zeolite at equilibrium, and mole of metal $i$ per unit mass of zeolite at equilibrium, respectively. The $q_i$ of each heavy metal was determined by Eq. (2) with the assumptions of $S=S_0$, $L=L_0$, and $q_{i,0}=0$. The yield of metal $i$, $Y_i$, was defined as,

$$Y_i = 1 - L_iC_i / L_0C_{i,0}$$  (2)

The adsorption isotherm of the Langmuir model is expressed as,

$$q_i = q_{\text{m,}i}K_iC_i/(1 + K_iC_i)$$  (3)

where $q_{\text{m,}i}$ is the adsorbed moles of metal $i$ per unit mass of zeolite at saturation, and $K_i$ is the Langmuir constant of metal $i$.

### 3.4. Yields of heavy metals

Figure 3 shows the yields of metal $i$ with both of zeolites. The $Y_i$ of all metals simply decreased with an increment of the metal concentrations. In the range of lower metal concentrations, $Y_i$ attained more than 0.9 in all cases. The $Y_i$ of Zn was the largest, followed by Mn and Cu. The $Y_i$ were higher with the zeolite2 than those with the zeolite1.

### 3.5. Adsorption isotherm

Figures 4 and 5 show the adsorption isotherms of the heavy metals with both zeolites. Both zeolites adsorbed all kinds of heavy metals. For each zeolite, $q_i$ of Zn was the largest, followed by Mn and Cu. The $q_i$ was larger with the zeolite2 than that with the zeolite1. The measured results were fitted by the Langmuir model to obtain $q_{\text{m,}i}$ and $K_i$, as listed in Table 3. The $q_{\text{m,}i}$ of Cu was approximately the same as in the previous study[2], however $q_{\text{m,}i}$ of Zn and Mn were larger in this study than those in the previous study. This might be caused by the difference in the equilibrium pH. The higher pH should enhance the adsorption of the cations. The pH with Zn was the largest followed by those of Mn and Cu, and pHs of Zn and Mn were larger than those in previous study. The $q_{\text{m,}i}$s were larger with the zeolite2 than those with zeolite1. The exchange of cations in zeolite should affect on the adsorption because the divalent cations should generally adsorb more than the univalent cations. Moreover the treatment with sodium acetate solution made the pH larger at equilibrium, causing larger $q_i$. Then the zeolite2, in which the cations were exchanged by Na, might show higher adsorbability of the heavy metals. However these effects were not so significant and the contribution degrees of these effects were unidentified.

### Table 3 Langmuir parameters for each heavy metal

<table>
<thead>
<tr>
<th>Zeolite1</th>
<th>Cu</th>
<th>Zn</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{\text{m,}i}$ [kmol/kg-Zeo]</td>
<td>$2.9 \times 10^4$</td>
<td>$4.1 \times 10^4$</td>
<td>$3.8 \times 10^4$</td>
</tr>
<tr>
<td>$K_i$ [m$^3$/kmol]</td>
<td>$46 \times 10^2$</td>
<td>$42 \times 10^2$</td>
<td>$50 \times 10^2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zeolite2</th>
<th>Cu</th>
<th>Zn</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{\text{m,}i}$ [kmol/kg-Zeo]</td>
<td>$3.3 \times 10^4$</td>
<td>$4.6 \times 10^4$</td>
<td>$4.3 \times 10^4$</td>
</tr>
<tr>
<td>$K_i$ [m$^3$/kmol]</td>
<td>$1.58 \times 10^7$</td>
<td>$6.2 \times 10^2$</td>
<td>$3 \times 10^7$</td>
</tr>
</tbody>
</table>

### 4. Conclusion

The natural zeolite from Mongolia could remove copper, zinc and manganese from the solution. The zeolite treated by the solution of high concentration of sodium acetate could improve its adsorbability of these heavy metals. This might be attributed to the exchange of some cations in the cations with divalent cation of sodium in the zeolite by the treatment. This treated zeolite enhanced the pH in the solution, improving the adsorbability as well. However the effects were not clarified and further study is necessary.

### Reference