Separation of Heavy metals from mine wastewater by adsorption using Mongolian natural zeolites

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モンゴル産天然ゼオライトを用いた吸着による鉱山廃水からの重金属の分離

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まず、Tsagaan Tsav鉱床産のゼオライト試料のキャラクタリゼーションを行い、これらのゼオライトがカルシウム型のクリノプチロライト、モルデナイト、シャバザイトなどを主成分とすることなどを明らかにした。ついでOyu Tolgoi銅鉱山の廃水を想定して、銅ならびに付随する亜鉛、マンガンを含むモデル水溶液を、上記ゼオライト試料により処理した。いずれのゼオライトもこれらの重金属を吸着し、最大で99 %程度除去できた。また、他の金属共存条件下でもゼオライトによる吸着を確認した。

1. Introduction

In Mongolia, the large deposits of gold, copper ores, etc. have been found in 2000, discovered by Ivanhoe Mines Ltd. of Canada. The deposits of the metals were estimated as 340 tons of gold, and 15 million tons of copper, and they may have great influence on the commodity market in the world. For the future, an Oyu Tolgoi copper deposit, Tavan Tolgoi coal deposits and other ore deposit are to be developed and the trade of these metals is planned to drastically increase from around 2013. However, the environmental contamination due to the mining development has become serious.
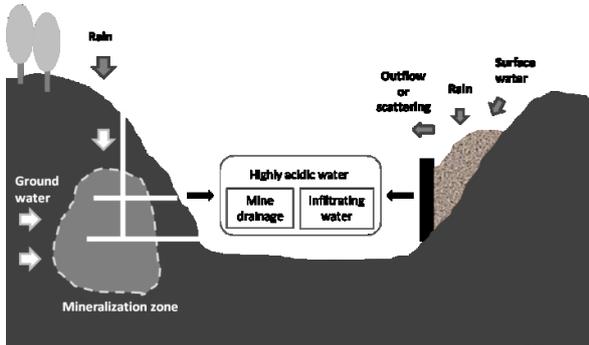

Fig. 1 Generation of mine wastewater [5]

When crushed or broken minerals in ore deposit contact with air and water, it generate acidic water called mine drainage. The sludge which has low metal concentration wastes is also cause of generation acidic water, infiltration water. Mine wastewater means both mine drainage and infiltrating water. It continues to flow out not only during mining development but also mine closing (**Fig. 1**).

The neutralization method is generally used for wastewater treatment. However this method has been pointed out to have many problems, such as generation of a lot of sludge, necessity of a large-scale facilities, high cost requirement, etc.

The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently. Treatment processes for metal contaminated waste streams include chemical precipitation, ion exchange, adsorption, ultra-filtration, etc; various treatment processes are available, among which ion exchange is considered to be cost-effective if low-cost ion exchangers such as zeolites are used.

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents. The exchangeable cations in the zeolites can participate in ion-exchange processes. The fact that zeolite exchangeable ions are relatively innocuous and makes them particularly suitable for removing undesirable heavy metal ions from wastewater.

Mongolia is abundant in metal resources and the natural zeolite deposits have been developed. It was prospected that Tsagaan Tsav deposit of natural zeolites should have a potency to produce about 4.8 million tons of zeolite minerals. However the destination of the zeolite has not been fully examined.

The use of natural zeolites as an adsorbent has gained interest among many researchers. Although still in developmental stage, T. Motsi, *et al.* studied the actual treatment of mine wastewater from Wheal Jane Mine by using Turkey natural zeolite. They found that natural zeolite had the potential to effectively remove heavy metals from relatively dilute mine wastewater [2]. T. Bolortamir. *et al.* studied wastewater treatment including chromium by using Mongolian natural zeolites. They revealed that Mongolian natural zeolites have potential to remove chromium (III and IV) from solutions [1].

This study aimed at the application of adsorption using Mongolian natural zeolite to mine wastewater treatment. As in its early stage, the characterization of Mongolian natural zeolites and batch equilibrium adsorption of model wastewater were carried out.

2. Experimental

2.1 Characterization of natural zeolites

The used sample of natural zeolite was obtained from Tsagaan Tsav deposit in Dornogovi province, Mongolia (**Table 1**). The zeolites were crushed, ground and passed through $150 \times 150 \, \mu m$ sieves and the moisture of the samples was controlled in the desiccators with saturated ammonia chloride.

Base component of the natural zeolites were

carried out using X-Ray diffraction (XRD). Surface elemental analysis was carried out with Energy Dispersive X-ray Spectroscopy (EDX). Surface areas were measured with nitrogen gas adsorption. The maximum quantity of total cations, Cation Exchange Capacity, was measured by Chapman method (1965). The aqueous phases were analyzed by ICP-AES (SPS 7800 Series, Seiko Instruments Inc.). Copper (Cu), Zinc (Zn), and Manganese (Mn) were selected as a model heavy metals. Since this study target at Oyu Tolgoi copper ore deposit, mine wastewater will contain copper and base metals such as Zn and Mn. Mine wastewater generally contains sulfate ions, and the analytical grade reagents of $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$ and $MnSO_4 \cdot 5H_2O$ (Wako Pure Chemical Industries, Ltd.) were used as the sources of the metals.

2.2 Batch adsorption studies

Batch adsorption studies were conducted by the conditions shown in **Table 2**. pH of the initial solution was adjusted with sulfuric acid. The mixture was shaken in 100×10^{-6} m^3 Erlenmeyer flask in a shaker. The final concentration after suction filtration and filtration with 0.45 μm membrane filter was determined by ICP-AES. The material balances of metals are represented by,

$$L_0 \times C_0 = L \times C + S \times q \qquad (1)$$

where L_0 is the mass of initial solution, C_0 is the initial metal concentration, L is the mass of solution, C is the equilibrium metal concentration, S is the mass of adsorbent, and q is the adsorbed amount of metals per unit mass of zeolite. q was determined by Eq. (1) with the assumption of $L=L_0$.

To marshal the adsorption data, Langmuir adsorption model was used.

$$q = q_m \times K \times C /(1 + K \times C) \qquad (2)$$

where q_m is the saturated adsorbed mass and K is the Langmuir constant. The isotherms were expressed by this equation.

3. Result and Discussion

3.1 Characterization of natural zeolites

From XRD measurement the frameworks of the used natural zeolites could be classified into three species according to the major components, such as Clinoptilolite (CLP), Mordenite (MOR), and Chabazite (CHA). All zeolites have Ca type frameworks. The Si/Al molar ratios were measured by EDX analysis. The mass fraction of each oxidized metal was determined with the assumption that all metals should exist in form of oxide metal and is shown in **Table 4**. The measured cation exchange capacity and these results were shown in **Table 3**. As expected from the results of EDX and CEC, natural zeolites have impurity such as quarts, Sanidine, Muscovite, and so on. It found that there is general correlation between Si/Al ratio and CEC.

3.2. Batch adsorption studies

Table 1 Information of Mongolian natural zeolites[1]

Sample	Deposit	Sampling depth [m]	Sampling date
CLP	Tsagaan Tsav	60	09/2004
MOR	Tsagaan Tsav	60	09/2004
CHA	Tsagaan Tsav	150	12/2005

Table 2 Conditions of adsorption run

Mass of initial solution, L_0 [g]	20
Initial concentration of metals, C_0 [g/m^3]	100 – 5000
Mass of zeolite, S [g]	1
Contacting time, t [h]	240
Initial pH of solution, pH$_0$	2.5 – 5
Temperature, T [K]	300

Table 3 Principal characteristics of Mongolian natural zeolites

	CLP	MOR	CHA
Surface area [m^2/g]	31.7	7.8	164.1
Cation exchange capacity $\times 10^{-3}$ [mol/100g]	62 - 76	48 - 69	31 - 43
Si/Al molar ratio [-]	7.88	9.28	8.87

Table 4 The oxidized metal composition

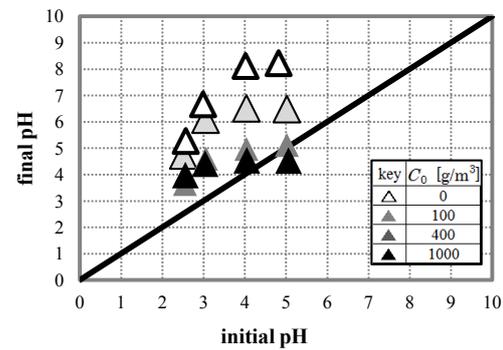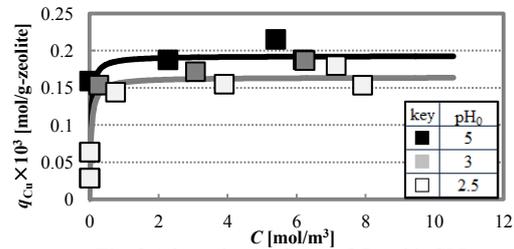| Wt %	CLP	MOR	CHA
Al$_2$O$_3$	7.17	5.10	6.70
SiO$_2$	66.62	55.80	70.05
SO$_3$	2.32	1.96	4.10
K$_2$O	9.36	10.54	7.94
CaO	3.91	22.36	5.52
Fe$_2$O$_3$	9.34	3.27	4.88
TiO$_2$	1.28	0.96	0.19
Mn$_2$O$_3$	—	—	0.61

Fig. 2 pH change of CLP in Zn sol.

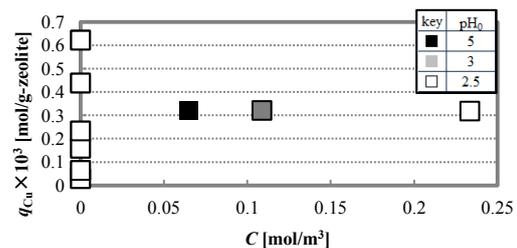**Fig. 3** Adsorption isotherm of Cu with CLP

Fig. 4 Adsorption isotherm of Cu with MOR

The natural zeolite could adsorb all kinds of metals. The adsorption of sulfur content was measured as well and the used zeolites could not adsorb it at all. To attain the adsorption equilibrium it was found that 240 hours were needed. The pH was elevated from 3 to around 4-7 by the addition of zeolite since the zeolite preferentially may adsorb H^+ from solution [2], as shown in **Fig. 2**. The equilibrium pH decreased slightly with initial concentration of metals. Especially with MOR, the equilibrium pH tends to rise up. The pH influences precipitation and dissolution of metals. The addition of the zeolites causes the dissolved metals to precipitate, such as $Cu(OH)_2$, $Zn(OH)_2$, and $Mn(OH)_2$.

The adsorption isotherms of metals on the natural zeolite are shown in **Fig. 3 to 11**. q_m and K are shown in **Table 5**. The results of $pH_0=5$ and $pH_0=3$ are almost same. The adsorption amount increase with an increase in initial pH, pH_0. The reason for this is that competitive adsorption between H^+ ion and metal ions were occurred.

Cu In the case of adsorption with MOR, equilibrium concentration of metal was 0. Since the equilibrium pH tends to be higher and copper hydroxide has low solubility to water, it may produce precipitation. Then, the most of adsorption data on MOR were not fit to Langmuir adsorption isotherm. The adsorbed amount follows the order: MOR, CLP, CHA. The legal concentration of Cu^{2+} in effluent standard is 3 mg/L [4]. It is seen that 1 g of CLP, MOR and CHA are able to treat 20 g of 200 mg/L, 600 mg/L and 200 mg/L solutions to below the legal requirement, respectively.

Zn MOR may made zinc hydroxide precipitation. The adsorbed amount follows the order: MOR, CLP, CHA. The legal concentration of Zn^{2+} in effluent standard is 2 mg/L [4]. It is seen that 1 g of CLP, MOR and CHA are able to treat 20 g of 100 mg/L, 50 mg/L and 100 mg/L, respectively.

Mn The adsorbed amount follows the order: MOR, CLP, CHA. The legal concentration of

Table 5 Principal characteristics of Mongolian natural zeolites

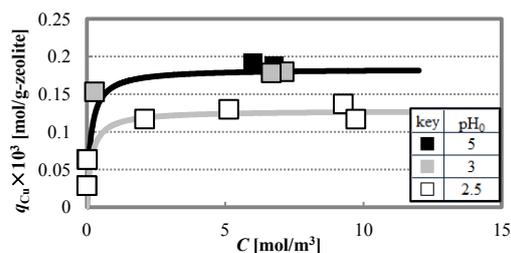| metal	zeolite	pH_0=high		pH_0=low	
		$q_m \times 10^3$ [mol/g-zeolite]	K [m³/mol]	$q_m \times 10^3$ [mol/g-zeolite]	K [m³/mol]
Cu	CLP	0.20	32.13	0.16	23.07
	MOR	—	—	—	—
	CHA	0.18	10.17	0.13	70.95
Zn	CLP	0.15	5.62	0.14	1.67
	MOR	0.84	1.96	0.83	0.98
	CHA	0.11	8.50	0.07	2.46
Mn	CLP	0.15	2.12	0.13	1.87
	MOR	0.17	0.11	0.17	0.05
	CHA	0.12	0.32	0.11	0.43

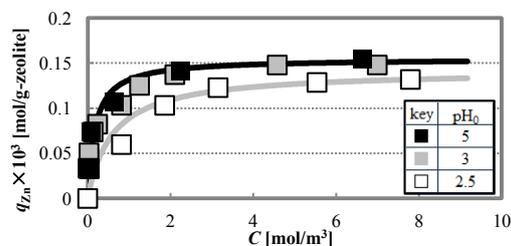**Fig. 5** Adsorption isotherm of Cu with CHA

Fig. 6 Adsorption isotherm of Zn with CLP
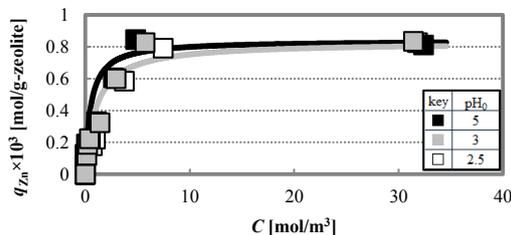

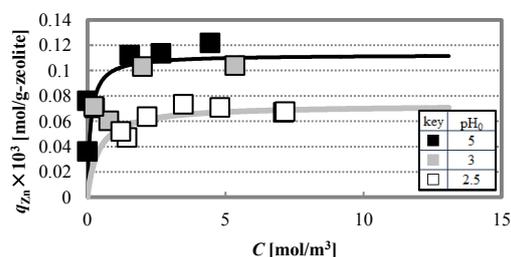**Fig. 7** Adsorption isotherm of Zn with MOR

Fig. 8 Adsorption isotherm of Zn with CHA
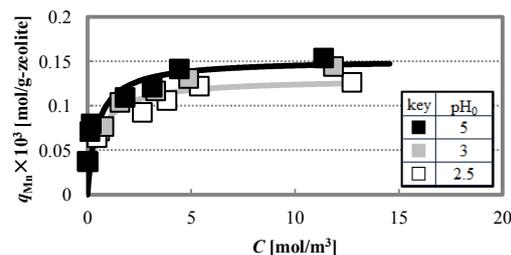

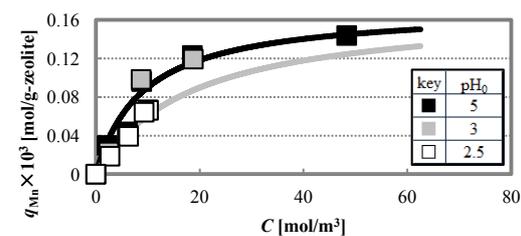
Fig. 9 Adsorption isotherm of Mn with CLP

Fig. 10 Adsorption isotherm of Mn with MOR

Mn^{2+} in effluent standard is 10 mg/L[4]. It is seen that 1 g of CLP, MOR and CHA are able to treat 20 g of 200 mg/L, 50 mg/L and 50 mg/L, respectively.

Despite that the CEC follow the order: CLP, MOR, CHA, adsorbed amount didn't follow the same order. It is because that there is an effect of precipitation of metal hydroxide.

<u>Adsorption from binary wastewater</u>

The adsorption of Zn and Mn in the binary system with CLP was carried out (**Fig. 12**). The gray line and dashed line shows the adsorbed isotherms of Zn and Mn in the single system and black key shows total adsorption amount of Zn and Mn in binary system. The $q_{m,Zn}$ and $q_{m,Mn}$ have almost the same adsorbed amount to black key. It is considered that Zn and Mn are adsorbed on same adsorption site.

<u>Adsorption from ternary wastewater</u>

The results of adsorption from ternary wastewater were shown in **Fig. 13** to **Fig. 15**. It is clear that adsorbed amount from ternary solution were lower than from single solution. With CLP, it was considered that Zn and Mn were adsorbed on same adsorption site in binary system, however, the results in ternary system was different. Because there may be other effects, such as competitive adsorption between H^+ and metal ion, change of pore size, etc. With MOR, Cu may produce hydroxide and the concentrations after equilibrium were 0. The adsorption isotherm of total metal shown as black lines were inaccurate due to hydroxide precipitation, and there is not leaving much room for discussion.

4. Conclusion

XRD pattern showed that Mongolian natural zeolites have Clinoptilolite, Mordenite and Chabazite mainly with Ca-type. Silica/Alumina molar ratio was 7.88, 9.28, and 8.87, and Cation Exchange Capacity was $62\text{-}76\times10^{-3}$, $48\text{-}69\times10^{-3}$, and $31\text{-}43\times10^{-3}$ mol/100g-zeolite, and surface area were 32, 8, 164 m^2/g-zeolite with CLP, MOR, and CHA respectively. These zeolites could remove copper, zinc and manganese. The adsorption amount increase with an increase in initial pH. Removal of the heavy metal ions was not only due to ion exchange but also due to precipitation of metal hydroxides. In binary system of Zn and Mn, it was considered that Zn and Mn adsorbed on same adsorption site with CLP.

Reference
[1] Bolortamir. Ts, *et al.*; *J. Chem. Eng. Japan*, **41**, 1003 (2008)
[2] Motsi, T.*et al.*; *Int. J. Miner. Process*, **92**, 42–48 (2009)
[3] Web site "Database of Zeolite Structures"
   http://www.iza-structure.org/databases/
[4] Environmental Bureau of the Tokyo Metropolitan Government
   http://www.kankyo.metro.tokyo.jp/water/pollution/regulation/emission_standard/hazardous_materials_except.html
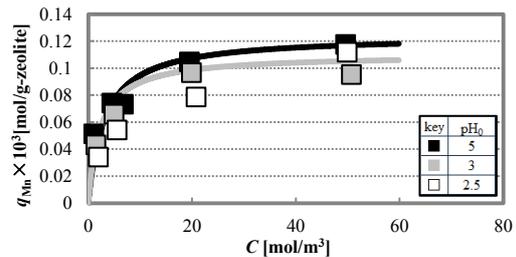[5] JOGMEC
   http://www.jogmec.go.jp/

Fig. 11 Adsorption isotherm of CHA in Mn sol.
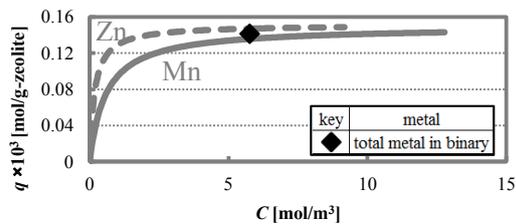

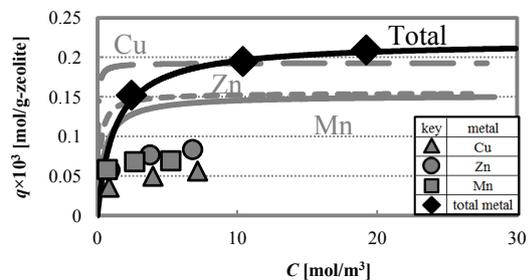**Fig. 12** Adsorption isotherm of Zn and Mn

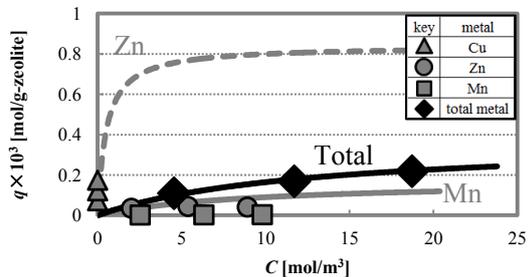**Fig.13** Adsorption isotherm with CLP from ternary system

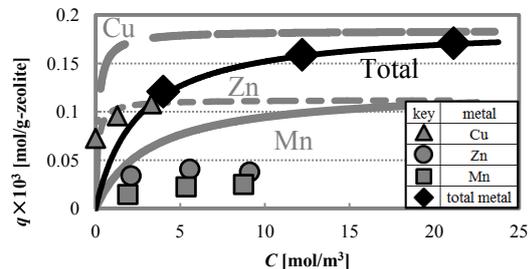**Fig.14** Adsorption isotherm with MOR from ternary system

Fig.15 Adsorption isotherm with CHA from ternary system

Nomenclature

CLP: Clinoptilolite, MOR: Mordenite, CHA: Chabazite, L_0: Mass of initial solution [g], C_0: Initial concentration of metals [g/m^3], C: Final concentration of metals [g/m^3], S: Mass of zeolite [g], t: Contacting time [h], pH_0: Initial pH of solution, pH: equilibrium pH, T: Temperature [K], q: adsorbed amount [mol/g-zeolite], q_m: maximum adsorption amount [mol/g-zeolite], K: Langmuir constant [m^3/mol]