

# Treatment of Acid Mine Drainage Using Indonesian Natural Zeolites

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This study focuses on the removal of the heavy metals and control of the  $pH$  in the model and real acid mine drainage (AMD) by natural zeolites. The zeolites obtained from Sukabumi and Bogor deposits, whose base components were clinoptilolite-Ca and mordenite, were chemically stable even in relatively low  $pH$  range ( $pH < 5$ ). In the batch equilibrium adsorptions, the samples could adsorb heavy metals contained in the solution; the sample from Bogor adsorbed the heavy metals, removed all of Fe, Cu, Zn and about 0.87 of Mn, and restored the  $pH$  from low range to higher than 7 in the real AMD.

## 1. Introduction

The rapid growth of coal mining industry in the last twenty years in Indonesia contributes an important role in the economic growth; however it has also resulted in environmental impacts such as water contamination caused by acid mine drainage (AMD). The high concentration of dissolved heavy metals and high acidity ( $pH < 5$ ) are the main characteristics of AMD. AMD is formed naturally when pyrite and sulfide minerals with the rock of coal seams are exposed to atmospheric conditions and are oxidized. The acid generation and the discharge may continue to occur even after mines are closed and abandoned. There are various techniques exist for treatment of AMD, and mainly divided into active and passive treatments. Lime neutralization have been studied extensively and mainly employed in both treatments. However, some treatment methods generate unrecovered sludge in huge amount.

The deposits of Indonesian natural zeolite were found abundantly in West Java Province and widespread in Java, Sumatera, Sulawesi, Lombok and Flores. The base components of the zeolites are mainly clinoptilolite and mordenite. Presently, they have been utilized mostly in agriculture and aquaculture industries; therefore further developments of these useful and abundant resources are highly expected. Zeolites are microporous materials that are capable of cation exchange and are used to adsorb and remove heavy metal cations from solution<sup>2</sup>.

The removal of heavy metal ions from mine waste waters using natural zeolite has been great interest among researchers. Egashira *et al.* (2013), Li *et al.* (2007), and Motsi *et al.* (2009) studied on the treatment of mine waste water using natural zeolite from Mongolia, Canada, and Turkey respectively, and revealed that the zeolite could adsorb and remove heavy metals from the solution. There have been no previous studies conducted addressing the possibility of utilizing Indonesian natural zeolite in treating real AMD from coal mine in Indonesia.

This study focuses on the removal of heavy metals and control of the  $pH$  in the model and real AMD. A number of experiments such as characterization of the zeolites, batch equilibrium adsorptions, and precipitation studies using lime in model and real AMDs under various conditions were performed.

## 2. Materials and Methods

### 2.1. Characterization of the zeolites

The natural zeolites were obtained from Sukabumi (SKB) and Bogor (BGR) deposits, West Java. The zeolites samples were crushed, ground and sieved to adjust the particle size smaller than  $150 \times 10^{-6}$  m. The comminuted samples were washed to remove any water soluble impurities such as soil and were then dried. The

prepared samples were kept in desiccators with a saturated ammonium chloride solution at room temperature to control the moisture of the zeolites samples, and were then provided for the following characterization and adsorption runs.

The base components of the zeolites samples were analyzed using X-ray diffraction (XRD). The specific surface areas of the particles in the samples were measured from their nitrogen-gas-adsorption isotherms and the Brunauer-Emmett-Teller (BET) method.

The hydrofluoric acid (HF) dissolution method was employed in the analysis of element composition of the zeolites samples. The cation exchange capacity (CEC) of the zeolites samples was measured using Method 9081 of the US Environmental Protection Agency (EPA)<sup>1</sup>. Those liquid phases were then analyzed using ICP-AES (SPS7800 Series, Seiko Instruments Inc.) in order to determine the concentrations of the metals present in them. The standard solutions used for chemical analyses were prepared from standard metal solutions from Wako Pure Chemical Ind., Ltd.

The experimental conditions of the structural stability studies of the zeolites are summarized in **Table 1**. Aqueous sulphuric acid solutions ( $H_2SO_4$ ) with the  $pH$  range from 2 to 5 covering the range of environment for AMD were mixed with the zeolites samples in  $100 \times 10^{-6}$  m<sup>3</sup> Erlenmeyer flask with screw cap. The mixtures were shaken using thermostatic shaking water bath machine at 300 K for 240 hours to obtain the equilibrium. The acid-treated zeolites samples were then characterized by XRD and HF dissolution.

### 2.2. Batch equilibrium adsorption studies

The experimental conditions of batch equilibrium adsorption studies are presented in **Table 1**. A single component aqueous solutions of analytical grade reagents of  $Fe_2(SO_4)_3 \cdot nH_2O$ ,  $CuSO_4 \cdot 5H_2O$ ,  $MnSO_4 \cdot 5H_2O$  and  $ZnSO_4 \cdot 7H_2O$  respectively (Wako Pure Chemical Ind., Ltd) were used as the model AMDs as the feed solution for the batch equilibrium adsorption studies using the natural zeolites and precipitation studies using lime. The mixtures of the zeolites samples and model AMD solutions in  $100 \times 10^{-6}$  m<sup>3</sup> Erlenmeyer flask with screw cap were shaken using thermostatic shaking water bath machine at 300 K for 240 hours to obtain the equilibrium. The liquid phases were then analyzed by  $pH$  meter and ICP-AES to determine the  $pH$  of the solutions and metal concentrations in the equilibrium solutions.

### 2.3. Precipitation studies using lime

The lime sample obtained from Bogor deposit was prepared as same as the preparation of the zeolites and was characterized in term of elemental contents prior to the precipitation runs. The experimental conditions of

**Table 1** Principal conditions of experimental run for structural stability, batch adsorption, precipitation and treatment of AMD

Feed solutions for structural stability studies of natural zeolites	Aqueous sulphuric acid solution (H <sub>2</sub> SO <sub>4</sub> )
Feed solutions for batch equilibrium adsorption studies and precipitation studies	Aqueous solutions of Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .nH <sub>2</sub> O, CuSO <sub>4</sub> .5H <sub>2</sub> O, MnSO <sub>4</sub> .5H <sub>2</sub> O and ZnSO <sub>4</sub> .7H <sub>2</sub> O
Feed solutions for the treatment of AMD	Real AMD from coal mining in Indonesia
Volume of feed solution, V <sub>0</sub> [m <sup>3</sup> ]	20 × 10 <sup>-6</sup>
Initial metals concentration, C <sub>i,0</sub> [kmol m <sup>-3</sup> ]	0 – 2.7 × 10 <sup>-2</sup>
Initial pH of feed solution, pH <sub>0</sub>	2 – 5 (adjusted by H <sub>2</sub> SO <sub>4</sub> solution)
Adsorbent for batch adsorption studies and treatment of AMD	Natural zeolites from Sukabumi and Bogor deposits
Mass of zeolite, S [kg]	1 × 10 <sup>-3</sup>
Lime for precipitation studies and treatment of AMD	Natural lime from Bogor deposit
Mass of lime [kg]	0 – 1 × 10 <sup>-3</sup>
Contacting time [hours]	240
Temperature [K]	300

precipitation studies are summarized in **Table 1**. The mixtures of lime and model AMD solutions were shaken using thermostatic shaking water bath machine at 300 K for 240 hours. The liquid phases were then analyzed by pH meter and ICP-AES to determine the pH of the solutions and metal concentrations in the solutions.

#### 2.4. Treatment of real AMD

The samples of AMDs were obtained from 2 different locations in coal mining site in Indonesia. The samples were analyzed by pH meter and ICP-AES to determine the pHs and metal concentrations in the solutions.

In this study, the treatment of AMD by adsorption using the natural zeolites was preliminarily compared with the precipitation method using lime. The experimental conditions of treatment of AMD are summarized in **Table 1**. The standing (STD) and shaking (SHK) tests were employed in this study. The samples of zeolites or lime were mixed with 20×10<sup>-6</sup> m<sup>3</sup> of real AMD. The mixtures were contacted for 240 hours in thermostatic shaking water bath machine at 300 K. The liquid phases were then also analyzed by pH meter and ICP-AES to determine the pH of the solutions and metal concentrations in the solutions.

### 3. Results and Discussion

#### 3.1. Characterization of the zeolites

Based on the XRD analysis result, the base components of the zeolites were clinoptilolite-Ca and mordenite; the zeolites also contained with small quantity of impurities such as albite (NaAlSi<sub>3</sub>O<sub>8</sub>) and cristobalite (SiO<sub>2</sub>). In the case of BGR, the sample also contained with calcite (CaCO<sub>3</sub>). The element compositions of the zeolites are presented in **Table 2**. It was confirmed that the zeolites contained with exchangeable cations such as Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup>. The principal characteristics of

the zeolites are summarized in **Table 3**. There was a relationship between Si/Al ratio and CEC in term of the amount of negative charge in the zeolite balanced by the exchangeable cations.

**Figure 1** shows the XRD results of untreated and treated zeolites. The result showed that no radical change in crystallinity of the zeolites even treated at pH<sub>0</sub>=2 during 240 hours. Nevertheless, the peak intensities of the treated zeolites have been reduced slightly. This might be due to the leaching of major elements in the structure of zeolite and dissolution of amorphous materials. However, the decreased of the volume of some elements in the zeolites such as Al, Fe, Ca, Na, K, and Mg was insignificant to the disruption of zeolites structure and framework due to the high ratio of Si in the framework<sup>(9)</sup>.

#### 3.2. Batch equilibrium adsorption studies

**Figure 2** shows the estimated solubility curve of metal hydroxides described as a solid line and the relation between the equilibrium pH values and the concentrations of the metals as determined from the adsorption runs. This figure clarifies that the precipitation of metal hydroxides occurred on the removal of Fe<sup>3+</sup> by SKB and BGR, and removal of Cu<sup>2+</sup> and Zn<sup>2+</sup> in model AMD by BGR. **Figure 4** shows the change of pH by adsorption. The greater values of equilibrium pH than the initial pH, pH<sub>0</sub> indicate that the zeolites could also adsorb the H<sup>+</sup> ions in solution; however, the difference between equilibrium pH and pH<sub>0</sub> demonstrated a descending tendency with the increment in metal concentration of the equilibrium solutions. It was clarified that the zeolites preferred to adsorb metal ions than H<sup>+</sup> ions.

The amount of metal adsorbed ion on the zeolite, q<sub>i</sub>, was calculated by material balance relationship with the concentrations in liquid phases. Since the change in the

**Table 2** The element composition of the zeolites

Elements	% -weight	
	Sukabumi	Bogor
SiO <sub>2</sub>	79.6	80.9
Al <sub>2</sub> O <sub>3</sub>	13.3	10.2
MnO	0.004	0.02
TiO <sub>2</sub>	0.3	0.2
ZnO	0.01	0.01
Fe <sub>2</sub> O <sub>3</sub>	1.3	1.1
MgO	1.9	1.9
CaO	1	1.4
Na <sub>2</sub> O	0.4	2.3
K <sub>2</sub> O	2.2	1.8

**Table 3** Principal characteristics of the zeolites

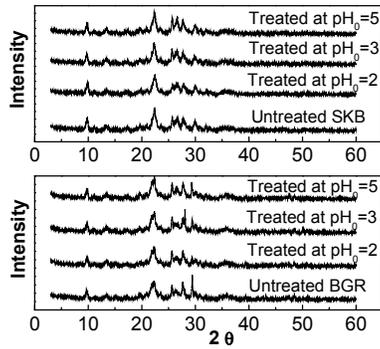
Deposit	Sukabumi		Bogor	
	Surface area × 10 <sup>3</sup> [m <sup>2</sup> kg-zeo <sup>-1</sup> ]	38.4	100.6	
CEC × 10 <sup>-4</sup> [kmol kg-zeo <sup>-1</sup> ]	11.3~14.3	6.7~7.5		
Si/Al ratio [-]	5.3	7		

**Table 5** Principal characteristics of real AMD and the quality standard of treated AMD in Indonesia

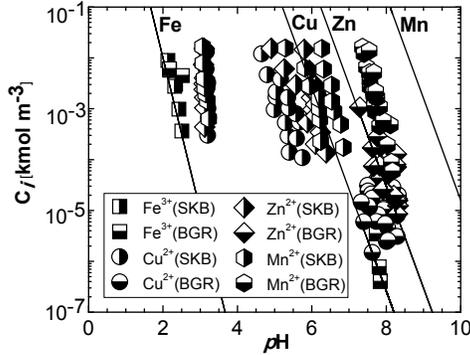
	Concentration [mg l <sup>-1</sup> ]				pH
	Fe	Mn	Cu	Zn	
Real AMD I	34.11	3.87	0.04	0.53	2.72
Real AMD II	28.45	3.7	0.13	1.14	2.66
The quality standard of treated AMD	< 7	< 4	< 2	< 5	6–9

**Table 4** The element composition of lime

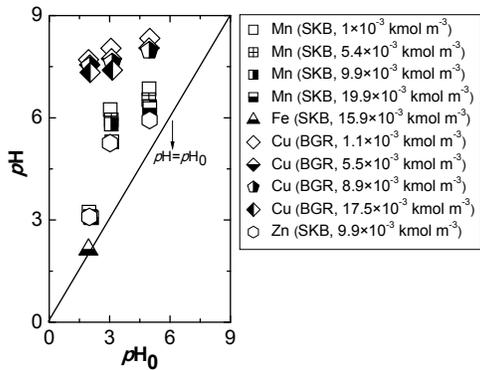
Elements	% -weight
	CaO
SiO <sub>2</sub>	2.4
Al <sub>2</sub> O <sub>3</sub>	1.6
CuO	0.02
MnO	0.05
TiO <sub>2</sub>	0.1
ZnO	0.2
Fe <sub>2</sub> O <sub>3</sub>	1
MgO	0.6
Na <sub>2</sub> O	0.2
NiO	0.01



**Figure 1** XRD patterns of the zeolites at different  $pH_0$  treated conditions



**Figure 2** Estimated solubility curves of the heavy metal hydroxides and the relation between the solution  $pH$  values and the concentrations of the metals as determined from the adsorption runs



**Figure 3** Changing  $pH$  in equilibrium solutions

volume of the feed solution after adsorption was negligible, the material balance relationship for the metals could be expressed by,

$$V_0 C_{i,0} = V_0 C_i + S q_i \quad (1)$$

and the fractional removal of metal  $i$ ,  $Y_i$ , was defined as,

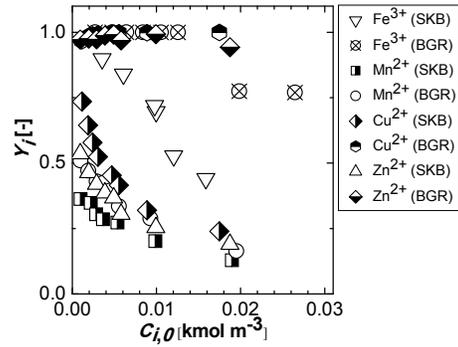
$$Y_i = (C_{i,0} - C_i) / C_{i,0} \quad (2)$$

This fractional removal of metals,  $Y_i$ , is shown in **Figure 4**. In general, the  $Y_i$  decreased with the increment of initial metal concentration,  $C_{i,0}$ . The  $Y_i$  of  $Cu^{2+}$  and  $Zn^{2+}$  by BGR in model AMD was almost 1 due to the precipitation of the metals.

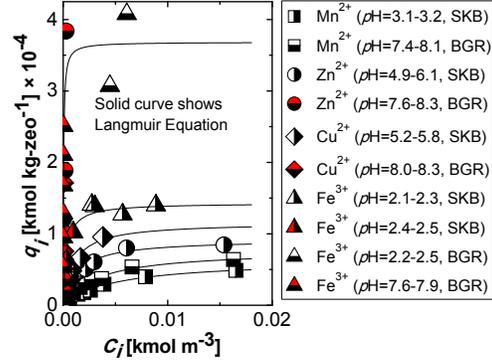
**Figure 5** shows the adsorption isotherms of the metals. The isotherms were examined using Langmuir equation:

$$q_i = q_i^* K_{L,i} C_i / (1 + K_{L,i} C_i) \quad (3)$$

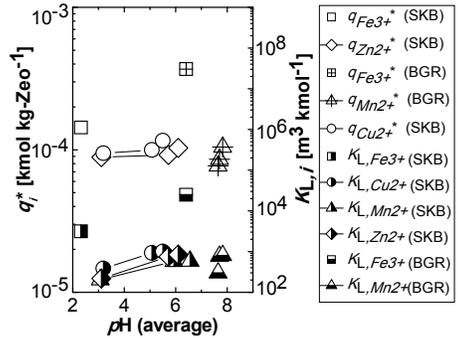
Generally, the amount of adsorbed metal,  $q_i$ , increased as the increment in metal concentration of the equilibrium solution until the tendency become constant. It means that



**Figure 4** Fractional removals of metals on the respective zeolites at  $pH_0=2$



**Figure 5** Comparisons of the adsorption isotherms for various heavy metal-zeolite combinations



**Figure 6** Effect of the equilibrium  $pH$  of solutions on the saturated adsorption amount,  $q_i^*$ , and adsorption coefficient,  $K_{L,i}$ , in Langmuir equation for various heavy metal-zeolite combinations

the maximum adsorbent sites on the zeolites surface have been attained. The  $q_i$  increased as the increment in  $pH$  of the equilibrium solutions. The red colored results refer to the occurrence of precipitation of metal hydroxides. The saturated adsorbed amounts,  $q_i^*$ , and the Langmuir constants,  $K_{L,i}$  in the equation estimated by fitting with the experimental results are summarized in **Figure 6**.  $K_{L,i}$  increased with  $pH$ , but the  $q_{Mn^{2+}}^*$  was almost constant. The  $q_{Fe^{3+}}^*$  and  $K_{L,Fe^{3+}}$  were higher than those of metals at any different  $pH$ . According to the Langmuir parameters, the adsorbability of the heavy metal ions on the zeolites were  $Fe^{3+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$ . This tendency was same as in the previous study<sup>2)</sup>. The difference in the adsorbability might attribute to the hydration diameters and solubility of the metals. The hydration radii of the cations are:  $r_H Cu^{2+}=4.19\text{\AA}$ ,  $r_H Zn^{2+}=4.30\text{\AA}$ ,  $r_H Mn^{2+}=4.38\text{\AA}$  and  $r_H Fe^{3+}=4.57\text{\AA}$ <sup>6)</sup>. The smaller particles should be adsorbed faster and much more quantities compared to the larger

particles. However, in the case of the  $\text{Fe}^{3+}$ , it is confirmed that the precipitation of iron hydroxide was the main mechanism in the removal of iron in model AMD by the zeolites. In addition, ion exchange was also responsible on its removal particularly on high concentration of iron with low  $\text{pH}$  in equilibrium solution. **Figure 7** shows the comparison of the total amount of leached exchangeable cations and the amount of adsorbed mangan by the zeolites. An enhanced amount of the exchangeable cations at equilibrium solution clarified that ion exchange was taken place. **Figure 8** shows the relationships between  $q_i^*$  and CEC on the adsorption of mangan by SKB and BGR. The  $q_{\text{Mn}}^*$  by BGR was greater than the  $q_{\text{Mn}}^*$  by SKB. In addition, the  $q_{\text{Mn}}^*$  by both zeolites were much lower than those predicted from the cation exchange capacity. It was because some of these exchangeable cations are located at inaccessible sites of the zeolite structure and the exchangeable cations might be components of impurities, and accordingly not possible to take part in ion exchange<sup>3)</sup>.

Compare to the previous study<sup>2)</sup>, the efficiency of Indonesian natural zeolites to adsorb and remove heavy metal cations from solution was lower than Mongolian natural zeolites. However, the utilization of Mongolian natural zeolites in Indonesia is not applicable due to the cost of material and transportation.

### 3.3. Precipitation studies using lime

The chemical composition of Indonesian lime is presented in **Table 4**. **Figure 9** shows the result of the precipitation studies such as the fractional removal of mangan and the changing  $\text{pH}$  at various initial mangan concentrations,  $C_{\text{Mn}^{2+},0}$ . The lime sample could adjust the  $\text{pH}$  to alkaline conditions ( $\text{pH} > 12$ ), thus removed all of the metals completely by precipitated them out.

### 3.4. Treatment of real AMD

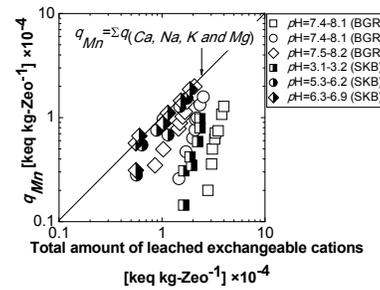
**Table 5** shows the characteristics of real AMDs and the standard of treated AMD in Indonesia. The  $\text{pH}$  values and iron concentration in real AMDs were over than the regulation. **Table 6** shows the fractional removal of metal and  $\text{pH}$  of treated AMD. The quality of the treated AMD using the zeolite from Bogor was complied with the level of quality standard in Indonesia by removed all of  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and about 0.87 of  $\text{Mn}^{2+}$ , and restored the  $\text{pH}$  from low range to higher than 7 either by standing or shaking test.

## 4. Conclusions

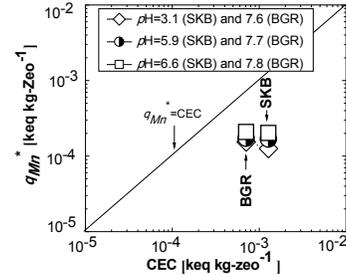
The base components of Indonesian natural zeolites were clinoptilolite-Ca and mordenite. They were chemically stable in AMDs treatment. The zeolites could adsorb and remove the heavy metals, and restore the  $\text{pH}$  to the appropriate level in AMD. Removal of the heavy metal ions was due to the adsorption, ion exchange, and precipitation of metal hydroxides. The removal of  $\text{Fe}^{3+}$  was larger than  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Mn}^{2+}$ . The efficiency of Indonesian natural zeolite in the adsorption of the heavy metals from AMDs would increase as the increment of initial  $\text{pH}$ . Based on the treatment of real AMD studies, the Indonesian natural zeolite has a great promising alternative adsorbent for the treatment of AMD.

### Nomenclature

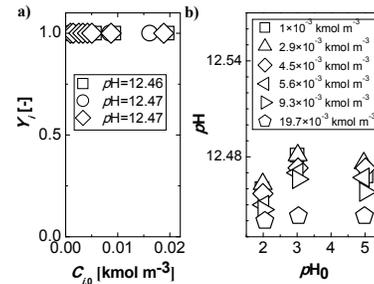
$C_i$ : concentration of metal  $i$  in liquid at equilibrium [ $\text{kmol m}^{-3}$ ],  $C_{i,0}$ : concentration of metal  $i$  in liquid at initial [ $\text{kmol m}^{-3}$ ],  $K_{L,i}$ :



**Figure 7** Relationship between the amount of total leached cations and adsorbed mangan at different  $\text{pH}$  and  $C_i$ .



**Figure 8** The relationships between  $q_i^*$  and CEC on the adsorption of mangan on respective zeolites



**Figure 9** The result of precipitation studies: a) fractional removal of Mn, b) changing  $\text{pH}$  at various  $C_{\text{Mn}^{2+},0}$

**Table 6** The  $Y_i$  [-] and  $\text{pH}$  of treated AMD

$Y_i$ [-]	SKB		BGR		Lime	
	AMD I	AMD II	AMD I	AMD II	AMD I	AMD II
Fe	STD	1	0.99	1	1	1
	SHK	1	1	1	1	1
Mn	STD	0.66	0.27	0.87	0.54	1
	SHK	0.66	0.27	0.87	0.54	1
Cu	STD	1	0.62	1	1	1
	SHK	1	1	1	1	1
Zn	STD	1	0.99	1	1	1
	SHK	1	1	1	1	1
pH	STD	4.46	4.11	7.9	7.8	12.5
	SHK	5.12	4.25	8.27	8.06	12.53

Langmuir constant [ $\text{m}^3 \text{kmol}^{-1}$ ]  $q_i^*$ : saturated adsorbed amount of metal  $i$  [ $\text{kmol kg-Zeo}^{-1}$ ],  $V_0$ : volume of liquid [ $\text{m}^3$ ],  $Y_i$ : fractional removal of metal  $i$  [-],  $\text{pH}_0$ : initial  $\text{pH}$  of solution,  $\text{pH}$ : equilibrium  $\text{pH}$ , S: mass of zeolite [kg], SKB: natural zeolite from Sukabumi, BGR: natural zeolite from Bogor, STD: standing test, SHK: shaking test

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