Evaluation of Geochemical Reaction Rates from Different Wet-Dry Cycle Intervals in Laboratory Kinetic Test

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Abstract

Characterization of acid mine drainage, as the early step in acid mine drainage management, is essential to plan and conduct minimization of negative environmental impacts. Kinetic tests in the laboratory using free draining column leach test method are commonly used to predict the weathering rate and geochemical reaction rate including sulfide oxidation, neutralization reaction, and the time until acid mine drainage is generated. The geochemical reaction rates further can be used in geochemical modeling for predicting water quality.

Based on Amira, 2022, the kinetic test using free draining column leach test methods is subjected to a wet-dry cycle by flushing the sample every 7th day and subjecting the samples to a fixed dry condition interval of 6 days. This wet-dry cycle may not represent the interval of rainfall events in Indonesia which can vary between daily and weekly in the wet season. Nevertheless, the geochemical reaction rates do not represent the actual varying rainfall interval. This study aims to evaluate the varying geochemical rates due to varying rainfall intervals which is represented by different wet-dry cycles.

Three different samples from coal mines are used in this study. Each sample is crushed and sieved into the same size distribution. Samples are placed into a Buchner funnel, triplicated, and subjected to 3 different wet-cycle intervals, i.e., daily wet-dry cycle, 3-day wet-dry cycle, and 7-day wet-dry cycle. The selection of wet-dry cycles is based on the most occurring rainfall interval in Indonesia (daily, 3-day, and weekly). The wet cycle is simulated by flushing the samples with distilled water (1:2 L/S ratio) and the dry cycle is simulated by heating the samples using an incandescent light bulb. The kinetic test ran for 100 days. Selected leachates are measured for physiochemical parameters and used as input for geochemical modeling. The geochemical modelling is using PHREEQC to estimate the reaction rate including sulfide oxidation for each sample.

The study shows that the 3-day wet-dry cycle produced the highest geochemical reaction rate of sulfide oxidation due to the optimal moisture and oxygen content ratio in the samples. The daily wet-dry cycle and 7-day wet-dry cycle produce less reaction rate due to higher moisture rate and lowest moisture rate, respectively. These varying reaction rates are important inputs for geochemical modeling used in acid mine drainage management.

Keywords: Geochemical reaction rates, wet-dry cycle intervals, coal mine, rainfall, PHREEQC, kinetic test

Introduction

Characterization of acid mine drainage, as the early step in acid mine drainage management, is essential to plan and conduct minimization of negative environmental impacts. Kinetic tests in the laboratory using free draining column leach test method are commonly used to predict the weathering rate and geochemical reaction rate including sulfide oxidation, neutralization reaction, and the time until acid mine drainage is generated. The geochemical reaction rates further can be used in geochemical modeling for predicting water quality.

Usually, the kinetic test using free draining column leach test methods is subjected to a wet-dry cycle by flushing the sample every 7th day and subjecting the samples to a fixed dry condition interval of 6 days. This wet-dry cycle may not represent the interval of rainfall events in Indonesia which can vary between daily and weekly in the wet season. Nevertheless, the geochemical reaction rates do not represent the actual varying rainfall interval. This study aims to evaluate the varying geochemical rates due to varying rainfall intervals which is represented by different wet-dry cycles from the kinetic test in the laboratory using free draining column leach test method (FDCLT).

Methods

Three samples of overburden from coal mines, named A1, A2, and A3 are characterized as claystone and were taken to the Mining Environmental Laboratory, Institut Teknologi Bandung Indonesia. The samples are crushed and sorted using standard sieves. Sieves of size #4, #8, #16, #20, and #25 mesh (size in millimetres are 4.760 mm, 2.380 mm, 1.190 mm, 0.841 mm, and 0.707 mm, respectively) are used for samples for the kinetic tests in the laboratory. All samples have the same size distribution for the kinetic test thus having the same surface area.

The samples are also subjected to static tests for geochemical characterization based on Amira, 2004, and mineralogical tests using *XRD Rigaku* Smart Lab, and *XRF Rigaku* Super Mini (XRD and XRF) to identify the mineralogical composition of the samples.

For the kinetic test, samples are placed into a Buchner funnel, triplicated, and subjected to three different wet-cycle intervals, i.e., daily wet-dry cycle, 3-day wet-dry cycle, and 7-day wet-dry cycle. The selection of wet-dry cycles is based on the most occurring rainfall interval in Indonesia (daily, 3-day, and weekly). The wet cycle is simulated by flushing the samples with distilled water (1:2 L/S ratio) and the dry cycle is simulated by heating the samples using an incandescent light bulb. The kinetic test ran for 100 days. All the samples started on the same day for all varying cycles.

Selected leachates are measured for physiochemical parameters and used as input for geochemical modeling. The geochemical modelling is using PHREEQC to estimate the reaction rate of pyrite/sulfide oxidation for each sample.

The calculation of the oxidation rate of pyrite is based on the molar transfer value of pyrite (from PHREEQC modeling) reacting to form leachate water, divided by the particle surface area and the interval of flushing. Mathematically, it can be written as follows.

$$\mathrm{r} = \frac{n_{FeS_2}}{A{*}\times t}$$

Which r denotes pyrite oxidation rate (mol/m^2.s) $nFeS_2$ denotes pyrite mol transfer modeling in PHREEQC (mol), A* denotes sample particle surface area (m^2), and t denotes duration or interval of flushing cycle (converted into second)

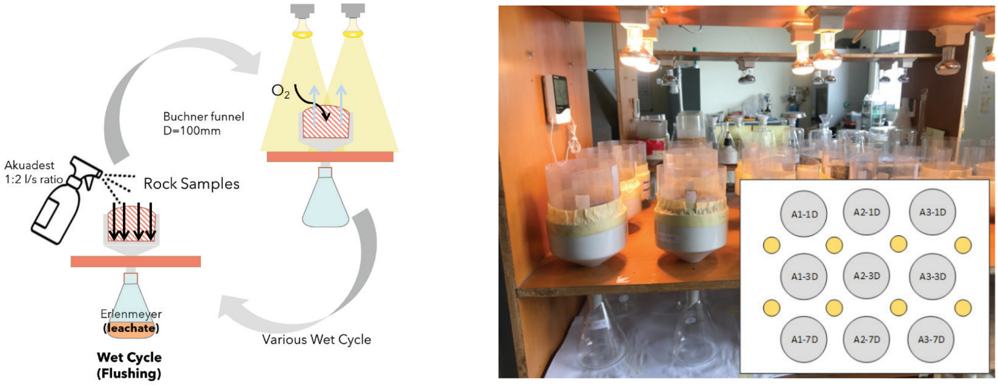

***Figure 1** Schematic of Kinetic Test in the Laboratory using FDCLT method and Various Wet-Dry Cycle*

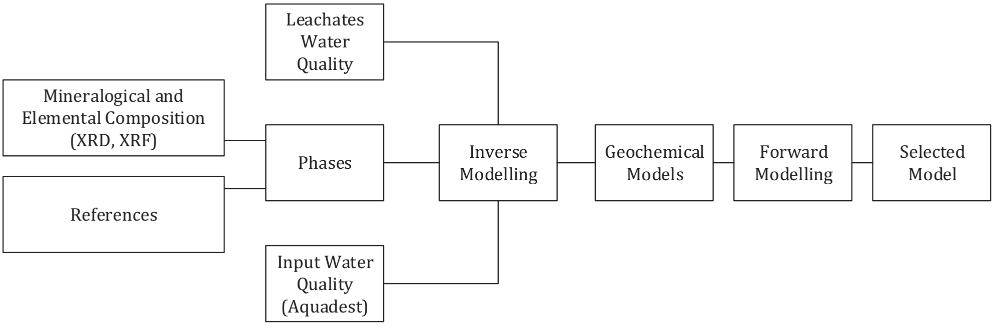

***Figure 2** Geochemical Modelling using PHREEQC for calculating the pyrite oxidation rate*

Results and Discussion

Static test results show that varying geochemical characteristics of samples A1, A2, and A3. Sample A1 are characterized as non-acid forming (NAF) and samples A2, and A3 are characterized as potentially acid forming (PAF).

Mineralogical analysis results are shown in Table 2. The NAF sample contains carbonate (calcite) whilst PAF samples have pyrite. For the geochemical modeling using PHREEQC, term phases are used for reacting minerals and other constituents, as gases. Oxygen and carbon dioxide thus are added to the phases list as shown in Table 2. Sample 1 composition is quartz, clay mineral, calcite as well as acid producing mineral (pyrite). In contrast, sample 2 and sample 3 do not have any neutralizing minerals as reflected in acid acid-neutralizing capacity of 0 kg H_2SO_4/t.

Kinetic test results (pH value) for all samples and various wet-dry cycle is shown in Fig. 3. All samples are producing leachates with pH values close to their NAG pH values. There are small variations of pH values for the same samples subjected to different wet-dry cycles.

***Table 1** Static test results*

Sample ID	pH Paste (1:2)	NAG Test			Acid-Base Accounting				NPR
		NAG pH	NAG pH=4,50	NAG pH=7,00	TS	MPA	ANC	NAPP	
			kg H_2SO_4/ton		%	kg H_2SO_4/ton			
A1	7.54	7.19	<0.05	<0.05	0.54	16.54	23.61	-7.07	1.43
A2	2.32	2.19	76.44	122.5	2.83	86.67	0	86.67	0
A3	3.35	3.08	13.23	21.85	1.7	52.06	0	52.06	0

Note: NAG=net acid generating; TS=total sulfur; MPA=maximum potential acidity; ANC=acid neutralizing capacity, NAPP=net acid producing potency; NPR=neutralization Potency Ratio

***Table 2** Phases for each sample based on mineralogical analysis and references*

Sample ID		
A1	**A2**	**A3**
Quartz	Quartz	Gypsum
Kaolinite	Pyrite	Goethite
Calcite	Gypsum	Pyrite
Dolomite(disordered)	K-Jarosite	CO_2(g)
Goethite	Dolomite(disordered)	O_2(g)
Pyrite	CO_2(g)	
CO_2(g)	O_2(g)	
O_2(g)		

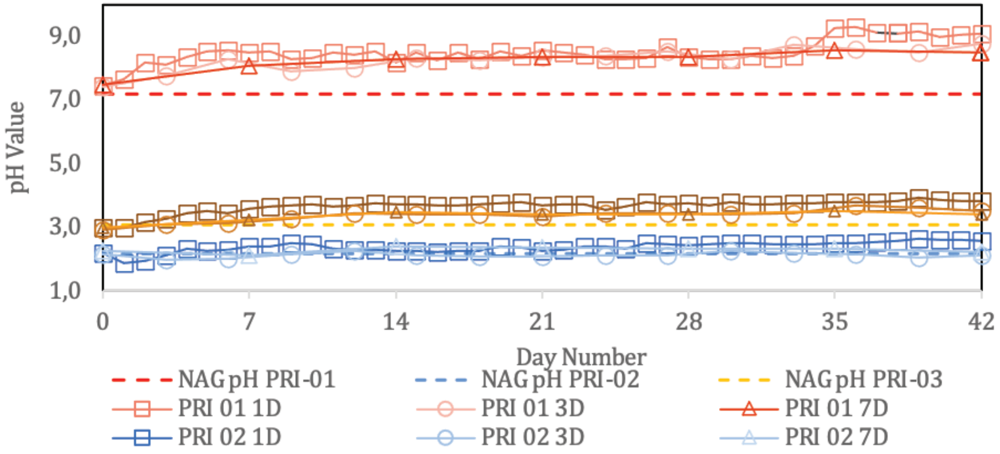

Figure 3 *pH leachate from Kinetic Test for all samples and various wet-dry cycle*

Table 3 *Physiochemical Analysis of Leachate from Kinetic Test (Day-21 and Day-42)*

Day Number	Sample ID	Cycle	pH	Major Anions (mg/L)				Major Cations (mg/L)					Metals (mg/L)	
				F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	Mn^{2+}	ΣFe
21	A1	Daily	8.55	2.36	5.36	6.35	9.29	14.24	8.28	12.42	33.06	0.85	0.09	0.87
		3-Days	8.36	2.43	4.80	13.55	105.48	8.68	14.93	13.60	34.14	0.82	0.03	0.79
		Weekly	8.35	2.48	5.62	34.34	341.47	20.49	25.30	32.18	72.94	0.90	0.03	0.83
	A2	Daily	2.26	2.24	4.96	6.05	1033.92	0.34	0.37	6.74	3.47	51.21	2.30	207.08
		3-Days	2.1	2.54	4.63	6.93	4548.48	0.16	-	37.66	30.72	191.31	13.80	1515.36
		Weekly	2.37	2.88	4.63	7.52	3552.00	0.09	-	50.56	61.21	201.22	18.32	1562.37
	A3	Daily	3.7	-	4.65	-	40.13	0.37	0.68	-	0.39	5.67	0.14	1.16
		3-Days	3.35	2.21	4.71	8.63	94.86	0.47	0.42	1.63	9.07	11.59	1.97	1.54
		Weekly	3.43	2.27	4.76	8.60	196.80	0.31	-	10.42	28.68	11.42	5.93	1.36
42	A1	Daily	9.1	2.26	4.78	-	253.82	7.51	5.79	17.96	49.93	0.49	0.44	0.81
		3-Days	8.77	2.48	10.02	6.82	33.05	4.41	19.27	9.08	26.23	0.44	0.03	0.69
		Weekly	8.49	2.35	5.01	12.38	107.03	6.96	9.99	11.34	28.26	0.75	0.03	0.62
	A2	Daily	2.57	2.19	4.69	8.07	247.58	0.94	0.21	0.15	1.21	9.74	0.52	39.38
		3-Days	2.11	2.29	4.64	7.22	1930.56	0.19	-	19.21	8.58	64.15	4.27	508.14
		Weekly	2.24	2.53	4.73	7.38	4147.20	0.34	-	30.75	33.59	176.69	12.64	1371.92
	A3	Daily	3.82	-	4.61	-	11.81	0.25	1.11	-	-	1.08	0.08	1.66
		3-Days	3.53	-	4.57	6.11	45.13	-	-	-	0.63	7.70	0.15	0.63
		Weekly	3.43	2.23	4.65	6.94	121.82	0.60	0.22	3.69	17.63	8.06	3.45	1.64

Leachates from the kinetic tests are selected for full-suite physiochemical analysis, using AAS (atomic absorption spectroscopy) and IC (ion chromatography). Leachates from day-21 and day-42, as they are coincidental days for all cycles, are selected and the results show in the Table 3.

Physiochemical analysis of the leachates shows small variations in pH value yet larger variations in dissolved elements/ions such as Ca, Mn, Fe, and sulfate. The variations are due to different geochemical rates of pyrite oxidation calcite dissolution, and acid neutralization for samples with

***Table 3** Calculated Pyrite Oxidation Rate using PHREEQC*

Day Number	Sample ID	Cycle	Transfer Mole (for Pyrite)	Sample Particle Surface Area (A*)	Pyrite Oxidation Rate (r)
			mole	m^2	mol/m^2.s
21	A1	Daily (86,400 s)	3.60×10^{-5}	5.67×10^{-1}	7.35×10^{-10}
		3-Days (259,200 s)	4.38×10^{-4}		2.98×10^{-9}
		Weekly (604,800s)	8.03×10^{-4}		2.34×10^{-9}
	A2	Daily (86,400 s)	5.30×10^{-3}	5.67×10^{-1}	1.08×10^{-7}
		3-Days (259,200 s)	2.14×10^{-2}		1.45×10^{-7}
		Weekly (604,800s)	2.18×10^{-2}		6.35×10^{-7}
	A3	Daily (86,400 s)	1.77×10^{-4}	5.67×10^{-1}	3.61×10^{-9}
		3-Days (259,200 s)	4.74×10^{-4}		3.22×10^{-9}
		Weekly (604,800s)	4.96×10^{-5}		1.45×10^{-10}
42	A1	Daily (86,400 s)	1.45×10^{-5}	5.67×10^{-1}	2.96×10^{-10}
		3-Days (259,200 s)	1.71×10^{-4}		1.17×10^{-9}
		Weekly (604,800s)	2.89×10^{-4}		8.42×10^{-10}
	A2	Daily (86,400 s)	1.46×10^{-3}	5.67×10^{-1}	2.97×10^{-8}
		3-Days (259,200 s)	1.01×10^{-2}		6.86×10^{-8}
		Weekly (604,800s)	2.07×10^{-2}		6.03×10^{-8}
	A3	Daily (86,400 s)	6.17×10^{-5}	5.67×10^{-1}	1.26×10^{-9}
		3-Days (259,200 s)	2.35×10^{-4}		1.60×10^{-9}
		Weekly (604,800s)	5.88×10^{-5}		1.72×10^{-10}

neutralization capacity. Calculated pyrite oxidation rates using PHREEQC based on above-mentioned method and equation are summarized in Table 3.

The calculated pyrite oxidation rates vary for each sample. Sample A1, characterized as NAF material has the lowest pyrite oxidation compared to all samples (2.34×10^{-9} – 7.35×10^{-10} m^2.s), whilst Sample A2 has the highest pyrite oxidation 1.08×10^{-7} – 6.35×10^{-8} mol/m^2.s. For all samples, among these leaching intervals, the three-day cycle was found to have the highest oxidation rate from PHREEQC modelling (1.17×10^{-9} – 1.45×10^{-7} mol/m^2.s), the result shows that the 3-day wet-dry cycle produced the highest geochemical reaction rate of sulfide oxidation due to the optimal moisture and oxygen content ratio in the samples following by weekly cycle and daily cycle.

Conclusions

During the kinetic testing of FDCLT leaching intervals, daily, three-day, and weekly intervals were conducted simultaneously and for the same number of weeks. Among these leaching intervals, the three-day cycle was found to have the highest oxidation rate from PHREEQC modelling (1.17×10^{-9} – 1.45×10^{-7} mol/m^2.s), supported by the correlation of pH values to the leaching water oxidation rate. Higher pH values tend to result in lower oxidation rates for the samples. In the other hand, the result shows that the 3-day wet-dry cycle produced the highest geochemical reaction rate of sulfide oxidation due to the optimal moisture and oxygen content ratio in the samples. The daily wet-dry cycle and 7-day wet-dry cycle produce less reaction rate due to higher moisture rate and lowest moisture rate, respectively. These varying reaction rates are important inputs for geochemical modeling used in acid mine drainage management

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