Evaluation of geochemical reaction rates from different wet-dry cycle intervals in laboratory kinetic test

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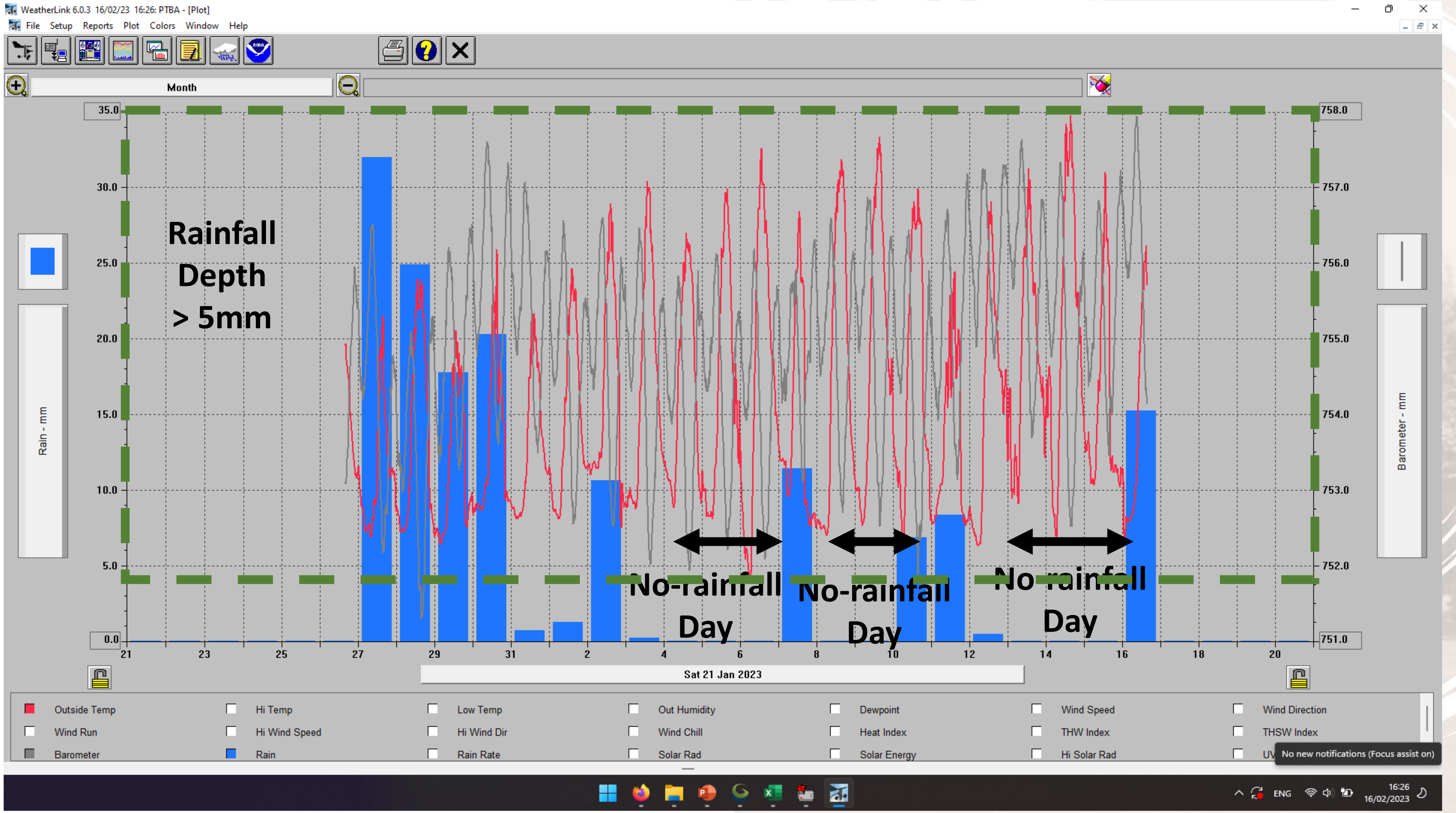
Presentation’s Outline

- Introduction
- Methods
- Results and Discussion
  - Static Test Results
  - Mineralogical Test Results
  - Kinetic Test results (pH values)
  - Selected Leachate Physico-chemistry Characteristics
  - Calculated Pyrite Oxidation Rate
- Conclusion
- Acknowledgement and References

Introduction

- Characterization of acid mine drainage,
  - an early step in acid mine drainage management,
  - essential to plan and conduct minimisation of negative environmental impacts.
  - Kinetic tests in the laboratory using free draining column leach test method
    - predict the weathering rate and geochemical reaction rate.
  - The geochemical reaction rates further can be used in geochemical modelling 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
  - 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 the free draining column leach test method (FDCLT).

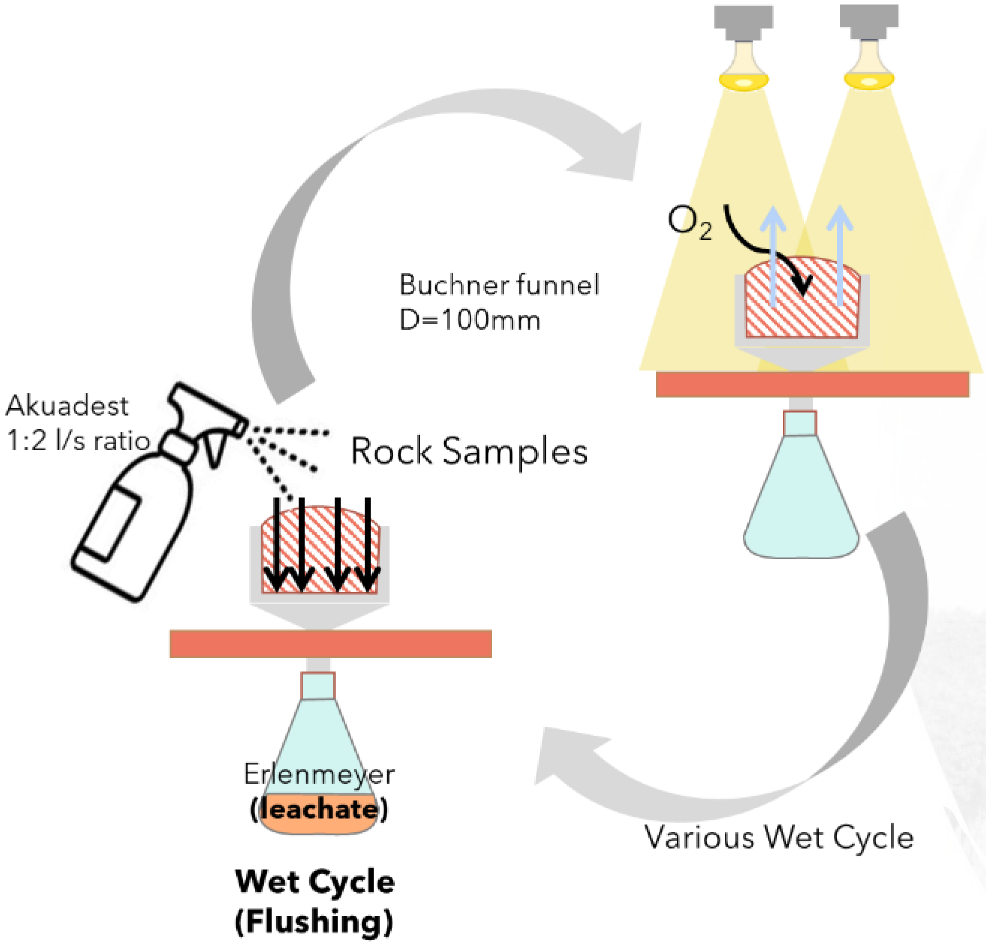
Introduction

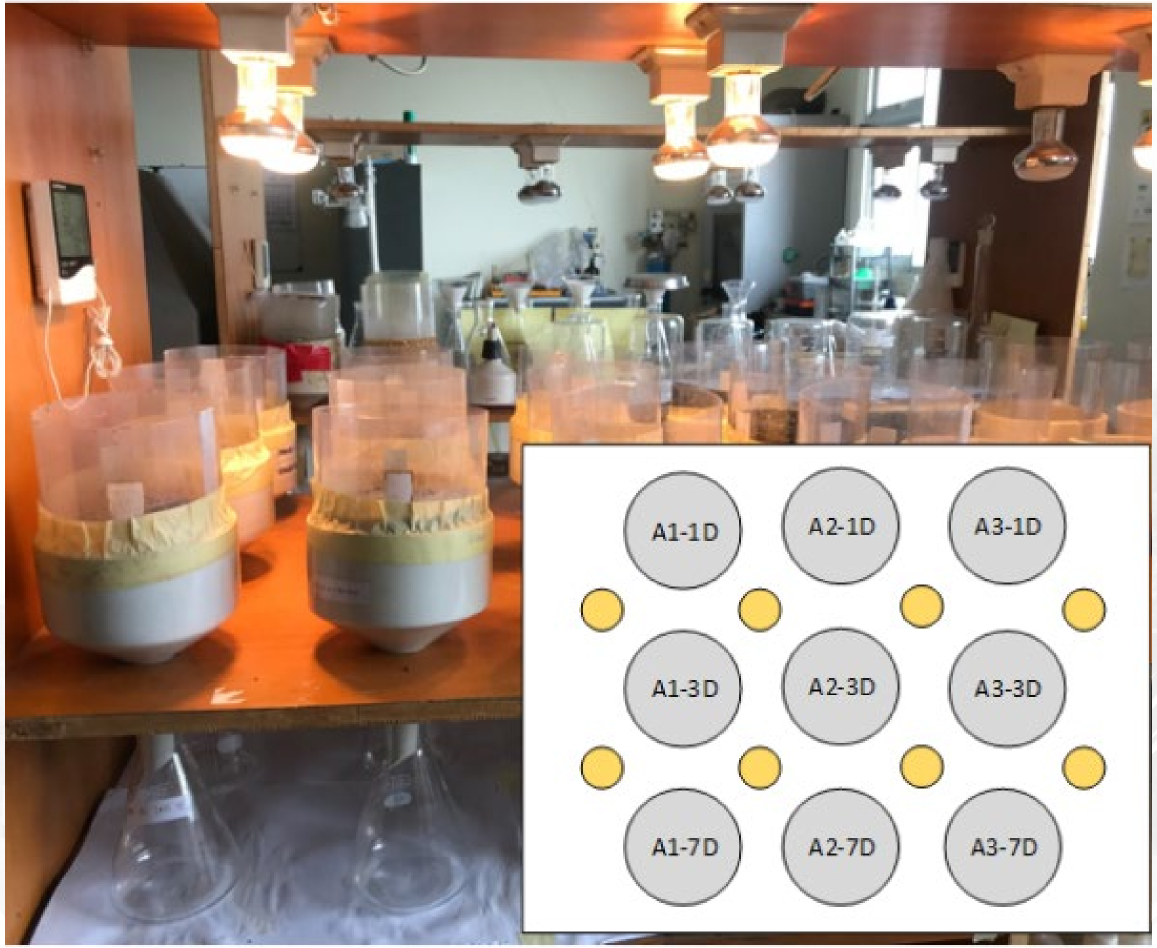


Methods (1/2)

- Three samples of overburden from coal mines,
  - named A1, A2, and A3 are characterized as *claystone*
  - The samples are crushed and sorted using standard sieves.
  - 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 dan XRF*
- For the kinetic test, samples are placed into a Buchner funnel,
  - 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.
- All the samples started on the same day for all varying cycles.

Methods (1/2)

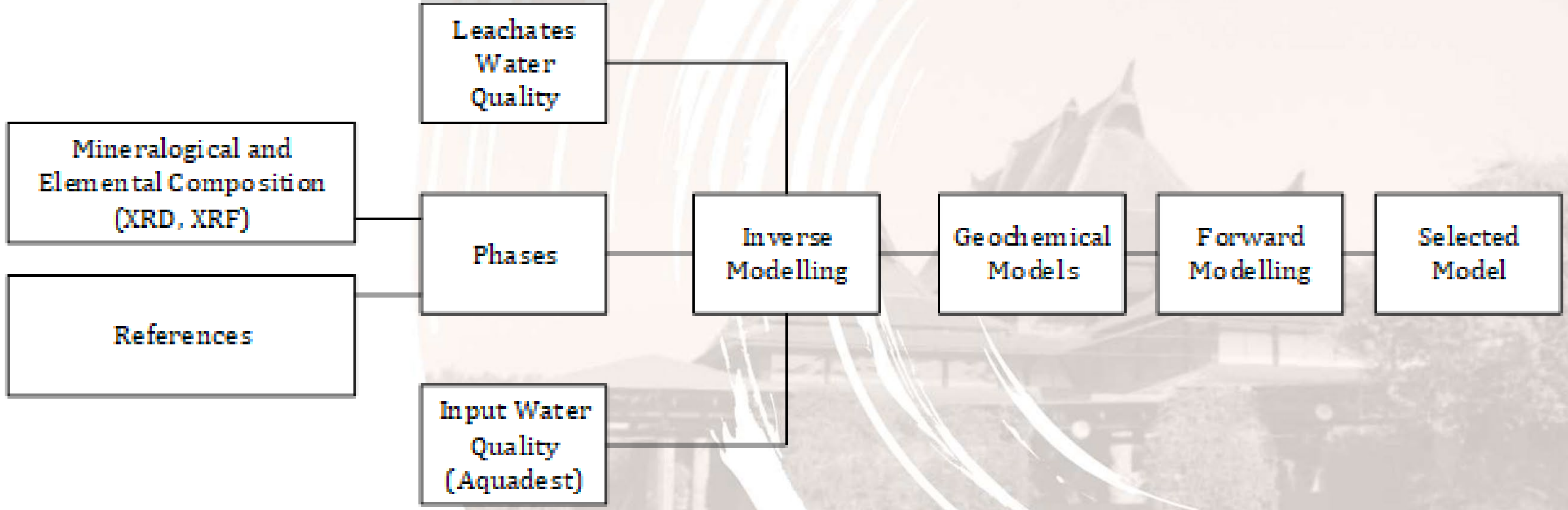




Schematic of Kinetic Test in the Laboratory using FDCLT method and Various Wet-Dry Cycle

Methods (2/2)
Geochemical Modelling

- 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. Geochemical Modelling using PHREEQC for calculating the pyrite oxidation rate are shown below:



- 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.

$$r = n_{FeS2}/(A^{*}\times t)$$

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

Results and Discussion
Static Test Results

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).

Sample ID	pH Paste (1:2)	NAG Test			Acid-Base Accounting				
		NAG pH	NAG pH=4,50	NAG pH=7,00	TS	MPA	ANC	NAPP	NPR
			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 generation, TS=total sulfur, MPA=maximum potency acidity, ANC=acid neutralizing capacity, NAPP=net acid producing potency, NPR=neutralizing potency ratio

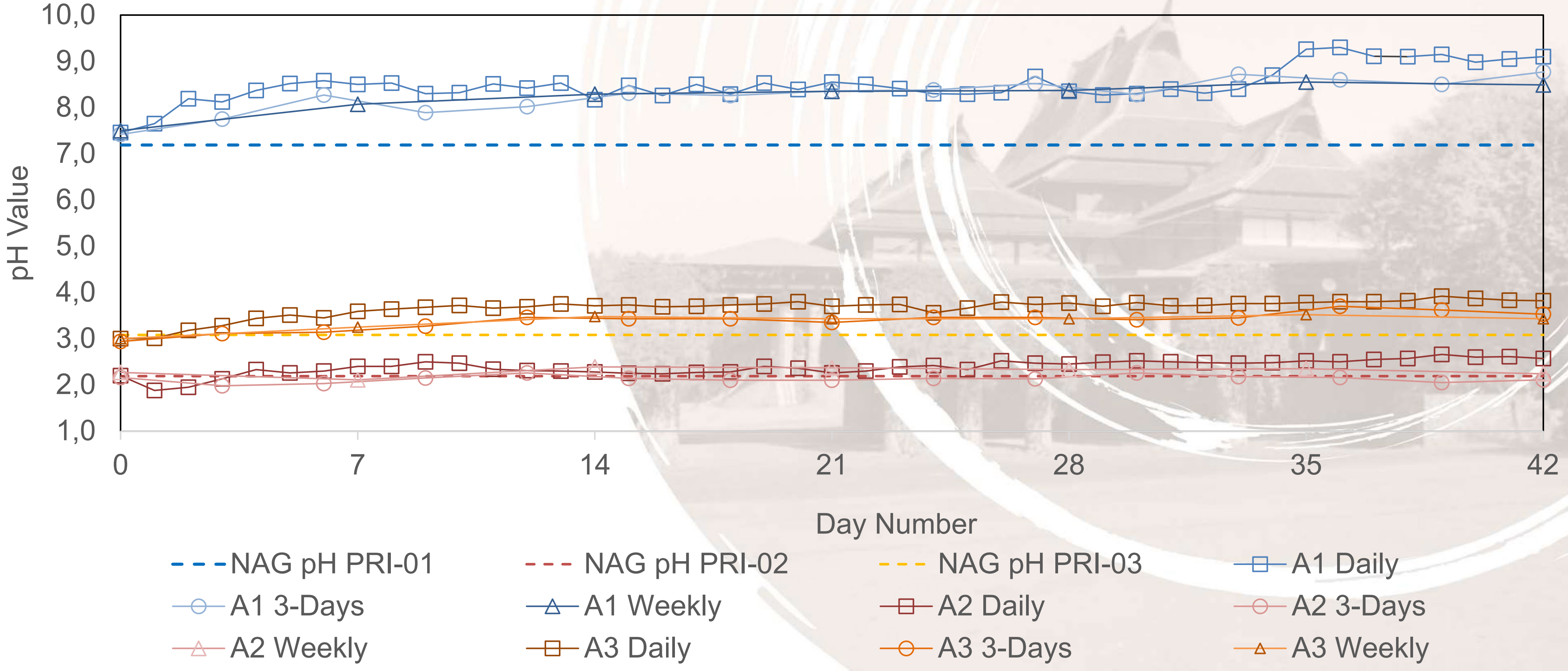
Mineralogical analysis results are shown below

- The NAF sample contains carbonate (calcite) whilst PAF samples have pyrite.
  - Sample 1 composition is quartz, clay mineral, calcite, and 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/ton.
- For the geochemical modelling 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 ID		
A1	A2	A3
Quartz	Quartz	Quartz
Kaolinite	Pyrite	Pyrite
Calcite	Gypsum	Gypsum
Dolomite(disordered)		
$Fe(OH)_3$	Dolomite(disordered)	Dolomite(disordered)
Pyrite	$Fe(OH)_3$	$Fe(OH)_3$
$CO_2(g)$	$CO_2(g)$	$CO_2(g)$
$O_2(g)$	$O_2(g)$	$O_2(g)$

Results and Discussion
Kinetic Test Results

- Kinetic test results (pH value) for all samples and various wet-dry cycle is shown below
  - 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.



Results and Discussion

Selected Leachate Physico-chemistry Characteristics

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.

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+}	∑Fe
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	4.8	13.55	105.48	8.68	14.93	13.6	34.14	0.82	0.03	0.79
		Weekly	8.35	2.48	5.62	34.34	341.47	20.49	25.3	32.18	72.94	0.9	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	2.3	207.08
		3-Days	2.1	2.54	4.63	6.93	4548.48	0.16	-	37.66	30.72	191.31	13.8	1515.36
		Weekly	2.37	2.88	4.63	7.52	3552	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	8.6	196.8	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	4147.2	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	7.7	0.15	0.63
		Weekly	3.43	2.23	4.65	6.94	121.82	0.6	0.22	3.69	17.63	8.06	3.45	1.64

Physiochemical analysis of the leachates shows

- small variations in pH value
- yet larger variations in dissolved
- The variations are due to different geochemical rates

Results and Discussion
Calculated Pyrite Oxidation Rate

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^{-8}
	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}

- 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

The calculated pyrite oxidation rates vary for each sample.

- Sample A1, characterized as NAF (non-acid material) has the lowest pyrite oxidation compared to all samples (2.34×10^{-9} – 7.35×10^{-10} mol/m^2.s), whilst Sample A2 has the highest pyrite oxidation (1.08×10^{-7} – 6.35×10^{-8} mol/m^2.s)
    - Due to low leachate pH value and the occurrence of neutralizing minerals in NAF sample.

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)
    - due to the optimal moisture and oxygen content ratio in the samples.
- These varying reaction rates are important inputs for geochemical modeling used in acid mine drainage management

Acknowledgements and References

Acknowledgements

The authors thank all parties who helped during sampling, laboratory work and sample analysis. The Research is funded through a grant of the PTUPT (Penelitian Terapan Unggulan Perguruan Tinggi – Applied Research of Higher Education) Scheme from the Ministry of Research, Technology and Higher Education in the year 2019.

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