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Model application for acid mine drainage treatment processes

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Abstract
This paper presents the utilization of the geochemical model, PHREEQC, to investigate the chemical treatment system for Acid Mine Drainage (AMD) prior to the discharge. The selected treatment system consists of treatment processes commonly used for AMD including settling pond, vertical flow pond (VFP) and caustic soda pond were considered in this study. The use of geochemical model for the treatment process analysis enhances the understanding of the changes in AMD's chemistry (precipitation, reduction of metals, etc.) in each process, thus, the chemical requirements (i.e., $CaCO_3$ and NaOH) for the system and the system's treatment efficiency can be determined. The selected treatment system showed that the final effluent meet the discharge standard. The utilization of geochemical model to investigate AMD treatment processes can assist in the process design.

Keywords: Acid mine drainage treatments; Acid mine drainage geochemical processes; PHREEQC model.

1. Introduction
Acid Mine drainage (AMD) is generally referred to an acidic metal-rich wastewater discharged from the mining industry. It has low pH and high concentrations of metals, which are the byproduct of the mining industries and/or chemically formed during the discharged process [1, 2]. The studies showed that the discharge of AMD causes environmental pollution in many countries having mining industries. Therefore, the AMD is required to be treated prior to the discharge by many countries. The treatment processes used to treat AMD are different from site to site depending on the water quality and its composition. However many studies reported that the combination of chemical treatment processes is the most effective technique used for AMD treatment [1-3]. That is because of their effectiveness in removing the metals out from the water and neutralization of the water pH [1, 2]. However as it was mentioned earlier, the treatment processes that work for one site may not work for another depending on AMD water quality at each site. Therefore, the investigation for treatment processes must be made for each site, thus, the suitable processes can be chosen for the site. Use of the geochemical, PHREEQC, model is a cost effective way for assessing the appropriate treatment processes for particular AMD water. PHREEQC (version 2) released by US Geological Survey (USGS) in 1999 is designed to perform a wide variety of aqueous geochemical calculations: speciation and saturation-index calculations, batch-reaction and one dimensional transport, etc [4, 5].The model can be used to estimate the efficiency and amount of chemical required for the treatment processes. This helps in supporting the decision making for selection

of treatment processes. The objective of this study is to illustrate the use of PHREEQC model for AMD treatment processes assessment. The model was employed to estimate the amount of chemical required for the treatment and to determine the effectiveness of the selected treatment processes. The same method can be applied for any particular site where the selection of appropriate AMD treatment process is needed.

2. Scenario Study

The following scenario is hypothetical. It assumes that a reclaimed mining site has two discharges released from different mining process plants within the site. The water quality and flow rate data of the two hypothetical discharges are show in Table 1. The hypothetical discharged water quality data in Table 1 represent a typical AMD water quality, which has low pH, high sulfate and high concentrations of various heavy metals, in scenario, are iron, manganese, aluminum, cadmium and arsenic.

Table 1. Discharge characteristics [6]

Parameter	Discharge # 1	Discharge # 2
Design flow, liter per second	0.63	1.12
Average Flow (median), liter per second	0.45	0.86
Alkalinity, mg/L	5	4
pH	3.1	3.5
Ferric Iron; Fe^{3+}, mg/L	5.0	0.45
Ferrous Iron; Fe^{2+}, mg/L	46.8	32.4
Manganese, mg/L	14.2	18.2
Aluminum, mg/L	1.14	0.95
Cadmium, mg/L	1.10	1.00
Arsenic, mg/L	0.90	0.53
Uranium, mg/L	0.85	0.75
Sulfate, mg/L	580	950
Dissolved Oxygen, mg/L	5.30	4.6

3. Methodology

The geochemical model PHREEQC (Version 2) was used to assess and evaluate the effectiveness of the selected AMD treatment process. PHREEQC calculates geochemical reactions at equilibrium based on the available database using the activity and mass-action equation. Precipitation of newly formed solid phases could chemically control the fate of AMD contaminants in the neutralization reactions. This process may be predicted from supernatant solutions by a thermodynamic model and must be corroborated by characterization of final solid products. Equilibrium geochemical speciation/mass transfer model PHREEQC with the database of the speciation model MINTEQ was applied to determine aqueous speciation and saturation indices of solid phases [SI = log(IAP/KS), where SI is the saturation index, IAP is the ion activity product and KS is the solid solubility product]. Zero, negative or positive SI values indicate that the solutions are saturated, undersaturated and supersaturated respectively, with respect to a solid phase. For a state of subsaturation, dissolution of the solid phase is expected and supersaturation suggests precipitation.

The selected treatment system is the combination of different treatment processes put in order: Rock-lined ditch, settling pond, vertical flow pond (VFP) and caustic soda pond. This study assumed that the two AMD were produced from different plants within the mine with different flow rates and qualities (Table 1). The estimation of the chemical requirements for the selected treatment process to treat both discharges was conducted using the models. The final effluent is determined to meet the water quality discharge criterion.

3.1 Selected treatment processes

In order to save money, both discharges will be combined and treated with single treatment system. The schematic of the selected treatment system is shown in Figure 1.

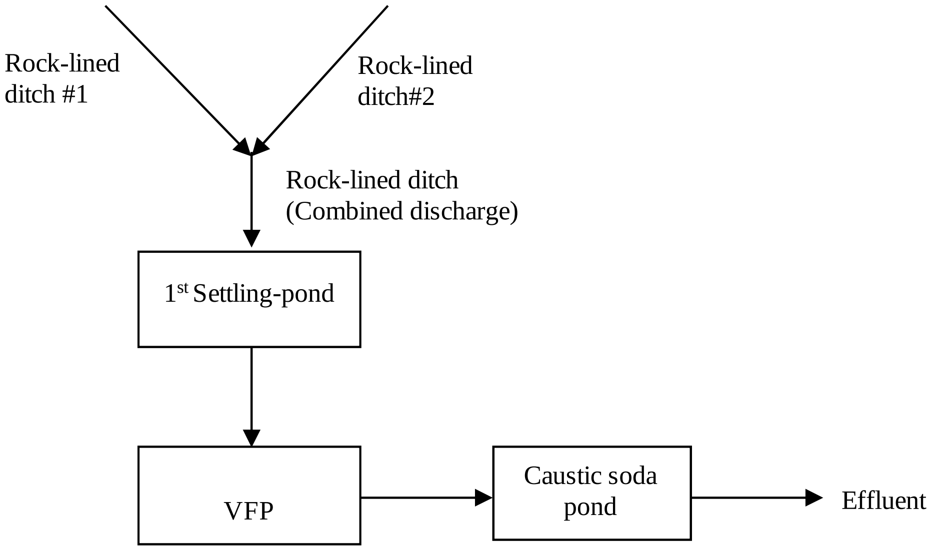

Figure 1. Schematic of selected AMD treatment process

3.2 AMD treatment processes description

Rock-line ditches

Two rock-lined ditches carry the discharges to the meeting point where the discharges are combined. The combined discharge then flows through another rock-lined ditched to the 1st settling pond. PHREEQC was used to calculate the precipitations and dissolutions that may occur after the waters are mixed. The results will be used for the settling pond design.

1st settling pond

This settling pond will hold the sludge volume that will be produced by the precipitation while maintaining a desired water retention time. The primary precipitation will be removed at this settling pond. The solution will then flow through the Vertical Flow Pond (VFP)

Vertical Flow Pond (VFP)

VFP or Vertical flow wetland, also known as Successive Alkalinity Producing System (SAPS), is designed to add alkalinity to net acidic discharges. The schematic of the VFP is shown in Figure 2.
The organic matter layer serves to remove dissolved oxygen (DO) from the water and promote the anaerobic environment with reducing conditions: that changes Fe^{3+} to Fe^{2+}, S^{6+} to S^{2-} and favors the precipitation of metal-sulfide [7, 8]. Reducing DO content in water will prevent the covering of limestone layer by the precipitated metals. The dissolution of limestone will then neutralize the acidity. The acidity of water is very important value for pond sizing design and sensitive to cost estimation. PHREEQC helped to determine the changes in water chemistry in reducing environment. That the calculation of the reductions (e.g., Fe^{3+} to Fe^{2+} and S^{6+} to S^{2-}) and the precipitation of metal-sulfide and other metals were made[7-9]. PHREEQC also used to estimate the amount of limestone needed to neutralize the acidity.

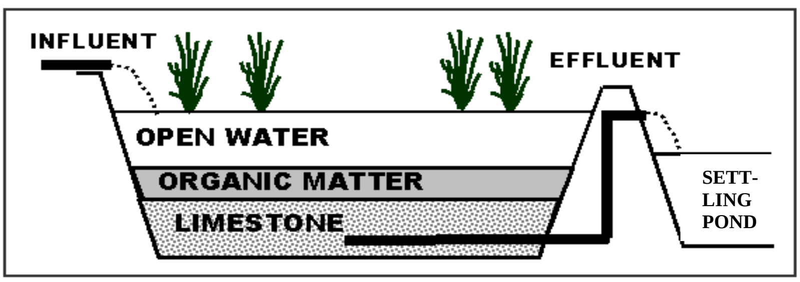

Figure 2. Schematic of Vertical Flow Pond (VFP) (modified after http://www.prp.cses.vt.edu)

Caustic soda pond

The purposes of caustic soda system are to be a backup system in case the VFP does not perform as expect and to remove the Mn since the VFP will not treat the Mn [8, 9, 10]. PHREEQC helped to calculate the caustic soda amount: the amount that will increase water pH to 9.5 where the precipitation of Mn occurs.

4. Results and discussions

The acidities of discharges #1 and #2 were calculated and shown in Table 2. The governing equations used in this model are shown in equations 1 to 3.

$$pH \text{ acidity (mg/L as } CaCO_3) = 50 \times 100 \times 10^{-pH} \quad (1)$$

$$Metal \text{ acidity(mg/L as } CaCO_3) = 50\left(\frac{2Fe^{2+}}{56} + \frac{3Fe^{3+}}{56} + \frac{3Al}{27} + \frac{2Mn}{55}\right) \quad (2)$$

$$Net \text{ acidity(mg/L as } CaCO_3) = 50\left(\frac{2Fe^{2+}}{56} + \frac{3Fe^{3+}}{56} + \frac{3Al}{27} + \frac{2Mn}{55} + 1000 x 10^{-pH}\right) \quad (3)$$

Table 2. The acidities of discharges

Parameters	Discharge #1	Discharge #2
pH acidity	39.72 mg/L as $CaCO_3$	15.81 mg/L as $CaCO_3$
Metal acidity	129.41 mg/L as $CaCO_3$	97.85 mg/L as $CaCO_3$
Net acidity	169.12 mg/L as $CaCO_3$	113.66 mg/L as $CaCO_3$

4.1 Combined discharge

PHREEQC was used to calculate the mixing of two discharges. Upon the mixing of these two discharges the pH behaved non-conservatively because of the release of CO_2(g). The result of combined discharge is shown in Table 3.

Table 3. The combined discharge characteristics

Parameter	Combined discharge
Design flow, liter per second	1.75
pH	3.63
Acidity, mg/L as $CaCO_3$	148.84
Ferric Iron; Fe^{3+}, mg/L	35.37
Ferrous Iron, Fe^{2+}, mg/L	3.73
Manganese, mg/L	16.41
Aluminum, mg/L	1.00
Cadmium, mg/L	1.02
Arsenic, mg/L	0.65
Uranium, mg/L	0.77
Sulfate, mg/L	797.86

4.2 1st settling pond

The combined discharge entered the settling pond as an influent while the chemical changes upon the mixing slowly took place. The precipitation of iron hydroxide (Ferrihydrite) upon mixing leads to metal removal from the pond. Metals adsorbed on precipitated iron hydroxide and were removed from the water [1, 2, 7]. Table 4 shows the pond effluent, the precipitated minerals and, percentage removals.

Upon mixing, the acidity was decrease, that is because Fe^{3+} was precipitated out from the water, moreover, the precipitation of $Fe(OH)_3$ also released H^+ (equation 4) [1, 2, 7, 9], thus both reactions led to the decrease in pH (3.6 to 3.2).

$$Fe^{3+} + H_2O = Fe(OH)_3 + 3H^+ \quad (4)$$

Table 4. The pond effluent, the precipitated minerals and, percentage removals

Parameter	Settling pond effluent	% Removal
Solution		
Design flow, liter per second	1.75	-
pH	3.24	-
Acidity	82.5 mg/L as $CaCO_3$	44.57%
Ferric Iron (Fe^{3+})	4.32 mg/L	87.80%
Ferrous Iron (Fe^{2+})	3.74 mg/L	-
Manganese	16.41 mg/L	-
Aluminum	1.00 mg/L	-
Cadmium	1.02 mg/L	-
Arsenic	0.29 mg/L	55.96%
Uranium	0.77 mg/L	
Sulfate	792.96 mg/L	0.61%
Precipitation		
Ferrihydrite, $Fe(OH)_3$	(SI = 0.9)	60.68 mg/L

4.3 VFP (Vertical Flow Pond)

The settling pond effluent then entered the VFP and the organic matter layer which has anaerobic condition (see Figure 2). The pe = -2 was assumed and fed to PHREEQC model in order to allow the occurrence of reducing condition, therefore, sulfate (S^{6+}) is reduced to sulfide (S^{2-}) and ferric (Fe^{3+}) to ferrous (Fe^{2+}) [9-11]. The effluent from organic matter layer then seeped through the limestone layer where the dissolution of limestone occurred and increased the pH of the discharge. This led to the precipitation of As-S, Cd-S and Fe-S and Al minerals [10-12]. The effluent from VFP treatment process is shown in Table 5.

Table 5. The results of VFP treatment process

Parameter	VFP influent	Organic matter layer effluent	Limestone layer effluent	% removal
Solution				
Design flow, liter per second	1.75	1.75	1.75	
pH	3.24	2.95	7.78	
Acidity mg/L as $CaCO_3$	82.5	91.53	0.95	> 98
Ferric Iron (Fe^{3+}),m mg/L	4.32	3.4×10^{-17}	~ 0.00	> 99
Ferrous Iron (Fe^{2+}), mg/L	3.74	0.008	3.6×10^{-6}	> 99
Manganese, mg/L	16.41	16.41	0.52	> 96
Aluminum, mg/L	1.00	1.00	1.8×10^{-4}	> 99
Cadmium, mg/L	1.02	3.98×10^{-4}	1.04×10^{-4}	> 99
Arsenic, mg/L	0.29	3.94×10^{-13}	3.9×10^{-13}	> 99
Uranium, mg/L	0.77	1.24×10^{-7}	1.24×10^{-7}	> 99
Sulfate (SO_4^{2-}), mg/L	792.96	~ 0.00	~ 0.00	
Sulfide (HS^-), mg/L	-	262.58	253.01	3.64%
Precipitation				
Greenockite, CdS, mg/L		1.31	-	
Orpiment, As_2S_3, mg/L		0.47	-	
Pyrite, FeS_2, mg/L		17.29	0.02	
Uraninite, UO_2, mg/L		0.88	-	
Diaspore, AlOOH, mg/L		-	2.26	
Greenockite, CdS, mg/L		-	0.00037	
MnS(green), mg/L		-	25.18	
Limestone needs, mg/L		-	461.1	

In this process, most of the SO_4 changed to HS^- and Fe^{3+} changed to Fe^{2+} in anaerobic condition resulting in removals of metal sulfide minerals. However, the rich HS^- in water decreased the water pH from 3.2 to 2.9. Water then flowed through the limestone layer. The dissolution of limestone increased the water pH to 7.7. The model calculated the amount of limestone needs by allowing limestone to dissolve in water until its saturation index (SI) reached 0, where the water is saturated with $CaCO_3$. The amount of limestone required was 461.1 mg/L. The increase in pH led to the precipitation of Al, Mn, Cd and Fe minerals thus these precipitated minerals were then removed out from the water [11-13]. VFP treatment increased the water pH and removed most of the metals from the water. However, the amount of Mn in VFP effluent was still greater than the discharge standard (Mn < 0.2 mg/L). Therefore, the further treatment is required.

4.4 Caustic Soda Pond

Recall that the purpose of caustic soda pond is to increase pH to 9.5 (based on the titration to 8.3) to remove Mn. The pond is an open air pond (pO_2 = 0.21 atm) therefore, the water in this treatment process has an aerobic condition. The effluent and the metal removals by this process are shown in Table 6.

Table 6. Treatment results of caustic soda pond

Parameter	influent	Effluent	% removal	Discharge Standard
Solution				
Design flow, liter per second	1.75	1.75		
pH	7.78	8.34		6.5 – 8.5
Acidity, mg/L $CaCO_3$	0.95	0.0002	> 99	
Ferric Iron (Fe^{3+}), mg/L	~ 0.00	5.6×10^{-9}	-	< 1
Ferrous Iron (Fe^{2+}), mg/L	3.6×10^{-6}	~ 0.00	-	
Manganese, mg/L	0.52	5.36×10^{-12}	> 96	<0.2
Aluminum, mg/L	1.8×10^{-4}	1.8×10^{-4}	-	-
Cadmium, mg/L	1.04×10^{-4}	1.04×10^{-4}	-	<0.01
Arsenic, mg/L	3.9×10^{-13}	3.9×10^{-13}	-	<0.05
Uranium, mg/L	1.24×10^{-7}	1.24×10^{-7}	-	<0.1
Sulfate, SO_4^{2-}, mg/L	~ 0.00	736.03	-	<2500
Sulfide, HS^-, mg/L	253.01	~ 0.00	-	-
Precipitation				
Calcite, $CaCO_3$, mg/L	-	21.3		
Hematite, Fe_2O_3, mg/L	-	5.3×10^{-6}		
Pyrolusite, MnO_2, mg/L	-	0.82		
NaOH needs, mg/L		10		

Since the water is aerated (pO_2 = 0.21 atm), Fe^{2+} was oxidized to Fe^{3+} and HS^- as S^{2-} to SO_4^{2-} as S^{6+} [13-15]. The 10 mg/L of NaOH was needed to rise the pH to 9.5. At water pH 9.5, some minerals; $CaCO_3$, Fe_2O_3 and MnO_2, were precipitated out from the water and this led to the decrease in water pH that precipitation of CaCO3 released CO_2(g) thus the pH decreased from 9.5 to 8.34 [11, 15, 16]. This treatment removed 96.8% of Mn out from the water. Thus, the final effluent met the discharge standard.

5. Conclusion

Using the geochemical models help to support the AMD treatment system design. The study points out that iron can be removed via the oxidation process in the settling pond. Most of metals were removed in the VFP. Although most of Mn was removed via VFP but in order to meet the discharge standard requirement the caustic soda pond was required. With employing the PHREEQC model, the optimum amount of chemical requirements for the treatment processes; to neutralize the pH of water and to remove the metals, could be calculated. The similar analysis method with the help of the PHREEQC model can be used to support the decision making for the most suitable treatment processes and system for particular AMD water quality, thus, the final effluent can meet the discharge standard requirement.

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