

AN APATITE DRAIN: NEW METHOD FOR IRON AND ALUMINUM REMOVAL FROM FROM HIGHLY CONTAMINATED ACID MINE DRAINAGE¹

by

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Abstract. The apatite drain system is a new method for acid mine drainage (AMD) treatment. Laboratory tests and the field experiment showed that this technique can be used for removal of high concentrations of iron and aluminum in the AMD with pH less than 4.0. In addition, this system removes both ferric and ferrous irons whereas constructed wetlands system remove only ferric iron when it is converted from ferrous iron in the wetlands. The geochemical model was then used to simulate the changes in concentration of aqueous constituents and in pH, and the potential mineral phase. The results of MINTEQ2 supports the conclusion of experiments. Apatite removed iron, sulfate, and aluminum from AMD and pH was inversely proportional to apatite added until it had reached the equilibrium point (pH=4.09 at 25°C). Nevertheless, the role of apatite as a precipitant and a pH buffer was restricted by the solubility of it.

INTRODUCTION

AMD forms when certain sulfide minerals are exposed to the atmosphere and oxidized in the absence of calcareous material. Although commonly associated with coal mines, the problem also occurs in areas where pyrite or marcasite becomes exposed during land disturbance such as in metallic sulfide mines, highway road cut, subway tunnels, etc.

In the process of AMD forming, sulfide minerals oxidized to form a series of soluble hydrous iron sulfates. Usually, these compound appear as white and yellow crusts on the weathered rocks or sediment surfaces. Natural waters readily dissolve the salts and hydrolyze to form acidic drainage with high concentration of sulfate and ferrous iron. Subsequently, the ferrous iron is oxidized to the ferric state, complexing with water to form a ferric hydroxides (yellow boy) that impart the red and yellow color characteristic of acid mine drainage.

¹ Paper presented at the annual meeting of the American Society for Surface Mining and Reclamation, May 19-25, 1996, Knoxville, TN.

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boy sludge). The water is then separated from the sludge in a series of settling basins or ponds and is discharged.

Alkaline reagents used in conventional AMD treatment are lime (CaO), limestone (CaCO₃), sodium hydroxide (NaOH), and sodium carbonate (Na₂CO₃). However, these reagents are expensive, potentially dangerous, and when misused can result in the discharge of excessive alkaline water. It is obvious that conventional treatment of run-off and seepage is not a long-term solution, because formation of AMD can persist for many decades.

Staged aerobic constructed wetlands offer a potential low-cost, natural, low maintenance, and long-term alternative to conventional treatment of AMD. In an aerobic wetlands system, oxidation reactions occur and the metals precipitate as oxides and hydroxides. Constructed wetlands contain cattails growing in a clay or spoil substrate. However, plantless systems have also been constructed and function in a similar way to systems containing plants. However, aerobic ponds are not recommended when the water entering the wetlands system has a pH less than 4. At such a low pH, iron oxidation and precipitation reactions are quite slow, and significant removal of iron in the aerobic pond would not be expected (Hedin et al., 1994).

The Anoxic Limestone Drain (ALD), which consists of a shallow, limestone-filled trench excavated into the source material and sealed from the atmosphere, passively introduces buffering capacity, as alkalinity, into the AMD and may comprise the initial component of a staged wetlands system. Changes in pH due to acid production from Fe hydrolysis in the wetlands are buffered due to the high alkalinity in the influent (Brodie, 1991). Dissolution of limestone added 100-200 mg/l of alkalinity as CaCO₃ to the water (Kleinmann et al., 1990).

However, not all water is suitable for pretreatment with the ALD. The primary chemical factors believed to limit the utility of the ALD are the presence of ferric iron,

aluminum and dissolved oxygen (DO). When acidic water containing any ferric iron or aluminum contact limestone, metal hydroxides will form. No oxygen is necessary. Ferric hydroxide can armor the limestone, limiting its further dissolution. Whether aluminum hydroxides armor the limestone has not been determined. The buildup of both precipitates within the ALD can eventually decrease the drain permeability and cause plugging. The presence of dissolved oxygen in mine water will promote the oxidation of ferrous iron within the ALD, and thus potentially cause armoring and plugging.

APATITE DRAIN SYSTEM

Seeps of some Indiana Abandoned Coal Mine sites show high concentration of ferric iron and aluminum and very low pH because refuse piles have weathered for several decades. Therefore, constructed wetlands system with ALD is not appropriate.

Laboratory tests by the authors showed a high potential for apatite where limestone has failed. Apatite removed iron and aluminum as a metal phosphate at low pH. According to the laboratory test using pebble to sand-sized apatite (50 mm to 0.6 mm) with aerobic condition, apatite removed iron from 100 to 1,200 mg/l and aluminum from 0 to 800 mg/l, and removal was inversely proportional to flow rates. Flow rate ranged between 1.17×10^{-4} to 1.43×10^{-3} cm/sec. In addition, pH increased to values as high as 3.2 in the effluent water from pH of influent water ranging from 2.1 to 2.2 (Choi and West, 1995a).

According to this result, an apatite drain was constructed on September 30, 1994 at the Green Valley Abandoned Mine site near Terre Haute in west central Indiana. The primary objective of this experiment is to evaluate the long-term ability of the apatite drain to mitigate AMD under field conditions. The drain was 9 m long, 3.3 m wide, and 0.75 m deep, and receives AMD seepage from reclaimed gob

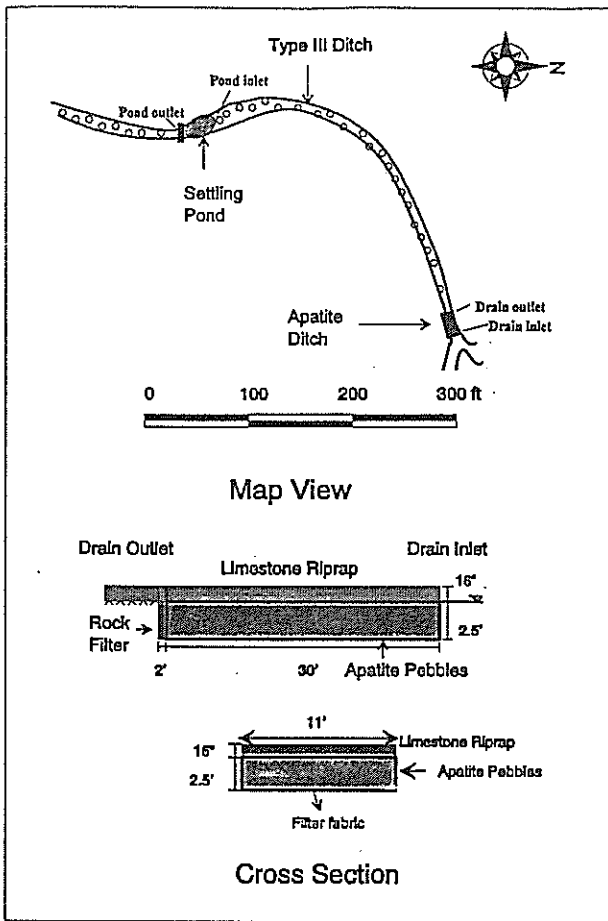


Figure 1. Schematic of an apatite drain design

piles (See Figure 1). The apatite drain was covered with limestone riprap ($D_{50}=36$ cm) and filter fabric (coefficient of permeability $>10^{-3}$ cm/sec) to protect the drain system from stormwater and siltation. Limestone riprap was also used as a rock filter at the end of the apatite drain. The drain consists of about 50 metric tones of 50 mm to 0.6 mm sized marine apatite (francolite) which came from Payne Creek Phosphate Mine in central Florida. A gabion structure was constructed downstream of the drain to create a settling pond to collect precipitates.

Apatite removed iron from 800 to 4,200 mg/l, aluminum from 120 to 830 mg/l and sulfate from 2,090 to 13,430 mg/l between the section of drain inlet and pond outlet during the nine month monitoring period (See Figure 2).

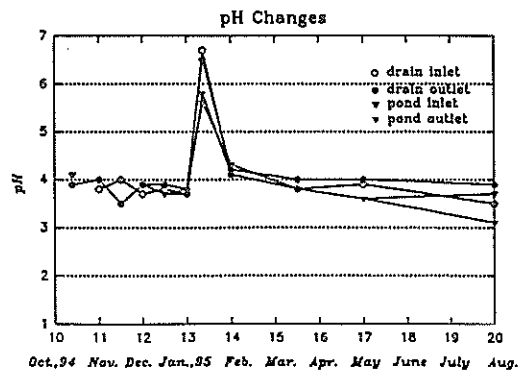
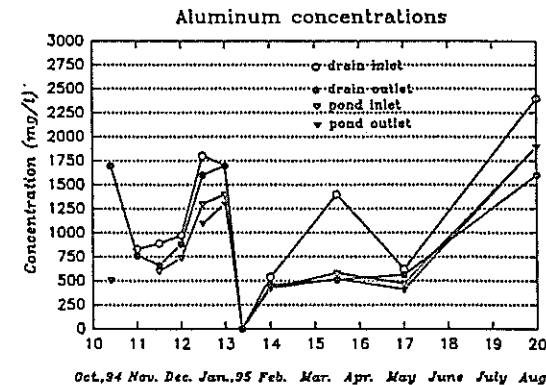
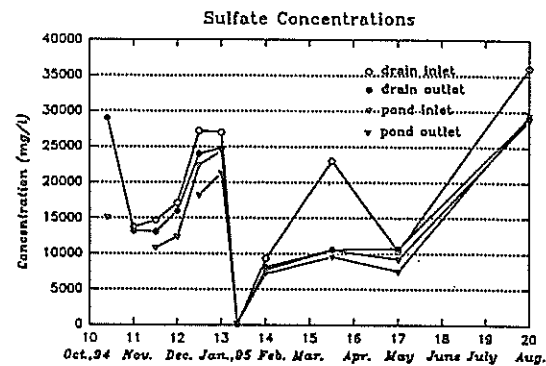
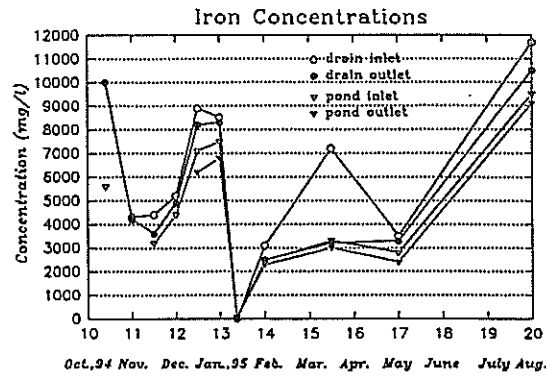


Figure 2. Iron, aluminum and sulfate removals, and pH changes

The pH is nearly constant for the influent and effluent, ranging between 3.1 and 4.3. Flow rate measured at the gabion structure ranged from 0.8 to 1.2 gpm except January 11, 1995 when a stormwater event was occurred (flow rate > 100 gpm). Precipitates of iron and aluminum phosphate (yellow and white suspended solids) continued to accumulate in the settling pond (Choi and West, 1995b).

OBJECTIVE OF STUDY

A preliminary question to consider is under what conditions an apatite drain system is effective. The effectiveness of an apatite drain seems to depend on pH, flow rate, and grain size.

According to the X-ray diffraction analysis, only gypsum was detected in the precipitates collected from the water in the settling pond. It seems that remaining precipitates consist of amorphous phosphates. Therefore, it is necessary to define the composition of the precipitates resulted from reactions between AMD and apatite.

To solve these problems, the MINTEQA2 computer program was used to simulate the experimental changes in concentration of aqueous constituent in the acid mine water. MINTEQA2 is a geochemical equilibrium speciation model capable of computing equilibrium among the dissolved, adsorbed, solid, and gas phases in an environmental setting (Allison et al., 1991). The model can be used to calculate the equilibrium composition of dilute aqueous solutions in the laboratory or in natural aqueous systems. It can be used to calculate the mass distribution between the dissolved, adsorbed, and multiple solid phases under a variety of conditions including a gas phase with constant partial pressure.

The objectives of this study is to apply MINTEQA2 to the attenuation problem of AMD, to predict the outcome solution chemistry, to compare it with the experimental

data, and to find out chemical processes responsible for the chemical composition of actual experiments.

GEOCHEMICAL MODELING

The apatite added to treat AMD was assumed to have homogeneous, ideal chemical composition, which can be represented by hydroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$). The elements of interest in this simulation were iron, aluminum, manganese and sulfate, which react mostly with three constituents, that is, calcium, phosphate and H_2O . Francolite was not considered because it has four more elements added to the system (See Table 1) and the iteration number to reach convergence may exceed the 200 maximum allowed by MINTEQA2 which could cause error of the iteration number. The chemical characteristics for the untreated water

Table 1. Chemical analyses of phosphate pebble (+1 mm) in weight percent (from Cathcart, 1989).

$\text{Ca}_{10-x-y}\text{Na}_x\text{Mg}_y(\text{PO}_4)_{6-z}(\text{CO}_3)_z\text{F}_{0.4z}\text{F}_2$	
P_2O_5	30.7-36.1
CaO	40.8-49.0
F	3.63-4.01
SiO_2	6.33-10.4
Al_2O_3	0.57-3.77
Fe_2O_3	0.55-1.38
MgO	0.14-0.35
Na_2O	0.11-0.57
K_2O	0.11-0.57
Ti_2O_8	0.04-0.06
MnO	0.01-0.03
S	0.10-0.52
CO_2	1.83-3.80
Ratios	
$\text{CaO}/\text{P}_2\text{O}_5$	1.40
$\text{F}/\text{P}_2\text{O}_5$	0.133

Table 2. Chemical data from laboratory testing to evaluate the effectiveness of apatite for AMD control using the seepage water collected from Seep 108 located at the toe of the southwestern edge of the Southeast Gob Pile at the Friar Tuck Abandoned Mine site near Dugger, Indiana (from Choi and West, 1995a).

Water Sample	pH	Eh	Alk. (eq.)	Acid. CaCO ₃	SO ₄ ²⁻ ()	Ca ²⁺	Mg ²⁺ mg/l	K ⁺	Na ⁺	Zn ²⁺ ()
August 29, 1991 - September 4, 1991										
Seep 108A	2.1	386	0	31200	36200	510	1300	28	50	100
Bottle A	2.4	333	0	29500	34100	620	1300	27	65	100
Bottle B	2.9	250	0	27400	33900	650	1300	27	90	100
Bottle C	3.0	237	0	25700	31300	610	1300	29	93	100
Bottle D	3.2	222	0	23900	29100	560	1500	31	96	100
Water Sample	Fe ²⁺ ()	Fe ³⁺	Al ³⁺ mg/l	Mn _{tot}	Si	TDS ()	Charge Balance	Flow rate (l/min/kg)		
August 29, 1991 - September 4, 1991										
Seep 108A	4600	800	3600	250	72	47600	0.2			
Bottle A	4500	300	3400	240	69	44700	-0.1	9.52 X 10 ⁻⁴		
Bottle B	4500	400	3500	250	73	44800	1.5	5.35 X 10 ⁻⁴		
Bottle C	4400	300	3200	250	75	41800	3.1	2.39 X 10 ⁻⁴		
Bottle D	4300	400	3000	250	77	39500	5.4	1.21 X 10 ⁻⁴		

were obtained from Choi and West (1995a) and are shown in Table 2. Precipitation was allowed but no oxidation/reduction reaction was permitted. The pH was allowed to change in response to the dissolution of hydraptite and precipitation of other constituents, whereas the Eh was ignored in the program runs. The hydraptite was considered as an infinite solid for the first run to calculate the maximum amount of hydraptite soluble in the solution with different water temperatures. Adsorption was not allowed in these runs because the data for the adsorption model such as a particular metal oxide and its surface area and sorption site concentration, could not be obtained from the experimental data. The trace elements which have a strong tendency to adsorb on ferric hydroxide were not considered in this geochemical modeling, either.

In order to simulate the pH variation with respect to the amount of apatite added and to find the reduction of metals and sulfate in the system, another run was executed with stepwise increasing apatite amount added at initial pH.

Additionally, an excution was performed to trace the sequence of mineral precipitation.

RESULTS AND DISCUSSION

Speciation calculations using MINTQA2 show that the dominant free ions and complexes for Al, Fe, and Mn include $AlSO_4^+$ and $Al(SO_4)_2^-$, Fe^{2+} , $FeSO_4$, $FeSO_4^+$ and $Fe(SO_4)_2^-$, and Mn^{2+} , and $MnSO_4$, respectively.

When the water temperature was set at 25°C, most of the dissociation of apatite occurred at pH below 3.8. When 0.04 mol of apatite was added to the solution, the pH of equilibrium solution was 3.8. Beyond this point, the increasing rate of pH was conspicuously reduced, which may be closely related to the solubility of apatite. The maximum dissolvable amount of apatite with Seep 108A was 0.082 mol/l at pH 4.09, beyond which pH was constant and surplus of hydraptite was not dissolved.

When the water temperature was set as 4°C, The maximum amount of apatite dissolvable in the solution was 0.046 mol/l at pH 4.62. The

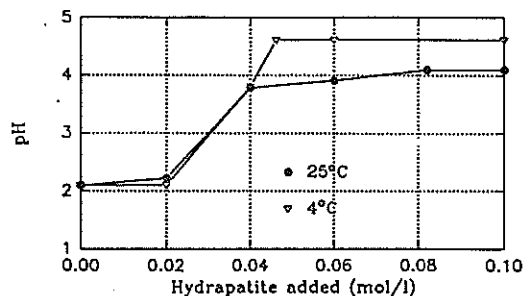


Figure 3. Simulation of MINTEQA2 on variation of pH as a function of amount of apatite added into solution and temperature

pH as a function of the added amount of apatite and temperature is shown in Figure 3.

When precipitation was allowed to occur, the possible minerals precipitated are listed in Table 3. Precipitation of manganese phosphate consumed H^+ . The dissolution of hydrapatite at low pH also removed H^+ from solution, which is supported by dissolved species of phosphate such as $FeH_2PO_4^+$, $H_2PO_4^-$, and $MgH_2PO_4^+$.

The solubility of apatite was closely related with the characteristics of its own chemical composition and chemistry of the solution. Especially, the solubility of hydrapatite is a function of Ca^{2+} activity in the solution (Wilson and Ellis, 1984). The Ca^{2+} is a more reactive ion component than PO_4^{3-} so that the solubility

Table 3. Potential minerals precipitated at equilibrium

PHOSPHATE	
Hydrapatite	$Ca_5(PO_4)_3OH$
Strengite	$FePO_4 \cdot 2H_2O$
Vivianate	$Fe_3(PO_4)_2 \cdot 8H_2O$
MnHPO4	
OXIDE	
Hematite	Fe_2O_3
Ca-Nontronite	$Ca_{0.167}Fe_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
Diaspore	$AlO(OH)$
SULFATE	
Gypsum	$CaSO_4 \cdot 2H_2O$
Alunite	$K Al_3(SO_4)_2(OH)_6$
AlOHSO ₄	

of hydrapatite is controlled by the activity of Ca^{2+} ion.

Fe^{3+} and Mn^{2+} were quickly removed as soon as hydrapatite was added. Once apatite was added, the first minerals possibly precipitated were strengite and $MnHPO_4$, which are iron phosphate and manganese phosphate, respectively. Strengite ($FePO_4(s)$) and variscite ($AlPO_4(s)$) are the stable solid phase when the phosphate is precipitated in the low pH range. However, the pH of minimum variscite solubility occurs at about 1 pH unit higher than that of strengite, so that the precipitation of variscite did not occur.

The modeled concentration of dissolved manganese as a function of PO_4^{3-} does not correlate very well with the actual analysis data (See Table 2). According to the data of simulation, manganese ion was completely precipitated as a mineral of manganese phosphate. However, the actual concentration of manganese apparently did not decrease and no precipitation was observed. This behavior of manganese can be explained in several ways. Differences between the two results can be accounted for by the assumption that the total concentration of Mn in the experimental data would consist of Mn^{2+} only. Secondly, microcrystalline manganese phosphate might be analyzed as a dissolved phase. This kind of error can be eliminated by filtering and centrifuging the solution before analysis.

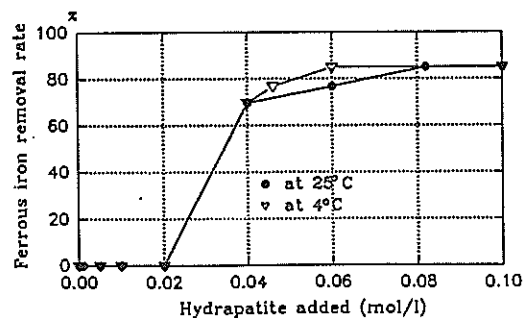


Figure 4. Ferrous iron removal rate as a function of amount of apatite added into solution.

Additionally, manganese ion can be formed in oxyhydroxides at low temperature. Therefore, it might exist in a state of flocculation in the solution and could be analyzed along with dissolved phase. Ferrous iron is a dominant cation in the acid mine drainage. Its chemical reactions have a significant effect on the mobility of other solutes. Exposure to atmospheric O₂ results in oxidation of much of ferrous state to ferric state. However, the rate of conversion of ferrous to ferric iron in the aerated solutions is very slow below pH 4.0. The precipitation of ferrous iron depends on the concentration of phosphate in the solution and on the solubility of hydroxapatite at low pH (See Figure 4). Therefore, the solubility of apatite is the key factor as a reagent for the treatment of AMD.

The aluminum concentration of the simulation data were clearly related to the pH control imposed on the system by the apatite solution. Nordstrom (1982) suggested that an aluminum sulfate ((Al₂SO₄)₃) solid may control aluminum solubility in some acid sulfate-rich waters. The

minerals Al(OH)SO₄, Diaspore (Al(OH)₃), and alunite (KAl₃(SO₄)₂(OH)₆) are all predicted to be supersaturated by MINTEQA2.

Lindsay (1979) mentioned that the solubility of SO₄²⁻ in soil is limited by the solubility of gypsum. The Ca²⁺, together with high SO₄²⁻ concentrations from pyrite oxidation, yields in a saturated condition with respect to gypsum. The simulation results show that gypsum and alunite as well as Al(OH)SO₄ were precipitated out of solution.

Another run of MINTEQA2 has been performed to trace the sequence of mineral precipitation (See Table 4). On the basis of the output of this run, the sequence of mineral precipitation and dissolution could be traced step by step. In case of ferric iron, first mineral precipitated was strengite. During this execution. However, when pH was increased, the phosphate from strengite combined with ferrous iron and vivianite was precipitated. On the other hand ferric iron was precipitated as hematite and/or Ca-nontronite. The sequence

Table 4. Variation of specific elements and mineral assemblages (0.06 mol/l hydroxapatite added)

STEP	ELEMENT (% precipitated)					(not dissolved, mmol/kg)			
	Fe ³⁺	Fe ²⁺	Al ³⁺	Mn ²⁺	SO ₄ ²⁻	Hydroxapatite			
1	0.0	0.0	0.0	0.0	0.0	0.0549			
2	100.0	0.0	0.0	0.0	0.0	0.0533			
3	100.0	0.0	0.0	0.0	0.0	0.0533			
4	100.0	0.0	94.0	0.0	0.0	0.0524			
5	100.0	0.0	90.1	100.0	0.0	-			
6	100.0	0.0	90.3	100.0	0.0	-			
7	100.0	0.0	99.9	100.0	77.1	-			
8	100.0	0.0	99.8	100.0	82.4	-			
9	100.0	79.3	99.8	100.0	92.1	-			
10	100.0	79.0	99.8	100.0	92.2	-			
11	100.0	78.9	99.8	100.0	92.2	-			
12	100.0	64.5	99.6	100.0	95.3	-			
13	100.0	76.7	99.7	100.0	93.0	-			
STEP	MINERAL PRECIPITATED (mmol/kg)								
	Strengite	Ca-nontronite	Hematite	Vivianite	Alunite	Diaspore	Al(OH)SO ₄	MnHPO ₄	Gypsum
1	0.0000	-	-	-	-	-	-	-	-
2	0.0150	-	-	-	-	-	-	-	-
3	0.0150	-	-	-	-	-	-	0.0048	-
4	0.0150	-	-	-	-	-	-	0.0048	-
5	0.0150	-	-	-	-	0.1317	-	0.0048	-
6	0.0150	-	-	-	-	0.1262	-	0.0048	-
7	0.0150	-	-	-	-	0.1265	-	0.0048	0.3149
8	0.0150	-	-	-	-	0.1265	0.0214	0.0048	0.3045
9	0.0150	-	-	0.0229	-	0.1185	0.0666	0.0048	0.2987
10	0.0136	0.0007	-	0.0228	-	0.0723	0.0673	0.0478	0.2974
11	0.0136	0.0007	-	0.0228	-	0.0712	0.0661	0.0478	0.2974
12	-	0.0007	0.0385	0.0186	0.0007	0.0416	0.0953	0.0478	0.2804
13	-	0.0007	0.0068	0.0221	0.0007	0.0658	0.0714	0.0478	0.2950

of aluminum precipitation started with diaspore and ended up with AlHSO_4 and alunite. The run of MINTEQA2 shows the precipitation sequence with time, which can be used to predict the mineral assemblage that is a product of the reaction of hydroapatite with AMD.

CONCLUSION

The apatite drain system is a new method for AMD treatment. A naturally occurred material was thought which will remove metals from AMD, produce insoluble and powdery precipitates, have buffering capacity or at the least maintain the pH after reaction, and dissolve slowly so that it lasts several years or several decades. Apatite from Florida satisfied these conditions.

Laboratory tests and the field experiment showed that this technique can be used for removal of high concentrations of iron and aluminum in AMD. In addition, this system removes both ferric and ferrous irons whereas constructed wetlands systems remove only ferric iron when it is converted from ferrous state in the wetlands. However, only gypsum was detected in the precipitates collected from the settling pond according to the X-ray diffraction analysis. Therefore, it seems that precipitates consist of amorphous phosphate.

A geochemical speciation model (MINTEQA2) was applied to simulate the precipitation of mineral phase, the solubility of apatite, pH variance with the apatite dissolution and the sequence of mineral precipitations. Hydroapatite, which is one of simple form of apatite and also has buffering capacity similar to francolite, was used for this simulation. The main conclusions are as follows:

- H^+ was neutralized primarily with phosphate mineral. These reactions were relatively rapid and resulted in a steep pH gradient over a narrow range of phosphate addition.
- The maximum amount of hydroapatite dissolvable in the solution was 0.082 mol/l

at pH 4.09 and 25°C, whereas it was 0.046 mol/l at pH 4.62 and 4°C.

- Ferric iron was quickly removed as strengite at low pH and was transformed into hematite and Ca-nontronite as pH rose.
- The concentration of ferrous iron in the treated AMD was controlled by precipitation of vivianite (iron phosphate). The oxidation of ferrous to ferric iron was apparently limited by low pH.
- It is likely that concentration of Al was controlled by the solubility of AlOHSO_4 at low pH. Diaspore and alunite were other potential solid phases at low pH.
- Manganese might be formed by the precipitation of manganese phosphate (MnHPO_4), which is the most stable Mn solid phases.
- Calcium and sulfate concentrations were controlled by the precipitation of gypsum.

The results of MINTEQA2 runs appeared to support the conclusion of the experimental works. Apatite is effective in removing iron, sulfate, and aluminum from AMD and pH was inversely proportional to flow rates until it had reached the equilibrium point (pH = 4.09 at 25°C).

However, further research on the apatite drain system is necessary to define the actual mechanism of the precipitation process and the constituents of those precipitates in order to optimize design of the apatite drain system.

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