

FERROUS FIASCO!

<input type="checkbox"/> Grade Level: High School	<input type="checkbox"/> Subject Areas: Chemistry, Environmental	<input type="checkbox"/> Setting: Classroom/Laboratory
<input type="checkbox"/> Duration: 60 min.	<input type="checkbox"/> PA Academic Standards: 1.5.8A,B; 1.5.11A,B; 2.2.11C,F; 2.8.11K; 3.7.10A,B,D; 3.7.12A,B;D; 4.3.7A	<input type="checkbox"/> Keywords: titration, pH, buffering, alkalinity, acidity, dilution

SUMMARY

Students will investigate the iron content in Abandoned Mine Drainage using a colorimetric technique.

OBJECTIVES

- Given a sample of mine water, the student will work cooperatively to prepare the sample for analysis.
- After determining the absorbance of the standards, the student will prepare a calibration graph using a computer program or graph paper.
- After producing a calibration graph, the student will determine the concentration of iron in the mine water using the calibration graph
- After completing the experiment, the student will prepare a laboratory report to meet teacher specifications.

MATERIALS (for each lab group)

A. Student Handouts

B. If analyzing with the HACH Kits:

1. HACH Acid Mine Drainage Kit
2. Graduated Cylinders
3. Distilled/Deionized Water
4. Pipets
5. Goggles

4. 10ml and 20 ml Pipets

5. Pipet Bulb

Glassware needed for each lab group:

1. 1 - 50 and 1 - 100 ml Volumetric Flask
2. Various Pipets for dilutions and reagent addition (10, 20 ml), or graduated Cylinders, although not as accurate
3. Pipet Bulb

OR

C. If analyzing with laboratory analysis:

Supplies Provided:

1. Ammonium acetate buffer solution
2. Phenanthroline solution
3. Iron Standards: 2.00ppm, 1.00ppm, 0.50ppm, 0.20ppm

Equipment Needed:

1. Spectrophotometer/Colorimeter
2. Cuvette
3. Goggles

BACKGROUND

The diversity of aquatic life in a stream is dependent upon the quality of the water found in that stream. There are many types of species, some which are tolerant to pollution and others that are very sensitive. Of all the contaminants in our waterways, Abandoned Mine Drainage is a very common pollution in South Western Pennsylvania. Aside from the unsightly orange colors associated with AMD, it introduces many metals to the stream. Aluminum, a metal found in acid abandoned mine drainage, is toxic at very low levels. The stream life is degraded because the orange iron oxide blocks the sunlight, stopping photosynthesis, causing the breakdown of the food chain.

The reaction oxidizing ferrous iron to ferric iron and the eventual formation of iron hydroxide, which is the familiar orange colored "yellow boy" common in areas with AMD.

FORMATION OF AMD

During mining operations, the coal seam was usually located below the groundwater level, so the mine would fill up with water if the mining company did not pump the water out of the mine during the mining operation.

In the roof of the mine, was pyrite or fool's gold, FeS_2 , to see information, makeup, uses, sources and other information about pyrite, check out the following web site. <http://www.minerals.net/mineral/sulfides/pyrite/pyrite.htm>. The two elements that make up pyrite are Iron and Sulfide. Pyrite is commonly found in the rock layers overlying coal seams.

When the mine was "played out" or had no more coal, the company abandoned the mine and stopped pumping the water out of the mine. Eventually, the roof would probably collapse and the mine would be filled with the rocks and minerals that were in the roof, things such as pyrite, sandstone, shale and limestone. Just like when you put sugar in water, the water will begin to dissolve the minerals, and the pyrite will dissolve into iron (Fe^{+2}) particles and sulfate (SO_4^{-2}) particles. When the mine is filled up with ground water, there needs to be an outlet, often times that outlet is a seep, or sometimes it is a borehole that was drilled for any of a number of reasons. When the water exits the mine, the reaction begins.

PROCEDURE

WARM UP

Hold up a flask of mine water and treated mine water, ask if the water is clean, pass it around.

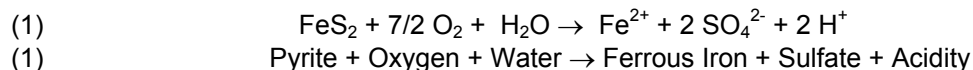
- Would you drink it? Why not? (Probably not the input because of the smell.)
- If sulfur smell is mentioned, ask what causes that smell?
- Do you think there is anything else in the water?
- How could we determine if there was anything in the water?
- What if I told you that this was mine water, what would you think was in the water?

Add hydrogen peroxide to the water and ask the students what happen, and what was produced.

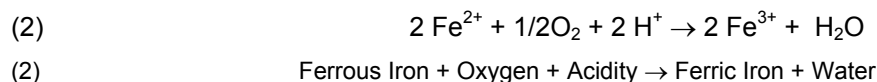
Go over the reaction that occurs in the mine and after the water exits the mine.

The Chemical Reaction of AMD

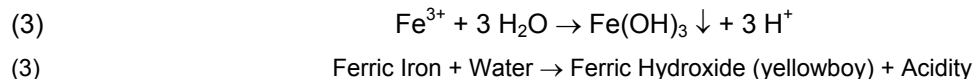
The first reaction, which occurs in the mine, is the physical and chemical weathering of pyrite, which includes the oxidation of pyrite by oxygen to produce sulfate and ferrous iron. This reaction generates one mole of ferrous iron for each mole of pyrite oxidized.



The second reaction, which occurs when the mine water comes in contact with oxygen, involves the oxidation of ferrous iron to ferric iron. Certain bacteria can increase the rate of oxidation from ferrous to ferric iron. This reaction rate is pH dependant with the reaction proceeding slowly under acidic conditions (pH 2-3) with no bacteria present and several orders of magnitude faster at pH values near 5. This reaction is referred to as the "rate determining step" in the overall acid-generating sequence.



The third reaction, which may occur, is the hydrolysis of iron. Hydrolysis is a reaction that splits the water molecule. The formation of ferric hydroxide precipitate (solid) is also pH dependant. The orange precipitate is seen more quickly if the pH is above about 3.5 but below pH 3.5 little or no solids will precipitate or will do so slowly.



Reference: http://www.dep.state.pa.us/dep/deputate/minres/bamr/amd/science_of_AMD.htm

- Why would we want to clean this pollution before it enters the streams? Degrades the streams, lowers the diversity of sensitive species of macroinvertebrates, decreases fish population...

When the mine water exits the ground, it reacts with oxygen and forms iron hydroxide, which will precipitate out of solution and as with any precipitate, it will eventually settle out and coat the bottom of the stream or animals. If we allow this reaction to occur before it reaches the stream, the water that enters the stream will have no iron and therefore no precipitation of iron hydroxide. The more iron in the mine water, the more iron hydroxide that will be deposited on the streambed.

THE ACTIVITY - FERROUS IRON DETERMINATION

The determination of ferrous in a sample of mine water is determined through the use of a colorimetric technique or a HACH Iron test found in the Acid Mine Drainage Kit (available from Saint Vincent College EEC).

To be prepared by the teacher if not provided

(Chemicals/solutions are available to public and private schools for use in laboratory settings; Home school organizations may contact the EEC for alternative options.)

I. Reagents

- A. Hydrochloric Acid (HCl): concentrated, containing less than 0.5ppm iron.
- B. Hydroxylamine solution
 1. Dissolve 10g of $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 100 ml of DI water.
- C. Ammonium acetate buffer solution
 1. Dissolve 250g of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ in 150 ml of DI water.
 2. Add 700ml of concentrated (glacial) acetic acid. Because even a good grade of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ contains a significant amount of iron, prepare new reference standards with each buffer preparation.
 3. Measure the pH of the solution; it must be between 2.9 and 3.5. Add more ammonium acetate to raise the pH or more acetic acid to lower it.
- D. Phenanthroline solution
 1. Dissolve 400mg (0.4g) of 1,10-phenanthroline monohydrate ($\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$) into 400 ml of DI water by stirring and heating to 80°C . Do not boil.
 2. Discard the solution if it darkens.
 3. Heating is unnecessary if 2 drops of conc. HCl are added to the water.
- E. Stock Iron Solution (200ppm Fe)
 1. Place 50ml of DI water in a 1-L volumetric flask.
 2. Slowly add 20ml of conc. H_2SO_4 .
 3. Add 1.404g of ferrous ammonium sulfate ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$)
 4. Add 0.1M Potassium permanganate (KMnO_4) dropwise until a faint pink color persists
 5. Dilute to the line with DI water and mix.
- F. Iron Standards
 1. First make a 10ppm stock solution
 - a. Pipet 25ml of the 200ppm standard to a 500ml volumetric flask and dilute to the line with DI water.
 2. Use the 10ppm standard made above to make the following standards
Add 0.5ml of conc. HCl to each standard before diluting to the line.
 - a. 2.00ppm standard: dilute 20ml of the 10ppm stock to 100ml.
 - b. 1.00ppm standard: dilute 10ml of the 10ppm stock to 100ml.
 - c. 0.50ppm standard: dilute 5ml of the 10ppm stock to 100ml.
 - d. 0.20ppm standard: dilute 2ml of the 10ppm stock to 100ml.

II. Running the standards (this step reduces all the iron in the standards to Fe^{+2})

- A. Pipet 50ml of the standard solution into a 125ml Erlenmeyer flask. Prepare a blank of DI water also.
- B. Add 0.5ml of conc. HCl, 1ml of the hydroxylamine solution, and a couple of boiling stones.
- C. Boil until the solution is reduced to about 15-20 ml.
- D. Cool to room temperature.

NOTE: These steps may be done a day before samples are run; if you want to store the standards, you must prevent contact w/air and thus oxidation of Fe^{+2} to Fe^{+3} .
- E. Transfer the solution to a 100ml volumetric flask.
- F. Add 10ml of ammonium acetate buffer solution and 4 ml of phenanthroline solution.
- G. Dilute to the mark with DI water.
- H. Read absorbance at 510nm within 5-10 minutes.

III. Running the Samples.

- A. Some samples will need diluted, especially the input mine waters.
- B. Prepare the dilution if needed.
- C. Pipet 50ml of the sample or diluted sample into a 100ml volumetric flask.
- D. Add 10ml of ammonium acetate buffer solution.
- E. Add 20 ml of phenanthroline solution.
- F. Dilute to the mark with DI water.
- G. Read absorbance at 510nm within 5-10 minutes.

IV. Calibration graph

- A. Prepare a calibration graph of absorbance vs. concentration.
- B. Determine the concentration of the samples, being sure to multiply by the dilution.

WRAP UP

Have the students determine the concentration of their ferrous iron in the mine water and complete the calculations required to determine iron loading, manganese loading and the size of the wetland needed.

Review with the students the importance of knowing the amount of iron in the mine water and how that iron precipitates out of solution to coat the streambeds and destroy ecosystems.

ASSESSMENT

- The teacher will visually monitor the preparation of the sample including cooperation. **(Objective 1)**
- The teacher will evaluate the calibration graph for accuracy and scored for accuracy. **(Objective 2)**
 - If completed on the computer, the correlation coefficient should be checked (=1).
 - Graph should include title, axis labels and units.
- The teacher will check the student's iron concentration with the actual concentration. **(Objective 3)**
- The teacher will check the laboratory reports for required specifications. **(Objective 4)**

EXTENSIONS

RESOURCES

INTRODUCTION:

Water plays an important role in the support of life. It is used for survival, recreation and transportation. Water also contains many ions, some of the ions are beneficial, while some are harmful, not only to humans, but to other creatures. Although iron is an essential mineral to humans, the different forms of iron can cause numerous problems in the environment.

One specific problem is AMD, once called acid mine drainage, but is now termed Abandoned Mine Drainage due to the fact that discharges in Pennsylvania that were acidic in the 1970's are now alkaline. AMD is a tremendous water pollution problem in Southwestern Pennsylvania, second only to agriculture. Over 2,400 miles of Pennsylvania's 54,000 miles of streams are polluted by AMD.

Although EPA and state agencies have taken action to clean up orange streams and prevent further degradation from proposed mining projects, much of the damage has already been done. Many past coal mining operations have left large amounts of waste products or overburden that were generated during mining operations. When this overburden is exposed to the atmosphere, precipitation, and ground or surface water, they may generate products that adversely affect the pH, and metal composition of nearby streams and the deposition of the metals can affect the overall stream quality.

In the past 200 years, over 10 billion tons of bituminous coal has been mined in 21 Pennsylvania counties. This is about one fourth of all coal ever mined in the United States. The counties containing coal mines are: Greene, Somerset, Armstrong, Indiana, Clearfield, Washington, Cambria, Jefferson, Westmoreland, Clarion, Elk, Fayette, Lycoming, Butler, Lawrence, Centre, Beaver, Blair, Allegheny, Venango and Mercer (ranked in order of production).

When coal is formed there are usually certain rocks and minerals associated with coal, primarily above the coal seam. Pyrite or Fool's gold is most commonly found in the roof material of the mine. Pyrite, FeS_2 , is made up of Iron and Sulfide.

Coal is often found near or below ground water level, so while miners were working, the company would pump the water out of the mine. After the mining of the coal was complete, the company no longer needed to remove the water, so pumping ceased. The mine would fill up with water. The only thing holding up the roof of the mine is a few wooden beams. The beams eventually rot and then there is nothing holding up the roof. The roof will collapse, and the mine will contain large piles of rubble containing iron sulfide or pyrite.

Pyrite or fool's gold, FeS_2 , (to see information, makeup, uses, sources and other information about pyrite, check out the following web site. <http://www.minerals.net/mineral/sulfides/pyrite/pyrite.htm>.) Pyrite is the most common mineral in mine overburden. Pyrite weathers in water to produce Iron (II) ions and Sulfuric acid. While the mine water is acidic and there is no oxygen present, the iron ions are kept in solution. Once the pH is raised, the iron reacts with oxygen to form Iron (III) hydroxide, a reddish-orange solid/sludge. This precipitate commonly called "yellow boy" coats the bottom of the streambed and blocks the sunlight from penetrating the water, thus stopping photosynthesis. If the drainage is acidic, the pH will usually increase with dilution from other water sources. In the case of Saint Vincent, there is a natural limestone layer above the mine, so the water coming from the mine is not acidic, and the reaction with oxygen begins upon exiting the mine.

- (1) $\text{FeS}_2 + 7/2 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2 \text{H}^+$
- (1) Pyrite + Oxygen + Water \rightarrow Ferrous Iron + Sulfate + Acidity

- (2) $2 \text{Fe}^{2+} + 1/2\text{O}_2 + 2 \text{H}^+ \rightarrow 2 \text{Fe}^{3+} + \text{H}_2\text{O}$
- (2) Ferrous Iron + Oxygen + Acidity \rightarrow Ferric Iron + Water

- (3) $\text{Fe}^{3+} + 3 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 \downarrow + 3 \text{H}^+$
- (3) Ferric Iron + Water \rightarrow Ferric Hydroxide (yellowboy) + Acidity

COPY ME



One Per Group

Wetland treatment systems are often created to treat the mine water and remove the iron from the water. The ferrous iron will change to ferric iron with exposure to oxygen. The ferric iron then changes to a precipitate, ferric hydroxide or yellowboy. A precipitate is particles suspended in solution, and they usually settle to the bottom with time. The Treatment systems also slow the water down to allow the precipitate to settle out and when the amount of precipitate is significantly decreased, vegetation, usually cattails will act as a filter and provide a surface for the precipitate to adhere.

In order to determine the size of the wetland treatment system, different parameters must be determined, two of the most important items, are the flow rate, and the iron concentration.

The following experiment will allow you the opportunity to determine amount of iron that the WELOS are hoping to remove from their stream with a passive treatment system.

COPY ME



One Per Group

FERROUS FIASCO!

GROUP NUMBER: _____
 PERIOD _____

NAME _____
 DATE _____

Standards

Concentration (mg/L)	Absorbance
0.00	
0.20	
0.50	
1.00	
2.00	

Sample Name	Dilution	Absorbance

INSTRUCTIONS

Analyzing the Standards

- A. Turn on Spectrophotometer and set wavelength to 510 nm.
- B. Set to absorbance, and zero the instrument with the 0.00 standard
- C. Read the absorbance of remaining standards and record on chart.

Analyzing the Samples

- A. Prepare the dilution if needed.
- B. Pipet 50ml of the sample or diluted sample into a 100ml volumetric flask.
- C. Add 10ml of ammonium acetate buffer solution.
- D. Add 20 ml of phenanthroline solution.
- E. Dilute to the mark with DI water.
- F. Read absorbance at 510nm within 5-10 minutes.

CALCULATING IRON CONCENTRATION

Calibration graph

- A. Prepare a calibration graph with absorbance on the vertical axis (y) and concentration on the horizontal axis (x).
- B. Determine the concentration of the samples.
- C. Multiply the concentration by the dilution used.

1. Calculate the lbs/day that would be deposited on the stream bed if the flow was 254 gal/min (HINT: Multiply the concentration in mg/L by the flow and do any required conversions to produce the answer in lbs/day).

2. If the manganese concentration of discharge is 5 mg/L, and the calculation for the wetland size is as follows, what size would the wetland have to be?

$$\text{Minimum Wetland Size} = [\text{Fe loading (lb/day)} / 180 \text{ (lb/acre/day)}] + [\text{Mn loading (lb/day)} / 9 \text{ (lb/acre/day)}]$$

COPY ME



One Per Group

COPY ME



One Per Group