

# pH, ALKALINITY, ACIDITY, OH MY!

<input type="checkbox"/> <b>Grade Level:</b> High School	<input type="checkbox"/> <b>Subject Areas:</b> Chemistry, Environmental Science, Mathematics	<input type="checkbox"/> <b>Setting:</b> Classroom/Laboratory
<input type="checkbox"/> <b>Duration:</b> 90 min.	<input type="checkbox"/> <b>PA Academic Standards:</b> 1.4.8B; 2.2.8A,B; 2.2.11E; 2.3.11C; 3.1.10E; 3.2.10B; 3.4.10A; 3.4.12A; 4.3.7A1	<input type="checkbox"/> <b>Keywords:</b> Titration, pH, buffering, alkalinity, acidity, calculations

## SUMMARY

Students examine the topic of buffers and analyze and calculate the alkalinity and or acidity content of Abandoned Mine Drainage using the HACH Kit or a titration. Given extra information, they can determine how the mine drainage can affect the streams the water flows into.

## OBJECTIVES

- Given an Abandoned Mine Drainage sample, the student will work cooperatively to determine the alkalinity and acidity or buffering ability of the sample.
- While completing the titration, the student will demonstrate proficiency in measuring pH and performing a titration.
- After determining the Alkalinity and Acidity, the student will identify any possible problems expected from discharging the AMD sample into a stream.
- While completing the titration, the student will accurately measure volumes of water for analysis.
- After completing the lab experiments, the student will prepare a formal write up/memo to the organization.

## MATERIALS

### A. Demonstration

Supplies Provided:

1. Buffer Solution
2. Distilled Water
3. 2-250 ml beakers
4. phenolphthalein indicator
5. bromcresol green indicator
6. 0.1M NaOH
7. 0.1M HCl

### B. Student Handouts

### C. If analyzing with HACH Kits

1. HACH Acid Mine Drainage Kit
  - i. Follow the Total Acidity Procedure
  - ii. Prior to class, test the alkalinity to determine which test (High or Low Range) is best.
2. Graduated cylinders
3. Deionized Water
4. Pipets
5. Goggles

OR

### D. If analyzing with laboratory analysis (for each lab group):

Supplies Provided:

1. Sodium Hydroxide (0.02N), 50 ml
2. Sulfuric Acid (0.02N), 100 ml
3. Bromcresol green (pH 4.5 indicator)
4. Phenolphthalein (pH 8.3 Indicator)

Glassware Needed per Sample (Alkalinity and Acidity):

1. 2 Beakers or Erlenmeyer Flasks
2. 2 Burets
3. Graduated Cylinder (50 ml)
4. 1 Buret clamp
5. 1 Ring stand
6. Various pipets for dilutions, or graduated cylinders, although not as accurate.

Equipment Needed:

1. pH, meter if not using indicators.
2. Goggles

## BACKGROUND

Water quality plays an important role in the life of humans, plants and animals; it is used for survival, recreation and transportation to name a few. Water also contains many ions, some of which are beneficial, and others that are harmful. Excessive amounts of any particular contaminant can result in imbalances in the water chemistry and destroy ecosystems. Long-term effects of this pollution can harm the food chain, and affect recreational activities. The water quality in many streams has dramatically decreased due to pollution, mostly caused by humans, entering water sources.

Pollution can be either point source or non-point source. Point source pollution can be identified from a single source, whereas, non-point source pollution is from a source that can't be directly pointed out, like stormwater runoff from land use. Mine Drainage can be both point and non-point source pollution because it can appear as a seep, where the actual source is not able to be determined or it can be a borehole or mine shaft or other point that is a definite, recognizable point. Mine drainage is the second largest water pollution problem in Southwestern Pennsylvania, second only to agricultural runoff. Current mining practices and required permits have greatly reduced the amount of AMD entering our streams, and many organizations have begun cleanup processes. The cleanup process is different for each site and discharge. The chemistry of the discharge must be determined in order to develop a cleanup plan. In order to determine the type of treatment system needed, it is necessary to determine several chemical parameters; three important tests are the pH, alkalinity, and acidity. The pH of the water determines the type of treatment system needed. If the pH is low, the metals will not precipitate out of solution until the pH is raised.

There are numerous factors that influence the quality and quantity of Abandoned Mine Drainage.

1. Amounts of oxygen and water present in the mine.
2. The amounts of carbonate materials in the mine and surrounding rocks.
3. Sizes of the minerals.

The pyrite in the mine overburden is the mineral that contaminates ground water. The contamination starts with the weathering of pyrite found in abandoned mine overburden or in "gob piles" from strip-mining. The weathering of the pyrite is dependent on the surface area exposed, (i.e. smaller the size of the pyrite, the larger the surface area that can be weathered). As pyrite is weathered or dissolved, ferrous iron, sulfate and acidity are produced. When the acid is produced, many other rocks and minerals found under the ground are often dissolved also. Some common minerals found in Pennsylvania are Calcite (Calcium Carbonate-Limestone), which is formed when the limestone cracks and the ground water flows through the limestone and dissolves it. Eventually this will harden and produce a white streak through the limestone. The other common mineral is Feldspar, which is a complex group of hard, rock-forming silicates containing aluminum, calcium, sodium, and potassium.

When the acid is produced, through the weathering of pyrite, it stays in the water until it comes in contact with something to increase the pH, such as limestone. The substance used to increase the pH usually adds a buffering ability to the water. When something is considered a buffer, it will allow water to resist a change in pH.

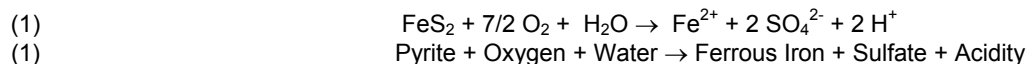
Two common types of chemical analysis for mine water are Alkalinity and Acidity. They are important concepts when investigating mine drainage, although both not pollutants, they refer to the ability of water to act as a buffer. They should not be confused with pH, although there is usually a connection; alkalinity is a measure of how much acid can be added to a liquid without causing a large change in pH, and acidity is a measure of how much base can be added to a liquid without causing a large change in pH.

Alkalinity is a quantitative measure of the water's ability to neutralize a strong acid to a designated pH. The presence of carbonates, bicarbonates and hydroxides is the most common cause of alkalinity in natural waters. In some communities, the mine may exist under a layer of limestone as in Latrobe at Monastery Run. This limestone layer, calcium carbonate, helps to neutralize the acid produced and the mine water discharge has a neutral pH and a considerable amount of alkalinity. When a discharge is alkaline, the treatment system is considerably easier and less costly.

Acidity is a quantitative measure of the water's ability to neutralize a strong base to a designated pH. The amount of acidity indicates the water's degree of corrosiveness. Acidity in mine drainage is caused by the weathering of pyrite which produces sulfuric acid. Ions that can hydrolyze such as iron aluminum and manganese, all of which are commonly found in mine drainage can also contribute to acidity. Mine water often times has a high acidity and therefore a lower pH due to the fact that acid is produced in the weathering of pyrite.

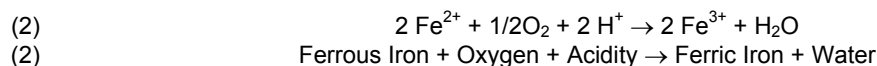
## AMD, Acidity and Alkalinity

The production of Abandoned Mine Drainage occurs through the weathering of pyrite, FeS<sub>2</sub> or fool's gold. Pyrite is usually associated with the formation of coal, and is usually found in the roof material of the coal mine. Once mining is complete, the roof may collapse and the mine will fill with ground water. The pyrite is dissolved over time by the groundwater, which is indicated by the reaction below. This reaction involves the oxidation of pyrite by oxygen to produce sulfate and ferrous iron. This reaction generates two moles of acidity for each mole of pyrite oxidized.

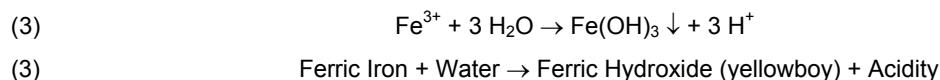


From looking at the reaction, it appears that the mine drainage would have to be acidic due to the fact that there is a production of hydrogen ions. The reaction can be altered if the rocks and soil the ground water flows through contains carbonates, as in limestone. Limestone provides carbonates to assist in the buffering of the acid, producing a net alkaline discharge. Also under investigation is the importance of the mine being flooded; research conducted by Duquesne University has found evidence that a mine that is flooded will have a net alkaline discharge, whereas an unflooded mine will have a net acidic discharge. The Scarlift report produced in 1972 indicated that most discharges in the Pittsburgh Coal seam were acidic. When they were analyzed again in the 1990s, several had changed to alkaline. It is not sure why this happened.

The second reaction is pH dependent and will proceed slowly under acidic conditions (pH 2-3) with no bacteria present and several orders of magnitude faster at pH values near 5. The reaction, which occurs when the mine water comes in contact with oxygen, involves the conversion of ferrous iron to ferric iron. The conversion of one mole of ferrous iron to one mole of ferric iron consumes one mole of acidity. Certain bacteria can increase the rate of oxidation from ferrous to ferric iron. 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. Three moles of acidity are generated as a byproduct. Many metals are capable of undergoing hydrolysis. The formation of ferric hydroxide precipitate (solid) is pH dependent. Solids form if the pH is above about 3.5 but below pH 3.5 little or no solids will precipitate.



Throughout the entire reaction acidity is being produced and consumed, but the production of acidity is far greater and without the limestone layer above the coalmine, the mine water discharge will be acidic.

## PROCEDURE

### WARM UP

#### DEMONSTRATION-BUFFERS - Alkalinity/Acidity

APPROX TIME 10 min.

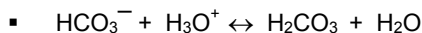
1. Make a buffer solution at pH 7 by dissolving 6.8 g of KH<sub>2</sub>PO<sub>4</sub> in water. Add 295 ml of 0.1M KOH and dilute the solution to 1L.
2. Place 50ml of distilled water and 50ml of the buffer solution into two separate 250ml beakers and place them on an overhead projector.
3. Add 2-3 drops of phenolphthalein indicator to both beakers. Using a dropper add 0.1M NaOH drop by drop to both solutions. The water solution should change color after a few drops, but the buffer solution will require over 7ml of the base before a color change occurs.
4. Repeat the demonstration using methyl orange or bromcresol green as the indicator and add 0.1M HCl drop by drop. Again a few drops of HCl are needed in the water solution, but several milliliters are needed to change the indicator's color in the buffer solution.

Safety: Wear safety goggles and a lab apron. Students should remain back at least 10ft.

Disposal: Combine all solutions and neutralize the mixture with 1M HCl or 1M NaOH as appropriate. Pour the neutralized solution down the drain.

## QUESTIONS:

- ❖ **What were some observations?**
- ❖ **Why did the one solution take more acid and base to change the color, and pH of the solution?** The solution contained a buffer. A buffered solution is one in which the pH can stay relatively constant when limited amounts of acid or base are added.
- ❖ **What are buffers?** Buffers usually consist of a solution of a weak acid and its salt or a weak base and its salt. For example, a solution containing a weak acid, carbonic acid,  $\text{H}_2\text{CO}_3$ , and its conjugate base, hydrogen carbonate ions,  $\text{HCO}_3^-$ . The hydrogen carbonate ions react with the  $\text{H}_3\text{O}^+$  ions from the added acid, and initiate the following equilibrium reaction.



Upon leaving the mine, the ground water can pass through sandstone and limestone, which contain calcium carbonate  $\text{CaCO}_3$ . If the ground water picks up the carbonate ions it will have an alkalinity value to buffer the acid in the water. Also adding to the buffering or alkalinity is the reaction between carbon dioxide and water to form carbonic acid.

This brings in Le Chatelier's principle where the addition of an acid places a stress on the equilibrium system. There is a net shift to the right as  $\text{HCO}_3^-$  neutralizes the added acid.

- ❖ **Can anyone give any examples of Buffers that are used in everyday life?**
- ❖ **If a stream contained no alkalinity and an acid was introduced to the water, would the stream would become acidic, or have a low pH?** Yes, without a strong buffering capability, the pH would change rapidly. In mining areas, a stream with a higher alkalinity is preferred, because, it protects the stream against rapid pH changes by acid mine drainage, thus, protecting fish and aquatic life.
- ❖ **What would an acidic stream do to the aquatic life?** Kill most every living thing in the stream.
- ❖ **What would happen to a well-buffered stream when acid mine drainage entered?** The stream could possibly be protected against rapid pH changes by acidic abandoned mine drainage, thus, protecting fish and aquatic life. Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0. Many species have trouble surviving if pH levels drop under 5.0 or rise above 9.0. Changes in pH can also alter the water chemistry; many metals are more soluble at a lower pH, thus creating toxic situations for aquatic species (i.e. aluminum).

In mine water, rocks, soils and salts usually influence buffering. The main sources of natural alkalinity are rocks containing carbonate, bicarbonate, and hydroxide compounds. Limestone is rich in carbonates, so water flowing through limestone regions has high alkalinity, and thus a good buffering capacity. The levels and types of alkalinity are directly dependent on the source of the water.

Alkalinity and acidity are determined using potentiometric titrations. In the alkalinity determination, sulfuric acid is added to the water sample in measured amounts until the three main forms of alkalinity (bicarbonate, carbonate, and hydroxide) are converted to carbonic acid. At pH 10, hydroxide (if present) reacts to form water. At pH 8.3, carbonate is converted to bicarbonate. At the end-point pH 4.5, all carbonates and bicarbonates have been converted to carbonic acid. The amount of acid required to reach a pH of 4.5 is expressed in milliliters. The carbonate ions ( $\text{CO}_3^{2-}$ ) and bicarbonate ( $\text{HCO}_3^-$ ) neutralize the acid in this reaction, and show the buffering capacity of the sample. From the amount of acid used, a calculation will indicate the amount of carbonate ( $\text{CO}_3$ ) involved in the reaction. This then is expressed as mg of  $\text{CaCO}_3/\text{L}$  even though actually part of the alkalinity may be contributed by  $\text{MgCO}_3$ ,  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ .

In the acidity determination, because mine drainage contains hydrolysable metals which can contribute to the acidity, it is necessary to remove those metals prior to determination of acidity. Mine drainage samples are treated with sulfuric acid to lower to pH to less than 4.0 and hydrogen peroxide is added and the solution heated to precipitate the metals. After the solution is cooled, the sample is titrated to a pH of 8.3 to determine the acidity.

Web sites to look at: <http://webpub.alleg.edu/group/creekconnections/alkalinity.html>

## THE ACTIVITY - Determination of Alkalinity in Abandoned Mine Drainage

The determination of the alkalinity of a sample of mine water is determined through the use of a titration, or a HACH alkalinity kit (available from Saint Vincent College EEC).

If using the HACH kit, follow instructions included with the kit.

### TITRATION

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

- A. Sodium Carbonate Solution (0.05N) – Provided if borrowing the module
  1. Dry 3 – 5 grams of standard  $\text{Na}_2\text{CO}_3$  at  $250^\circ\text{C}$  for 4 hours and cool in a desiccator.
  2. Mass 2.5 g with an analytical balance.
  3. Transfer to a 1 L volumetric flask.
  4. Fill flask to the mark with distilled water
  5. Mix.
  6. Do not keep for longer than 1 week.
- B. Sulfuric Acid (0.02N) – Provided if borrowing the module
  1. Dilute 200.00 ml of 0.1000N standard Sulfuric Acid Solution to 1000ml with distilled or deionized Water.
  2. Standardize by potentiometric titration of 15.00ml of 0.05N  $\text{Na}_2\text{CO}_3$  mixed with 15.00 ml of distilled water in a beaker to a pH of 4.5.
- C. Bromcresol green (pH 4.5 indicator) – Provided if borrowing the module) Dissolve 100 mg of bromcresol green sodium salt in 100 ml distilled water.
- D. Beakers/Erlenmeyer Flasks
- E. Burets
- F. Buret clamps
- G. Ring stands
- H. Oven For drying chemicals, or chemicals bought at correct concentration
- I. Pipettes/graduated cylinder

### Procedure

1. Fill buret to the top with  $\text{H}_2\text{SO}_4$ , remove all air bubbles from the tip and empty the buret to 0.00.
2. Record the initial reading from the buret.
3. Record the concentration of the  $\text{H}_2\text{SO}_4$  solution.
4. Place 50.0 ml of the sample in a clean beaker or Erlenmeyer flask
5. Add a clean stir bar and place on stir plate if available, if not, swirl beaker with your hand after each addition of  $\text{H}_2\text{SO}_4$ .
6. Add 5 drops of indicator, bromcresol green, the solution will be blue if the pH is above 4.5.
7. If the pH is below 4.5 discontinue, there is no alkalinity present.
8. Titrate slowly with 0.02N  $\text{H}_2\text{SO}_4$  to a pH of 4.5 (light violet gray) being careful to stir thoroughly after each addition.
9. Allow the pH to reach equilibrium before adding more acid.
10. When the end point is near, add  $\text{H}_2\text{SO}_4$  dropwise.
11. Titrate to the endpoint pH of 4.5 (light violet gray).
12. Record the volume of  $\text{H}_2\text{SO}_4$  added to the sample.

### Calculation of Alkalinity

#### Titration to a pH of 4.5

$$\text{Alkalinity, mg/L CaCO}_3 = [(\text{ml H}_2\text{SO}_4) * (\text{Normality of H}_2\text{SO}_4) * (50,000)] / [\text{ml of sample used}]$$

## THE ACTIVITY - Determination of Acidity in Abandoned Mine Drainage

The determination of the acidity of a sample of mine water is determined through the use of a titration, or the HACH Acidity kit (available from Saint Vincent College EEC).

If using the HACH kit, follow instructions for Total Acidity included with the kit.

For Titration to be completed, the following items need to be available:

- A. Potassium Hydrogen phthalate solution (KHP) (0.05N) – Provided if borrowing the module
  1. Crush 15-20 g of primary standard  $\text{KCH}_8\text{H}_4\text{O}_4$  and dry at  $120^\circ\text{C}$  for 2 hours.
  2. Cool in a desiccator.
  3. Weigh 10.0000 g to the nearest mg.
  4. Transfer to a 1 L volumetric flask, and dilute to 1000ml.
- B. Sodium Hydroxide (0.02N) – Provided if borrowing the module
  1. Mass out .80 g of NaOH on a watch glass
  2. Transfer to a 1 L volumetric flask.
  3. Fill flask to the mark with distilled water
  4. Mix.
  5. Standardize with 15.00 ml of KHP to the inflection point, which should be close to pH 8.7.
  6. Determine the concentration of your NaOH:
$$\text{Normality} = \frac{A \times B}{204.2 \times C}$$

A = g KHP weighed into 1 L flask  
B = ml of KHP solution used for titration  
C = ml of NaOH solution needed for titration
- C. Sulfuric Acid (0.02N) – Provided if borrowing the module
  1. Dilute 200.00 ml of 0.1000N standard Sulfuric Acid Solution to 1000ml with distilled or deionized Water.
  2. Standardize by potentiometric titration of 15.00ml of 0.05N  $\text{Na}_2\text{CO}_3$  mixed with 15.00 ml of distilled water in a beaker to a pH of 4.5.
- D. Phenolphthalein (pH 8.3 Indicator)
  1. Dissolve 5g of phenolphthalein disodium salt in 500 ml of 95% ethyl or isopropyl alcohol and add 500 ml distilled water.
  2. If necessary, add 0.02N NaOH dropwise until a faint pink color appears in solution.
- E. Burets
- F. Buret clamps
- G. Ring stands
- H. Pipettes/graduated cylinders
- I. Beakers/Erlenmeyer Flasks

### Procedure (Hot Peroxide)

- A. Fill burets to the top with NaOH and  $\text{H}_2\text{SO}_4$ , remove all air bubbles from the tip and empty the buret to 0.00
- B. Record the initial reading from the buret.
- C. Record the concentration of the NaOH and  $\text{H}_2\text{SO}_4$  solutions.
- D. Place 50.0 ml of the sample in a clean beaker or Erlenmeyer flask.
- E. Add a clean stir bar and place on stir plate if available, if not, swirl beaker with your hand after each addition of titrant.
- F. Measure the pH of the sample with pH paper, if the pH is above 8.3, discontinue, there is no alkalinity present
- G. If the pH is above 4.0 add standardized  $\text{H}_2\text{SO}_4$  in 5ml increments to lower the pH to 4.0 or below. If you have completed the alkalinity, it should give you a feel for the amount of  $\text{H}_2\text{SO}_4$ . Test the pH with pH paper.
- H. Add the amount of  $\text{H}_2\text{SO}_4$  needed to bring the pH to less than 4.
- I. Add 5 drops of 30%  $\text{H}_2\text{O}_2$  to the sample.
- J. Boil for 2-5 minutes.
- K. Cool to room temperature.
- L. Add 5 drops of indicator, phenolphthalein. The solution should be colorless.
- M. Titrate slowly with 0.02N NaOH being careful to stir thoroughly.
- N. Allow the pH to obtain equilibrium before adding more NaOH.
  1. Titrate to the endpoint of a pH of 8.3, pink.

## Calculation of Acidity

### Titration to a pH of 8.3.

Acidity, mg/L  $\text{CaCO}_3 = [(A * B) - (C * D)] * 50,000 / [\text{ml of sample used}]$

A = ml of NaOH used

B = normality of NaOH

C = ml of  $\text{H}_2\text{SO}_4$  used

D = normality of  $\text{H}_2\text{SO}_4$

## WRAP UP

1. Review what the results mean.

If the alkalinity was high a high number, if acid was added to the stream or discharge, would the pH immediately drop or would the pH change very slowly?

If the alkalinity was 0, could the stream buffer or stop the pH from changing immediately?

2. Can you think of anyway that Watershed organizations can increase the alkalinity of mine water when there is a very low value associated with the current alkalinity?
3. Review the results
4. Have the students prepare a formal write up/memo to the organization that the mine water is from.

## ASSESSMENT

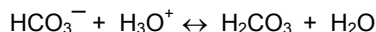
- The teacher will evaluate cooperation between the students while completing the experiment. **(Objective 1)**
- The teacher will evaluate proficiency while measuring pH and performing the titration. **(Objective 2)**
- The teacher will verbally question students to determine their understanding of the impact of AMD on streams. **(Objective 3)**
- The teacher will observe students while measuring volumes during the experiment. **(Objective 4)**
- The teacher will evaluate the lab write up/memo for accuracy, grammar, and technical information. **(Objective 5)**

## EXTENSIONS

# Analysis of pH, Alkalinity and Acidity in Mine Drainage

## Introduction:

A buffered solution is one in which the pH can stay relatively constant when limited amounts of acid or base are added. Buffers usually consist of a solution of a weak acid and its salt or a weak base and its salt. For example, a solution containing a weak acid, such as carbonic acid,  $\text{H}_2\text{CO}_3$ , and its conjugate base, hydrogen carbonate ions,  $\text{HCO}_3^-$  is a buffer system. The hydrogen carbonate ions react with the  $\text{H}_3\text{O}^+$  ions from the added acid, and initiate the following equilibrium reaction.



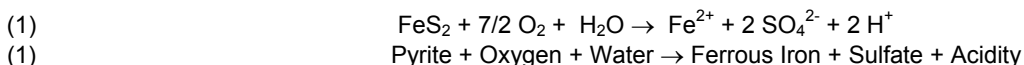
Two common types of chemical analysis for mine water are Alkalinity and Acidity. They are important concepts when investigating mine drainage, although both not pollutants, they refer to the ability of water to act as a buffer. They should not be confused with pH, but there is usually a connection; alkalinity is a measure of how much acid can be added to a liquid without causing a large change in pH, and acidity is a measure of how much base can be added to a liquid without causing a large change in pH.

Acidity is a quantitative measure of the water's ability to neutralize a strong base to a designated pH. The amount of acidity indicates the water's degree of corrosiveness. Acidity in mine drainage is caused the production of the sulfuric acid through the weathering of pyrite. Ions that can hydrolyze such as iron aluminum and manganese, all of which are commonly found in mine drainage also contribute to acidity. Mine water often times has a high acidity and therefore a lower pH due to the fact that acid is produced in the weathering of pyrite.

Alkalinity is a quantitative measure of the water's ability to neutralize a strong acid to a designated pH. The presence of carbonates, bicarbonates and hydroxides is the most common cause of alkalinity in natural waters. In some communities, the mine may exist under a layer of limestone as in Latrobe at Saint Vincent College. This limestone layer, calcium carbonate, helps to neutralize the acid produced through the weathering of pyrite and the mine water discharge has a neutral pH and a considerable amount of alkalinity. When a discharge is alkaline, the treatment system is considerably easier and less costly.

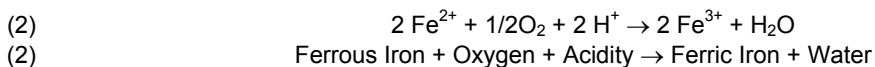
## AMD, Acidity and Alkalinity

The production of Abandoned Mine Drainage occurs through the weathering of pyrite,  $\text{FeS}_2$  or fool's gold. Pyrite is usually associated with the formation of coal, and is usually found in the roof material of the coal mine. Once mining is complete, the roof may collapse and the mine will fill with ground water. The pyrite is dissolved over time by the groundwater, which is indicated by the reaction below. This reaction involves the oxidation of pyrite by oxygen to produce sulfate and ferrous iron. This reaction generates two moles of acidity for each mole of pyrite oxidized.



From looking at the reaction, it appears that the mine drainage would have to be acidic due to the fact that there is a production of hydrogen ions. The reaction can be altered if the rocks and soil the ground water flows through contains carbonates, as in limestone. Limestone provides carbonates to assist in the buffering of the acid, producing a net alkaline discharge. Also under investigation is the importance of the mine being flooded; research conducted by Duquesne University has found evidence that a mine that is flooded will have a net alkaline discharge, whereas an unflooded mine will have a net acidic discharge. The Scarliff report produced in 1972 indicated that most discharges in the Pittsburgh Coal seam were acidic. When they were analyzed again in the 1990s, they had changed to alkaline. It is not sure why this happened.

The second reaction, which occurs when the mine water comes in contact with oxygen, involves the conversion of ferrous iron to ferric iron. The conversion of one mole of ferrous iron to one mole of ferric iron consumes one mole of acidity. Certain bacteria can increase the rate of oxidation from ferrous to ferric iron. This reaction rate is pH dependent 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.



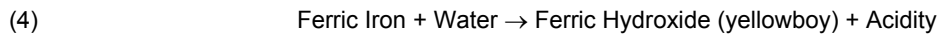
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**One Per Group**



The third reaction, which may occur, is the hydrolysis of iron. Hydrolysis is a reaction that splits the water molecule. Three moles of acidity are generated as a byproduct. Many metals are capable of undergoing hydrolysis. The formation of ferric hydroxide precipitate (solid) is pH dependent. Solids form if the pH is above about 3.5 but below pH 3.5 little or no solids will precipitate.



Throughout the entire reaction acidity is being produced and consumed, but the production of acidity is far greater and without the limestone layer above the coalmine, the mine water discharges will be acidic.

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**One Per Group**

## The Activity: Determination of Alkalinity in Abandoned Mine Drainage

The determination of the alkalinity of a sample of mine water is determined through the use of a titration, or the HACH alkalinity kit provided.

If using the HACH kit, follow instruction included with the kit.

### Materials:

- Sulfuric Acid (0.02N)
- Beakers/Erlenmeyer Flasks
- Burets
- Buret clamps
- Ring stands
- Oven For drying chemicals, or chemicals bought at correct concentration
- Pipettes/graduated cylinder
- Indicators - bromcresol green, metacresol purple or phenolphthalein

### I. Procedure

- A. Fill buret to the top with  $\text{H}_2\text{SO}_4$ , remove all air bubbles from the tip and empty the buret to 0.00.
- B. Record the initial reading from the buret.
- C. Record the concentration of the  $\text{H}_2\text{SO}_4$  solution.
- D. Place 50.0 ml of the sample in a clean beaker or Erlenmeyer flask
- E. Add a clean stir bar and place on stir plate if available, if not, swirl beaker with your hand after each addition of  $\text{H}_2\text{SO}_4$ .
- F. Add 5 drops of indicator, bromcresol green, the solution will be blue if the pH is above 4.5.
  1. If the pH is below 4.5 discontinue, there is no alkalinity present.
- G. Titrate slowly with 0.02N  $\text{H}_2\text{SO}_4$  to a pH of 4.5 (light violet gray) being careful to stir thoroughly after each addition.
- H. Allow the pH to reach equilibrium before adding more acid.
- I. When the end point is near, add  $\text{H}_2\text{SO}_4$  dropwise.
- J. Titrate to the endpoint pH of 4.5 (light violet gray).
- K. Record the volume of  $\text{H}_2\text{SO}_4$  added to the sample.

### II. Calculation of Alkalinity

Titration to a pH of 4.5

$$\text{Alkalinity, mg/L CaCO}_3 = [(\text{ml H}_2\text{SO}_4) * (\text{Normality of H}_2\text{SO}_4) * (50,000)] / [\text{ml of sample used}]$$

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**One Per Group**

# ALKALINITY OF MINE DRAINAGE

GROUP NUMBER: \_\_\_\_\_

NAME \_\_\_\_\_

PERIOD \_\_\_\_\_

DATE \_\_\_\_\_

Normality of Titrant (H<sub>2</sub>SO<sub>4</sub>) \_\_\_\_\_

Volume of Sample \_\_\_\_\_

Volume of H <sub>2</sub> SO <sub>4</sub> (from buret)	Color

**INSTRUCTIONS**

- A. Fill buret to the top with H<sub>2</sub>SO<sub>4</sub>, remove all air bubbles from the tip and empty the buret to 0.00.
- B. Record the initial reading from the buret.
- C. Record the concentration of the H<sub>2</sub>SO<sub>4</sub> solution.
- D. Place 50.0 ml of the sample in a clean beaker or Erlenmeyer flask.
- E. Add a clean stir bar and place on stir plate if available, if not, swirl beaker with your hand after each addition of H<sub>2</sub>SO<sub>4</sub>.
- F. Add 5 drops of bromcresol green indicator the solution will be blue if the pH is above 4.5.
- G. If the pH is below 4.5 discontinue, there is no alkalinity present
- H. Titrate slowly with 0.02N H<sub>2</sub>SO<sub>4</sub> to a pH of 4.5, light violet/gray, being careful to stir thoroughly after each addition.
- I. Record the volume of H<sub>2</sub>SO<sub>4</sub> after each addition.
- J. Allow the color to mix completely before adding more acid.
- K. When the end point is near, add H<sub>2</sub>SO<sub>4</sub> slowly or even drop by drop.
- L. Titrate to the endpoint pH of 4.5, light violet/gray.
- M. Record the total volume of H<sub>2</sub>SO<sub>4</sub> added to the sample.

**CALCULATING ALKALINITY**

mg CaCO<sub>3</sub>/L = [(ml H<sub>2</sub>SO<sub>4</sub> used) \* (Normality of H<sub>2</sub>SO<sub>4</sub>) \* (50,000)] / [ml of sample used]

Alkalinity = \_\_\_\_\_ mg CaCO<sub>3</sub>/L

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**One Per Group**

## The Activity: Determination of Acidity in Abandoned Mine Drainage

The determination of the acidity of a sample of mine water is determined through the use of a titration, or the HACH alkalinity kit provided.

If using the HACH kit, follow instruction included with the kit.

For Titration to be completed, the following items need to be available:

- Sodium Hydroxide (0.02N)
- Sulfuric Acid (0.02N)
- Beakers/Erlenmeyer Flasks
- Burets
- Buret clamps
- Ring stands
- Pipettes/graduated cylinders
- Indicators - phenolphthalein

### I. Procedure (Hot Peroxide)

- A. Fill burets to the top with NaOH and H<sub>2</sub>SO<sub>4</sub>, remove all air bubbles from the tip and empty the buret to 0.00
- B. Record the initial reading from the buret.
- C. Record the concentration of the NaOH and H<sub>2</sub>SO<sub>4</sub> solutions.
- D. Place 50.0 ml of the sample in a clean beaker or Erlenmeyer flask.
- E. Add a clean stir bar and place on stir plate if available, if not, swirl beaker with your hand after each addition of titrant.
- F. Measure the pH of the sample with pH paper, if the pH is above 8.3, discontinue, there is no alkalinity present
- G. If the pH is above 4.0 add standardized H<sub>2</sub>SO<sub>4</sub> in 5ml increments to lower the pH to 4.0 or below. If you have completed the alkalinity, it should give you a feel for the amount of H<sub>2</sub>SO<sub>4</sub>. Test the pH with pH paper.
- H. Add the amount of H<sub>2</sub>SO<sub>4</sub> needed to bring the pH to less than 4.
- I. Add 5 drops of 30% H<sub>2</sub>O<sub>2</sub> to the sample.
- J. Boil for 2-5 minutes.
- K. Cool to room temperature.
- L. Add 5 drops of indicator, phenolphthalein. The solution should be colorless.
- M. Titrate slowly with 0.02N NaOH being careful to stir thoroughly.
- N. Allow the pH to obtain equilibrium before adding more NaOH.
- O. Titrate to the endpoint of a pH of 8.3, pink.

### I. Calculation of Acidity

Titration to a pH of 8.3.

$$\text{Acidity, mg/L CaCO}_3 = [(A * B) - (C * D)] * 50,000 / [\text{ml of sample used}]$$

A = ml of NaOH used

B = normality of NaOH

C = ml of H<sub>2</sub>SO<sub>4</sub> used

D = normality of H<sub>2</sub>SO<sub>4</sub>

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**One Per Group**

## ACIDITY OF MINE DRAINAGE

GROUP NUMBER: \_\_\_\_\_

NAME \_\_\_\_\_

PERIOD \_\_\_\_\_

DATE \_\_\_\_\_

Normality of Titrant (NaOH) \_\_\_\_\_

Normality of Titrant (H<sub>2</sub>SO<sub>4</sub>) \_\_\_\_\_

Volume of Sample \_\_\_\_\_

Volume of H<sub>2</sub>SO<sub>4</sub> added to pH <4 \_\_\_\_\_

Volume of NaOH (from buret)	Color

**INSTRUCTIONS**

- A. Fill burets to the top with NaOH and H<sub>2</sub>SO<sub>4</sub>, remove all air bubbles from the tip and empty the buret to 0.00
- B. Record the initial reading from the buret.
- C. Record the concentration of the NaOH and H<sub>2</sub>SO<sub>4</sub> solutions.
- D. Place 50.0 ml of the sample in a clean beaker or Erlenmeyer flask.
- E. Add a clean stir bar and place on stir plate if available, if not, swirl beaker with your hand after each addition of titrant.
- F. Measure the pH of the sample with pH paper, if the pH is above 8.3, discontinue, there is no alkalinity present
- G. If the pH is above 4.0 add standardized H<sub>2</sub>SO<sub>4</sub> in 5ml increments to lower the pH to 4.0 or below. If you have completed the alkalinity, it should give you a feel for the amount of H<sub>2</sub>SO<sub>4</sub>. Test the pH with pH paper.
- H. Add the amount of H<sub>2</sub>SO<sub>4</sub> needed to bring the pH to less than 4.
- I. Add 5 drops of 30% H<sub>2</sub>O<sub>2</sub> to the sample.
- J. Boil for 2-5 minutes.
- K. Cool to room temperature.
- L. Add 5 drops of indicator, phenolphthalein. The solution should be colorless.
- M. Titrate slowly with 0.02N NaOH being careful to stir thoroughly.
- N. Allow the pH to obtain equilibrium before adding more NaOH.
- O. Titrate to the endpoint of a pH of 8.3, pink.

**CALCULATING ACIDITY**

$$\text{mg/L CaCO}_3 = \frac{[(A \cdot B) - (C \cdot D)] \cdot 50,000}{[\text{ml of sample used}]}$$

A = ml of NaOH used      B = normality of NaOH  
 C = ml of H<sub>2</sub>SO<sub>4</sub> used      D = normality of H<sub>2</sub>SO<sub>4</sub>

Acidity = \_\_\_\_\_ mg CaCO<sub>3</sub>/L

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**One Per Group**