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, H_2CO_3, and its conjugate base, hydrogen carbonate ions, HCO_3 is a buffer system. The hydrogen carbonate ions react with the H_3O^+ ions from the added acid, and initiate the following equilibrium reaction.

$$HCO_3^- + H_3O^+ \leftrightarrow H_2CO_3 + H_2O$$

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 quantative 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 quantative 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 Acid Mine Drainage occurs through the weathering of pyrite, 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.

(1) $$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$

(1) Pyrite + Oxygen + Water → Ferrous Iron + Sulfate + Acidity

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, 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.

(2) $$2\ Fe^{2+} + 1/2O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + H_2O$$

(2) Ferrous Iron + Oxygen + Acidity → Ferric Iron + Water

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.

(3) $Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 \downarrow + 3\ H^+$

(4) Ferric Iron + Water → Ferric Hydroxide (yellowboy) + Acidity

Throughout the entire reaction acidity if 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.