HYDROGEOCHEMISTRY AND TREATMENT OF ACID MINE DRAINAGE IN SOUTHERN CHINA[1]

by

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Abstract. Coal mines and various sulfide ore deposits are widely distributed in Southern China. Acid mine drainage associated with coal and metal sulfide deposits affects water quality in some mined areas of Southern China. Mining operations accelerate this natural deterioration of water quality by exposing greater surface areas of reactive minerals to the weathering effects of the atmosphere, hydrosphere, and biosphere. Some approaches to reduce the effects of acid mine drainage on water quality are adopted, and they can be divided into two aspects:

(a) Man-made control technology based on long-term monitoring of acid mine drainage; and,

(b) Neutralization of acidity through the addition of lime. It is important that metals in the waste water are removed in the process of neutralization.

A new method for calculating neutralization dosage is applied. It is demonstrated that the calculated value is approximately equal to the actual required value.

Key Words: acid mine drainage, oxidation, sulfide, neutralization, lime, neutralization dosage calculation

Introduction

Coal mines, iron-sulfide and multi-metal ore are widely distributed in China. Sulfur and iron disulfide minerals contained in coal and associated strata or metal sulfide deposits can produce acid mine water due to the oxidation of these minerals during mining operations. Acid mine drainage is not only harmful to the worker's health but also corrodes drainage facilities, mine haulage rails and the other equipment underground. After reaching the earth's surface, this acid water can contaminate soil and surface water; thereby, affecting aquatic life. Therefore, it is very important for commercial operations to study hydrogeochemical origins and treatment of acid mine drainage.

Acid mine drainage occurs mainly in several areas of Southern China. These waters have iron (or manganese) and sulfate ion concentrations that characteristically exceed background values. At present, effective measures to protect water from contamination by acid mine drainage have been adopted in some mined areas

of Southern China: First, environmental monitoring stations have been set up that analyze chemical compositions in coal mine drainage regularly. From these analyses, corresponding approaches can be adopted which will aid in the reduction of possible degradation of water quality. Second, mine drainage is treated to neutralize the acidity and lower metal concentrations before it is discharged.

The purpose of this paper is to explain the hydrogeochemical origin of acid mine drainage and to identify those areas where surface water is greatly influenced by coal mine drainage. This paper also discusses treatment principles and neutralization dosage calculations. Some examples of acid water abatement are also presented.
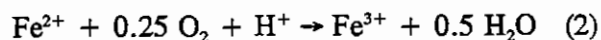
Hydrogeochemistry of Acid Mine Drainage

The production of acidic coal mine drainage is primarily associated with mining operations of high sulfur coal. The amount of sulfur contained in coal beds reflects differences in depositional environments. When mining occurs, the exposure of iron disulfides in coal deposits to water and oxygen results in the oxidation of sulfur and iron; thus producing sulfate, ferrous, ferric, and hydrogen irons, as well as the ferric iron hydroxide precipitate.

1. Oxidation of Iron Disulfides

Dissolution of pyrite:

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow$$
$$Fe^{2+} + 2\ SO_4^{2-} + 2\ H_2O \qquad (1)$$
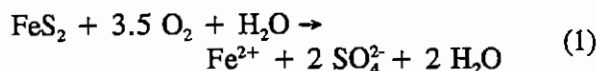
Oxidation of ferrous iron to ferric iron:

$$Fe^{2+} + 0.25\ O_2 + H^+ \rightarrow Fe^{3+} + 0.5\ H_2O \quad (2)$$

Hydration of ferric iron:

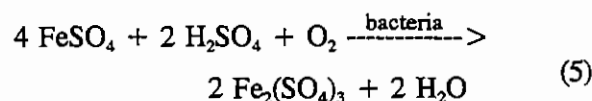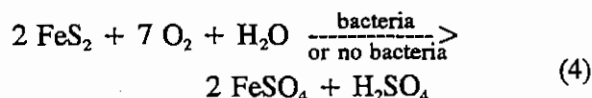$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3\downarrow + 3\ H^+ \qquad (3)$$

In the preceding reactions, four moles of hydrogen ion are produced from the oxidation of one mole of iron disulfide. As the water moves through the coal seam, oxidation of pyrite occurs, generating acidity which at first is neutralized by the alkalinity in the groundwater. If the acidity generated is greater than the initial alkalinity of the water, all the alkalinity will be consumed and acid water will result. Fine-grained pyrite is very reactive, so the total sulfur content of coal by itself, may be a poor predictor of potential acidity problems (Caruccio, 1975).

2. Catalysis by Bacteria

The bacteria that catalyze the acidity-producing reaction thrive only under acid conditions, so once acidity is initiated, acid production becomes more rapid and the acidity problem increases rapidly (Drever, 1982).

If the above-mentioned reaction is accompanied by bacteria (e.g. thiobacilli), it will accelerate the oxidation of ferrous iron, and promote production of ferric sulfate and sulfuric acid. The ferric iron, in turn, serves as an oxidant of pyrite, serving to generate more ferrous iron for the bacteria to oxidize.

$$2\ FeS_2 + 7\ O_2 + H_2O \xrightarrow[\text{or no bacteria}]{\text{bacteria}}$$
$$2\ FeSO_4 + H_2SO_4 \qquad (4)$$

$$4\ FeSO_4 + 2\ H_2SO_4 + O_2 \xrightarrow{\text{bacteria}}$$
$$2\ Fe_2(SO_4)_3 + 2\ H_2O \qquad (5)$$

Water Quality and Its Harmful Effects in Acid Mine Areas of Southern China

In the 81 water samples of coal mines and metal sulfide ore, studies indicated that acid mine drainage is present in 11 mine sites in Southern China.

Selected water quality parameters measured in several regions of China are shown in

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Table 1. The high concentrations of total iron and sulfate ion result from inorganic sulfide in the form of iron sulfide associated with coal.

Groundwater and streamwater in Southern China is not highly mineralized. This condition exists because regional precipitation exceeds potential evaporation. Under this condition, chemical constituents are continually leached from the rocks and removed in low concentrations in streamwater. Dissolved constituents resulting from coal mine drainage are readily identifiable against this low concentration background water quality (Table 1). Lower pH and greatly increased concentrations of sulfate ion and total iron are obviously observed in drainages from these mined areas.

Water contamination from acid mine drainage is not only detrimental to mine drainage facilities, but also adversely affects human health and the environment because of the potentially adverse effects of mine drainage on drinking water and aquatic life. In Southern China, an example of these effects is substantiated by data taken from a multi-metal sulfide ore of Yongping, Jiangxi Province, where a severe mine-drainage contamination problem exists (Table 2). Acid groundwater drained from the ore, flowed into the neighboring Jiaoji River and contaminated the streamwater. This resulted in the death of fish and shrimp, the occurrence of withered hydrophytes, and an increase in some trace metals in the river (Table 2). With the passage of time, this acid water continuously contaminated the whole river system. Thus, streamwater along 25 KM of the river cannot be used as drinking water due to the fact that some chemical constituents (metal ions and pH) exceed national water quality standards.

When streams become contaminated by acid mine drainage, adjacent vegetation dies and precipitation of ferric hydroxide occurs over long distances. Some trace elements associated with acid water are relatively innocuous to humans, but even at low concentrations are toxic to fish and other aquatic organisms. These ecological environmental problems are gradually being addressed by environmental and governmental agencies in China.

Table 1. Water quality data from acid mine drainage
in various mined areas of Southern China.

Sampling locations	pH	Total iron (mg/L)	Sulfate ion (mg/L)
1. Jiangsu Province			
Lishan	4.0	128.00	2000.0
Baishan	2.5	292.00	570.0
Jinshan	3.0	113.60	570.0
Tanshan*	2.3	926.00	
Chuanbu	2.96	12.00	
2. Jiangxi Province			
Santian	6.8	460.00	1370.0
Yongping*	4.0	27.00	
3. Hubei Province			
Songshan	4.6	6.98	1545.9
Jianyanhe	3.6		700.0-920.0
Tongzegou	4.0	671.60	4181.9
4. Zhejiang Province			
Dongfengje . . .	2.1-2.6	800.0-1300.0	2800.0-2900.0

*Metal sulfide ore mines (the others being coal mines).

Table 2. Water quality data from a multi-metal sulfide ore,
Yongping, Jiangxi Province

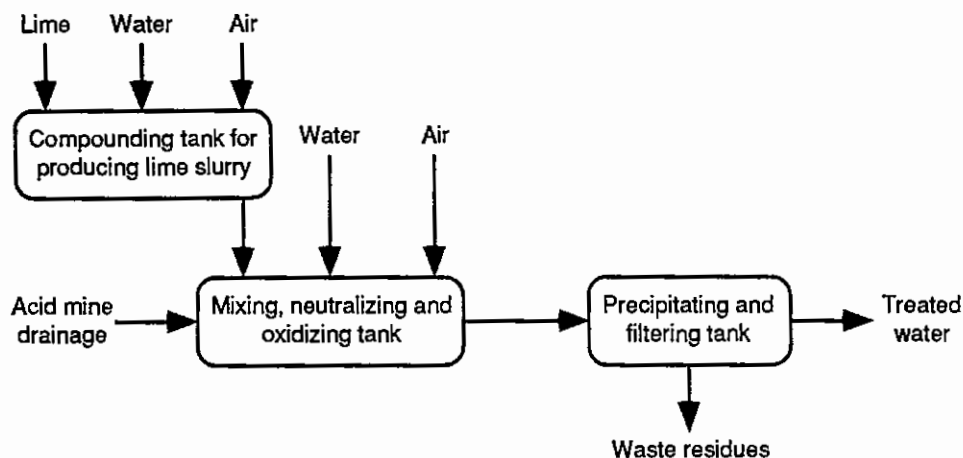| Sampling locations	pH	Copper (mg/L)	Zinc (mg/L)	Total iron (mg/L)	Fluorine (mg/L)
Jiaoji River	4.0	13.00	0.970	27.00	2.04
Tongmu River	5.9	.20	.083	.36	.37
Xinjanghekou town . .	6.0	.02	.005	.88	.37

Figure 1. Neutralization process.

Treatment Methods and Neutralization Dosage Calculation

Treatment Methods

In recent years, some environmental monitoring stations, regularly analyzing chemical constituents, have been established in mining areas. In addition, some effective measures, such as closing abandoned mines and building rational drainage systems, have been adopted in these areas so as to reduce the potential degradation of water quality.

At present, in some mining areas, acid produced in mine drainage by sulfide oxidation is neutralized by the alkalinity produced from lime and limestone. However, it should be noted that limestone, as a neutralizer, has some disadvantages, e.g., a slow reaction rate, and carbon dioxide produced by the reaction can hinder a neutral reaction from decreasing the acidity. In view of this, lime as a neutralizer is widely applied in the treatment of acid mine drainage as shown in Figure 1.

Lime containing 67-81% CaO is first made into a reactive lime slurry with 5-10% CaO, and then added in a neutralizing and aeration tank, along with water and air. Through precipitation and filtration, treated water rises to the national discharge standard (pH 6.5-9) and is permitted to be discharged or reused. Many kinds of metal ions (e.g., iron and manganese etc.) in treating water are transferred into hydroxide precipitants with a stable and low solubility product and can be removed after filtration.
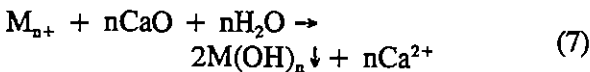
Neutralization Dosage Calculation

When neutralizing acid mine drainage, the dosage of lime is generally determined on the basis of pH-lime dosage curves resulting from practical experimentation. This method of dosage calculation is suitable in the case of stable

water quality. However, it can be seen by many experiments that water quality of acid mine drainage is often unstable in water treatments, and it is difficult or inaccurate to calculate lime dosage needed for neutralization according to the pH-lime dosage curves. For this reason, a new calculation method, based on water quality of treated water, is developed and replaces the previous one. It has been demonstrated that the calculated value for lime dosage is approximately equal to the actual required value. The theoretical basis for the new calculation method is as follows:
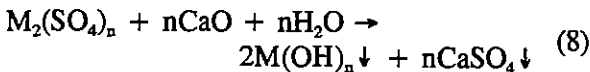
When acid produced by oxidation in mine drainage is neutralized by CaO from lime, a calcium-bearing precipitant will occur:

$$H_2SO_4 + CaO + H_2O \rightarrow \\ CaSO_4\downarrow + 2\,H_2O. \quad (6)$$
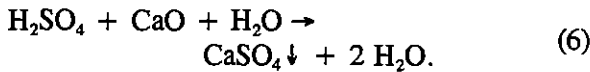
Some chemical compounds containing metal ions (e.g. Fe^{2+}, Fe^{3+}, Mn^{2+}, Cu^{2+}, Mg^{2+}, etc.) react with lime and produce hydroxide precipitants with a low solubility product, as shown in the following reactions,

$$M_{n+} + nCaO + nH_2O \rightarrow \\ 2M(OH)_n\downarrow + nCa^{2+} \quad (7)$$
or

$$M_2(SO_4)_n + nCaO + nH_2O \rightarrow \\ 2M(OH)_n\downarrow + nCaSO_4\downarrow \quad (8)$$

where M is metal ion. If CaO in lime reacts with a negative ion cluster (e.g., F^-, PO^- etc.), precipitants of a calcium-bearing compound will be produced.

$$CaO + H_2O + F^- \rightarrow CaF_2\downarrow + (OH)^- \quad (9)$$

On the basis of chemical equivalent fundamentals, the relation which neutralizes CaO in reaction (6) is as follows:

If $pH \leq 7$, acid consumption in neutral reaction G_c^I will be

$$G_c^I = 28.04 \times 10^3(10^{-pH1} - 10^{-pH2}). \quad (10)$$

When $pH > 7$, G_c^I will be

$$G_c^I = 28.04 \times 10^3(10^{-pH1} - 10^{-(14-pH2)}), \quad (11)$$

where pH is the pH in waste water before disposal, exponent pH is the pH in waste water after the neutralization reaction, and 28.04 represents the gram equivalent weight of CaO.

The relation which consumes CaO in reactions (7) and (8), can be written as follows:

$$G_c^{II} = 28.04 \times \sum \frac{n(S_{i1}-S_{i2})}{M_i}, \quad (12)$$

where S_{i1} is the metal ion concentration (mg/L) in waste water before disposal, S_{i2} is the metal ion concentration (mg/L) in waste water after neutral reaction, n is the reaction coefficient for a metal ion, and M_i is the atomic weight for a metal ion.

The relation which consumes CaO in reaction (9) can be written

$$G_c^{III} = 28.04 \times \sum \frac{I(S_{k1}-S_{k2})}{N_i}, \quad (13)$$

where S_{k1} is the concentration (mg/L) for negative ion cluster in waste water before disposal, S_{k2} is the concentration (mg/L) of negative ion cluster that remains in the waste water after neutralization, I is the reaction coefficient for a negative ion cluster, and N_i is the atomic weight for a negative ion cluster.

In conclusion, the amount of lime consumed by neutralization can theoretically be calculated as

$$G = \frac{1}{\eta}(G_c^I + G_c^{II} + G_c^{III}), \quad (14)$$

where η is the amount of effective CaO (%) contained in lime involved in the neutralization reaction.

When $pH \leq 7$, G is

$$G = \frac{1}{\eta} [28.04 \times 10^3(10^{-pH1}-10^{-pH2}) + \\ 28.04 \times \sum \frac{n(S_{i1}-S_{i2})}{M_i} + \\ 28.04 \times \sum \frac{I(S_{k1}-S_{k2})}{N_i}]. \quad (15)$$

If pH > 7, G is given by

$$G = \frac{1}{\eta} [28.04 \times 10^3 (10^{-pH1} - 10^{-(14-pH2)}) +$$
$$28.04 \times \sum \frac{n(S_{i1}-S_{i2})}{M_i} +$$
$$28.04 \times \sum \frac{I(S_{k1}-S_{k2})}{N_i}] . \qquad (16)$$

Results

A new calculation method for neutralization dosage was developed and applied in an example of treatment of acid mine drainage in a coal mine. The calculated result (Table 3) is satisfactory according to the above-mentioned method.

According to equation (15), the total lime required for neutralization in the case of the data shown in Table 3 is calculated to be 1697 g/m³. The actual consumption of lime at the coal mine was 1710 g/m³. This demonstrates the accuracy of this neutralization calculation.

Another example of treatment of acid mine drainage by lime neutralization is demonstrated below for acid mine drainage from an iron sulfide ore, Tanshan, Jiangsu Province, Southern China (Table 4).

The required retention time in the precipitation and filtering tank is 3-4 hours.

Summary

Oxidation of the iron disulfide minerals associated with coal deposits degrades water quality. This process is accelerated by mining activities and results in acid mine drainage.

Effects of acid mine drainage on water quality by coal mining in some areas of Southern China is serious. Neutralization of acidity through the addition of lime or powdered limestone is the most common means of treating mine effluent, which is high in acidity and dissolved metals. Neutralizers such as lime and

Table 3. Calculated values for neutralization (CaO) dosage referred to treatment of acid mine drainage from a coal mine, Southern China. The amount of effective CaO contained in lime is assumed to be 70%.

Chemical constituents	Concentrations before neutral reaction (mg/L)	Concentrations after neutral reaction (mg/L)	Calculated values for CaO (g/m³)
pH	2.0	8.0	280.40
Calcium	3.5	1.0	2.21
Ferrous ion . . .	296.0	22.7	274.80
Manganese . . .	160.0	13.3	387.70
Magnesium . . .	188.0	2.0	1.80

Table 4. Water quality data for treatment of acid mine drainage from and iron sulfide ore, Tanshan, Jiangsu Province, Southern China

Chemical constituents	Concentrations before disposal	Concentrations after disposal
pH	2.3	7.8
Total iron (mg/L) . .	926.0	0.1-0.2
Sulfate ion (mg/L) . .	3660.0	200.0-250.0
Arsenic (mg/L) . . .	1.6	0.02
Fluorine (mg/L) . . .	10.0	1.0

limestone have a low cost and are easily obtained from nearby regions. Neutralization dosage calculation is a key to effective treatment of acid mine drainage in the process of neutralization. The removal of some metals (e.g., iron and manganese etc.) that remain in treated water is also addressed.

Most acid mine drainage problems result directly from past mining activities and practices. Therefore, man-made control technology, such as closing acid-producing conditions and long-term monitoring of water quality, should be advocated in those areas that deal with acid mine drainage.

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