MONTANA STATE UNIVERSITY

Acid mine drainage treatment in an open limestone channel emphasizing aeration & retention
by Daniel John Franti

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Rehabilitation
Montana State University
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Abstract:
Acid mine drainage (AMD) can contaminate both surface and groundwater supplies with low-pH, poor-quality water. Contamination is often severe enough to render these waters harmful or toxic to both plants and animals. Neutralization of AMD in Montana's Great Falls Coal Field is a challenge due to the extremely poor quality of the water and number of acid springs involved. Researchers have applied passive AMD neutralization systems successfully in the eastern U.S.; however, colder climates and poorer water quality have impeded direct transfer of these technologies to the Rocky Mountain region.

It was hypothesized that promoting AMD aeration and retention in an open limestone channel (OLC) might enhance its treatment efficiency, particularly with respect to iron removal and acidity neutralization. Fifty-seven aeration and retention structures were installed in a 316-meter long OLC near Stocked, Montana, to study the effects of such structures on AMD treatment. Each structure possessed three gates along its cross-channel length. The gates were opened or closed to control the flow path and promote aeration by a fall from each gate. Water levels were raised behind each structure, or baffle, promoting retention. Water quality parameters measured were flow rate, pH, conductivity, temperature and redox potential, along with concentrations of oxygen, carbon dioxide, titratable acidity, sulfate, sulfur, organic carbon, total iron, ferric iron, aluminum, calcium, manganese, zinc, nickel, and magnesium. Limestone armoring and dissolution were also studied.

Iron removal was 30 to >300 percent more efficient after the baffles were installed. However, iron removal varied seasonally with outflow concentrations ranging from 453 to 601 mg L^-1 while inflow concentrations held around 831 mg L^-1. The most tortuous routing of AMD produced the greatest iron removal. While titratable acidity neutralization appeared greater after baffle installation, the difference was not confirmed statistically. Dissolved oxygen concentrations increased, particularly in slow-moving water, after baffle installation. However, oxygen saturation was reached at concentrations as low as 3 to 5.5 mg L^-1 limiting oxidation and hydrolysis reaction rates. Little improvement in pH occurred after baffle installation; values remained around pH 2.9. Treatment failed to increase pH sufficiently to precipitate significant quantities of aluminum and trace metals, apparently due to high sulfate concentrations. Sulfate concentrations were typically 5200 mg L^-1 at the OLC outflow and 5500 mg L^-1 at the inflow. At these concentrations sulfate buffers pH at low values and promotes gypsum precipitation over limestone dissolution. The mass of limestone dissolved per day was calculated to be at best 9 percent of the requirement needed for complete acid neutralization.

If pH and acidity are of primary concern, successful neutralization might not be achieved for AMD containing >2000 mg L^-1 SO4^2-. However, and according to these data, OLCs can be effective at iron removal. Thus, and since they are relatively low-cost, OLCs could be a good design to decrease iron concentrations in the Great Falls Coal Field.

ACID MINE DRAINAGE TREATMENT

IN AN OPEN LIMESTONE CHANNEL

EMPHASIZING AERATION & RETENTION

by

Daniel John Franti

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

in

Land Rehabilitation

MONTANA STATE UNIVERSITY-BOZEMAN
Bozeman, Montana

January, 1998

APPROVAL

of a thesis submitted by

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Acid mine drainage (AMD) can contaminate both surface and groundwater supplies with low-pH, poor-quality water. Contamination is often severe enough to render these waters harmful or toxic to both plants and animals. Neutralization of AMD in Montana's Great Falls Coal Field is a challenge due to the extremely poor quality of the water and number of acid springs involved. Researchers have applied passive AMD neutralization systems successfully in the eastern U.S.; however, colder climates and poorer water quality have impeded direct transfer of these technologies to the Rocky Mountain region.

It was hypothesized that promoting AMD aeration and retention in an open limestone channel (OLC) might enhance its treatment efficiency, particularly with respect to iron removal and acidity neutralization. Fifty-seven aeration and retention structures were installed in a 316-meter long OLC near Stockett, Montana, to study the effects of such structures on AMD treatment. Each structure possessed three gates along its cross-channel length. The gates were opened or closed to control the flow path and promote aeration by a fall from each gate. Water levels were raised behind each structure, or baffle, promoting retention. Water quality parameters measured were flow rate, pH, conductivity, temperature and redox potential, along with concentrations of oxygen, carbon dioxide, titratable acidity, sulfate, sulfur, organic carbon, total iron, ferric iron, aluminum, calcium, manganese, zinc, nickel, and magnesium. Limestone armoring and dissolution were also studied.

Iron removal was 30 to >300 percent more efficient after the baffles were installed. However, iron removal varied seasonally with outflow concentrations ranging from 453 to 601 mg L^{-1} while inflow concentrations held around 831 mg L^{-1}. The most tortuous routing of AMD produced the greatest iron removal. While titratable acidity neutralization appeared greater after baffle installation, the difference was not confirmed statistically. Dissolved oxygen concentrations increased, particularly in slow-moving water, after baffle installation. However, oxygen saturation was reached at concentrations as low as 3 to 5.5 mg L^{-1}, limiting oxidation and hydrolysis reaction rates. Little improvement in pH occurred after baffle installation; values remained around pH 2.9. Treatment failed to increase pH sufficiently to precipitate significant quantities of aluminum and trace metals, apparently due to high sulfate concentrations. Sulfate concentrations were typically 5200 mg L^{-1} at the OLC outflow and 5500 mg L^{-1} at the inflow. At these concentrations sulfate buffers pH at low values and promotes gypsum precipitation over limestone dissolution. The mass of limestone dissolved per day was calculated to be at best 9 percent of the requirement needed for complete acid neutralization.

If pH and acidity are of primary concern, successful neutralization might not be achieved for AMD containing >2000 mg L^{-1} SO$_4^{2-}$. However, and according to these data, OLCs can be effective at iron removal. Thus, and since they are relatively low-cost, OLCs could be a good design to decrease iron concentrations in the Great Falls Coal Field.

BACKGROUND AND OBJECTIVES

Acid Mine Drainage Control and Treatment

Acid mine drainage (AMD) results when sulfide minerals are oxidized in the presence of water. Techniques to limit AMD production often concentrate on either sealing acid producing material with a waterproof barrier to reduce transport (Meek, 1996; Ziemkiewicz and Skousen, 1996) or inundating the material with water to limit oxygen transport (Evangelou, 1995; Ziemkiewicz and Skousen, 1996). Both water barriers and inundation techniques often incorporate alkalinity generating minerals such as carbonates and phosphates to increase pH and aid in metal complexation (Ziemkiewicz and Skousen, 1996).

A third preventive control technique is the use of bactericides, or anionic surfactants, to control microbial oxidation rates, thus limiting the rate of AMD production. However, bactericides may not provide a permanent solution to AMD production since the compounds eventually either leach out or are decomposed within the acid producing mineral source (Ziemkiewicz and Skousen, 1996). Therefore, the two most permanent ways to control AMD production remain sealing and inundation.

Where sealing or inundating the acid producing source is impractical, neutralizing the AMD itself becomes necessary. The commonly used techniques for AMD neutralization include treatment with chemicals and treatment with artificially constructed wetlands (Gusek, 1995).

While the success of chemical treatment can in theory be predicted by simple stoichiometric balancing, the success of wetland treatment relies on less well-understood biological loading rates and chemical processes. The practicality of either method ultimately relies on the ability of the treatment system to either absorb or adjust to physical or chemical changes. Chemical treatment requires neutralizing agents be metered into the AMD at rates appropriate to the acidity and flow rate of the drainage, which can be variable and interdependent.

The appeal of chemical treatment is that through proper monitoring and chemical application, neutralization can be virtually guaranteed. The disadvantages of chemical treatment, however, include the

potential danger of chemicals and the financial cost of monitoring and chemicals, conceivably into perpetuity. Wetland treatment, on the other hand, is appealing due to its passive nature. If sized appropriately, a wetland should adjust to acidity and flow rate variations through changes in bacterial populations. Thus, although the initial cost of constructing a wetland might be high, if successful at neutralizing AMD, the only long-term expense for wetland treatment might be periodic cleaning and disposal of precipitates.

The Great Falls Coal Field

The Great Falls Coal Field covers about two-hundred thirty-three square kilometers (90 mi^2) and lies east/southeast of Great Falls, Montana. Most of the area within the perimeter of the Coal Field contains abandoned underground workings, and most of the watershed has been affected in some way by AMD produced from the abandoned mines. This is the largest concentration of abandoned AMD-discharging coal mines west of the Mississippi River (Hiel and Kerins, 1988).

Both Federal and State regulations mandate the State of Montana to oversee the reclamation of all its abandoned mines with funding from coal taxes. The regulations also further stipulate that reclamation of all abandoned coal mines must occur before coal tax money can be spent on reclaiming other abandoned mine types (e.g., hard-rock). While the State of Montana is currently reclaiming hard-rock mines, a mandate remains for the State to reclaim the entire 233 km^2 Great Falls Coal Field.

Reclamation Efforts in the Great Falls Coal Field

Technologies exist to reclaim the land in the Great Falls Coal Field. Techniques that have been successfully applied include deep limestone incorporation, or acid neutralization, and revegetation of the neutralized area. Reclamation of the AMD sources by barriers or inundation, on the other hand, is not technologically feasible. AMD control techniques are due to the inter-connectivity of the underground workings and porous nature of the shale and sandstone within which the workings lie, along with the size of the area.

It has been proposed that AMD production might be controlled by managing recharge of the underground workings. Crop selection and summer-fallow discontinuation on the upland benches has been suggested as a strategy to limit recharge, especially since the recharge-discharge relationship for most AMD

springs in the Coal Field are believed to be local (Osborne *et al.*, 1983). However, examination of the topography reveals that aquifer recharge probably begins about twelve to fifteen kilometers (7.5-9 mi) away from the Coal Field in the Little Belt Mountains. Thus about two-thousand square kilometers might need to be managed by the State to reduce water in the abandoned works. Until technologies are developed for successful large-scale underground AMD control, the most reasonable option available is therefore treatment of the AMD as it flows from its discharge points.

Osborne *et al.* (1983) identified at least seventeen AMD springs in the region around Stockett and Sand Coulee in the Coal Field (Figure 1). A chemical analysis of the spring waters reveals that all have low pH values (pH 2.3-5.4), undergo little dilution via recharge, have acidity concentrations ranging from 108 to 6002 mg L^{-1} (as $CaCO_3$), and are dominated by ferrous iron, aluminum, and sulfate. Iron ranges from 12 to 1065 mg L^{-1} and aluminum ranges from <2 to 752 mg L^{-1}. Many waters are also saturated with respect to gypsum.

Between 1990 and 1992 the Montana Department of State Lands (DSL) Abandoned Mine Reclamation Bureau (AMRB) constructed three wetlands in the Great Falls Coal Field. Included were wetlands constructed at French Coulee near Belt, Montana (not shown in Figure 1), near Centerville, Montana (labeled CS04 in Figure 1), and near Stockett, Montana (labeled CS10 in Figure 1). All three wetlands failed to provide sufficient neutralization of acidity and precipitation of metals to comply with even the least restrictive water quality standards such as for livestock water. The three wetlands also encountered a variety of physical flow control problems such as fouling of buried pipe systems with inorganic precipitates and bacterial slime, plus winter freezing and subsequent loss of containment. Anoxic limestone drain (ALD) pretreatment at both the Centerville and Stockett wetlands failed because metal and sulfate concentrations were too high for this technology (Schafer and Associates, 1994).

Two wetlands were also constructed in the summer of 1986 near Tracy, Montana (labeled CS01 and CS02 in Figure 1). These two earlier-constructed wetlands were also ineffective in improving AMD water quality, both being undersized and possessing minimal AMD/substrate interaction (Hiel and Kerins, 1988).

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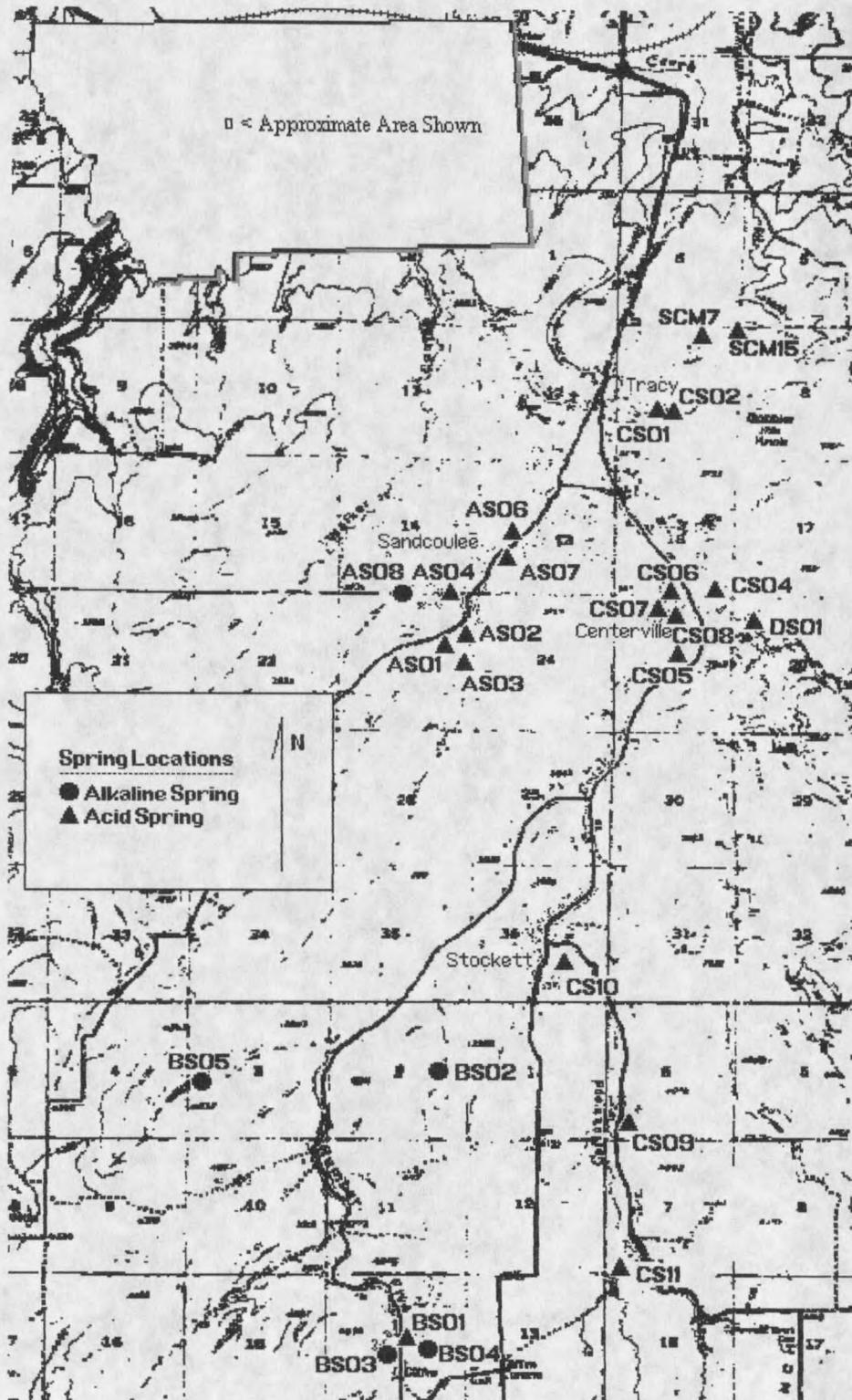
Figure 1. Location of Springs and Acid Discharges in the Stockett-Sandcoulee Area
(from Osborne *et al.*, 1983)

In the summer of 1995, the AMRB constructed an open limestone channel (OLC) to treat an AMD spring seeping from the abandoned #6 Coal Mine near Stockett, Montana (labeled CS09 in Figure 1). Construction of the OLC coincided with the apparent successful AMD neutralization by similar channels in West Virginia reported by Ziemkiewicz *et al.* (1994). Construction involved lining an existing AMD transport channel with a semipermeable geotextile liner and backfilling the channel with limestone rock. Although no performance expectations were set for the #6 Coal Mine OLC, results were less impressive than those shown by Ziemkiewicz *et al.* (1994).

In October 1995, an Ameri-Corps crew was hired by the AMRB to install aeration structures within the #6 Coal Mine OLC. These structures consisted of a series of PVC pipes that captured AMD flowing along the bottom of the OLC. The AMD thus entrained was piped downstream and discharged back into the OLC either from the raised lower downstream-ends of the pipes or from small holes punched into the raised lower end of pipes that had their down-gradient ends capped, creating sprinklers. Both techniques were designed to introduce oxygen into the AMD and precipitate metals by enhancing oxidation and hydrolysis.

Comparison of water quality from AMRB data before and after installation of the aeration structures is presented in Table 1. Water samples were collected at both the inflow and outflow of the #6 Coal Mine OLC. Installation of the aeration structures appeared to have greatly increased the amount of iron removed between the channel inflow and outflow. According to these preliminary data, iron removal efficiency [(inflow-outflow)/inflow • 100] appeared to grow from -4.6 to -24.3 percent by installing simple aeration devices. Acidity removal efficiency might have improved as well.

These preliminary data appeared to agree with the findings of Wilmoth (1974) and Jageman *et al.* (1988) who determined that limestone neutralization of AMD was most effective under conditions that promoted aeration. Ackman and Kleinmann (1984) concluded that limestone AMD neutralization was most efficient when aeration was combined with retention. Installation of the PVC aeration structures, however, did nothing to increase retention in the channel.

Table 1. Comparison of Water Quality Before and After Installation of PVC Aeration Structures in an OLC.

	Before Installation of Aeration Structures		After Installation of Aeration Structures	
	Inflow 10/23/95	**Outflow** 10/23/95	**Inflow** 10/26/95	**Outflow** 10/26/95
pH (std. units)	2.72	2.87	2.74	2.84
EC (mS cm^{-3})	4.94	4.66	5.14	4.68
SO$_4^{2-}$ (mg L^{-1})	4830	4680	4980	4610
Acidity (mg L^{-1})	3880	3960	3950	3600
Al^{3+} (mg L^{-1})	366	366	368	359
Mn (mg L^{-1})	1.44	1.46	1.42	1.48
Fe$_T$ (mg L^{-1})	754	719	756	572
Zn^{2+} (mg L^{-1})	44.1	43.9	44.4	44.1

Problem and Study Objectives

Neutralization of AMD in the Great Falls Coal Field is of paramount importance due to the extreme poor quality of the water and size of the area affected. Chemical treatment, while certainly possible, may be prohibitively expensive due to the number of AMD springs in the area. Passive treatment, on the other hand, would be an attractive alternative if neutralization could be achieved. While passive systems have been used successfully in the eastern U.S., colder climates and greater amounts of heavy metals in the Rocky Mountains have impeded direct transfer of this technology to many western areas (Emerick *et al.*, 1988).

Oxidative enhancement in an OLC might improve iron and acidity removal from AMD. The purpose of this study is to further enhance the aeration and retention capabilities of the #6 Coal Mine OLC and study the effects these changes have on AMD chemistry. The specific objectives of this study are as follows:

1) Investigate the ability to improve OLC performance with aeration and retention structures.

2) Determine whether OLC technology is a suitable AMD treatment alternative for the Great Falls Coal Field.

LITERATURE REVIEW

Open Limestone Channels

Open limestone channels are free-flowing, limestone-lined AMD transport channels within which low-pH AMD reacts with limestone to neutralize acidity and precipitate metals. Exposure of AMD to the atmosphere accelerates metal hydrolysis and releases excess proton acidity, H^+, into solution further dissolving limestone. Hydrolysis, however, also produces metal-hydroxides or "floc", which often coat or armor the limestone surfaces, thus reducing the ability of limestone to neutralize acidity unless the coatings are removed either by abrasion or under conditions of high-velocity flow.

The first studies on the neutralization of AMD in open channels were conducted in the 1970s by Pearson and McDonnell (1975a, 1975b, 1977). Iron-hydroxide armoring of permeable beds of crushed limestone placed across AMD-bearing streams was found to reduce the efficiency and solubility of limestone to 20% of the unarmored limestone rate. From these studies, it was concluded that neutralization of AMD would require five times as much armored limestone as clean limestone.

More recently, Ziemkiewicz et al. (1994, 1996a, 1996b) analyzed water chemistry and limestone from several AMD-bearing limestone-filled channels in northern West Virginia and Pennsylvania. The general conclusions drawn by the authors were that OLCs work best on steep slopes, where settling of precipitates is inhibited, and are more efficient when they contain large limestone particles (15 to 30-cm, 6 to 12-in) to maximize void space and water velocity within the voids. In these studies, the efficiency and solubility of armored limestone was found to decrease to 66-75% of the unarmored limestone rate. They also suggested that OLCs could be inexpensive, pre-treatment steps if placed upstream of conventional AMD treatment systems.

Other minerals, such as apatite (ideally $Ca_5(PO_4)_3OH$) have also been used as open channel substrates in AMD neutralization (Choi and West, 1996), particularly where limestone neutralization has
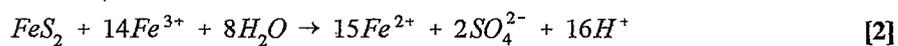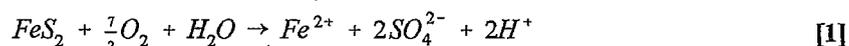
failed. The idea behind the use of phosphate substrates to remove metals is that metal-phosphate precipitates can form at much lower pH than can metal-hydroxide precipitation.

Acid Mine Drainage Formation

Acid mine drainage (AMD) occurs when sulfide-bearing minerals are exposed to oxidizing conditions in the presence of water. Oxidizing conditions exist either as abiotic oxygenation of the mineral or microbial oxidation, the latter having a rate independent of oxygen concentration. Water provides a means by which the oxidation products are desorbed, preventing oxidation-impeding build-ups of products on mineral surface "reactive sites" (Smith and Shumate, 1970), but serving as the vector for AMD transport.

While there is a host of acid producing minerals, the most often referred to source of AMD is pyrite, FeS_2, the most commonly occurring of sulfide-forming minerals (Morse *et al.*, 1987). Pyrite is implicated as the primary AMD source due to its great abundance in eastern United States coal fields (Stumm and Morgan, 1996, p. 690), western hard-rock mines in California and Colorado (Taylor *et al.*, 1984), and its ability to enhance the oxidation rate of other sulfides (Hamilton and Woods, 1981).

Pyrite oxidizes to release soluble ferrous iron, Fe^{2+}, along with sulfuric acid, H_2SO_4, and proton acidity, H^+, according to the following two well-known reactions:

$$FeS_2 + \tfrac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad [1]$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad [2]$$

where oxygen, O_2, and ferric iron, Fe^{3+}, are the primary oxidants (Singer and Stumm, 1970a; Brown and Jurinak, 1989).

Ferric iron, or the oxidizing agent in reaction two, is formed by the slower abiotic oxidation of Fe^{2+} according to reaction three:

$$Fe^{2+} + \tfrac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}H_2O \qquad [3]$$
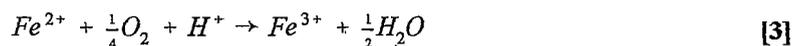
or by much more rapid microbial oxidation by bacteria such as *Thiobacillus ferrooxidans*. Once oxygen has initiated oxidation, however, reaction one is no longer important because reaction two becomes the major oxidant of pyrite (Kleinmann *et al.*, 1981) and may proceed by as much as 10^6 times faster than the abiotic rate, or reaction one (Singer and Stumm, 1970a).
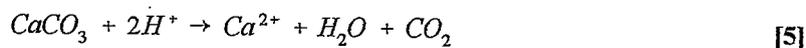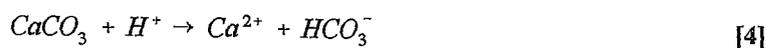
Acid Neutralization by Limestone

Limestone, $CaCO_3$, neutralizes acid according to the simple reactions:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad [4]$$

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2 \qquad [5]$$

where limestone neutralizes proton acidity by transforming H^+ into either bicarbonate, HCO_3^-, or water, H_2O. According to reaction four, there are only three concentration variables in the dissolution of limestone: a_{H^+}, $m_{Ca^{2+}}$, and $m_{HCO_3^-}$, since according to reaction five the three variables are: a_{H^+}, $m_{Ca^{2+}}$, and P_{CO_2} (Morse, 1974a) where a equals activity, m equals total molality (free ions plus ion pairs), and P equals partial pressure. According to reaction four, the primary mechanism for limestone dissolution at pH >6.4 is single proton attack of limestone which releases calcium, Ca^{2+}, and produces HCO_3^- ions. In reaction five, dominant at pH <6.4, which consumes two protons, Ca^{2+} is released, and H_2O and carbon dioxide, CO_2, are produced.

Limestone also neutralizes acidity produced during the process of iron hydrolysis at pH <6.4 through summary reaction six:

$$Fe^{2+} + \tfrac{1}{4}O_2 + CaCO_3 + \tfrac{3}{2}H_2O \rightarrow Fe(OH)_3 + Ca^{2+} + CO_2 \qquad (6)$$
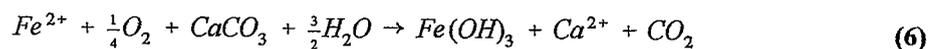
which is the combination of reactions three and five, along with the general hydrolysis reaction for Fe^{3+}. According to reaction six the ultimate iron-containing product of hydrolysis in the presence of limestone is iron hydroxide, $Fe(OH)_3$. In reality, there are intermediate hydrolysis products including $FeOH^{2+}$, $Fe(OH)_2^+$, .

and FeOOH, plus poynuclear hydrolysis products, carbonates, metal-intergrades, and sulfates. Reaction six is therefore written to represent complete hydrolysis of Fe^{2+} to its most stable stoichiometric hydroxide form at the surface of the earth, $Fe(OH)_3$, to maintain continuity with the remainder of the equations.

In an open system, and when limestone dissolves according to reactions five or six, the assumption is often made that there is complete outgassing, of CO_2. The exsolution of CO_2 is assumed to simplify the chemistry provided by reaction seven:

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad [7]$$

where CO_2 produced by reactions five and six reacts with water to form carbonic acid, H_2CO_3, a weak acid. The theoretical fraction of CO_2 converted to H_2CO_3 is less than 1% of dissolved CO_2 (Lasaga, 1984). Nevertheless, carbonic acid also reacts with limestone according to reaction eight:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \qquad [8]$$

where limestone and carbonic acid react releasing one mole of Ca^{2+} and two moles of HCO_3^- for each mole of limestone dissolved and enabling solution buffering above about pH 6.4 (Cravotta *et al.*, 1990).

While exsolution of CO_2 from open systems is often tacitly assumed, it must be remembered that the solubility of CO_2 is higher than that of oxygen. It should also be pointed out that the solubility of CO_2 increases in the presence of alkaline earth metals or alkali earth metals (first and second columns of the periodic table). In fact, when the metals are abundant, CO_2 abandons the precepts of Henry's law and the potential for the formation of bicarbonate increases substantially (Cole, 1994, p. 267).

The significance of this phenomenon is twofold: First, in the presence of alkaline or alkali earth metals, increased bicarbonate formation raises the buffering capacity, or alkalinity, of the water. Second, a measurable increase in the concentration of CO_2 should then signify the occurrence of reactions five and six, or the production of alkalinity by extension through reactions seven and eight. However, if CO_2 evolved from limestone dissolution exsolves to equilibrium atmospheric concentrations ($p_{CO_2} = 10^{-3.5}$), the maximum buffering, or alkalinity, that can be added to solution is only about 60 mg L^{-1} (as $CaCO_3$) and the maximum