

## **COST-EFFECTIVE ACID ROCK DRAINAGE WATER TREATMENT APPLIED TO MINING-IMPACTED WATERSHEDS<sup>1</sup>**

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**Abstract.** The application of three different Acid Rock Drainage (ARD) water treatment technologies will be discussed. The first water treatment technology results discussed are from laboratory and field treatability studies that used low volumes of high Total Dissolved Solids (TDS) ARD water to treat much larger volumes of lower TDS water to reach applicable ecological standards in the effluent stream. The low volumes of high (TDS) lime neutralized water were mixed with the high volumes of low TDS stream water to optimize the removal efficiencies of aluminum, cadmium, cobalt, copper, iron, lead, and zinc. Average removal efficiencies of the metals from the stream water were generally greater than 95%. Flow conditions of the low volume high TDS water tested ranged from 10 to 300 gpm and flow of the low TDS water ranged from 3,000 to over 25,000 gpm. Iron precipitation reactions and pH values in the effluent (ranging from 6 to 8.5) were accurately controlled. The precipitated iron-rich sludge from the neutralization reactions was deposited into a large open pit. Significant cost savings using this water treatment strategy was realized when compared to a conventional lime neutralization ARD water treatment system. The second water treatment technology to be discussed uses a lime mixing apparatus (The Neutra-Mill<sup>®</sup>) and its application to ARD impacted water-bodies. Results from hydrated lime neutralization of an approximate 90 million gallon ARD impacted tailings impoundment will be discussed. The third water treatment technology describes a system, which grinds limestone to ultra-fine grain sizes (The HALT system) resulting in rapid neutralization reactions occurring in ARD impacted water. Limestone is generally cheaper than most other sources of alkalinity and the maximum pH value that can be reached during dissolution is 8.5.

Additional Key Words: Neutra-Mill<sup>®</sup>, HALT, acid neutralization

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## **Introduction**

There are many watersheds throughout the US and World, which show elevated metals concentrations due to ARD (ICARD, 2000 and Skousen et al, 1998). ARD is generated when sulfide minerals, such as pyrite are oxidized by either atmospheric oxygen or dissolved oxygen in water (Rimstidt and Vaughn, 2003). Other oxidants, such as ferric iron can also oxidize the sulfide minerals (Rimstidt et al, 1994).

The oxidation of sulfide minerals occurs naturally and its effects can also be enhanced significantly during both metal and coal mining operations (ICARD, 2000 and Skousen et al, 1998). Mining generally increases the surface area and/or exposure pathways to oxygen and water of the sulfide minerals. The oxidation reactions occurring have been described by numerous authors (Rimstidt and Vaughn, 2003) and there are many different chemical and biological controls on these reactions. Generally these reactions produce waters which range in pH from 2 to 5, contain elevated metals and sulfate concentrations. Examples of elevated metals include; aluminum, arsenic, cadmium, cobalt, copper, iron, lead, manganese, and zinc. Iron is the one metal that is generally pervasive in all ARD waters, found in the highest concentrations, and is present in the reduced (ferrous) and/or oxidized (ferric) state (Langmuir, 1997).

One of the major considerations in choosing an ARD water treatment technology is determining what concentrations of the individual constituents in the effluent the treatment system is trying to attain. Generally, the lower the concentrations required, the more expensive the water treatment costs. The utilization of pH adjustment to treat acidic water that contains elevated concentrations of metals is a demonstrated technology that can remove metals to acceptable levels and is capable of treating large volumes of water (Smith, 2000 and Skousen et al, 1998). Low pH water can be neutralized or made alkaline by the addition of readily available additives such as sodium hydroxide (NaOH), calcium hydroxide (hydrated lime,  $\text{Ca}(\text{OH})_2$ ) or calcium oxide (lime, CaO). The mechanism for removal of constituents is primarily through precipitation, co-precipitation, and/or sorption reactions. As acidic waters increase in pH, many metals become supersaturated with respect to various mineral phases and precipitate from solution and/or sorb to mineral surfaces (Stumm and Morgan, 1981 and McKenzie, 1980). In

addition, kinetic limitations on redox reactions and the formation of certain mineral phases are overcome at more alkaline pH levels (Cornell and Schwertmann, 1996).

The geochemical reactions that occur during neutralization of ARD water with alkalinity are complicated and are generally controlled by the most abundant heavy metal in the water, iron. Therefore, the reactions of this constituent will tend to control the mobility and availability of the less abundant cationic metal species. Iron in most soil and near surface environments is typically found in one of two oxidation states, as ferrous ( $\text{Fe}^{2+}$ ) or ferric ( $\text{Fe}^{3+}$ ) iron (Langmuir, 1997). The oxidation of ferrous iron below a pH of about 6 is very slow. However, in solutions of  $\text{pH} \geq 5$ , the rate of iron oxygenation is first order with respect to the concentration of both  $\text{Fe(II)}$  and  $\text{O}_2$ , and second order with respect to  $\text{OH}^-$  ion (Stumm and Morgan, 1981). Thus, for each unit increase in pH there is a 100-fold increase in the rate of iron oxidation as described by equation 1.

$$\frac{-d[\text{Fe(II)}]}{dt} = k[\text{Fe(II)}][\text{OH}^-]^2 p_{\text{O}_2} \quad (1)$$

Therefore, addition of a base and the concomitant increase in pH to values greater than 7, potentates the rapid conversion of ferrous to ferric iron. The ferric iron formed at near neutral pH and in the presence of  $\text{O}_2$  is very unstable and rapidly converts to oxyhydroxide mineral phases, such as ferrihydrite ( $\text{Fe(OH)}_3$ ), which precipitate and are removed from solution. The iron compounds formed under oxidizing conditions and found in these environments are in fact classified as oxides, hydroxides, or oxide hydroxides (oxyhydroxides), but for simplicity will generally be referred to as iron oxyhydroxides in this paper.

The precipitation and removal of iron oxyhydroxide from solution in turn affects the concentrations of other metals in the aqueous phase through sorption and coprecipitation reactions. Adsorption of cations on iron oxyhydroxides can be specific, involving interaction with deprotonated surface hydroxyl groups to form mono- and bi-nuclear complexes, or nonspecific involving ion pair formation (Cornell and Schwertmann, 1996). The strength of metal cation adsorption onto iron oxyhydroxides varies with the mineral phase. For example, the strength of metal adsorption on goethite ( $\alpha\text{-FeOOH}$ ) is  $\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Co} > \text{Ni} > \text{Mn}$ ,

which is approximately the same order observed with hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ). In contrast, the strength of adsorption observed on ferrihydrite is  $\text{Cr} > \text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni}$  (as reviewed in Cornell and Schwertmann, 1996). The pH range over which the metal cations adsorb varies with the cation involved with Cu, Pb, and Zn generally being adsorbed more strongly at lower pH values than are Co, Ni, and Mn. However, all of these species are adsorbed over a pH range from about 4 to 8. Aluminum ( $\text{Al}^{3+}$ ) also readily adsorbs to iron oxyhydroxides over a pH range from about 3 to 8.5, and desorption is very slow, with adsorption being only partially reversible.

In summary, increasing the pH of ARD water should significantly increase the rate of iron oxidation and cause the formation of iron oxyhydroxides. The precipitation of these iron minerals will remove iron from solution and facilitate the removal of other metals via sorption or coprecipitation reactions.

This article will describe in detail the application of three different ARD water treatment technologies using neutralization and discuss the associated reduction of trace metal concentrations using these technologies at each Site. The trace metals associated with the ARD are often the treatment cost drivers and treatment success is judged by these constituents reaching levels below applicable standards. Depending on the constituents found in the ARD solutions this may have large effects on water treatment costs and the water treatment technology selected. Individual trace metals in ARD solutions are highly site specific and depend on numerous different geologic and chemical controls.

### **Treatment Technology I – Neutralization of low TDS Creek water**

Laboratory and field studies were conducted using low volumes of high Total Dissolved Solids (TDS) ARD water to treat much larger volumes of lower TDS Creek water to reach applicable ecological standards in the effluent stream. The commingling of high TDS water and low TDS water can be used to control the chemistry of treated water. The low TDS water in this example ranged in pH from 3.7 to 5.6 and the acidity concentrations range from 5 mg/L to 50 mg/L (as  $\text{CaCO}_3$ ). In contrast, the high TDS water has consistent chemistry with a pH value of about 4.6 and acidity concentrations of 1,050 mg/L (as  $\text{CaCO}_3$ ). Creek flows of the low TDS

during the treatment scenarios were measured and ranged from 4,000 gpm to greater than 25,000 gpm.

Laboratory experiments involving the titration of the high TDS and low TDS ARD water to various endpoints using alkaline additives were conducted to evaluate the potential and possible limitations of pH adjustment for the reduction of metal concentrations. Water collected was shipped in zero-headspace 1-liter amber glass bottles. Amber glass bottles with no headspace were used to minimize oxidation and iron/metal precipitation in transit. Once opened, samples were used immediately in experiments. Iron concentration and pH were monitored frequently to assure that large changes in water chemistry did not occur. Table 1 shows typical concentrations of the low and high TDS ARD waters. Total acidity measured in the high TDS water is on the order of 40 to 50 times greater than that of the low TDS water.

The titration of ARD water with calcium hydroxide will be discussed. The high TDS water was anoxic, and results from aerated experiments will be discussed. Water quality data collected at two titration end points are shown in Table 1.

Table 1. Water quality of low TDS and High TDS water and neutralized water

	Low TDS Water	Neutralized	High TDS Water	Neutralized
Acidity, mg/L	20.6	< 5	1020	< 5
Alkalinity	< 5	26.9	< 5	26.9
Aluminum, mg/L	1.06	0.0357	0.901	<0.20
Cadmium, mg/L	0.0008	<0.001	0.0011	<0.001
Calcium, mg/L	34.8	68.8	308	721
Cobalt, mg/L	0.0311	0.00034	0.073	0.0033
Copper, mg/L	0.125	<0.025	0.0258	<0.025
Iron, mg/L	5.24	<0.10	559	<0.10
Lead, mg/L	0.00069	<0.001	0.00032	<0.001
Magnesium, mg/L	12.4	0.594	231	231
Manganese, mg/L	1.96	<0.015	37.1	13.4
Nickel, mg/L	0.0066	0.0009	0.0224	0.0099
Sulfate, mg/L	142	159	2890	2910
Zinc, mg/L	0.801	0.0192	0.898	0.0209
pH, s.u.	4.7	9.91	4.6	8.5
TDS, mg/L	198	242	4027	3890

A typical titration curve of the high TDS water titrated with calcium oxyhydroxide ( $\text{Ca}(\text{OH})_2$ ) is shown in Fig. 1. The pH at which the ferrous iron is converted to ferric iron can be seen as the first horizontal step in Fig. 1.

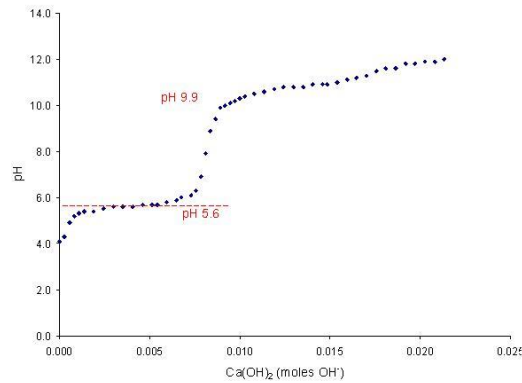
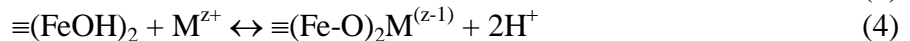
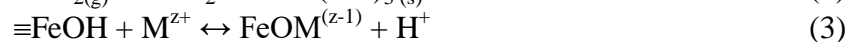
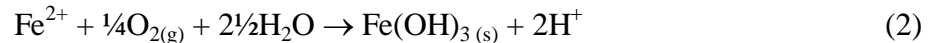


Figure 1. Neutralization of high TDS water using hydrated lime

Numerous proton generating reactions are occurring between pH ~ 5.2 to pH ~ 6.2, which consume hydroxyl ions ( $\text{OH}^-$ ) and result in the consumption of the added  $\text{OH}^-$  with only a very slight increase in pH. During this portion of the titration reaction, iron and other constituents are removed from solution as described by Equations 2 through 5.



Equation 1 describes the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  coupled to the formation of hydrous ferric oxyhydroxide (HFO) or amorphous ferrihydrite. Equations 3 and 4 represent the specific adsorption reactions of metal cations to surface hydroxyl groups of the ferric oxyhydroxide to form mono- and bi-nuclear inner sphere complexes. Equation 5 shows the adsorption of trivalent metal ions (represented by Al) on ferric oxyhydroxides, which appear to adsorb as surface hydroxo species (from Cornell and Schwertmann, 1996). The upward inflection observed at pH 6.1 is the point at which all the ferrous iron in solution has been consumed and most of these proton generating reactions have occurred.

After the development of the titration curve, it was important to determine at what pH values and to what extent iron and other constituents were removed from solution. Analytical data from samples collected at various endpoint pH values were in agreement with theoretical predictions based on current literature, Fe, Cu, and Zn were removed from solution at about pH 6.5. In addition, other constituents (Al, Cd, and Pb) were all either at non-detectable levels or at concentrations well below initial concentrations. Cobalt is removed from solution at somewhat higher pH values of approximately 8.5. This observation agrees with current literature regarding Co sorption onto iron oxyhydroxides, which suggest Co is sorbed at higher pH values than are Pb, Cu, and Zn and can be kinetically limited (Cornell and Schwertmann, 1996). An example of the water quality changes that occur during neutralization of the high TDS water is shown in Table 1.

Manganese sorbs to iron oxyhydroxides much less strongly than do the majority of other metals (i.e., Cu, Pb, Zn, Cd, and Co). In addition, the oxidation of manganese is much slower than the oxidation of iron, and experimental results suggest that the manner of Mn(II) oxygenation is autocatalytic, as described by Equation 6 (Stumm and Morgan, 1981).

$$\frac{-d[\text{Mn(II)}]}{dt} = k_0[\text{Mn(II)}] + k[\text{Mn(II)}][\text{MnO}_2] \quad (6)$$

Thus, total removal of manganese from solution was found to occur at pH values greater than approximately 9.0. However, the concentration of manganese was observed to decrease from its original level as the pH increases.

#### Iron Oxyhydroxide Floc Formation

For treatment of the low TDS water to be successful, the iron oxyhydroxides formed during the pH adjustment phase of treatment need to be rapidly removed from solution by precipitation. Studies in which the pH of low TDS water was adjusted showed that there was insufficient iron present in the low TDS water to get nucleation and precipitation of iron oxyhydroxide within a reasonable time frame and it was also difficult to maintain a stable solution pH. Therefore, high TDS water was added to the low TDS water to provide enough iron in solution to promote nucleation, growth, and production of flocs that were of adequate size and density to settle quickly. Systems in which low TDS and high TDS waters were mixed to provide 25 mg/L, 50

mg/L, and 100 mg/L total dissolved iron were tested for floc formation upon neutralization. Rapid floc formation was observed in all test systems. It was determined that a mixing ratio of high TDS to low TDS water of about 1:10 was near the maximum level at which the high TDS water could be added to get good flocculation and rapid conversion of iron to Fe(III) and precipitation of ferric oxyhydroxide. In addition, the lower limit for mixing the high TDS water with the low TDS water and still get reasonable floc formation would be near the ratio of 1:40.

### Treatability Field Study

Results from these laboratory tests indicated that pH adjustment through the addition of lime to a mixture of low TDS and high TDS water would effectively reduce concentrations of iron as well as the other constituents. While these results provide support for implementation of this treatment method, it was difficult to predict the results when implemented on a larger scale in the field due the difference in scale of the volume of water to be treated. A relatively small volume of water was incorporated in the bench-scale testing as compared to the large volume of water to be treated in the field.

A treatability field study was conducted to verify that the results obtained in laboratory studies could be reproduced under full-scale environmental conditions encountered in the field. This section describes a general description of the field study treatment plant operation, example water quality data collected during the monitoring, and the results.

Treatment Plant Operation. The field study treatment plant utilized during the treatability field study was assembled at a site located northeast of a large pit (Fig. 2). During the field studies, as shown in Figure 2, low TDS water was pumped from a creek approximately 250 meters upstream from the discharge to a large pit. Water was pumped at a rate of approximately 3,000 gpm. The 12-inch HDPE discharge pipe from the pump was routed to a steel tank, approximately 12 feet in diameter and 12 feet deep, that was used as a rapid mix tank (Fig. 3). In route from the pumps to the rapid mix tank, lime slurry was injected into the HDPE pipe to raise the pH of the low TDS water to values between 10 and 12.

Simultaneously with pumping of the low TDS water, approximately 300 gpm of high TDS water was pumped to the rapid mix tank. This water was pumped from a depth of approximately



40 feet in the Pit utilizing a submersible pump hung from a small barge. In the rapid mix tank, the pH adjusted low TDS water was combined with high TDS water pumped from the pit. Following the rapid mixing phase, water was discharged from the rapid mix tank via an overflow pipe to a 16-inch diameter gravity pipe that discharged back to the Creek downstream of the intake.

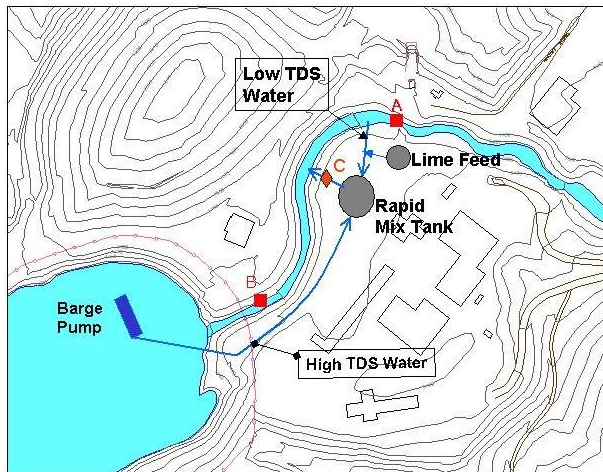


Figure 2. Schematic showing general location of treatment system.



Figure 3. Rapid mix tank

The water discharged generally had a pH value that ranged from 7.5 to 10.0. Higher pH values from the discharge point were found to be necessary to keep pH values of the entire creek flow above 6.5 during higher flow conditions in the Creek.

Lime feed was accomplished using an approximately 3,000-gallon lime-dissolving tank, shown in Fig. 4. Hydrated lime was batch mixed in the tank by mixing hydrated lime with water pumped from the Creek. A one-ton, semi-bulk lime container (super-sack) was lifted above the lime mixing tank using a forklift, and hydrated lime was dispensed into the tank, as depicted in Fig. 4. A mechanical mixer was used to mix the lime in the lime dissolving tank. The lime slurry prepared ranged in concentration from about 12% to 20%. Lime was fed to the rapid mix tank by pumping from the lime dissolving tank to the 12-inch HDPE pipe carrying low TDS water. An in-line valve installed in the lime feed pipe allowed for adjustment of the lime slurry feed rate so the desired pH of treated creek water could be maintained as the slurry concentration varied.

Implementation and Monitoring. The operating times for a low flow and high flow water treatment scenario were as follows: Scenario 1 – Low flow conditions in Creek, August 13-14 from 19:00 to 8:30 (13.5-hour test) and Scenario 2 – High flow conditions in Creek, August 12-13 from 15:00 to 9:00 (18-hour test).

The field studies were conducted under two flow scenarios, such that various flow conditions in the Creek could be simulated and treatment effectiveness could be evaluated. During low flow conditions in the creek the majority of the low TDS water was pumped into the treatment system. During high flow conditions in the Creek the water pumped from the Creek represented approximately 15% of the total water that was treated. Because the tests were conducted during the summer months of July and August, 2002, which are typically low flow periods on the Creek, staged storm event simulations utilizing controlled releases from a diversion dam were utilized.



Figure 4. Lime mixing tank

Monitoring was conducted to evaluate water treatment effectiveness and water quality results during operation of the treatability field study and the location of the sampling points are shown on Fig. 2. Sampling location A was in the creek approximately 25 meters upstream from the pump inlet to the water treatment system. Sampling location B was in the Creek approximately 75 meters downgradient of the treatment system discharge. Sampling location C was located on the discharge line from the rapid mix tank. Sampling location C water represents a mixture of

the lime combined with the low TDS creek water, after it has also had time to neutralize the high TDS water.

The monitoring included field measurements and laboratory analysis of samples collected from locations A, B, and C. Specific conductance and pH measurements were obtained at locations A and B every 15 minutes with Hydrolab<sup>®</sup> instrumentation. Additional field measurements, including pH, specific conductance, manganese concentrations, ferrous iron concentrations, and dissolved total iron concentrations, were collected in different combinations. Once per day water quality samples during each operating scenario were analyzed for acidity, alkalinity, dissolved metals, and sulfate.

Results from Treatability Field Studies

Scenario 1 - Low Flow Conditions on Creek, August 13– August 14. These studies began at 19:00 on August 13 when the treatment system was turned on and continued until 8:30 on August 14 (13.5-hour test) when treatment was suspended.

Field data collected during this test period are shown on Fig. 5, and laboratory data are shown in Table 2. The pH data show that the water in the creek at sampling point A was initially approximately 3.6 and was raised to values of approximately 7.0 at sampling point B during the test.

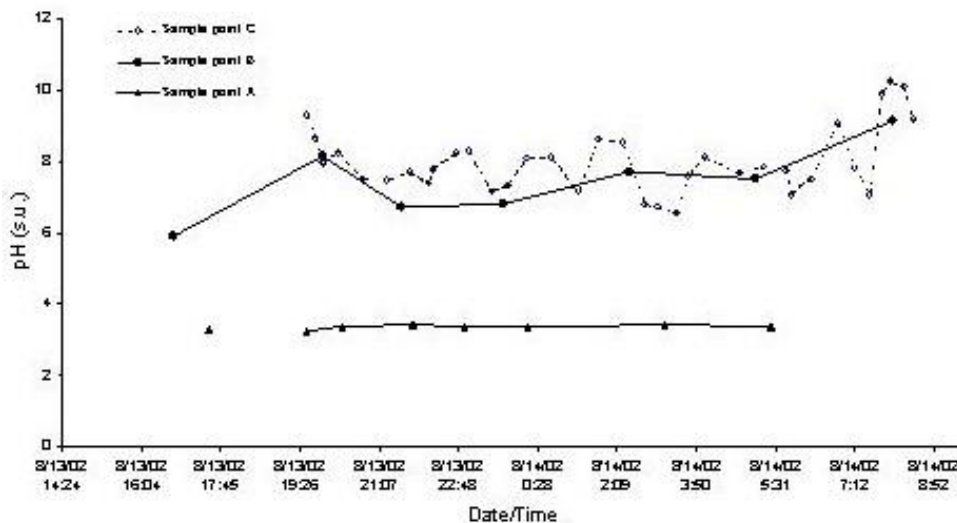


Figure 5. pH data collected during low flow conditions at sampling locations A (upgradient of treatment system), B (effluent exiting the rapid mix tank), and C (downgradient).

The decreases in constituent loading in the Creek is demonstrated by the reduced metals concentrations measured at sampling location A as compared to those measured at sampling location B (Table 2). Table 2 shows a significant decrease in concentrations of dissolved constituents transported in the creek measured at A (upstream of treatment plant) when compared to B (post-treatment).

Table 2 – Water quality of Sampling points A, B, and C during the low flow scenario, 2002.

Sampling Location	A	A	B	C
Date, Time	9-31, 10:15	8-14, 5:25	8-14, 8:00	8-14, 5:50
Acidity, mg/L	45	n.m.	<5	<5
Alkalinity	<5	n.m.	n.m.	n.m.
Aluminum, mg/L	2.58	n.m.	0.0447	0.0268
Cadmium, mg/L	0.00093	n.m.	0.00006	<0.001
Calcium, mg/L	66.7	n.m.	209	211
Cobalt, mg/L	0.0385	n.m.	0.000082	0.00086
Copper, mg/L	0.156	n.m.	<0.025	<0.025
Iron (Lab), mg/L	6.83	n.m.	<0.10	<0.10
Iron (Field), mg/L	6.55	0.56	<0.10	<0.10
Iron (Fe <sup>2+</sup> ), mg/L	5.35	0.91	<0.10	<0.10
Lead, mg/L	0.0041	n.m.	<0.000034	<0.001
Magnesium, mg/L	25.1	n.m.	24.5	48.6
Manganese, mg/L	3.65	1.96	0.027	2.84
Mn (field), mg/L	3.6	n.m.	0.2	0.8
Nickel, mg/L	0.0091	n.m.	0.0021	0.002
Sulfate, mg/L	288	n.m.	612	680
Zinc, mg/L	1.24	n.m.	<0.020	<0.020
pH, s.u.	3.6	3.4	9.2	7.07
Conductivity, us/cm	620	643	1113	1193

n.m. – not measured

Scenario 2 - High Flow Conditions in Creek, August 12 – August 13. Evaluation of Scenario 2, high flow on Creek, began at 15:00 on August 12 and continued until 9:00 on August 13 (18-hour test).

Creek water backed up behind a dam was released at an initial flow rate of approximately 17,500 gpm with flows ranging from 14,000 gpm to 27,000 gpm during the treatment scenario.

During treatment, the pH was measured at sampling points A, B, and C and the results are shown on Fig. 6. The pH data show that the water in the Creek at sampling point A was initially 3.6 and was raised to values of approximately 7.0 at sampling point B during the test. Notice that the pH values at sampling point C needed to be higher than in Scenario 1 in order to increase observed pH values in the Creek measured at sampling point B. The flow as measured at a weir at sampling point B ranged from 15,000 gpm to 25,000 gpm during the test.

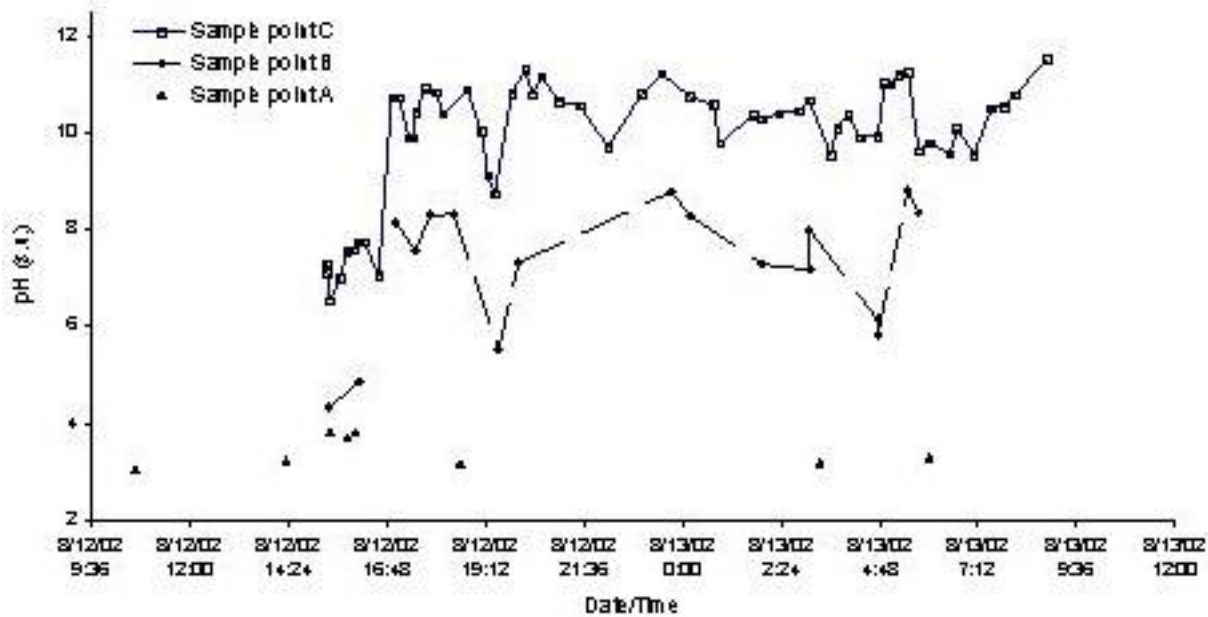


Figure 6. pH data collected during high flow conditions at sampling locations A, B, and C. Due to the high flow conditions in the Creek much higher pH values at sample point B were needed.

The decreases in constituent loading in the Creek is demonstrated by the reduced metals concentrations measured at sampling location B as compared to those measured at sampling location A (Table 3). Table 3 shows a significant decrease in concentrations of dissolved constituents transported in the creek measured at A (upstream of treatment plant) when compared to B (post-treatment).

### Summary of the Treatability Field Study

With the exception of manganese, all constituents were removed very efficiently using this method of treatment during both the low flow and high flow scenarios. Averaged decreases in mass loading in the Creek for individual constituents for the data presented were Al, >96%; Cu, >98%; Fe, >99.5%; Zn, >99.5%; Cd, >90%; Co, >85%; and Pb, >99%. Concentrations of these constituents in the treated Creek water were also well below the most-stringent ecological risk water quality standards. These results confirm laboratory investigations and show that treatment of the Creek water by pH adjustment can significantly reduce metals loading.

Table 3. Water quality of Sampling points A, B, and C during the high flow scenario, August 12, 2002.

Sampling Location	A	B	C
Time	18:35	18:25	18:10
Acidity, mg/L	38.8	<5	<5
Alkalinity	<5	35.6	401
Aluminum, mg/L	2.26	0.126	0.0189
Cadmium, mg/L	0.0013	0.00012	<0.001
Calcium, mg/L	109	147	323
Cobalt, mg/L	0.0474	0.0044	0.00017
Copper, mg/L	0.256	<0.025	<0.025
Iron (Lab), mg/L	1.47	<0.10	<0.10
Iron (Field), mg/L	1.39	<0.10	<0.10
Iron (Fe <sup>2+</sup> ), mg/L	0.89	<0.10	<0.10
Lead, mg/L	0.0233	<0.000036	<0.001
Magnesium, mg/L	36.5	36.1	1.24
Manganese, mg/L	4.13	2.81	<0.015
Mn (field), mg/L	4.3	0.2	0.0
Nickel, mg/L	0.0099	0.0043	0.0054
Sulfate, mg/L	459	509	785
Zinc, mg/L	1.66	0.0046	0.0298
pH, s.u.	3.2	8.3	10.4
Conductivity, us/cm	913	949	1527

The field demonstrations conducted verify the findings of the laboratory studies and indicate that treatment of a mixture of low-TDS and high-TDS water by pH adjustment will significantly reduce the concentration of most constituents in the Creek and, cost-effectively remove metals from high volumes of low TDS water using lime neutralization.

### **Treatment Technology II – Neutra-Mill<sup>®</sup>**

The second water treatment technology discussed is the Neutra-Mill<sup>®</sup> system. The Neutra-Mill technology was developed by Earth Systems Pty, Ltd. (Melbourne, Australia) to address the need for a portable, low-cost alternative to fixed plant treatment systems for ARD. Portable systems have a role to play when the cost of pumping acid water to a central plant is greater than deploying a small plant at the body of water. The technology is based around a small, efficient, partly submerged mixing chamber. Reagent is fed into the rotating chamber through a feed chute, mixed with water and dispensed as a fine grained suspension from an opening at one end

of the chamber. Coarser material remains in the chamber until the rotating action abrades the material to a fine enough grain size to exit the Neutra-Mill as a suspension. Dispensing rates can be controlled by adjusting the rotation speed of the chamber. This technology allows mixing and dispensing of chemical reagents to be conducted either within or immediately adjacent to the ARD affected water body (i.e., quicklime, hydrated lime). Such systems are capable of dispensing up to 5 tonne of dry powdered reagent per hour when configured with automated reagent storage and feed systems.

One of the key benefits of *insitu* treatment (treatment at a water body), is a reduction in the costs associated with sludge handling and disposal. Using portable treatment systems, the treatment sludge remains in the affected water body (eg. tailings pond, pit lake), or a separate sump can be used for treatment and then the sludge buried. In addition, if the treatment system is placed in the affected water, as water-based Neutra-Mills are, pumping and piping costs are avoided. Land-based Neutra-Mills offer similar cost benefits in situations where the floating systems can not be deployed.

Neutra-Mill technology has been applied to ARD treatment at a number of sites world-wide where the lack of infrastructure or other site requirements make fixed treatment plants either unsuitable or uneconomic. One example from Northern Nevada will be discussed where this technology and conventional lime reagents have cost-effectively neutralized ARD and improved water quality by lowering dissolved metal concentrations.

The neutralization field example used the Neutra-Mill<sup>®</sup> in a 90 million gallon tailings pond. The ARD was generated from a pyrite-rich waste rock pile and was discharged into the tailings pond for a period of several years. The acidity of the discharged water has been consistently monitored and had an acidity of approximately 9,760 mg/L CaCO<sub>3</sub>, iron and aluminum concentrations exceeding 1,000 mg/L, and moderate amounts of arsenic, copper, manganese, and zinc.

During the 28-day treatment test period acidity and alkalinity inputs to the tailings pond were carefully tracked. An average of approximately 1300 kg of dry hydrated lime was added daily through the Neutra-Mill<sup>®</sup> to the acidic tailings pond, totaling 36,800 kg (Fig. 7). ARD from the pyrite-rich waste rock pile was intermittently discharged at an average rate of 49 gpm totaling



1.976 million gallons over the 28-day trial. Water quality changes and removal efficiencies that occurred during neutralization of the ARD are shown in Table 4.



Figure 7. Treating a large tailings pond with a Neutra-Mill. The cloudy plume surrounding the floating mill is largely metal hydroxide precipitates from the reaction between the lime slurry being dispensed and the metalliferous ARD. For this treatment task the Neutra-Mill was loaded manually rather than using the automated reagent storage and delivery system.

Table 4. ARD and treated pond water quality.

	ARD	Treated Pond Water	Percent Reduction
pH, s.u.	2.5	5.8	---
Acidity, mg/L	9,760	11	>99
Aluminum, mg/L	1,500	1.1	>99.9
Arsenic, mg/L	9.5	0.01	>99
Cadmium, mg/L	0.35	0.008	>97
Copper, mg/L	21	0.1	>99
Iron, mg/L	1,100	0.5	>99.9
Lead, mg/L	0.07	0.002	>97
Manganese, mg/L	60	1.7	>97
Sulfate, mg/L	14,000	4,600	67
Zinc, mg/L	35	0.6	>98

Examination of the pond water quality following treatment suggests that the majority of aluminum and iron are likely to have been removed as hydroxides as a result of the rise in pH. The reduction in other metals is also likely to have been associated with decreased solubility associated

with increasing pH in combination with adsorption. Adsorption of arsenic, cadmium, and copper onto ferric iron hydroxide, and to a lesser degree onto aluminum hydroxide, is a well known process for the reduction of the dissolved concentrations of these trace metals. Manganese, lead, and zinc, which tend to exist in solution at neutral and acidic pH values, may have been partially removed by the large amount of iron and aluminum that precipitated. The reduction in sulfate (67%) is attributed to gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) saturation and precipitation due to increased dissolved calcium concentrations associated with the lime treatment.

Comparing the amount of alkalinity added to the pond, to the volume of acidity added, showed that the efficiency of the hydrated lime addition using the Neutra-Mill<sup>®</sup> was approximately 85% for the 28 day period. The Neutra-Mill has been successfully used as an ARD water treatment system in more than 50 different pit lakes, tailings ponds, and other water storage facilities in the United States, Australia, Indonesia, Peru, and South Africa.

### **Treatment Technology III – The HALT System**

The third treatment technology discussed is a hydro-active lime treatment (HALT) system developed by Earth Systems Pty. Ltd.. The HALT system grinds aggregate limestone ( $\text{CaCO}_3$ ) to produce an ultra-fine grained, highly reactive lime slurry which reacts very quickly with ARD solutions. The system cost-effectively treats acid drainage using one of the lowest cost reagents possible, carbonate (eg. limestone, dolomite or magnesite) (Fig. 8). The two key issues associated with efficient use of carbonate for neutralization are (1) relatively slow reaction rates (kinetics), and (2) armoring of the carbonate particles with treatment precipitates. Unless these two issues can be addressed, treatment with carbonate becomes highly inefficient and consequently can be expensive, even relative to conventional treatment reagents such as hydrated lime.

The simplest, and most effective approach to improving both carbonate dissolution kinetics and minimizing armoring of carbonate surfaces is to use very fine grained carbonate powder. The HALT system utilizes the fundamental principles of conventional ball mills to produce a highly reactive ultra fine grained slurry. A dual chamber ball mill grinds the aggregate under water, and produces fine particles at a controlled rate. The limestone slurry is screened to control grain size and is dosed into an acidic water body or stream. The rate of slurry production

is influenced by the nature of the feed material and the output grain size set via a particle screen. Output rates can also be controlled by adjusting the systems operating parameters such as mill rotation rate. The reactive carbonate slurry is then discharged into a highly acid, and ideally high energy environment, where the bulk of the neutralization occurs during sustained contact between the carbonate particles and acid water. This treatment system is unique in that acid water is not neutralized within the mill, but in the affected water body as the reactive plume is released. pH values of between 7.0 – 7.5 are achievable using this technology and limestone. A key benefit of this technology is that acid water cannot be accidentally over-treated to pH values above 8.5 using limestone.



Figure 8. The HALT System. Low cost limestone gravel is fed to the system (foreground), from a storage hopper (background). Using a partly submerged modified rotating ball mill, the system grinds the limestone to produce an ultra fine grained slurry. The slurry is then dispensed into the receiving environment where reaction between the slurry and affected water body results in neutralization *insitu*.

The effectiveness of this technology relies on the ultra fine grain size of the limestone slurry generated which is essential for rapid neutralization and highly efficient limestone use. The average particle size of the HALT mill output can be as low as 2-7  $\mu\text{m}$ , which compares favorably with that of the autogenous mills (Zurbuch et al, 1996). Particle size distribution data from slurry output indicates that 33% of material is less than 0.48 microns.

High efficiencies of limestone use are significantly promoted by the fine grain sizes, but are also a function of the energy of the receiving environment. Higher energy receiving environments assist in abrading carbonate particles thereby maintaining their reactivity. Positioning of the systems is therefore an important consideration for maximizing the systems efficiency.

The HALT system was used to neutralize ARD run-off from an area containing acid sulfate soils. Acid sulfate soils are organic rich soils which contain iron sulfides and produce ARD when exposed to oxidizing conditions. They are naturally occurring and are formed in seawater or brackish water environments and are common in estuarine environments. The iron sulfides are generally stable and do not produce ARD when the soils remain water saturated.

This case study was conducted along coastal New South Wales, Australia. Drainage works have exposed these soils leading to the production of up to 400 tonnes of acid annually. The acid has numerous impacts to the region, especially on aquatic fauna including commercially farmed oysters. The acid is produced in the dryer months and accumulates in the soil. During rain events the acid is mobilized or flushed out into a nearby Creek. The ARD is produced over short time periods with relatively high acid loads.

Over an approximate 10-day period the pH of the creek upgradient of the HALT system was approximately 3.2 – 3.6 and after treatment using the HALT system was approximately 7.0 – 7.5. The system delivered an average of 750 kg of limestone in slurry form through 250 micron (0.25mm) screens, from a starting material of minus 4mm limestone gravel per 24 hour period. The ultra-fine grained, highly reactive limestone slurry was highly cost effective, prevents over treatment of the system, and helped protect the local ecosystems.

### **Summary**

Examples of three different lime-neutralization ARD treatment technologies were discussed showing associated improvements in water quality. The type of treatment chosen is highly dependent on site-specific conditions and water quality goals. Understanding site-specific geochemical reactions can aid in the choice of a cost-effective water treatment system that meets water quality goals.



**Literature Cited**

- Cornell, R.M. and U. Schwertmann. 1996. The Iron Hydroxides. Structure, Properties, Reactions, Occurrence and Uses. VCH Verlagsgesellschaft, Weinheim, Federal Republic of Germany.
- ICARD 2000. Proceedings from the Fifth International Conference on Acid Rock Drainage. Society for Mining, Metallurgy, and Exploration, Inc. (SME). Volumes I and II.
- Langmuir, Donald. 1997. Aqueous Environmental Geochemistry. Prentice Hall. Upper Saddle River, New Jersey.
- McKenzie, R.M. 1980. The adsorption of lead and other heavy metals on oxides of manganese and iron. Aust. J. Soil Res. Vol. 18, pages 61-73. <http://dx.doi.org/10.1071/SR9800061>.
- Rimstidt, J.D., Chermak, J.A., and Gagen, P.M. 1994. Rates of reaction of Galena, Sphalerite, Chalcopyrite, and Arsenopyrite with Fe (III) in acidic solutions. *In: Environmental Geochemistry of Sulfide Oxidation* edited by C.N. Alpers and D.W. Blowes, ACS Symposium Series 550, pages 1-13.
- Rimstidt, J.D., and Vaughn, D.J. 2003, Pyrite Oxidation: A state-of-the-art assessment of the reaction mechanism. *Geochimica et Cosmochimica Acta*, Vol. 67, No. 5, pages 873-880. [http://dx.doi.org/10.1016/S0016-7037\(02\)01165-1](http://dx.doi.org/10.1016/S0016-7037(02)01165-1).
- Skousen J., A. Rose, G. Geidel, J. Foreman, R. Evans, and W. Hellier. 1998. A Handbook for Avoidance and Remediation of Acid Mine Drainage. National Mine Land Reclamation Center. West Virginia University.
- Smith, J.H. 2000. AMD treatment, it works but are we using the right equipment? Tailings and Mine Waste 2000. Proceedings of the Seventh International Conference on Tailings and Mine Waste. Fort Collins, Colorado, USA, January 23-26, 2000.
- Sobek, A.A., W.A. Schuller, J.R. Freeman, and R.M. Smith. 1978. Field and Laboratory Methods Applicable to Overburdens and Mine Soils. U.S. Environmental Protection Agency, EPA 600/2-78-054. Cincinnati, Ohio.
- Stumm, Werner and James J. Morgan. 1981. Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters. 2<sup>nd</sup> Edition. John Wiley and Sons. New York, Chichester, Brisbane, Toronto and Singapore.

Zurbuch, P. E., Menendez, R. and Clayton, J. L., 1996, Limestone neutralization of Dogway Fork, West Virginia, by means of a rotary-drum system. Restoration Ecology, Vol. 4, No. 3, pages 206-219 <http://dx.doi.org/10.1111/j.1526-100X.1996.tb00174.x>.