

MINING INFLUENCED WATERS: THEIR CHEMISTRY AND METHODS OF TREATMENT¹

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Abstract. More and more often, in treating waters associated with mining projects, it is not acid rock drainage that is the focus of concern. Consequently, we have coined a new phrase “mining influenced waters” to include all the types of water that can be encountered. These waters can be divided into four categories. For acid rock drainage (ARD) the primary treatment problem is the elimination of mineral acidity in the form of soluble iron and aluminum. For mineral processing waters, the water is usually basic and the primary treatment problem is usually the elimination of cyanide, arsenic and selenium. For marginal waters, the water is circum-neutral but contains contaminants slightly above aquatic standards. For these waters, the treatment problem is often reducing small concentrations of contaminants in high flows of water. Finally, for residual waters, the primary treatment problem is the removal of high levels of total dissolved solids. For residual waters, there are few treatment options and these waters are becoming a serious environmental problem in some mining operations.

Additional Key Words: aquatic chemistry, acid mine drainage, water treatment, mineral processing, and total dissolved solids

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Introduction

After working for 15 years on the chemistry and treatment of mining waters, it has become evident to us that not all waters found in mining and industrial operations are the same. In particular, labeling all these waters as acid rock drainage misses the treatment objectives for many industrial waters that have different chemistry. Not understanding the chemistries of these waters can lead to missing the cause of the contamination and this leads to inappropriate ideas for source control of contaminants. Missing the treatment objectives can cause costly errors in the cleanup method. The purpose of this paper is to introduce the term mining influenced waters (MIW) that was coined by Schmiermund and Drozd, 1997, and describe in this paper four categories of mining influenced waters that have different chemistries and require different types of treatment.

A mining influenced water (MIW) is defined as any water whose chemical composition has been affected by mining or mineral processing. Acid rock drainage (ARD) is a MIW that has mineral acidity. The term acid rock drainage is used instead of acid mine drainage because this includes all waters that have mineral acidity that could be found on a mining operation and not just water flowing from adits and shafts. In particular, ARD from waste rock piles, pit walls, and overburden are included. In addition, ARD can include water with mineral acidity that occurs in other situations such as the ARD found on the Halifax Airport that was caused by cutting into pyritic shales during construction (Hicks, 2003). Besides ARD, there are at least three other types of MIW:

Marginal Waters have alkalinity and pHs around 7. However, they have one or two inorganic contaminants that are above the concentration standards for aquatic organisms.

Mineral Processing Waters have alkalinity and pH's above 7. However, they contain soluble anions such as arsenate and selenate that persist through the mineral processing circuit. Also, those waters from cyanide processing circuits contain that constituent and other metals such as iron and copper that are complexed by cyanide.

Residual Waters have pH's above 7 and have a high level of total dissolved solids. The constituents that make up the dissolved solids are cations such as sodium and potassium and anions such as chloride and sulfate that persist in water all the way to the sea.

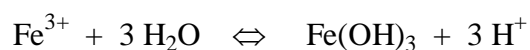
In the sections that follow, examples of each category of MIW are given, the chemistry critical to treatment is defined, and the treatment objectives are discussed.

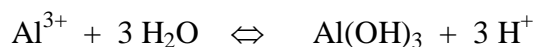
Acid Rock Drainage (ARD)

Table 1. Concentrations in mg/L of constituents in typical examples of acid mine drainage waters associated with mining operations.

	Quartz Hill	Big Five	Coal	Buckeye
pH	2.5	2.9	3.0	5.9
Al	60	20	37	21
Fe	750	50	57	580
Mn	80	30	6.4	20
Cu	55	2.0		0.03
Zn	150	10		0.24
Cd	0.80	0.03		
Pb	0.14	0.01		0.02
As	1.5	0.10		0.01
SO ₄	4000	2100	1300	750

Table 1 gives examples of ARD. The Big Five Tunnel and the Quartz Hill Tunnel are in the Central City / Idaho Springs Superfund site in Colorado (Machemer, et al, 1993, Bolis, et al, 1991). They represent typical examples of ARD from mineral mining operations. The coal mining water is an average of ARD from coal mining sites in Illinois (Wildeman, 1991). The Buckeye water comes from a landfill site in Ohio that covered a number of coal waste piles. What these waters have in common is not pH, but the high concentrations of Fe and Al. These two elements hydrolyze in water according to the following reactions.



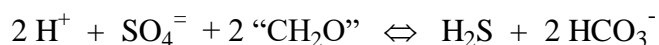


For Fe this reaction happens between a pH of 3.0 and 3.5, and for Al between a pH of 4.5 and 5.0 (Wildeman, et al, 1997b). To begin to have carbonate alkalinity in water, the pH has to be above 5.0 (Stumm and Morgan, 1996). Consequently, all the Fe and Al have to be removed before carbonate alkalinity can be achieved. The Buckeye is an excellent example of an ARD with mineral acidity. The pH of the water is 5.9, however, the high concentration of iron in the water existing as Fe(II) controls the chemistry of the water. Fe(II) will oxidize to Fe(III) and this will hydrolyze to Fe(OH)₃ and the pH will drop to about 3 until all the Fe is removed from the water (Wildeman, 1991). Note that in the examples of metal mining ARD there are considerable concentrations of heavy metals such as Cu, Zn, Cd and Pb. Because the hydroxides of these metals are more soluble than those of Fe(III) and Al, it is still the case that these two metals have to be removed before treatment of heavy metals can begin.

Treatment of ARD

The treatment objective for ARD is obviously to add alkalinity to the water. In active treatment of ARD, a number of reactants are used to provide this alkalinity with NaOH and Ca(OH)₂ being the most popular (Skousen, et al, 1998, Evangelou, 1996). In active treatment, the pH is usually increased to about 10 and, under these alkaline conditions, most all metals of concern are precipitated as hydroxides. In passive treatment, providing alkalinity is more problematic, especially in a case of severe ARD such as the Quartz Hill Tunnel water. Natural alkaline materials such as limestone do not dissolve rapidly enough (Skousen, et al, 1998). Still, limestone treatment is used in open limestone drains and in anoxic limestone drains. Alkaline byproduct materials from coal-fired power plants usually cement when they come in contact with water and lose their ability to easily dissolve. It appears that steel slag may be one alkaline constituent that can provide significant alkalinity over a long period of time and not cement (Simmons et al, 2002).

If microbial methods of passive treatment are considered, aerobic methods of treatment are unacceptable because in these systems, Fe(II) will be oxidized to Fe(III) and then the above hydrolysis reaction of Fe(III) will occur lowering the pH to around 3 (Wildeman and Updegraff, 1998). One microbially catalyzed reaction that will add alkalinity is anaerobic sulfate reduction:



In this reaction “CH₂O” represents the organic material in an anaerobic sulfate reduction system. The issue in sulfate reduction is that the reaction works best when the pH is between 5 and 8. So adding severe ARD’s puts the bacteria under stress. Also, sulfate reduction is primarily used for precipitation of heavy metal constituents as sulfides and using the reaction to provide large amounts of alkalinity is inefficient (Gusek and Wildeman, 2002). Consequently, treatment of the mineral acidity in ARD can be accomplished by active treatment but this is an expensive approach relative to using passive treatment. However, adding alkalinity rapidly enough to severe ARD water in a passive treatment system is not easily accomplished at this time and this area of treatment needs an infusion of research and development.

Marginal Waters

Table 2. Concentrations in mg/L of constituents in typical examples of marginal waters associated with mining operations.

	Westfork	Ferris Haggarty	MSF	Rico	Aquatic Stds
pH	7.9	6.6	7.1	7.0	6 – 8.5
Mn	0.01	0.03	0.37	0.66	1.0
Ni		0.05	7.5	0.01	0.20
Cu	0.02	20.6	0.015		0.01
Zn	0.21	0.07	0.20	11.4	0.10
Cd	0.002	0.003	0.009	0.03	0.005
Pb	0.70				0.020
SO ₄	63	48	1005	450	
Alk.	156		33	595	

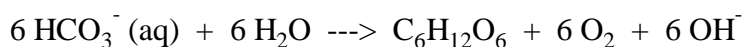
Table 2 contains four waters that are representative of the marginal water category of MIW. These waters have alkalinity, and pHs around 7. The concentrations of Fe and Al are low because these two constituents cannot remain in the water under aerobic conditions at these pHs

(Stumm and Morgan 1996). The treatment issue for these waters is the concentrations of contaminants of concern that are significantly above typical water quality criteria for aquatic organisms. The aquatic standards column five in Table 2 represent the cold water standards for Colorado for a water hardness of 100 mg CaCO₃ per liter (Herron, private communication, US EPA, 2002). The Westfork water is from an underground lead mine in the New Lead Belt in Missouri (Gusek et al, 1999), and here lead exceeds the aquatic limit. The Ferris-Haggarty water is from a copper mine in southern Wyoming (Reisinger et al, 2000), and Cu is the contaminant of concern. The MSF water is from the Mineracao Serra de Fortaleza (MSF) Nickel Mine, in Fortaleza de Minas, Minas Gerais State, Brazil, and Ni and Mn are the contaminants of concern. The Rico water is from the Rico-Boy adit in the town of Rico in southwest Colorado, and Zn and Cd are above aquatic limits. In an aerobic environment typical of most places where aquatic organisms reside, heavy metal constituents would precipitate as hydroxides or carbonates. However, these forms of Zn, Ni, Mn, and Cd are quite soluble even at the pH of 7 (Stumm and Morgan, 1996). Consequently, removing these more soluble metals is often the treatment objective for these waters.

Treatment of Marginal Waters

At first glance, treatment of marginal waters appears to be the simple increase of pH to about 10 so that even soluble metal hydroxides would be removed. This would be the first approach to active treatment of these waters. However, there are a number of issues that make this treatment scheme not that easy. First, it is often the case that these waters are of reasonably good quality because they have been diluted by large volumes of good water, so large flows are an issue (Gusek et al., 1998). Second, active treatment of these waters involves the removal of a small amount of precipitate from a large volume of water. This may require a coagulation agent or a special filtering apparatus. Finally, in the case of Pb, and Zn, the form of the metal in the water is primarily a carbonate or hydroxide complex (Wildeman, et al., 1997a, Stumm and Morgan, 1996). Addition of more carbonate or hydroxide in an active process may cause the metal to be more stable in water and not cause precipitation. Consequently, an active treatment program for a water of this type requires bench- and pilot-scale testing to insure that removal will be lowered to concentrations required for aquatic standards.

On the other hand, passive treatment of these types of water work well even with flows up to 1200 gallon per minute (Gusek, et al. 1999, Reisinger, et al., 2000). These waters have carbonate alkalinity, and there is usually no problem with eliminating mineral acidity. In sulfate-reducing systems the pH is optimal for the microbes; and, for aerobic systems, photosynthesis using the bicarbonate in the water provides oxygen and hydroxides by the following reaction (Wildeman and Updegraff, 1998):



In aerobic systems, when Mn remains in the water it is oxidized and precipitates as MnO₂, the surfaces of this oxide provide excellent sites for adsorption of contaminant metals. Adsorption sites can also be provided by rock surfaces. Examples of full-scale passive treatment of marginal waters include the Westfork system (Gusek et al., 1999), the Duluth Complex system (Eger, et al. 1997), and the recently completed MSF system (Wildeman, et al., 2003).

Mineral Processing Waters

Table 3. Concentrations in mg/L of constituents in typical examples of mineral processing waters associated with mining operations.

	RPM	Gilt Edge	Rain	CMM
pH	8.6	9.0	8.0	5.5
Fe	0.5	470	0.05	0.60
Mn			0.47	187
Cu	8.3	78	3.3	0.024
Zn	0.06			657
Cd		0.09		1.9
As	20		0.09	
Se	0.05		0.2	
CN (Total)	~100	230	4	
SO ₄	1300	300	400	5800

Table 3 contains four waters that are representative of the mineral processing category of MIW. The waters in the first three columns come from cyanide circuits. The RPM water from a gold mine in Brazil and the Gilt Edge water from South Dakota are spent waters coming directly from the mineral processing circuit. The Rain Mine water from Nevada comes from the tailings pond that is fed by the circuit (Wildeman, et al., 1994). The CMM water is a spent liquor coming from a zinc refinery in Brazil.

The cyanide waters represent a special category of mineral processing waters because the cyanide causes three problems. First, it is a contaminant and must be destroyed. The second problem is that a significant portion of the cyanide is tied up in metal complexes and these have to be broken before the cyanide and contaminant metal can be removed. This is especially the case in the Gilt Edge water where there is far much more Fe and Cu in the water than should be present at a pH of 8.0. The final problem is that cyanide processing often releases arsenic and selenium from the ore minerals. These contaminants exist in the water as soluble oxyanions and their removal can prove to be difficult.

Treatment of Mineral Processing Waters

There are standard methods for the active treatment of cyanide containing waters (Gusek, 2002). These methods concentrate on oxidizing the cyanide and mineralizing it into carbon dioxide and nitrogen, two non-contaminants. Removal of arsenic and selenium by active treatment usually relies on the adsorption of the oxyanions by ferric hydroxide. These treatment methods are quite different than those normally used for ARD. For waters such as CMM, precipitation of the metals as hydroxides, like for ARD, is often the method of treatment.

Passive treatment studies have been done on all of the waters in Table 3. For the cyanide waters, destruction of the cyanide in a sulfate-reducing system has been shown to be possible. The first study of this type was a laboratory study on the Gilt Edge water. The Fe, Cu and CN^- were all removed to below 1.0 mg/L (Filas and Wildeman., 1992). Laboratory studies on the Rain Tailings water proved in principle that the cyanide, arsenic, and selenium could be removed by either anaerobic or aerobic processes (Wildeman et al., 1994). An aerobic pilot system was built to treat this water and was reported to have removed the contaminants. For the RPM water, laboratory studies showed that the arsenic in the water can be removed by sulfate reduction and by the use of zero valent iron (Pinto, at al., 2001). These methods of removal are currently being

used in a pilot scale study. Finally, the CMM water is unusual because it has large concentrations of Zn and Mn, hardly any Fe and Al, and has a pH close to 7. The treatment objectives for this water are to bring the Zn and Mn down to 1.0 mg/L. Currently, sulfate reduction is being tried with pre-treatment cells using limestone and cement clinker to reduce the concentrations of Zn and Mn as much as possible before the sulfate reduction step.

Residual Waters

Table 4. Concentrations in mg/L of constituents in typical examples of residual waters associated with mining operations.

	Wyoming	Coal	Oil Shale	Refinery
pH	8.2	7.1	7.9-8.8	7.8
Na	800	940	1000	180
K	92	3	743	82
Ca	260	290	47	160
Mg	34	100	33	170
Cl	1040	1000	69	350
SO ₄	900	1600	3000	600
Alk	280	200	371	
TDS	3500	4200	5300	

Table 4 contains four waters that are representative of the residual water category of MIW. The term residual is used because the constituents in the water represent what is left when everything else is easily removed. However, the source of the constituents in these waters probably is due to the water interacting with soluble salts either in the overburden or in the mineral deposit. The Wyoming water comes from the Naval Oil Reserve. The Coal water is from Illinois and is ground water that has flowed through a coal waste pile. The Oil Shale water is from Colorado and is the residual water from oil shale retorting. The refinery water is contaminated ground water from an oil refinery in Oklahoma. The chemistry of residual waters is characterized by high values of TDS, alkaline pHs, and high concentrations of sulfate, which is often flagged as the contaminant of concern.

Treatment of Residual Waters

The treatment objectives for residual waters usually focus on the total dissolved solids or the sulfate. Both of these parameters have regulatory limits that are often ignored or dealt with by that adage that “the solution to pollution is dilution”. However, in the last few years more requests are coming forward for treating sulfate to the drinking water limit of 250 mg/L or to a limit for agricultural waters or ground waters of 500 mg/L. That there are no references for this section attests to fact that standard methods for treatment of this type of MIW are scarce and expensive. The International Network for Acid Prevention (INAP) funded Lorax Environmental to do a review of the treatment of sulfate and their report is available on the Internet (ADTI, 2003). The report is an excellent summary of technologies that are available. In the review, two observations stand out:

All the recommended options from reverse osmosis to sulfate reduction are active or semi-passive methods and truly passive methods for sulfate reduction are not now available.

The leader in the removal of sulfate is South Africa. Because of a lack of water resources, this country has put considerable funds into the removal of sulfate from MIW so that the water can be used for agriculture and drinking water (Pulles, et al., 2003).

Typical passive sulfate reduction systems do not need to reduce that much sulfate for metals removal (Machemer et al., 1993, Wildeman and Updegraff 1998, ADTI, 2003). Even in laboratory studies where sulfate reduction is allowed to proceed for a long time, it is difficult to reduce the concentration of sulfate to below 250 mg/L (Wildeman, et al. 1994). The best attempt at a passive system is the four stage sulfate reducing / sulfide oxidizing system that has been developed by Pulles and others (2003). Consequently, at this time passive treatment of residual waters is not an option.

Conclusions

Considering other types of MIW besides ARD opens the door to many other treatment possibilities than the addition of alkalinity. When this broader category of waters is considered, there are a number of treatment issues that have to be kept in mind:

- The necessity to keep in mind cyanide complexes in mineral processing waters and other metal complexes in marginal waters.

- The need for a low cost and hopefully passive method to remove sulfate from residual waters.
- The need to find materials that will passively provide large amounts of alkalinity to ARD over an extended period of time.
- The ability to remove contaminants to aquatic concentration limits even when flows are large.

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