ROLE OF ACCELERATED OXIDATION FOR REMOVAL OF METALS FROM MINE DRAINAGE[1]

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Abstract. The kinetics of iron oxidation can dictate the effectiveness of both passive and active mine drainage treatment systems. Iron oxidation rates can be improved by increasing pH and by aeration. Devices that aerate mine water may also increase pH in many mine waters by causing dissolved carbon dioxide to out-gas. This paper briefly documents several case histories where accelerated oxygen transfer was used to reduce water treatment costs. At two sites where the water was net alkaline, AMDTreat was used to calculate comparative costs for the Maelstrom Oxidizer and conventional passive treatment systems. This comparison indicated that using the Oxidizer at those two sites decreased the land required for settling ponds by a factor of ten to twenty and decreased capital and maintenance costs by over 50% due to the high iron loading. The system was also effective in treating acidic mine water; a cost comparison at one site indicated a chemical cost savings of 46%.

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Introduction

The kinetics of iron oxidation can dictate the effectiveness of both passive and active mine drainage treatment systems. Iron is the most common contaminant of concern in mine water, but is present in solution as ferrous (Fe^{2+}) iron, which may or may not be complexed with other ions. For efficient and stable iron precipitation, the Fe^{2+} must be oxidized to ferric iron (Fe^{3+}), which readily hydrolyses and precipitates in near-neutral water. Iron oxidation depends on the concentration of dissolved oxygen (D.O.), Fe^{2+}, and hydroxide (OH^-), and is typically represented by some version of the following equation:

$$-d[Fe^{2+}]/dt = k_{Fe}\,[Fe^{2+}]\,[O_{2\,(aq)}]/[H^+]^2 \qquad (1)$$

where: $k_{Fe} = 3x10^{12}$ (mol/L)/min, at 20º C (room temperature); $[Fe^{2+}]$ = the concentration of Fe^{2+}, in mol/L; $[O_{2\,(aq)}]$ = the concentration of D.O., in mol/L; and $[H^+]$ = the concentration of hydrogen ions, again, in mol/L (Stumm and Lee, 1961; U.S. Environmental Protection Agency, 1983). You will note that one of the terms, $[H^+]$ is squared, which means that an increase in pH of 0.5 standard units increases the oxidation rate 10 times, so that an increase in pH from 6 to 7 increases the oxidation rate 100 times.

However, Hustwit et al. (1992) pointed out that equation (1) is only valid at relatively low concentrations of Fe^{2+}; oxygen is consumed as the Fe^{2+} oxidizes, and even if the water was fully saturated with oxygen initially, by the time that about 63 mg/L of Fe^{2+} is oxidized, all of the oxygen initially dissolved in the water is gone. In general, oxygen transfer into mine water becomes the rate-limiting step.

In active treatment plants, mechanical aerators are used to introduce air into the mine water but these are not very efficient, forcing treatment plant operators to accelerate iron oxidation by adding more alkalinity (typically, lime) (Ackman and Kleinmann, 1991). Alternatively, sedimentation basins sometimes serve a dual purpose, as oxidation ponds, but the slow rate of diffusion of oxygen into water means that this can require large areas of land.

The same limitations constrain the design of passive treatment systems, where high iron loads are extremely difficult to deal with (Hedin et al., 1994). Even if small waterfalls or riffles are constructed between the wetland areas, large areas of land have to be converted to aerobic wetlands.

This paper briefly describes a few sites where an alternative aeration device, the Maelstrom Oxidizer, has been used to accelerate oxygen transfer. A side benefit of the system is that the turbulence in the device also accelerates the degassing of any dissolved carbon dioxide (CO_2) that may be present, which increases the pH.

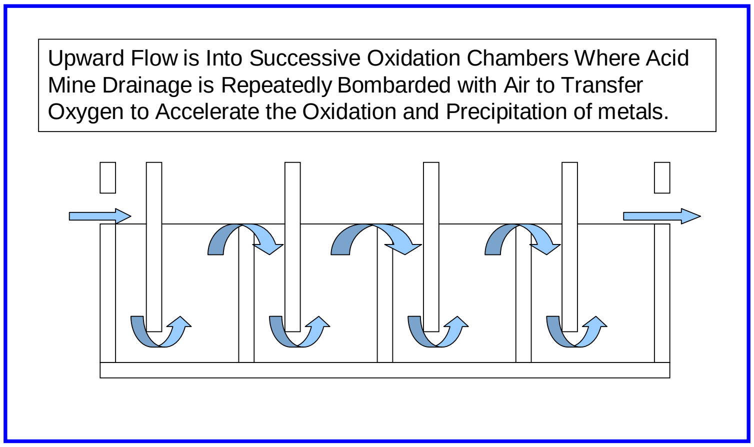
Method and Apparatus for Accelerated Oxidation

Maelstrom Oxidizer

The Maelstrom Oxidizer is a commercially-available, gravity-flow system that transfers oxygen into water by injecting high volumes of low-pressure air by means of a blower, which is the only moving part in the system. It differs from most mechanical aerators in that as oxygen is consumed by oxidation, it is replenished in subsequent reaction chambers to maintain oxygen saturation. It creates wake flow turbulence that out-gasses carbon dioxide. Every gallon of mine drainage flows sequentially through the system and oxygen saturation is achieved within minutes.

Figure 1. Maelstrom Oxidizer

Maelstrom Oxidizer Flow Pattern



Upward Flow is Into Successive Oxidation Chambers Where Acid Mine Drainage is Repeatedly Bombarded with Air to Transfer Oxygen to Accelerate the Oxidation and Precipitation of metals.

Figure 2. Flow pattern through the Maelstrom Oxidizer

Case Histories

Penn Allegh Mine

The Penn Allegh Mine, located in western Pennsylvania, had a mine water outbreak that was polluting a clean stream. The mine had been out of operation for many years, but the Penn Allegh Coal Co. was still in business. The initial discharge water contained, on average, 130 mg/L of total iron. The decision was made to pump water from the mine to lower and maintain the mine pool level below the breakout level. The Maelstrom Oxidizer shown in Fig. 1 was installed to treat the 1,890 L/min (500 gallons/minute (gpm) of discharge water. Once the mine pool was lowered, the average total iron in the discharge decreased to 105 mg/L. The water was alkaline (238 mg/L, as $CaCO_3$) but contained only 0.9 mg/L of D.O. Passage through the Maelstrom Oxidizer increased the measured D.O. to 9 mg/L, and increased the pH to 7.2 Fig. 2. The water then flows into two sedimentation ponds, where the sludge settles in a compact area (Budeit, 2001).

Given the fact that the water is net alkaline, one might wonder if the water could have been more cost effectively treated using an aerobic wetland. The two options were compared (Table 1), using the actual costs (where available) for the Maelstrom Oxidizer, and the costs of the passive system, as calculated using AMDTreat, a computer program available for downloading (http://amd.osmre.gov/amdtreat.asp) from the U.S. Office of Surface Mining (McKenzie, 2005). AMDTreat considers over 400 variables in estimating costs, and uses default values if cost data are not available; this aspect was used to calculate some of the costs for the installation of the Maelstrom Oxidizer. Specifically, the costs of excavating the ponds, clearing and grubbing the land, site engineering and design, etc. were calculated, using the same cost values as was used to estimate the costs of the passive treatment system. Annual maintenance costs include sludge removal and electric power (for the Maelstrom Oxidizer) (Budeit, 2003)

Table 1. Penn Allegh cost comparison

	Passive Treatment	Maelstrom Oxidizer
Land area required	2.3 ha (7 acres)	.0836 ha (0.25 acres)
Capital cost	$399,000.00	$166,000.00
Annual maintenance	$32,000.00	$6,400.00
$ per 3,780 L (1,000 gallons)	$0.18	$0.056

This site has now been in operation for more than 5 years (Fig. 3). It is monitored monthly by the Pennsylvania Department of Environmental Protection and has never been in violation of its permit. No chemicals are used to treat this net alkaline flow. Total iron in the effluent is 0.6 mg/L in all seasons.

Figure 3. Penn Allegh Pond 1.

Dundee Outfall---Nanticoke Creek---Pennsylvania

The Dundee Outfall (Fig. 4) has an average flow of 13,230 L (3,500 gallons) per minute and an estimated maximum flow of twice that. It is net alkaline with a near-neutral pH of 6.2 and contains 60 mg/L of iron. The U.S. Army Corps of Engineers published their study of 26 alternative methods for treatment of the water at this site for public review; (Nanticoke Creek Report published by the U.S. Army Corp of Engineers 2005). The Maelstrom Oxidizer was recommended for implementation at this site and at the Espy Run site.

Figure 4. Dundee Outfall---Nanticoke Creek

The costs were compared to the costs of passive treatment in the same way as in the previous example (Table 2).

Table 2. Dundee Outfall cost comparison

	Passive Treatment	Maelstrom Oxidizer
Land area	19 ha (57 acres)	1.6 ha (4.8 acres)
Capital cost	$3,203,935	1,094,698
Annual maintenance	$90,058	$18,067
$ per 3780 L (1000 gallons)	$0.119	$0.035

<u>Maple Creek Mine</u>

The Maple Creek Mine, in Pennsylvania has acidic water with a pH of 3.1 and an average total iron concentration of 1,800 mg/L. The treatment flow is 1,850 L (500 gallons) per minute. A Maelstrom Oxidizer was installed with a 15 horse power blower to supply the oxygen demand of 64 pounds per hour. Sodium hydroxide (NaOH) was used to increase the pH. In Fig. 5, the water is turning green in the first reaction chamber. As it leaves the second reaction chamber, 15 seconds later, it is already brown from the oxidation of the iron Fig 6.

Figure 5. Maple Creek Mine Maelstrom Oxidizer

Figure 6 Maple Creek---Outflow to Pond

Canterbury Mine

When the owner of the Maple Creek Mine shut down operations, the system was dismantled and trucked to his Canterbury Mine (Fig. 7), where it was retrofitted into his existing treatment system. Raw water at this site contains manganese as well as iron. The site has a lime silo and uses lime slurry in the treatment process. The site also had a high pressure aeration system, which was replaced by the Maelstrom Oxidizer system. According to the operator, chemical costs were reduced 41%.

Figure 7. Canterbury Mine

Crossville Coal Pit---Tennessee

A 150 foot deep pit reportedly contained 265 million L (70,000,000 gallons) of acidic water with a pH of 2.9, 150 mg/L of total iron and 148 mg/L of total manganese. The pit was overflowing and in violation of U.S. Office of Surface Mining and Tennessee Department of Environment and Conservation permits. Within six days of initial contact, Environmental Solutions LLC installed a Maelstrom Oxidizer system and was processing 7.56 million L (2.0 million gallons) per day (Fig. 9). Sodium hydroxide was used to treat the water. The white arrow in Fig. 8 shows the location of a 3 meter (10 foot) berm that was added after the pit overflowed. The photo was taken prior to start up of the Maelstrom Oxidizer system.

Figure 8. Crossville Coal Pit

Figure 9. The 7.56 million L (2 million gallons) per day Maelstrom Oxidizer

Take note of the coloration of the settling pond immediately below the white arrow in Fig. 9. The iron and manganese is already oxidized and settling out in the compact area at the front of the pond. At this point in time, the treatment system has been operating 24 hours a day for three weeks.

It became readily apparent that the 1.33 ha (4.0 acre) pit was drawing water from 30.66 ha (92 acres) of underground mine pools. A second system was fabricated and brought to the site to double the treatment capacity to 15.12 million L (4.0 million gallons) per day Fig. 10. The effluent pH is now 8.4, and the iron and manganese concentrations are within the permit values.

Figure10. 15.1 million (4.0 million) gallon per day system

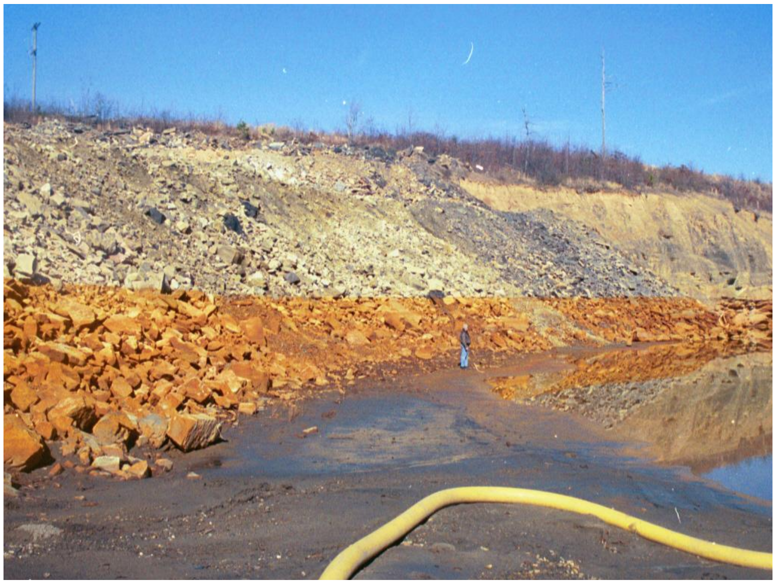


Figure 11. Crossville Coal Pit after 60 days.

Espy Run Wetland

The Espy Run wetland (Fig. 12) is part of the Nanticoke Creek Project in central Pennsylvania. The wetland has been in place for several years, and treats a total flow of 189 to 756 L (50 to 200 gallons) per minute. Average total iron is 19.3 mg/L, dissolved iron averages 18.5 mg/L, and average net alkalinity is 288 mg/L (as $CaCO_3$). It has a pH of 7 and high alkalinity, so it would appear that all of the iron should be removed, but the effluent contains 11.9 mg/L (57% of the original 19.3 mg/L).

Figure 12. Espy Run wetland

The system is obviously not operating efficiently, and so the U.S. Environmental Protection Agency has provided funds to assist the U.S. Army Corp of Engineers in installing a Maelstrom Oxidizer.

Conclusions

Enhancing oxygen transfer can be critical to successful water treatment at sites with high iron and manganese concentrations. Based on cost comparisons for two such sites, it appears that accelerated oxidation can be a cost-effective alternative to strictly passive treatment when the water is net alkaline but the iron loading is high. Land area can be reduced by a factor of 10 or more, capital and maintenance costs can be reduced by 50% or more.

Installing a Maelstrom Oxidizer at a conventional active treatment facility reduced chemical costs at that site by 46%. The system was also effective in meeting permit requirements at all of the other sites that were reviewed, though since it did not replace a more conventional system, actual cost comparisons are not possible.

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