

USE OF OZONE TO REMEDIATE MANGANESE FROM COAL MINE DRAINAGE WATERS¹

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Abstract. Manganese is an aesthetically undesirable metallic element that is difficult to remove from mine drainage that has acidic to neutral pH. In spite of the thermodynamic prediction that oxygen in the atmosphere or in solution should oxidize dissolved manganese (Mn^{2+}) to an oxide or a hydroxide, this does not happen in acidic aqueous solutions. The capability of ozone to oxidize and precipitate manganese as an oxide was proven in bench-scale experiments at U.S. Geological Survey (USGS) labs, and the process was granted U.S. patent no. 6,485,696. Ozone (O_3) oxidizes Mn^{2+} to MnO_2 (Mn^{4+}) as follows:



(Gibbs free energy $\Delta G = -38.985$ kcal at 10^0 C; Roine, 1999).

In order to test the method in the field, the USGS installed a pilot-scale treatment facility at the Little Toby Creek Treatment Plant in Elk County, PA, which is a limestone-based acid mine drainage treatment plant run by the Pennsylvania Department of Environmental Protection. The manganese treatment system was commissioned in March 2004. Ten pairs of mine drainage water samples, collected prior to and following ozone treatment, were analyzed for manganese and trace metals. In addition to Mn, the treatment should also precipitate as oxides or hydroxides: iron, nickel, cobalt, lead, silver, palladium, bismuth and thallium, if present. Dissolved manganese concentrations in the treated effluent were lowered by about 98 percent, iron by 99 percent, cobalt by 78 percent, and nickel by 8 percent. Measurements of Eh-pH values in the water samples subjected to ozone treatment demonstrate a shift from the Mn^{2+} field into the manganese dioxide (Mn^{4+}) stability field.

Additional Key Words: acid mine drainage, water treatment, manganese

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Introduction

Current treatment systems for the removal of dissolved Mn from mine drainage include both passive and active methods. Active treatments often use sodium hydroxide, which can add significantly to operating expenses. The U.S. Geological Survey (USGS) developed a new active treatment method to remove dissolved manganese (Mn^{2+}) from mine drainage water using ozone (Sato and Robbins, 2000) and this method was granted US patent number 6,485,696 in November 2002. Following successful bench-scale testing in USGS labs, a pilot-scale system was built by Ozotech, Inc. in Yreka, CA. A U.S. Geological Survey proposal was submitted to Southern Alleghenies Conservancy (<http://www.saconservancy.org>) to test the pilot-scale system at the Little Toby Creek Treatment Plant, operated by the Pennsylvania Department of Environmental Protection (PADEP). The system was shipped to the plant in July, 2003 where final plumbing and wiring were completed; operation commenced in March 2004 (Tewalt et al, 2004).

The Little Toby Creek Treatment Plant is located near the village of Dagus Mines in Elk County, PA. The plant is located on a hillside and takes advantage of gravity flow to move drainage from two abandoned underground mines and one partially reclaimed surface mine through limestone treatments contained in several buildings. The USGS treatment system is located in the lowermost building of the plant. The sources of abandoned mine drainage are likely in the Dagus coal, also known as the Lower Kittanning coal, in the Allegheny Formation (Keystone Coal Industry Manual, 2004). Although dissolved Mn^{2+} and aluminum (Al) are present in the drainage, iron (Fe^{2+}) is more predominant.

The Little Toby Creek treatment plant uses limestone neutralization to raise pH so that iron (Fe) can be precipitated. Collected sludge is disposed of at a nearby operating mine. The State of Pennsylvania is working with industry to try to make use of the sludge byproducts created from mine drainage treatment systems that currently cost the State about \$12 million per year. The sludge can be used as pigment or as a source to recover valuable metals and minerals (Platts, 2004). This paper summarizes the results of testing the abiotic oxidation of dissolved Mn^{2+} and the precipitation of manganese dioxide during a run of the system in May 2004.

Methods

Theory

In oxidizing aqueous environments, the slowness of molecular oxygen (O_2) reactions with dissolved metals (such as Fe^{2+} and Mn^{2+}) causes complications in treating mine drainage. Fig. 1 shows the Eh-pH stability fields for Mn species at conditions of 25° C and at 1 bar pressure (Sato and Robbins, 2000). Additionally, this diagram shows dashed lines labeled [a] through [e] that represent different equilibrium conditions for system parameters. Line [a] indicates the boundary between hydrogen gas (H_2) and water at 1 bar (H_2 gas is stable below the line and bound in water above the line). Line [b] is the oxygen gas (O_2) and water equilibrium boundary (below the line oxygen is bound in water and above oxygen is gaseous). If free oxygen is present, oxidation starts occurring at line [c] and above. However, in the natural environment, oxidation of Mn by oxygen progresses only to line [d]. An example of this phenomenon is sea water, which has been in contact with oxic air for a few billion years, but for which Eh values remain between lines [c] and [d] (Sato, M., 1960; Bass Becking et al., 1960). Theoretically, if the Eh can be shifted toward line [b], the dissolved Mn^{2+} should be precipitated as MnO_2 . The

maximum redox potential obtainable by ozonated air is represented by line [e], i.e. the practical upper limit of Eh for a solution saturated with ozonated ambient air. Above line [e], permanganate (MnO_4^{1-}) is the dominant species.

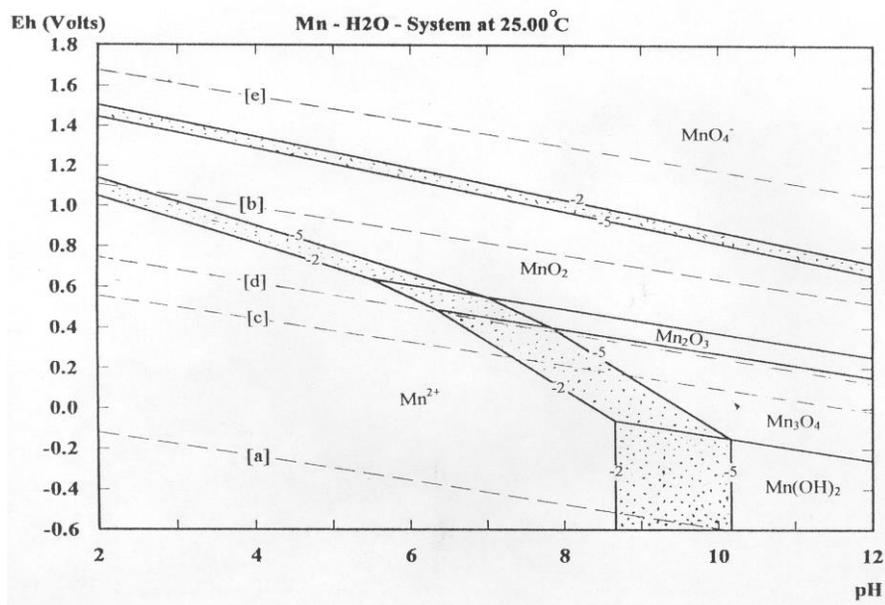
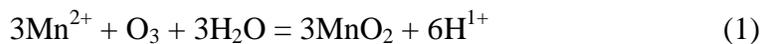


Figure 1. Mn-H₂O stability fields at 25 degrees C and 1 bar pressure (approximately 1 atmosphere). Lines [a] through [d] indicate redox potential lines for the hydrogen/oxygen/water system (from Sato and Robbins, 2000). Line [e] represents the maximum redox potential obtainable by ozonated air. See text for further explanation. Patterned areas represent Eh-pH areas of active dissolution/precipitation of MnO₂; the numbers on these lines are the powers of activity for Mn²⁺ or MnO₄¹⁻ ions.

In aqueous solutions, O₂ kinetically prefers to form hydrogen peroxide (H₂O₂) as an intermediate (Latimer, 1954, p. 43). Bench-scale tests showed that H₂O₂, being inherently unstable, is quickly decomposed back to water and oxygen. The decomposition is accelerated in the presence of dissolved Fe and Mn, which act as catalysts for the reaction. Direct addition of H₂O₂ to mine drainage failed to precipitate Mn in acidic solutions. Ozone (O₃) is a much stronger and faster oxidizer than either O₂ or H₂O₂. In the laboratory experiments with acidic solutions, O₃ rapidly precipitated manganese, iron, nickel, cobalt, lead, and silver metallic oxides (Sato and Robbins, 2002). Ozone (O₃) oxidizes Mn²⁺ to MnO₂ (Mn⁴⁺) as follows:



(Gibbs free energy $\Delta G = -38.985$ kcal at 10^oC; Roine, 1999). Release of H¹⁺ during the reaction lowers the pH of the treated water. Ozone should be capable of oxidizing nine metals with similar Eh-pH stability fields (manganese, iron, nickel, cobalt, lead, and silver, palladium, bismuth and thallium) if they are present in mine drainage water.

System description

The USGS pilot-scale system pumps about 25 gallons per minute (gpm), less than one-tenth of the average flow of water at the Little Toby plant, into a 345 gallon fiberglass reactor tank

(Fig. 2). The ozone generator system uses an air compressor to push air through an air dryer and into an oxygen concentrator composed of two tanks of zeolite material. The oxygen concentrator uses a pressure swing absorption mechanism to remove ambient nitrogen to less than 10 percent volume of the processed air (Fig. 2). The oxygen-enriched air is stored in a tank and fed to two ozone-generating cells, capable of producing 8 pounds of ozone per day. The ozone flows through Teflon tubing and is injected through a Venturi injector into recirculating water within the reactor tank, where dissolved Mn oxidizes to form very fine-grained MnO₂ particles. Ozonated water and precipitate flow out of the bottom of the reactor tank into the filtration/collection system. The sand filtration system uses air, split off from the compressor, to lift and scrub the precipitate from the sand. Partial recovery of the MnO₂ precipitate is accomplished with a fabric-lined (Tyvar) trough. Initial system design called for two sedimentation ponds to capture the precipitate for possible resource recovery, but there was insufficient space available for installation of ponds at the site. The current footprint of the pilot system is 15 by 17 feet.

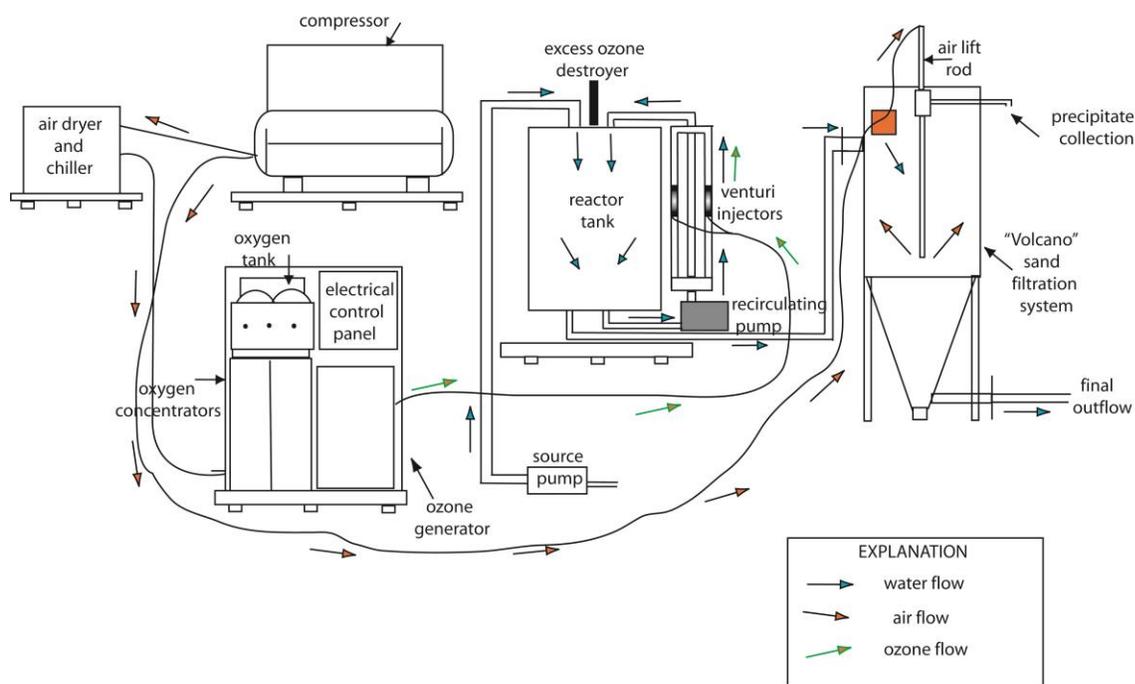


Figure 2. Schematic diagram of ozone remediation system indicating air, water and ozone flow (not to scale).

In the laboratory bench-scale experiments prior to construction of the pilot-scale system, ozone was continuously pumped into the reaction vessel and the mine drainage solution became saturated in ozone. However, the pilot-scale system was designed with a controller that would shut down and restart ozone production and flow into the reactor tank at a preset oxidation-reduction potential (ORP) value in millivolts (mv). An ORP meter in the final outflow stream is connected to a digital display controller for the ozone generator, where the cutoff value can be set.

Results and Discussion

Data collection

The Little Toby Creek Treatment Plant pipes mine drainage water from three intakes (designated A, B and C) into its limestone treatment system. For the water year June 2003 through June 2004, average pH values for intakes A, B and C were 2.97, 3.67, and 4.66 respectively and average Fe concentrations were 41.1, 3.78 and 17.84 mg/L (ppm) respectively (data from PADEP, written communication, 2004). Flow rates from these intakes are variable depending on precipitation. Average water quality of PADEP's final effluent from the polishing lagoon at the plant was 6.01 for pH and 11.6 mg/L for Fe for the same water year (PADEP, written communication, 2004). Mn concentrations are not determined for the plant by PADEP.

The ozone remediation followed limestone treatment, so the pH of input water to the USGS system was approximately 6.0. In May, 2004 the USGS collected ten pairs of water samples. The first sample pair was a baseline sample taken from the water flow before and after the system, but with no ozone being generated. Nine other pairs of samples were taken pre- and post-ozone treatment. All water samples were filtered. One subset was acidified to preserve metal concentrations and analyzed by the USGS for trace element concentrations by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). Non-acidified samples were also collected for anion analysis by ion chromatography (IC). Table 1 shows the analytical values for Mn, Fe, and Al in water samples collected pre- and post-ozone system, plus arithmetic mean values for the nine sample pairs. Overall removal averages about 98 percent for Mn, 99 percent for Fe; and about 66 percent for Al. The concentration of Al was also lowered in the baseline sample that had no ozone treatment, so it is likely that Al is precipitating mostly in response to circa 6.0 pH levels resulting from limestone treatment.

Excess ozone was evident during initial sample collection, so the cutoff value for ozone generation was reset from the manufacturer's value of 700 mv to 600 mv prior to collecting samples 4 through 7 shown in Table 1. Tracking the stabilization range for ORP values on the controller's visual display led to another reduction of the cutoff value to 450 mv prior to the collection of samples 8 and 9 shown in Table 1. All samples were collected with the system's status at approximately the same conditions, when the ORP sensor was above the critical value and the cells were not actively producing ozone. There is no obvious reason for the decrease in the amount of Mn and Al precipitation in the last sample collected.

Table 1. USGS analytical results for dissolved trace metal concentrations in water samples (measured in parts per billion, ppb) for pre- and post-ozone treatment system. In table 1, the ORP setting was set at 700 mv for samples 1 through 3; ORP at 600 for samples 4 through 7; and ORP at 450 for samples 8 and 9. ‘Less than’ values assigned detection limit values in order to calculate means.

<i>Sample</i>	<i>Mn pre</i>	<i>Mn post</i>	<i>Fe pre</i>	<i>Fe post</i>	<i>Al pre</i>	<i>Al post</i>
Baseline	12000	12000	12700	12200	131	84.3
1 - 5/26 10AM	11800	301	12400	<20	155	60.8
2 - 5/26 11AM	11700	141	12400	72.7	139	63.6
3 - 5/26 12PM	11800	27.7	12500	<20	162	53.1
4 - 5/26 3PM	11700	112	12400	115	83.7	61.9
5 - 5/26 4PM	11700	28.4	12000	<20	178	66.2
6 - 5/27 10AM	11600	212	12000	<20	140	52.9
7 - 5/27 12PM	12400	160	15600	27.8	961	115
8 - 5/27 2PM	11600	26.6	12300	<20	150	50.7
9 - 5/27 4PM	11400	517	12100	21.4	173	179
Mean (of 9)	11600	156	12640	37.4	227	78.1

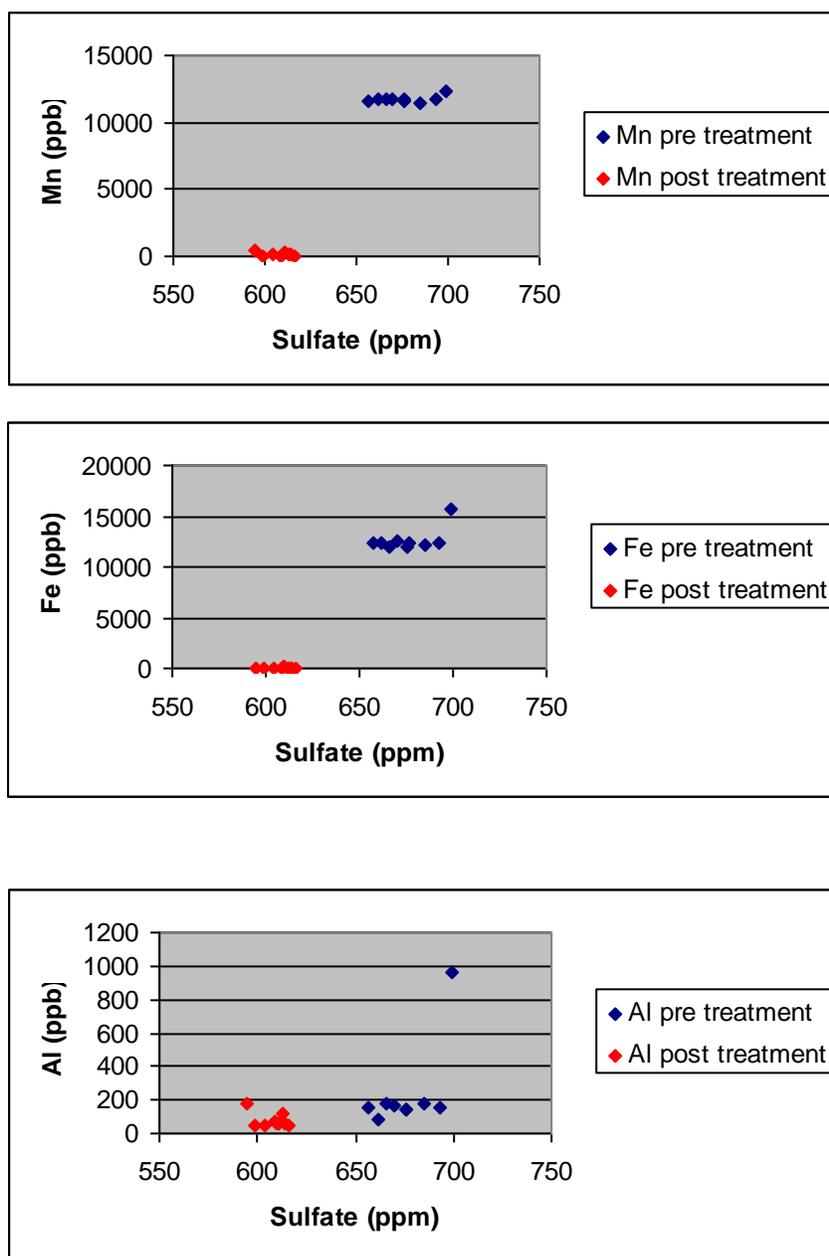


Figure 3. Plots of dissolved Mn, Fe and Al concentrations (in parts per billion, ppb) versus SO_4^{2-} (in parts per million, ppm) for pre- and post-treatment water samples.

The effect of ozone treatment is shown in Fig. 4, a plot of Eh versus pH generated from field measurements of pH and ORP taken in conjunction with the water sampling program. ORP values were constantly changing as measurements were taken, so an average was calculated from the range of values in a 30 second timeframe. Eh values were calculated from the ORP readings, converted to volts, and corrected for temperature (Nordstrom, 1977). The plot shows

the shift into the MnO_2 stability field for post-ozone treatment final outflow water samples (purple squares).

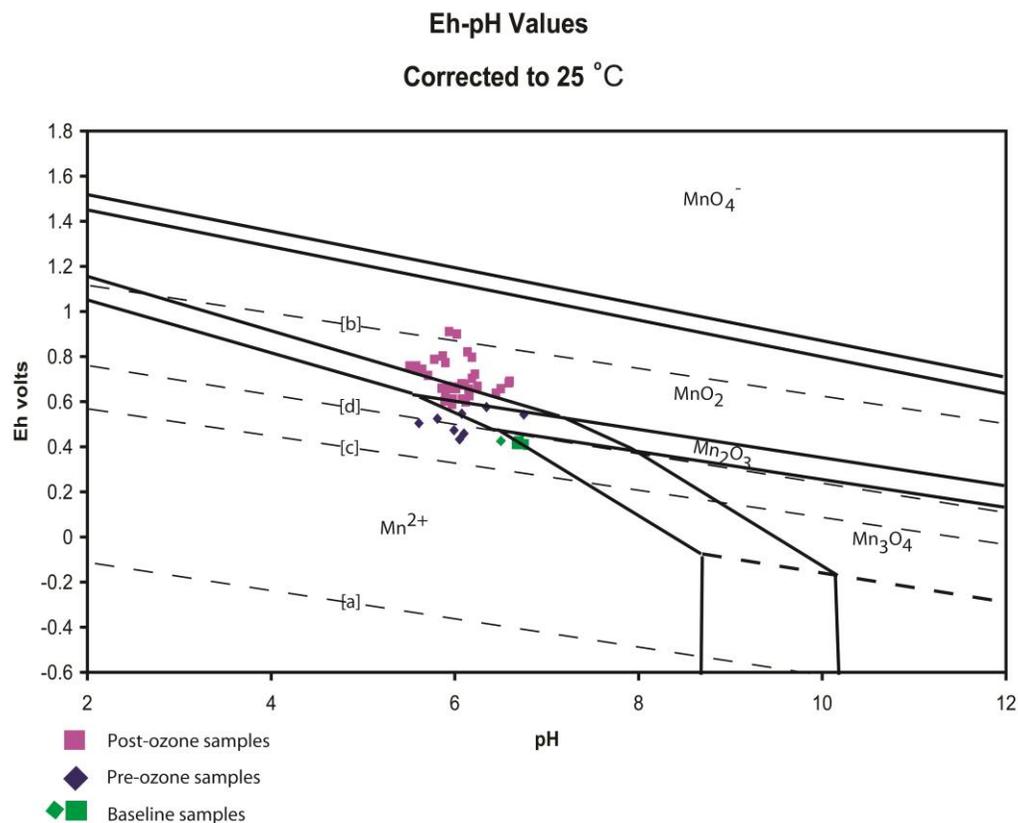


Figure 4. Plot of Eh (in volts) and pH from field measurements for baseline, pre- and post-ozone treatment samples. Samples at three different locations in the post-ozone effluent were measured, so there are 27 post-ozone points plotted. Dashed standard redox potential lines [a] through [d] are the same as those in figure 1.

Resource recovery

Although manganese concentrations of the Little Toby drainage are approximately 11,000 ppb (11 ppm) only a small volume is pumped into the reactor tank and ultimately (about 10 gpm) is passed by the sand filtration system onto the precipitate collection fabric. Thus only a small amount of Mn-rich sludge is recovered. Examination of the precipitate by scanning electron microscopy shows a poorly crystallized, fine grained material (Fig. 5a). The composition of the

precipitate is largely Fe and Mn, as shown by an energy dispersive x-ray spectrum (fig. 5b).

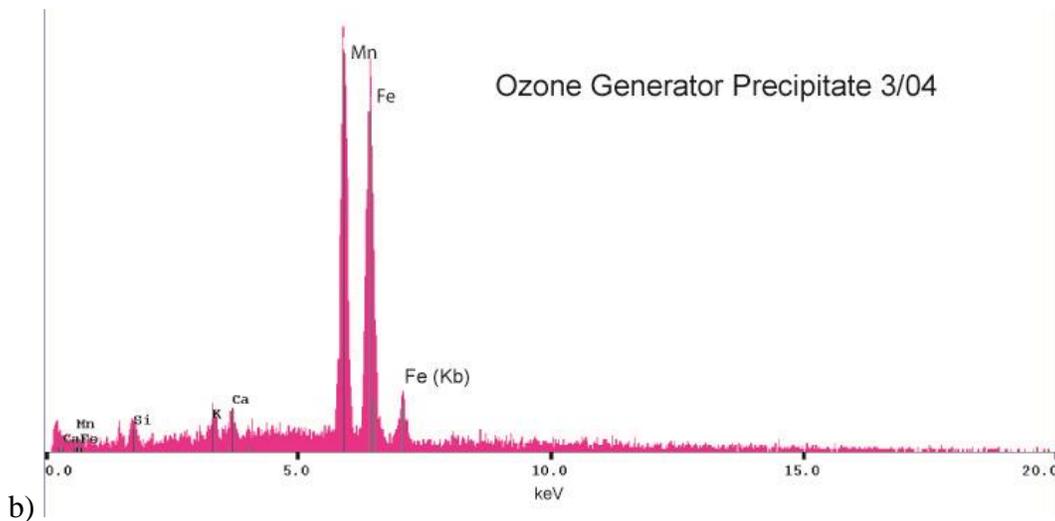
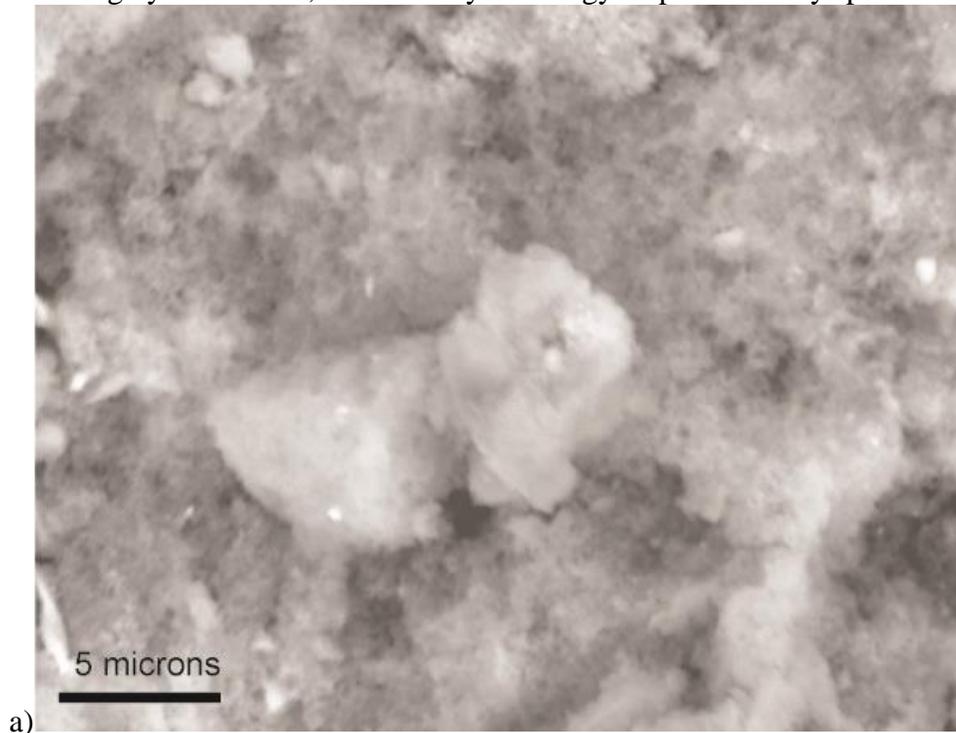


Figure 5a). Scanning electron micrograph of precipitate from treatment system; entire view is MnO_2 b) results of energy dispersive x-ray microanalysis showing peaks for Mn and Fe in precipitate collected in March, 2004. Fe (Kb) is the only visible beta peak. A complete analysis of the precipitate is not yet available.

Much of the precipitate is likely sub-micron in size, so that a large amount escapes the current filtration system, which was designed to capture 10-micron sized sediment at fairly low flow rates. Captured precipitate has a high water content; other mine sludges contain about 98

percent water (Ackman, 1982). Settling of MnO₂ solids in sedimentation ponds may still be a better method of capture.

Recovery of the MnO₂ precipitate was incomplete, but with improved capture efficiency and placement at another site with higher dissolved concentrations of Mn, commercial recovery of MnO₂ may be feasible. The economic aspects of this process could not be evaluated during the short test period of operation.

Conclusions

The pilot ozonation system successfully precipitated MnO₂ from mine drainage water and also precipitated dissolved Fe remaining after limestone treatment at the Little Toby Treatment Plant. Operation of the system confirms theoretical and bench-scale results for which a patent was granted to the USGS. Further work testing MnO₂ precipitation from acidic, instead of circumneutral, drainage is planned.

The present filtration system is inadequate to capture all of the solids created; recovery of precipitate could be enhanced through the use of sedimentation ponds or use of a capture system capable of filtering finer sediment sizes. Additionally, estimation of the settling rate and sludge volume generated by the system would be useful for determining improved capture methods.

Additional trials with longer operational times will be required to determine whether the resource recovery of Mn would be economically beneficial to promoting this remediation process.

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