REVIEW OF MANGANESE REMOVAL TECHNOLOGIES FROM COAL MINING-ASSOCIATED WATERS AND EVALUATION OF CORRESPONDING COSTS TO THE COAL MINING INDUSTRY

PRESENTED TO	PRESENTED BY
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Executive Summary

This report was prepared by Dr. William Burgos, Professor of Environmental Engineering at The

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Quality Division (PADEP WQD) to review water treatment technologies for the removal of manganese

(Mn) from coal mining-associated waters and to evaluate corresponding costs to the coal mining

industry. The Environmental Quality Board (EQB) adopted a proposed rulemaking that would update the

water quality standard for manganese on December 17, 2019. This proposed rulemaking includes the

following updates to 25 Pa. Code Chapter 93: 1) deleting the Potable Water Supply criterion of 1.0 mg/L

from § 93.7, Table 3 and 2) adding a more restrictive Human Health toxics criterion of 0.3 mg/L to §

93.8c, Table 5. This report includes: 1) summaries of measured concentrations of total Mn in waters in

the Commonwealth; 2) descriptions of mineralogical controls on the solubility of Mn in water; 3)

evaluations of treatment technologies for the removal of Mn(II) from coal mining-associated waters with

specific considerations regarding the size/flow rate of the sites; 4) recommendations for the most cost-

effective treatment technology for various size sites, and; 5) estimations of capital and operating costs

associated with these sites. Based on various water chemistry data sets (Cravotta, 2008; Cravotta and

Brady, 2015), Mn concentrations are <0.3 mg/L total Mn in 26% of permitted coal-mining/coal-

processing sites (n = 46), and <0.3 mg/L total Mn in 4% of abandoned coal mine drainage (CMD) outfalls

(n = 140). Presumably, permitted coal facilities with existing water quality-based Mn limits will be

required to achieve more stringent Mn limits once the 0.3 mg/L total Mn criterion is adopted into

regulation. Some of these facilities will likely need to adjust their existing operations to add Mn(II)

removal to their treatment systems. Few 'single-stage' treatment processes are available for the

simultaneous removal of acidity, iron, aluminum, and manganese. Instead, a dedicated 'sequential-

stage' treatment process, such as oxidative filtration, will likely be required following conventional

treatment of coal mining-associated waters. Because the current and proposed manganese water

quality criteria are based on total concentrations (i.e., unfiltered samples), the importance of adequate solids removal cannot be overstated, regardless of the specific technology selected for Mn(II) removal. A Mn(II) removal technology selection flowchart was developed based on mine water chemistry. Because treatment technology selection is also dependent on the size/flow rate of each site, recommended treatment technologies and associated costs were prepared for 'small' (Q = 50 gallons/minute; 25% of sites), 'average' (Q = 170 gal/min; 65% of sites), and 'large' sites (Q = 2,700 gal/min; 10% of sites). Costs for Mn(II) removal technologies were based on results from the US Office of Surface Mining Reclamation and Enforcement's (OSMRE) program AMDTreat and from discussions with technology vendors. There are approximately 706 mining sites in Pennsylvania with National Pollutant Discharge Elimination System (NPDES) permits that currently contain manganese monitoring and report requirements and/or manganese effluent limitations. Based on a reported distribution of site sizes and the different corresponding options for Mn(II) removal technologies, if all 706 sites needed to add unit operations for Mn(II) removal treatment, total costs to the industry caused by the proposed Mn water quality criterion were estimated to range from $0 (repurpose all existing unit operations) to $489 million in capital costs and from $32.7 million to $81.2 million in annual costs. However, it is highly unlikely that all 706 sites will need to add Mn(II) removal treatment and very likely that any site would select the most cost-effective treatment option. Therefore, a more refined estimate of <u>total costs to the industry caused by the proposed Mn water quality criterion would range from $137 to $143 million in capital costs and from $33.0 million to $46.2 million in annual costs</u> based on the assumption that 530 sites (i.e., 75%) will need to add Mn(II) removal treatment. If 50% of the sites (i.e., 353 sites) need to add Mn(II) removal treatment, total costs to the industry would range from $91.1 to $95.3 million in capital costs and from $22.0 million to $30.8 million in annual costs. Because the number of sites requiring additional treatment and the number of sites that may be able to utilize more cost-effective Mn(II) removal technologies are unknown, <u>there are considerable uncertainties with these costs estimates</u>.

1. Background

The purpose of this report is to review technologies capable of removing manganese (Mn) from coal mining-related discharges, and to estimate costs for the implementation and operation of these technologies. This report has been prepared for the PADEP WQD. Based on their own review of NPDES permits in Pennsylvania, there are approximately 706 mining sites with permits that currently contain manganese monitoring and report requirements and/or manganese effluent limits. The EQB is currently proceeding with a final-form regulation to adopt a more restrictive human health toxics criterion for manganese of 0.3 mg/L total Mn. The current water quality criterion of 1.0 mg/L total Mn is for the protection of the Potable Water Supply use and is not based on health effects. The current Best Available Technology Economically Achievable (BAT) effluent limitation guidelines (ELGs) for active surface and underground mining areas with acid mine drainage discharges and post-mining areas with underground acid mine drainage discharges are 2.0 mg/L total Mn as a monthly average, 4.0 mg/L total Mn as a daily maximum, and 5.0 mg/L total Mn as an instantaneous maximum.

The Pennsylvania Coal Alliance (PCA) submitted public comments on the proposed rulemaking regarding the proposed changes to the manganese water quality criterion and point of compliance, including a treatment technology report by their consultant Tetra Tech Inc. Based on Tetra Tech's report, PCA noted that 'the proposed rulemaking would impose significant, unnecessary costs to the coal mining industry.' Specifically, PCA claimed that capital improvements required to meet lower effluent limits for manganese 'are estimated to result in additional costs upwards of $200 million', and 'if the proposed criterion is adopted, annual treatment costs for the coal mining industry are estimated to increase by $44 to $98 million.'

The following sections will present information on manganese geochemistry and Mn(II) removal technologies to address some of the assumptions used by Tetra Tech in its approach to estimate costs to the coal mining industry to meet the proposed water quality criterion for manganese.

2. Manganese in the Environment

Manganese concentrations vary depending on the category of the water source – e.g., surface waters vs. groundwater vs. coal mine drainage (CMD) from surface mines vs. CMD from deep mines vs. CMD from coal-processing sites (Table 1). Geochemical characteristics of CMD also vary greatly depending on the coal seam and surrounding geologic strata, on whether the coal mine is abandoned or active, and other operational aspects. Manganese concentrations also vary considerably within each category.

Table 1. Concentrations of total manganese in coal-associated waters collected in Pennsylvania. All values are reported in mg/L total Mn.

Concentration distributions – percentile rank	Abandoned coal mine drainage (CMD) [1]	CMD influent to active coal sites [2]	CMD effluent from active coal sites [2]
10%	0.63	0.38	0.037
25%	1.4	2.2	0.23
50% (median)	2.4	8.3	0.91
75%	5.0	21	2.8
90%	11	47	7.3
# samples in dataset	140	46	46

1 – from Cravotta (2008a); 2 – from Cravotta and Brady (2015)

3. Mineralogical Controls on the Solubility of Manganese

The chemistry of manganese is complex and affects its removal from water. Manganese can exist in a variety of oxidation states including 0, +2, +3, +4, and +7. Mn(0) is elemental manganese and Mn(VII) is permanganate, a strong oxidant. Mn(II) is the most common oxidation state of dissolved manganese and primarily exists as the divalent cation Mn^{2+}. Depending on the pH of the water and the amount of alkalinity, Mn(II) can also exist as the soluble complexes $Mn(OH)^+$ and $Mn(CO_3)(aq)$. These complexes will increase the solubility of Mn(II) minerals such as manganese hydroxide ($Mn^{II}(OH)_2(s)$) and affect chemical precipitation water softening for Mn(II) removal. Mn(III) and Mn(IV) are typically present as sparingly soluble manganese oxides such as manganate, $Mn^{III}OOH(s)$, and manganese oxide, $Mn^{IV}O_2(s)$. For this report, manganese(III/IV) oxides will be referred to as $MnO_x(s)$.

The solubility of Mn(II) depends on the formation of $Mn^{II}(OH)_2(s)$, $Mn^{III}OOH(s)$, or $Mn^{IV}O_2(s)$ and the solubilities of these minerals are strongly pH-dependent (Figure 1). For chemical precipitation water softening to remove Mn(II) to 0.3 mg/L total Mn, the pH of the water must be raised to ca. pH 10.5. In comparison, because oxidized $Mn^{III}OOH(s)$ and $Mn^{IV}O_2(s)$ are much less soluble than $Mn^{II}(OH)_2(s)$, Mn(II) concentrations far below the proposed water quality criterion of 0.3 mg/L total Mn can be achieved at pH values as low as ca. pH 5.
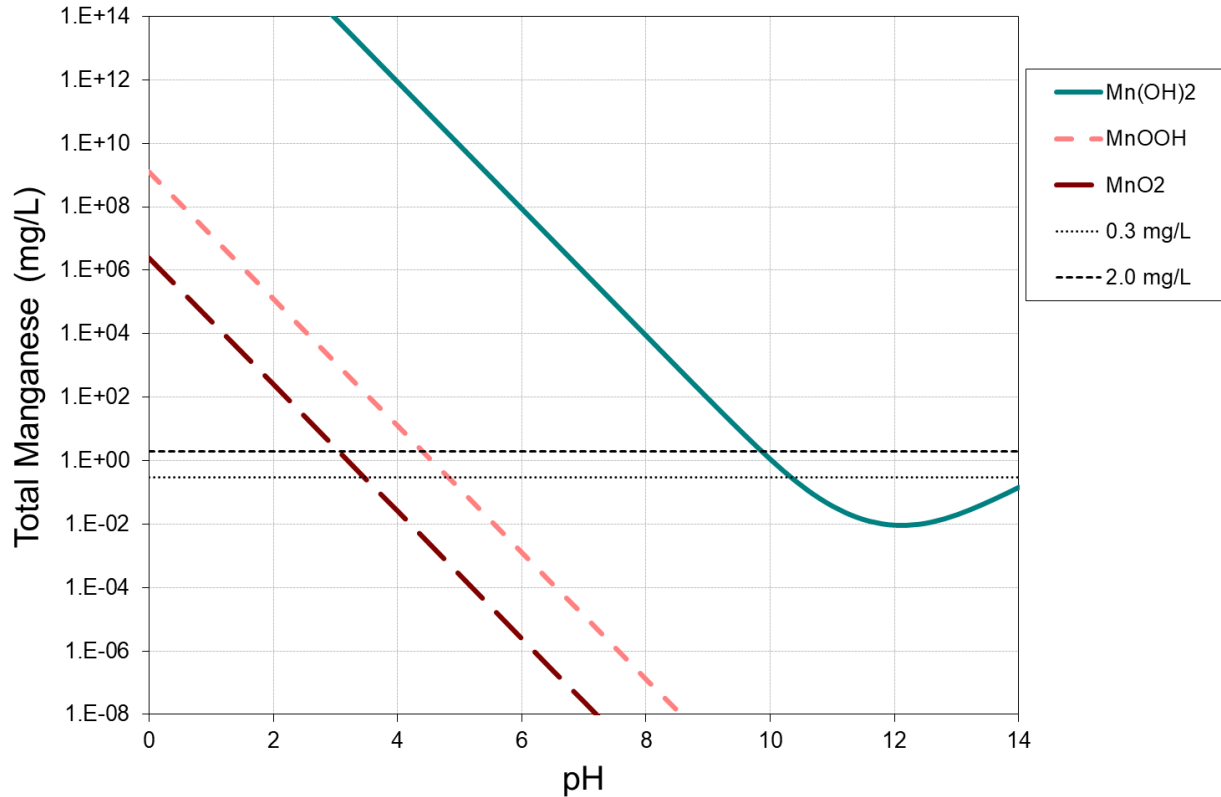
Figure 1. Comparison of pH-dependent solubilities of manganese minerals. Conceptually, at a specified

pH, dissolved concentrations above the mineral-equilibrium lines will precipitate out of solution until

equilibrium is attained. Treatment system pH can be adjusted to control dissolved Mn(II)

concentrations. Manganese hydroxide ($Mn^{II}(OH)_2(s)$) is the targeted phase to form in chemical

precipitation water softening. Oxidized forms of manganese such as manganate, $Mn^{III}OOH(s)$, and

manganese oxide, $Mn^{IV}O_2(s)$, are the targeted phases to form in oxidative filtration. The oxidized

Mn(III/IV) minerals are less soluble than $Mn^{II}(OH)_2(s)$ at all pH values. Mineral solubilities are based on

thermodynamic data provided in the WATEQ4F chemical speciation code from USGS. Horizontal lines

show Mn(II) concentrations of 0.3 mg/L and 2.0 mg/L total Mn.

Note that solubility predictions shown in Figure 1 are in terms of *dissolved* Mn. Properly designed solids removal systems (i.e., clarification or filtration) will be critical for Mn removal to ensure that all solids are captured and *total* Mn concentrations (regulated parameter) do not increase due to the presence of unsettled particulate Mn (e.g., colloids of $Mn^{II}(OH)_2(s)$ or $Mn^{III}OOH(s)$).

The pH-dependent solubility of $Mn^{II}(OH)_2(s)$ is quite sensitive to the amount of total inorganic carbon (TIC) in the water (Figure 2). Increased solubility of $Mn^{II}(OH)_2(s)$ is particularly important in the pH range used for chemical precipitation water softening (ca. pH 10.5) because of aqueous complexation between Mn^{2+} and carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-). The formation of Mn(II)-carbonate complexes is directly proportional to the amount of TIC in the water. A higher concentration of TIC favors the formation of higher concentrations of Mn(II)-carbonate complexes and increases the solubility of $Mn^{II}(OH)_2(s)$. Typical concentrations of TIC in coal mine drainage (ca. 20 mg/L C; Table 2) will make the attainment of an effluent concentration of 0.3 mg/L total Mn more difficult if trying to remove Mn(II) as $Mn^{II}(OH)_2(s)$. For example, if a chemical precipitation water softening system were operated at pH 10.5, an effluent concentration of 0.3 mg/L total Mn could not be attained unless the TIC concentration was at least 0.6 mg/L C (Figure 2). Therefore, decarbonation of the water before chemical precipitation water softening would likely be required when trying to remove Mn(II) as $Mn^{II}(OH)_2(s)$. As detailed below, decarbonation is an expensive process in terms of both capital and annual costs.
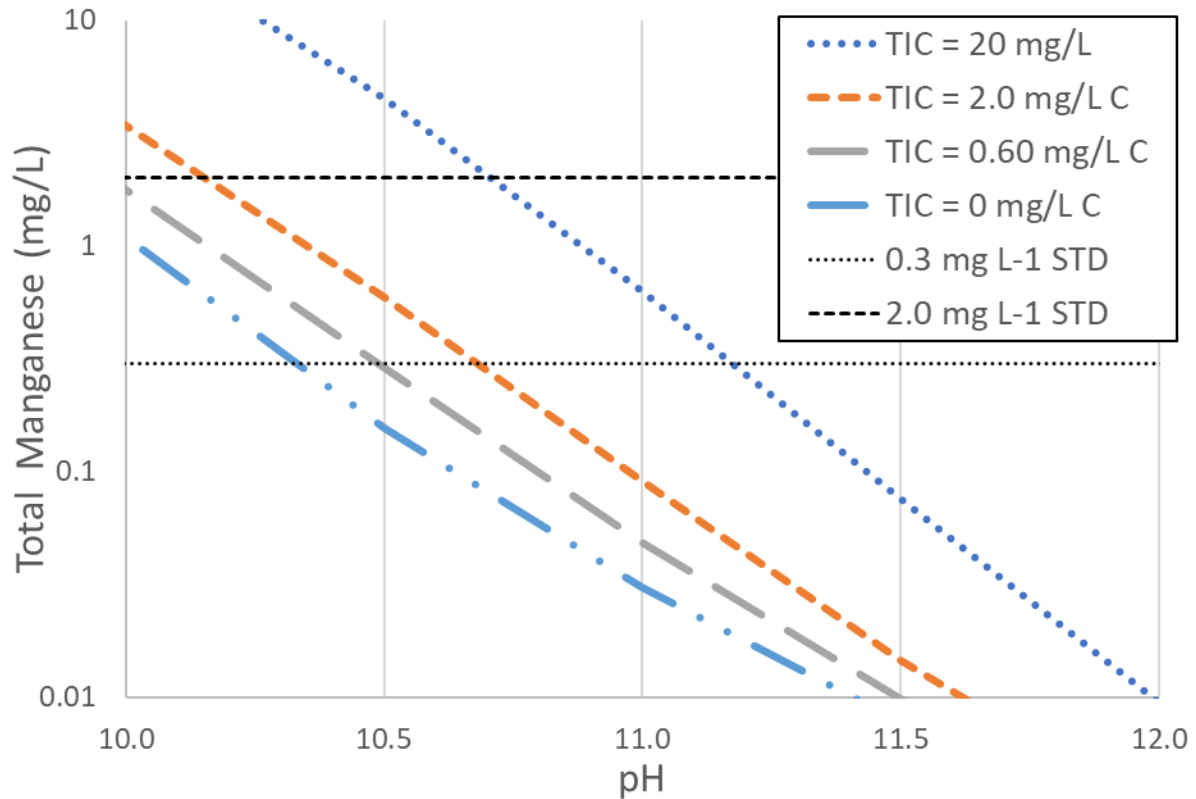
Figure 2. Impact of total inorganic carbon (TIC) and carbonate complexation on the solubility of manganese hydroxide ($Mn^{II}(OH)_2(s)$). Concentrations of total Mn(II) are shown for variable concentrations of TIC. Dissolved concentrations of Mn(II) will increase when manganese carbonate complexes form under high pH conditions. Chemical precipitation water softening for Mn(II) removal aims to operate at ca. pH 10.5. If a treatment plant had to reach the most stringent effluent standard of 0.3 mg/L total Mn, then decarbonation would be required to reduce the TIC concentration to below 0.6 mg/L C. Mineral solubility and complexation reactions are based on thermodynamic data provided in the WATEQ4F chemical speciation code from USGS.

Oxidation of Mn(II) to Mn(III) or Mn(IV) will dramatically affect the solubility of Mn (Figure 1). Oxidation of Mn(II) by dissolved oxygen $O_2(aq)$ can occur in solution (homogeneous) or on a mineral surface (heterogenous). Homogeneous oxidation of Mn(II) by $O_2(aq)$ is notoriously slow (Hem, 1981; Diem and Stumm, 1984). In contrast, heterogenous oxidation of Mn(II) on the surface of an $MnO_x(s)$ is orders of magnitude faster (Davies and Morgan, 1989; Morgan, 2005). Heterogenous oxidation of Mn(II) becomes important in sand filters where the media begins to develop coatings of $MnO_x(s)$. Heterogenous oxidation first requires Mn(II) to sorb to the mineral surface before $O_2(aq)$ reacts to form more $MnO_x(s)$. If sorbed Mn(II) is not oxidized, Mn(II) will 'breakthrough' the filter once Mn(II) sorption capacity is exhausted. Heterogenous oxidation of Mn(II) by $O_2(aq)$, therefore, becomes autocatalytic where the oxidized product provides more sorption capacity for Mn(II) and promotes more Mn(II) oxidation. Sorption of Mn(II) and solid-phase growth of $MnO_x(s)$ improves the capture of total Mn either by 'oxidative filtration' or by improved settling of larger oxide particles during clarification.

Several chemical oxidants have been used to oxidize Mn(II) for removal from drinking water. Chemical oxidants offer advantages compared to $O_2(aq)$ because of greater operational control, however, this comes with increased costs. Chemical oxidants for Mn(II) include chlorine (Cl_2), chlorine dioxide (ClO_2), ozone (O_3), and permanganate (MnO_4^-). While peroxide (H_2O_2) is commonly used as an oxidant for Fe(II) in CMD treatment, it is not effective for Mn(II) oxidation (Knocke et al., 1987). As with $O_2(aq)$, chemical oxidants can react directly with Mn(II)(aq) in a homogeneous reaction or with Mn(II) sorbed onto $MnO_x(s)$ in a heterogeneous reaction. MnO_4^- and ClO_2 (Knocke et al., 1991a) and O_3 (Reckhow et al., 1991) are all capable of rapid homogeneous oxidation of Mn(II). Regardless of the oxidant, the rate of Mn(II) oxidation increases significantly as pH increases – often 10-times faster per pH unit (Davies and Morgan, 1989).

4. Manganese Removal Treatment Technologies

Dissolved Mn(II) can be removed from water via chemical precipitation water softening as $Mn^{II}(OH)_2(s)$, oxidative precipitation as $MnO_x(s)$ using $O_2(aq)$ (e.g., limestone beds), oxidative precipitation using chemical oxidants (e.g., permanganate addition before sand filters), oxidative filtration (e.g., greensand filters), and sorption onto and/or co-precipitation into other solids formed in conventional CMD treatment systems (e.g., ferric hydroxide). In conventional CMD treatment systems, lime (CaO) or caustic soda (NaOH) are added to neutralize acidity and precipitate iron (Fe) as ferric hydroxide ($Fe(OH)_3(s)$) and aluminum (Al) as aluminum hydroxide ($Al(OH)_3(s)$). Alkali addition to reach pH values of $7 - 8$ is often used for the neutralization of acidity and removal of Fe and Al.

Chemical precipitation water softening

Chemical precipitation of Mn(II) as $Mn^{II}(OH)_2(s)$ requires an elevated pH. This is typically accomplished with the addition of caustic soda ($NaOH(l)$), lime slurry, or hydrated lime. The choice of alkali depends on the size/flow rate of the site, where 'small' sites tend to use caustic soda and 'large' sites tend to use hydrated lime. To remove Mn(II) to ≤0.3 mg/L total Mn the pH must be increased to ca. pH 10.5 (Figure 1) but will also be controlled by the amount of TIC in the water (Figure 2). Based on solubility predictions for $Mn^{II}(OH)_2(s)$ shown in Figure 2, the TIC concentration would have be less than 0.6 mg/L C to achieve a Mn(II) concentration below 0.3 mg/L total Mn at pH 10.5. Typical TIC concentrations in CMD are ca. 20 mg/L C (Table 2). Therefore, decarbonation of the water would be required before increasing the pH to precipitate $Mn^{II}(OH)_2(s)$. As detailed below, decarbonation is an expensive process in terms of both capital and annual costs. After chemical precipitation and physical settling, the pH of the water must be decreased to meet permit requirements, likely pH $6 - 9$. This can be accomplished with mineral acid (e.g., H_2SO_4, HCl) or $CO_2(g)$ addition.

There are several operational challenges associated with chemical precipitation water softening for Mn(II) removal from CMD. If a 'single-stage' configuration is used, several other minerals will

precipitate from solution (in addition to $Mn^{II}(OH)_2(s)$) causing increased solids production. Tetra Tech noted that sludge volumes were expected to double for chemical precipitation water softening operated at pH 10.5 as compared to solids produced at a conventional plant operated at pH 7.

It is quite difficult to quantify the total increased cost due to increased sludge volumes. While sludge handling costs can be estimated with reasonable certainty (e.g., using defaults in AMDTreat), costs associated with sludge disposal back into mines through injection boreholes are not easy to predict. For example, if sludge volumes are doubled, then the life cycle of sludge pumps and injection boreholes may be cut in half. Injection boreholes can only be installed into 'hydrologically dead' portions of mines and it may require either acquiring new access easements or property to reach new injection sites. Trenching and extending sludge conveyance lines is expensive and may require boring under streams, railroads, and roads. The costs of sludge disposal and additional injection borehole capacity may at some point eliminate the consideration of chemical precipitation softening.

A second operational problem with 'single-stage' softening is that aluminum hydroxide will re-dissolve at high pH causing a potential violation of the water quality-based effluent limitations for aluminum in some NPDES permits. This is most likely a concern for NPDES-permitted discharges to waters with approved total maximum daily loads (TMDLs) for metals, including Fe, Mn, and Al. Due to either an approved TMDL or a lack of assimilative capacity in the receiving waterbody, the current water quality criterion for Al of 0.75 mg/L may be included in some NPDES permits as an end-of-pipe effluent limitation. Alkali addition to CMD will promote the precipitation of $Fe(OH)_3(s)$ and $Al(OH)_3(s)$. The solubility of $Fe(OH)_3(s)$ reaches its minimum at ca. pH 8 and remains relatively low even at ca. pH 11. In contrast, the solubility of $Al(OH)_3(s)$ reaches its minimum at ca. pH 6 and then increases with pH such that the effluent aluminum concentration will exceed 0.75 mg/L total Al above ca. pH 10. 'Single-stage' chemical precipitation water softening for the simultaneous removal of Fe, Al, and Mn, therefore, would

not be recommended for Mn removal if the influent Al concentration exceeds 0.75 mg/L total Al (current water quality-based criterion).

Instead, 'sequential-stage' treatment would be required where Fe and Al are removed in the first-stage of the process (operated at ca. pH 7 – 8) and then Mn(II) would be removed in the second-stage of the process (operated at ca. pH 10.5). Effective clarification in the first-stage would be critical to ensure that a minimum amount of Al(OH)$_3$(s) is conveyed into the second-stage system. Decarbonation of the water would be recommended before increasing the pH further to avoid increased solubility of Mn(II) caused by the formation of Mn(II)-carbonate complexes (Figure 2). This configuration would require additional capital costs for the second-stage components (e.g., decarbonation, chemical feed systems, reactor tankage, solids collection, acidification) and increased operation and maintenance costs for alkali chemicals and solids management and disposal.

*Oxidative precipitation of MnO$_x$(s) using O$_2$(*aq*)*

Oxidative precipitation of Mn(II) to form MnO$_x$(s) is strongly dependent on the presence of a catalytic metal oxide surface, pH, and an effective oxidant. One of the best catalysts for Mn(II) oxidation are MnO$_x$(s) because of the rapidity and selectivity of Mn(II) sorption to these oxides. Heterogeneous oxidation of Mn(II) by O$_2$(aq) is rapid at circumneutral pH values and kinetics increase as pH increases (Davies and Stumm, 1989). Several bacteria and fungi are also known to oxidize of Mn(II) in oxygenated waters. Filter media coated with MnO$_x$(s) and/or containing Mn(II)-oxidizing microbes can effectively remove Mn(II) with only O$_2$(aq). This configuration is cost-effective because the oxidant, O$_2$(aq), is essentially free. However, biofilters used for Mn(II) removal from drinking water were found to be temperature sensitive, performing poorly below 15°C (Evans et al., 2021).

Oxidative precipitation of MnO$_x$(s) using O$_2$(aq) is a readily scalable treatment technology. For 'small' low-flow sites (e.g., Q = 50 gal/min), a bed of limestone can be an effective filtration media. This configuration is common in passive treatment systems. Over time, the limestone becomes coated with

$MnO_x(s)$ and the bed becomes populated with Mn(II)-oxidizing microbes. In passive systems, a hydraulic residence time of 48-hours may be required to ensure complete removal of influent Mn(II) (Means and Rose, 2005). Because the bed effectively functions as a filter, no further clarification is required. However, because $MnO_x(s)$-coated limestone effectively captures $MnO_x(s)$ that clog the porosity of the bed, maintenance is required to remove the accumulated solids and restore bed porosity. Maintenance frequency is dependent on the influent Mn(II) concentration where higher Mn(II) concentrations will clog the bed more quickly.

Oxidative precipitation of MnO_x(s) using chemical oxidants

In drinking water treatment systems, chemical oxidation of Mn(II) is commonly followed by sand filtration for several reasons. First, rapid oxidation of Mn(II) leads to the formation of very small $MnO_x(s)$ particles that are difficult to settle (Knocke et al., 1991b). Second, the secondary standard for manganese in finished drinking water is 0.05 mg/L total Mn, a concentration difficult to consistently attain via clarification. Third, as $MnO_x(s)$ coatings develop on the filter media, heterogeneous oxidation of Mn(II) by $O_2(aq)$ becomes an effective removal mechanism and decreases the chemical oxidant demand, in turn decreasing annual costs. The presence of 3 – 5 milligrams of $MnO_x(s)$ coatings per gram of filter media has allowed drinking water treatment plants to remove Mn(II) without continuous addition of chemical oxidants (Knocke et al., 1991b).

Several chemical oxidants can oxidize Mn(II) but this process will require removal of Fe beforehand (i.e., 'sequential-stage' configuration). When comparing chemical oxidants using similar experimental systems at ca. pH 7 – 8, Knocke et al. (1991a,b; Reckhow et al., 1991) found the following order for Mn(II) oxidation kinetics – permanganate > ozone ≈ chlorine dioxide >> chlorine. For MnO_4^-, O_3, and ClO_2, Mn(II) oxidation occurred within seconds to minutes. For Cl_2, Mn(II) oxidation occurred within tens-of-minutes, however, it occurred rapidly if $MnO_x(s)$ was present. Mn(II) oxidation required stoichiometric amounts of potassium permanganate (1.92 mg/mg Mn), sodium permanganate (1.73

mg/mg Mn), ozone (0.93 mg/mg Mn), chlorine dioxide (2.45 mg/mg Mn), and chlorine (1.29 mg/mg Mn).

Oxidative filtration

Mn(II) can be removed from water via oxidative filtration, for example using a so-called greensand filter. The active material in a greensand filter is the Fe(III)-rich clay glauconite. In this process, Mn(II) sorbs to the clay, is oxidized by clay-Fe(III), and retained in the filter media as $MnO_x(s)$. Solid-phase clay-Fe(III) is the oxidant, however, when it is reduced it remains in the filter media as solid-phase clay-Fe(II). As clay-Fe(III) is consumed, clay-Fe(II) must be reoxidized, often using potassium permanganate or chlorine. The advantages of this approach are Mn is physically filtered out of the water and the modularity of these filters is scalable for a range of flow rates. The disadvantage of this approach is the capital and annual costs. Greensand media is heavy and requires high-flow pumping equipment to fluidize the bed during regeneration steps. While the greensand media can oxidize Mn(II) it must be regenerated with a chemical oxidant. Essentially Mn(II) is oxidized by the chemicals purchased for regeneration of the greensand media.

Sorption and co-precipitation onto other solids formed in conventional CMD treatment

The most cost-effective means to remove Mn(II) from CMD would be to promote its sorption onto or co-precipitation into $Fe(OH)_3(s)$ and $Al(OH)_3(s)$. This removal mechanism will be favored at sites with higher influent concentrations of Fe and Al. Greater amounts of Fe and Al hydroxides generated from higher influent concentrations of Fe and Al will produce more solids to react with and remove Mn(II). The adsorption of Mn(II) onto $Fe(OH)_3(s)$ may not be substantial until ca. pH 9.0 (Figure 3). However, if a 'single-stage' CMD treatment system were operated at pH 9, Mn(II) removal may occur without the resolubilization of $Al(OH)_3(s)$. Note that influent and effluent samples from coal sites showed Mn removal through a variety of processes not explicitly designed for Mn removal (Table 1).
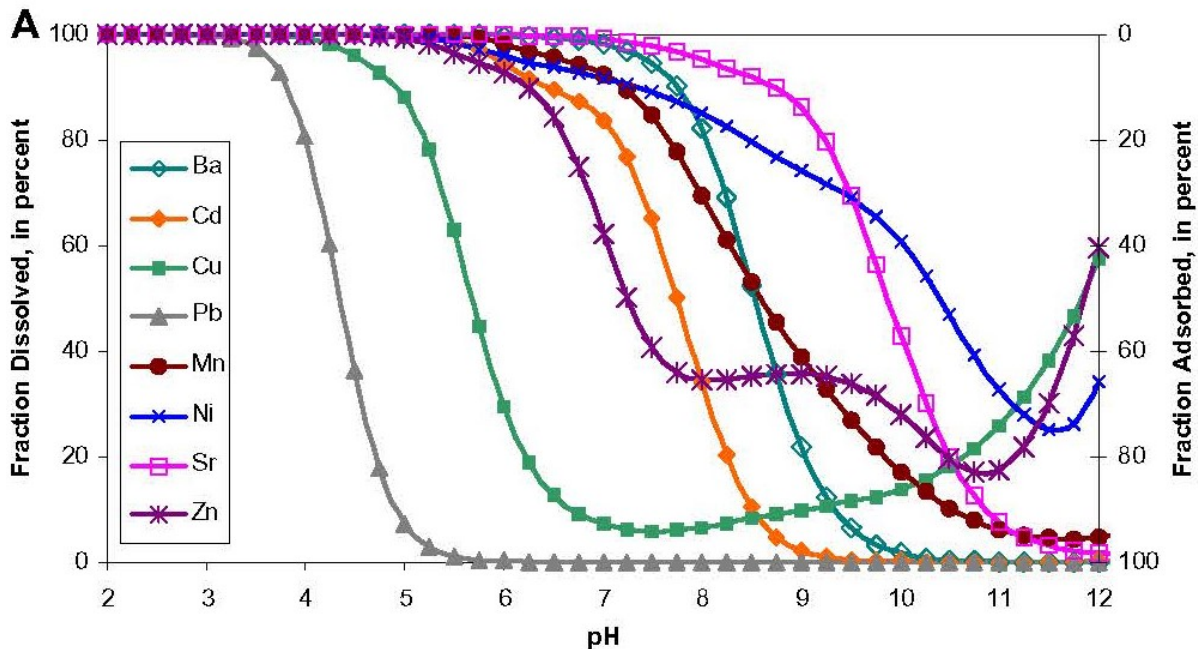
Figure 3. Simulations of cation sorption to iron hydroxides, $Fe(OH)_3(s)$, as a function of pH. The curve for Mn(II) (purple circles) indicates that substantial sorption of Mn(II) to $Fe(OH)_3(s)$ will not occur until ca. pH 9. From Cravotta (2008b).

Recent research has demonstrated that Mn(II) can be co-removed from CMD at ca. pH 8.0 – 9.0 (Kim et al., 2018). Experiments were conducted with various concentrations of Fe(II), Fe(III), Al, and Mn(II) to determine Mn(II) removal mechanisms (i.e., coprecipitation, sorption) as a function of pH. The authors found greatest Mn(II) removal in systems where $Fe^{3+}(aq)$ formed 'fresh' Fe(III) hydroxides and Mn(II) was removed via both coprecipitation and sorption. Significant removal of Mn(II) at ca. pH 8.0 – 9.0 occurred when the Fe-to-Mn weight ratio (m/m) was rather high – ca. >20 m/m. This weight ratio may only be common in CMD from deep mines with active treatment (Table 2), but these discharges are particularly important with respect to the coal industry in Pennsylvania.

Table 2. Median concentrations (50th percentile) of metals and other constituents in coal-associated waters collected in Pennsylvania. All metals are reported in mg/L.

Element	Abandoned coal mine drainage (CMD) [1]	CMD influent to active coal sites [2]	CMD from deep mines with active treatment [2]	CMD from surface mines with active treatment [2]
Iron (Fe)	32	9.7	20	8.3
Manganese (Mn)	2.4	8.3	3.5	14
Fe/Mn ratio (m/m)	8.1	2.1	48	0.75
Aluminum (Al)	1.3	0.57	0.83	3.4
Calcium (Ca)	88	190	120	190
Magnesium (Mg)	38	87	44	88
Acidity (mg/L as $CaCO_3$)	52	63	65	85
Alkalinity (mg/L as $CaCO_3$)	9.5	27	61	5.0
Total Inorganic Carbon (TIC) (mg/L C)	n.r.	23	27	20
# samples in dataset	140	46	9 (of 46)	20 (of 46)

1 – from Cravotta (2008a) n.r. = not reported; 2 – from Cravotta and Brady (2015)

5.   Treatment Technology Recommendations for Mn(II) Removal

The selection of a technology to remove Mn(II) from CMD will depend on both influent water chemistry and the size/flow rate of the site. While technology selection will essentially be done on a site-by-site basis, some generalizations can be used for guidance. A flowchart for Mn(II) removal technology recommendations was motivated by similar guidance developed for the design of passive treatment systems for the remediation of CMD (Figure 4). In general, the selection of the Mn(II) removal technology is based on water chemistry (specifically the concentrations of Fe, Al, and Mn) while the size of the process is based on contaminant loading (where Mn load = Mn concentration × flow rate). However, technology selection is also influenced by the size/flow rate of the site. For example, a limestone bed that requires a 48-hour hydraulic retention time is likely not a practical option for a high-flow rate site. Similarly, oxidative filtration (with automated chemical feed systems and backwash pumps) is not likely a practical option for a low-flow rate site.

A flowchart for selecting a Mn(II) removal technology was developed based on influent concentrations of Mn(II), Fe(II), and Al (Figure 5), and assumes that all sites essentially treat net acid water (Table 2). Furthermore, these technology recommendations assume that existing active treatment systems treat the CMD via alkali addition, aeration (if required), and solids clarification. Technology recommendations for passive treatment options are limited and provided below. As noted above, Mn(II) removal will occur at sites that may also need to meet permit requirements for Al. Because chemical precipitation water softening may resolubilize Al, influent concentrations of Al will affect technology selection. Because a high Fe(II)-to-Mn weight ratio can promote Mn(II) removal via coprecipitation and sorption, influent concentrations of Fe(II/III) will also affect technology selection.

Characterize Mine Water

Net alkaline   **Net acid**

DO, Fe^{3+}, Al all < 1 mg/L (high Fe^{2+})   *DO, Fe^{3+}, Al any > 1 mg/L*   *DO, Fe^{3+}, Al any > 1 mg/L Fe < 10 mg/L*

Anoxic Limestone Drain

High Fe^{2+}

Net Alkaline   *Net acid*

Ox/Settling Pond   Ox/Settling Pond   Vertical Flow Pond   Oxic Limestone Bed (drainable)

Repeat As Needed

Aerobic Wetland   Ox/Settling Pond   Settling Pond

Mn   Oxic Limestone Bed   ←   *Mn*   Aerobic Wetland

Final Discharge

Figure 4. A flowchart based on chemical characterizations of mine water for the selection of appropriate processes for passive treatment of coal mine drainage. Adapted from Hedin and Nairn (1992).

Characterize Mine Water

Influent Conditions	Net acid Mn > 2.0 mg/L Al > 0.75 mg/L Fe(II)/Mn > 20	Net acid Mn > 2.0 mg/L Al > 0.75 mg/L Fe(II)/Mn < 20	Net acid Mn > 2.0 mg/L Al < 0.75 mg/L Fe(II)/Mn > 20	Net acid Mn > 2.0 mg/L Al < 0.75 mg/L Fe(II)/Mn < 20
Assumed Existing Treatment System operated at pH 7-8	Aeration + Alkali Addition → Solids Removal	Aeration + Alkali Addition → Solids Removal	Aeration + Alkali Addition → Solids Removal	Aeration + Alkali Addition → Solids Removal
Most cost-effective option	Reconfigure treatment system for coprecipitation at pH 9 → Success = $[Mn]_T < 0.3$ mg/L $[Al]_T < 0.75$ mg/L / Failure = Try Next Technology		Reconfigure treatment system for coprecipitation at pH 9 → Success = $[Mn]_T < 0.3$ mg/L $[Al]_T < 0.75$ mg/L / Failure = Try Next Technology	Choose from
Intermediate cost options	Enhanced solids removal	Choose from	Add treatment system for oxidative precipitation at pH 8 using chemical oxidants or $O_2(aq)$	Add system for Decarbonation → Reconfigure treatment system for single-stage water softening at pH 10.5
Most expensive option	Add system for Decarbonation → Add system for sequential-stage water softening at pH 10.5 → Add system for enhanced solids removal → Add system for Acidification to pH 7		Add system for enhanced solids removal	Add system for enhanced solids removal → Add system for Acidification to pH 7

Final Discharge

Figure 5. Technology selection flowchart for removal of Mn(II) at coal sites with active treatment plants.

In Figure 5, technology recommendation options are presented in order of their cost-effectiveness. For CMD with a high Fe(II)/Mn mass ratio (i.e., >20 mg/mg), the most cost-effective means to remove Mn(II) could be via coprecipitation and sorption to $Fe(OH)_3(s)$. Note that Mn(II) removal is more effective when Fe(II) is oxidized to 'fresh' $Fe(OH)_3(s)$ allowing for both coprecipitation and sorption as compared to Mn(II) sorption to pre-formed $Fe(OH)_3(s)$. Thus, Mn(II) removal from CMD with elevated concentrations of Fe(III) may not be substantial enough to meet lower Mn(II) effluent limits. Based on chemical characterizations of coal-associated waters collected in Pennsylvania (Table 2), this treatment option may be viable at active deep mine sites where the median Fe/Mn mass ratio was 48 (n=9). Note that sources for data in Table 2 (Cravotta, 2008a; Cravotta and Brady, 2015) did not distinguish between concentrations of Fe(II) and Fe(III).

Assuming that coprecipitation and sorption to $Fe(OH)_3(s)$ can achieve the *chemical* goals of a final Mn concentration below any new effluent limit (e.g., 0.3 to 2.0 mg/L total Mn) and a final Al concentration below effluent limitations based on the existing water quality criterion of 0.75 mg/L total Al, the system must still rely on a *physical* process to effectively and consistently remove suspended solids from the water. Coprecipitation and sorption to $Fe(OH)_3(s)$ is presented as the most cost-effective option because an existing active treatment plant could be readily modified to add more alkali to operate at a higher pH (e.g., pH 9 instead of pH 7) to promote these removal mechanisms. However, because removal of suspended solids from CMD is crucial to permit compliance, the flowchart specifies some form of enhanced solids removal (Figure 5). This may amount to a polymer feed system for improved coagulation, an additional clarifier or pond for extended settling times, or a sand filter. Therefore, engineering services and treatability studies would be required on a site-by-site basis to evaluate this treatment option.

If Mn(II) cannot be removed via coprecipitation and sorption to $Fe(OH)_3(s)$, then oxidative precipitation as $MnO_x(s)$ or chemical precipitation water softening as $Mn^{II}(OH)_2(s)$ are essentially the

only remaining treatment options (membrane filtration was not considered for this report because of its higher costs). If influent Al concentrations are <0.75 mg/L total Al such that high-pH resolubilization of $Al(OH)_3(s)$ is not an operational concern, then so-called 'single-stage' water softening could be incorporated into an existing active treatment plant. Compared to the operation of a conventional active treatment plant, additional alkali would be required to meet the target pH of ca. 10.5 and additional solids would be generated. Decarbonation would have to be added to the system because the solubility of $Mn^{II}(OH)_2(s)$ is very sensitive to the concentration of TIC (Figure 2). Water softening will also require re-acidification to meet an acceptable effluent pH. It should be noted that this process is not particularly efficient when considering that the mass of $Mn^{II}(OH)_2(s)$ (formed from an assumed influent concentration of 8.3 mg/L total Mn – Table 2) in the sludge will be low compared to the mass of $CaCO_3(s)$ (formed from 190 mg/L Ca – Table 2), $Mg(OH)_2(s)$ (formed from 87 mg/L Mg – Table 2) and any other mineral solids captured in the clarifier. As noted in Tetra Tech's report to PCA, these operational adjustments will significantly increase CMD treatment costs.

If influent Al concentrations are >0.75 mg/L total Al such that high-pH resolubilization of $Al(OH)_3(s)$ is an operational concern, then an even more expensive 'sequential-stage' water softening configuration would be required. In this case, the existing active treatment plant would continue to be used for the removal of Fe and Al at ca. pH 7 – 8. A completely new water softening plant would then have to be added onto the existing plant. Because of operational inefficiencies noted above compounded with significant additional capital costs, this treatment option may never be selected.

Compared to chemical precipitation water softening, Mn(II) removal via oxidative precipitation using chemical oxidants may be easier to incorporate into an existing active treatment plant. As noted above, $MnO_x(s)$ can be dissolved by Fe(II), therefore, Mn(II) removal via oxidative precipitation must occur in a 'sequential-stage' configuration after Fe(II) has been oxidized and Fe(III) solids have been removed (i.e., downstream of existing plant). Chemical oxidation of Mn(II) would require chemical feed

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system(s) for the oxidant(s) (e.g., permanganate) and a rapid-mix tank to initiate the reaction. Mn(II) oxidation kinetics by permanganate at ca. pH 7 – 8 are rapid (required hydraulic residence times of ca. seconds to minutes) such that the system could be relatively compact. A system for enhanced solids removal would be the largest component of this system. While a clarifier or a pond could be used, clarification may be challenging because of the relatively low solids concentration produced in this process and the relatively small size of $MnO_x(s)$ particles produced via chemical oxidation. Therefore, sand filtration is likely best to remove this low concentration of TSS.

While chemical oxidation of Mn(II) combined with sand filtration will almost certainly allow a site to meet a manganese effluent limit of 0.3 mg/L total Mn, the major disadvantages of this option are the capital and annual costs (discussed in detail in next section) and finding the room on-site for these unit operations. Both of these costs will depend on the size/flow rate of the site while the annual cost will also be dependent on the influent Mn(II) concentration.

Instead of chemical oxidants, Mn(II) can also be oxidized by $O_2(aq)$ provided an abundant amount of $MnO_x(s)$ are present. A large amount and/or surface area of $MnO_x(s)$ can be developed and collected in a passive limestone bed. Long-term monitoring of Mn-removal limestone beds has demonstrated that these systems are effective in producing effluent concentrations <0.3 mg/L total Mn (Means and Rose, 2005). One concern with limestone beds is that startup of these systems may produce waters that do not initially meet Mn effluent limits.

Flow rates from coal-mining/coal-processing sites vary depending on the category of the water source – abandoned CMD vs. CMD from deep mines vs. CMD from surface mines (Table 3). Flow rates are generally far greater from active deep mines as compared to active surface mines (Cravotta and Brady, 2015). This is also consistent with abandoned CMD where sites that drain underground mine complexes have much higher flow rates as compared to 'average' surface mine sites.

Table 3. Flow rates from coal-associated discharges in Pennsylvania. All values reported in gal/min.

Flow rate distributions – percentile rank	Abandoned coal mine drainage (CMD) [1]	CMD from all active coal sites studied [2]	CMD from deep mines with active treatment [2]	CMD from surface mines with active treatment [2]
10%	36.3	12.5	197	11.2
25%	92.1	49.4	462	44.9
50% (median)	292	166	1,540	112
75%	1,030	595	3,340	227
90%	3,190	2,740	10,300	312
# samples in dataset	140	46	9 (of 46)	20 (of 46)

1 – from Cravotta (2008a); 2 – from Cravotta and Brady (2015)

6. Cost Estimates for the Coal Industry

CMD treatment costs are directly related to the influent water chemistry. The majority of costs presented in this report were determined using the OSMRE software program AMDTreat. Cost estimates made for unit operations selected in AMDTreat often require several chemical concentrations as inputs. Median concentrations for coal-mining/coal-processing facilities presented in Table 2 were used in all cases except when noted. One important exception was for the condition when the Fe(II)/Mn mass ratio was assumed to equal 20. Under this condition, favorable removal of Mn(II) may occur via coprecipitation and sorption to $Fe(OH)_3(s)$. In this case, the Mn(II) concentration remained 8.3 mg/L Mn while the Fe(II) concentration was increased to 166 mg/L Fe.

The pH of the treatment operation also significantly affects the amounts of chemicals consumed and sludge generated. In this report it has been assumed that an existing conventional treatment plant operated at pH 7.0 can continue to operate at pH 7.0 if oxidative precipitation is selected for Mn(II) removal. If Mn(II) removal via coprecipitation is selected (i.e., Fe(II)/Mn ratio must be >20 mg/mg), then an existing plant would have to be operated at pH 9.0. If Mn(II) removal via chemical precipitation water softening is selected (i.e., Al must be <0.75 mg/L), then an existing plant would have to be operated at pH 10.5. The additional alkali needed to attain these higher pH values were estimated using the PHREEQ-N-AMDTreat ParallelTreatment tool with median values in Table 2. This tool calculated that, compared to pH 7.0, three-times as much alkali would be required to reach pH 9.0 and six-times as much alkali would be required to reach pH 10.5. The alkali demand at pH 7.0 was assumed to equal the influent acidity, a value of approximately 60 mg/L $CaCO_3$ (Table 2). Compared to the sludge volume produced at pH 7.0, sludge volumes were assumed to increase by 1.5-times at pH 9.0 and increase by two-times at pH 10.5. These assumptions were used throughout the following cost estimates. Mn(II) removal technologies were then made for each size site for the range of influent conditions included in Figure 5 to generate three options for each size site.

CMD treatment costs are related to the size/flow rate of the site. Tetra Tech based all of their treatment cost estimates (both capital and annual) on an average flow rate of 200 gal/min and applied these costs to 700 (of 706) coal mining-related NPDES-permitted sites. Based on the distribution of flow rates presented in Table 3, Mn(II) removal technology selections and associated cost estimates were prepared for 'small' (Q = 50 gal/min), 'average' (Q = 170 gal/min), and 'large' (Q = 2,700 gal/min) sites. The site population distribution was assumed to be 25% 'small' sites (0 – 25th percentile in Table 3), 65% 'average' sites (26th – 90th percentile in Table 3), and 10% 'large' sites (91st – 100th percentile in Table 3).

While a relatively small fraction of the site population will have 'large' flow rates (10%, Table 3), the corresponding costs to the coal mining industry from these few sites could be disproportionately large. This is also similar to coal production where just a few large mines produce most of the coal in Pennsylvania and, presumably, the majority of profit for the industry. Fortuitously, large deep coal mines have high Fe/Mn mass ratios (Table 2) that could be exploited to utilize the most cost-effective Mn(II) removal technology – coprecipitation and sorption to $Fe(OH)_3(s)$ at pH 9.0. If indeed the most cost-effective Mn(II) removal technology can be used at the majority of the largest coal mines, the total cost to the coal mining industry could end up below the low range of cost estimates in this report.

Costs at small sites

For small sites (Q = 50 gal/min) the most practical Mn(II) removal technology would likely be oxidative precipitation using $O_2(aq)$ in a limestone-based manganese removal bed (assuming land is available). A limestone bed would also provide enhanced solids removal. Costs were estimated using the Manganese Removal Bed module in AMDTreat with a design flow of 50 gal/min, dissolved Mn of 10 mg/L (fixed value), and a retention time of 48 hours (conservative value from Means and Rose (2005)). Capital costs for this unit operation were estimated at $177,000 and annual costs were estimated at $3,540 (Table 4).

Alternatively, oxidative precipitation using a chemical oxidant followed by a limestone bed could be considered. For a small site, sodium permanganate ($NaMnO_4$) delivered as a concentrated liquid (20% w/w) would be simpler than using potassium permanganate ($KMnO_4$). $KMnO_4$ is delivered as a solid powder and would require mixing with makeup water. Even though $NaMnO_4$ is more expensive than $KMnO_4$, lower capital costs and simpler operation may be preferred for small sites. Costs for a $NaMnO_4$ system were estimated using the Permanganate module in AMDTreat with a design flow of 50 gal/min, dissolved Fe(II) of 0.1 mg/L Fe, dissolved Mn(II) of 8.3 mg/L Mn, the non-bulk delivery option (263 gallons estimated to last ca. 60-days), and a 500-gal dose tank. Capital costs for Na-permanganate oxidation were estimated at $57,800 and annual costs were estimated at $20,700. A limestone bed is less expensive than a manganese removal bed because a shorter residence is required. A limestone bed also provides enhanced solids removal. Costs were estimated using the Limestone Bed module in AMDTreat with a design flow of 50 gal/min, a net acidity concentration of 60 mg/L $CaCO_3$ (fixed value), and a retention time of 24 hours. Capital costs for the limestone bed were estimated at $56,700 and annual costs were estimated at $1,130 (Table 4). Combined capital costs for this configuration were estimated at $115,000 and annual costs were estimated at $21,800.

If the Fe(II)/Mn mass ratio is greater than 20 mg/mg and unit operations for alkali addition, aeration, and solids removal are pre-existing, then it would be worthwhile to pilot test the feasibility for Mn(II) removal via coprecipitation and sorption to $Fe(OH)_3(s)$ at pH 9.0. If successful, enhanced solids removal may be required. Capital costs for this treatment system were estimated at $0 (i.e., repurpose all existing unit operations) to $32,200 to add a settling pond. Capital costs for the pond were estimated using the Ponds module in AMDTreat with a design flow of 50 gal/min. To estimate annual costs, concentrations of 166 mg/L Fe(II), 0 mg/L Fe(III), 0.57 mg/L Al, and 8.3 mg/L Mn were specified. Annual costs for the pond were estimated at $2,760. Because this process requires operation at pH 9.0 instead of pH 7.0 (assumed for conventional system), additional alkali is needed to attain this higher pH. This

alkali demand was estimated at 180 mg/L CaCO$_3$ (= 3 × 60 mg/L CaCO$_3$) as described above. Annual costs

for this alkali were then estimated at $15,700 using the Caustic Soda module in AMDTreat with a design

flow of 50 gal/min, net acidity of 180 mg/L CaCO$_3$, and a caustic soda concentration of 20 wt. %. Capital

costs for alkali addition were assumed to equal $0 and annual costs were estimated at $15,700. Sludge

handling costs are about $0.05 to $0.10 per 1,000 gallons treated based on calculations provided in

AMDTreat (same values used by Tetra Tech). Assuming sludge volumes increase by 1.5-times from

increasing the treatment pH from 7.0 to 9.0, then the annual cost for increased sludge handling would

be $660 to $1,310. Combined capital costs for this configuration were estimated at $0 to $32,200 and

annual costs were estimated at $19,100 to $19,800.

Chemical precipitation water softening for Mn(II) removal would not be recommended for small

sites.

Costs at average sites

For average sites (Q = 170 gal/min) the most practical Mn(II) removal technology would likely be

oxidative precipitation using chemical oxidants and sand filtration. For an average site, either NaMnO$_4$

or KMnO$_4$ could be considered. Costs for a NaMnO$_4$ system were estimated using the Permanganate

module in AMDTreat with a design flow of 170 gal/min, dissolved Fe(II) of 0.1 mg/L Fe, dissolved Mn(II)

of 8.3 mg/L Mn, the non-bulk delivery option (263 gallons estimated to last ca. 17-days), and a 500-gal

dose tank. Capital costs for Na-permanganate oxidation were estimated at $57,800 and annual costs

were estimated at $48,300. Costs for a KMnO$_4$ system were estimated using the Permanganate module

in AMDTreat with a design flow of 170 gal/min, dissolved Fe(II) of 0.1 mg/L Fe, dissolved Mn(II) of 8.3

mg/L Mn, the bulk container delivery option (330 lb drums to last ca. 10-days), a 500-gal mix tank, and a

1,000-gal dose tank. Capital costs for K-permanganate oxidation were estimated at $72,900 and annual

costs were estimated at $41,700. Sand filtration will provide the enhanced solids removal required to

meet a stringent total Mn effluent limit. Costs for sand filters for a design flow of 170 gal/min were

provided by anonymous vendors. Capital costs for a sand filter were estimated at $135,000 and annual

operating costs were estimated at $10,100. Combined capital costs for this configuration were

estimated to range from $193,000 to $212,000 and annual costs were estimated to range from $58,000

to $73,100.

If the Fe(II)/Mn mass ratio is greater than 20 mg/mg and unit operations for alkali addition,

aeration, and solids removal are pre-existing, then it would be worthwhile to pilot test the feasibility for

Mn(II) removal via coprecipitation and sorption to $Fe(OH)_3(s)$ at pH 9.0. If successful, enhanced solids

removal may be required. Capital costs for this treatment system were estimated at $0 (i.e., repurpose

all existing unit operations) to $44,700 to add a pond to $729,000 to add a clarifier. Capital costs were

estimated using the Ponds module in AMDTreat with a design flow of 170 gal/min, and annual costs for

the pond were estimated at $8,150. Capital costs were estimated using the Clarifier module in

AMDTreat with a design flow of 170 gal/min and a hydraulic loading of 0.50 gpm/ft^2. To estimate annual

clarifier costs, concentrations of 166 mg/L Fe(II), 0 mg/L Fe(III), 0.57 mg/L Al, and 8.3 mg/L Mn were

specified. Annual costs for the clarifier were estimated at $16,300. To reach a treatment pH of 9.0, an

additional alkali demand of 180 mg/L $CaCO_3$ will be required. Alkali could be added in forms of caustic

soda (NaOH), lime slurry, or hydrated lime. Capital costs for this unit operation were assumed to equal

$0 and it was assumed any site would continue to use its current form of alkali. Annual costs for NaOH

were estimated at $51,400 using the Caustic Soda module in AMDTreat with a design flow of 170

gal/min, net acidity of 180 mg/L $CaCO_3$, and a caustic soda concentration of 20 wt. %. Annual costs for

lime slurry were estimated at $25,100 using the Lime Slurry module in AMDTreat with a design flow of

170 gal/min, net acidity of 180 mg/L $CaCO_3$, and a % solids slurry of 37 wt. %. Annual costs for hydrated

lime were estimated at $38,300 using the Lime Products module in AMDTreat with a design flow of 170

gal/min, net acidity of 180 mg/L $CaCO_3$, and a hydrated lime purity of 96 %. Sludge handling costs are

about $0.05 to $0.10 per 1,000 gallons treated based on calculations provided in AMDTreat. Assuming

sludge volumes increase by 1.5-times from increasing the treatment pH from 7.0 to 9.0, then the annual

cost for increased sludge handling would be $2,240 to $4,470. Combined capital costs for this

configuration were estimated to range from $0 to $729,000 and annual costs were estimated to range

from $35,500 to $72,200.

If the influent aluminum concentration is <0.75 mg/L total Al, then 'single-stage' chemical

precipitation water softening for Mn(II) removal could be considered. Decarbonation and enhanced

solids removal will have to be added to an existing treatment system (assumed to include alkali addition,

aeration, and solids removal). Costs were estimated using the Decarbonation module in AMDTreat with

a design flow of 170 gal/min, raw pH of 5.7, temperature of 13°C, and TIC of 23 mg/L C (Table 2). Based

on the solubility enhancement of $Mn^{II}(OH)_2(s)$ by the formation of Mn(II) carbonate complexes,

decreasing the TIC concentration to ca. 0.6 mg/L C would be recommended (Figure 2). However, none of

the decarbonation equipment options in AMDTreat were able to achieve this TIC concentration.

Nonetheless, cost estimates are provided along with predicted effluent TIC concentrations. Capital costs

for a surface aerator with a retention time of 120 min (maximum allowable; effluent TIC of 6.9 mg/L C)

were estimated at $183,000 and annual costs were estimated at $10,400. Capital costs for a fine bubble

diffuser with a retention time of 120 min (maximum allowable; effluent TIC of 3.8 mg/L C) were

estimated at $196,000 and annual costs were estimated at $20,600. Capital costs for a Maelstrom

aerator with a retention time of 1.8 min (fixed value; effluent TIC of 4.4 mg/L C) were estimated at

$52,600 and annual costs were estimated at $6,480. Note that if the TIC concentration is too high,

chemical precipitation water softening may never be able to achieve an effluent manganese

concentration of <0.3 mg/L total Mn.

Because more solids will be produced by operating the treatment system at pH 10.5 as

compared to pH 7.0, enhanced solids removal will have to be added to an existing treatment system.

Capital costs for a clarifier were estimated at $729,000 and annual costs were estimated at $16,300.

Capital and annual costs for these unit operations were estimated using AMDTreat as described above.

To reach a treatment pH of 10.5, an additional alkali demand of 360 mg/L $CaCO_3$ (= 6 × 60 mg/L $CaCO_3$ as described above) will be required. Alkali could be added in forms of caustic soda (NaOH), lime slurry, or hydrated lime. Capital costs for this unit operation were assumed to equal $0 and it was assumed any site would continue to use its current form of alkali. Annual costs for NaOH were estimated at $102,000 using the Caustic Soda module in AMDTreat with a design flow of 170 gal/min, net acidity of 360 mg/L $CaCO_3$, and a caustic soda concentration of 20 wt. %. Annual costs for lime slurry were estimated at $41,200 using the Lime Slurry module in AMDTreat with a design flow of 200 gal/min, net acidity of 360 mg/L $CaCO_3$, and a % solids slurry of 37 wt. %. Annual costs for hydrated lime were estimated at $47,400 using the Lime Products module in AMDTreat with a design flow of 170 gal/min, net acidity of 360 mg/L $CaCO_3$, and a hydrated lime purity of 96 %. Sludge handling costs are about $0.05 to $0.10 per 1,000 gallons treated based on calculations provided in AMDTreat. Assuming sludge volumes are doubled from increasing the treatment pH from 7.0 to 10.5, then the annual cost for increased sludge handling would be $4,470 to $8,940. Capital costs for this configuration were estimated to range from $782,000 to $925,000 and annual costs were estimated to range from $68,500 to $139,000.

If the influent aluminum concentration was >0.75 mg/L total Al, 'sequential-stage' chemical precipitation water softening for Mn(II) removal would not be recommended for these average sites. Instead, oxidative filtration would be recommended.

Costs at large sites

For large sites (Q = 2,700 gal/min) where high Fe/Mn mass ratios (>20 mg/mg) may be expected (Table 2) it will be worthwhile to pilot test the feasibility for Mn(II) removal via coprecipitation and sorption to Fe(OH)$_3$(*s*) at pH 9.0. If successful, enhanced solids removal may be required. Capital costs for this treatment system were estimated at $0 (i.e., repurpose all existing unit operations) to $2,190,000 to add a clarifier (a pond is not recommended for large sites). Capital costs were estimated

using the Clarifier module in AMDTreat with a design flow of 2,700 gal/min and a hydraulic loading of 0.50 gpm/ft^2. To estimate annual clarifier costs, concentrations of 166 mg/L Fe(II), 0 mg/L Fe(III), 0.57 mg/L Al, and 8.3 mg/L Mn were specified. Annual costs for the clarifier were estimated at $26,100. To reach a treatment pH of 9.0, an additional alkali demand of 180 mg/L CaCO$_3$ will be required. For large sites, only lime slurry and hydrated lime would be considered. Capital costs for this unit operation were assumed to equal $0 and it was assumed any site would continue to use its current form of alkali. Annual costs for lime slurry were estimated at $264,000 using the Lime Slurry module in AMDTreat with a design flow of 2,700 gal/min, net acidity of 180 mg/L CaCO$_3$, and a % solids slurry of 37 wt. %. Annual costs for hydrated lime were estimated at $174,000 using the Lime Products module in AMDTreat with a design flow of 2,700 gal/min, net acidity of 180 mg/L CaCO$_3$, and a hydrated lime purity of 96 %. Sludge handling costs are about $0.05 to $0.10 per 1,000 gallons treated based on calculations provided in AMDTreat. Assuming sludge volumes increase by 1.5-times from increasing the treatment pH from 7.0 to 9.0, then the annual cost for increased sludge handling would be $35,500 to $71,000. Combined capital costs for this configuration were estimated to range from $0 to $2,190,000 and annual costs were estimated to range from $236,000 to $361,000.

If Mn(II) removal via coprecipitation is unsuccessful or unfavorable, Mn(II) removal by oxidative precipitation using chemical oxidants and sand filtration should be considered. For a large site, only KMnO$_4$ would be considered. Costs for a KMnO$_4$ system were estimated using the Permanganate module in AMDTreat with a design flow of 2,700 gal/min, dissolved Fe(II) of 0.1 mg/L Fe, dissolved Mn(II) of 8.3 mg/L Mn, the bulk container delivery option (330 lb drums to last ca. 0.64-days), a 5,000-gal mix tank, and a 5,000-gal dose tank. Capital costs for this unit operation were estimated at $152,000 and annual costs were estimated at $560,000. Sand filtration will provide the enhanced solids removal required to meet a stringent total Mn effluent limit. Costs for sand filters for a design flow of 2,700 gal/min were provided by anonymous vendors. Capital costs for a sand filter were estimated at

$1,040,000 and annual operating costs were estimated at $57,000. Capital costs for a greensand filter were estimated at $850,000 and annual operating costs were estimated at $42,500. Combined capital costs for this configuration were estimated to range from $1,000,000 to $1,190,000 and annual costs were estimated to range from $603,000 to $617,000.

If the influent aluminum concentration is <0.75 mg/L total Al, then 'single-stage' chemical precipitation water softening for Mn(II) removal could be considered. As described above, both decarbonation and enhanced solids removal would need to be added to an existing treatment system. Costs were estimated using the Decarbonation module in AMDTreat with a design flow of 2,700 gal/min, raw pH 5.7, temperature of 13°C, and TIC of 23 mg/L C (Table 2). Capital costs for a surface aerator with a retention time of 120 min (maximum allowable; effluent TIC of 6.9 mg/L C) were estimated at $974,000 and annual costs were estimated at $97,800. Capital costs for a fine bubble diffuser with a retention time of 120 min (maximum allowable; effluent TIC of 3.8 mg/L C) were estimated at $1,130,000 and annual costs were estimated at $215,000. Capital costs for a Maelstrom aerator with a retention time of 1.13 min (fixed value; effluent TIC of 6.0 mg/L C) were estimated at $248,000 and annual costs were estimated at $56,400. It should be noted that if the TIC concentration is too high, chemical precipitation water softening may never be able to achieve an effluent manganese concentration of <0.3 mg/L total Mn. Capital costs for a clarifier were estimated at $2,190,000 and annual costs were estimated at $26,100 using AMDTreat as described above.

Because more solids will be produced by operating the treatment system at pH 10.5 as compared to pH 7.0, enhanced solids removal will have to be added to an existing treatment system. Capital costs for a clarifier were estimated at $2,190,000 and annual costs were estimated at $26,100. Capital and annual costs for these unit operations were estimated using AMDTreat as described above. To reach a treatment pH of 10.5, an additional alkali demand of 360 mg/L $CaCO_3$ (= 6 × 60 mg/L $CaCO_3$ as described above) will be required. Only hydrated lime would be considered for large sites requiring large

amounts of alkali. Capital costs for this unit operation were assumed to equal $0 and it was assumed any large site would be equipped to use this form of alkali. Annual costs for hydrated lime were estimated at $319,000 using the Lime Products module in AMDTreat with a design flow of 2,700 gal/min, net acidity of 360 mg/L $CaCO_3$, and a hydrated lime purity of 96 %. Sludge handling costs are about $0.05 to $0.10 per 1,000 gallons treated based on calculations provided in AMDTreat. Assuming sludge volumes are doubled from increasing the treatment pH from 7.0 to 10.5, then the annual cost for increased sludge handling would be $71,000 to $142,000. Combined capital costs for this configuration were estimated to range from $2,440,000 to $3,320,000 and annual costs were estimated to range from $473,000 to $702,000.

If the influent aluminum concentration was >0.75 mg/L total Al, 'sequential-stage' chemical precipitation water softening for Mn(II) removal would not be recommended for these large sites. Instead, oxidative filtration would be recommended.

Table 4. Cost estimates for possible plant reconfigurations required for Mn(II) removal from 'small' coal-associated discharges in Pennsylvania. Small sites were assumed to have a flow rate = 50 gal/min and represent the 0th – 25th percentile of coal sites in Pennsylvania.

Configuration description	Mn-removal bed	Coprecipitation	NaMnO$_4$ + limestone bed	Representative value for cost to industry
Capital costs	$177,000	$0 – $32,000	$115,000	$0 – $177,000
Annual costs	$3,540	$19,100 – $19,800	$21,800	$3,540 – $19,800

Table 5. Cost estimates for possible plant reconfigurations required for Mn(II) removal from 'average' coal-associated discharges in Pennsylvania. Average sites were assumed to have a flow rate = 170 gal/min and represent the 26th – 90th percentile of coal sites in Pennsylvania.

Configuration description	MnO$_4^-$ + sand filter	Coprecipitation	Water softening	Representative value for cost to industry
Capital costs	$193,000 – $212,000	$0 – $729,000	$782,000 – $925,000	$0 – $729,000
Annual costs	$58,000 – $73,100	$33,600 – $82,000	$68,500 – $139,000	$33,600 – $82,000

Table 6. Cost estimates for possible plant reconfigurations required for Mn(II) removal from 'large' coal-associated discharges in Pennsylvania. Large sites were assumed to have a flow rate = 2,700 gal/min and represent the 91st – 100th percentile of coal sites in Pennsylvania.

Configuration description	Coprecipitation	KMnO$_4$ + sand filter	Water softening	Representative value for cost to industry
Capital costs	$0 – $2,190,000	$1,000,000 – $1,190,000	$2,440,000 – $3,320,000	$0 – $2,190,000
Annual costs	$236,000 – $361,000	$603,000 – $617,000	$473,000 – $702,000	$236,000 – $617,000

Costs to the coal industry

Cost summaries for the various treatment configurations for the various sized sites are summarized in Tables 4 – 6. From these options, it was assumed that a facility would not select the most expensive option. Therefore, a 'representative cost to the industry' range was determined from the two lower-priced options. As shown in Tables 5 and 6, chemical precipitation water softening for Mn(II) removal was never the least expensive treatment option. Using Equation (1), these representative costs were then combined with the assumed facility size distribution to calculate an 'aggregate industry cost per site' range as follows:

Aggregate cost per site = 0.25*small site costs + 0.65*average site costs + 0.10*large site costs (1)

where the 0.25 represents the 0-25th percentile of small sites, 0.65 represents the 26th-90th percentile of average sites, and the 0.10 represents the 91st-100th percentile of large sites. This formula was used to estimate both the capital costs and the annual costs. Using Equation (1) and the representative costs presented in Tables 4 – 6, aggregate industry costs per site were found to range from $0 (repurpose all existing unit operations) to $693,000 in capital costs and range from $46,300 to $115,000 in annual costs. Using Equation (2), total costs to the coal industry were then estimated as follows:

Total industry cost = # sites requiring additional treatment * Aggregate cost (2)

where this formula was used to estimate both the total industry capital costs and the annual costs. If all 706 sites were assumed to require additional treatment operations to remove Mn(II), then the total industry capital costs are estimated to range from $0 (repurpose all existing unit operations) to $489 million and total industry annual costs were estimated to range from $32.7 million to $81.2 million. Both estimates agree with Tetra Tech who estimated capital 'treatment improvements in excess of $200 million' and 'annual treatment costs…to be $44 to $88 million'.

Because the number of sites requiring additional treatment and the number of sites that may be able to utilize more cost-effective Mn(II) removal technologies are unknown, there are considerable uncertainties with these costs estimates. For example, it is highly unlikely that all 706 sites will need to add Mn(II) removal treatment to reach the most stringent effluent standard of 0.3 mg/L total Mn and it is very likely that any site would select the most cost-effective treatment option. Therefore, a more refined estimate of total costs to the industry caused by the proposed Mn water quality criterion was determined based on an assumed % of sites that will need to add Mn(II) removal treatment and costs for the 'most likely' option selected for treatment (shaded columns in Tables 4 – 6 based on author's best professional judgement). Using Equation (1) and the 'most likely' costs shaded in Tables 4 – 6, aggregate industry costs per site would range from $258,000 to $270,000 in capital costs and range from $62,700 to $87,200 in annual costs. Using these aggregate costs and assuming 530 sites (i.e., 75%) will need to add Mn(II) removal treatment, total costs to the industry would range from $137 to $143 million in capital costs and from $33.0 million to $46.2 million in annual costs. If 50% of the sites (i.e., 353 sites) need to add Mn(II) removal treatment, total costs to the industry would range from $91.1 to $95.3 million in capital costs and from $22.0 million to $30.8 million in annual costs.

7. Concluding Remarks

Tetra Tech argues that removing Mn(II) at municipal drinking water treatment (DWT) plants would be more cost-effective than removing Mn(II) at private coal facilities. This is not a fair argument. If influent Mn(II) concentrations were to increase in a DWT plant's source water, then that DWT plant would have to add similar Mn(II) removal technologies described in this report. A DWT plant would also have to meet a more stringent treatment goal (0.05 mg/L total Mn) than the most stringent treatment goal for a CMD plant (0.3 mg/L total Mn). It is likely that DWT plant operators would select oxidative filtration. On an equal flow rate basis, capital costs for both the DWT industry and the coal industry would be similar. On an equal Mn(II) load (concentration × flow rate) basis, annual costs for both the DWT industry and the coal industry would be similar. In other words, it is not less expensive for a DWT plant to remove the same amount of Mn(II) as compared to a CMD plant.

The EQB's proposed rulemaking to lower the water quality standard for manganese to 0.3 mg/L total Mn will require some coal-mining/coal-processing facilities to add Mn(II) removal technologies to meet more stringent effluent guidelines as NPDES permits are updated. While chemical precipitation water softening was used by Tetra Tech as the likely Mn(II) removal technology for the coal industry for estimating costs to the industry, this may not be the best choice at most sites. This technology may not meet an effluent limit of 0.3 mg/L total Mn unless decarbonation is also included, may lead to compliance issues associated with Al, will require additional alkali, and will produce additional solids. This technology was never the least expensive treatment option (Table 5 and 6). Instead coal companies should consider oxidative filtration and investigate coprecipitation to $Fe(OH)_3(s)$ to reduce costs.

For oxidative filtration, permanganate was selected for all cost estimates because it is a built-in option in AMDTreat. However, there are less expensive oxidants such as chlorine, chlorine dioxide, ozone, and $O_2(aq)$. While permanganate is a good choice because of its rapid oxidation of Mn(II), once $MnO_x(s)$ coatings develop on filter media, heterogenous oxidation of Mn(II) by chlorine, and

autocatalytic oxidation of Mn(II) by O_2(aq) could be exploited to reduce annual costs. After MnO_x(s)

coatings form on the filter media, heterogeneous oxidation of Mn(II) by dissolved chlorine

(hypochlorous acid/hypochlorite) will become rapid and heterogeneous oxidation of Mn(II) by O_2(aq)

will become an important Mn(II) removal mechanism. Under these operating conditions (which could be

most of the filter cycle run), chemical oxidants may only be needed intermittently or not at all (Knocke

et al., 1991b). Properly designed and operated, this chemical oxidation system would use the most

expensive oxidant (permanganate) for the shortest time possible, followed by the intermittent longer-

term use of the less expensive oxidant (chlorine) and exploit the use of a free oxidant (oxygen).

Therefore, estimates of annual costs for oxidative filtration provided in this report likely represent the

most conservative maximum values. This is an important point because oxidative filtration was the most

cost-effective treatment option for average-size sites (Table 5).

Total costs to the coal industry are extremely challenging to predict and include considerable

uncertainty. Actual costs at each site will be determined by unique site-specific conditions including e.g.,

influent water chemistry, flow rate, effluent permit limits, and land availability. It is currently unknown

how many site permits will change to include a lower Mn effluent limit and the numerical limit in each

permit. It does appear that some of the large deep mines may be able to remove Mn(II) with relatively

lower additional capital and annual costs.

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