

MANGANESE REMOVAL IN DRINKING WATER SYSTEMS



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ABSTRACT

Manganese exists naturally in some soils and enters into ground water or is washed down to surface water reservoirs. If not oxidised, manganese(II) ions will escape through water treatment processes into the supply system. Once in the system, the ion is gradually oxidised to insoluble manganic dioxide causing dirty water problems.

Manganese(II) can be oxidised to insoluble manganic dioxide and removed by clarification and filtration. Oxidation can be achieved by aeration, chlorination or chemical oxidation using potassium permanganate.

South Gippsland Region Water Authority (SGRWA) has manganese problems in most of their surface water reservoirs. This paper shares the experiences of SGRWA in removing manganese and compares the advantages and disadvantages of alternate oxidation methods with plant scale data.

KEYWORDS

Manganese, Aeration, Potassium permanganate, Chlorine, Sodium Hypochlorite, pH, detention time, dosage

1.0 INTRODUCTION

South Gippsland Region Water Authority (SGRWA) owns and operates ten water treatment plants and supplies 21 small towns. The main water supply for the treatment plants is surface water. Four SGRWA plants obtain their water directly from rivers. The remaining plants source their water from reservoirs. Since manganese exists naturally in the South Gippsland region as insoluble manganic oxide and soluble manganese ion almost all the plants have manganese problems. Although the storage reservoirs supply water of a consistent quality for most parameters, the manganese levels in the raw water vary significantly with time. The insoluble manganic dioxide in the raw water tends to settle to the bottom of the reservoirs. Where dissolved oxygen levels are low the manganese ion is released into the water from the manganic oxide.

Manganic dioxides that have not settled in the reservoir can be readily removed by coagulation, sedimentation and filtration processes. However, since the removal of soluble manganese cannot be achieved by such processes, the soluble manganese which enters the supply system is gradually oxidised to manganic dioxide by the disinfection process causing problems for customers. Generally customer complaints are received at manganese concentrations as low as 0.03 mg/L. According to the Australian Drinking Water Guidelines (ADWG) manganese is not a health consideration unless the concentration exceeds 0.5 mg/L.

The descriptions of complaints resulting from manganese in the supplied water vary from dirty water, black water, or brown water. Where bleach is added to laundry, manganese ions are oxidised to manganic dioxide forming stains on washed clothes. Maintenance of the water supply pipeline is also a problem. Low levels of iron and manganese in the supply water enhance the growth of iron bacteria that produce black slimes.

These slimes increase the chlorine demand and reduce the available chlorine residual in the distribution system. They also cause taste and odour problems. If not flushed regularly the bacteria slimes and manganic oxide sediments accumulate in the pipes. During peak demand periods they slough off and cause problems. As a result normal water flushing at the hydrant is not sufficient to maintain pipelines. Regular air scouring of the mains is required and undertaken by SGRWA.

In addition, manganic dioxide also stains the sample pipelines and on-line monitoring equipment such as pH probes, turbidity meters and chlorine residual analysers. The sample lines coated with manganic dioxide absorb and release manganese ions. Where long sample lines exist this results in misleading manganese levels being monitored.

Soluble manganese can be oxidised to manganic dioxide and then removed by coagulation, sedimentation and filtration. Oxidation can be achieved by aeration or by oxidation agents such as chlorine, sodium hypochlorite or potassium permanganate.

2.0 OXIDATION OF MANGANESE

2.1 Aeration

Aeration can be used to oxidise manganese ions to manganic dioxide. However, the kinetics of oxidation by oxygen is slow in typical water treatment conditions and so a long detention time is required (AWWA, 1990). Aeration is useful as an option to oxidise manganese in reservoirs. Manganic dioxide can release manganese ions back into the water at DO levels as high as 4 mg/L. Generally aeration involves high capital costs and high running costs. Aeration alone cannot completely oxidise all manganese. Aeration is ineffective in oxidising organically bound manganese. As a result aeration can only be used as a preliminary treatment to oxidise manganese. Where further oxidation is necessary an oxidising agent must be introduced to reduce the manganese levels.

Aeration is used in several SGRWA reservoirs to provide artificial destratification to control algal blooms, iron and manganese. However, manganese levels in the raw water can increase significantly on occasions. Increasing levels have been observed where algal blooms have been treated using algaecide. It is believed that this is due to oxygen depletion resulting from the sudden death and decomposition of the algal cells (AWWA research Foundation, 1995).

2.2 Chlorine

Chlorine is a stronger oxidising agent than oxygen. Chlorine forms hypochlorous acid when dissolved in water. For manganese oxidation chlorine needs to be added at the head works or just before filtration. Pre-chlorination has a higher potential to react with organic compounds and to produce trihalomethane (THM) which is carcinogenic. At SGRWA chlorine gas is delivered in cylinders to the water plants. Chlorinators and appropriate safety equipment are required to dose chlorine.

2.3 Sodium Hypochlorite

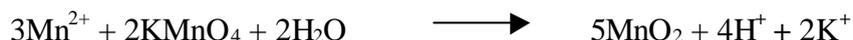
Sodium hypochlorite also forms hypochlorous acid when dissolved in water. The sodium hypochlorite reaction slightly increases the pH whereas the reaction of chlorine gas slightly reduces the pH. Commercially available sodium hypochlorite has a concentration of 12.5 %. Even though sodium hypochlorite is about twice the cost as equivalent chlorine gas, sodium hypochlorite is used only in small systems at SGRWA due its ease of handling and safety.

2.4 Potassium Permanganate

Potassium permanganate is a stronger oxidant than chlorine and sodium hypochlorite. Whilst it is effective in oxidising manganese, it has also been used for the treatment of taste and odour problems in water supplies (AWWA Research Foundation, 1995). Unlike chlorine, the reaction of potassium permanganate with organic compounds will not produce trihalomethanes but will actually reduce them (Singer, 1988).

Potassium permanganate is supplied as a powder in 50 kg drums. Potassium permanganate is

mixed on site with water to a concentration between 0.5 to 2.0 % before dosing. The stoichiometric equation for manganese ion oxidation by potassium permanganate is given as below.



According to the stoichiometric equation, it would require 1.92 mg of potassium permanganate to oxidise 1 mg of manganese ion. A comparison of the oxidants required to oxidise manganese according to stoichiometry is given in Table 1.

Table 1: *Comparison of Oxidants for oxidation of manganese*

Oxidant	Theoretical weight to oxidise 1 mg of manganese ion
Oxygen, mg	0.29
Chlorine, mg	1.30
Sodium hypochlorite, mg	1.36
Potassium Permanganate, mg	1.92

Even though, the stoichiometric requirement of chlorine and hypochlorite is less than potassium permanganate, in practice the chlorine requirement has been found to be much higher due to the chlorine demand by organic carbon.

3.0 JAR TEST STUDIES

A series of jar tests were completed to compare the effectiveness of potassium permanganate and sodium hypochlorite to oxidise manganese. The pH, oxidant dosage and detention time were identified as the controlling parameters for manganese removal. The tests were designed to simulate the conditions at a water plant where levels of manganese were high. The jar testing procedure performed is as follows:

- 1) Initial pH adjustment to the required pH;
- 2) Mixing at 100 rpm;
- 3) Oxidant addition (potassium permanganate or sodium hypochlorite);
- 4) Mixing at 100rpm for the required detention time;
- 5) Alum addition (40mg/L concentration for all jars);
- 6) Rapid mixing at 100 rpm for 1 minute;
- 7) Slow mixing at 60 rpm for 5 minutes;
- 8) Slow mixing at 10 rpm for 10 minutes;
- 9) Settling time (10 minutes);
- 10) Decanting 50ml of sample from the top of the jars;
- 11) Filtration of sample through 0.45um filter;
- 12) Analysis of filtrate for manganese.

Jar test results are summarised in Table 2. The objective of the tests was to reduce the manganese concentration below 0.02 mg/L.

3.1 pH

The pH of the water is the most important parameter for manganese removal. Required levels of manganese removal occurred above a pH of 7.5. Pre pH adjustment was made using a 10% soda ash solution. The lowest manganese concentration of 0.026 mg/L was obtained at an initial pH of 8.3 (Test No.12). Alum addition decreased the pH to approximately 5.8.

3.2 Detention Time

Generally a detention time of 5 to 15 minutes is recommended for manganese removal (Sank, 1980). According to a study by Desjardins, oxidation of manganese by potassium permanganate occurred in less than 5 minutes where the manganese was not in a complexed form (AWWA Research Foundation, 1995). Jar tests were performed at 2 to 3 minute intervals to simulate the conditions of the existing plant where the maximum available detention time during average demand is approximately 3.0 minutes. Results from the tests indicated no significant difference in manganese removal for the time range tested.

Experience in one SGRWA plant, (Lance Creek WTP), indicates that a detention time of 10 minutes is adequate to provide complete oxidation of manganese with potassium permanganate. It should be noted however that the detention time for manganese oxidation has to be provided before alum addition. After alum addition, the pH drops below 7.0 slowing the kinetics of potassium permanganate oxidation.

3.3 Permanganate Dosage

The theoretical potassium permanganate dosage required is approximately double the concentration level of manganese in the raw water. Manganese in the raw water varied between 0.15 to 0.38 mg/L during the tests. Best results were obtained using a potassium permanganate dosage of 0.4 to 0.5 mg/L.

Slight overdosing of permanganate (up to 0.1 mg/L) has been found not to cause any adverse effects. Currently, potassium permanganate is used at five of the water treatment plants at SGRWA to remove manganese. Installation of dosing systems at the remaining water treatment plants is presently occurring.

3.4 Sodium Hypochlorite Dosage

Trials with the addition of sodium hypochlorite indicated that sodium hypochlorite was not effective within short detention times. The kinetics of oxidation by chlorine is very slow and therefore longer detention times are required.

Pre chlorination is not preferred because of THM formation especially for high coloured raw water.

Table 2: Jar Tests Results

Test No.	Jar No.	Test Sample		Jar Testing conditions			Filtrate Sample
		Manganese	pH	KMnO ₄ dose	Sodium Hypochlorite Dose	Detention Time	Manganese
		mg/L		mg/L	mg/L	Minutes	mg/L
1	1	0.275	6.70	0.5	0	3	0.163
	2		6.70	1.0	0	3	0.219
	3		6.70	2.0	0	3	0.524
2	1	0.275	6.70	0.2	0	3	0.177
	2		6.70	0.5	0	3	0.162

3	3	0.275	6.70	0.7	0	3	0.138
	1		6.70	0.2	7.5	3	0.177
	2		6.70	0.7	7.5	3	0.137
4	1	0.181	6.90	0.5	0	3	0.090
	2		7.40	0.5	0	3	0.061
	3		8.70	0.5	0	3	0.100
5	1	0.181	7.10	0.6	0	3	0.133
	2		7.10	0.8	0	3	0.136
	3		7.10	0.9	0	3	0.151
6	1	0.181	7.02	0.2	0	3	0.140
	2		7.02	0.4	0	3	0.144
7	1	0.147	7.70	0.2	0	2.5	0.086
	2		7.70	0.5	0	2.5	0.037
	3		7.60	0.8	0	2.5	0.041
	4		7.60	0.9	0	2.5	0.081
8	1	0.147	6.90	0.5	0	2	0.122
	2		7.35	0.5	0	2	0.082
	3		7.35	0.4	0	2	0.120
	4		7.35	0.6	0	2	0.119
9	1	0.151	6.70	0.5	0	3	0.135
	2		7.04	0.5	0	3	0.095
	3		7.27	0.5	0	3	0.056
	4		7.52	0.5	0	3	0.038
10	1	0.151	7.54	0.5	0	2	0.067
	2		7.94	0.5	0	2	0.037
	3		7.58	0.4	0	2	0.061
	4		8.30	0.5	0	2	0.026
11	1	0.644	7.3	0	4	3	0.432
	2		7.2	0	8	3	0.402
	3		7.1	0	16	3	0.362
	4		6.9	0	20	3	0.002

Jar tests can give an indication of the pH and dosage requirement for manganese removal. However, jar tests alone cannot exactly predict the treated water manganese level. This is because filtration simulated in the jar tests uses 0.45um filter paper whereas water treatment plant filtration involves granular media filtration.

Granular media filters play a major role in manganese removal. Manganic dioxide solids that are deposited on the granular media during filtration act as catalysts in manganese oxidation reactions. The manganic dioxide is also found to adsorb the manganese ion which will be eventually oxidised in time (Water Quality and Treatment, 1990).

4.0 CASE STUDY

4.1 Korumburra Ness Creek Reservoir

The Korumburra Reticulation System provides water for the township of Korumburra with a population of 4200. The system also includes two industrial customers, (Korumburra Saleyards and Burra Foods), and a hospital.

The raw water is sourced from three reservoirs, Coalition Creek, Bellview Creek and Ness Creek as shown in Figure 1. Coalition Creek Reservoir is the only storage used all year round. Water from the other two reservoirs is pumped as required.



In the summer of 2000-2001, the Korumburra Township had to be placed on water restriction due to inadequate water at the reservoirs. Unfortunately the manganese level in Ness Creek Reservoir increased to a level where it was not possible to use the water without contaminating the water supply in the Coalition Reservoir. Therefore as a temporary solution it was decided to treat the manganese at the reservoir by oxidation and settling. Once treated the water would then be pumped to the Coalition Reservoir.

Samples were taken at the reservoir at different locations and depths to determine the manganese levels in the reservoir. The Ness Creek Reservoir has a floating off-take approximately 1m deep. The manganese level at this off-take was measured at 0.38 mg/L.

Table 3: *Manganese Testing at Korumburra Ness Creek Reservoir*

Location No.	Description	Sample No.	Depth	Manganese mg/L
1	Off take	1	1m	0.375
		2	5m	2.472
2		1	1m	0.375
3		1	1m	0.318

4.2 Potassium Permanganate Dosing

Potassium permanganate dosing in the reservoir was considered as an immediate and viable option. However, potassium permanganate as a long-term solution was not preferred because of the total mass of manganese compounds that would settle and remain in the reservoir. Therefore as a trial a small amount of potassium permanganate was dosed. Approximately 15kg of potassium permanganate was dissolved in approximately 900L of water. This solution was then sprayed into the reservoir from a boat to give an overall potassium permanganate concentration of 0.19 mg/L.

The total water volume in the reservoir at the time of application was approximately 80ML. Samples taken after two days indicated that the manganese levels had increased to 0.5 mg/L at 1m sampling depth. Most of the manganese appeared to be in a dissolved form. This is most likely due to the mixing effect of the boat in the reservoir which increased the manganese concentration at the surface of the water.

4.3 Aeration

Temporary aeration was introduced into the basin as a second step to reduce the manganese. Samples were taken at the reservoir weekly. Initially the manganese levels increased, however, after three weeks, the soluble manganese concentration decreased below 0.5 mg/L. Whilst the total manganese level was still high at approximately 0.5 mg/L, this indicated that most of the manganese has been oxidised to manganic dioxide and remained in suspension.

The manganic dioxide in the reservoir could now be removed by coagulation, clarification and filtration treatment. However, transferring manganic dioxide solids into the main reservoir was still not considered as a good option.

4.4 Alum addition

Flocculating the manganic dioxide solids with alum addition was considered in order to settle as much manganese as possible in the reservoir. Approximately 800 kg of alum powder was evenly distributed from a boat to achieve an overall alum concentration of approximately 10 mg/L in 80 ML of water. After alum addition aeration was continued for one more day to provide adequate mixing. The aerator was then turned off to allow settling of the manganic dioxide-alum flocs. A week later the measured manganese levels had decreased below 0.1 mg/L. The water from the Ness Creek Reservoir was then pumped to the Coalition Creek Reservoir, the main reservoir that feeds the water treatment plant.

4.5 Permanent Solution

Treating the water at the reservoir was considered as a temporary, emergency option. Providing a permanent aeration system at the Ness Creek Reservoir is currently under consideration.

5.0 CONCLUSIONS

Comparison of oxidants to remove manganese brought the following conclusions.

- ◆ Aeration at the reservoir should be considered as primary treatment. However, aeration alone cannot oxidise all of the manganese and therefore oxidising agents are necessary at the treatment plants to reduce manganese to low levels.
- ◆ Potassium permanganate dosing is very effective. However, if the raw water manganese level fluctuates significantly, adjusting the permanganate dosing according to manganese levels may be operationally difficult. Slight overdosing of permanganate (up to 0.1 mg/L) has been found not to cause any adverse effects.
- ◆ Higher pH (pH above 8) resulted in improved manganese removal. However, if the resulting pH after alum addition is above 6.5, alum coagulation would be affected. Whilst alum coagulation is good at a slightly acidic pH (5.5 to 6.5), it is not always economical to add more pH correcting chemical. Plant performance indicates that a pre pH correction up to 7.5 to 8.0 with a detention time of 10 minutes before alum addition gives adequate manganese removal.
- ◆ Chlorine is not as effective as potassium permanganate in oxidising manganese. The chlorine requirement has been found to be in excess of the stoichiometric requirement. This is due to chlorine demand by organic compounds.

6.0 ACKNOWLEDGEMENTS

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