

Oxidation of manganese in drinking water systems using potassium permanganate

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Abstract South Gippsland Region Water Authority experience manganese problems in most of their surface water reservoirs. Manganese is present in the form of manganese(II) ions and manganic dioxide solids. At low dissolved oxygen levels, the manganic dioxide is reduced to the manganese(II) ion. If not oxidised, the manganese(II) ion escapes through water treatment facilities and enters the supply system. Once in the system, the manganese ions are gradually oxidised to insoluble manganic dioxide causing dirty water problems which can stain clothes and bathing equipment. As part of the water treatment process, manganese(II) can be oxidised to insoluble manganic oxide and then removed by clarification and filtration. Generally, oxidation can be achieved by aeration or chemical oxidation by addition of an oxidising agent such as potassium permanganate (KMnO_4) or chlorine. However, due to fluctuations of manganese levels in raw water, treatment techniques are often very difficult. This paper shares the experiences of South Gippsland Water in using potassium permanganate as part of the water treatment process to remove manganese in its surface water reservoirs. Whilst consideration is given to the advantages and disadvantages of alternative oxidation methods, this paper primarily focuses on the use of KMnO_4 to remove manganese and the resulting analytical problems associated with monitoring manganese levels.

Keywords Aeration; chlorine; detention time; manganese; potassium permanganate; pH

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, and the remaining plants source their water from reservoirs. Manganese exists naturally in the SGRWA's water catchment and 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 dioxide solids 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 (NHMRC and ARMCANZ, 1996).

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 adsorb 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.

Oxidation of manganese

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 (Benefield and Morgan, 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, as it is ineffective in oxidising organically bound manganese. As a result, aeration can only be used as a preliminary treatment to oxidise manganese, and 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, on occasion, increase significantly. Increasing levels have been observed where algal blooms have been treated using algacide. It is believed that this is due to oxygen depletion resulting from the sudden death and decomposition of the algal cells.

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.

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%. Since sodium hypochlorite costs about twice the equivalent chlorine gas, sodium hypochlorite is used only in small systems at SGRWA for its ease of handling and safety.

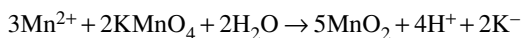
Potassium permanganate

Potassium permanganate (KMnO_4) 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. Unlike chlorine, the reaction of KMnO_4 with organic compounds will not produce trihalomethanes, but will actually

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

reduce them (Singer, 1988). Potassium permanganate is supplied as a powder in 50 kg drums and is mixed on site with water to a concentration between 0.5–2.0% before dosing. The stoichiometric equation for manganese ion oxidation by KMnO_4 is given as:



According to the stoichiometric equation, it would require 1.92 mg of KMnO_4 to oxidise 1 mg of manganese ion. A comparison of the oxidants required to oxidise manganese according to stoichiometry is given in Table 1. Even though the stoichiometric requirement of chlorine and hypochlorite is less than KMnO_4 , in practice the chlorine requirement has been found to be much higher due to the chlorine demand by organic carbon.

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 100 rpm for the required detention time;
5. alum addition (40 mg/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 50 ml of sample from the top of the jars;
11. filtration of sample through 0.45 μm 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.

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.

Detention time

Generally a detention time of 5–15 minutes is recommended for manganese removal (Sanks, 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 (Desjardins, 1995). Jar tests were performed at 2–3 minute intervals to simulate the conditions of the existing plant where the maximum available detention time during average demand is approximately 3 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 KMnO_4 . 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 KMnO_4 oxidation.

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. Prechlorination 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 (mg/L)	pH	KMnO_4 dose (mg/L)	Sodium Hypochlorite dose (mg/L)	Detention time (minutes)	Manganese (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		6.70	0.7	0	3	0.138
3	1	0.275	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

Permanganate dosage

The theoretical KMnO_4 dosage required is approximately double the concentration level of manganese in the raw water. Manganese in the raw water varied from 0.15–0.38 mg/L during the tests. The best results were obtained using a KMnO_4 dosage of 0.4–0.5 mg/L.

Jar tests are generally conducted to select the optimum dose rate of KMnO_4 . Although a suitable dosing rate can be determined, operational difficulties exist in changing dosing rates with sudden fluctuations of manganese in the raw water. Such difficulties can be overcome by slight overdosing of KMnO_4 .

In order to quantify the allowable overdosing of KMnO_4 , an experiment was conducted in the laboratory using different strengths of KMnO_4 solutions prepared with deionised water. Since there is no demand for permanganate ion in the deionised water, all the KMnO_4 added to the solution is considered as overdosing amount. Solutions were left in a closed bottle and analysed for manganese, colour, and turbidity after 0 hours, 24 hours, 48 hours, and 72 hours to simulate the detention time in the distribution system. Table 3 shows the results of the experiment.

Manganese levels are analysed in water treatment laboratories using calorimetric methods. South Gippsland Water uses the Hach 1-(2-Pyridylazo)-2-Naphthol (PAN) test method to determine manganese in water. Using this method first all manganese compounds including manganic oxide and permanganate, are reduced to manganese(II) ion by the addition of ascorbic acid as a reducing agent. Alkaline cyanide reagent and PAN indicator are then added to mask interferences and complex the manganese ion.

Where permanganate is overdosed in the treatment process, excess permanganate ion will remain and be detected as manganese. In order to differentiate the permanganate ion during analysis, addition of ascorbic acid to the water sample has been skipped and the permanganate ion is no longer reduced or detected. Manganese levels that are recorded without ascorbic are due to the soluble manganese in the water.

Table 3 Tests for simulation of permanganate overdosing

KMnO_4 solution strength (mg/L)	Time (hours)	Manganese (mg/L)		Colour (HU)	Turbidity (NTU)
		Tested with ascorbic acid	Tested without ascorbic acid		
0.05	0	0.017	0.000	0	0.12
	24	0.012	0.000	0	0.15
	48	0.007	0.000	0	0.19
	72	0.005	0.000	0	0.19
0.1	0	0.034	0.000	0	0.45
	24	0.027	0.000	0	0.43
	48	0.021	0.000	5	0.43
	72	0.012	0.000	5	0.38
0.2	0	0.068	0.000	5	0.47
	24	0.056	0.000	20	0.63
	48	0.057	0.000	25	0.68
	72	0.043	0.000	25	0.62
0.3	0	0.100	0.000	10	0.82
	24	0.091	0.000	30	0.94
	48	0.084	0.000	40	1.01
	72	0.073	0.000	40	0.95
0.4	0	0.124	0.000	10	1.08
	24	0.118	0.000	35	1.41
	48	0.110	0.000	45	1.51
	72	0.098	0.000	50	1.27
0.5	0	0.156	0.000	15	0.44
	24	0.135	0.000	45	0.95
	48	0.135	0.000	55	0.94
	72	0.121	0.000	55	0.99

In the experiments with the potassium permanganate solutions, the pink colour was not visible to the naked eye below 0.3 mg/L potassium permanganate. As shown in Table 3, no significant colour development (>10 HU) was identified up to 72 hours of testing for the concentrations of 0.05 mg/L and 0.1 mg/L as potassium permanganate. The results indicated that slight overdosing up to 0.1 mg/L does not cause any adverse effects in the distribution system. On the other hand surplus permanganate ion (MnO_4^-) assures full oxidation of the manganese ion in the supply system.

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 0.45 μm 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 (Benefield and Morgan, 1990).

Conclusions

Comparison of oxidants to remove manganese led to the following conclusions.

- Aeration at the reservoir should be considered as a 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 (5.5–6.5), it is not always economical to add more pH correcting chemical. Plant performance indicates that a pre-pH correction up to 7.5–8.0 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.

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