



## Purate<sup>®</sup> Technical Bulletin

# Advantages of Chlorite Reduction with Ferrous Ion



by

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## **Summary**

Chlorine dioxide is used effectively in hundreds of drinking water plants to oxidize iron and manganese, to provide disinfection, to reduce TTHM and HAA<sub>5</sub> formation, and for many other benefits. Chlorite, a byproduct of chlorine dioxide use, has an MCL limit and is occasionally associated with “cat urine” odors, and these issues have combined to limit the dosage that a utility can apply. But ferrous salts can be used to eliminate the chlorite byproduct while simultaneously oxidizing the ferrous to ferric, thus providing an extra benefit to the coagulation and sedimentation portions of the treatment plant.

## **Chlorine Dioxide Treatment Benefits**

Future USEPA regulations will mandate increased disinfection capabilities and lower disinfection byproduct levels from water treatment plant processes <sup>(1)</sup>. Advanced oxidants, such as chlorine dioxide, will be needed to substitute for chlorine in pre-disinfection in order to increase disinfection capabilities and lower TTHMs and HAA<sub>5</sub> levels in distribution systems <sup>(2)</sup>.

Chlorine dioxide will also be utilized in pretreatment to:

- Reduce taste and odors in raw water
- Oxidize natural iron and manganese
- Reduce color
- Improve coagulation and flocculation
- Improve filtration
- Minimize taste and odors from chloramination treatment in distribution systems <sup>(3,4,5,6)</sup>

Although there are many benefits from chlorine dioxide treatment, there are two limitations cited in its use. They are:

1. The USEPA 1.0 ppm chlorite MCL (maximum contaminant level) limits the chlorine dioxide dosage to 1.4 ppm
2. The chlorite residual re-forms chlorine dioxide in free chlorine distribution systems, which causes an occasional “cat urine” odor at the tap when it reacts in the air with new carpet glue volatiles in a poorly ventilated room.

Therefore, with chlorite reduction implemented at the water plant, it is possible to apply higher chlorine dioxide dosages without exceeding the chlorite MCL and to eliminate the potential for “cat urine” complaints from water customers <sup>(4)</sup>.

## **Chlorite Reduction by Ferrous Ion**

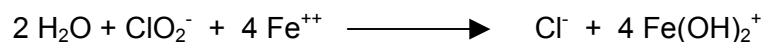
When chlorine dioxide reacts in water, it forms a stable byproduct called chlorite (ClO<sub>2</sub><sup>-</sup>), which can be safely consumed below the 1.0 ppm MCL level at the water tap. Typically, about 60-70% of the chlorine dioxide applied converts to the byproduct chlorite. So in order to maintain the chlorite level below 1.0 ppm, the water plant operator often limits the applied chlorine dioxide dosage to 1.4 ppm. However, some plants are using more than 1.4 ppm of chlorine dioxide and therefore must reduce the chlorite level within the plant process by using ferrous chloride or ferrous sulfate.



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Based on laboratory testing and full plant usage of chlorine dioxide, each ppm of chlorite can be reduced by 3.1 ppm of ferrous as Fe from ferrous chloride or ferrous sulfate solutions <sup>(7,8,9,10)</sup>. The ferrous ion is oxidized to the ferric ion by the chlorite while the chlorite is reduced to chloride. The “best of both worlds” are accomplished by this reaction because both results benefit the water plant. The ferrous ion has now become a strong coagulant in the ferric form while the chlorite has been transformed to the safe chloride form. The reaction of ferrous to ferric is a very fast reaction. It is often added at the flash mixer where the reaction is completed within the retention time of the flash mixer. The chemical equation is:



Dissolved oxygen in the water will also oxidize ferrous to ferric, but at a much slower rate. Therefore, dissolved oxygen acts as a safety net when a slight excess of ferrous is used. Also, some plant operators prefer to add a small amount of chlorine (<0.5 ppm) at the flash mixer or the filter influent point as an additional safety factor for assuring complete ferrous oxidation before it reaches the filter effluent. The small amount of chlorine will decay rapidly which will minimize TTHM formation.

### **Ferrous Chloride versus Ferrous Sulfate**

Ferrous chloride or ferrous sulfate is effective in reducing chlorite byproduct levels. The choice of which one to use will depend on one or more of the following issues. The issues involved are: availability, cost, raw water chemistry, chemical storage capacity and % iron content of the chemical. The lowest delivered cost of either chemical will often depend upon their transportation cost from the chemical supplier to the local water plant.

Some plants determine their choice based on the raw water chemistry at the plant. If a water supply has high sulfates, then ferrous chloride is used to prevent sulfate addition. On the other hand, if a water supply has high chloride levels, then ferrous sulfate becomes the best choice.

Many plants prefer to use ferrous chloride because it has a greater iron content (10%) as compared to ferrous sulfate (5%), which makes ferrous chloride more convenient to use in terms of required chemical storage capacity and pumping rate. Also, ferrous sulfate is more likely to precipitate in storage tanks in colder climates unless the storage tank temperature is controlled <sup>(11)</sup>.

The amount of ferrous solution fed at the flash mixer will depend upon the amount of chlorine dioxide applied, the % iron content of the solution, and the total residual oxidants' (chlorite plus chlorine dioxide) level at the flash mixer.



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Example

A plant feeding 1.4 ppm of chlorine dioxide to the raw water will have a total residual oxidants' level of about 0.98 ppm ( $1.4 \times 0.70 = \text{mg/l ClO}_2^-$ ) at the flash mixer.

If a 12% (as Fe) ferrous chloride solution is used, then the amount of ferrous chloride solution needed is 25.3 mg/l as calculated in equation 1.

Equation 1:

$$\frac{(\text{ClO}_2 \text{ Dose, mg/l} \times 0.70 \times 3.1 \text{mg as Fe/mg ClO}_2^- \times 100)}{\% \text{ Ferrous as Fe}} = \text{mg/l Ferrous chloride solution}$$

If a water plant wanted to use ferrous as their primary coagulant, then a jar test evaluation should be done with ferric chloride or sulfate to determine the ideal ferric dose. Based on this information, the amount of total residual oxidants' level required from the chlorine dioxide dose can be easily determined as the amount of ferrous as Fe needed using equation 1. This plant treatment example should result in non-detectable chlorite residuals in the finished water while providing coagulation capability from the ferrous to ferric reaction. The amount of ferric coagulant needed for low settled water turbidities will depend upon the amount of total residual oxidants' levels available for the ferrous to ferric reaction.

In El Paso Texas, the 40 MGD Canal (Umberhauer/Robertson) Water Plant is able to meet proposed Stage 2 Disinfection and Disinfection By Products' levels (Figure 1). Despite having high turbidity raw water, the plant's settled water turbidity is less than 2.0 ntu using 3.0 ppm chlorine dioxide dose (Figure 2) with about 54 ppm of ferrous chloride solution while having a non-detectable chlorite level in the distribution system (8,9, 10). On the other hand, water plants having a low turbidity raw water supply may be able to obtain adequate settled water turbidity levels by adding chlorine dioxide dosages in the 1.0 to 1.4 ppm range with 25 ppm of ferrous chloride dose.

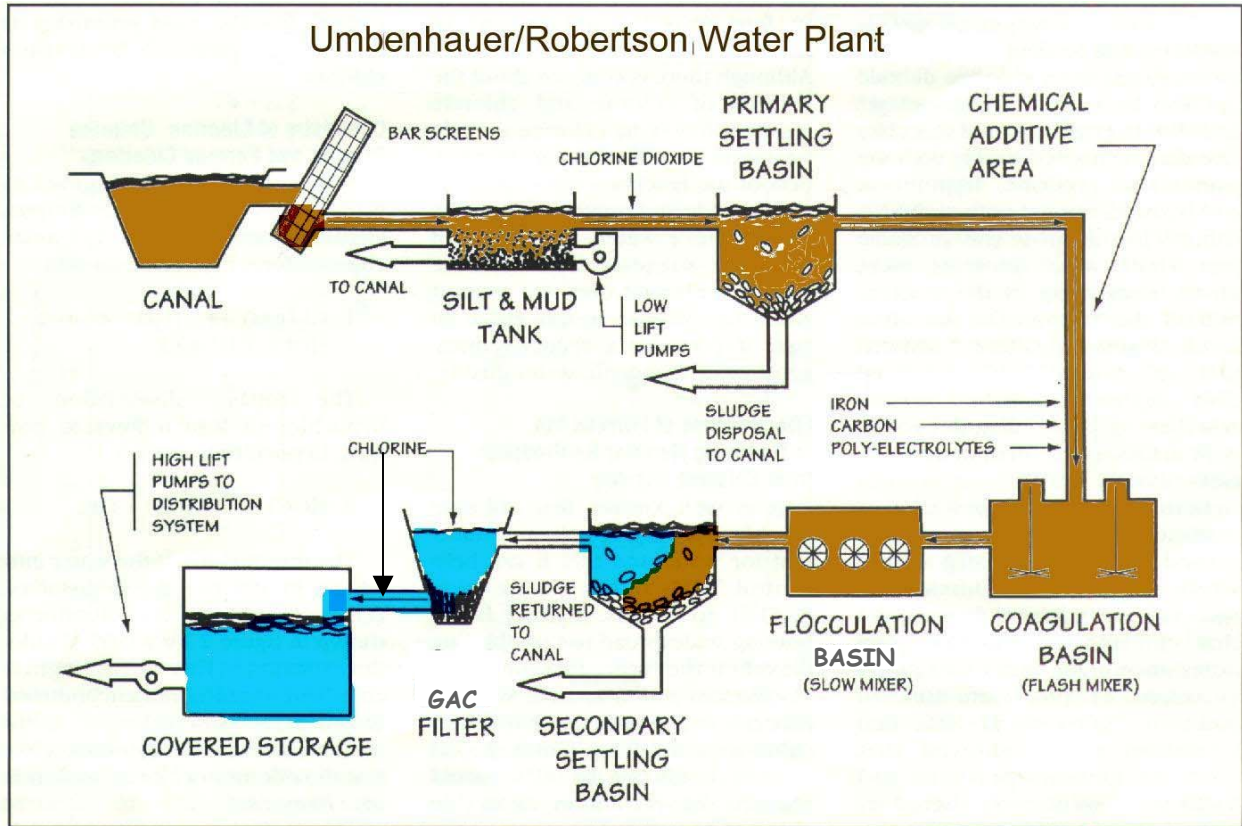


Figure 1 – Umbenhauer/Robertson Flow Schematic



Figure 2 – Eka Chemicals SVP-Pure® Chlorine Dioxide Generator



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### **Potential Water Plant Applications**

There are many water plants that are good candidates for using ferrous to ferric chemistry. They are:

1. Water Plants using chlorine dioxide that want to reduce or eliminate chlorite residuals.
2. Water Plants using free chlorine treatment with high disinfection byproduct levels.
3. Water Plants wanting to reduce coagulant and chlorine chemical cost in order to implement chlorine dioxide treatment.
4. Water Plants that want to increase chlorine dioxide doses above the 1.4 ppm level.

If a water plant is concerned about “cat urine” odors at the tap, then chlorite elimination can be done by ferrous chemical addition. The ferrous chemical could be supplemental to the existing aluminum or ferric ion based coagulants. The additional cost of ferrous chemical should reduce the cost of existing coagulants while gaining the benefit of a non-detectable chlorite residual in the distribution system.

For concerns with high TTHMs and/or HAA<sub>5</sub> levels, reducing or eliminating pre-chlorination by replacing it with chlorine dioxide treatment followed by ferrous treatment for chlorite reduction should substantially reduce TTHMs and HAA<sub>5</sub> levels in the distribution system. This could be done while providing increased disinfection capability and improved taste and odor treatment.

If a water plant wants to reduce coagulant and chlorine chemical cost in order to implement chlorine dioxide treatment, then reducing or eliminating pre-chlorination and using the cheaper ferrous chemical may be very cost effective.

To allow the use of chlorine dioxide doses above 1.4 ppm level, the less expensive ferrous can often offset some of the extra cost from the higher chlorine dioxide dose and other coagulants in use.

### **Conclusions**

The following conclusions can be made with reasonable certainty:

1. Future USEPA regulations will mandate increased disinfection capability and lower disinfection byproduct levels from water treatment plant processes.
2. Based on laboratory testing and full plant use of chlorine dioxide, each ppm of chlorite can be reduced by 3.1 ppm of ferrous as Fe from ferrous chloride or ferrous sulfate solutions.
3. Chlorine dioxide in pretreatment can effectively lower TTHMs and HAA<sub>5</sub> levels.
4. Elimination of chlorite prior to discharge to the distribution system prevents “cat urine” odors at the tap.
5. The use of ferrous ion solutions for chlorite reduction may reduce coagulant cost.
6. Chlorite reduction by ferrous ion is necessary for plants adding more than 1.4 ppm of chlorine dioxide.



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## REFERENCES

1. USEPA. Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR). [www.epa.gov/safewater/lt2/grand.html](http://www.epa.gov/safewater/lt2/grand.html). Aug. 2003
2. Blanck, Clarence A., Plant Operations as Related to Trihalomethanes, 70<sup>th</sup> Annual Meeting Illinois Section American Water Works Association, Oak Brook, Illinois, March 21, 1979; 24 pages.
3. Suffet, I.H., et al. Advances in Taste-and-Odor Treatment and Control, AWWARF. Denver, CO., 1995.
4. Benninger, Robert W. & Hoehn, Robert C., Rosenblatt, Aaron A. "Chlorine-Free Chlorine Dioxide Gas for Drinking Water Treatment at Roanoke County, Virginia," Proceedings 1996 Water Quality Technology Conference Part II, AWWA, 6666 W. Quincy Ave., Denver, CO., 1997.
5. Steynberg, M.C., Pieterse, A.J.H. & Geldenhuys, J.C., "Improved Coagulation and Filtration of Algae as a Result of Morphological and Behavioural Changes Due to Pre-Oxidation," Aqua (Journal of Water Supply Research and Technology), AWWA, 6666 W. Quincy Ave., Denver, CO, Dec., 1996.
6. McGuire, Michael J; Lieu, Nancy I., Pearthree, Marie S., "Using Chlorite ion to Control Nitrification," Journal AWWA, 6666 W. Quincy Ave., Denver, CO., Oct., 1999.
7. Knocke, William R., Iatrou, Angela. "Chlorite Ion Reduction by Ferrous Iron Addition," AWWA—AWWARF, 6666 W. Quincy Ave., Denver, CO, 1993.
8. Rittmann, D., "Can You Have Your Cake and Eat It Too with Chlorine Dioxide", Water Engineering and Management, April, 1997.
9. Rittmann, D., Impact of Cl<sub>2</sub> in the Generation of ClO<sub>2</sub> on DBPs in Drinking Water. Doctoral Dissertation, University of Texas at El Paso Library, El Paso, Texas, July, 1999.
10. Rittmann, D., "Impact of Mixing Chlorine with Chlorine Dioxide on TTHMs Formation", Water Engineering and Management, August & September, 2002.
11. Mills, Jack, "Interview with Jack Mills Concerning Ferrous Iron Salts", Environmental Chemical Services, PO Box 95, La Marque, Texas 77568, August, 2003

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