

Chlorate Ion in Drinking Water

Sources and Control of Chlorate Ion

Chlorate ion (ClO_3^-) is primarily present in drinking water as a result of the use of chlorine dioxide or hypochlorite solutions for oxidation/disinfection in the treatment process. It may also be present in the untreated source water, but the ClO_3^- concentrations contributed to drinking water by ambient water are generally much lower than those resulting from the treatment process.

The American Water Works Association (AWWA) Disinfection Systems Committee tracks disinfection practices in US community water systems. Their most recent comprehensive survey (completed in 1998) estimated that approximately 20% of the systems serving populations greater than 10,000 use sodium hypochlorite (2% generated it on-site), 8% use chlorine dioxide, and <1% use calcium hypochlorite. (AWWA, 2000a) For systems serving populations less than 10,000, the survey estimated that approximately 34% use sodium hypochlorite, none use chlorine dioxide, and at least 4.5% use calcium hypochlorite. (AWWA, 2000b)

Chlorine Dioxide: The use of chlorine dioxide can introduce ClO_3^- into the finished water by several routes. Drinking water plants generally use sodium chlorite as a starting material in the production of chlorine dioxide. Chlorate ion may be present as a contaminant in the feedstock material (usually less than four percent of the active chlorite is chlorate). A typical range of ClO_3^- carryover to the finished water from chlorite feedstock contamination is about 50 $\mu\text{g/L}$ for a 1-mg/L dose of chlorine dioxide. (Gates, 1998) Technology to generate chlorine dioxide using sodium chlorate is now available to the drinking water industry, which introduces the possibility of ClO_3^- carryover to the finished water from the chlorate feedstock.

Chlorate ion may also be produced due to inefficient generation of chlorine dioxide. Excess chlorine will favor the production of ClO_3^- over chlorine dioxide, as will keeping the generator mixtures at highly alkaline ($\text{pH} > 11$) or acidic ($\text{pH} < 3$) conditions. If the concentrations of feedstock reactants are too low or too much dilution water is added during the reaction, ClO_3^- formation is also favored.

Chlorite ion (ClO_2^-) is a major degradation product resulting from the reaction of chlorine dioxide with inorganic and organic constituents in the water. When free chlorine is used after the application of chlorine dioxide in the treatment process, ClO_2^- is oxidized to ClO_3^- . This conversion will continue over time as the water travels through the distribution system. Chlorate ion is also formed by photodecomposition of chlorine dioxide when treated water is exposed to bright sunlight in open basins.

The primary ways in which water systems can control the levels of ClO_3^- in the finished water is through high efficiency operation of their chlorine dioxide generators and by reducing ClO_2^- concentrations prior to the addition of free chlorine. Careful control of the generation process minimizes ClO_3^- formation. Ferrous ion, which is a coagulant aid, can be used to convert ClO_2^- to chloride ion and thus prevent it from reacting with free chlorine to form ClO_3^- .

Hypochlorite: Some water systems use sodium hypochlorite or calcium hypochlorite as their source of free chlorine. Chlorate ion can be formed in these products during the manufacturing process, but the decomposition of hypochlorite solutions during storage is the more significant source of ClO_3^- in systems using hypochlorite. Sodium hypochlorite is usually purchased as a solution, and ClO_3^- concentrations increase between the time of manufacture and delivery to the water plant. Calcium hypochlorite is a solid, and thus ClO_3^- concentrations don't increase until calcium hypochlorite solutions are prepared for use at the water treatment plant.

The rate at which hypochlorite ion (OCl^-) disproportionates to ClO_3^- is influenced by concentration of OCl^- , pH, and temperature. The rate of decomposition increases as the concentration of OCl^- increases, so water systems can use dilution as one control strategy. The pH should be in the 12 to 13 range to minimize decomposition; a pH below 11 greatly increases the rate of decomposition. Hypochlorite solutions should be protected from high temperatures and sunlight. Storage time should be minimized; both from the time of manufacture to delivery and from the time of delivery to use.

Chlorate Ion Occurrence Data

Data on the occurrence of ClO_3^- in drinking water are available from two primary sources: the Information Collection Rule (ICR) Auxiliary 1 Database, Version 5.0 (USEPA, 2000) and the AwwaRF research study on the control of ClO_3^- in hypochlorite solutions (Gordon et al, 1995).

Information Collection Rule: The most extensive data on the occurrence of ClO_3^- in drinking water is from the ICR (USEPA, 1996). Source water and drinking water were monitored for ClO_3^- between July 1997 and December 1998. Water systems serving a population of at least 100,000 were required to monitor for ClO_3^- at treatment plants using chlorine dioxide or hypochlorite solutions in the treatment process. Plants using chlorine dioxide collected monthly samples of the source water entering the plant, the finished water leaving the plant, and at three sample points in the distribution system (near the first customer, an average residence time and a maximum residence time). Plants using hypochlorite solutions were only required to collect quarterly samples of the water entering and leaving the plant. If chlorine dioxide or hypochlorite solutions were used intermittently at a plant, ClO_3^- samples were only required in sample periods in which they were in use.

Chlorine dioxide was used by 22 water systems (29 treatment plants) during at least one of the 18 monthly ICR sampling periods. Data from 413 samples collected at the entry point to the distribution system showed ClO_3^- concentrations ranging from $< 20 \mu\text{g/L}$ to $1,600 \mu\text{g/L}$. The ClO_3^- concentrations ranged from $< 20 \mu\text{g/L}$ to $2,200 \mu\text{g/L}$ in the 1084 samples collected in the distribution system. The distribution of average ClO_3^- concentrations calculated for each treatment plant and sample point are summarized in Table 1. The distribution system average concentrations determined for each water plant by averaging the data from the three distribution system sample points are summarized in the last column of Table 1. The median distribution system average concentration is $129 \mu\text{g/L}$ with a range from $< 20 \mu\text{g/L}$ to $691 \mu\text{g/L}$.

Sodium hypochlorite solutions were in use in 44 water systems (61 treatment plants) during the six quarterly ICR sampling periods. (None of the systems reported using calcium hypochlorite as the source of their chlorine solutions.) Data from 312 samples were reported with concentrations ranging from < 20 µg/L to a maximum of 1,400 µg/L. The average ClO₃⁻ concentration in the finished drinking water for each treatment plant ranged from < 20 µg/L to 502 µg/L with a median concentration of 99 µg/L. Table 1 summarizes the distribution of average ClO₃⁻ concentrations calculated for each plant.

Table 1. Chlorate Concentrations¹ (µg/L) - ICR Data

	Hypochlorite Plants	Chlorine Dioxide Treatment Plants				
	Finished	Finished	Near First Customer	Average Retention Time	Maximum Retention Time	Distribution System Average ²
10 th Percentile	23	56	52	55	35	52
20 th Percentile	37	77	95	84	71	79
50 th Percentile	99	119	126	132	138	129
80 th Percentile	155	195	203	232	230	217
90 th Percentile	239	226	239	282	301	264
Maximum	502	687	632	735	707	691
# WTPs	61	29	27	27	27	27
# PWSs	44	22	21	21	21	21

¹The average chlorate concentration was calculated for each sample point at each WTP over the entire ICR monitoring program. The distribution of these averages is presented in this table.

²The distribution system average chlorate concentration was calculated for each WTP using the three distribution system sample points. The distribution of these averages is presented in this column.

AwwaRF Hypochlorite Project: The American Water Works Association Research Foundation sponsored a project to study how water systems could minimize ClO₃⁻ formation in the hypochlorite solutions they use for disinfection. As part of the data gathering effort, they obtained information from 185 water systems concerning their use of hypochlorite solutions. Samples of source water, hypochlorite solution, and finished drinking water from 111 of the water systems were analyzed for ClO₃⁻. Only one set of samples was collected for each system.

Background information on the subset of 111 water systems that provided samples was not reported separately from the 185 systems who answered the questionnaire. Therefore, the ClO₃⁻

concentrations cannot be directly related to the size of the water system or type of hypochlorite solution in use. However, 73.5 % of the systems who responded to the questionnaire served populations less than 100,000 with a subset of 66% serving populations less than 10,000. There is a possibility that a few systems using calcium hypochlorite were sampled in the AwwaRF project, since 13% of the 185 systems reported using calcium hypochlorite and 85% reported using sodium hypochlorite.

The ClO_3^- concentrations reported in the finished water are summarized in Table 2. The median concentration in the finished water is 161 $\mu\text{g/L}$. The ClO_3^- concentrations in the hypochlorite solutions ranged from 0.03 to 113 g/L.

Table 2. Chlorate Concentrations - AwwaRF Project
(PWSs using Hypochlorite Solutions)

	Finished Water Chlorate Concentration ($\mu\text{g/L}$)
Minimum	<10
10 th Percentile	15
20 th Percentile	41
50 th Percentile	161
80 th Percentile	611
90 th Percentile	1,160
Max	9,180
# PWSs	111
# States	13

Chronic Exposure to Chlorate Ion

Even though the ICR ClO_3^- sampling was targeted to systems suspected of having ClO_3^- contamination due to the treatment process in use, it is reasonable to assume that there were not significant ClO_3^- levels in the systems in the same size category that were not sampled. This is based on earlier drinking water studies that found ClO_3^- concentrations in source water were too low to impact the levels in drinking water on the same scale as treating the water with either chlorine dioxide or hypochlorite (Bolyard et al, 1993).

The ICR data confirm the presence of ClO_3^- in source water (75 of 744 samples of water entering the treatment plants contained measurable ClO_3^-), but also demonstrate that the concentrations are

generally very low, can vary considerably over time at the same sample site, and are minor compared to those observed from chlorine dioxide or hypochlorite use. Data were reported from 105 treatment plant influent sample points in the ICR and samples from 33 of those sites contained ClO_3^- concentrations of 20 $\mu\text{g/L}$ or greater. Chlorate concentrations were reported in influent samples from both surface and ground water sources. Samples from fifteen of the 33 sites contained measurable ClO_3^- in more than one sampling period, but with one exception, the concentrations were all $\leq 120 \mu\text{g/L}$; 70% were between 20 and 50 $\mu\text{g/L}$. One influent water had a ClO_3^- concentration of 944 $\mu\text{g/L}$ in one sample period, but the concentrations were $\leq 100 \mu\text{g/L}$ in the other sample periods. Three influent waters contained a high ClO_3^- concentration (1,300 to 1,600 $\mu\text{g/L}$) in one sample period and none in the other sample periods. The ICR data indicate that the influence of source water ClO_3^- (as reflected by the influent samples) on the concentrations in finished drinking water is minimal compared to the contribution from using chlorine dioxide or hypochlorite solutions in the treatment process.

The ICR data set provides the best available estimate of long term exposure to ClO_3^- from drinking water, because multiple samples were collected over an 18 month period. Only systems serving populations of at least 100,000 were sampled during the ICR. Even though this size category includes roughly one percent of the total number of drinking water systems in the United States, it serves almost 60 percent of the population. During the ICR, there were 296 water systems in this size category; 7% used chlorine dioxide and 15% used hypochlorite solutions.

When chlorine dioxide is the source of ClO_3^- in drinking water, it is appropriate to use the average concentration in the distribution system to estimate exposure. This is because the concentration is expected to change within the system due to the conversion of ClO_2^- to ClO_3^- in the presence of chlorine. Fifty percent of the chlorine dioxide plants had average distribution system ClO_3^- concentrations of $\leq 129 \mu\text{g/L}$. Ninety percent had concentrations $\leq 264 \mu\text{g/L}$.

The average ClO_3^- concentration at the entry point to the distribution system can be used to estimate exposure when hypochlorite solutions are the source of the ClO_3^- contamination. No additional ClO_3^- is expected to be formed in the distribution system. Fifty percent of the plants using hypochlorite solutions had finished water ClO_3^- concentrations of $\leq 99 \mu\text{g/L}$. Ninety percent had concentrations $\leq 239 \mu\text{g/L}$.

The AwwaRF data set is much smaller than the ICR data set, because the 111 systems from 13 states were only sampled once. Low levels of ClO_3^- were measured in almost 20% of the source waters with 90 percent of the samples having concentrations less than 35 $\mu\text{g/L}$. (Over 30% of the source waters sampled during the ICR contained measurable concentrations of ClO_3^- with 90 percent having concentrations less than 23 $\mu\text{g/L}$.) The finished water ClO_3^- concentrations measured in the AwwaRF study are generally higher than those observed in the ICR. This difference could be the result of a number of factors such as: 1) The AwwaRF data represents a single point in time while the ICR data reflects an average over 18 months; 2) Most of the AwwaRF samples were collected from utilities that served population of less than 100,000, while all of the ICR samples were from utilities serving at least 100,000; and 3) Hypochlorite treatment

practices may have changed between when the AwwaRF samples were collected (1993) and the ICR samples were collected (1997-98).

References

AWWA Water Quality Division Disinfection Systems Committee, Committee Report: Disinfection at Large and Medium-Size Systems, May 2000a, p 32-43.

AWWA Water Quality Division Disinfection Systems Committee, Committee Report: Disinfection at Small Systems, May 2000b, p 24-31.

Bolyard, M., Fair, P.S., and Hautman, D.P. "Sources of Chlorate Ion in US Drinking Water," *Journal AWWA* Vol 85(9) 81-88, 1993.

Gates, D.J. *The Chlorine Dioxide Handbook*. American Water Works Association, Denver, CO, 1998.

Gordon, G.G., Adam, L., and Bubnis, B. *Minimizing Chlorate Ion Formation in Drinking Water When Hypochlorite Ion is the Chlorinating Agent*. American Water Works Association Research Foundation, Denver, CO, 1995.

USEPA, 1996. National Primary Drinking Water Regulation: Monitoring Requirements for Public Drinking Water Supplies: *Cryptosporidium*, *Giardia*, Viruses, Disinfection Byproducts, Water Treatment Plant Data and Other Information Requirements. Final Rule. FR 61:94:24354-24388 (May 14, 1996).

USEPA, 2000. *ICR Auxiliary 1 Database*. EPA 815-C-00-002. Office of Water, Cincinnati, OH, April 2000.