

Banish Bromate

“Managing bromate formation in your ozone disinfection process”

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An increasing shift toward ozone-based disinfection processes has raised awareness of bromide concentrations in raw water and the potential to form bromate through the disinfection process.

Until the last decade, bromate was seldom a topic of concern for most treatment facilities. However, an increasing shift toward ozone-based disinfection processes has raised awareness of bromide concentrations in raw water and the potential to form bromate through the disinfection process.

Fortunately, most plants looking to use ozone can confidently address bromate formation by properly understanding their ozone demand and how it interacts with bromate chemistry.

In this article we will review the basic concepts of bromate control for a ‘typical’ ozone disinfection application. We will also apply these lessons to data from an actual application whose demand and decay curve are show below.



Chemistry is Key

One of the first and probably best discussions of bromate chemistry was published in the AWWA Journal almost 20 years ago by Dr. Urs von Gunten, the summary of which is presented below. While initially a little intimidating, the key aspect of this chart is the reaction sequence 2, 3, 6 and 8 near the center of the chart. The goal is to influence the formation of hypobromous acid (HOBr) by keeping the re-

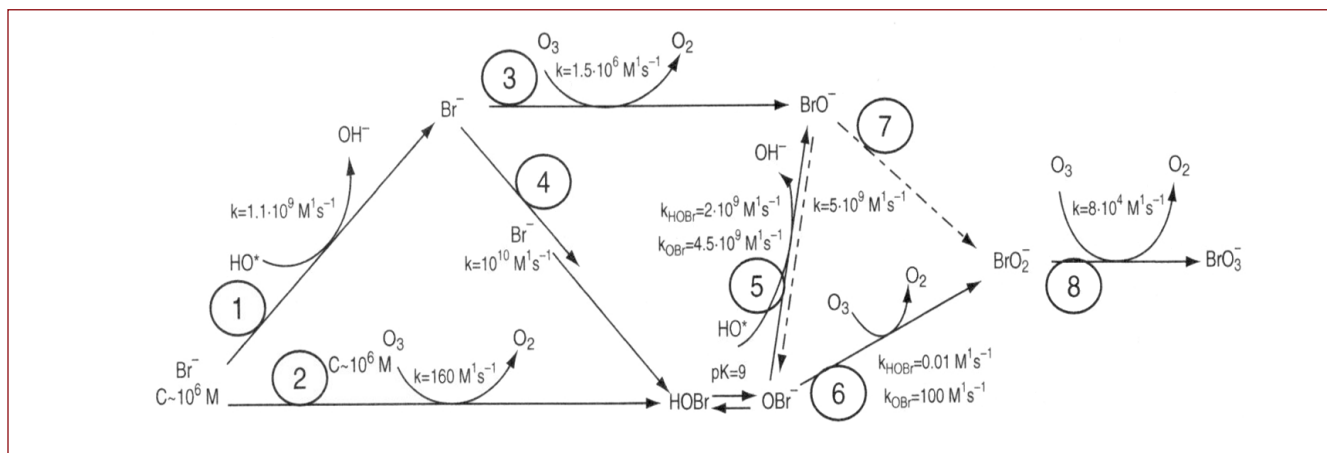


Illustration 1 - von Gunten, Urs et.al. “Bromate Formation in Advanced Oxidation Processes,” *Journal AWWA*, June 1996

action pathway along the bottom of the chart. Fortunately, we have several tools at our disposal including pH, contact time and ozone dose which are discussed further below.

A 'Typical' Disinfection Project

The best way to illustrate bromate control for a 'typical' ozone disinfection project is by example. The demand curve shown below is for a medium sized water treatment facility in the north-central US. The surface water source sees cold clear conditions during the winter that are punc-

tuated by high-turbidity events from snowmelt, with periodic T&O events during warmer summer months. Even the small amount of ozone demand data presented shows us keys to managing bromate control in this process.

pH and Alkalinity Control

Like most other aqueous reactions, bromate formation is strongly influenced by pH. For many applications even a modest adjustment to lower pH (-0.2 to -0.5 units) produces a higher concentrations of HOBr (for pH above

7). This is good since the reaction constants (the "k" values) show that HOBr reacts about 10,000 times slower with ozone compared to hypobromite (BrO^-). Effectively, this gives us time for ozone to react with other contaminants such as organics or pathogens, whose reaction rates are much faster. However, the effectiveness of pH suppression can be different for each water source since there are many competing factors such as dissolved organics, transition metals, hydrogen sulfide, and alkalinity, etc. The best way to evaluate bromate formation and pH control is to run a series of demand studies at varying pH and ozone doses. The resulting family of curves should show the level of bromate formation control that is possible for your water.

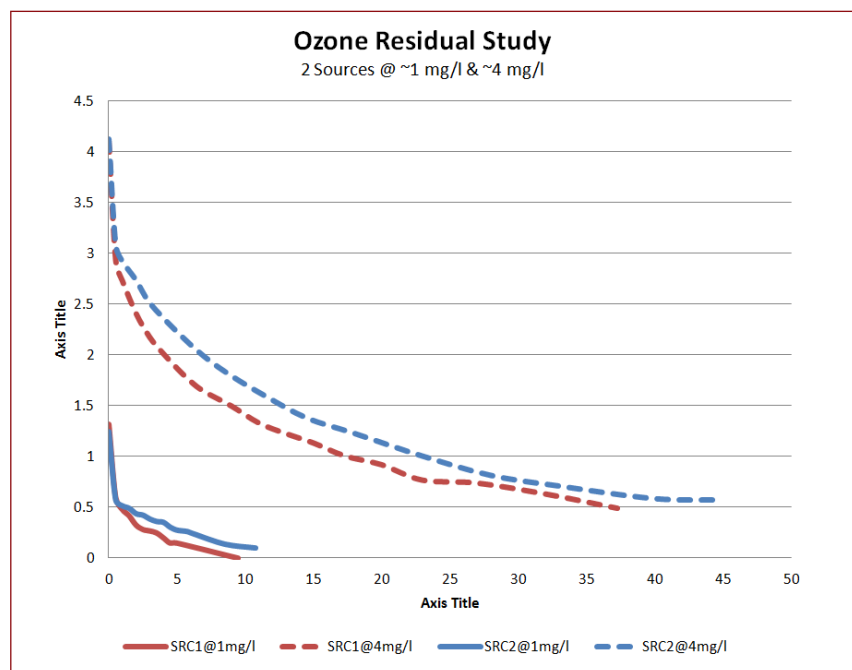


CHART 1

TABLE 1: Ozone Residual Study Selected Data						
Sample ID	Source1 Raw	Source1 Lo Dose	Source1 Hi Dose	Source2 Raw	Source2 Lo Dose	Source2 Hi Dose
Ozone Dose (mg/L)	-	1.311	4.101	-	1.241	4.124
Temperature (°C)	-	0.63	0.35	-	0.89	0.85
pH	8.04	8.01	7.90	7.89	7.93	7.86
Alkalinity (mg/L)	147.9	144.1	133.6	143.8	135.0	134.0
Conductivity (µS/cm)	668.5	654.9	629.1	662.8	566.8	628.5
TDS (mg/L)	466.7	457.2	436.2	458.8	393.9	431.8
DOC (mg/L)	3.83	4.01	3.89	3.91	3.84	3.89
TOC (mg/L)	4.01	4.29	4.00	3.99	4.00	3.88
Bromide (µg/L)	35.1	44.3	30.5	37.5	40.5	32.6
Bromate (µg/L)	-	<1	11.8*	-	<1	4.9

* Value is above the National Primary Drinking Water Regulation of 10 µg/L

NOTES:

- 1) Raw water quality data is fairly consistent between the two sources.
- 2) Note the slightly lower pH in Source 2 yields significantly lower bromate formation at the hi ozone dose. Even modest pH suppression should significantly reduce the potential to form bromate.
- 3) Looking at the data for both sources and the demand curves, doses above ~1 mg/l allow excess ozone to react and form bromate. Limiting ozone dose will reduce bromate formation potential.

For our example application, we see that even a moderate lowering of pH (from ~8.0 to ~7.8) helps reduce bromate formation. Suffice it to say, pH adjustment is the first and most powerful tool in our bromate control toolbox for ozone disinfection. However, there are several other factors at play which can offer us another level of control.

Limit Ozone Dose

Accurate control of ozone dose is also a key to managing bromate formation. The goal here is to provide 'just enough' ozone to completely (and quickly) react with the water matrix and achieve disinfection. This limits the availability of excess ozone to react with bromide in the raw water.

The demand curves from our example project help illustrate the point. Approximately 1 mg/l of ozone demand can be seen within the first minute after ozone injection. The flatter portion of the curve shows slower ozone reaction kinetics after the first minute. So, in effect, the excess ozone will be more available to react with the bromide ion to potentially create more bromate. This offers an opportunity to limit the ozone dose to reduce both the bromate formation potential and the overall operating cost.

Timing is Everything

Ozone reaction rates can be fast, but are different for each water matrix. Reactions with many organics are fairly quick. Conversely, reaction times with HOBr are much slower. We can use this difference to our advantage. Shorter contact times generally reduce bromate formation since there is less time and opportunity for ozone to create the BrO^- ion and then further react to form bromate. The goal of your design should be to minimize the total contact time needed to achieve your disinfection or treatment goals.

Here again, our demand curve tells the story. Reducing both excess ozone dose and contact time will help prevent bromate formation, as long as the required disinfection credits can still be met. The slower decay portion of the curve after about the first 1 minute shows us that the medium to fast reacting organics are consumed quite quickly. Thus, the ozone residual should be managed with as much precision as possible in the order to mitigate bromate formation while still achieving the level of disinfection required by the plant's process design.



Tying It All Together

Effective bromate control for ozone disinfection is a matter of understanding water chemistry and the parameters that control it. Balancing a combination of pH, ozone dose, and contact time controls is key to managing most bromate issues. Certainly, there are some sites where the specific mix of dissolved organics, alkalinity, pH, bromide concentration and ozone dose is beyond the basic toolset presented here. In such cases, additional steps such as peroxide addition or even alternate disinfection methods may be warranted.

Even so, the principals presented here can still apply. Armed with a little knowledge, most systems should be able to banish bromate issues with the proper application of the tools presented here and a good understanding of their water chemistry.

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