



Technical Brief: Bromide and Chromium Oxidation

Bromide and chromium ions are naturally occurring species found in soil and numerous drinking and groundwater sources throughout the United States.

The bromide ion (Br^-) is present in low but significant levels in drinking water resources due to pollution, saltwater intrusion, and bromide from natural resources.¹ However, this form of bromine ion is of little concern due to its low degree of toxicity.

Chromium ions are similarly distributed in the earth's crust, ranging from oxidation states 2^+ to 6^+ .² The main focus in ozone water remediation has been on the chromium(III) and (VI) ions. The 3^+ ion has been shown to naturally predominate in soil, while the 6^+ ion has been introduced to the environment through human activities and industrial processes.² This is of concern because the chromium(VI) ion is classified as Group 1 (carcinogen to humans) by the International Agency for Research on Cancer (IARC).³ Unlike its positively charged (VI) cousin, chromium(III) has been found to be harmless to human consumption, and is not mutagenic or carcinogenic.

Bromide (Br^-) and chromium(III) ions have been the focus of concern in ozone water remediation and treatment processes because these ions react with O_3 to produce bromate (BrO_3^-) and chromium(VI) ions, respectively. These disinfection by-products (DBP) are highly toxic and if not removed from treated water, can cause numerous health problems in humans.

Bromate (BrO_3^-) can be produced through a direct reaction of the existing bromide ion (Br^-) in solution with molecular ozone (O_3). In this instance, hypobromous acid (HBrO), hypobromite (BrO^-), and bromite (BrO_2^- , Br^-) act as intermediates in the series of reactions leading to bromate synthesis.

The initial bromide ion reacts with ozone to produce oxygen gas and hypobromite. The hypobromite product can then undergo two different reactions with ozone to produce a bromite ion (BrO_2^- or Br^-).^{4,5} The final step reacts the BrO_2^- ion with ozone to produce the bromate ion and oxygen gas. This series of four reactions is known as the molecular ozone pathway, see Table 1.

No.	Reaction
1	$\text{Br}^- + \text{O}_3 \longrightarrow \text{O}_2 + \text{OBr}^-$
2	$\text{O}_3 + \text{OBr}^- \longrightarrow 2\text{O}_2 + \text{Br}^-$
3	$\text{OBr}^- + \text{O}_3 \longrightarrow \text{BrO}_2^- + \text{O}_2$
4	$\text{BrO}_2^- + \text{O}_3 \longrightarrow \text{BrO}_3^- + \text{O}_2$

Table 1: Molecular Ozone Pathway reaction mechanism⁴

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No.	Reaction
1	$\text{Br}^- + \text{OH}^- \rightarrow \text{BrOH}^-$
2	$\text{BrOH}^- \rightarrow \text{Br} + \text{OH}^-$
3	$\text{Br} + \text{Br}^- \rightarrow \text{Br}_2^-$
4	$\text{Br}_2^- + \text{Br}_2^- \rightarrow \text{Br}_3^- + 2\text{Br}^-$
5	$\text{Br}_2^- + \text{OBr}^- \rightarrow \text{BrO} + 2\text{Br}^-$
6	$\text{OH} + \text{OBr}^- \rightarrow \text{BrO} + \text{OH}^-$
7	$\text{OH} + \text{HOBr} \rightarrow \text{BrO} + \text{H}_2\text{O}$
8	$\text{CO}_3^- + \text{OBr}^- \rightarrow \text{BrO} + \text{CO}_3^{2-}$
9	$\text{CO}_3^{2-} + \text{OH}^- \rightarrow \text{OH}^- + \text{CO}_3^-$
10	$\text{HCO}_3^- + \text{OH}^- \rightarrow \text{OH}^- + \text{HCO}_3$
11	$\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-}$
12	$\text{HCO}_3 \rightarrow \text{H}^+ + \text{CO}_3^-$
13	$2\text{BrO} + \text{H}_2\text{O} \rightarrow \text{BrO}^- + \text{BrO}_2^- + 2\text{H}^+$
14	$\text{BrO}_2^- + \text{OH}^- \rightarrow \text{BrO}_2 + \text{OH}^-$
15	$\text{BrO}_2^- + \text{CO}_3^- \rightarrow \text{BrO}_2 + \text{CO}_3^{2-}$
16	$2 \text{BrO}_2 \rightarrow \text{Br}_2\text{O}_4$
17	$\text{Br}_2\text{O}_4 + \text{OH}^- \rightarrow \text{BrO}_3^- + \text{BrO}_2^- + \text{H}^+$

Table 2: Bromate formation through hydroxyl radical pathway⁶

Numerous studies have also suggested that bromate formation can be achieved by reacting bromide via a pure hydroxyl radical pathway created by hydrogen peroxide (H₂O₂) Advanced Oxidation Processes. Studies by von Gunten and Oliveras (1998) and von Gunten and Hoigne (1994) have determined hypobromous acid/hypobromite (HBrO/BrO⁻) is a requisite intermediate when bromate is created through this hydroxyl radical pathway—meaning that bromate formation cannot occur unless bromide is first oxidized to HBrO/BrO⁻.^{5,6} A mechanism derived by von Gunten and Hoigne for the bromate synthesis through hydroxyl radical pathway is shown in Table 2.

Reactions 8-12 show the production of carbonate radicals through the reaction of bicarbonate with hydroxyl radical. These carbonate radicals then oxidize the intermediate hypobromite to bromite, which is further oxidized by ozone to the final bromate product.⁶

Bromate formation concentrations can be reduced through the manipulation of specific parameters including the following: pH depression, ammonia addition, hydroxyl radical scavenger addition and temperature.

A decrease in the pH of the aqueous solution has been demonstrated to be one of the more effective methods employed to control bromate formation. In a study conducted by Song, pH depression from 8 to 7 to 6 resulted in a general reduction of bromate formation of 30-50% per unit of pH decreased.⁷ This is due to the inability of hypobromous acid to dissociate at low pH (< 7) thus limiting the amount of hypobromite ion (BrO⁻) available to react with ozone.⁷ Depressed pH levels also reduce generation of hydroxyl radicals, decreasing the likelihood that bromate formation will occur through the hydroxyl radical pathway. While a pH reduction results in higher control of bromate formation, there has been a recorded increase in the concentration of brominated organic compounds formed within solution at these conditions.⁷

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Bromide Treatment

Ammonia

Ammonia addition has proven effective due to its tendency to react with bromine intermediates to form bromamines. Bromamines do not contribute to bromate formation, and therefore the addition of ammonia can minimize—but not extinguish—the creation of bromate by eliminating the pathways that require bromine intermediates.⁴ Unfortunately, bromamine product stability is dependent on the type of species formed, and the conditions in which the species was created. Instability results in the decay of bromamine to bromide and nitrate, and the eventual oxidation of all ammonia in solution will ultimately result in the reproduction of the bromate ion.⁴

Temperature

Bromate formation under variable temperatures has been suggested to be a function of increasing reaction rates with bromide species. Studies conducted at high bromide concentrations (1000 ug/L or greater) in semi-batch reactor experiments recorded an increase in bromate formation by 20% as temperature was increased from 20 to 30%.⁴ Low bromide waters have not been studied in detail, but it is expected that a decrease in temperature will also result in bromate reduction.

Hydroxyl Radical Scavenger

The addition of a hydroxyl radical scavenger such as tertiary butanol has also proven effective in limiting bromate formations that occur through the hydroxyl radical pathway.⁴

Chromium Treatment

The hexavalent chromium(VI) ion forms from the oxidation of trivalent chromium(III) or other non Cr(VI) Cr-containing materials in water with ozone. Mechanisms for this reaction have not been studied in detail, but it is noted that hydroxyl radicals play a likely part in the oxidation of the chromate ion.⁸

However, because of hexavalent chromium's high

toxicity level, focus has been directed towards determining water conditions that will decrease the production of the (VI) ion. In this realm, variables effective for bromate reduction such as pH depression and decreased water temperature have been proven to also have positive effects on chromium(VI) reduction. Decreasing the ozonation contact time between the gas and aqueous phase is also an effective method for hexavalent chromium ion reduction.⁸

Contaminants such as bromide and chromium ions found in ground or drinking water are capable of removal through in-situ or ex-situ chemical oxidation with ozone gas. However, remediation process conditions for these ions must be carefully monitored due to their potential to undergo ozonation to toxic and undesirable disinfection by-products (DBP) such as bromate and chromium(VI) ions.

pH and temperature depression of the aqueous phase have proven effective in reducing final concentrations of both bromate and hexavalent chromium. Ammonia addition, hydroxyl radical scavenger introduction, and limited ozonation contact time are also effective methods to reduce these harmful substances.

At Piper Environmental Group, Inc. we are able to accommodate any modifications to our ozone remediation systems and methods as needed in order to minimize the oxidation effects of O₃ on these contaminants.

¹ "Chemistry of Disinfectants and Disinfectant By-products." *Chemistry of Disinfectants and Disinfectant By-products*. World Health Organization, n.d. Web. 20 June 2013. http://www.who.int/ipcs/publications/ehc/216_disinfectants_part_2.pdf.

² World Health Organization, comp. *Chromium in Drinking-water*. N.p.: n.p., 2003. Print.

³ Imanaka, S., and H. Hayashi. *Behavior of Hexavalent Chromium in Water Supply System by IC-ICP-MS Method*. N.p.: n.p., n.d. Print.

⁴ Gillogly, Thomas, and Issam Najm. *Bromate formation and control during ozonation of low bromide waters*. N.p.: Awwa Research Foundation and American Water Works Foundation, 2001. Print.

⁵ Von Gunten, Urs, and Yvonne Oliveras. "Advanced Oxidation of Bromide-Containing Waters: Bromate Formation Mechanisms." *Environ. Sci. Technol.* 32 (1998): 63-70. Print.

⁶ Von Gunten, Urs, and Jurg Hoigne. "Bromate Formation during Ozonation of Bromide-Containing Waters: Interaction of Ozone and Hydroxyl Radical Reactions." *Environ. Sci. Technol.* 28 (1994):1234-42. Print.

⁷ Song, Rengao, et al. "Empirical modeling of bromate formation during ozonation of bromide-containing waters." *Wat. Res* 30.5 (1996): 1161-68. Print.

⁸ Van der Merwe, W., JP Beukes, and PG Van Zyl. *Cr(VI) formation during ozonation of Cr-containing materials in aqueous suspension--implications for water treatment*. N.p.: n.p., 2012. Print.

Company Profile

Piper Environmental Group, Inc. offers ozone technology, equipment, and services for a wide-range of environmental applications. The company designs, manufactures, and integrates ozone systems and related equipment for short and long-term projects, offering equipment for rent or purchase. Services include project design assistance, oxidation pilot studies, contract service, equipment repair, consulting. Our area of expertise is large remediation projects.