**Project Title:** Strategies to Control Bromate and Bromide

**Project Number:** 156

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**Objectives:** The primary objective of this study was to evaluate, both at the bench- and pilot-scale, treatment options for bromate ion (BrO$_3^-$) minimization (during ozonation) and BrO$_3^-$ removal (after ozonation). A secondary objective was to assess options for bromide ion (Br$^-$) removal before ozonation.

**Background:** BrO$_3^-$ is formed upon ozonation of waters containing Br$^-$ through one of two general pathways, a molecular ozone pathway and a hydroxyl radical pathway. The continued use of ozonation for microbial inactivation will be contingent upon developing control strategies for reducing BrO$_3^-$ levels in ozonated waters, with the proposed MCL of 10 ug/L defining the present constraint. The general options are to minimize BrO$_3^-$ formation during ozonation, through either chemical addition or modified contactor design and operation, or to remove BrO$_3^-$ after its formation by chemical conversion back to Br$^-$.

**Highlights:** BrO$_3^-$ minimization by acid addition, ammonia (NH$_3$) addition, hydrogen peroxide (H$_2$O$_2$) addition, hydroxyl radical addition, and tapered (versus) single stage ozonation were evaluated. The most consistent, predictable minimization approach was pH depression (acid addition). BrO$_3^-$ removal by ferrous iron (Fe$^{2+}$) reduction, granular activated carbon (GAC) surface reduction, and decomposition by UV light irradiation were studied, with Fe$^{2+}$ providing the most effective reduction but being constrained to application following pre-ozonation. Only NF (and RO) membranes represented an effective Br$^-$ removal technique.

**Research Approach:** A wide range of natural waters with varying water qualities were tested at both the bench- and pilot-scale. Bench-scale ozonations were conducted over a range of pH conditions, ammonia concentrations, hydrogen peroxide concentrations, and hydroxyl radical concentrations. Pilot- and bench-scale evaluations were performed to assess tapered (multi-stage) versus single-stage addition. Bench-scale evaluations of Fe$^{2+}$, GAC, and UV light reduction of BrO$_3^-$ were performed with varying spiked levels of BrO$_3^-$; subsequent pilot tests were performed for all BrO$_3^-$ removal techniques. Bench-scale tests of Br$^-$ removal by coagulation, softening, GAC, ion exchange, and NF membranes were performed. In many cases, BrO$_3^-$ measurements were accompanied by Br$^-$ measurement to help define a mass balance for Br-species.

**Results/Findings:** pH depressions proved to be the most effective approach in minimizing BrO$_3^-$ for conditions in which either the molecular ozone or hydroxyl radical pathway were dominant. NH$_3$ additions was more effective in interrupting the molecular ozone pathway. H$_2$O$_2$ addition provided mixed results, with pH conditions being very influential. Hydroxyl radical addition was effective, but would likely be subject to institutional constraints. Pilot- and demonstration-scale contactor studies indicated that
chemical factors (e.g., ozone dose) were more influential than hydrodynamic factors (e.g., CT) in minimizing BrO₃⁻ formation. While bench-scale results with Fe²⁺ were encouraging, pilot tests showed premature turbidity breakthrough, a result rectified by simultaneous addition of both Fe²⁺ and Fe³⁺ (ferric iron) salts. While both lab- and pilot-scale results for GAC were encouraging, the pilot tests were not run long enough to assess the effects of biofilm development on GAC. Medium (versus low) pressure UV lamps proved most effecting in BrO₃⁻ decomposition. Br⁻ was found to be conservative through the coagulation, softening, and GAC processes; sulfate ion was found to greatly impair uptake by ion exchange; nanofiltration membranes provided about 50 % rejections of Br⁻.

**Impact:** The results of this research provide water utilities with several tools for controlling BrO₃⁻ and permitting continued use of ozone for microbial inactivation. For utilities with a potential to form high levels of BrO₃⁻, it may be necessary to employ a combination of minimization/removal options. There is little opportunity for Br⁻ removal before ozonation.

**Participating Utilities:** Metropolitan Water District of Southern California, Contra Costa Water District, Alameda County Water District, Santa Clara Valley Water District, Los Angeles Department of Water and Power.