

Electrochemical process for the removal of bromide from California state project water

David Eugene Kimbrough and I. H. "Mel" Suffet

ABSTRACT

Although bromide is generally considered non-toxic at concentrations found in most drinking water sources, it reacts with a variety of commonly used disinfectants, most notably ozone and chlorine, to produce by-products that are of serious public health concern. There are not currently any demonstrated technologies that can remove bromide in a cost effective fashion. This paper examines an electro-chemical process on a pilot-scale to remove bromide from a widely used surface water source, the California State Water Project (SWP). The process consists of oxidizing bromide to bromine and volatilizing the bromine. SWP water was passed through this unit under various conditions and the bromide removal was measured as well as the formation potential for various organic by products. This study shows up to 35% of the bromide was removed and there were up to 60% less disinfection by-products measured.

Key words | bromide, DBPs, electrolysis, oxidation, THMs, TOC

INTRODUCTION

One of the greatest concerns in drinking water treatment, is the formation of brominated disinfection by-products (DBPs) through the addition of chlorine, chloramines, or ozone to waters containing bromide and natural organic matter (NOM) (Kargalioglu *et al.* 2002; Klotz *et al.* 1998; Morris *et al.* 1992; Pegram *et al.* 1997; Plewa *et al.* 2002; Plewa *et al.* 2003). The brominated DBPs that occur in the greatest concentrations are thought to have the greatest risk are the trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), and bromate, although the formation of brominated haloketones, haloaldehydes, and halonitromethanes are also known to occur. Brominated DBPs in general are thought to pose a much greater health risk than those that are only chlorinated (Kargalioglu *et al.* 2002). As Kargalioglu *et al.* note; "quantitative structure function analysis of the brominated vs. the chlorinated analogs of the haloacetic acids showed that brominated acetic acids had a higher mutagenic potency."

In a recently published paper, a bench-top process was presented which removed bromide from water that contained significant quantities of bromide and total organic

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carbon (TOC), which react during chlorine disinfection to form DBPs (Kimbrough & Suffet 2002). The process used a flow-through electrolysis reactor, which appeared to oxidize bromide to bromine, and a batch air stripper, which then appeared to volatilize the bromine. The removal of bromide from the water resulted in lowering the concentration of brominated THMs (tribromomethane, bromodichloromethane, dibromochloromethane). While promising, it is difficult to determine the practicality of this process from a small bench-top experiment. This paper presents an attempt to take this bench-top semi-batch bromide removal process to a pilot-scale continuous flow-through process.

Reactions, mechanisms and kinetics

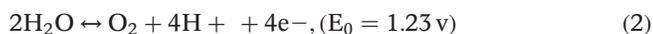
The approach used in this study involves two processes; one is electrolytic oxidation of bromide (Br^-) to bromine (Br_2). The second is the volatilization of the bromine on the surface of the electrode by the gases formed during electrolysis. Industrial processes used to manufacture chlorine and bromine use a two stage process, with

oxidation occurring in one unit process and volatilization in a second unit process, usually with air stripping, pH adjust, heating, and/or vacuum. In the approach that was used in this study, the volatilization will occur in the same unit process as the oxidation. This will be referred to as "self-stripping".

The oxidation of bromide to bromine in water has three steps, the bromide ion migrates toward the anode by diffusion or turbulent flow of the water, the bromide ion gives up an electron to the anode producing a reactive intermediate bromine atom, and two bromine atoms react to form molecular bromine.

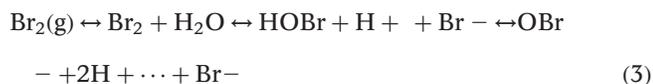


($E_0 = 1.09$ volts) (all standard potentials are versus a hydrogen electrode from CRC Handbook 1978). However, during electrolysis of bromide to bromine in water at the anode, other reactions occur. Water can also be oxidized to oxygen gas and hydrogen ions.



Oxygen bubbles produced in this fashion are very fine, with a very favorable surface area to volume ratio for phase transfer of bromine from water to the oxygen bubbles. If these very fine oxygen bubbles can be produced in sufficient quantities bromine could be removed from the water phase.

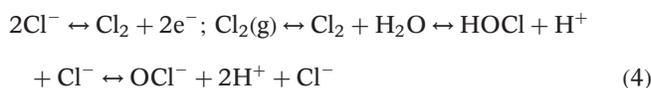
If bromine is not volatilized, it will dissolve in the water. The bromine will be hydrolyzed and can exist in one of three states, molecular bromine (Br_2), hypobromous acid (HOBr), or as hypobromite ion (OBr^-), all of which are in equilibrium with each other.



The equilibrium constant for the hydrolysis of molecular bromine at 25°C has been measured to be between 5.2 and $7.2 \times 10^{-9} \text{ M}^{-2}$ (Radford 1966; Downs & Adams 1973) at pH 7 ($\text{pK}_a = 8.7$) (Radford 1966). However, the equilibrium constant is highly pH dependent, with low pHs being more favorable to Br_2 and higher pHs favoring hypobromous acid and hypobromite (Downs & Adams 1973). Br_2 is the dominant species at pH less than 3.5 and OBr^-

dominates at pH above 9 (Johnson & Sun 1975), and HOBr dominates at pH levels in between.

The oxidation of water also produces a very low pH through the formation of hydrogen ions around the anode (Kimbrough *et al.* 1999a; Krasner *et al.* 1996), which creates conditions favoring bromine over hypobromous acid and hypobromite (Yaron 1966; Radford 1966; Downs & Adams 1973). The Henry's Law Constant (HLC) for hypobromous acid is $6.1 \times 10^3 \text{ M/atm}$ (Frenzel *et al.* 1998) while the HLC for bromine is $7.6 \times 10^{-1} \text{ M/atm}$ (Dean 1992). The electrolysis can oxidize bromide to bromine in water, can produce large quantities of very fine oxygen bubbles, and very low pH all in the same location, around the anode. It is the intent of these experiments to see if this will occur. Chloride will also be oxidized to chlorine under these conditions.



However, no volatilization of chlorine was observed in the previous papers (Kimbrough & Suffet 2002). The equilibrium constant for the hydrolysis of chlorine to hypochlorous acid is 4.2×10^{-4} at 25°C (Cotton & Wilkinson 1976) The Henry's law constant for Cl_2 is 9.3×10^{-2} (Dean 1992) but 6.6×10^2 for HOCl (Huthwelker *et al.* 1995). Cl_2 is the dominant species at pHs of less than 2 but HOCl is dominant above pH 2 while OCl^- is dominant above pH 7.4 (Grotheer 1998). This means that under conditions favorable to the volatilization of bromine ($\text{pH} < 3.5$), chlorine may not be volatilized.

EXPERIMENTAL SECTION

Analytical techniques

- (1) Bromide and chloride ions were measured by ion chromatography (DIONEX DX-500) using USEPA Method 300.0 (Standard Methods 1995). This method cannot measure bromine, hypobromous acid, or hypobromite.
- (2) Free Available Bromine (Br_2 , HOBr , or OBr^-) was measured by collecting samples in duplicate and adding excess sodium thiosulfate (STS) to one of the samples.

The STS reduced any bromine, hypobromous acid, or hypobromite that is present to bromide. The bromide was measured in both samples by ion chromatography (above). The difference between the bromide with and without STS was the Free Available Bromine. Samples for bromide, chloride, and chlorine and pH were collected in 100 ml polypropylene bottles.

- (3) THMs were measured by gas chromatography combined with electrolytic conductivity detector (ELCD or Hall Detector) on a Varian 3400 using USEPA Method 502.2 (USEPA 1998). Samples were collected in zero-headspace vials preserved using STS.
- (4) HAAs were measured by USPEA Method 552.2 (USEPA 1998) with a gas chromatograph with an electron capture detector by the Water Quality Laboratory of the Metropolitan Water District of Southern California. All nine HAAs were analyzed. Samples were preserved using ammonium chloride as described in the method.
- (5) HANs were measured by USEPA Method 551.1 (USEPA 1998) with a gas chromatograph with an electron capture detector by the Water Quality Laboratory of the Metropolitan Water District of Southern California. Samples were preserved using a phosphate buffer and ammonium chloride as described in the method.
- (6) Total Organic Halides (TOX) was measured using SM 5320 (Standard Methods 1995) and was analyzed at the Laboratory at the City of Long Beach Water Department. Samples for TOX were collected in amber glass bottles with STS.
- (7) The Free Available Chlorine/Bromine (HOCl/OCl^- and HOBr/OBr^-) were measured by Ferrous Ammonium Sulfate (FAS)/N,N - Diethyl - p - Phenylene Diamine (DPD) colorimetric titration using Standard Methods 4500-Cl F (Standard Methods 1995). This method cannot distinguish HOCl from HOBr.

Materials and equipment

For most of these experiments, water from the California State Water Project (SWP) was used. The SWP is a system

of dams, conveyances, and pumping stations spanning 1,000 km (600 miles) and supplies drinking water to 20 million Californians. The SWP has four termini, one of which is Castaic Lake in Northern Los Angeles County, in southern California. The water delivered by the SWP has historically had high bromide concentrations (100 to 400 $\mu\text{g}/\text{l}$), high TOC concentrations (2 to 9 mg/l), and a potential to form high concentrations of DBPs, particularly of the brominated species. It had an ionic strength of less than 0.02.

An electrolytic reactor was constructed which consisted of a 2 m section of clear poly-vinyl chloride (PVC) tube with 6.35 cm (2.5 inch) inside diameter with an overall volume of 3,300 ml. On the inside walls three 316 stainless steel rod cathodes 3 m in length and 6.25 mm (1/4 inch) in diameter, were placed at equal distances from each other and held in place by nylon binders. Three dimensionally stable anodes (DSAs), (titanium rods coated with a proprietary coating of RuO_2 and TiO_2 (EC-600), (ELTECH Systems Corporation, Fairport Harbor, Ohio) (Grotheer 1998) of dimensions equivalent to the cathodes were placed in a similar fashion between the cathodes. A fourth DSA was placed in the center of the reactor supported by an inert material. The total surface area of the four DSAs was 1440 cm^2 . The electrodes extended above the highest possible water level and were connected there in parallel. The wires were connected to the power source (for low power tests a PS-1850D, Instek Laboratories Inc., Industry, California; for high power tests, an Agilent 6674 A, Hewlett-Packard, Palo Alto California was used). The power source held a constant applied current and displayed both current and voltage.

Experiment 1: Changes in DBP formation through the reactor

SWP from Castaic Lake was fed into the reactor at 0.75 l/min (contact time was about 260 seconds), while several different applied currents (0 to 7 amps) and potentials (0 to 17 volts) were applied. The water containing bromide, free available bromine, and THMs was collected from the reactor effluent. A 1 liter sample was collected in an amber bottle and then had sufficient chlorine added to produce a final concentration of 18 mg/l of free available chlorine after the demand was met. These samples were

incubated for 6 days and then analyzed for THMs, HAAs, HANs, and TOX. These conditions were designed not to mimic actual water treatment or distribution conditions but to produce the maximum possible DBP concentrations. The influent water contained $174 \mu\text{g/l}$ bromide and the pH was 8.0. The TOC concentration in Castaic Lake water was 3.5 mg/l . The TOC and bromide concentrations in Castaic Lake water does not change rapidly.

Experiment 2: Oxidation & volatilization of bromide in the reactor

The same experiment conditions were used as above but the water was fed into the reactor at several different flow rates (1.5, 3, 4, 7, and 14 l/min), different applied currents (0 to 35 amps), and associated potentials (0 to 60 volts). Bromide, free available bromine, free available bromine and chlorine, and THMs were measured. These experiments were conducted over a series of weeks. The influent bromide concentrations varied somewhat during this period, between 240 and $290 \mu\text{g/l}$. The influent TOC concentrations varied somewhat during this period, between 2.4 and 2.6 mg/l .

RESULTS AND DISCUSSION

Experiment 1

Figure 1 shows the effect of electrolysis on bromide, free available bromine, and brominated THMs. As a result of the formation of bromine and chlorine, small concentrations of THMs were formed through the reactor. The amount of chloride was the same before and after electrolysis thus no chlorine was volatilized. The key observation is that as more current is applied, more bromide is oxidized to bromine and more bromine is volatilized. The rate of volatilization appears to be less than the rate of oxidation. This would suggest that oxidation precedes volatilization.

Figure 2 shows the formation of brominated THMs during the course of six days of contact with 18 mg/l HOCl (initial concentration). The concentrations of brominated THMs declined with declining bromide concentrations. This would indicate that the apparent volatilization of the bromine gas was not an analytical artifact but a reflection of

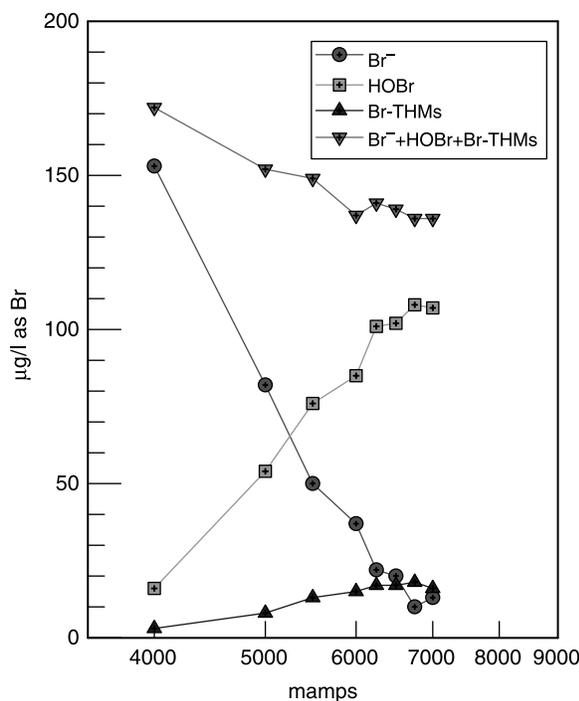


Figure 1 | Bromide oxidation & bromine volatilization in the pilot plant at different applied currents at a flow of 0.75 l/min .

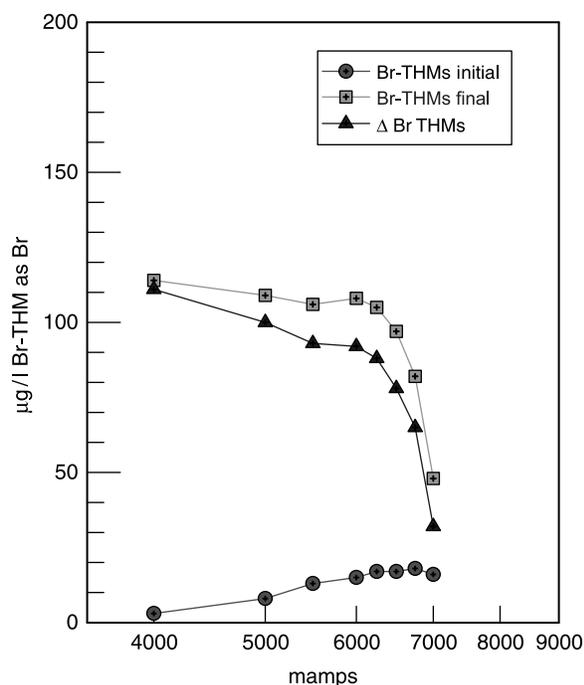


Figure 2 | THMs as Br before and after incubation for 6 days at different applied currents at a flow of 0.75 l/min .

an actual change in bromide concentration. Figure 3 shows similar results for other brominated organic DBPs as well as for TOX. The concentrations of brominated HANs appear to have increased, but the concentrations are so small that it is not possible to assess whether this is a significant increase.

Experiment 2

Figure 4 shows the removal rates of bromide at several different flows and currents. Several trends can be observed in the results from Experiment 2. One is that the applied current needed to completely oxidize the bromide increases as the flow increases and the contact time decreases. This is to be expected given that the contact time decreases with increasing flow rates. The second trend is for the amount of self-stripping to decrease as water flow rate increases. These results would indicate that both the oxidation and volatilization of bromide are controlled by the applied current and the contact time in the reactor. As the contact time decreases, the amount of time available for stripping by the oxygen formed at the anode decreases. Since, the influent bromide concentration varied during the course of

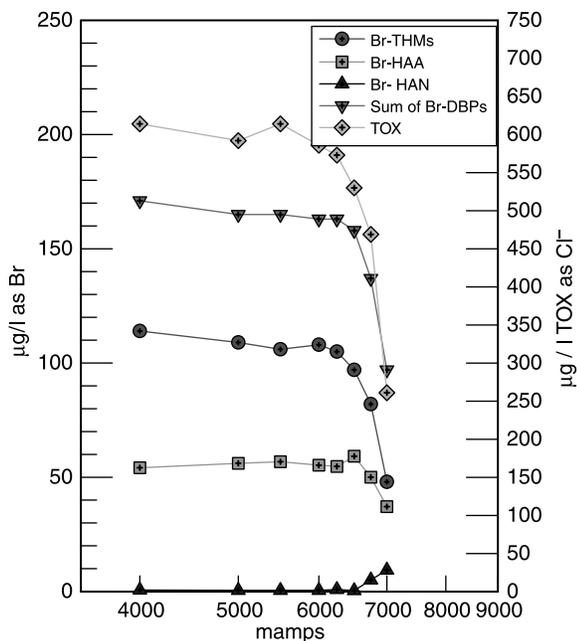


Figure 3 | THMs HAAs, HANs, & TOX after for 5 days incubation at different applied currents at a flow of 0.75 l/min.

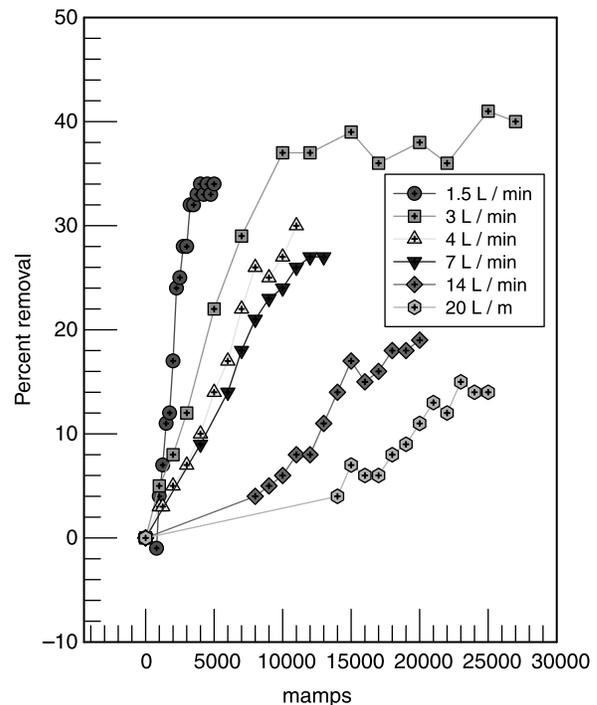


Figure 4 | The effect of water flow (contact time) on "Self-Stripping" in electrolytic reactor removal rates.

these experiments, the results are presented as percent removal relative to the control sample with the power off.

The "self-stripping" observed in Experiment 1 was also observed at each experimental flow, but the rate of self-stripping was proportional to the contact time in the reactor. This is shown more clearly in Figure 5, which indicates that the volatilization rate is a direct function of the applied current. From each of the curves on Figure 4, the sample point with the highest volatilization rate ($\mu\text{g}/\text{min}$) was taken and plotted against the applied current. The bromide was completely oxidized to bromine (results not shown in this figure). Only 40 percent of the bromine was volatilized. The unvolatilized bromine was hydrolyzed to HOBr. Each point on Figure 5 represents a different flow condition for Experiment 2.

The results of these experiments would indicate that self-stripping, using constant current electrolysis to simultaneously oxidize bromide to bromine, produces large quantities of very fine oxygen bubbles, and low pH conditions around the anode to volatilize bromine did occur. The process was certainly incomplete as less than 50% of the

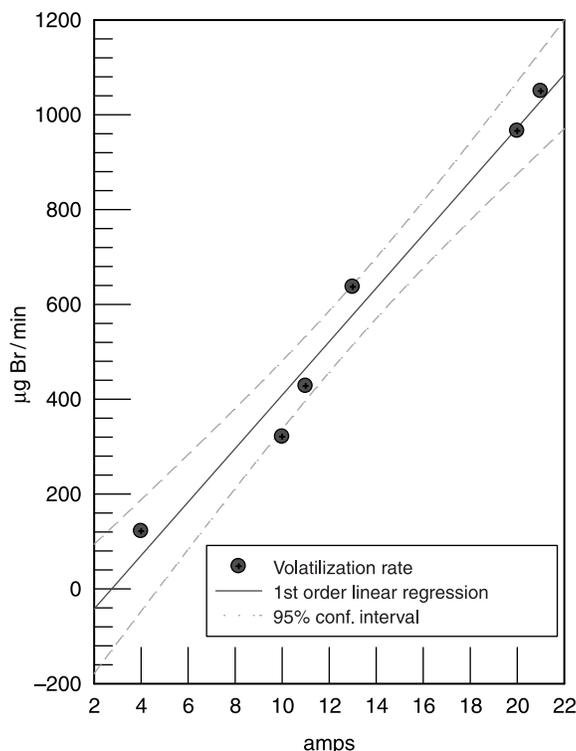


Figure 5 | Volatilization rates of bromine as a function of applied current.

bromine was volatilized. The brominated THMs were reduced in concentration by somewhat more than 50%, whereas the brominated HAAs were reduced in concentration by less than 50%. The TOX, which includes chlorinated species, was significantly reduced in concentration. The relationship between the amount of bromine volatilized and the reduction in the amount of DBPs produced does not appear to be linear but rather shows greater reduction in DBP concentration than expected for the THMs and TOX and less than expected for the HAAs. This is consistent with previous research which shows increases in bromide concentration produce greater than expected increases in THM formation (Krasner *et al.* 1996; Symons *et al.* 1997). This was achieved in low ionic strength natural waters containing bromide at concentrations of concern, such as the Castaic Lake waters used in these experiments.

Implications for full-scale treatment plants

If such a process could be made cost-effective for large scale treatment, drinking waters negatively impacted by

brominated DBPs could benefit. Two unexamined issues are the impact of electrolysis on conventional surface water treatment for example coagulation, sedimentation, and filtration. The other is the impact of electrolysis on disinfection. There are several studies that indicate that electrolysis enhances disinfection of bacteria (Kimbrough *et al.* 1999a; 1999b; 2006) however, there is little or no research on the impact of electrolysis on viruses and protozoan parasites.

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