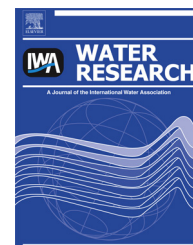


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Selective oxidation of bromide in wastewater brines from hydraulic fracturing

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ABSTRACT

Brines generated from oil and natural gas production, including flowback water and produced water from hydraulic fracturing of shale gas, may contain elevated concentrations of bromide (~1 g/L). Bromide is a broad concern due to the potential for forming brominated disinfection byproducts (DBPs) during drinking water treatment. Conventional treatment processes for bromide removal is costly and not specific. Selective bromide removal is technically challenging due to the presence of other ions in the brine, especially chloride as high as 30–200 g/L. This study evaluates the ability of solid graphite electrodes to selectively oxidize bromide to bromine in flowback water and produced water from a shale gas operation in Southwestern PA. The bromine can then be outgassed from the solution and recovered, as a process well understood in the bromine industry. This study revealed that bromide may be selectively and rapidly removed from oil and gas brines ($\sim 10 \text{ h}^{-1} \text{ m}^{-2}$ for produced water and $\sim 60 \text{ h}^{-1} \text{ m}^{-2}$ for flowback water). The electrolysis occurs with a current efficiency between 60 and 90%, and the estimated energy cost is $\sim 6 \text{ kJ/g Br}$. These data are similar to those for the chlor-alkali process that is commonly used for chlorine gas and sodium hydroxide production. The results demonstrate that bromide may be selectively removed from oil and gas brines to create an opportunity for environmental protection and resource recovery.

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1. Introduction

Large volumes of brine are produced during hydraulic fracturing to recover oil and natural gas from deep shale formations (Gregory et al., 2011). Aqueous fluids are pumped into the formation to fracture the rock and increase the permeability. A fraction of the hydraulic fracturing fluids returns to the surface as a concentrated brine that is referred to as “flowback water” and/or “produced water”. “Flowback water” is the brine recovered from the well immediately following hydraulic fracturing, while “produced water” is the brine recovered from the well during well gas production all over the lifetime of the

well (Gregory et al., 2011). Both brines can contain total dissolved solids (TDS) as high as 5 times that of seawater (Gregory et al., 2011). Although the high TDS (mainly NaCl) does not present a direct threat to humans and ecosystems, it does limit the potential reuse of the oil and gas brines for irrigation, livestock watering, and other various uses (e.g., vehicle washing and power plant makeup water). Such brines may also contain constituents which are of health concern, including emulsified or dissolved organic compounds (e.g., heavy and light hydrocarbons, phenols, ketones), chemical additives (surfactants, biocides, scale inhibitors and corrosion inhibitors), bacteria, metals (e.g., zinc, lead, manganese, iron,

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and barium) and naturally occurring radioactive material (Veil et al., 2004; Wilson and Van Briesen, 2012). Thus, the brines need to be properly treated before reuse or discharge to protect groundwater and surface water resources. Traditional brine treatment technologies in oil and gas mining industry include oil–water separation (skimming, flotation, etc.) and suspended solids removal (settling or filtration) (Veil et al., 2004), but little is done to remove TDS. These primarily treated brines are then disposed by deep-well injection, reused for on-site hydraulic fracturing, applied to roads for dust or ice control, or introduced into municipal wastewater treatment plants followed by surface discharge (Gregory et al., 2011; Wilson and Van Briesen, 2012).

Among the dissolved constituents in produced and flowback water, bromide (at concentration of ~ 1 g/L), has garnered recent attention, considering its potential release into surface waters that may serve as a drinking water source (States et al., 2011). The concern with bromide is primarily due to the potential to form carcinogenic brominated disinfection byproducts (DBPs) upon chlorination for drinking water disinfection (World Health Organization, 2000). Since elevated concentrations of bromide will favor the formation of brominated DBPs over chlorinated DBPs, and the brominated DBPs are generally considered more hazardous than their chlorinated analogs (World Health Organization, 2000), it is highly desirable to remove bromide from industry brines/wastewater before discharge or surface application for dust control. Diluting the high concentrations of bromide by discharging the brine into surface water can lower the DBPs formation risk, but may not completely eliminate the risk. For example, in southwestern Pennsylvania, simultaneous increases in brominated DBPs, TDS, and bromide concentrations have been observed in drinking water utilities using the Monongahela River (Handke, 2009) and Allegheny River (States et al., 2011) as source water, while these rivers have received treated brine discharges from oil and gas mining (Wilson and Van Briesen, 2012).

However, there are few techniques for effective bromide removal from industrial brines. Methods have been proposed for bromide removal in drinking water applications, such as adsorption using silver-doped activated carbon aerogels (Sánchez-Polo et al., 2006) or aluminum coagulation (Ge and Zhu, 2008), but in both processes chloride competes with bromide removal. Since the concentration of chloride (and other ions) in oil/gas brines is orders of magnitude higher than bromide, the adsorption and coagulation approaches become ineffective for selective bromide removal. Alternatively, bromide may be removed along with all other TDS using standard desalination processes. However the available techniques (e.g., thermal distillation, reverse osmosis, nanofiltration, electrodialysis, and capacitive deionization) can be prohibitively energy intensive (Gregory et al., 2011), especially when the primary need is to remove bromide ions while the presence of other ions (e.g., high concentration of Na^+ , Cl^-) is not problematic or regulated. There is a need for cost-effective, selective bromide removal from oil/gas brines. Assuming the brine has the common characteristics as reported oil/gas brines from the Marcellus formation (median values in Table 2 in Gregory et al. (2011)), the estimated theoretical minimum energy consumption for reverse osmosis, capacitive

Table 1 – Properties of brine samples used in this study.

	Flowback water	Produced water
Total dissolved solids (g/L)	46.4 ± 0.3^a	184.6 ± 1.1^a
Dissolved volatile solids (g/L)	4.7 ± 0.3^a	15.4 ± 0.6^a
pH	6.93	4.74
Conductivity (mS/cm)	86 ± 18^a	287 ± 18^a
Alkalinity (mg/L as CaCO_3)	402	7
Hardness (g/L as CaCO_3)	9	60
Dissolved organic carbon (mg/L)	26.7	16.9
Dissolved inorganic carbon (mg/L)	47.2	1.2
Chloride (g/L)	23	110
Bromide (g/L)	$0.24/1.2^b$	1.7

Notes:

a Mean of triplicate measurements $\pm$ standard deviation.

b The original bromide concentration in flowback water sample was 0.24 g/L; in the bromide removal experiment it was amended with KBr up to 1.2 g/L in order to compare the result with other tested water samples.

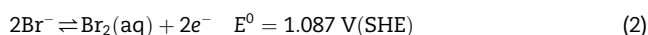
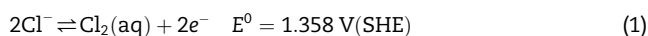
deionization, and thermal distillation are 11, 412, 2142 kJ/g-Br, respectively, while the theoretical minimum energy consumption of selective electrolysis proposed in this study is calculated to be 1.3 kJ/g Br, as shown in Table S-1 in Supporting Information. Thus, the selective bromide electrolysis has an economic advantage when bromide is the

Table 2 – Species with lower standard equilibrium potential (E^0) than bromide that may exist in oil/gas brines. Data from Lide (2011) and Madigan and Martinko (2006); data in Madigan and Martinko (2006) were converted from equilibrium potentials at pH = 7 to standard states (pH = 0) to compare with data from Lide (2011); pH observed in the anolyte was below 2. E^0 for bromide oxidation is 1.09 V vs. SHE.

Species	Oxidation half reaction	E^0 (V vs. SHE)
Formic acid	$\text{HCOOH} \rightleftharpoons \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$	-0.017
HS^-	$\text{HS}^- \rightleftharpoons \text{S} + \text{H}^+ + 2\text{e}^-$	-0.064
Acetic acid	$\text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^-$	0.123
Ethanol	$\text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e}^-$	0.216
Lactic acid	$\text{CH}_3\text{CH}(\text{OH})\text{OH} \rightleftharpoons \text{CH}_3\text{COCOOH} + 2\text{H}^+ + 2\text{e}^-$	0.223
HS^-	$\text{HS}^- + 4\text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^-$	0.245
	$\text{HS}^- + 3\text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + 6\text{H}^+ + 6\text{e}^-$	0.297
Succinic acid	$\text{HOOCCH}_2\text{CH}_2\text{COOH} \rightleftharpoons \text{HOOCCH} = \text{CHCOOH} + 2\text{H}^+ + 2\text{e}^-$	0.38
I^-	$2\text{I}^- \rightleftharpoons \text{I}_2 + 2\text{e}^-$	0.536
	$3\text{I}^- \rightleftharpoons \text{I}_3^- + 2\text{e}^-$	0.536
FeCO_3	$\text{FeCO}_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + \text{CO}_2 + \text{H}^+ + \text{e}^-$	0.613
Fe^{2+}	$\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{e}^-$	0.771
Mn^{2+}	$\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{4+} + 2\text{e}^-$	0.798
I^-	$\text{I}^- + \text{H}_2\text{O} \rightleftharpoons \text{HIO} + \text{H}^+ + 2\text{e}^-$	0.987
	$\text{I}^- + 2\text{H}_2\text{O} \rightleftharpoons \text{IO}_3^- + 6\text{H}^+ + 6\text{e}^-$	1.085

targeted ionic contaminant and removal of other ions is not necessary for the end-use or disposal of the water.

Electrolytic oxidation may be an effective method for transforming bromide in oil/gas brines. A similar process is used commercially in the chlor-alkali industry to oxidize chloride to chlorine (Equation (1)) using brine or seawater as the chloride source. Direct bromide oxidation to bromine (Equation (2)) by electrodes has been studied for both drinking water source treatment (Bo, 2008; Kimbrough and Suffet, 2002; 2006) and bromine production from bromide-containing brine (Qi and Savinell, 1993a, b; Yalçin et al., 1997). However, the former only treated relatively clean water with very low bromide concentration (~200 ppb), while the later focused on bromine production and did not address the need for low residual bromide concentration of the processed brine. It is thus unclear whether electrolytic treatment can be successfully applied in a chemically heterogeneous brine to achieve a low bromide residual.



Therefore, in this study, an electrolysis method to remove bromide in complex brines was proposed and tested, as shown in Fig. 1. The bromide-containing brine is processed in an electrolyzer, with the anode and cathode chambers separated by a cation-permeable membrane. Bromide is oxidized to bromine at the anode (Equation (2)). The produced bromine was stripped out of the electrolyte with air and recovered in separate containers by potassium iodide reduction. At the same time protons are reduced to form hydrogen gas at the cathode. This method may be competitive for treating brines, because the high salinity in brines provide natural electrolyte for the electrochemical reaction, and thus lowers the energy consumption. Applying such selective bromide removal from brines containing chloride need to address an important engineering challenge that the standard oxidizing potential for bromide is only 0.27 V lower than for chloride (Equations (1) and (2)) (Lide, 2011). Since chloride exists in the brine in high concentration but is not a risk to human health, precise control of the electrical potential is crucial to ensure only bromide is oxidized.

Compared to the industrial bromide production process, where a high potential is used to oxidize chloride to chlorine first, and then uses the produced chlorine to oxidize bromide to bromine, the direct bromide electrolysis proposed in this study has the advantage of requiring less energy input, not only because a lower electric potential is needed for bromide oxidation than chloride oxidation, but also because no excess reagent (chlorine) has to be produced or added to achieve complete bromide removal. The elimination of chlorine as the primary oxidant also creates safer reactions and a product stream that is easier to purify the commodity bromine.

In order to prevent bromide from entering waterways and ultimately lead to DBP formation, electrolytic bromide removal from oil/gas brines can be performed either during treatment of the brines or when it arrives (diluted) at a drinking water treatment plant. In practice, the former option has several advantages over the later: (1) The high TDS in

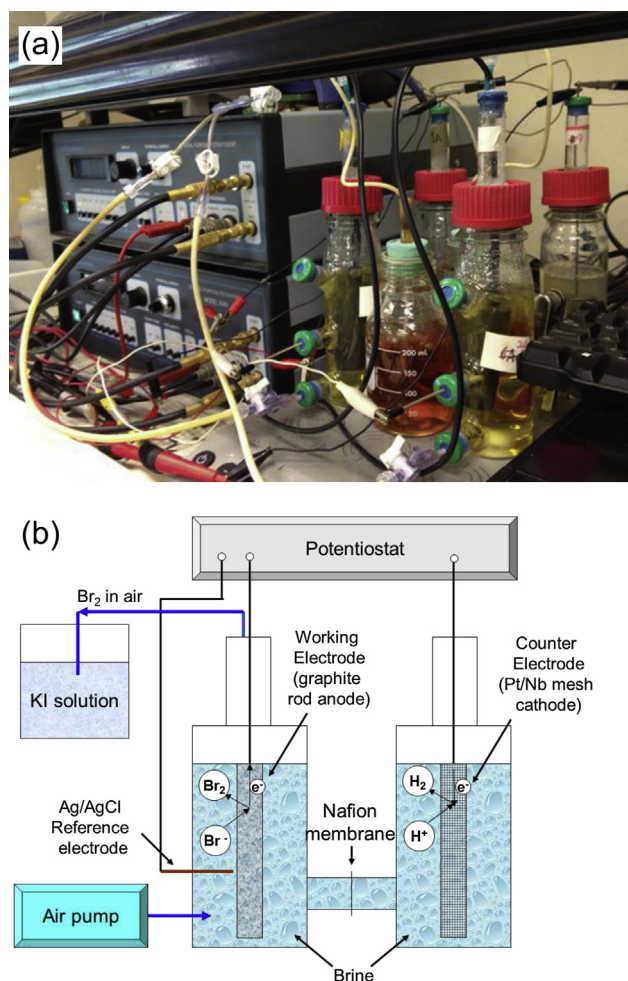


Fig. 1 – Picture (a) and scheme (b) of the experimental setup for bromide removal by selective electrolysis from brines (coupled with hydrogen production) in H-cell reactors.

brine provides strong electrolyte support for electrolysis and thus less energy consumption than what would be expected for low ionic strength drinking water. (2) A much lower volume of brine has to be treated compared to the drinking source water, requiring smaller reactors and electrodes. (3) The bromide concentration in the treated brine does not have to be as low as in drinking water treatment, because dilution will further reduce the bromide concentration in receiving water. (4) DBPs are not regulated in brine discharge, but are strictly regulated in drinking water.

The objective of this work is to evaluate the feasibility of selective bromide removal from flowback and produced water by electrolysis, and to make preliminary estimation for the energy inputs required for a scaled-up process for treating these brines. Specifically, the feasibility of selective bromide removal in the presence of high concentrations of chloride was determined. The bromide oxidation rate and current efficiency afforded by graphite electrodes was determined at different chloride concentration, and in produced water and flowback water collected from oil and gas wells in the Marcellus formation in southwestern Pennsylvania.

2. Materials and methods

2.1. Chemicals

All chemicals were reagent grade unless otherwise noted. Sodium chloride (NaCl), sodium sulfate (Na_2SO_4), potassium bromide (KBr), potassium iodide (KI), soluble starch, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), Eriochrome black T, disodium ethylenediamine tetraacetate dihydrate ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), ammonium chloride (NH_4Cl), sodium carbonate (Na_2CO_3), sodium bicarbonate (NaHCO_3), triethanolamine ($\text{C}_6\text{H}_{15}\text{NO}_3$), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) were supplied by Fisher Scientific (Pittsburgh, PA). Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was purchased from Acros (Geel, Belgium). Calcium carbonate (CaCO_3 , special reagent low in heavy metals, alkalis, and magnesium) and ammonium hydroxide (NH_4OH) were purchased from Aldrich Chemical (Milwaukee, MI).

2.2. Flowback and produced water samples

Flowback and produced water samples were collected from hydraulic fracturing wells of the Marcellus shale in southwestern Pennsylvania (USA). Both samples were stored at 4°C until use. Samples were filtered with $20\ \mu\text{m}$ ashless quantitative filter paper (Grade 41, Whatman, Piscataway, NJ) before use. Properties of the brines including hardness, alkalinity, pH, conductivity, total dissolved solid (TDS) and dissolved volatile solids (DVS), dissolved organic and inorganic carbon content (DOC and DIC) were determined using standard analytical methods as described below.

To determine whether the bromide removal rates would be affected by hardness and scaling, a group of experiments were conducted with softened brines. In these experiments, excess amounts of Na_2CO_3 , Na_2SO_4 and NaOH was added to brine to precipitate cations contributing to the brine hardness (Ca^{2+} and Mg^{2+}) and other divalent ions (Sr^{2+} and Ba^{2+} , etc.). Then the brine was filtered using a $20\ \mu\text{m}$ filter paper and the pH was adjusted back to the initial pH before softening.

2.3. Electrode materials

Graphite anodes were historically used in chlor-alkali processes because of their low cost and resistance to poisoning. In this study solid graphite rods (described below) were chosen as the anode. Graphite felt (10 cm long $\times$ 4 cm wide $\times$ 1/4 inch thick, Wale Apparatus Co., Inc., Hellertown, PA) was also tested and found to be not selective enough for bromide over chloride.

2.4. Linear voltammetry

Linear voltammetry of bromide and chloride oxidation was carried out in 250 ml media bottle using a potentiostat (mode 2049, AMEL Instrument, Milano, Italy) to demonstrate selective bromide oxidation over chloride and water oxidation, and to determine the proper anode potential for bromide electrolysis. Graphite rods (0.25"OD $\times$ 3"L, GraphiteStore.com, Inc., Buffalo Grove, IL) were used as both the working and

counter electrodes. The electrode potential was scanned between 0 and 2 V against the Ag/AgCl reference electrode (Electrolytica, Inc., Amherst, NY) at a scan rate of 50 mV/s, and reported as vs. standard hydrogen electrode (SHE) values. Tested electrolytes included buffer solution (5 mM phosphate buffer at pH 7), pure bromide solution (buffer + 0.5 M KBr), pure chloride solution (buffer + 0.5M NaCl) and a combined bromide/chloride solution (buffer + 0.5 M KBr + 0.5 M NaCl). During scans, the electrolytes were constantly mixed using a magnetic stir bar at 500 rpm at room temperature ($23 \pm 2^\circ\text{C}$).

2.5. Selective bromide removal from brines

Bromide removal experiments were performed at room temperature in glass H-cell reactors as previously described (Sun et al., 2012). Each cell is separated into a cathode chamber and an anode chamber by a cation-exchange membrane (Nafion 117; Electrosynthesis Inc., Lancaster, NY). Each chamber contained 90 ml of headspace and 220 ml of electrolyte (synthetic or real brines), and was well mixed using a magnetic stir bar. In these experiments graphite rods (1"OD $\times$ 3"L, Graphite Engineering & Sales Co., Greenville, MI) were used as the anode, and Ag/AgCl was used as the reference electrode. Pd/Nb meshes (1"OD $\times$ 3"L, Scribner Associates Inc., Southern Pines, NC) were used as the cathode to lower the energy consumption in the cathode side reactions. The anode potential was poised at 1 V vs. Ag/AgCl (1.22 V vs. SHE) by the potentiostat. Duplicate H-cells were used for each experiment to determine reproducibility. Bromide removal experiments were conducted in either flowback water, produced water, or KBr solution at common concentration in hydraulic fracturing brines (1.2 g/L bromide, or 15 mM) (Gregory et al., 2011) with different chloride concentrations. KBr was added to the flowback water to provide an initial concentration of 1.2 g/L for comparison to the synthetic brine. Air was constantly pumped into the anode chamber to strip out the formed bromine (Br_2). The outlet gas was directed to a separate bottle containing 15 mM KI to collect the produced bromine for quantitative analysis.

2.6. Calculation of the bromide removal rate, current efficiency and energy consumption

The bromide concentration in anolyte was monitored over 6.5 h, and was tested for the hypothesis that bromide removal was first-order with respect to the bromide concentration. For all experiments, a $R^2 > 0.98$ was achieved for the model fits. The first order kinetic rate constant was used to compare the rates achievable under the various electrolyte conditions used.

Current efficiency was calculated using Equations (3) and (4).

$$\text{Current efficiency} = \frac{C_{\text{Br}^- \text{ initial}} - C_{\text{Br}^- \text{ end}}}{\text{Current equivalent of Br}^-} \quad (\text{dimensionless}) \quad (3)$$

$$\text{Current equivalent of Br}^- = \frac{\int_0^{t_{\text{total}}} \text{Idt}}{F} \times \frac{\text{MW}}{\text{Vol}} \quad (\text{g/L}) \quad (4)$$

where I is the cell current (A), t_{total} is the total reaction time (s), F the Faradic constant (96,485 °C/mol), MW is the molecular weight of bromide (80 g/mol), and Vol is the volume of electrolyte in the anode chamber (0.22 L).

Energy consumption was calculated using Equation (5).

$$\text{Energy consumption} = \frac{\int_0^{t_{\text{total}}} V I dt}{(C_{\text{Br}^- \text{ initial}} - C_{\text{Br}^- \text{ end}}) Vol} \text{ (J/g)} \quad (5)$$

where V is the cell voltage (V).

2.7. Analytical methods

The hardness of the produced and flowback waters was determined by EDTA titration (standard method 2340C); alkalinity was determined by H_2SO_4 titration to pH 4.3 (standard method 2320B); pH and conductivity were determined using a pH and conductivity probe, respectively (Fisher Scientific, Pittsburgh, PA); TDS and DVS were determined by heating the water sample at 104 °C and 550 °C, respectively; DOC and DIC were measured using an O.I. Analytical 1010 liquid TOC analyzer (College Station, TX).

The bromide and chloride concentration in the anolyte were determined by ion chromatography (IC) (Dionex, Sunnyvale, CA) using an AS14A column and conductivity detector. The mobile phase was 8 mM Na_2CO_3 /1 mM NaHCO_3 at 1.0 ml/min. Bromine captured by KI adsorption was reduced to bromide and quantified by IC as well. Bromine remaining in the H-cells was determined by titrating the electrolyte with $\text{Na}_2\text{S}_2\text{O}_3$ and the KI-starch indicator. The total produced bromine concentration was calculated as the sum of bromine captured in KI and bromine remaining in the anolyte.

3. Results and discussion

3.1. Linear voltammetry and selective bromide oxidation

Although the standard potential for bromide oxidation (1.09 V vs. SHE) is 0.27 V lower than chloride oxidation (1.36 V vs. SHE), in practice this gap may not be significant enough to allow selective bromide oxidation. The standard potentials are determined for 1 M conditions, while the higher concentrations of chloride in brine will lead to a lower oxidation potential for chloride, and lower than 1 M concentrations of bromide will lead to a higher oxidation potential for bromide. For example, for chloride and bromide present at their common concentration in flowback and produced water from the Marcellus formation (76 g/L and 1.2 g/L, respectively (Gregory et al., 2011)), the theoretical chloride and bromide oxidation potential become, 1.34 V and 1.20 V, respectively, leading to the theoretical gap only 0.14 V. Moreover, the electrodes may require different overpotentials for bromide and chloride oxidation. If the required overpotential for bromide oxidation is greater than for chloride oxidation, the practical gap will become even smaller. Thus, special attention is needed to avoid the chlorine side reaction.

Another important side reaction during bromide oxidation is water electrolysis. Theoretically oxygen production starts at

a lower potential (0.82 V vs. SHE) than bromine production at pH 7. Many commonly used electrode materials require large overpotentials for oxygen generation, and in practice oxygen production typically does not occur under 2 V. However it is still necessary to verify whether oxygen production is an important side reaction with the graphite electrodes used in this study. If oxygen and chlorine production do start at the same potential as bromine production, selective bromide removal would become unfeasible because of the high concentrations of water and chloride.

To demonstrate the possibility of selective bromide oxidation over chloride and water oxidation, and to determine the proper anode potential for selective bromide oxidation, linear voltammetry of buffer solution (5 mM phosphate buffer at pH 7), 0.5 M bromide in buffer, 0.5 M chloride in buffer, and a combined 0.5 M bromide/0.5 M chloride solution in buffer was conducted (Fig. 2). The onset of bromide oxidation occurred at ~1.0 V vs. SHE, while chloride oxidation began at ~1.5 V vs. SHE. Water oxidation was not observed in the potential range tested. Compared to the theoretical potentials, it appears that the graphite electrodes used in this study require a very low or negligible overpotential for bromide oxidation, a moderate overpotential for chloride oxidation, and a significant overpotential for oxygen production. Thus, bromine formation is favored over chlorine and oxygen formation at potentials between 1.0 V and 1.5 V vs. SHE. The behavior of the combined Br^-/Cl^- solution was the same as in the Br^- only solution before the onset of chloride oxidation, and only had higher current than in the Br^- solution after chloride oxidation started, suggesting the presence of chloride did not interfere with bromide oxidation at potential less than 1.5 V vs. SHE. Since there is ~0.5 V gap between bromide oxidation and chloride oxidation, and even a greater gap between bromide oxidation and water oxidation, selective bromide removal in chloride-rich solution appears possible.

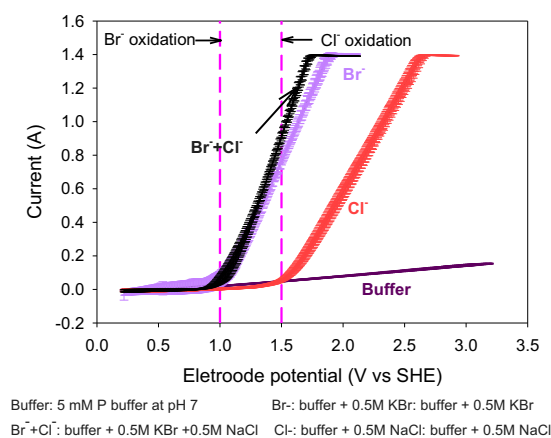


Fig. 2 – Linear voltammetry of 0.5 M Br^- and Cl^- solutions with graphite electrodes. Solutions were constantly stirred with magnetic bars at 500 rpm at room temperature. Voltammetry conditions: Scan rate: 50 mV/s; step width: 100 ms; step height: 5 mV. Error bars represent standard deviations of 5 replicate scans for each solution. The onset of bromide oxidation occurs at 1.0 V vs. SHE with and without the presence of 0.5 M chloride. Water oxidation was not observed over the range of potentials tested.

While the linear voltammetry indicates that bromide can be selectively oxidized in the presence of an equal molar concentration of chloride, the selective oxidation of bromide in waters containing much higher chloride to bromide concentrations ratios (which is common in oil/gas brines) needs to be determined. This experiment was conducted in closed H-cell reactors where the bromide, chloride, and water oxidation products (bromine, chlorine, and oxygen, respectively) can be measured. As shown in Fig. 3, a concentrated chloride solution (76 g/L, or 2.1 M) was poised at 1 V vs. Ag/AgCl (1.22 V vs. SHE) for 20 h. No chlorine generation was detected using the $\text{Na}_2\text{S}_2\text{O}_3$ titration, and the cell current was constantly low, indicating that neither chloride oxidation nor water oxidation was taking place. However, once a comparatively low concentration of bromide (1.2 g/L, or 15 mM) was added into the anolyte, there was an immediate jump in both cell voltage and current, and the anolyte turned to a yellow-green color, indicating that bromide was oxidized to bromine. The voltage and current gradually decreased and returned to the initial level as bromide was consumed. These results suggest, even at high concentration and prolonged reaction time, chloride is not oxidized at the poised potential (1 V vs. Ag/AgCl electrode) while bromide at roughly a two orders of magnitude lower concentration can be selectively oxidized when the anode potential is carefully controlled. IC analyses showed that bromate (a DBP) was below detection limits during electrolytic bromide oxidation at the poised potentials examined in these studies.

3.2. Effect of chloride concentration on bromide removal

The removal of bromide from synthetic brine containing 0.015 M (1.2 g/L) bromide and different chloride concentrations was measured to determine the effect of chloride concentration on bromide oxidation. The bromide concentrations used here were selected based on the median

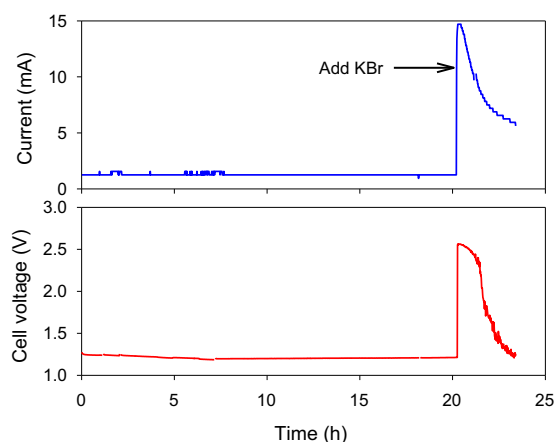


Fig. 3 – Current and cell voltage profile in the H-cell reactor containing 2.1 M (76 g/L) chloride solution before and after adding 15 mM (1.2 g/L) bromide. Cell voltage was measured between the graphite anode and the Pt/Nb cathode. The anode was poised at 1 V vs. Ag/AgCl (1.22 V vs. SHE). Initial electrolyte was NaCl only, and KBr was added after 20 h. Chlorine gas production was below detection limit.

concentration in oil/gas brines from the Marcellus formation (Gregory et al., 2011), and the chloride concentration was selected to represent a low (32 g/L), median (76 g/L), and high (148 g/L) concentration. Equal chloride and bromide concentration (1.2 g/L) was also examined. Fig. 4 is a typical profile of the measured bromine and bromide concentration over time. Within 6.5 h, all the bromide in the electrolyte was oxidized to bromine and removed from the solution by air stripping. The current efficiency, determined using Equation (3), was ~80%, and no chlorine was detected in the KI adsorption solution.

The measured bromide removal rate constant vs. chloride concentration is shown in Fig. 5. The data indicate that the presence of even low concentration of chloride significantly slowed bromide removal. When chloride is present in the electrolyte at twice of the bromide concentration (34 mM Cl^- /15 mM Br^-), the bromide removal rate constant was reduced by 30% compared to the absence of chloride. However, when chloride concentration was further increased, the decrease in the bromide removal rate constant was much less severe. Given that chloride is not oxidized at the anode, it is likely that competitive adsorption between chloride and bromide on the anode surface depresses the bromide removal. Previous electrosorption studies revealed competitive adsorption between chloride and bromide (Xu et al., 2008). Their findings show that chloride adsorbed by carbon electrodes is 20 times greater than bromide using brackish water with 93 mM Cl^- and 0.63 mM Br^- .

However, chloride also has a positive impact on the overall process. The presence of chloride increases the electrolyte conductivity, thereby reducing the energy consumption for bromide removal by a factor of 6–11. In practice, the lower energy demand will likely compensate for the lower reaction rate, although a lower reaction rate necessitates longer retention times and hence larger reactors (higher capital) for a given flow rate. The current efficiency for bromide removal, however, was relatively unaffected by the chloride concentration (Fig. 5).

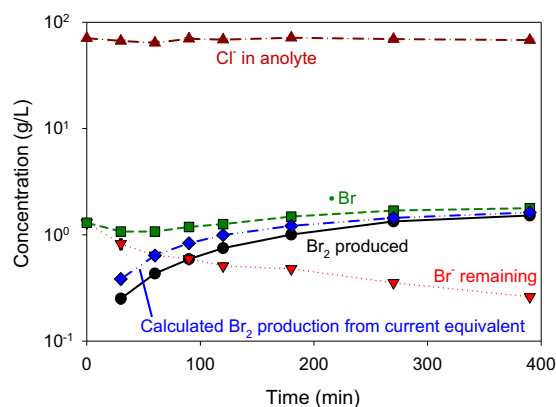


Fig. 4 – Bromide removal and bromine production in a 15 mM (1.2 g/L) Br^- + 2.1 M (76 g/L) Cl^- solution by a graphite rod anode poised at 1 V vs. Ag/AgCl (1.22 V vs. SHE). The results are the means of replicate reactors, and error bars represent standard deviation. In separate control experiments (Fig. 3), chlorine gas was not detected.

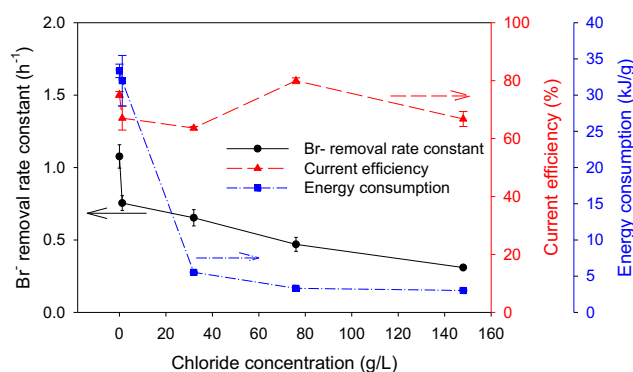


Fig. 5 – Effect of chloride concentration on the bromide removal rate constant, current efficiency and energy consumption in synthetic brine using a graphite rod anode poised at 1 V vs. Ag/AgCl (1.22 V vs. SHE) Initial bromide concentration is 0.015 M (1.2 g/L) in all cases. The results are the means of replicate reactors, and error bars represent standard deviation.

3.3. Bromide removal from flowback and produced water

Two kinds of oil/gas brine (one flowback water sample, one produced water sample) were tested for selective bromide removal by electrolysis. The properties of the brine samples are summarized in Table 1.

Fig. 5 suggests there is a linear relationship between the chloride concentration and the bromide removal rate constant for the chloride concentration range tested (1.2–148 g/L Cl⁻). Thus, the bromide removal rate in synthetic brine with the same concentration as that in the two brine samples can be estimated. Fig. 6 compares the bromide removal rate constants, energy consumption and current efficiency measured in flowback water and produced water, and compared these to that estimated for the synthetic brine (pure bromide and chloride solution) with the same chloride concentration. The bromide removal rate was 44% lower in flowback water than in synthetic brine, and 84% lower in produced water than in synthetic brine (Fig. 6a), suggesting that besides chloride, other components in oil/gas brines also have a negative impact on the bromide removal rate. One possible factor is the hardness of the real brines, which can lead to precipitation of carbonate and sulfate minerals on the electrode surfaces. To test this hypothesis, bromide removal experiments were also conducted in softened flowback and produced water samples (as described in Material and Method section). The softened brine had similar bromide removal rates compared to the original brine, suggesting hardness was not responsible for the decrease in the bromide removal rate. Similarly, pH, alkalinity, and DIC (HCO₃⁻ and CO₃²⁻) are not likely reasons for the observed differences; in all the experiments, regardless of which brine was used, the pH of the anolyte dropped to ~2.5 with 30 min after power on, diminishing any pH, alkalinity or DIC differences in initial brine samples.

Table 2 lists several chemical species that may exist in oil/gas brine with standard oxidation potential lower than bromide. Although their concentrations are low, they may be

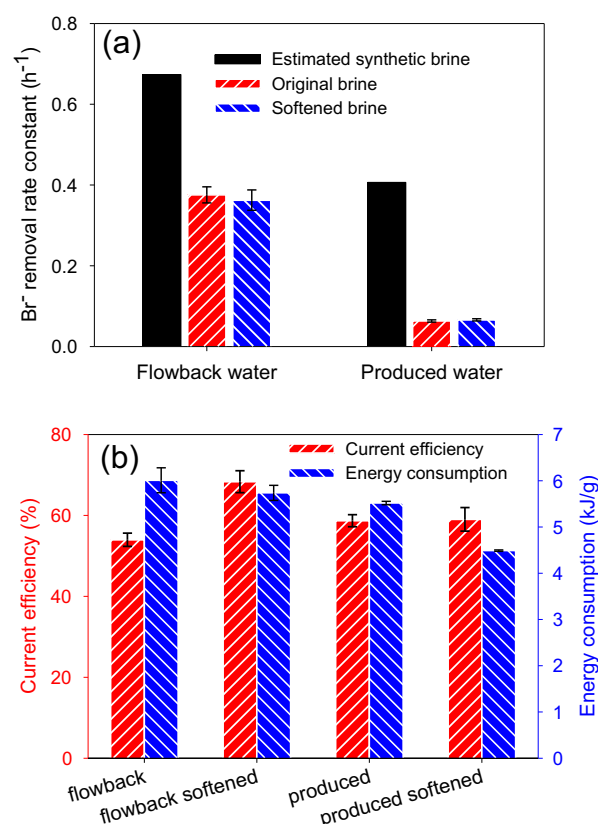


Fig. 6 – Bromide removal rate constant (a), and current efficiency and energy consumption (b), in synthetic brines, flowback waters, and produced waters using a graphite anode poised at 1 V vs. Ag/AgCl (1.22 V vs. SHE). The estimated removal rates in synthetic brine are interpolated from the relationship between chloride concentration and bromide removal rate constant (Fig. 5) based on the measured chloride concentration in each brine sample. The other results are the means of replicate reactors, and error bars represent standard deviation.

preferentially oxidized at the anode and thereby compete with bromide oxidation. However, further studies on which of these components may be responsible for the observed decrease in the bromide removal rate were not conducted.

Energy consumption and current efficiency in all tested brine solutions are close to the levels in synthetic brine (Figs. 6b and 5). These results suggest that electrodes can selectively and effectively remove bromide present in produced and flowback waters containing up to two orders of magnitude higher chloride concentration than bromide. Further, similar results from different brine samples with very different properties suggest that such treatment has considerable tolerance to various properties of the brine.

3.4. Engineering considerations

The bromide removal rate constants achieved in this study ranged from 0.4 h⁻¹ for flowback water to 0.06 h⁻¹ for produced water. When normalized to the anode surface area (64 cm²), the removal rate constants is ~60 h⁻¹ m⁻² in

flowback water and $\sim 10 \text{ h}^{-1} \text{ m}^{-2}$ in produced water. Using the configuration of an electrolyzer in the chlor-alkali process and bromide oxidation rates obtained in this study, the required size of electrolyzers suitable for bromide removal from flowback and produced water was estimated. A key assumption here is that bromide removal is first order with respect to bromide concentration, which should be verified in future studies for very low bromide concentrations. It is also assumed that the slow step in the process is bromide oxidation rather than removal of the produced bromine.

Based on the characteristics of reactors for several chlor-alkali industrial facilities (Mantell, 1931), the median electrode area per cell is $\sim 3 \text{ m}^2$, and the cell volume is $\sim 0.5 \text{ m}^3$. If such an electrolyzer is used for bromide removal, and the treatment target is to reduce bromide concentration from 1 g/L ($10^6 \text{ }\mu\text{g/L}$) to $50 \text{ }\mu\text{g/L}$ (allowable bromide level for drinking water sources regulated in California), the retention time (t) required for electrolysis is

$$\ln\left(\frac{C}{C_0}\right) = -k_s S t$$

$$\Rightarrow t = \frac{-\ln(C/C_0)}{k_s S} = \frac{-\ln(50/10^6)}{60 \text{ h}^{-1} \text{ m}^{-2} \times 3 \text{ m}^2} = 0.055 \text{ h} = 3.3 \text{ min for flowback water}$$

$$\text{Or } t = \frac{-\ln(C/C_0)}{k_s S} = \frac{-\ln(50/10^6)}{10 \text{ h}^{-1} \text{ m}^{-2} \times 3 \text{ m}^2} = 0.33 \text{ h} = 20 \text{ min for produced water}$$

where C and C_0 are influent and effluent bromide concentration, respectively; k_s is the surface area normalized reaction rate constant ($60 \text{ h}^{-1} \text{ m}^{-2}$ or $10 \text{ h}^{-1} \text{ m}^{-2}$); S is the total anode surface area.

An estimate of the required reactor volume can then be made based on the flow rates of brine generation. The flow rate of brine varies from as high as $10,000 \text{ barrels/day}$ (or $1600 \text{ m}^3/\text{day}$) at the initial stage of fracturing (flowback water) to as low as 2 barrel/day (or $0.3 \text{ m}^3/\text{day}$) after 50 days (produced water) (Acharya, 2011). Thus the total reactor volume needed is: $1600 \text{ m}^3/\text{day} \times 0.055 \text{ h} \times \text{day}/24 \text{ h} = 3.7 \text{ m}^3$ for the high flow rate flowback water and $0.3 \text{ m}^3/\text{day} \times 0.33 \text{ h} \times \text{day}/24 \text{ h} = 4.1 \times 10^{-3} \text{ m}^3$ for low flow rate produced water.

These calculations indicate that several electrolyzers, each with a size of 0.5 m^3 are needed to run in parallel to treat the flowback water at the highest rate (in the case of peak flow $10,000 \text{ barrels/day}$, 8 reactors are needed), while only one electrolyzer of 0.5 m^3 volume would be sufficient for handling the low flow rate produced water. That means the comparatively low bromide removal rate in produced water can be compensated using a longer retention time to achieve the required treatment goal since the flow rate of produced water is low.

The cell current during electrolysis of all the water samples decreased from $\sim 100 \text{ mA}$ to $\sim 2 \text{ mA}$ as the reaction proceeded, but generally the integrated average is about 20 mA , and thus the current density is about 3 A/m^2 . This is much lower than the current density used in chlor-alkali cells which are typically several kA/m^2 (O'Brien et al., 2005).

The energy consumption (calculated using Equation (5)) required for bromide removal in this study is $\sim 6 \text{ kJ/g Br}$, not including the energy needed for stripping of the produced bromine from solution. Not surprisingly, this is higher than the theoretical minimal energy consumption as calculated in supporting information and summarized in Table S-1, because the current efficiency is not 100% and an over-potential exists in practice. When the observed energy consumption is converted to chlorine equivalent, it is about 3760 kWh/ton Cl . This value is higher than the energy consumption in membrane chlor-alkali cells used in the industry ($2600\text{--}2800 \text{ kWh/ton Cl}$) (O'Brien et al., 2005) but is of similar magnitude. The higher energy consumption for bromide removal than in the chlor-alkali process is a result of: (1) the higher chloride concentration in the feed brine in the chlor-alkali process ($170\text{--}190 \text{ g/L}$) (O'Brien et al., 2005) compared to 1 g/L bromide in flowback and produced water, while reaction efficiency usually decreases with decreasing substrate con-

centration; and (2) the need to remove bromide to very low levels (several mg/L or even $\mu\text{g/L}$ level) in brine management, whereas this is not necessary in the chlor-alkali process (the recommended minimum chloride concentration in the depleted brine is 103 g/L) (O'Brien et al., 2005).

The cost of a proposed treatment process for brines must be considered in any assessment. While it is too early in the development process for a comprehensive cost estimate, it should be noted that the recovery of produced bromine may offset the cost of brine treatment. In 2010, the average value of exported bromine (including cost, insurance and freight) was $\$1760/\text{ton}$ (Ober, 2011). The energy cost for bromide oxidation is relatively low compared to this number. The average wholesale price for electricity in Western Pennsylvania in 2010 was $\$54/\text{MWh}$ (U.S. Energy Information Administration, 2012), which is about $\$1.5 \times 10^{-5}/\text{kJ}$. Thus the energy cost for electrolytic bromide removal is approximately $\$1.5 \times 10^{-5}/\text{kJ} \times 6 \text{ kJ/g} = \$9 \times 10^{-5}/\text{g}$ or approximately $\$90/\text{ton}$. While a very preliminary cost, this zero-order estimate suggests that electrolytic bromine recovery from these oil/gas brines is feasible.

4. Conclusions

This work demonstrates that it is both thermodynamically and kinetically feasible to use graphite electrodes to selectively remove bromide from complex flowback and produced water from hydraulic fracturing without generating chlorine or oxygen. The presence of high concentrations of chloride and other unknown components in the brine decreases the

bromide removal rate, but the reaction remains fast enough for treatment in electrolytic cells that are of a reasonable size. The energy consumption of this process is comparable with industrial chlorine production in the chlor-alkali process. Industrial chlor-alkali electrolyzers could meet the treatment requirements for bromide removal in the oil/gas brine in terms of both electrode surface area and reactor volume. These results suggest that an electrode-based system for removing bromide from flowback and produced water before discharge is a promising technology and that additional work to scale up the process and to develop a three electrode system for use at the industrial scale is warranted.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2013.04.041>.

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