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Produced water softening using high-pH catholyte from brine electrolysis: reducing chemical transportation and environmental footprints

Golnoosh Khajouei [a], Hoil Il Park [b], Harry O. Finklea [c], Paul F. Ziemkiewicz [d], Edward F. Peltier [e], Lian-Shin Lin [a,*]

[a] Wadsworth Department of Civil and Environmental Engineering, West Virginia University, Morgantown, WV, 26505, United States
[b] Valent BioSciences LLC, Osage, Iowa, 50461, United States
[c] C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV, 26505, United States
[d] West Virginia Water Research Institute, Morgantown, WV, 26505, United States
[e] Department of Civil, Environmental and Architectural Engineering, The University of Kansas, Lawrence, KS, 66045, United States

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ABSTRACT

This study evaluates the benefits of using brine electrolysis for generating caustic soda (NaOH) and free chlorine for on-site produced water (PWs[1]) treatment. A two-compartment electrochemical cell was shown to generate NaOH solutions (pH > 12, faradic efficiency 93%) and chlorine (faradic efficiency 32%) from a NaCl brine solution at a current density of 10 mA/cm^2. The catholyte was used for softening field-collected PWs. The degree of Mg removal depends mostly on the catholyte/PW mixture pH with pH 11 achieving >90% removal. Ca removal is poor (<10%) due to low bicarbonate alkalinity in the PWs. Soda ash alone at a dose equivalent to the total hardness of the PWs helps $CaCO_3$ precipitation and Ca removal (>90%). The combined treatment of the catholyte and a reduced quantity of soda ash achieves better or comparable Ca removal compared to the full stoichiometric amounts of soda ash alone. Ba and Sr removal patterns closely follow those of Ca, suggesting co-precipitation of these cations as the primary removal mechanism. Organic removal is negligible during chemical softening; however, activated carbon filtration achieves >90% of total organic carbon (TOC) removal in all PWs. A treatment scheme is proposed for field generation of caustic soda and chlorine from PW. The economic analysis demonstrates the significant cost-effectiveness of the approach compared to purchasing the NaOH.

1. Introduction

Oil and gas (O&G) production plays a significant role in modern civilization as an important source of energy [1]. However, a critical issue concerning these forms of energy production is the generation of liquid waste defined as “produced water” (PW) [2]. PW constitutes the industry’s most important waste stream based on the volume [3]. Currently, up to 890 billion gallons of produced water are generated each year from O&G production in the United States [4]. PW can contain a wide variety of chemicals including organic compounds, metals, radioactive materials, production solids (e.g., corrosion, scale, and formation solids), and dissolved gases [5,6]. PW is also highly saline, as a result of interactions between reservoir fluids and the formation materials [2,5]. Thus, the actual composition of these waters depends heavily on the geology of the field in production, and concentrations of individual constituents can vary over several orders of magnitude [5]. In the Eastern U.S. Marcellus gas field, the total dissolved solids (TDS) in PW increases rapidly after well completion, then stabilizes often at concentrations exceeding 150,000 mg/L [7].

Produced water can be managed in different ways including 1) avoiding the production of water to the surface by using a polymer gel, 2) injecting produced water into the formations (a practice which may need some treatment to reduce fouling and scaling agents as well as bacteria), 3) discharge of the PW after adequate treatment, 4) reuse oil and gas operations (drilling, stimulation, and workover operation), 5) beneficial reuse of PW such as irrigation, rangeland restoration, cattle, and animal consumption, and drinking water for private use or public water system [8,3]. Discharge or reuse of the PWs may require different degrees of treatment to remove specific constituents depending on their disposal and reuse options. A produced water treatment structure is

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* Corresponding author at: Wadsworth Department of Civil and Environmental Engineering, West Virginia University, Morgantown, WV, 26505, United States.
E-mail address: lianshin.lin@mail.wvu.edu (L.-S. Lin).

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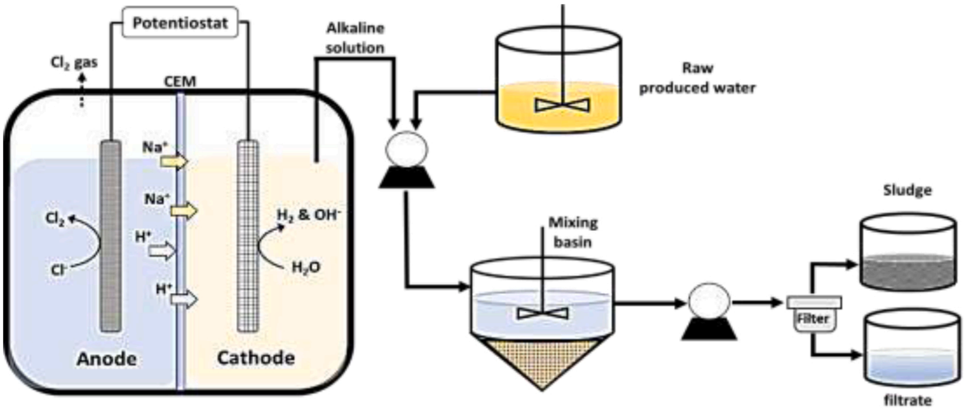

Fig. 1. Schematic diagram of produced water softening in a continuous mode.

often selected based on the overall treatment objectives. To achieve treatment objectives, in many cases a series of individual processes rather than a single process is required for contaminant removal [9].

Various physical, chemical, and biological methods have been used individually or in combination for the treatment of PW [5]. Membrane separation processes such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are among those treatment methods that have been evaluated frequently for removal of suspended solids (SS) and dissolved solids from PW [5,10,11] . However, due to the high concentration of divalent cations (e.g., Ba^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}) as well as organic and colloidal materials in PW, fouling poses a serious challenge for these membrane technologies [12]. Consequently, PW softening to reduce multi-valent ions has often been used as a pretreatment in combination with other treatment methods [9,13] .

Alkalization technology is an economical softening method that uses alkaline materials such as lime ($Ca(OH)_2$), soda ash (Na_2CO_3), and caustic soda (NaOH) to raise pH and promote chemical precipitation of divalent cations. However, the transportation of alkaline chemicals and the required space for handling and storage facilities are among the disadvantages of this method for PW treatment. Compared to the chemical addition for softening, the nanofiltration (NF) membrane is considered as an economical technology to separate divalent ions. However, for waters with high TDS such as PWs in the current study, a reasonable amount of brine at the maximum-allowed applied pressure cannot be obtained by the NF membrane. Besides, the fouling problem still exists with NF technology [14]. Therefore, onsite production of alkaline chemicals (e.g., NaOH) using brine electrolysis [15] represents an attractive approach for PW softening. For this treatment method, the brine solution can be obtained from PW after the removal of multi-valent ions and organic content using electricity generated from onsite natural gas or a diesel generator. In addition, this electrochemical approach provides an emerging method for PW treatment through the production of products such as active chlorine in the form of gaseous chlorine, hypochlorous acid, or hypochlorite ions at the anode [16]. Due to the significant production of PW in often remote areas, the application of conventional physical, chemical, or biological methods is restricted [17]. Electrochemical methods have the advantages of high efficiency, mild operating conditions, ease of automation, versatility, and low cost, especially when they are powered by renewable energy [18].

The ultimate objective of this study, as described later, is to use treated produced water as the feed for the brine electrolysis. To reduce the energy requirements, the electrolysis is performed at room temperature rather than at the high temperatures typical for the chlor-alkali process [19]. Issues concerning brine electrolysis for softening of PWs include kinetics of NaOH generation, electrical power consumption, and PW softening efficiency. This study focuses on developing a brine electrolytic system for generating caustic soda using an electrochemical cell for softening as a PW management tool. Mehmood et al. describe a three-chamber cell for generating NaOH and hydrochloric acid from brine [15]. A commercially available lab unit has been studied for the generation of sodium hypochlorite from water softener spent brine [20]. In this study, a two-chambered electrolytic cell typical of the Chlor-alkali process is used to generate NaOH and chlorine from NaCl solutions. The electrochemical characteristics are examined to identify the controlling factors of NaOH generation kinetics and power consumption. Optimal conditions for NaOH generation are identified by measuring pH and electrical power requirements. The high-pH catholyte is then used in the softening treatment of three field-collected PWs and the efficiency is quantified. The sludge materials from the softening treatment are characterized using spectroscopic analyses to help illustrate softening mechanisms. Given the often-remote locations of O&G production wells, such brine electrolysis for on-site generation of useful chemicals for produced water treatment can provide the advantages of a small environmental footprint and minimal chemical transportation.

2. Materials and methods

2.1. Electrochemical Cell

A two-compartment electrolytic cell (Fig. 1) was constructed using acrylic plates. The two compartments were separated by a cation exchange membrane (CEM, Nafion115, DuPont, 5.5 × 5.5 cm^2, effective area 30 cm^2, 0.013 cm thick). Each compartment contained a working volume of 170 mL and was equipped with ports for fluid input and output. A dimensionally stabilized RuO_2/IrO_2 coated titanium anode (geometric dimension of 5.5 × 5.5 cm^2, 0.1 cm thick, Edgetech Industries LLC.,) and a type 304 stainless steel mesh cathode (geometric dimension of 5.5 × 5.5 cm^2, 0.1 cm thick, McMaster-Carr) were used. RuO_2 based coating is very stable for chlorine evolution reaction. However, they are unstable for anodic oxygen evolution reaction and undergo heavy corrosion in acidic conditions. The addition of iridium oxide (IrO_2) which is stable for oxygen evolution while has a lower electro-catalyst to ruthenium oxide (RuO_2) has a synergistic effect and improves the stability of RuO_2 based oxide anodes in harsh corrosive conditions [21]. For the fabrication of the electrode, the precious metal mixture was painted on the titanium substrate and then sintered at high temperature. As cathode, 304 stainless steel is more corrosion resistant than galvanized steel. It is known as a very inexpensive electrode and has an active surface area three times larger than a flat sheet. Cathodes of this material with high specific surface area showed performance similar to carbon cathode containing a platinum catalyst [22]. The two electrodes were 1 cm apart. Brine solutions of various concentrations were prepared using analytical grade sodium chloride (Fisher Scientific, Chicago, Illinois, USA) and deionized water.

Generation of NaOH occurs in the cathode compartment according to reactions 1 and 2. The CEM permits the passage of hydrated sodium ions

Table 1
Produced water characteristics.

Parameters			Units	Result		
				PW 1	PW 2	PW 3
pH			–	6.2	8.0	7.2
Conductivity			mS/cm	102	52	166
Acidity			mg/L as $CaCO_3$	79	42	113
Alkalinity			mg/L as $CaCO_3$	107	280	226
Inorganic Ions		**Chloride**	mg/L	48,000	19,600	88,000
		Sulfate	mg/L	0.3	4	213
Chemical Oxygen Demand (COD)			mg/L	300	120	400
Suspended solids (TSS)			mg/L	350	135	180
Dissolved solids (TDS)			mg/L	87,700	40,800	153,600
Total Organic Carbon (TOC)			mg/L	10.0	3.0	7.0
Color			–	Brown	Clear yellow	Light Gray
Odor			–	Not significant	Not significant	Significant
Metals	**Calcium, Ca**		mg/L	7,700	650	7,880
	Magnesium, Mg		mg/L	640	303	2100
	Sodium, Na		mg/L	18,900	12,800	42,000
	Iron, Fe		mg/L	78	12	1.2
	Barium, Ba		mg/L	3,860	176	6.0
	Strontium, Sr		mg/L	1,883	83.5	2,113
	Manganese, Mn		mg/L	2.7	0.4	0.1
	Aluminum, Al		mg/L	<0.038	<0.038	<0.038

from the anode compartment to the cathode compartment where sodium hydroxide is produced [23,24].

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2)$$

An added advantage of this method as discussed in the introduction section is production of chlorine/hypochlorous acid in the anode compartment (reactions 3 and 4):

$$2\ Cl^- \rightarrow Cl_2 + 2e^- \quad (3)$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \quad (4)$$

A fraction of the current at the anode drives water oxidation:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (5)$$

The cell was first examined for its electrochemical characteristics including cell and membrane resistances, and mass transfer limitation under various current densities. Specifically, electrochemical impedance spectroscopy (EIS) was conducted using a potentiostat/galvanostat (Reference 3000, Gamry Instrument) to measure cell and membrane ohmic resistances. Galvano-dynamic current scans were conducted to identify mass transfer limiting processes. The coulombic efficiency of charge transfer for OH^- formation was quantified. The electrolysis was driven by a potentiostat/galvanostat under controlled current densities (10 - 30 mA/cm^2, equivalent to 300 – 900 mA), operation time (0 – 60 minutes), feed solution concentrations (0.2, 0.5, and 1 M NaCl), and different solution feeding modes (batch and circulation). The cell voltage and pH of the anolyte and catholyte were monitored during electrolysis to determine NaOH generation kinetics. Titration of the catholyte with standard HCl was used to determine the coulombic efficiency of OH- production [25]. Both chlorine gas and dissolved free chlorine (HOCl/OCl) generated from the anode were also collected and analyzed.

The high-pH catholyte solutions were subsequently used to remove multivalent cations from PW waters as a softening treatment. In addition, sodium carbonate (Fisher Scientific, Fair Lawn, New Jersey) was used to supplement carbonate in the softening treatment for comparisons.

2.2. Produced Water Samples and Characterization

Three PW water samples were collected from different production wells, including one at the Industrial Park in Morgantown, WV (PW1), and the other two in Kansas, Douglas County (PW2), and Reno County (PW3). These samples represent three distinctly different produced water characteristics and were analyzed as received to characterize their physical and chemical properties (Table 1).

Table 2
Continuous produced water softening using catholyte from brine electrolysis (0.5 M NaCl, 10 mA/cm^2).

Flow rate (ml/min)		Flow rate ratio (Catholyte: PW)	Catholyte hydraulic retention time (min)
Catholyte	PW		
1.5	1.5	1	113
3.0	1.5	2	57
7.5	1.5	5	23

2.3. Softening Treatment

Softening experiments using the high-pH catholyte were conducted in both batch and continuous flow modes. The batch experiments were carried out over a range of catholyte to PW volume ratios (0.1 – 5) using Jar tests. Briefly, mixtures of a range of volumetric ratios of catholyte: PW were subject to 5 minutes rapid mixing at 120 revolutions per minute (rpm) and then 40 minutes slow mixing at 40 rpm. The mixing was then stopped to allow the formed precipitates to settle for one hour, followed by filtration of samples using glass microfiber filters (Grade GF/F, Cat. No. 1825-047, Whatman, UK). Both the filtrate and precipitates were collected for analysis. In the continuous mode, the NaCl brine solution was continuously fed to the cathode for continuous NaOH generation under a current density of 10 mA/cm^2, and both the catholyte and PW were pumped continuously at a range of predetermined flow ratios (catholyte: PW 1 – 5) to a mixing basin (Fig. 1, Table 2). The mixed solution was permitted to form precipitates in the basin for one hour before it was vacuum-filtered to separate the solids from the solution. Both the precipitate and filtrate were collected for analysis. For experiments in continuous mode, the operation time was set to 60 minutes, where the first 15 minutes were crucial for NaOH to reach a pH of at least 12 and the last 45 minutes were for the NaOH and PW to form precipitates.

Softening experiments were also conducted with Na_2CO_3 in Jar tests with and without the catholyte to study any synergistic effects in

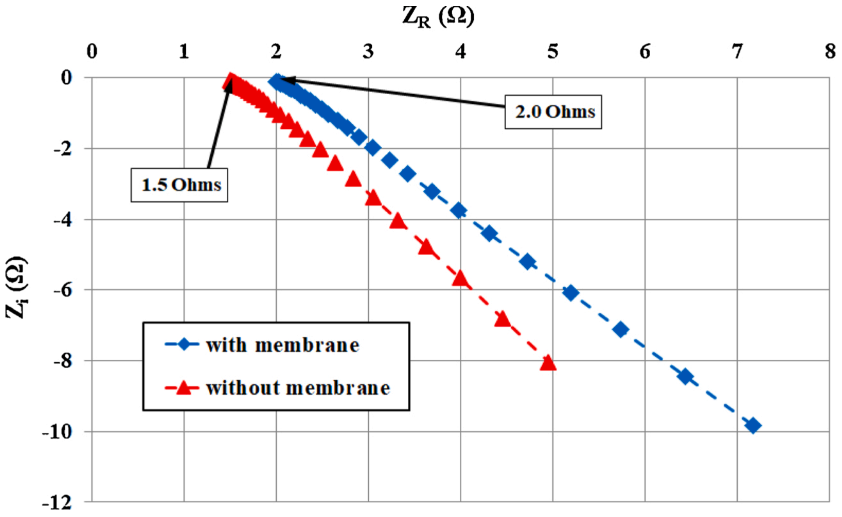

Fig. 2. Nyquist plot of the electrolytic cell with membrane and without membrane.

removing various divalent cations. Soda ash was added to the samples at a range of stoichiometric ratios based on each sample's hardness, calculated as the total of major multi-valent cations including calcium, magnesium, barium, and strontium (i.e., soda ash: total hardness molar ratio = 0.2, 0.5, and 1).

2.4. *Activated Carbon Filtration*

Activated carbon filter (ARIESFILTERWORKS, VP series, dimension: 43.18 cm × 8.9 cm) was used to remove organic carbon from the softened water. The effective volume of the filter was approximately 0.6 L and water was fed at a flow rate of 0.021 m^3/hr. The water circulated through the unit until the TOC concentration of PWs was reduced to <1 mg/L.

2.5. *Chemical and Microscopic Analyses*

All chemicals used in the analyses were analytical grade and chemical concentrations were measured following the Standard Methods [26]. Metal concentrations were measured using atomic absorption spectrometer (Perkin-Elmer, 3100). Given the high chloride content of the PWs and its potential interference with chemical oxygen demand (COD) measurement, an improved COD analysis was applied [27]. Briefly, mercuric sulfate ($HgSO_4$) was added to samples at the ratio of $HgSO_4$: Cl = 20:1 to mask the chloride effects through mercury chloride complex formation. Total organic carbon (TOC) was measured with a TOC analyzer (Shimadzu TOC-L). Analysis of both chlorine gas and dissolved free chlorine was conducted according to the standard iodometric method [26].

The morphology of the precipitated materials was characterized by scanning electron microscopy (SEM, Hitachi, S-4700) and the chemical composition was analyzed by energy dispersive spectroscopy (EDS, PV7746/58 ME, EDAX Inc., Mahwah, NJ, USA) with excitation energy set at 20 kV. The sludge samples were coated with gold under vacuum in a sputter coater (SPI-module^{TM} sputter, SPI Supply, West Chester, PA, USA) before the SEM/EDS analysis.

3. Results and Discussion

3.1. *Electrochemical characteristics*

Experiments with a range of current densities (10-30 mA/cm^2), operation time (0-60 min), NaCl concentrations (0.2 M, 0.5 M, and 1.0 M), and different flow rates showed no significant impact on the production rate of high pH catholyte. Consequently, 0.5 M NaCl, 10 mA/cm^2 current density for 15 minutes, and the Nafion 115 CEM were selected as the optimal operating conditions for further experiments. Under this condition, a catholyte with a volume of 170 mL at a pH > 12 is generated with a power consumption of 4.5 watts/L.

Estimates of OH- formation and expected pH change show that 100% current efficiency during operation at 300 mA (10 mA/cm^2) for 15-min requires a total charge of 270 coul, corresponding to 0.0028 moles of electrons and a theoretical hydroxide concentration of 0.016 M (pH 12.2). Under this operating condition, 0.015 M OH- is produced corresponding to 93% columbic efficiency. Similarly, 100% faradaic efficiency for the same operating conditions theoretically generates 0.0028 equivalents of chlorine (99 mg). Total free chlorine of 32 mg (both gas and dissolved) was measured yielding a faradaic efficiency of 32%. The rest of the current is assigned to water oxidation according to reaction 5. These efficiencies remain almost constant even at the higher current densities of 20 and 30 mA/cm^2. This finding is supported by galvanodynamic (GD) current scans. GD scans with the electrochemical cell filled with 0.5 M NaCl in both chambers were performed up to currents of 900 mA (30 mA/cm^2). The plots of voltage vs current are linear and do not show any evidence for mass transfer limiting behavior (Figure S1). Consequently, water dissociation at the membrane, a process that would lower the current efficiency for NaOH production, should not be occurring even at the highest currents.

With 0.5 M NaCl in both chambers, the cell EIS was measured at an open-circuit voltage of 0.8 V with the Nafion 115 membrane and 0.9 V without a membrane in a frequency range of 10 to 10,000 Hz and an AC voltage amplitude of 10 mV. From the high-frequency intercept on a Nyquist plot (Fig. 2), an ohmic resistance of 2.0 ohms (61 ohm cm^2) with the membrane and 1.5 ohms (45 ohm cm^2) without the membrane is obtained. The difference of 0.53 ohm (16 ohms cm^2) is attributed to the Nafion 115 membrane.

3.2. *PWs Softening*

3.2.1. *PWs softening by the generated catholyte*

After the PWs softening treatment using the catholyte in batch and continuous modes, manganese (Mn) and aluminum (Al) are not detectable in the filtrate for all mixing ratios. Mg removal exceeds 90% in PW1 and PW2 at higher catholyte: PW ratios when corresponding pHs are greater than 11 (Fig. 3). The lower removal efficiency of PW3 (less than 40%) is due to its higher acidity (113 mg/L) which results in pHs below 11. In contrast, Ca removal is poor - approximately 10% for PW2 and negligible for PW1 and PW3 (data not shown). This low removal

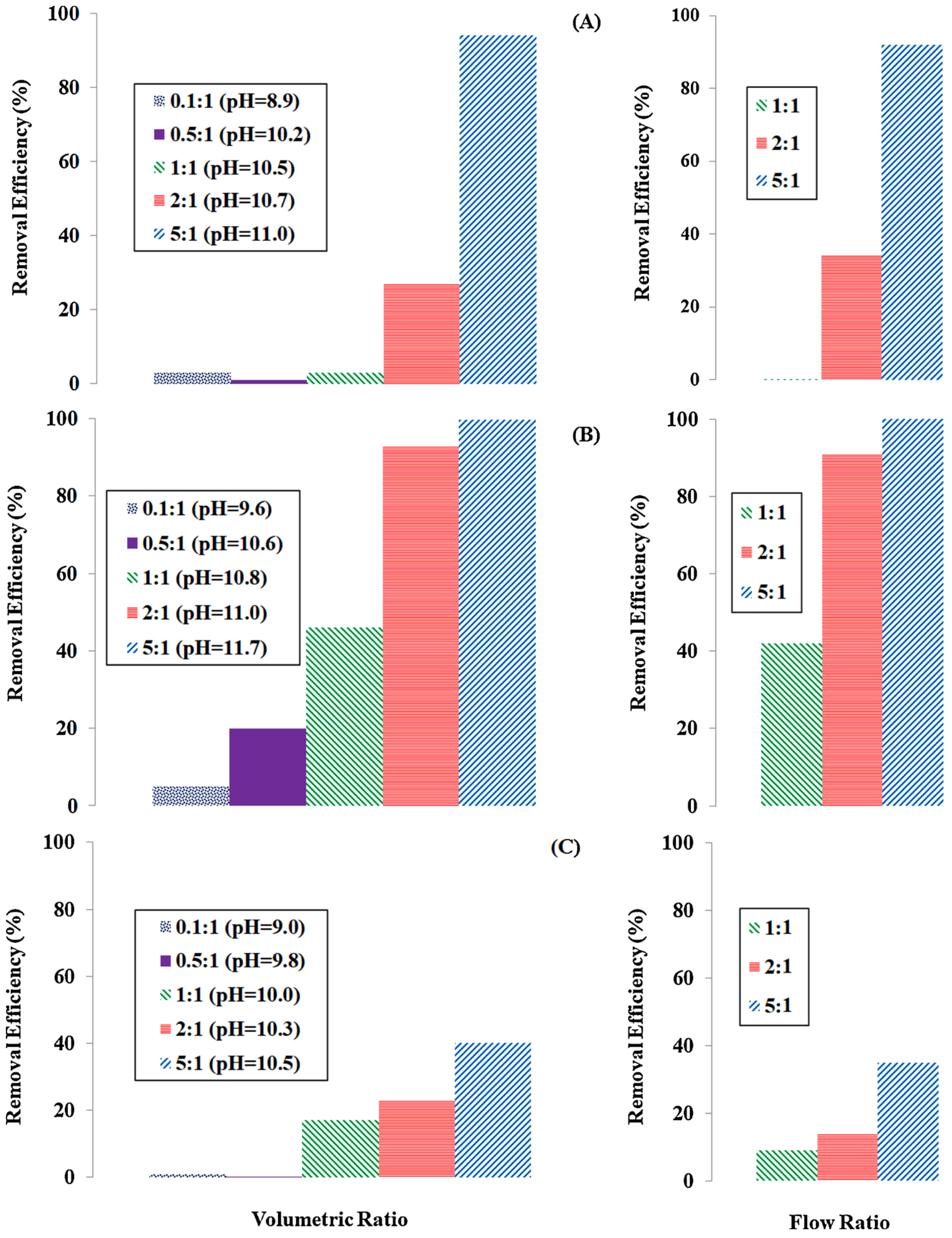

Fig. 3. Magnesium removal efficiency with (A) PW1, (B) PW2, and (C) PW3 using the catholyte in batch mode (left-hand graphs, catholyte to PW volume ratio = 0.1-5) and continuous mode (right-hand graphs, catholyte to PW flow ratio = 1, 2, and 5).

efficiency is attributed primarily to the high solubility of calcium hydroxide ($Ca(OH)_2$) (Table S1). Also, because of low bicarbonate alkalinity in the PW samples and despite pH higher than 10 of the catholyte/PW mixture in all experiments, insignificant calcium removal is achieved. PW2 exhibits relatively higher removal efficiency because of its higher alkalinity (280 mg/L as $CaCO_3$).

Barium (Ba) removal is essentially negligible in all samples. Less than 16% strontium (Sr) removal is obtained for PW3 and no strontium removal occurs with PW1 and PW2. Sr removal from PW3 is attributed to higher sulfate concentration (213 mg/L) in the sample resulting in precipitation of $SrSO_4$. However, the formation of $BaSO_4$ is retarded despite its lower solubility than $SrSO_4$, which is likely because of the very low initial Ba concentration of this sample (6 mg/L) compared to its high initial Ca and Sr concentrations. Also, ionic strength effects caused by high Ca concentration increases $BaSO_4$ solubility and decreases its supersaturation [28].

The insignificant removal of Ca, Ba, and Sr with catholyte alone is attributed to the absence of carbonate to precipitate these cations as carbonate salts or to improve sorption of Ba and Sr to $CaCO_3$ precipitates, and the higher solubility of $Sr(OH)_2$ and $Ba(OH)_2$ (Table S1) [29,30]. Overall, the catholyte treatment results in varying degrees of Mg removal depending on the PW acidity, and poor removal of Ca due to low alkalinity in the PWs. Removal of Ba and Sr is poor indicating that their removal is not associated with Mg $(OH)_2$ precipitation.

3.2.2. *PWs softening by sodium carbonate (soda ash)*

Although one of the main purposes of this study is to minimize chemical consumption, due to lack of enough carbonate concentration in PWs especially PW1 to precipitate carbonate salt, softening was conducted by adding different amounts of soda ash (Soda ash to total hardness molar ratio = 1.5, 1, 0.5, and 0.2 to 1). Ca, Ba and Sr removal have similar patterns indicating Ba and Sr removal are closely associated with $CaCO_3$ precipitation (Fig. 4). Ba and Sr removal are relatively lower in PW1 compared to PW2 and PW3. This observation is attributed to the

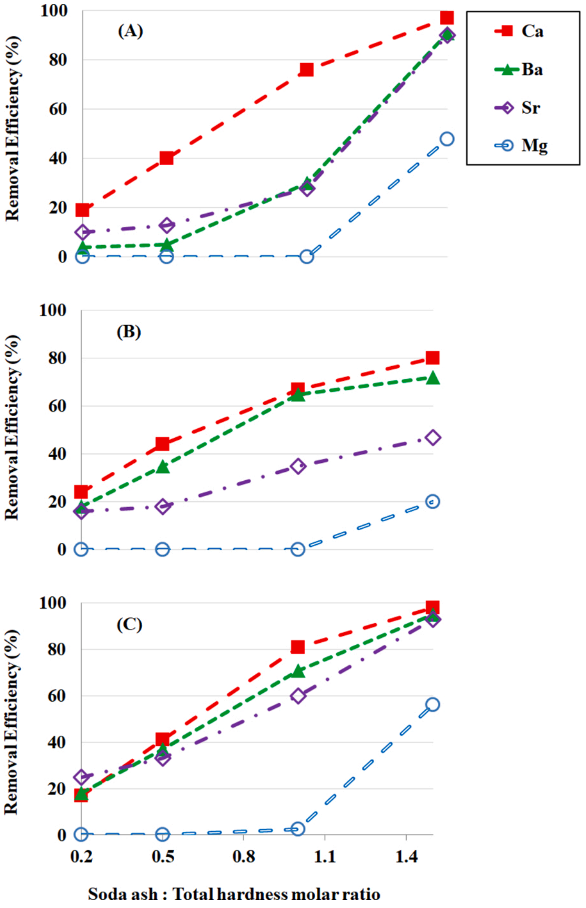

Fig. 4. Effect of soda ash on removal efficiency of calcium, barium, strontium, and magnesium from (A) PW1, (B) PW2, and (C) PW3 with different amount of soda ash (soda ash to hardness molar ratio of 0.2, 0.5, 1.0, and 1.5 to 1).

high concentration of Ba and Sr in PW1. In PW2, concentrations of Ba and Sr are lower than PW1, and in PW3 barium content is negligible (6 mg/L).

Around 80% of Ca is removed from PW1 and PW3 at the soda ash to hardness molar ratio of 1 to 1. Lower removal efficiency from PW2 is attributable to the lower total hardness which results in a lower quantity of soda ash added to PW2 (Table S2). Mg removal from the PWs is negligible with all added quantities of soda ash except the soda ash to total hardness molar ratio of 1.5 to 1. Given that the mixture pHs are all below 10 (Table S2), the Mg removal is attributed to mostly co-precipitation with and/or sorption to $CaCO_3$.

3.2.3. PWs softening by catholyte and soda ash

PW softening batch tests were also conducted by supplementing different quantities of soda ash (soda ash: total hardness = 1, 0.5, and 0.2) to the mixtures of catholyte and PWs (catholyte: PW volume ratio = 1 and 2). Compared to the samples mixed with soda ash alone, Ca removal is enhanced with the combined use of catholyte and soda ash (Fig. 5). Specifically, a soda ash-to-hardness molar ratio of 0.5 to 1 with the catholyte achieves comparable (square marked lines) or higher Ca removal than twice the amount of soda ash (i.e., soda ash to hardness molar ratio of 1 to 1) without the catholyte (solid bars). Mg removal follows a similar pattern as calcium. The degree of enhancement in Ca and Mg removal varies with the original acidity and alkalinity in the PWs. Presumably, the catholyte eliminates the PW acidity that otherwise would consume the added carbonate, thereby enhancing the yields of the Ca and Mg precipitates. As a result of increased $CaCO_3$ precipitates, Ba, and Sr removal is improved by enhanced sorption to the surface of formed precipitates [28,29]

This finding is supported by SEM-EDS analysis (Fig. 6). Specifically, only Mg and a relatively lower abundance of Ca are found in PW1 precipitate from the catholyte treatment alone, and Sr and Ba are absent (Fig. 6A). In contrast, precipitates from the treatment of soda ash alone show a dominant presence of Ca as well as a noticeable amount of Ba and Sr (Fig. 6B). The precipitate from the combined treatment of the catholyte and soda ash exhibits increased abundances of Sr and Ba compared to the precipitates by soda ash alone (Fig. 6C). The SEM micrographs show more particles attached to the surface of $CaCO_3$ from the combined

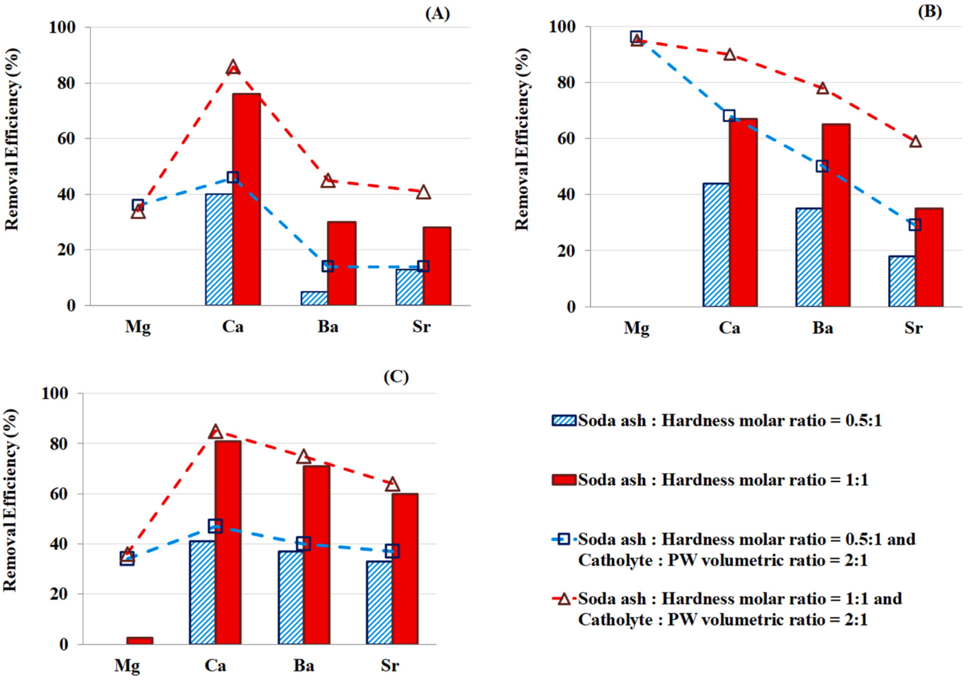

Fig. 5. Calcium, barium, strontium, and magnesium removal (%) from (A) PW1, (B) PW2, and (C) PW3 with catholyte and/or soda ash.

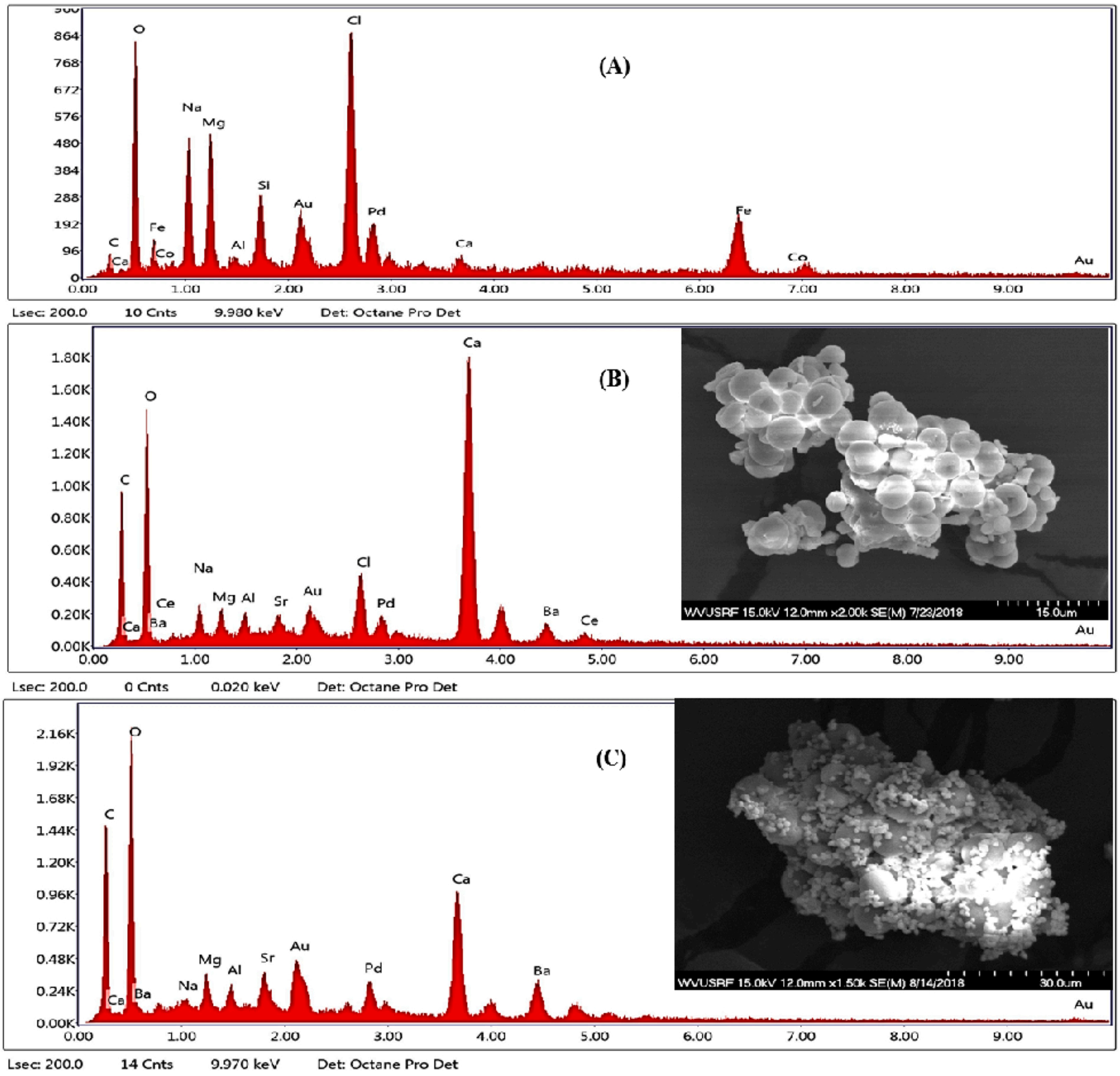

Fig. 6. EDS and SEM spectra of PW1 precipitates from softening treatment with (A) catholyte, (B) sodium carbonate, and (C) combination of catholyte and soda ash (Catholyte: PW volumetric ratio = 2:1, and soda ash: hardness molar ratio = 0.5:1).

treatment of the catholyte and soda ash (Fig. 6C) than those with soda ash alone (Fig. 6B).

4. Organic removal

The PWs have a low TOC content (< 10 mg/L). TOC removal from PW2 is ~40% using catholyte alone (catholyte: PW volume ratio of 2:1) while TOC removal from PW1 and PW3 is negligible. This is attributed to the higher level of $Mg(OH)_2$ formation from PW2 than PW1 and PW 3 (Fig. 3). The result is consistent with $Mg(OH)_2$ precipitation as a mechanism for removing of many organic contaminants from the water in chemical softening [31].

Another way for organic compounds to be removed during softening is through adsorption to the surface of growing $CaCO_3$ precipitates, which is referred to as co-precipitation [28]. Softening of PWs using soda ash (soda ash: hardness molar ratio of 0.5) results in 20%, 26%, and 17% TOC removal for PW1, PW2, and PW3, respectively. However, the combined treatment of catholyte and soda ash yields little or no TOC removal. This observation is contrary to a previous study reporting improved or comparable TOC removal by $CaCO_3$-$Mg(OH)_2$ [32].

By using activated carbon filtration, however, TOC concentration decreases to less than 1 mg/L after seven complete circulations of PW1 and PW3 and three complete circulations of PW2 through the system. The associated retention time is approximately 15 minutes for PW1 and PW3 and 5 minutes for PW2.

5. Cost analysis of NaOH production

The work-energy associated with NaOH production is the integral of the product of voltage and current throughout the galvanostatic experiments. With 0.5 M NaCl, current of 10 mA/cm^2 (0.3 A), the voltage is nearly constant at ~3.0 V. The specific energy calculated as kilowatt-hours (KW·h) per mol of the product (NaOH) is 0.086 KW·h/mol. Using an estimated price of \$0.15/ KW·h for distributed electricity, the cost of sodium hydroxide production is \$0.32/kg which is far below the bulk NaOH price of at least \$1.5/kg. Shipping and storage for purchased chemicals would significantly increase the energy footprint. This analysis shows the significant benefits of on-site generation of NaOH and its on-site use for softening.

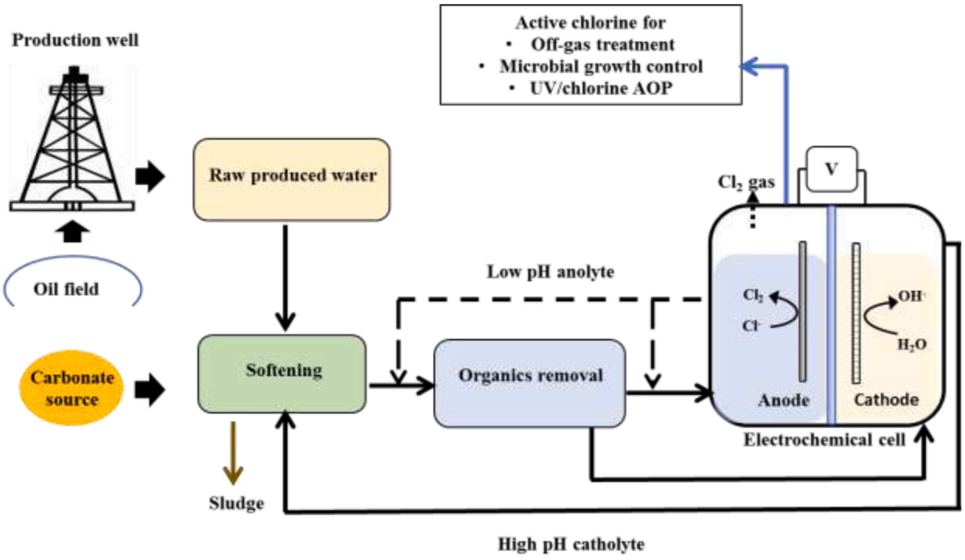

Fig. 7. Potential treatment scheme of using brine electrolysis for produced water management.

6. Proposed treatment scheme

A conceptual treatment scheme that incorporates the brine electrolysis is proposed (Fig. 7). The treatment method can take advantage of highly saline PW to generate two useful products on-site from the PW for treatment of the PW itself in order to reduce the environmental footprint of the treatment process. The raw PW is first treated by the high-pH catholyte with or without soda ash addition for softening. The effluent is then treated in a unit for organics removal (e.g., activated carbon) yielding a brine solution which contains no or little organics, carbonate, and scale-forming cations. The brine solution is then fed into the electrolytic cell to generate free chlorine in the anode and high-pH catholyte in the cathode for the softening of the PW. The acidic anolyte (Figure S3) can be used to eliminate any residual carbonate in the effluent from the softening or organics removal unit, and to adjust pH of the feed brine solution. The generated chlorine can be used as a biocide for controlling microbial activities in the PW impoundment or storage tank, as an oxidant for treating off-gas from PW storage (e.g., H_2S), or as a chemical for advanced oxidation applications (e.g., UV/Cl_2 [33]). The whole process is driven by electricity which can be generated either by a diesel generator or on-site natural gas. Given the insufficient alkalinity in PWs to remove Ca, soda ash is likely needed if a high degree of calcium removal is required. In remote areas, the proposed on-site treatment of produced water may be economical due to reduced transportation costs.

7. Conclusion and Future Work

The main conclusions of this study are summarized as follows.

1 Caustic soda is generated at high faradic efficiency from the brine electrolysis and successfully used in softening treatment of raw produced water with or without carbonate addition. In the case where carbonate is added, the use of the high-pH catholyte achieves better or comparable removal efficiencies of the cations using only half of the amount of carbonate compared to the treatment with carbonate alone.
2 This treatment method adopts green principles of utilizing wastes (high salt content of produced water) as a resource for generating useful products (i.e., NaOH and Cl2) and can potentially reduce the environmental footprint of the treatment process and chemical transportation significantly.
3 This electrolytic method can be used in combination with membrane and/or thermal desalination treatment to generate a low-salinity stream and concentrated stream (i.e., 10-lb Brine) as a saleable product. The treatment approach can also be used in other applications such as treatment and reuse of blowdown water to supplement makeup water for cooling tower operation at thermoelectric power facilities.

While this study was conducted with a simple brine solution in the electrochemical cell, the future work will include the use of produced water product as a feed solution to electrolysis cell after softening and organic removal steps. To lower equipment costs, higher current densities will be explored. The results then will be compared in terms of NaOH production efficiency and energy consumption and the feasibility of the method will be evaluated.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jwpe.2020.101911.

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