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Electrode effects on temporal changes in electrolyte pH and redox potential for water treatment

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Abstract

The performance of electrochemical remediation methods could be optimized by controlling the physicochemical conditions of the electrochemical redox system. The effects of anode type (reactive or inert), current density and electrolyte composition on the temporal changes in pH and redox potential of the electrolyte were evaluated in divided and mixed electrolytes. Two types of electrodes were used: iron as a reactive electrode and mixed metal oxide coated titanium (MMO) as an inert electrode. Electric currents of 15, 30, 45 and 60 mA (37.5 mA L⁻¹, 75 mA L⁻¹, 112.5 mA L⁻¹ and 150 mA L⁻¹) were applied. Solutions of NaCl, Na₂SO₄ and NaHCO₃ were selected to mimic different wastewater or groundwater composition. Iron anodes resulted in highly reducing electrolyte conditions compared to inert anodes. Electrolyte pH was dependent on electrode type, electrolyte composition and current density. The pH of mixed-electrolyte was stable when MMO electrodes were used. When iron electrodes were used, the pH of electrolyte with relatively low current density (37.5 mA L⁻¹) did not show significant changes but the pH increased sharply for relatively high current density (150 mA L⁻¹). Sulfate solution showed more basic and relatively more reducing electrolyte condition compared to bicarbonate and chloride solution. The study shows that a highly reducing environment could be achieved using iron anodes in divided or mixed electrolytes and the pH and redox potential could be optimized by using appropriate current and polarity reversal.

Keywords

Electrochemical; wastewater treatment; redox; iron electrolysis; physicochemical; electrocoagulation

INTRODUCTION

Electrochemical processes and electrochemically enhanced biological processes are effective methods for treatment of organic contaminants (e.g., chlorinated hydrocarbons, perchlorinated ethene, trichlorinated ethene) and heavy metals (e.g., As, Cu, Cr) in

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contaminated soil, water, sediment, and other environmental media. The contaminants can be transformed to less toxic byproducts by direct oxidation or reduction on the electrode surface or by indirect biological, chemical or physicochemical transformation in the electrolyte,^[1, 2] such as electrochemically-assisted biological reduction,^[3] chemical reduction,^[4] electrocoagulation,^[5] electroflotation^[6] and electroflocculation.^[7]

Electrochemical reduction of aqueous contaminants have been evaluated at the cathode using inert anodes, in different mass transfer conditions including batch, circulated and flow through electrolyte systems. The reduction efficiencies of aqueous contaminants are dependent on a variety of operating parameters, including electrode types and electrolyte conditions. For instance, cathode materials such as silver,^[8] iron,^[9] copper,^[9, 10] palladium,^[11] Pt- or Pd-coated ceramic,^[12] bare and polymer coated nickel^[13] and mixed metal oxide (MMO)-coated titanium mesh cathodes^[14] demonstrated different performances for reductive electrolytic dechlorination of chlorinated solvents in aqueous solution. The electrolyte pH and constituting components also impact the efficiency of electrochemical treatment of water contaminated with chlorinated hydrocarbons.^[15]

On the other hand, electrochemical oxidation is another way that can be applied to the treatment of aqueous contaminants, through either direct oxidation on the electrode surface or indirect oxidation with electrochemically-produced by-products. Many anode materials have been evaluated for direct electro-oxidation of different contaminants, including granular graphite,^[16] planar graphite,^[17] glassy carbon,^[18] lead dioxide, tin dioxide and iridium oxide,^[19] Ebonex,^[20] diamond film electrode^[21] and MMO mesh electrodes.^[22] Indirect electrochemical oxidation has been demonstrated by the electrochemically-generated hydrogen peroxide^[23] and electrically-generated ozone.^[24] These oxidative intermediates can accelerate the removal of the target contaminants by their liquid phase reactions.

Generally, research on electrochemical water treatment have shown that efficiency of electrochemical process is impacted not only by electrodes' surface reactivity and reactions, but also by the temporal changes on the physical and/or chemical properties of electrolyte. Electrolyte pH and redox potential are important chemical parameters that could alter the reduction or oxidation potential of target compounds; since protons are involved in many reactions, and electrolyte redox reflects the existence of oxidizing or reducing substances. Redox potential of electrolyte can greatly change the electrochemical efficiency of TCE dechlorination.^[25] Understanding temporal changes in electrolyte pH and redox potential is important for developing treatment methods that are based on electrolyte chemistry rather than surface reactions of electrolysis.

Iron (cast iron, mild steel, etc.) electrolysis is an important electrochemical treatment process, and has been extensively studied for the electrocoagulation treatment of different types of wastewater, such as dairy wastewater^[26] and the effluents containing phenol compounds,^[27] nitrogen and phosphorus,^[28] and mercury(II).^[29] Although many examples using iron electrolysis can be found in the literatures, the information regarding the chemical changes of the electrolyte as a function of electrode types, background electrolyte, current intensity and polarity configuration is rarely reported. In this study, cast iron (as a reactive anode) is compared with mixed metal oxide coated titanium electrode (inert anode) under different electrolysis conditions, and the effects of reactive and inert anode materials on pH and redox change of the electrolyte are evaluated. Furthermore, to understand temporal changes in the electrolyte, the current density is discussed with respect to electrolyte volume (mA L^{-1}), instead of using current density based on electrode surface.

MATERIALS AND METHODS

Chemicals and Reagents

The chemicals and reagents used include NaCl (100%, Fisher Scientific), Na₂SO₄ (99%, BDH), NaHCO₃ (99–100%, Fisher Scientific), o-Phenanthroline (0.25% w/v, LabChem Inc.), hydroxylamine hydrochloride (98.5%, Fisher Scientific), ammonium acetate (98.1%, Fisher Scientific), hydrochloric acid (37.3%, Fisher Scientific), and glacial acetic acid (99.9%, Fisher Scientific). All the solutions were prepared by deionized water and without pH adjustment.

Experimental Procedures

An experimental program was designed to evaluate the effect of electrode type, current density, background electrolyte composition and polarity reversal on temporal changes in the pH and redox potential in divided- and/or mixed-electrolytes. The divided- and mixed-electrolyte batch experiments were conducted in a glass electrochemical cell with two electrode compartments as shown in Figure 1. In each compartment, the liquid and headspace volume were 200 mL and 100 mL, respectively. Gas from electrolysis was collected in 150 mL syringe connected to each compartment to maintain a closed system. Cast gray iron (McMaster Carr, USA) and mixed metal oxide coated titanium (mesh type, 3N International, USA) were used as anodes. The working surface area for the each electrode was 7 cm² with a length of 7 cm. The center to center spacing between anode and cathode was 13 cm. The electrical current was applied by Agilent E3612A DC power supply. In the divided-electrolyte, the anolyte and catholyte were isolated by a Nafion[®] membrane (Nafion[®] 112, ElectroChem Inc, USA). The anolyte and catholyte compartments were continuously stirred at the same speed during testing. The surface of iron electrodes were polished with sand paper, etched in 1.3 M HCl, and then washed with distilled water prior to assembly.

Analytical Methods

The pH and the oxidation reduction potential (ORP) were measured by microelectrodes probes (Microelectrodes Inc., USA), an aliquot of 0.5 mL electrolyte was sampled from compartments for pH and ORP measurements. Total dissolved iron and precipitated iron concentration were determined using 1, 10 Phenanthroline method.^[30] For the measurement of total dissolved ferrous ions concentration, 1 mL sample taken from cell was filtered with 0.45 µm syringe filter and immediately diluted by 0.05 M H₂SO₄ solution, then placed in centrifuge tubes. Afterwards, 200 µL ammonium acetate buffer (14.30 g ammonium acetate and 40 mL glacial acetic acid in 150 mL distilled water) and 1 g L⁻¹ phenanthroline solution were added subsequently to the centrifuge tube. The absorbance of solution at 510 nm wavelength was measured using UV-VIS spectrophotometer (UVmini-1240, Shimadzu). For the measurement of the total dissolved iron concentration (ferrous and ferric), 25 µL hydroxylamine hydrochloride (15 g of hydroxylamine hydrochloride in 150 mL distilled water) was added to the filtered sample as a reductant and the sample was mixed for 5 minutes to allow all ferric ions to reduce to ferrous ions. Then, the same reagents (ammonium acetate buffer and phenanthroline) mentioned above were added prior to spectrophotometer measurement. For the determination of concentration of total iron precipitates, 1 mL samples were collected from electrochemical cell and were placed in 1.5 mL centrifuge tube and 100 µL concentrated HCl was added to the tube. The tube was stored for 1 day to allow all forms of iron precipitates to dissolve. The sample was then subjected to the same procedure explained above to measure the total iron concentrations (dissolved and solid form).

RESULTS AND DISCUSSION

Effect of Electrode Types

A summary of the results is presented in Table 1. Temporal chemical changes in divided- and mixed-electrolytes were evaluated in 0.02 M NaSO₄ background electrolyte. As shown in Figure 2a, the pH of mixed electrolyte with inert electrodes did not change significantly since the H⁺ produced at the anode neutralizes the OH⁻ produced at the cathode. The electrolyte pH with iron electrodes increased to 10.5 (Fig.2b) because there is no or limited formation of H⁺ ions at the iron anode to neutralize the OH⁻ released from the cathode. Instead, the dissolution of iron is the dominating reaction on the anode as shown in Equation 1.

Depending on electrolyte pH, the ferrous ions might subsequently form ferrous hydroxides (Fe(OH)_{2(s)}, pK_{so} = 15.1).^[31] The ORP data in Figure 2 shows critical differences. The ORP values of the mixed electrolyte with inert electrodes decreased from 217 mV to 160 mV in the first 2 hours then stabilized around 150 mV as shown in Figure 2a. In contrast, the ORP of the mixed electrolyte with iron electrodes steadily dropped to -444 mV in 5 hours (Fig. 2b), showing buildup of a reducing electrolyte condition.

When the anolyte and catholyte were divided by an ion exchange membrane, the pH in the anolyte was acidic (≈ 2) and that in the catholyte was alkaline (≈ 11.5) when MMO electrodes were used (Fig. 2a). The iron anode limits the change in the anolyte pH due to little or no H⁺ production. A slight decrease was observed in the first 2 hours in the anolyte (Fig.2b). This could be explained by the oxidation of the ferrous species by the dissolved oxygen in electrolyte. The formation of solid ferric hydroxides (pK_{so} of Fe(OH)_{3(s)} is 38.8)^[31] produces protons, leading to a slight pH drop, as given by:

The ORP of the anolyte with MMO anode was highly oxidizing (≈ 450 mV) due to oxygen production from water electrolysis by the inert anode (Fig. 2a). By contrast, the anolyte ORP was low and more chemically reducing (11 mV, Fig.2b) with an iron anode. The main reason is that ferrous ions, instead of oxygen gas, were produced at the anode. Based on Equation 2, the ferrous species showed reducibility to consume the oxidative components, such as dissolved oxygen, in the electrolyte. Furthermore, with increasing pH, the reducibility of ferrous species (such ferrous hydroxides) increased progressively.^[31] Changes in pH and ORP values in catholyte were consistent for both inert and iron electrodes because cathodic reactions are the same. The pH increased to 11.5 and the ORP decreased to -340 mV in one case and -250 mV in the other case (Fig. 2). The reducing potential (negative ORP) is due to the production of hydrogen gas and the basic environment.

The above observations show significant differences on the effect of using iron (reactive) versus MMO (inert) electrodes on the pH and redox change of the electrolytes. Water oxidation is the main reaction at the anode of inert electrodes, therefore oxygen gas (O₂) and hydrogen ion (H⁺) are produced at the anode of inert electrodes. Iron dissolution is the governing reaction at the anode of iron electrodes and ferrous ions (Fe²⁺) are produced as main product. The main cathodic reaction is water reduction that is same for iron and inert

electrodes. The oxidation rates of iron and the flux of ferrous ions per electrolyte volume are controlled by the electric current. The rate can be calculated following Faraday's law,

$$J_{\text{Fe(II)}}^e = \alpha \frac{I}{n_{\text{Fe(II)}} V_a F} = \alpha \frac{I}{2 V_a F} \quad (3)$$

$$\alpha = \frac{2 V_a F J_{\text{Fe(II)}}^e}{I} \quad (4)$$

$$\bar{\alpha}_{0 \rightarrow t} = \frac{2 V_a F J_{\text{Fe(II)}}^e}{I \Delta t} \quad (5)$$

where $J_{\text{Fe(II)}}^e$ is the rate of electrolytic oxidation (in mol/m³ s) of Fe(0) into Fe(II), $n_{\text{Fe(II)}}$ is the number of electron transferred, V_a is the volume of the anolyte (for divided-electrolyte) or total electrolyte volume (for mixed electrolyte), I is the electric current, α is instant iron dissolution efficiency and $\bar{\alpha}_{0 \rightarrow t}$ is the average iron dissolution efficiency from time zero to time t . In Equation 3 the current is divided by the electrolyte volume to evaluate the current per volume of electrolyte (A m⁻³). This is mainly because it is important to evaluate the impact of electrolysis on the dynamics of electrolyte chemistry.

Other electrolysis reactions may occur at the anode include the oxidation of ferrous (Eq. 6, $E^0 = 0.77$ V vs. SHE) and the water decomposition (Eq. 7, $E^0 = 1.23$ V vs. SHE),

Comparing the electrochemical standard potential shows that the electrolytic transform of iron to Fe(II) has a significantly lower standard potential (−0.44 V). Therefore, oxidation of Fe(0) to Fe(II) is the dominant electrolytic reaction at the anode. In the mixed-electrolyte condition (Exp. No 3 in Table 1), the high average iron dissolution efficiency (85.1%) supports this fact. As a result, the electrolyte pH and redox potential significantly changed due to the ferrous species.

Effect of Background Electrolyte Types on Iron Electrolysis

Electrolyte composition has significant effects on chemical and physicochemical change induced by iron electrolysis due to the complexation of ferrous and ferric ions with existing anions and the precipitation of produced solid species. Mixed- electrolyte experiments were conducted using 0.02 M NaCl, Na₂SO₄ and NaHCO₃ solution and change in electrolyte pH and ORP values were recorded. In addition, iron speciation and the average iron dissolution efficiency ($\bar{\alpha}$) within 5 hours in different background electrolytes were compared. In Figure 3a, the pH of mixed bicarbonate solution was stable around 8 in the first 4 hours due to its buffer capacity. Afterwards, the buffer capacity was exceeded by the OH[−] released from the cathode and pH increased to 8.9. The pH values of the mixed sulfate and chloride electrolytes increased steadily as a result of electrolysis. At the end of the experiment, the pH of Na₂SO₄ (≈10.5) electrolyte was slightly higher than that of the chloride solution (≈10.0).

Initially, the ORP value of the bicarbonate solution was lower (87 mV) than sulfate and chloride solutions (Fig. 3a) because initial alkaline pH caused the bicarbonate solution to be relatively more reducing. The final ORP values are associated with the final pH of these three solutions. High buffer capacity of bicarbonate solution caused the lowest final pH value, thus the highest final ORP value. The sulfate electrolyte showed the highest final pH value, thus the lowest ORP value (−444 mV).

Although chloride, sulfate and carbonate anions can form ferrous ions complexes, based on the equilibrium data, the primary metal ligands in the solution were ferrous hydroxides. Some ferrous ions can be further oxidized to ferric ions in the presence of dissolved oxygen. Ferric ions produce some ferric complexes with existing ligands as well. Ferric hydroxides precipitations (yellow to brownish color) were observed at the early stage of the experiment and ferrous hydroxides precipitations (dark green color) were observed at the end of the experiment. Dissolved iron, ferrous and ferric precipitates are summarized in Table 2 for varying electrolyte composition. Dissolved iron was not observed in the bicarbonate solution because of the high initial pH (≈8). Dissolved iron was detected in sulfate solution (7.3%) and in chloride solution (4.4 %) in the first hour, however, at the later stages of experiments, all dissolved iron precipitated due to pH increase. At the end of 5-hours electrolysis, the ratio of ferrous precipitates to ferric precipitates was higher in chloride and sulfate solutions compared to bicarbonate solution that leads more reducing condition. Total iron concentrations were 8.9 mM for sulfate solution, 6.9 mM for chloride solution and 9.6 mM for bicarbonate solution. The average iron dissolution efficiencies were 85%, 66% and 92% in sulfate, chloride and bicarbonate solutions, respectively. Chloride solution showed lower efficiency compared to sulfate and bicarbonate solution. We speculate the evolution of chlorine on iron anode may be the reason of lower iron dissolution efficiency. Kobya reported that the following reaction may occur during an iron electrocoagulation process if the potential of anode is higher to a certain value.^[32]

As a competitive process on anode, chlorine evolution may decrease the iron dissolution efficiency to even lower value since it is easier to occur than oxygen evolution in chloride solution.^[33] Based on experimental results, the pH increase in chloride solution is lower than that in sulfate solution. It is inferred that the reaction of chlorine gas in solution (Eq. 9 and Eq.10) may be the reason.

Effect of Different Current Densities on Iron Electrolysis

The current density is another important parameter which may pose significant effects on electrolyte chemistry. The amount of electrolysis products is directly related with the level of current density. The first observation is that the electrolyte pH slightly decreased from 5.6 to 4.9 for the lowest current density (37.5 mA L^{−1}) in the first 2 hours in Figure 3b because ferrous ions oxidation with existing oxygen leads H⁺ production. The pH value then increased slightly to 5.8 and stabilized. Therefore, if high alkaline condition is not desired in the electrolyte, applying low current density can be the first choice. When current density is increased, OH[−] production at the cathode and accordingly the electrolyte pH increase. Based

on Figure 3b, the maximum observed pH was 10.7 for 150 mA L^{-1} . The ORP values for different current densities also showed similar trends with pH. The most reducing solution was observed under 150 mA L^{-1} . According to the pe-pH diagram^[31] of iron species, the basic pH enables more $\text{Fe}(\text{OH})_2(\text{s})$ precipitation and a more reducing condition (lower ORP).

Based on Figure 4, dissolved iron species are available in the electrolyte after 1 hour for all current densities. As the electrolysis progresses, the dissolved iron gradually disappears and only 37.5 mA L^{-1} shows dissolved iron after 5 hours electrolysis. The data is in agreement with the pH data in Figure 3b. According to the pH data, the pH values after 2 hours under 37.5 mA L^{-1} and 75 mA L^{-1} were less than 7, which allows the presence of the dissolved ferrous ions.

Polarity Reversal with Iron Electrolysis

Polarity reversal is a convenient and useful method to clean the scale and fouling on electrode, and prevent the passivation of iron electrode. The effect of polarity reversal of iron electrolysis on redox and pH conditions in divided anolyte and catholyte is also evaluated. After application of the current for 5 hours, the polarity was reversed for the next 5 hours. In the first 5 hours, the pH in the anolyte dropped from 5.4 to 4.2 in 2 hours and then increased up to 5.8 (Fig. 5a) due to the formation of ferrous and ferric hydroxides; and the pH in the catholyte increased up to 12 (Fig. 5b) due to water electrolysis. After polarity reversal, the pH in the new catholyte in Figure 5a was stable for about one hour because the OH^- being produced is reacting with existing ferrous and ferric ions. The pH then sharply increased up to 12 since all ferrous ions immediately precipitated mostly in the form $\text{Fe}(\text{OH})_2(\text{s})$. As shown in Figure 5b, the pH change in the new anolyte was not significant for 2 hours, but the pH dropped after that because of precipitation of ferrous hydroxides. The final pH in the anolyte was around 6.5 (Fig. 5b).

The ORP value in the anolyte (Fig. 5a) decreased to -150 mV in the first 5 hours due to ferrous production at the anode, and the ORP in the catholyte (Fig. 5b) dropped to below -300 mV in the first 5 hours due to $\text{H}_2(\text{g})$ generation in basic environment. When the polarity was reversed, the ORP in the new catholyte (Fig. 5a) continued to decrease to -600 mV while the pH increased. The ORP in the anolyte (Fig. 5b) was stabilized at around -400 mV . At the end of the experiment, neutral pH and highly reducing environment (Fig. 5b) was achieved in the anolyte.

CONCLUSION

The results shown in this study demonstrate that pH and redox of electrolytes are affected by a variety of electrolysis conditions. The efficiency of electrochemical method can be optimized by controlling the pH and redox of electrolytes. When iron electrode is used as anode for electrochemical remediation processes, a reducing electrolyte environment can be created in a divided- or mixed electrolyte. This environment is crucial for the reductive transformation of some contaminants. Inert anode creates more oxidizing environment which limits reductive transformation but enhances oxidative transformation of contaminants. While inert anodes do not cause a significant change in the pH of mixed-electrolyte, iron anodes increase pH of mixed-electrolyte during electrochemical processes. Electrolyte composition significantly affects the pH, ORP, iron speciation and electrolysis efficiency of iron electrolysis. Sulfate solution showed the highest pH value and the most reducing ORP value compared to bicarbonate and chloride solutions. Polarity reversal can be engineered to control and/or maintain neutral pH and reducing environment with two-iron electrodes in divided-electrolyte cell.

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Figure 1. Divided glass electrochemical cell: 1) cathode side; 2) anode side; 3) electrolyte; 4) gas release port to the syringe; 5) magnetic stirrer; 6) membrane connection; 7) sampling port.

Figure 2. pH and ORP profiles in divided-electrolyte and mixed-electrolyte, 0.02 M Na₂SO₄ background electrolyte, 112.5 mA L⁻¹ current density (a) MMO electrodes (b) Iron electrodes.

Figure 3. pH and ORP profiles (a) in different electrolyte compositions using iron electrodes, 112.5 mA L^{-1} current density, mixed-electrolyte; (b) with different current densities (mA L^{-1}), using iron electrodes, in 0.02 M Na_2SO_4 mixed-electrolyte.

Figure 4. Iron speciation at different current densities (37.5, 75, 112.5, 150 mA L⁻¹). The asterisk (*) means under detection limit.

Figure 5. pH and ORP profiles under polarity reversal using iron electrodes, 112.5 mA L^{-1} current density and $0.02 \text{ M Na}_2\text{SO}_4$ background electrolyte (a) first 5 hours served as anolyte then polarity reversed and then served as catholyte from 5 hours to 10 hours (b) first 5 hours served as catholyte then polarity reversed served as anolyte from 5 hours to 10 hours.

Table 1

Summary of experimental results with different electrode materials, background electrolytes and current densities.

Exp. No	Anode	Cathode	Electrolyte	Current (mA L ⁻¹)	pH (ini-fin) ^a	ORP (mV vs Ag/AgCl) (ini-fin) ^a	ζ (mS cm ⁻¹) (ini-fin) ^a	$\bar{\alpha}$ (%)
1	MMO	MMO	Na ₂ (SO ₄)-mixed	112.5	5.4-5.7	217-156	4.01-4.07	NA
2	MMO	MMO	Na ₂ (SO ₄)-divided	112.5	5.4-2.5/5.4-11.4	271-449/275(-251)	3.93-6.02/3.93-7.23	NA
3	Cast Iron	Cast Iron	Na ₂ (SO ₄)-mixed	112.5	5.5-10.5	217(-444)	4.02/4.05	85.1
4	Cast Iron	Cast Iron	Na ₂ (SO ₄)-divided	112.5	5.6-5.7/5.6-11.4	240-11/249(-340)	4.03-3.21/4.03-7.96	-
5	Cast Iron	Cast Iron	Na ₂ (SO ₄)-mixed	112.5	5.5-10.5	217(-444)	4.02-4.05	85.1
6	Cast Iron	Cast Iron	NaCl-mixed	112.5	5.7-10.0	226(-385)	2.42-2.46	66.0
7	Cast Iron	Cast Iron	Na(HCO ₃)-mixed	112.5	7.7-8.9	87(-299)	1.73-1.80	91.9
8	Cast Iron	Cast Iron	Na ₂ (SO ₄)-mixed	37.5	5.6-5.8	188-52	4.05-4.11	87.1
9	Cast Iron	Cast Iron	Na ₂ (SO ₄)-mixed	75	5.4-9.7	218(-376)	4.05-3.99	70.8
10	Cast Iron	Cast Iron	Na ₂ (SO ₄)-mixed	112.5	5.5-10.5	217(-444)	4.02-4.05	85.1
11	Cast Iron	Cast Iron	Na ₂ (SO ₄)-mixed	150	5.6-10.7	228(-494)	3.97-4.20	93.4
12 ^b	Cast Iron	Cast Iron	Na ₂ (SO ₄)-divided	112.5	5.4-12/5.4-6.6	240(-572)/240(-389)	-	-

^aThe first value is in the anolyte and second value is in the catholyte.

^bThe polarity of direct current was reversed so the initial values were in the anolyte and catholyte at the beginning of the experiment, final values were in the catholyte and anolyte at the end of the experiment

Table 2

Iron Speciation in sulfate, chloride and bicarbonate solutions at different times, 112.5 mA L⁻¹ current density, mixedelectrolyte (total volume 400 ml), and two iron electrodes

Time, h	0.02 M Na ₂ SO ₄				0.02 M NaCl				0.02 M NaHCO ₃			
	Dissolved Iron, %	Fe ²⁺ precipitates, %	Fe ³⁺ precipitates, %	Dissolved Iron, %	Fe ²⁺ precipitates, %	Fe ³⁺ precipitates, %	Dissolved Iron, %	Fe ²⁺ precipitates, %	Dissolved Iron, %	Fe ²⁺ precipitates, %	Fe ³⁺ precipitates, %	Fe ³⁺ precipitates, %
1	7.3	13.2	79.5	4.4	8.4	87.2	0	10.9	0	89.1	89.1	89.1
2	0	33.5	66.5	1.1	23.5	75.3	0	6.8	0	93.2	93.2	93.2
3	0	45.0	55.0	0.5	36.4	63.1	0	20.4	0	79.6	79.6	79.6
4	0	52.4	47.6	0.5	45.9	53.7	0	32.1	0	67.9	67.9	67.9
5	0	59.7	40.3	0.3	55.6	44.0	0	40.5	0	59.5	59.5	59.5