MAKING PRODUCED WATER WORK: IMPROVED ELECTROCOAGULATION DESIGN FOR PRACTICAL SUCCESS IN THE OIL FIELD

Jiasheng Cao and Daryl McCracken
Baker Hughes Incorporated

ABSTRACT

It has become increasingly attractive and necessary to reuse treated produced water for frac fluids, especially in remote locations or limited water source regions to minimize freshwater usage. Electrocoagulation (EC), a traditional water remediation technology, was recently introduced to oilfield application. However, the complicated components in produced water are challenging for traditional EC systems.

A new EC apparatus has exhibited cost-efficient remediation of produced water, especially in the removal of iron and suspended solids that have reduced barriers for making frac fluids. This unique EC system has demonstrated fast reduction in iron from over 900 ppm to less than 5 ppm from high-concentration oil contained water, and efficient removal of hydrogen sulfide (H_2S), heavy metals, bacteria, and other contaminants. The system has been successfully used for treating produced water for numerous operators in the Utica and Permian Basin, reducing operating costs more than 20% while reducing freshwater demand and trucking over 90%.

INTRODUCTION

Electrocoagulation has been investigated and applied for water remediation for decades (1-6). In general, EC systems consist of one or more pairs of cathode and anode electrodes, which are both electric conductive material. Primarily, aluminum (Al) or iron (Fe) electrodes are used, which reacts with water with electrical current and forms coagulants of $Al(OH)_3$ or $Fe(OH)_3$ (1-6). Compared with chemical coagulation or chemical precipitation processes, EC provides higher efficiency in removal of many metal ions, total suspended solids, bacteria, biochemical oxidation demand (BOD), and chemical oxidation demand (COD) (7-8). EC requires fewer chemicals and generates less waste sludge than chemical methods. To improve the total treatment performance, EC systems are usually combined with other treatment processes, such as flotation, filtration, and adsorption, to treat different waters. (9-11).

The challenge for EC systems using Al or Fe electrodes is that quick consumption of Al or Fe electrodes reduces the EC treatment efficiency, and the replacement of the electrodes results in nonproductive time (NPT). An alternative is to use non-sacrificial electrodes, such as graphite, doped diamond, Ti/SO2, and Ti/PbO2, which can be used for long periods of time (12).

Recently, an EC system was developed for oilfield application to efficiently remove metal ions, suspended solids, oil, colloids, and bacteria from produced water (13-14). Iron is problematic for produced water reuse since it can inhibit hydraulic fracturing fluid formulation (15-16). Scale problems may also occur when iron is introduced into the well (17). EC has been shown to be highly efficient for iron removal by oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) and forming low soluble ferric hydroxide precipitate. Suspended solids may cause problems for drilling by plugging the proppant's pore space (18) and damaging fluid formation with filter cake (19). Total suspended solids (TSS) removal from produced water with EC has been shown to increase permeability of proppant up to 40% (18). However, the complicated and inconsistent components in produced water are challenging for traditional EC systems.

In this paper, a new EC system with a unique design is introduced that employs non-sacrificial electrodes and sacrificial filling material (Al or Fe) between cathode and anode. The selection of the sacrificial filling material is based on the water chemistry and treatment goal. The system has demonstrated fast and complete removal of iron from over 940 mg/L to less than 1 mg/L, over 99% removal of sulfide ions, and over 98% removal of silica.

EQUIPMENT STRUCTURE

This EC system uses multiple pairs of non-sacrificial cathode and anode electrodes, and sacrificial filling material between the cathode and anode. During EC treatment, the electrodes do not dissolve, which helps maintain a consistent electric current input into the water, ensuring steady treatment performance. This also reduces the replacement interval for the electrodes, lowering cost and NPT. This is one key advantage of the patent-pending design that cannot be achieved in traditional EC with sacrificial anodes.

Another advantage of this new EC system is the generation of bubbles and coagulants. Electrocoagulation treatment involves the process of electroflotation, electroflocculation, electrooxidation, and electroreduction. Electroflotation is formed by EC-generated bubbles, which raise some coagulants and precipitates to the top of water surface. Bubbles could be generated from cathode, anode, and filling material between cathode and anode; the coagulants are generated from the filling material and then have good distribution in the treated water samples. In traditional EC, bubbles are generated primarily from cathode, and coagulant is generated from dissolution of anode.

Aluminum has been used as the filling material in this system. The aluminum provides the seed ions by slowly dissolving into the water with the direct electric current and forms coagulants of $Al(OH)_2$ and $Al(OH)_3$. The selected Al material can be in a variety of forms that is selected to optimize the EC process. The type and volume of the Al material selection also depends on the water chemistry and treatment goal. Al material with high edge surface area and small thickness works best for water samples with low conductivity (or total dissolved solids), and large volume Al media generate a large amount of coagulant and provide high removal efficiency of oil, suspended solids, and some specific ions.

Iron is another low-cost and environmentally preferred material that has been used for environmental remediation water treatment. In this EC system, iron, such as stainless steel, can generate Fe^{2+} and Fe^{3+} ions and $Fe(OH)_3$ coagulants. Fe^{2+} ion reacts with sulfide ion (S^{2-}) and forms FeS precipitate, thus iron can be used in EC for removal of sulfide and other particular contaminants.

Mixtures of Al and Fe may also be useful for optimal treatment of water requiring both $Al(OH)_3$ and $Fe(OH)_3$ coagulants.

IRON REMOVAL

Iron is the primary contaminant to be reduced for reuse of treated produced water since iron ions (Fe^{2+} and Fe^{3+}) may cause scale issues for drilling and inhibit proper frac fluid formulation. In produced water, iron has varying concentrations from below 10 mg/L to over 900 mg/L, and has different oxidation states (Fe^{2+} and Fe^{3+}).

Ferric hydroxide ($Fe(OH)_3$) has low solubility (Ksp: 2.8×10^{-39}) in water and could precipitate at water pH > 3.5, while ferrous iron hydroxide ($Fe(OH)_2$) has relatively high solubility(Ksp: 4.9×10^{-17}), thus forming $Fe(OH)_3$ is the most efficient way for iron removal. When Fe^{2+} is the primary iron ion in the target water, oxidation of Fe^{2+} to Fe^{3+} is necessary for the removal of iron by forming $Fe(OH)_3$. In chemical treatment methods, oxidants, such as hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), or chlorine dioxide (ClO_2), are used to oxidize Fe^{2+} to Fe^{3+}. When treating high concentration of Fe^{2+} water, adding large amounts of chemicals into the water is required, which is not cost-efficient, or further treatment is needed to remove the generated second pollutant from the added chemicals.

In this case, the unique EC system was tested for treatment of produced waters containing an extremely high concentration of iron and over 60% (v/v) oil and grease. The total iron concentration in raw water was 946 mg/L, and over 97% (920 mg/L) of the iron was Fe^{2+}. The water sample had over 330,000 mg/L total dissolved salt and high concentrations of calcium (Ca), magnesium (Mg), manganese (Mn), strontium (Sr), zinc (Zn), and other contaminants.

In the testing, Al was selected as filling material for the EC lab unit. The oil in raw water was separated by taking out the free oil on the water sample surface. Next, two gallons of oil separated water were pumped into the EC unit and treated for 2.5 minutes residence time. Then, the EC-treated water was drained out from the unit. The post-EC water pH dropped to 4 and was adjusted to 6.5 with 25% NaOH. The sample was then filtered through 25 um filter paper and analyzed with inductively coupled plasma (ICP) for iron and other ion concentration.

The ICP analysis of the treated water sample in **Table 1** shows that EC treatment lowered the total iron concentration from 946 mg/L to 0.6 mg/L, representing over 99.9% iron removal. Removal of other ions was also observed from the EC treatment, such as 95% Zn removal; over 98% Si reduction; 51% Mn removal; and over 20% removal of boron (B), Mg, and SO_4. It is necessary to point out that using Al material in EC did not increase, but rather reduced the Al ion concentration in treated water.

If chemical oxidation methods for iron removal were employed on the same water samples, the calculated amount of oxidant (H_2O_2, $KMnO_4$, and ClO_2) for completed oxidation of 920 mg/L Fe^{2+} to Fe^{3+} are listed in **Table 2**. Recently, oxidants have been used for water treatment to remove iron and bacteria. From the number in Table 2, at least 221.8 mg/L ClO_2 is required to oxidize 920 mg/L Fe^{2+} to Fe^{3+} to obtain complete iron removal. However, the actual usage of ClO_2 or other oxidants is much higher than the data in Table 2 due to the oxidation of other contaminants like bacteria, oil, and grease. With $KMnO_4$, over 180 mg/L of Mn^{2+} ions were generated and need to be removed. Compared with the chemical methods, EC does not require any of these chemicals or special equipment; therefore, no further treatment was necessary.

Another advantage of EC for iron removal from the produced water sample is the complete iron removal with a consistent treatment parameter without any adjustment or change. Over a 24-hour period, the iron concentration in raw water changes in a range from over 100 mg/L to 940 mg/L. The normal EC treatment parameter, as discussed above, has been efficient for complete iron concentration reduction from 940 to less than 1 mg/L, which indicated it could provide complete iron removal when the iron concentration was below 940 mg/L. For iron removal from the same water using a chemical method, an accurate analysis of iron concentration on time is needed to adjust chemical usage so that the chemical is not overdosed or inadequate, which can be challenging and incurs additional cost for analysis.

SULFIDE (S^{2-}) REMOVAL

Hydrogen sulfide (H_2S) has high toxicity and may pose a scaling problem in oil and gas drilling. Chemical methods for H_2S or sulfide ion (S^{2-}) removal include oxidation with ClO_2 or H_2O_2, or an Fe^{2+} containing compound to form ferrous sulfide precipitate.

Iron filling material in the reported EC system can dissolve into water with direct electrical current and generate Fe^{2+} and Fe^{3+} ions. S^{2-} ions react with generated Fe^{2+} and Fe^{3+} and produce FeS and Fe_2S_3 precipitates.

Lab scale testing was conducted with the EC system and industry waste stainless steel for sulfide removal from synthetic produced water. The water samples were prepared by adding sodium sulfide (Na_2S), sodium chloride (NaCl), and crude oil. The water solution pH was adjusted with 15% hydrochloric acid (HCl).

The first water sample had 156 mg/L S^{2-} ion and 50,000 mg/L TDS as NaCl, and S^{2-} ions were completely removed after 2.5 minutes of treatment time. Analysis of the generated precipitates indicated that FeS was the primary compound formed for S^{2-} removal. The S^{2-} removal with EC is fast and complete.

S^{2-} ion initial concentration in the second water sample was 650 mg/L. At preset treatment times, the S^{2-} ion concentration and water solution pH are illustrated in **Figure 1**. Over 50% S^{2-} concentration reduction was achieved at 2.5 minutes, and after 7 minutes, the S^{2-} concentration was below 1 mg/L. Solution pH increased when S^{2-} formed FeS and precipitated from the solution, since H_2S is a weak acid.

It is important to point out that the Fe ion concentration in the EC-treated water in the two tests conducted was below 2 mg/L, which means that using iron filling material in the EC won't increase iron concentration, because without S^{2-}, the generated Fe^{2+} was oxidized to Fe^{3+} and precipitate.

TOTAL SUSPENDED SOLID (TSS) REMOVAL

Two processes contribute to the suspended solid removal with EC: suspended solids get electrically charged and form bigger particles and then precipitate, or suspended solids combine with coagulant and precipitate. **Figure 2** illustrates that the size of 90% of particles in the produced water sample are below 10 microns, which caused a problem for regular filtration with 20 micron filter media. After EC treatment, the average size was larger than 25 microns, which can easily be filtered from water with 20 micron filter media.

Produced water treatment with the reported EC system has been proven efficient for TSS removal: over 60% removal has been frequently observed in field treatment and lab scale testing. The TSS removal efficiency could be improved by adjusting EC treatment parameters for challenging water samples. For example, long residence time and high electric density in EC will generate a large volume of coagulants ($Al(OH)_3$ or $Fe(OH)_3$), and then provide high TSS reduction. **Figure 3** shows TSS removal from lab scale testing at the pH range of 5 to 9, indicating the consistent TSS removal at normal EC treatment pH range.

APPLICATION

A field unit of this EC system with non-sacrificial electrodes has been utilized in the United States and other countries for produced water treatment. The system has successfully run for 24 hours per day for up to15 continuous days with efficient treatment for iron and other contaminant removal and no NPT. While treating produced water for numerous operators in the Permian Basin, operating costs have been reduced by more than 20% while reducing freshwater demand and trucking over 90%.

CONCLUSION

The reported EC system has a unique design with non-sacrificial electrodes and sacrificial filling material that requires little maintenance or replacement of electrode and provides consistent parameters for a continuous treatment process. Both lab scale testing and field treatment with the EC system have shown fast and complete removal of high concentrations of iron, sulfide, and other contaminants from produced water.

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Table 1 - Water chemistry of raw water and EC treated water

Ion	Ion concentration (mg/L) Raw water	Ion concentration (mg/L) Treated water	Ion removal (%)
Al	8.94	4.4	50.8
B	35.4	25	29.4
Ba	610	548	10.2
Ca	25200	22560	10.5
Fe	946	0.60	99.9
K	3040	2884	5.1
Mg	2040	1596	21.8
Mn	1070	520	51.4
Na	49800	48,800	2.0
SO4	148	105.6	28.6
Si	23.9	0.32	98.7
Sr	1680	1524	9.3
Zn	621	27.6	95.6
pH	5.82	6.5	N/A
Calculated TDS	224,300	217,900	2.9

Table 2 - Chemical needed for oxidation of 920 mg/L Fe^{2+}

Oxidant	Required amount (mg/L)	Generated ion (mg/l)
H_2O_2	279.3	none
$KMnO_4$	519.1	Mn^{2-}: 180.7
ClO_2	221.8	Cl^{-}: 116.6

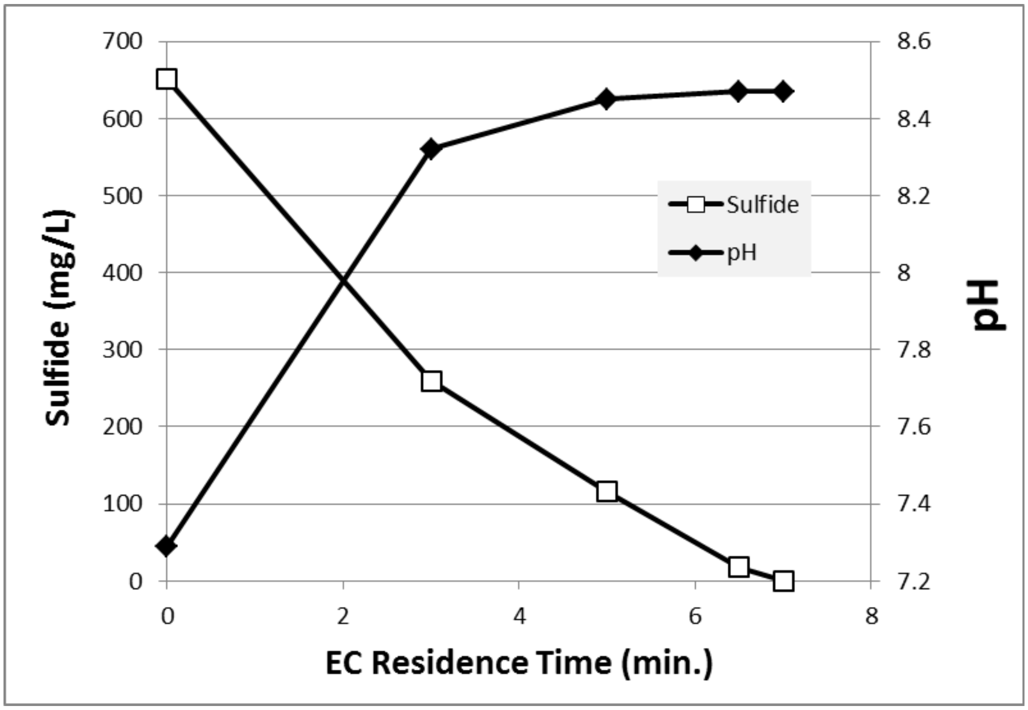

Figure 1 - Sulfide removal and pH change during EC treatment process

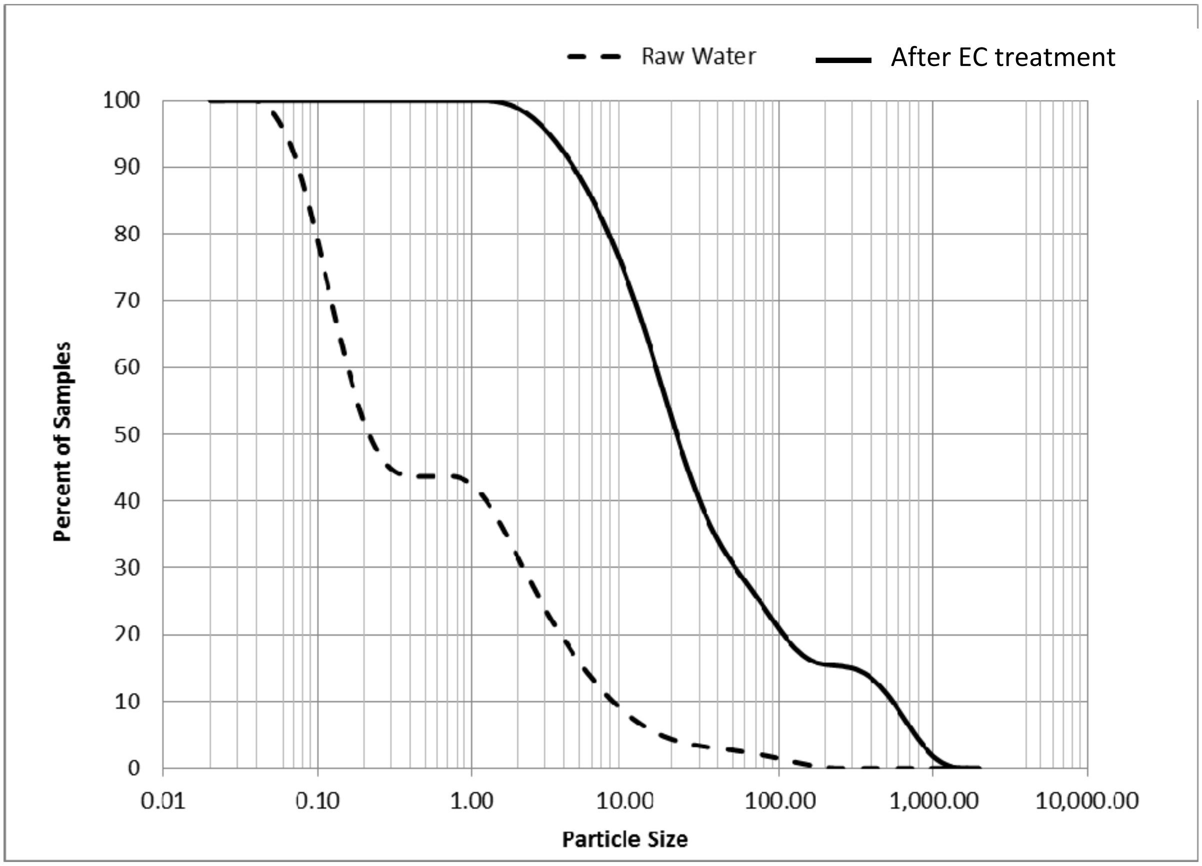

Figure 2 - Particle size distribution of raw water and EC-treated water sample (20)

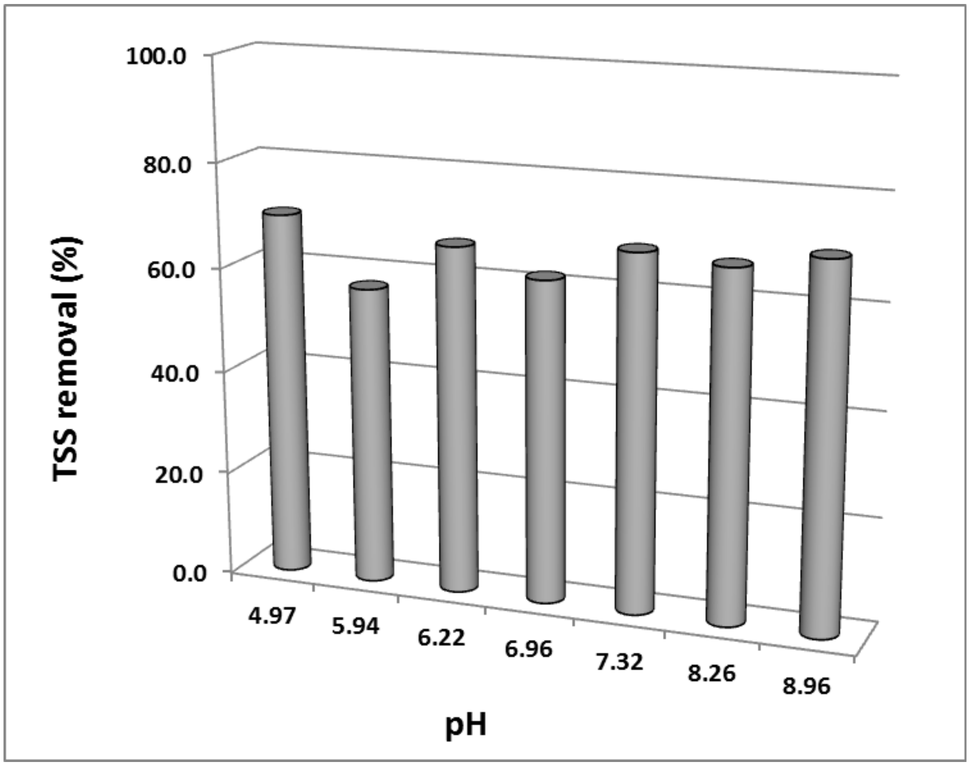

Figure 3 - TSS removal with EC