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Impact of Aluminum and Iron (III) Ions on Removal of Fluoride Ion (F^-) by Calcite

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Abstract

Matrix acidizing adds high concentrations of hydrofluoric acid into the oil production well for the purpose of well stimulation and thus, the return fluids could contain high fluoride ion (F^-) concentrations. Depending on the fate of the return fluids, high F^- concentrations, if untreated, could negatively affect public health and/or the environment. This article shows that calcite ($CaCO_3$) can remove F^- ions from solutions containing 200 mg/L of F^- and 200 mg/L of aluminum ion (Al^{3+}) or 200 mg/L of iron (III) ion (Fe^{3+}) by precipitation mechanism in batch mode. Al^{3+} and Fe^{3+} are among metallic ions that are present in the subsurface and, therefore, may appear in a typical matrix acidizing return fluid. Al^{3+} and Fe^{3+} can potentially form complexes with F^- and negatively affect F^- precipitation. F^- concentration was measured at fixed intervals during a 3-h period. The results showed that F^- removal efficiencies of up to 95% could be achieved when dissolved calcite is used on distilled water containing 200 mg/L of F^- at $[Ca^{2+}]/[F^-]$ ratio of 2:1. In addition, the presence of Al^{3+} or Fe^{3+} and their complexes did not hinder, and in some instances improved the F^- removal efficiency. The PHREEQC geochemical software was utilized as a predictive tool, which verified the study findings regarding the complexes and their role in chemical precipitation of F^- compounds.

Keywords: calcite; fluoride removal; matrix acidizing return fluid; PHREEQC geochemical model

Introduction

California has some of the highest reserves of oil in the world, and thus, oil and gas production remains a major California industry. For example, the Long Beach oil field in the Los Angeles Basin, once contained about 5 billion cubic meters (three billion barrels) of oil within an area of <7 km^2 (2,000 acres) (Long *et al.*, 2015). According to the California Division of Oil, Gas, and Geothermal Resources (DOGGR, 2017), there are 52 oil fields in the state, each with >16 million cubic meters (100 million barrels) of known recoverable oil.

For the past 60 years, well stimulation techniques, such as matrix acidizing, have been used to enhance oil and gas production as California oil fields mature. The modern-day era of acid use in well stimulation began in the 1930s when corrosion inhibitors were discovered to stop acid attack on metal. Commercial use of acids began in the 1950s (Williams *et al.*, 1979). The idea of using acids for well stimulation or cleaning a wellbore is an old concept, but the chemicals, volumes, and techniques used in acidizing have changed.

Matrix acidizing is used to remove formation damage around the wellbore and/or increase reservoir permeability. Operators inject acid solutions, such as hydrofluoric acid (HF), hydrochloric acid (HCl), or mud acid (HF/HCl) into the well at pressures below fracture pressure (Robertson *et al.*, 1989). Acids etch the reservoir silica rock creating channels for oil and gas to flow. The mechanisms involved include etching the mineral surfaces by dissolving the minerals and mobilizing particles by decomposing the rock structure (Mcleod, 1986). In California, matrix acidizing is conducted at depths ranging from 2,000 to 11,000 feet (Abdullah *et al.*, 2016) and are in use throughout central California, especially in Kern Country, and throughout the Southern California region. From April 2013 to September 2015, >600 instances of acidizing took place in urbanized Southern and Central California. During this period, the average amount of HF added during matrix acidizing events reported to California South Coast Air Quality Management District (SCAQMD) and DOGGR are 258 kg and 1,869 kg per treatment, respectively (Abdullah *et al.*, 2016). Reacted HF leaves F^- behind, and excessive F^- can be detrimental (Abdullah *et al.*, 2016). From September 2014 to September 2015, 23 matrix acidization activities were reported to DOGGR to comply with California Senate Bill 4 (SB4) enacted in 2013. SB4 sets the framework for regulation of well stimulation technologies in California. In all cases, the return fluids were discharged into

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underground injection control wells, which could potentially contaminate our groundwater and affect human health.

Shuchart (1995) analyzed several sets of well returns after HF acidizing treatments and reported Al^{3+} and Fe^{3+} concentrations in a typical return fluid sample to range from 35 to 1,111 mg/L and from 0 to 10,000 mg/L, respectively. The concentration (in mg/L) ratio of F^- to Al^{3+} ranged from 0.58 to 2.44.

F^- concentrations of >1.5 mg/L in drinking water can cause fluorosis, and adverse effects have been found from F^- concentrations as low as 0.5 mg/L (Ayoob and Gupta, 2007). High concentrations of F^-, above levels causing dental fluorosis, have been detected in the groundwater in portions of aquifers in five desert regions of southern California: the Coachella Valley (22%), the Colorado River basin (20%), the Mojave River area (10%), Owens Valley (3%), and the Antelope Valley (3%) (Wong and Stenstrom, 2017). Discharging Matrix acidizing return fluids into the subsurface can add more F^- to the already impacted groundwater and affect human health.

Several fluoride removal methods are currently in use, including coagulation and adsorption. Coagulation processes use chemical reagents such as lime, calcium, magnesium salts, polyaluminum chloride, and alum to form a precipitant with fluoride (Wong and Stenstrom, 2017). Adsorption uses sorption media that is often packed in columns. Water containing F^- is cycled through the columns, and the media can be regenerated, renewed, or disposed. The use of calcite to remove F^- at concentrations of 5–10 mg/L from drinking water and wastewater has been extensively studied. Dissolution of calcite increases calcium concentration until saturation is reached and CaF_2 precipitation occurs. Precipitation of CaF_2 occurs only at higher concentrations of F^- (10–20 mg/L or more) (Wong and Stenstrom, 2017).

A few studies have also been conducted on F^- removal by calcite in the presence of some specific metals. Cai *et al.* (2017) used calcite to remove F^- in the presence of barium ions (Ba^{2+}) and cadmium ions (Cd^{2+}) at ~10 mg/L by a batch reactor and a column test. Cai *et al.* (2017) refers to the need to treat the F^- impacted groundwater in Australia caused by leaching of the aluminum production by-product, spent pot lining (SPL). Ba^{2+} and Cd^{2+} are part of the chemical make-up of SPL. Results indicated that neither Ba^{2+} nor Cd^{2+} had any significant impact on F^- removal. However, other metallic ions such as Al^{3+} or Fe^{3+} have not been studied. In addition, no study focusing on F^- removal from matrix acidizing return fluids that would address the complications associated with mineral–fluoride complexation has been published.

The objectives of this article are the following:

- Present potential environmental problems caused by matrix acidizing; increase awareness on the composition and makeup of the recovered matrix acidizing fluids, and the potential impact of untreated F^- in matrix acidizing recovered fluids on human health and the environment.
- Present a simple and effective method of removing F^- from matrix acidizing return fluids.
- Present the results of using calcite in both the dissolved and saturated phase to remove F^- at concentrations higher than previously studied from solutions containing F^-, Al^{3+}, and Fe^{3+} ions at high background concentrations of Al^{3+} and Fe^{3+}. These solutions were prepared to model acidizing return fluids samples that could be recovered in the field. Considering the Al^{3+} and Fe^{3+} concentrations in a typical acidizing return fluid, the impact of these ions on the ability of calcite to precipitate F^- needs to be investigated. Therefore, the findings of this study should be viewed as primary steps in developing a comprehensive batch process of F^- removal from matrix acidizing return fluids at high concentrations of F^- and high background concentrations of Al^{3+} and Fe^{3+}.

Table 1. Removal Processes Involving Calcium, Aluminum, and Iron

Reaction (precipitation)	K_{sp}[a]
$Ca^{2+}(aq) + CO_3^{2-}(aq) \leftrightharpoons CaCO_3(s)$	3.3×10^{-9}
$Ca^{2+}(aq) + 2F^-(aq) \leftrightharpoons CaF_2(s)$	8.5×10^{-11}
$Al^{3+}(aq) + 3OH^-(aq) \leftrightharpoons Al(OH)_3(s)$	3×10^{-34}
$Al^{3+}(aq) + 3F^-(aq) \leftrightharpoons AlF_3(s)$	2×10^{-17}
$Fe^{3+} + 3OH^- \leftrightharpoons Fe(OH)_3(s)$	7.76×10^{-38}
Reaction (complex formation)	K[b]
$Al^{3+} + F^- \rightleftarrows AlF^{2+}$	$10^{6.12}$
$Al^{3+} + 2F^- \rightleftarrows AlF_2^+$	$10^{11.15}$
$Al^{3+} + 3F^- \rightleftarrows AlF_3$	10^{15}
$Al^{3+} + 4F^- \rightleftarrows AlF_4^-$	$10^{17.74}$
$Al^{3+} + 5F^- \rightleftarrows AlF_5^{2-}$	$10^{19.37}$
$Al^{3+} + 6F^- \rightleftarrows AlF_6^{3-}$	$10^{19.84}$
Reaction (complex formation)	K[c]
$Fe^{3+} + F^- \rightleftarrows FeF^{2+}$	$10^{5.2}$
$Fe^{3+} + 2F^- \rightleftarrows FeF_2^+$	$10^{10.6}$
$Fe^{3+} + 3F^- \rightleftarrows FeF_3$	$10^{13.7}$
$Fe^{3+} + 4F^- \rightleftarrows FeF_4^-$	N/A
$Fe^{3+} + 5F^- \rightleftarrows FeF_5^{2-}$	N/A
$Fe^{3+} + 6F^- \rightleftarrows FeF_6^{3-}$	N/A

[a]Generalic (2019).
[b]Complexation equilibrium coefficients (Hem, 1968).
[c]Complexation equilibrium coefficients (Inczedy, 1976).
N/A, not available.

Chemistry

Removal processes involving the ions of interest are governed by the reactions presented in Table 1. The formation of fluorite (CaF_2), aluminum fluoride (AlF_3), aluminum hydroxide [$Al(OH)_3$], and iron (III) hydroxide [$Fe(OH)_3$] depends on the solution pH as shown in Table 2.

Experimental Design

This study was conducted in two phases as shown in Table 3. In phase I, calcite was used in solid state. In phase II,

Table 2. The pH Dependence of Calcium, Aluminum, Iron, and Silica Chemistry in Return Fluid Waters

Reaction
$Ca^{2+}(aq) + 2F^-(aq) + H^+ + CO_3^{2-} \leftrightharpoons CaF_2(s) + HCO_3^-$
$Al^{3+}(aq) + 3OH^-(aq) \leftrightharpoons Al(OH)_3(s)$
$Al_2Si_2O_5(OH)_4(s) + 18HF(aq)$ $(2H_2SiF_6(aq) + 2AlF_3(s) + 9H_2O(l)$
$Fe^{3+}(aq) + 3OH^-(aq) \leftrightharpoons Fe(OH)_3(s)$

Table 3. Amounts and Concentrations of Reagents Used in the Study

Sample	Na^+ (mg/L)	F^- (mg/L)	Al^{3+} (mg/L)	Fe^{3+} (mg/L)	Cl^- (mg/L)	NaF (mg)	$AlCl_3$ (mg)	$FeCl_3$ (mg)	$CaCO_3$ Phase I (g)	$CaCO_3$ Phase II (mg/L)
Blank	241	200	—	—	—	176	—	—	13.32	900
Al-sample	241	200	200	—	790	176	396	—	13.32	900
Fe-sample	241	200	—	200	380	176	—	232	13.32	900
Al+Fe sample	241	200	200	200	1,179	176	396	232	13.32	900

Volume of deionized water = 400 mL.

calcite was used in aqueous state. ''Blank sample'' refers to the mixture of $NaF + CaCO_3$. ''Al-sample'' refers to the mixture of $NaF + AlCl_3 + CaCO_3$. ''Fe-sample'' refers to the mixture of $NaF + FeCl_3 + CaCO_3$. ''Combined ($Al^{3+} + Fe^{3+}$) sample'' refers to the mixture of $NaF + AlCl_3 + FeCl_3 + CaCO_3$.

Phase I

Sodium fluoride, aluminum chloride, and iron (III) chloride were dissolved in 400 mL of distilled water to produce solutions with starting concentrations of 200 mg/L each for F^-, Fe^{3+}, and Al^{3+} ions. 13.32 g of solid calcite was then added to the solutions. The solutions were continuously stirred and were either analyzed immediately or left for 2 days to reach equilibrium, as done by Cai *et al.*, (2017). F^- concentration and pH were measured for a 3-h period.

Phase II

Sodium fluoride, aluminum chloride, and iron (III) chloride were dissolved in 400 mL of distilled water to produce solutions with starting concentrations of 200 mg/L each for F^-, Fe^{3+}, and Al^{3+} ions. Calcite was completely dissolved in distilled water by lowering the pH using HCl to achieve a concentration of 900 mg/L for calcite in each case as described in Table 3. This concentration of calcite was used to achieve a $[Ca^{2+}]/[F^-]$ molar ratio of $\sim$2:1 and to ensure a F^- limiting environment.

The pH was raised to the desired value using NaOH as shown on the pH plots indicating the starting pH. Solutions were continuously stirred and were analyzed for F^- and pH for a 3-h period.

Experimental protocol

F^- concentration was measured using an ion-selective electrode (American Scientific Corporation, Portland, OR) and a silver chloride 900100, single junction, reference electrode (Thermo Fisher Scientific, Waltham, MA) following the procedure given hereunder:

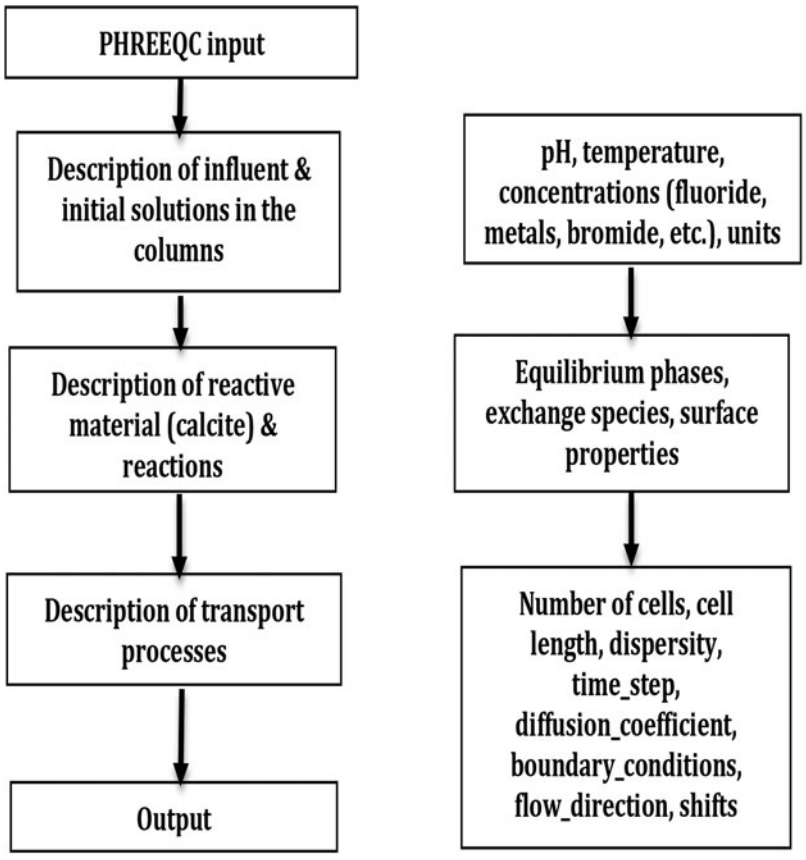

FIG. 1. General framework of PHREEQC input file (Cai *et al.*, 2017).

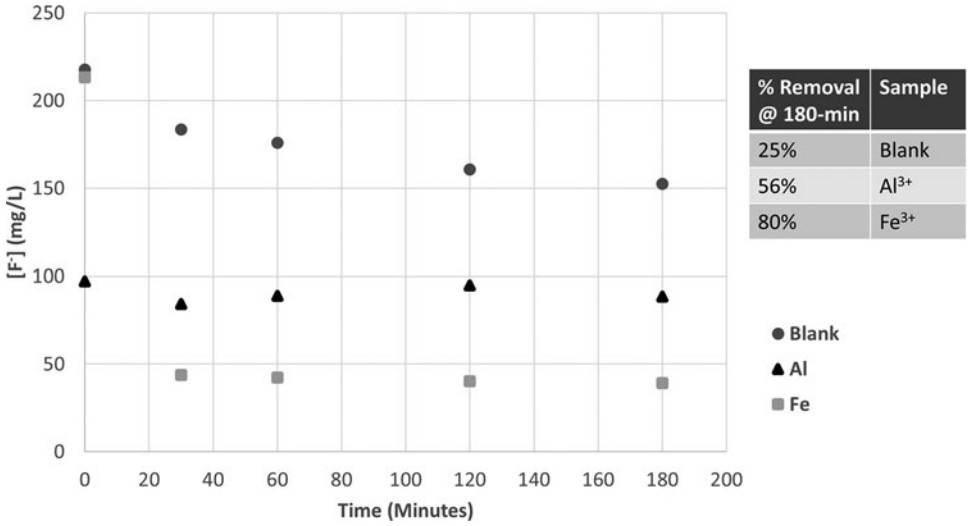

FIG. 2. Effect of 200 mg/L Al^{3+} and Fe^{3+} on removal of 200 mg/L fluoride samples analyzed immediately after $CaCO_3$ addition.

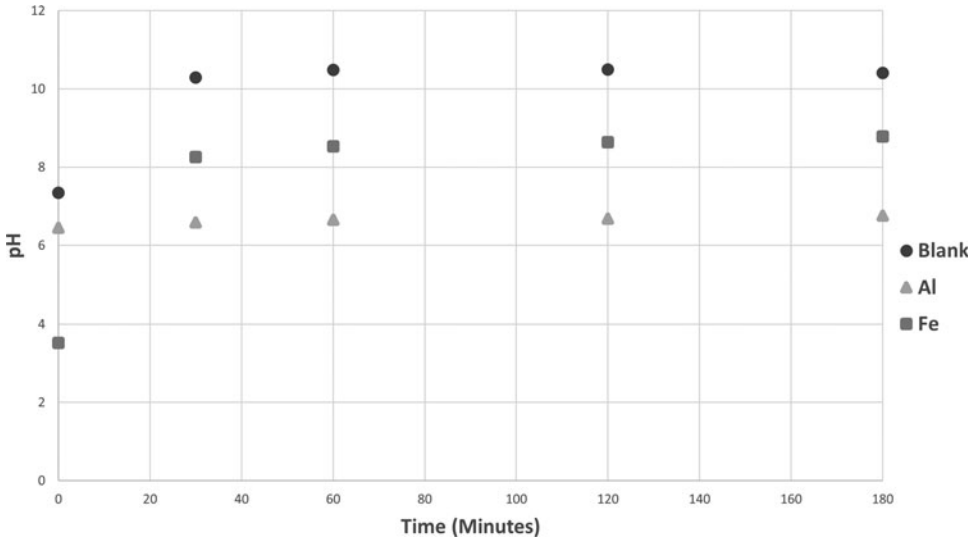

FIG. 3. pH versus time plot—effect of 200 mg/L Al^{3+} and Fe^{3+} on removal of 200 mg/L fluoride samples analyzed immediately after $CaCO_3$ addition.

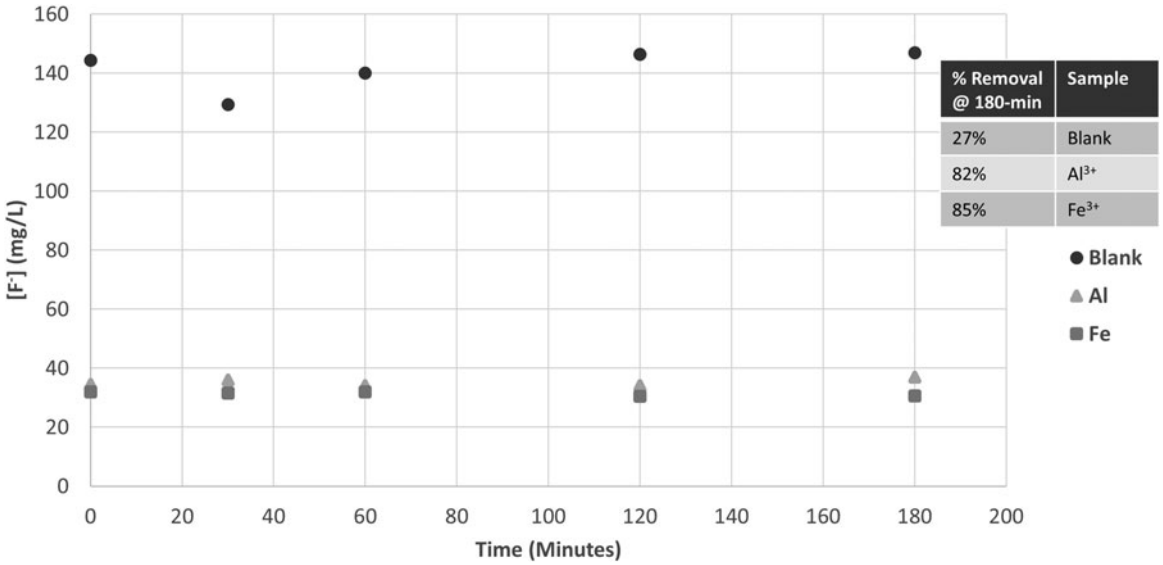

FIG. 4. Effect of 200 mg/L Al^{3+} and Fe^{3+} on removal of 200 mg/L fluoride samples analyzed 2 days after $CaCO_3$ addition.

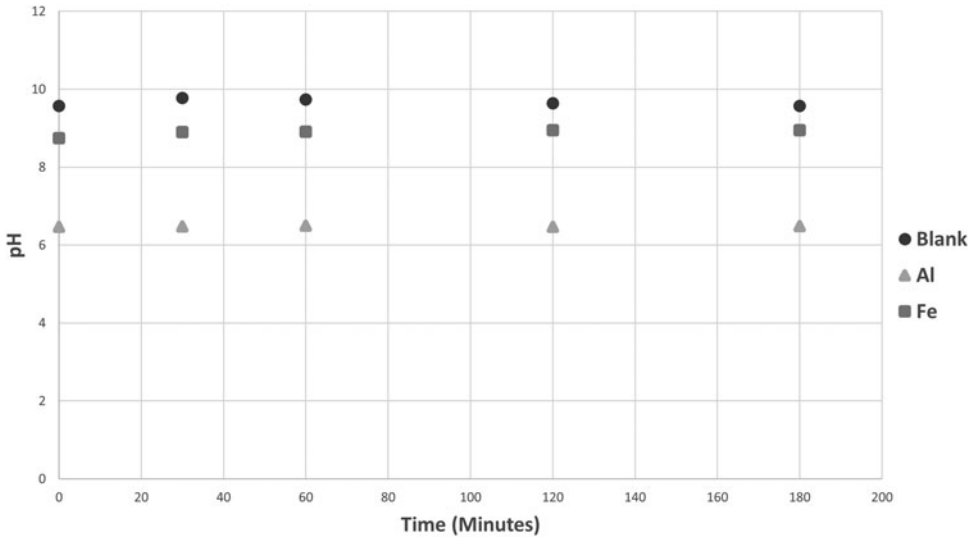

FIG. 5. pH versus time plot—effect of 200 mg/L Al^{3+} and Fe^{3+} on removal of 200 mg/L fluoride samples analyzed 2 days after $CaCO_3$ addition.

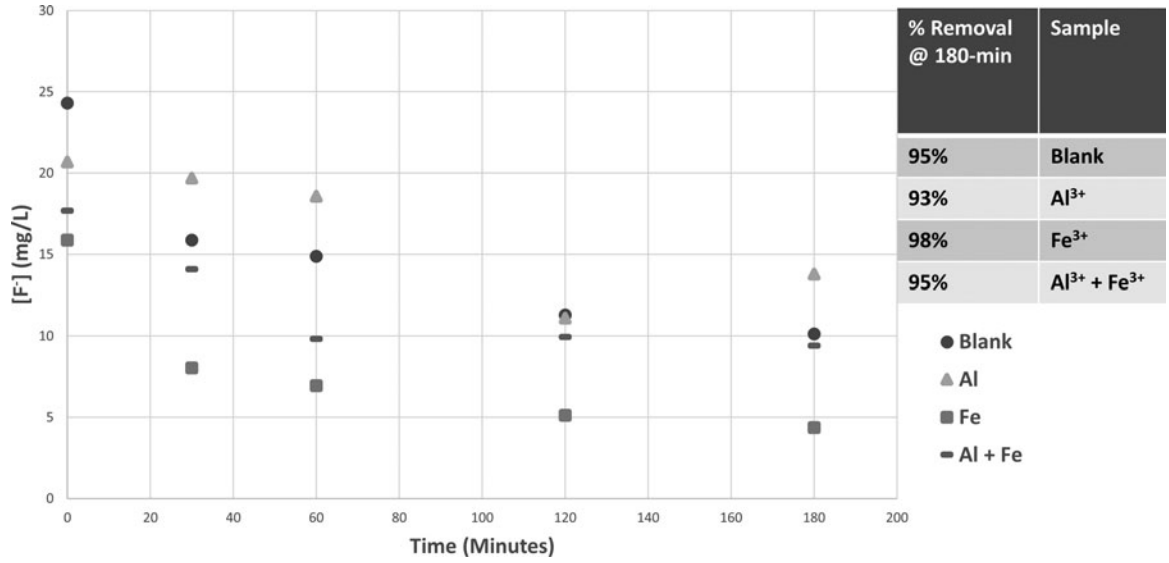

FIG. 6. Effect of 200 mg/L Al^{3+} and Fe^{3+} on removal of 200 mg/L fluoride at starting pH = 10. $CaCO_3$ made completely soluble.

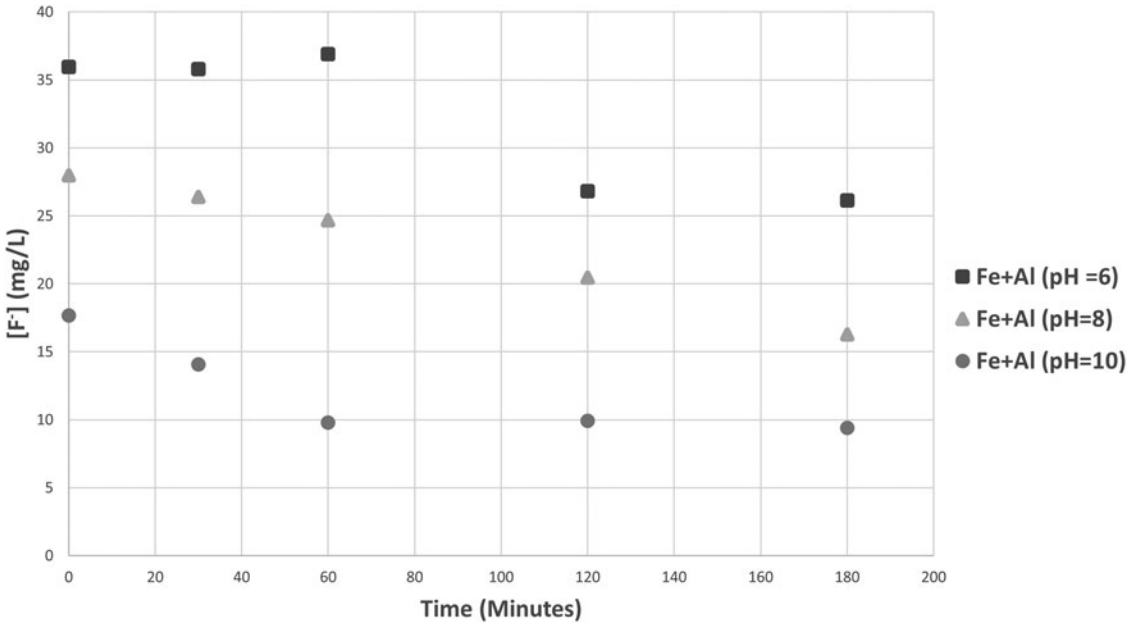

FIG. 7. Effect of 200 mg/L combined Al^{3+}+Fe^{3+} on removal of 200 mg/L fluoride at different starting pH. pH 10 offers higher removal with soluble $CaCO_3$.

(1) Using solid NaF, a 1,000 mg/L F^- stock solution was prepared in ''Total Ion Selective Addition Buffer'' (TISAB) III (Aqua Solutions, Inc., Deer Park, TX). The stock solution was then diluted to make standards of the following concentrations prepared with the addition of TISAB III.
   (a) 500 mg/L
   (b) 100 mg/L
   (c) 50 mg/L
   (d) 10 mg/L
(2) The sample to be analyzed was transferred into a clean dry beaker large enough to contain two electrodes. Ten milliliters of TISAB III was added for every 100 mL sample to be analyzed.
(3) The potential difference of the standard solutions was measured by a PHI 350 Digital pH/temperature/mV meter (Beckman Coulter, Inc., Pasadena, CA). The lowest to highest concentration was followed considering the initial fluoride concentrations of the sample to be analyzed.
(4) A clean and dry fluoride ion-selective electrode as well as reference electrode were inserted into the solution and swirled gently.
(5) The potential difference on the meter was recorded using the voltage scale after it was stabilized.
(6) To determine the F^- concentration of the sample to be analyzed, a standard calibration curve was prepared showing the measured potential difference versus the log of F^- concentration.
(7) A best-fit curve was created, and the equation of the curve was used to calculate the concentration of F^- in the sample.

Plastic laboratory ware was used for storage of standard solutions to prevent potential reaction of F^- with glass over time.

Geochemical Modeling

PHREEQC software (Parkhurst and Appelo, 2013), a geochemical model for simulating chemical reactions and transport processes in natural or polluted water, was used in this study. PHREEQC is capable of simulating chemical reactions, such as aqueous equilibria, mineral dissolution and precipitation, ion exchange, surface complexion, solid solutions, gas–water equilibrium, and kinetic biogeochemical reactions. The general framework for the PHREEQC simulations is presented in Fig. 1.

The software was used as a speciation program to calculate saturation indices (SIs) and the distribution of aqueous metal/F^- species, and ultimately, to verify the experimental results as follows:

TABLE 4. INDICES—BLANK SAMPLE

Phase	*SI*	*log IAP*	*log K_{sp} (298 K, 1 atm)*
Calcite ($CaCO_3$)	0.00	−8.48	−8.48
Fluorite (CaF_2)	1.98	−8.09	−10.07

IAP, ionic activity product; SI, saturation index.

TABLE 5. INDICES—AL^{3+} SAMPLE

Phase	*SI*	*log IAP*	*log K_{sp} (298 K, 1 atm)*
$Al(OH)_3$	2.49	−31.51	−34
Calcite ($CaCO_3$)	0.00	−8.48	−8.48
Fluorite (CaF_2)	1.49	−9.11	−10.60
AlF_3	−2.04	−19.30	−17.27

(1) Solution composition, pressure, and temperature were entered into the program.
(2) The program was set to adjust the equilibrium pH to achieve charge balance.
(3) The batch reaction modeling feature of the program was used to predict how the solution reacts with a solid phase or aqueous phase of $CaCO_3$.

Results and Discussion

Phase I

Immediate analysis after calcite addition. Figure 2 shows that the presence of Fe^{3+} had a positive impact on F^- removal by calcite. For example, at 180-min mark, an 80% F^- removal was achieved in the sample containing 200 mg/L Fe^{3+} as compared with a 25% F^- removal in the blank sample. The presence of Al^{3+} also improved F^- removal, but to a lesser extent. Although the starting concentration of F^- in all cases was 200 mg/L, the concentration of F^- dropped immediately upon measurement at time zero as shown in Figs. 2, 4, 6, and 7. In some instances, the measured initial concentration of F^- was slightly above the starting value of 200 mg/L, which could be due to instrumentation error.

The pH of the solutions after the initial rise was generally stable after 60 min (Figure 3).

The positive saturation indices of CaF_2 for all three cases calculated by PHREEQC (Tables 4, 5, and 7) verify that F^- removal is governed by the formation of CaF_2. Zero saturation indices calculated by PHREEQC for calcite for all three cases indicate that the calcium ions favor combining with the F^- ions over the carbonate ions.

In case of Al^{3+}, PHREEQC shows that considerable amounts of aqueous Al-F complexes, including AlF_3, are expected (Table 6). However, a negative saturation index for AlF_3 suggests that AlF_3 is undersaturated, and the removal of F^- is due only to the formation of solid CaF_2 (Table 5).

In case of Fe^{3+}, as Table 7 shows, the positive saturation indices of CaF_2 and FeF_3 point to the likelihood that F^- removal is achieved through the formation of both CaF_2 and FeF_3.

TABLE 6. PHREEQC OUTPUT—AL^{3+} SAMPLE

Species	*Concentration (mol/kg)*
AlF_2^+	2.986×10^{-3}
AlF_3	1.392×10^{-3}
AlF^{2+}	2.237×10^{-4}
F^-	5.327×10^{-5}
AlF_4^-	2.951×10^{-5}
NaF	2.233×10^{-7}
HF	1.553×10^{-8}
HF_2^-	3.175×10^{-12}
Equilibrium pH	6.627

Table 7. Indices—Fe^{3+} Sample

Phase	*SI*	*log IAP*	*log K_{sp} (298 K, 1 atm)*
$Fe(OH)_3$	4.75	−32.36	−37.11
Calcite ($CaCO_3$)	0.00	−8.48	−8.48
Fluorite (CaF_2)	3.79	−6.81	−10.60
FeF_3	2.49	−16.77	−19.26

Fluoride analysis 2 days after addition of calcite in solid state. Figure 4 shows that the presence of Al^{3+} and Fe^{3+} significantly improved F^- removal for samples left for 2 days before analysis. For example, at 180-min mark, 85% F^- removal was achieved in the sample containing 200 ppm Fe^{3+} as compared with 27% F^- removal in the blank sample.

F^- removal was slightly improved compared with the samples containing Fe^{3+} analyzed immediately after calcite addition (85% vs. 80%, Fig. 2). Figure 5 shows that the pH of the solutions in each case was generally constant throughout the reaction.

Phase II—addition of aqueous calcite

In Phase II, a combined (Al^{3+} + Fe^{3+}) sample was investigated. As Figs. 6 and 7 show, the F^- removal efficiency in the combined (Al^{3+} + Fe^{3+}) samples was second best after Fe^{3+} samples.

The presence of Fe^{3+} and Al^{3+} ions enhanced F^- removal when calcite was made completely soluble. As Fig. 7 shows, the combined (Al^{3+} + Fe^{3+}) samples performed best at pH of 10. Since the recovered fluids will likely contain iron and aluminum ions, the pH should be raised to 10 to obtain the highest removal. In addition, allowing solid calcium carbonate to dissolve completely in the return fluid offers much better F^- removal compared with using solid calcium carbonate. The positive saturation index of CaF_2 (Table 8) indicates that F^- removal is achieved through the formation of CaF_2.

Tables 8 and 9 present PHREEQC outputs for the combined (Al^{3+} + Fe^{3+}) samples.

Conclusion

The PHREEQC geochemical model verified the laboratory study findings regarding the complexes and their role in chemical precipitation of F^- compounds in the presence of both Al^{3+} and Fe^{3+} ions. As the results show, the F^- removal process in the presence of both Al^{3+} and Fe^{3+} ions was most efficient at pH of 10. Therefore, a starting pH of 10 in the soluble calcite scenario is recommended. The presence of silicon may complicate our findings and, therefore, needs to be further researched. In addition, the cost-effectiveness of the method presented should be further studied. Owing to the limited amount of information available to the public on the specifics of matrix acidizing operation, very few sources for referencing analytical data on actual return fluid samples were available. California SB4 requires matrix acidizing operators to report analytical results of return fluid sampling. However, there are limitations associated with self-reported information. Therefore, a system that would allow government agencies to access the wells being stimulated or acidized is needed, so that split samples of actual return fluids can be collected and analyzed independently.

Table 8. Indices—Combined Fe^{3+} and Al^{3+} Sample

Phase	*SI*	*log IAP*	*log K_{sp} (298 K, 1 atm)*
$Fe(OH)_3$	5.11	−32.00	−37.11
Calcite ($CaCO_3$)	2.00	−6.48	−8.48
Fluorite (CaF_2)	3.59	−7.01	−10.60
Hematite (Fe_2O_3)	24.01	20.01	−4.01
Geothite (FeOOH)	11.00	10.00	−1.00
$Al(OH)_3$	1.18	−32.82	−34

Table 9. PHREEQC Output—Combined Fe^{3+} and Al^{3+} Sample

Species	*Concentration (mol/kg)*
$Al(OH)_4^-$	6.077×10^{-3}
$Fe(OH)_3$	2.75×10^{-3}
AlF_4^-	9.173×10^{-4}
AlF_3	4.106×10^{-4}
$Fe(OH)_2^+$	1.003×10^{-4}
$Fe(OH)_4^-$	7.367×10^{-4}
$Al(OH)_3$	1.091×10^{-5}

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