A NEW METHOD TO ASCERTAIN THE HF STRENGTH OF ACIDIZING FLUIDS USING ION SELECTIVE ELECTRODE

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ABSTRACT

Successful sandstone acid stimulations have been widely reported using organic-HF acid systems. Unlike traditional mud acids, organic-HF acid systems are slow reacting fluids and show low dissolution with HCl-sensitive clay minerals. Furthermore, the conjugate base of organic acids chelates different metal ions such as iron, aluminum and silicon, thus preventing formation and reprecipitation of solubilized products and maintaining long term post-stimulation well productivity.

Ion selective electrode (ISE) meter can measure the equilibrium concentration of free fluoride ions of organic-HF acids via measurement of electrode potential of the solutions. Ammonium fluoride or ammonium bifluoride solutions are usually hydrolyzed by organic acids to generate HF acids. Unlike hydrochloride acid that ionizes completely in solutions, organic acids are very weak acids and only partially ionize in aqueous solutions. Nevertheless during acids treatments, the slow dissociation of weak organic acids generates more HF in-situ. However during acid treatments, long soaking time could result in formation of hydrated silica, a formation plugging precipitate. Consequently, the fluoride source may not be fully hydrolyzed to release the desired strength of organic-HF acid. The hydrolysis reaction becomes even more complicated when multi-protic organic acids with multiple dissociable protons such as in citric acid and 1-hydroxyethane 1,1-diphosphonic acid (HEDP) are used. The release of these protons in multi-protic organic acids is controlled by solution pH. Therefore, there is the need to ascertain the HF strength of organic-HF acid systems in order to achieve effective sandstone acid treatments.

In this study, several organic-HF acids were prepared with ammonium fluoride and their HF strength determined via measurement of the electrode potential of the solutions. Several coreflow studies were performed with the organic-HF acids to determine their effective sandstone stimulation capabilities. Coreflow effluent samples were also collected and the concentration of major ions such as Si, Al, Fe, Ca and Mg were determined via Inductively coupled Plasma (ICP) analysis. Finally, coreflow data and coreflow effluent ICP metal analysis clearly show the advantage of optimizing organic-HF acid systems with the aid of the ISE meter.

INTRODUCTION

Matrix stimulation is performed to mainly remove or bypass formation damage and increase well productivity (Martin 2004). Formation damage is mainly caused by the invasion of drilling fluids, completion fluids and treating fluids that could result in clay swelling, clay dispersion and scale precipitation (Di Lullo 1998; Martin 2004). Regular full strength mud acids (HCl-HF) have traditionally been used to remove formation damage. However, their reactions with clay sensitive minerals have resulted in the precipitation of formation plugging hydrated silica (Nasr-El-Din et al. 1998, Thomas et al. 2001). Retarded acids such as organic-HF acids when compared with mud acids show minimal dissolution with HCl-sensitive clay minerals and also keep solubilized products from reprecipitating (Di Lullo 1998; Rodgers 1998). Organic-HF acids are less corrosive, buffered systems and control the release of HF thereby ensuring deeper live acid penetration into the formation (Al-Dahlan et al. 2001).

Several organic HF acids have been used to effectively treat carbonate and sandstone formations (Wehunt et al. 1993; Motta et al. 1996; Schuchart et al. 1996, Di Lullo 1998; Yang et al. 2012). Some examples of the retarded organic-HF acid systems are acetic-HF, formic-HF, citric-HF, HEDP-HF (1-hydroxyethane 1,1-diphosphonic acid-HF), etc and a combination of these acid systems. However, unlike hydrochloric acid that completely ionizes in solution to fully hydrolyze the fluoride ion source, organic acids are weak acids and only partially ionize in aqueous solutions. The strength of organic acids is controlled by the pK_a of the acids. Thus, organic acids with low pK_a

values are stronger than organic acids with higher pK_a values. The use multi-protic organic acids to generate HF acids further complicate the problem. Multi-protic organic acids such as citric acids and etidronic acid (HEDP) have multiple ionizable protons. The ionization of these protons is controlled by the solution pH.

Some reports have shown that even with retarded HF acid systems, secondary and tertiary reactions with aluminosilicate minerals are likely to occur with increased soaking time (Al-Dahlan et al. 2001; Qin Ji et al. 2014). Secondary and tertiary reactions of HF acids with aluminosilicates generate formation damaging hydrated silica precipitates that reduce formation permeability to hydrocarbon production (Gdanski, 1996; 1999; 2000). As a result of the problems associated with increasing the soaking time during organic-HF acid treatments, the reaction equilibrium may not shift completely to the right. This may lead to fluid designs that are not fully optimized for effective sandstone stimulation. Therefore, the use of ion selective electrode to accurately ascertain the strength of organic-HF acid systems becomes very necessary.

EXPERIMENTAL STUDIES

Materials

All hydrochloric acid solutions were prepared from concentrated hydrochloric acid 22 Baume ACS grade. All organic acids were supplied in liquid form with acetic acid having an assay of more than 99%. Formic acid was received as 90% solution, citric acid (50%) and HEDP (60%). Ammonium fluoride was received as a 36% solution, while and ammonium bifluoride was received as a solid. All solutions were prepared using laboratory deionized (DI) water. The Buff Berea core plugs were 3 inch in length by 1.5 inch in diameter and were used in all coreflow studies.

Preparation and Measurement of HF Acid Systems

Standard mud acids (9 wt% HCl-1.0 wt% HF, 10 wt% HCl-1.5 wt% HF, 10 wt% HCl-2.0 wt% HF and 12 wt% HCl-3.0 wt% HF) were prepared with ammonium bifluoride salt and used only in construction of the HF calibration curve. Another 10 wt% HCl-1.5 wt% HF was prepared with the liquid ammonium fluoride and used in the coreflow study. All organic-HF acid systems were prepared with the liquid ammonium fluoride and different organic acids. The free fluoride ion concentration was measured by accumet® Basic (AB) 250 pH/mV/Ion selective electrode. A redox buffer was used as a calibration reference standard for the instrument. The pH of the HF acid solutions was usually adjusted to between 5.4 and 5.7 followed by the addition of total ionic strength buffer to provide a constant background ionic strength.

Coreflow Experiments

Coreflow studies were conducted to compare the effectiveness of the different HF acid treatment fluids in stimulating Buff Berea sandstone. The Berea core plugs were saturated in 5% NH_4Cl under nitrogen vacuum and used in the coreflow studies. After the core plug has been loaded into the core holder, an overburden pressure of 1000 psi and a back pressure of 200 psi were applied. The 5% NH_4Cl solution was injected at a flow rate of 0.5cc/min until the core reached target temperature. The 5% NH_4Cl solution was also used to establish initial and final core permeability. The HF treatment fluids were injected at a constant flow rate of 2cc/min to minimize fines movement within the core. A four hour shut-in pump schedule was incorporated in the acid fluid treatment sequence to drive the hydrolysis of ammonium fluoride to completion. At the end of each coreflow experiment, the regained core permeability was calculated using Darcy's law. Coreflow effluents were collected during acid injection and analyzed for silicon (Si), aluminum (Al), iron (Fe), calcium (Ca) and magnesium (Mg) using the Teledyne Lab Prism Inductively Coupled Plasma (ICP) equipped with the Salsa software.

RESULTS AND DISCUSSIONS

HF Acid Calibration and Measurements

Mud acids with four different HF strengths were prepared from ammonium bifluoride salt and their pH measurements recorded **(Table 1)**. A fluoride ion selective electrode was used to measure the equilibrium concentration of the free fluoride ions via electrode potential measurements **(Table 2)**. The electrode potential of the free fluoride ions was then used to construct an HF calibration curve **(Figure 1)**. Thereafter, the electrode potentials of organic-HF acids were measured and their HF strengths determined from the HF calibration curve **(Figure 1)**.

In comparison with hydrochloric acids, organic acids are relatively very weak acids with very small ionization constants (**Table 3**), (Serjeant and Dempsey; 1979). In aqueous solutions, organic acids partially dissociate to slowly release protons. Therefore, subsequent generation of HF acids from organic acids is controlled by slow equilibrium dissociation of the weak organic acids. This enables deeper live HF acids penetration into the formation during acidizing treatments. Formic and acetic acids are mono-protic acids and therefore have one ionizable proton per molecule. Citric acid and HEDP (etidronic acid) have three and four ionizable protons per molecule, respectively (**Table 3**). **Table 4** shows the amount of NH_4F required to generate approximately 1.5% HF acid with the different organic acids. According to the results, 12% acetic acid with pK_a 4.76 required 3.96 wt% NH_4F to generate approximately the same amount of free fluoride ions as 12% formic acid that required only 3.67 wt% NH_4F (**Table 4**). Formic acid has a pK_a value of 3.75 and therefore is a stronger acid than acetic acid (**Table 3**). Similarly, citric acid required 3.38 wt% NH_4F to generate approximately the same amount of free fluoride ions as HEDP that required only 3.24 wt% NH_4F. Citric acid is a weaker acid (pKa 1 is 3.13) when compared with the stronger HEDP acid with pK_a 1 value of 1.35. The much stronger HCl required the least amount of NH_4F (3.02 wt%) to generate approximately the same amount of free fluoride ions as all acids (**Table 4**). From the data provided in **Table 4**, it is very clear that the stronger the organic acid, the more easily it ionizes to release protons to hydrolyze the fluoride ion source.

Coreflow Results

Coreflow tests were performed to evaluate the effectiveness of the different organic-HF acids to stimulate clean Berea core plugs. The Berea core mineralogy determined by X-Ray powder Diffraction (XRD) is presented in **table 5** and indicated high quartz content (86%), potentially migrating clay mineral (kaolinite, 5.8%), mica (5.6%) and small amounts of calcium carbonate mineral (2.5%). Initial core permeability was determined via Darcy's Law after injecting 5wt% NH_4Cl solution through the core plug and a constant differential pressure (ΔP) was achieved. This was followed by 5 pore volume (PV) of the main acid treatment fluid. A postflush with 5%wt NH_4Cl was performed until a constant ΔP was re-established and the regained permeability determined.

Based on the data presented in **table 6**, citric-HF acid system produced the highest regained permeability of 104%. This may be due to the fact that citric-HF acid is very effective at keeping solubilized products in solution and preventing them from reprecipitating (*Rodgers et al. 1998*). More importantly, the citrate ion binds very strongly to Al and Fe (*Martell and Smith, 1976*), thereby minimizing the likelihood of aluminum trifluoride and iron hydroxide precipitates formation. Berea core treatment with HEDP-HF resulted in 102% regain permeability (**Table 6**). Berea core treatments with acetic-HF and formic-HF acids resulted in small permeability losses. Similarly, Berea core treatment with the mud acid (HCl/HF, 10wt%-1.5wt%) resulted in 94% regained permeability (**Table 6**). The permeability reduction is likely due to reprecipitation of initially solubilized products and also formation of silica gel precipitates. Silica gel precipitates are usually formed via secondary and tertiary aluminosilicate reactions with HF acids, and are damaging to formation permeability (Gdanski 1998, 1999 and 2000).

Coreflow studies also were performed with damaged Buff Berea core plugs (**Table 7**). Citric-HF and fluoroboric acid treatments resulted in 110% and 112% regained permeability, respectively (**Table 7**). However, acetic-HF and formic-HF treatments resulted in only 97% and 102% regained permeabilities (**Table 7**).

The concentration of dissolved Si, Al, Fe, Ca and Mg ions in coreflow effluent samples of clean Berea core plugs are presented in **Table 8**. Citric-HF acid was very effective in leaching aluminum, iron, calcium and magnesium ions from the Berea core (**Table 8**). This could be due to the fact that the citrate ion binds very strongly to Al and Fe compared when to the formate or acetate ions (Martell and Smith 1976). The strong binding affinity of the citrate ion to metal ions is most likely is responsible for the highest regain permeability (104%) recorded with the citric-HF treatment. Formic-HF and acetic HF were not as effective in leaching aluminum and magnesium from the Berea core plug as much as the citric-HF acid system. On the other hand, HEDP-HF leached the highest amount of calcium ions (2012 mg/L) from the Berea core (**Table 8**). Phosphonates such as HEDP are known to bind very strongly to calcium ions (Przybylinski et al., 1999; Amjad and Zuhl, 2004). The inorganic mud acid (HCl/HF, 10:1.5) leached the least amount of silicon (275 mg/L) from the core plug (**Table 8**). This is most likely due to formation and precipitation of formation damaging silica gel ($SiO_2.2H_2O$) resulting in lower regained permeability. Finally, the fluoroboric acid treatment was not effective in leaching aluminum from the Berea core plug (**Table 8**). However, the fluoroboric acid treatment fluid leached significant amounts of Si, Fe, Ca and Mg from the core plug, resulting in 99% regain permeability (**Table 6**).

CONCLUSIONS

- Accurate determination of organic-HF acid systems ensures fluid optimization.
- Organic acids with smaller pK_a values required lesser amount of ammonium fluoride solution to generate HF acids of similar strength as organic acids with higher pK_a values that typically require more ammonium fluoride.
- The use of an ISE meter enables direct measurement of HF strength of multi-protic HF acid systems such as citric-HF and HEDP-HF that have distinct dissociable protons.
- At 150°F, citric-HF improved the Berea core permeability the most without any noticeable damage.
- Formic-HF acid was most effective at leaching silicon from the Berea sandstone.
- Citric-HF acid was most effective at dissolving aluminum and iron from the Berea sandstone.
- Citric-HF and HEDP-HF acid stimulation may not require HCl preflush for sandstones containing calcium carbonate mineral.

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Table 1 - Composition of inorganic mud acids made from the reaction of hydrochloric acid with ammonium bifluoride

Acid System (wt%)	ABF (g)	pH of HF Acids
HCl/HF, 9:1	1.43	1.6
HCl/HF, 10:1.5	2.14	1.3
HCl/HF, 10:2	2.85	1.3
HCl/HF, 12:3	4.28	0.6

Table 2 - Inorganic mud acids generated with ammonium bifluoride salt solutions, their respective Ion Selective Electrode (ISE) and HF measurements. The ISE measurements and percent HF were used in the free fluoride ion calibration.

Acid System	ISE Reading Millivolts (mV)	HF (wt%)
HCl/HF, 9:1	-131.7	0.94
HCl/HF, 10:1.5	-139.8	1.52
HCl/HF, 10:2	-145.3	2.09
HCl/HF, 12:3	-156.2	2.95

Table 3 - Organic and inorganic acids pK_a's (Serjeant and Dempsey; 1979)

Acids	pKa 1	pKa 2	pKa 3	pKa 4
Acetic Acid	4.76	-	-	-
Formic Acid	3.75	-	-	-
Citric Acid	3.13	4.76	6.40	-
Etidronic Acid (HEDP)	1.35	2.87	7.03	11.3
HCl	-6.3	-	-	-

Table 4 - Acid compositions, pH, and corresponding ISE/HF measurements

Acid System	Ammonium Fluoride (wt%)	pH of HF Acids	ISE Reading Millivolts (mV)	HF (wt%)
Acetic Acid, 12wt%	3.96	5.5	-139.5	1.50
Formic Acid, 12wt%	3.67	4.5	-139.3	1.48
Citric Acid, 15wt%	3.38	4.6	-139.1	1.47
HEDP, 15wt%	3.24	4.4	-139.9	1.53
HCl, 10wt%	3.02	2.3	-139.2	1.48

Table 5 - The mineralogy of Buff Berea sandstone core plug used in coreflow studies

Mineralogy (XRD)	Wt%
Quartz	86.1
Kaolinite	5.8
Phengite	5.6
Calcite	2.5

Table 6 - Coreflow test results with Clean-Buff Berea Core Plugs performed at 150^{o}F with different HF acid systems

Base Fluid (Pre-/Post-Flushes)	Main Treatment Fluids	pH of Acid Systems	Shut-in Period	Regain Permeability	Permeability Enhancement, %
5 wt% NH_4Cl	Acetic Acid/NH_4F (12 wt%/1.5 wt% HF)	5.5	4 hours	98	-1.9
5 wt% NH_4Cl	Formic Acid/NH_4F (12 wt%/1.5 wt% HF)	4.5	4 hours	99	-1.1
5 wt% NH_4Cl	Citric Acid/NH_4F (15wt%/1.5 wt% HF)	4.6	4 hours	104	3.7
5 wt% NH_4Cl	Etidronic Acid/NH_4F (15 wt%/1.5 wt% HF)	4.4	4 hours	102	2.1
5 wt% NH_4Cl	Fluoroboric Acid (7.8%)	0.9	4 hours	99	-0.87
5 wt% NH_4Cl	HCl/NH_4F (10 wt%/1.5 wt% HF)	2.3	4 hours	94	-5.6

Table 7 - Coreflow test results with Damaged-Buff Berea Core Plugs performed at 150^{o}F with different HF acid systems

Base Fluid (Pre-/Post- Flushes)	**Main Treatment Fluids**	**Shut-in Period**	**Regain Permeability**	**Permeability Enhancement, %**
5 wt% NH_4Cl	Acetic Acid/NH_4F (12 wt%/1.5 wt% HF)	30 minutes	97	-3.4
5 wt% NH_4Cl	Formic Acid/NH_4F (12 wt%/1.5 wt% HF)	30 minutes	102	1.7
5 wt% NH_4Cl	Citric Acid/NH_4F (15wt%/1.5 wt% HF)	30 minutes	110	6.4
5 wt% NH_4Cl	Fluoroboric Acid (7.8%)	30 minutes	112	12

Table 8 - Elemental analysis (ICP) of coreflow effluents during acid injection

Elemental Analysis (ICP)	**(Si, mg/L)**	**(Al, mg/L)**	**(Fe, mg/L)**	**(Ca, mg/L)**	**(Mg, mg/L)**
Acetic-HF	862	0	180	1340	694
Formic-HF	481	0	238	658	41
Citric-HF	330	37.8	496	1658	2850
HEDP-HF	603	0	391	2012	627
Fluoroboric Acid (7.8%)	883	0	413	1356	811
HCl-HF, 10:1.5	275	34.9	405	1012	2502

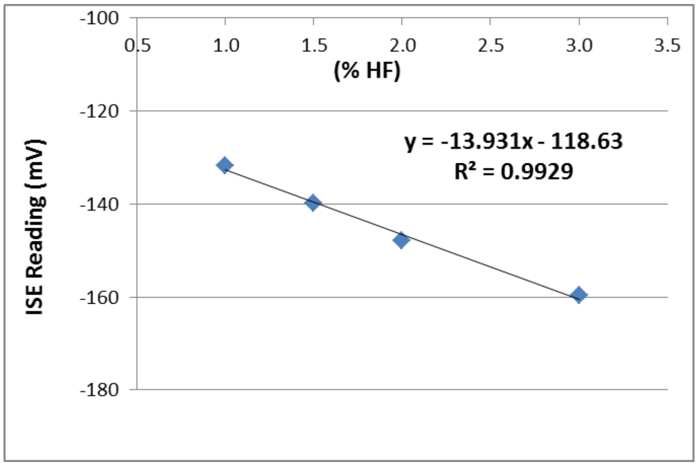

Figure 1 - Free fluoride ion calibration curve using four HCl/HF acids prepared with ammonium bifluoride salt solution.