A NEW CONCEPT IN HYDROCHLORIC-HYDROFLUORIC ACID MIXTURES FOR ACIDIZING LOW PERMEABILITY SANDSTONE FORMATIONS

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INTRODUCTION

To indicate a new concept in Hydrochloric-Hydrofluoric acidizing is perhaps an overstatement, but one which is necessary to promote the significance of a known, but seldom discussed feature of HCl-HF systems. This feature is the efficiency of low concentrations of *both* HCl and HF coupled with alcohol and/or surfactants which are gelled with a nonresidue polymer for a fracture-acidization application in low permeability, low porosity, well-consolidated, sandstone reservoirs.[1]

Two-thirds of the world's oil is found in sandstone formations. Problems with regard to treatment technique and type range from saturation and clay swelling to regarding clay particle migration, and fluid-formation compatibility.[2]

Reactions and reaction products have been extensively researched,[3] and it is not within the scope of this paper to dwell upon or challenge them.

Applications of low concentration HCl-HF treatments have been successful in several instances, although seldom has it been proposed utilizing the system as a combination pad volume and a complete fracture-acidizing treatment. Actual concentrations for hydrochloric acid in the system range between 2% and 6%, while hydrofluoric acid concentrations range between 0.6% and 1.2%.

Thickening for fracturing purposes is accomplished with low residue or nonresidue cellulosic or natural polymers, or by incorporation of a gelled amount (30%) of the weak HCl-HF fluid as the external portion of an emulsion involving an internal phase (70%) of a liquid hydrocarbon, usually kerosene or condensate.[4]

The material presented in this paper will discuss the use of such a system with selected example formations, and the illustration of the testing done on two examples of different character which was followed with actual treatment based on that testing. Both formations, the "J" Sand of Colorado, and the Delaware Sand of West Texas yielded successful treatments, each with a unique variation in design, based on formation location, and properties. (See Table 1).

TABLE 1—AREAS OF CORE TESTING AND TREATMENT

Formation	County	State	Field	Permeability	Depth
(1) "J" Sand	Weld	Colo.	Wildcat	0.1 md	7093 ft
(2) Delaware Sand	Reeves	Tex.	Worsham	3-10 md	5800 ft

PRINCIPLES OF LOW CONCENTRATION HCl-HF MIXTURES

The principle which is most significant about low concentration or "weak" HCl-HF acidization-fracturing systems is that of new acid-fracturing situations where only fracturing had been considered previously. Acid-fracturing of sandstone reservoirs, where conventional HCl-HF systems had been considered, tested, and failed, is a virgin territory for the "weak" HCl-HF systems.

Weak HCl-HF systems are prepared via the reaction of ammonium bifluoride in a 2-6% hydrochloric acid solution at concentrations of 50-100 pounds per 1000 gallons. Previous researchers have determined that this method of preparing HCl-HF mixtures is less likely to cause precipitation of calcium salts in formations with greater than expected HCl, solubility, and less likely to produce fluosilicates, which is attributed to the use of ammonium bifluoride for HF production.[5] Associated with the HCl-HF mixture is an often-used pretreatment of the formation with 2% KCl water to prevent swelling, and the precipitation of insoluble potassium hexafluosilicate, which results when KCl is run in solution with the HCl-HF mixture. To allow KCl to be run in the acid solution, the ammonium bifluoride again provides the guard against hexafluosilicate precipitation.[6]

Optimum concentrations for HCl or HF have been investigated only in a narrow range of circumstances, with 6-11% being considered optimum for HCl and 2-4% for HF.[5] Comparisons to lower concentrations were available for only the HF, and virtually no comparisons have been made to combination low concentration HCl and HF systems.

Where large permeability increases have been evident with conventional HCl-HF mixtures, (i.e., 12% HCl + 3% HF), there has almost always been an initial permeability decrease which is only recovered, and improved upon, after flowing many more pore volumes of the fluid, provided that reduction of flow was not too severe.[5] Weak HCl-HF systems combat this by creating a lower intensity reaction in the formation matrix (further retarded by gelation or emulsification), and not causing the initial permeability damage prior to a permeability increase.

Experimentation has shown that when hydrofluoric acid concentration is reduced, initial damage to flow characteristics is reduced or eliminated. However, larger volumes of acid were still required to effectively provide the same permeability increase as with the more concentrated HCl-HF systems. In both the previous cases, the HCl concentration was given very little consideration. Attention to HCl concentration has been limited to statements that a minimum of 6% HCl should be used in conjunction with HF, with concentrations of 8-11% HCl yielding the best improvement in a series of medium permeability situations (30-130 md).[5] Reasons for providing any HCl concentration at all center toward maintaining by-product solubility after the HF has spent, and providing a conversion medium for ammonium bifluoride to hydrofluoric acid. Also HCl provides a faster reaction medium where trace amounts of interstitial calcite are encountered within a sandstone matrix.[6] This allows conservation of the hydrofluoric acid with respect to preventing its spending on the hydrochloric-acid-soluble material and thus maintaining its intensity for reaction with the sandstone.

Three percent HCl with 0.6% HF, and 6% HCl with 1.2% HF are two of the successful treatment concentrations which, when applied to low permeability sandstone reservoirs, seem to provide a maximum response toward permeability restoration and/or improvement. Maximum response may be defined as an acid reaction which requires the least volume and concentration to initiate a permeability increase. The most significant principle which may be added to the previous statements on behalf of low concentration HCl-HF systems is that the low intensity reaction is probably responsible for preventing "acid reaction sloughing" which usually leads to permeability reduction via clay particle migration and subsequent blockage.

Gelation or incorporation of gelled low concentration HCl-HF acids in emulsion systems provide for retardation, thus allowing additional penetration. Also, if these weaker HCl-HF systems were applied without this retardation effect, they might tend to become spent prematurely, and leave the HF acid without by-product solubility control.

Acid reactivity is still maintained effectively and competitively with superior flow rate increases, in addition to being nondamaging. Where water-block or excess clay fines are a problem, suitable quantities of an alcohol and/or a silt-suspending surfactant may be employed, preferably of a non-ionic nature to eliminate surfactant plate-out within the pore spaces.

LABORATORY EVALUATIONS

The utilization of lower concentration HCl-HF combinations follows a well-known premise, that low concentration acid solutions ionize more readily, and in downhole situations, provide a more efficient candidate for removing or preventing emulsions. This fact is in addition to providing effective permeability increases in tight sandstone reservoirs while limiting, or totally preventing damage in tight problem formations, such as the "J" Sand in the Wildcat areas of Colorado and the Delaware Sand of the Worsham Field in West Texas. Other problem formations are candidates for this system, including the Canyon Sand formation of Sutton County, Texas and the stubborn Morrow Formation in southeastern New Mexico.

The "J" Sand and Delaware Sand were investigated via standard tests including solubility, sensitivity, X-ray diffraction and coreflow sequences.

Solubility and sensitivity evaluations were conducted by simply exposing known quantities of formation rock, ground into one-gram, 10-mesh samples, and added to controlled temperature solutions being tested for a period of 24 hours exposure. These routine tests coupled with commercial X-ray diffraction analysis were followed by selected coreflow tests utilizing 1-in. long by 1-in. wide cylindrical core sections mounted in a polyester resin sleeve, and placed in a commercial "ampcoloy" flow cell with facilities for temperature and pressure control. Tests were conducted at 1000 psig and at 110°F for the Delaware Sand, and 100°F for the "J" Sand. Various fluids were introduced to the core sections in an injection direction after determination of a reference hydrocarbon flow from a production direction. Following the acid-fracture fluid injection, a second reference fluid production flow rate was determined, thereby providing a simple means for determining flow rate damage or improvement. Precautions were taken to provide clean test fluids for flow tests. See Tables 2, 3, 4, and 5 for selected results.

Coreflow sequences were as follows under the above prescribed conditions.

1. Flow kerosene reference in production direction and time flow for 100 cc volume.
2. Flow selected acid solution in an injection direction after flowing a 2% KCl pad volume.
3. Backflow kerosene reference fluid in a production direction; time flow rate for 100 cc volume.
4. Figure improvement or damage according to change toward folds of increase or decrease in the original reference flow rate of kerosene. (See Table 5 for a summary of results).

SIGNIFICANCE OF RESULTS

The solubility tests signify obvious increased solubility in increasing ammonium bifluoride derived, HF concentrations. This is a desirable result in any formation except in the cases of the previously described formations where such concentrations tended to lower permeability. This could be attributed to reaction sloughing of formation fines, since precautions were taken in fluid design to prevent contamination by solids, by-product formation, swelling, fluid saturation, or water-block.

The research of others has pointed to formation fines migration being the result of every mechanism from pH and salinity changes to effects of pressure drawdown and the chemical composition of water.[5,6,7] However, it has only rarely been implied that more or less intensive acid solutions provide a mechanism for more or less severe damage to formation permeability.

X-ray diffraction showed the "J" Sand core to have a tendency to swell and the same tendency was insignificant in the Delaware Sand. The Delaware Sand cores showed a tendency to water-block when successive quantities of fresh water were flowed through the samples, and the damage was corrected by following with alcohol. However, significant damage remained which could probably be attributed to particle migration following the acid stimulation treatments. Such treatments were designed to cope with water-block via the use of alcoholic, low concentration HCl-HF acid. The swelling effect noted in the "J" Sand was controlled by implementing KCl within the acidizing system, or as a pretreatment with a 1% or 2% solution of KCl.

Flow tests with these two examples have been followed by successful field results as shown in Table 6, and subsequent treatments are being pursued. Results and further testing will be continued to further substantiate this information. Flow test data is shown very simply to indicate a folds-of-increase or decrease in flow rate, after subjecting the core samples to the test sequence outlined in the previous *Laboratory Evaluation* section.

It was noted that the Delaware Sand cores responded much better when the HCl-HF acid system was run as the external phase of an emulsion with kerosene, rather than as a straight gelled acid system. In fact, no response was obtained with the straight gelled HCl-HF weak acid system, whereas the results as tabluated were obtained using the HCl-HF weak acid as the external phase of an emulsion. Since the gelled acid was only 30% of the emulsion system, the medium concentration HCl-HF system was necessary (6% HCl + 1.2% HF). This was necessary probably due to the retardation effect of the acid being dispersed throughout a larger volume, although as the external phase.[4] An insignificant difference was noted between the 6% HCl - 1.2% HF system and the 12% HCl - 3% HF system, thereby showing for this particular instance the higher concentrations of both HCl and HF were essentially a waste. The "J" Sand was stimulated in test cores and actual treatments with the alcoholic and non-alcoholic 3% HCl + 0.6% HF system, and showed success over the more concentrated systems. However, it was again seen that the acid external emulsion system with the 6% HCl + 1.2% HF yielded the most effective treatment, and has been highly successful in the one field application of 35,000 gal. in a Wildcat well in the "J" Sand of Colorado.

CONCLUSIONS

Hydrochloric - hydrofluoric acid systems have been successfully applied to many oilfield problems encountered in attempting to stimulate sandstone reservoirs. As mentioned earlier, two-thirds of the world's oil is found in sandstone formations, and application of HCl-HF acidization techniques is generally restricted to consideration of maximum solubilization for permeability increase, by-product damage effects, and water sensitivity. Little regard is given problems encountered as a result of physical and chemical intensity of the system with regard to sloughing and dispersion blocking by formation fines. Regard should be given to the idea of a complete acid-fracture fluid which can effectively stimulate by utilizing the effects of *both* acidizing and fracturing.

Use of a pad volume or entire treatment composed of low concentration HCl-HF acids with tested alcoholic-surfactant-nonswelling additives has shown to be a qualified but successful method practically and economically for stimulating low permeability, low porosity, well consolidated, "problem" sandstones.

Hopefully, application will continue from the realms of the "J" Sand of Weld County, Colorado, and the Delaware Sand of the Worsham Field in West Texas to the tight Canyon Sands of Sutton County, Texas, and Morrow Sand in southeastern New Mexico.

SUMMARY

Lessened reaction intensity, coupled with alcoholic-surfactant sytems, and nondamaging gels make the low concentration HCl-HF fracture-acidizing systems more efficient with regard to promoting restored or increased permeability. Utilization of large volume treatments can be based on "total effectiveness", rather than having the necessary volume (pore volumes) to overcome the initial damaging effects encountered when using conventional HCl-HF systems, (i.e., 12% HCl + 3% HF).[5]

Gelation or emulsion of low concentration HCl-HF acids provides added effectiveness via retardation to preserve the maximum intensity of the weaker systems to obtain maximum penetration.

Low concentration HCl-HF systems provide a qualified economical and effective means of treating low permeability or reduced permeability sandstone reservoirs. These systems have characteristics to compensate for problems which have been encountered in the past, and are a relatively new concept for gaining treatment efficiency using lower concentrations of both hydrochloric and hydrofluoric acid.

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TABLE 2—SOLUBILITY OF 1 GRAM SAMPLE IN 50 ML. FLUID

(1) Formation: Delaware Sand
Permeability: 1 md to 5 md
Field: Worsham
Porosity: 10-20 per cent
County: Reeves
State: Texas
Depth: 5,800 feet

Fluid	Per Cent Solubility @ 110°F. and 24 hours
(a) Water	0.05%
(b) 15% HCl	5.07%
(c) 3% HCl + 0.6% HF	7.59%
(d) 6% HCl + 1.2% HF	12.24%
(e) 12% HCl + 3% HF	17.25%

(2) Formation: "J" Sand
Permeability: 0.1 md
County: Weld
Porosity: 8.8 per cent
State: Colorado
Depth: 7,093 feet

Fluid	Per Cent Solubility @ 100°F. and 24 hours
(a) Water	0.0%
(b) 15% HCl	1.82%
(c) 3% HCl + 0.6% HF	11.00%
(d) 6% HCl + 1.2% HF	23.60%
(e) 12% HCl + 3% HF	58.01%

TABLE 3—X-RAY DIFFRACTION ANALYSIS

(1) Delaware Sand:	Alpha Quartz	81.2%
5,800'	Feldspar	1.2%
(tight consolidation)	*Amorphous	14.4%
	Fines	3.2%

Fines: Kaolinite 2.9% + chlorite 0.3%

(2) "J" Sand	Alpha Quartz	76.0%
7,093'	Feldspar	2.0%
(medium consolidation)	*Amorphous	18.9%
	Fines	3.1%

Fines: Illite - 1.7% Illite-Montmorillonite - 0.8% Chlorite - 0.4%
Alpha - Quartz - 0.2%

*Note: Amorphous materials probably consist of one or a combination of the following: 1) chert, 2) volcanic glass, 3) weathered feldspar, 4) iron oxides, and/or 5) amorphous silica.

TABLE 4—FLUID SENSITIVITY (SWELLABLE CLAYS)

(1) Formation: Delaware Sand @ 5,800'

No sensitivity was detected in aqueous or hydrocarbon fluids.

(2) Formation: "J" Sand @ 7,093'

The presence of mixed layer clay, i.e., illite-montmorillonite, rendered this section sensitive to fresh water and low salinity brines.

TABLE 5—SAMPLE COREFLOW EVALUATIONS

	Formation	Fluid: Type of Acid	Test Temperature	Flow Rate Folds of Increase or Decrease
(1)	Delaware 5,800'	3% HCl + 0.6% HF as 30% of acid external emulsion Surfactant conc. = 0.1%, Alcohol Conc. = 10.0%	110°F.	1.83 Increase
(2)	Delaware 5,800'	6% HCl + 1.2% HF as 30% of acid external emulsion Surfactant Conc. = 0.1%, Alcohol Conc. = 10.0%	110°F.	17.84 Increase
(3)	Delaware 5,800'	12% HCl + 3.0% HF as 30% of acid external emulsion Surfactant Conc. = 0.1% & Alcohol Conc. = 10.0%	110°F.	17.85 Increase
(4)	Delaware 5,800'	15% HCl as 30% of acid external emulsion Surfactant Conc. = 0.1%, Alcohol Conc. = 10.0%	110°F.	0.25 Increase
(5)	"J" Sand 7,093'	3% HCl + 0.6% HF 2% KCl, 20% Alcohol 40 lb. Cellulose Gel	100°F.	10.06 Increase
(6)	"J" Sand 7,093'	40 lb. Cellulose Gel 6% HCl + 1.2% HF 2% KCl, 20% Alcohol	100°F.	3.15 Increase
(7)	"J" Sand 7,093'	40 lb. Cellulose Gel 15% HCl + 3% HF 2% KCl, 20% Alcohol	100°F.	2.0 Decrease
(8)	"J" Sand 7,093'	40 lb. Cellulose Gel 15% HCl + 6% HF 2% KCl, 20% Alcohol	100°F.	4.2 Decrease
(9)	"J" Sand 7,093'	6% HCl + 1.2% HF as 30% of acid external emulsion. Surfactant Conc. = 0.1% & Alcohol Conc. = 10.0%	100°F.	12.4 Increase

TABLE 6—FIELD RESULTS

Formation	Field	Treatment*	Prior Production	Post-Production (30 days+)
Delaware	Worsham	10,000 gal.	250 MCFPD	520 MCFPD
Delaware	Worsham	10,000 gal.	Dead	270 MCF + 2 BOPD
J-Sand	Wildcat	35,000 gal.	None	3,000 MCFPD

*Selected treatments were recent applications of the acid external emulsion with kerosene, utilizing the alcoholic, and surfactant treated 6 per cent HCl + 1.2 per cent HF system.