

STIMULATION FLUID FACTORS IN A STUDY OF FORMATION DAMAGE IN SEVERAL MORROW SANDS

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INTRODUCTION

Coreflow studies, X-ray diffraction, and a variety of other investigative techniques have been used in the study of the design for stimulation fluids for a number of years. Recently, the concern for the design of nondamaging stimulation fluids to treat "problem", well-consolidated, low-permeability low-porosity sandstone reservoirs has heightened. A typical example of a problem sandstone in the Pennsylvanian age group is the overall Morrow sand. The Morrow is considered to be in southeastern New Mexico, the Texas Panhandle, the Oklahoma Panhandle, and west-central Oklahoma at varying depths. The heterogeneity of the Morrow is displayed by the inclusion of laboratory investigation data which are necessary to point out the reasoning for the fluid types recommended in the Morrow in the above-mentioned areas. Following presentation of the investigative data, various case histories will be presented to substantiate the successful use of the recommended fluid systems in what has been labeled by operators, problem areas.

The significance of fluid pH, low surface/interfacial tension, iron chelation, and low-residue gelling materials, has been the premise for the treatment type which is being recommended for Morrow sections in the majority of the areas documented. Core data point to a general need to encounter or avoid specific components in the matrices of the Morrow sands. Core studies have shown that a recently developed combination of a weak HCl, weak HF acid system (3% HCl plus 1.2 HF) and a highly effective fluorocarbon surfactant provided significant improvement in the ability of a

fluid to successfully act on the inherent problems within the matrices of most Morrow sands. This implies that the Morrow is a candidate for damage, regardless of the considerations made to complete and/or stimulate it with "so-called" nondamaging fluids such as "clean" gels or condensate. The inherent potential for damage initiated by stimulation lay in the strategic location of migrating fines, iron compounds and extraneous clays within actual permeability and porosity. To avoid particulate matter damage with even minor penetration from commercially available fluid-loss additives for either oil or water frac systems, the amount used should be carefully considered.

The core studies which were run in the Morrow sections listed in Table 1 were intended to indicate the design which was most compatible and successful from the standpoint of encountering matrix conditions, and not to determine volumes to be utilized in treatment. The engineering aspects of these designs for the field followed contemporary computer methods. The flow tests were run with constant volumes for relative comparison purposes to show that significant pore volume concentrations could provide correlating data with actual recommendations followed by treatment.¹ The scanning electron microscope has been useful in identifying the location of potentially damaging particles within the permeability and porosity of the

TABLE 1—CORE STUDY AREAS AND ROCK DESCRIPTION

	Depth	County	State	Permeability	Porosity	Field
1.	10,000'	Roberts	Texas	0.1-1.5md	10-12%	Wildcat
2.	11,000'	Roberts	Texas	7.6md	17%	Parsell
3.	7,940'	Ochiltree	Texas	1.5-2.5md	12-14%	Wildcat
4.	6,135'	Texas	Oklahoma	1.0-4.0md	10.4%	Wildcat
5.	6,175'	Texas	Oklahoma	0.1-0.7md	11.1%	Wildcat
6.	7,900'	Blaine	Oklahoma	0.2md	7.0%	Northwest Okeene
7.	7,950'	Blaine	Oklahoma	0.1md	4.2%	Northwest Okeene
8.	11,400'	Eddy	New Mexico	0.6-3.5md	5-18%	South Carlsbad
9.	11,000'	Canadian	Oklahoma	0.2-0.5md	17.1%	Calumet
10.	5,600'	Cimarron	Oklahoma	0.2-1.0md	14.0%	Wildcat

Morrow which have been documented by X-ray diffraction.

FLUID pH CONTROL

The effects of any aqueous-phased system in the Morrow sands investigated were most easily attributed to the pH of the system used plus the overall strength of the acidity. Neutral aqueous fluids or strong acids (7-1/2% or greater) tend to impair permeability via ionic effects which disturb the iron and clay complex placement in the permeability matrix system. Weak HCl-HF (i.e. 3% HCl plus 0.6% HF or 6% HCl plus 1.2% HF) systems, besides their ability to cope with fines migration, provide a system which is not overly reactive so as to destroy matrix cementation, but rather a means of solubilizing iron complexes and less than 2 μ sized migratory fines as exhibited by the X-ray diffraction analyses in Table 2. Low pH should be maintained even after fluid is recovered, since the probability of iron product precipitation is

high. The weak HCl-HF treatments which have been performed have, for the most part, returned unspent. However, the factor of potential iron precipitation is sufficient evidence for utilizing some form of organic acid chelation method.

CHEMICAL CHELATION

Methods to control iron precipitation or reprecipitation are not new, but it has been determined that citric acid performs well at temperatures between 120°F and 200°F. Weak HCl-HF, as mentioned, seldom returns spent owing to the fact that the system is *not acidizing* the reservoir, but rather cleaning the matrix, sand pack or fracture, during and after treatment.²

LOW-RESIDUE GEL SYSTEMS

When the weak HCl-HF system is used as the total fluid in a fracturing fluid, or is used as a pad volume ahead of an efficient "clean" fluid, the gelling agent should be of the lowest residue nondamaging variety. For the most part, fracturing

TABLE 2—MORROW X-RAY DIFFRACTION ANALYSES

(1) Roberts Co., Texas @ 10,000'

α -Quartz	86.6%		
Dolomite	2.2%		
Feldspar	8.2%		
Fines (<2 μ)	3.0%	Chlorite	2.4%
		Illite	0.1%
		α -Quartz	0.5%

No water sensitive clays. Chlorite is iron-rich variety.

(2) Roberts Co., Texas @ 11,000'

α -Quartz	83.6%		
Feldspar	1.1%		
Amorphous	5.2%		
Fines (<2 μ)	10.1%	α -Quartz	6.7%
		Chlorite	3.4%

No water sensitive clays. Chlorite is iron-rich variety.

(3) Ochiltree Co., Texas @ 7940'

α -Quartz	89.1%		
Feldspar	5.7%		
Fines (<2 μ)	5.2%	Chlorite	1.5%
		Kaolinite	1.2%
		Illite	0.7%
		Feldspar	0.2%
		α -Quartz	1.6%

No water sensitive clays other than sloughing Kaolinite. Chlorite is of the iron-rich variety.

(4) Texas Co., Oklahoma @ 6135'

α -Quartz	75.8%		
Feldspar	4.3%		
Dolomite	1.6%		
Amorphous fines	12.8%		
Fines (<2 μ)	5.5%	Kaolinite	2.0%
		Iron Chlorite	0.7%
		Illite	0.9%
		α -Quartz	1.6%
		Feldspar	0.2%
		Dolomite	0.1%

No water sensitive clays. Chlorite is of the iron-rich variety.

(5) Texas Co., Oklahoma @ 6175'

α -Quartz	77.4%		
Feldspar	5.1%		
Dolomite	2.4%		
Amorphous fines	9.9%		
Fines (<2 μ)	5.2%	Kaolinite	1.8%
		Iron Chlorite	1.0%
		Illite	0.4%
		α -Quartz	1.1%
		Feldspar	0.9%

No water swellable clays. Chlorite is of the iron-rich variety.

(6) Blaine Co., Oklahoma @ 7900'

α -Quartz	52.8%
Illite	16.0%
Montmorillonite	11.6%
Iron Chlorite	10.8%
Kaolinite	8.8%

Water sensitive clays are present. Extremely rich in iron chlorite.

(7) Blaine Co., Oklahoma @ 7950'

α -Quartz	84.9%
(Siderite) Iron Carbonate	2.8%
Iron Chlorite	9.4%
Kaolinite	2.9%

Iron compounds are extremely prevalent.

(8) Eddy Co., New Mexico @ 11,400'

α -Quartz	90.7%		
Feldspar	2.0%		
Dolomite	6.0%		
Clay Fines (Amorphous)	1.3%	Kaolinite	0.8%
		Illite	0.2%
		Illite-Montmorillonite	0.1%
		Iron Chlorite	0.2%

(9) Canadian Co., Oklahoma @ 11,000'

α -Quartz	71.2%		
Calcite	3.0%		
Amorphous fines	18.9%		
Fines (<2 μ)	6.9%	Iron Chlorite	2.3%
		Kaolinite	1.5%
		α -Quartz	1.7%
		Calcite	1.4%

Iron oxide hydrate is also a portion of the iron.

(10) Cimarron Co., Oklahoma @ 5600'

α -Quartz	79.2%		
Feldspar	5.1%		
Dolomite	2.4%		
Amorphous fines	8.5%		
Fines (<2 μ)	4.8%	Kaolinite	1.8%
		Iron Chlorite	1.2%
		α -Quartz	0.8%
		Illite	0.5%
		Feldspar	0.3%
		Dolomite	0.2%

was accomplished in the Morrow with a hydroxyalkyl guar material in the weak HCl-HF or with a 15 lb/1000 gal. crosslinked system following a large prepad volume of 3% HCl plus 0.6% HF. The hydroxyalkyl guar was developed from a chemically substituted clean guar with less than 1% residue by weight, and greater tolerance to weak acids for gelation purposes (i.e. 1% - 7 1/2% HCl) than conventional, nonchemically substituted guar. Temperature stabilization may be employed chemically in the deeper Morrow.

LOW SURFACE/INTERFACIAL TENSION

Flow studies in the Morrow have indicated that a variety of fluids (aqueous) can be made more compatible with the Morrow by the use of an ultra-low surface tension agent in the group of compounds known as fluorocarbons. When carried in the proper solvent blend, these materials provide an excellent means to lower aqueous fluid surface tension to 16.5-18.0 dynes/cm from an original surface tension of 72-73 dynes/cm. More important, coreflow tests in the Morrow have shown that fluorochemical surfactants greatly affect the backflow or clean-up flow sequence of the coreflow test. Fluorochemical surfactants also exhibit a low tendency for adsorption as opposed to the highly adsorptive nature of the majority of hydrocarbon surfactants. Ionic charges (cationic, anionic, nonionic) are not the principal consideration when applying a fluorocarbon surfactant solution to a low-permeability, low-porosity sand such as the Morrow. The mechanism for surfactant plateout is physically adsorptive with most hydrocarbon types, but more an electrochemical charging effect with fluorosurfactants, so that the amount of surface-tension reducing efficiency affected is not nearly as great as many nonionic hydrocarbon surfactants.¹

The mechanism which allows faster clean-up from reservoirs which have been treated with aqueous fluids containing a fluorosurfactant, is that of providing a lower interfacial tension between the rock and treating fluid. The surface tension of 17 dynes/cm mentioned earlier will provide an interfacial tension between the Morrow cores tested and 3% HCl plus 0.6% HF of 5.6 dynes/cm. This provides a more efficient means of coverage within the matrix due to improved wettability, plus

allowing for a lower imbibition or fluid-holding tendency. This, in turn, provides a more efficient and more complete recovery mechanism to aid in getting the fluid back from the reservoir after treatment.¹

The properties of fluorocarbon surfactants for use in stimulation fluids are suspected to be many in number, but their development is a recent venture which is still continuing. The proven clean-up help in weak HCl-HF treatments is a beginning; but work is also being done to show fluorosurfactants as corrosion inhibitors, antishwelling agents, and effective synergistically with many other materials such as paraffin dispersants, scale inhibitors and scale converters.

Tabular data are presented to show areas of core study, and the effects of various types of fluid systems from the standpoint of matrix effect. This information is correlated to actual application by a series of case histories which follow. There have not been a large number of these treatments done, since they are done as stimulation treatments to combat suspected problems that conventional treatments such as regular HCl acid or condensate or other aqueous-phased fluids have not dealt with successfully.

The economics of the weak HCl-HF treatment (including the fluorosurfactant, iron sequestering agent and even gelling agent) will run 15-20% higher than most conventional-type treatments. Careful selection of candidates (plus the more efficient clean-up gained by using a nondamaging system of this type in the problem-prone Morrow) has proven more economical due to longer sustained production increases and faster clean-up after treatment, which means getting the well on production and selling gas or oil sooner.

CASE HISTORIES

Treatment A

In the Shreiky Morrow Field of the Texas Panhandle, core studies showed weak HCl-HF mixtures to be an optimum treating fluid in association with a fluorocarbon surfactant. The Morrow (with a porosity of 17.4% and 7.6 md permeability at 11,100 ft) was treated with 6400 gal. of the weak HCl-HF, fluorosurfactant mixture. The well cleaned-up rapidly and made dry gas in two hours and open flow tested at 78 MMCFD.

A direct offset to this well (which has a greater net thickness and more porosity) was treated with Morrow condensate which was shown to cause damage in core tests. After a lengthy period to clean up the well (several days), this well potentialled for 34 MMCFD. The cost here was comparable to the condensate treatment. The production is holding up after several months on the weak HCl-HF treatment, but has declined steadily where the condensate was used.

Treatment B

In the Hansford Upper-Morrow of the Texas Panhandle, core studies in 0.2 md and 7.0% porosity core again showed that low surface tension, weak HCl-HF treatments would be applicable. The Morrow interval to be treated was from 7094-7102 ft. The well was fractured with 35,000 gal. of a low-residue, hydroxyalkyl polymer gelled 3% HCl plus 0.6% HF fluid containing 3 gal. fluorosurfactant per 1000 gal. Mechanical problems caused a two-week delay in beginning load recovery, which according to the operator usually results in the inability to recover any of the treatment load. However, once load recovery was begun, the fluid returned quickly *without swabbing* (other than two initial pulls) to kick the well off. After testing, the well showed 4.4 MMCFD. Offset production that was treated with gelled condensate and gelled 2% KCl water tested for 1-3 MMCFD, on the average.

Treatment C

Another example of the ability of the low surface tension, low concentration HCl-HF combinations to clean up the damage caused by the misuse of another type fluid is in the Morrow sand of the Mocane-Laverne field of Oklahoma at a depth of 6667-6712 ft. The well had been fractured with a gelled KCl water system. Load recovery had been extremely slow and production was low. As noted in the Morrow core studies made from the area, capillary imbibition and migratory fines appeared to cause problems when conventional water surfactants were used. After treatment with 5000 gal. iron-stabilized 3% HCl plus 1.2% HF plus 3 gal. fluorosurfactant per 1000 gal., production was increased by 50%. Three months after treatment, production was still up by 41%, and five months later still 41%.

Summary

The above case histories illustrate not only the formation damage prevention gained by careful fluid design, but also show how existing damage was successfully dealt with utilizing the low surface tension, weak HCl-HF combination treatments with or without the clean hydroxyalkyl guar gelling material, and properly designed iron control.

CONCLUSIONS

The coreflow results exemplified in Table 3 were the premise for recommending or applying stimulation to several Morrow sections in those areas. The weak HCl-HF combinations can be seen to dominate the optimum effectiveness realm in comparison to the other systems tested for matrix flow. This led to implementing these fluid systems into fracturing or acidization designs which were planned to invade the migratory fines there, and either solubilize or reduce the particle size to a colloidal dispersion. This should aid in the ability to return load fluid more effectively. The fluorosurfactant's low surface-tension effect appears to aid the system by allowing it to overcome some of the holding effects in the rock matrix (capillary imbibition). A clean gelling agent is certainly an assumed requirement when proppant carriage with fracturing is desired. A highly efficient gelling additive which is utilized is a member of the hydroxyalkyl guar derivatives, and has shown to be a very clean and very effective viscosifier even in weak acid systems.

Iron control should not be added simply as an insurance factor to guard against the dangers of iron-complex reprecipitation, but rather considered carefully with regard to the amount of iron present in the rock. From 0.2% or greater, quantities of iron within the rock matrix or permeability can cause these problems, and in a sandstone such as the Morrow, iron stabilization or chelation should certainly be considered necessary.

With this test data, it has been determined that fluids of the design types previously discussed can be utilized as either all or portions of stimulation fluid systems. A composition is considered successful where it demonstrates an effectiveness at encountering the matrix without damage, and, in fact, with improvement being the end result. This

TABLE 3—COREFLOW TESTS IN VARIOUS MORROW SECTIONS WITH RESULTS SHOWING IMPROVEMENT (+) OR DAMAGING (-) FOLDS OF PERMEABILITY CHANGE AFTER 100cc TREATMENT AND BACKFLOW.

FLUID TYPES (HS=Hydrocarbon Surfactant) (F.S.=Fluorosurfactant)	(1) Roberts Co., Tx @ 10,000'	(2) Roberts Co., Tx @ 11,000'	(3) Chiltree Co. @ 7940'	(4) Texas Co., Ok @ 6135'	(5) Texas Co., Ok @ 6175'	(6) Blaine Co., Ok @ 7900'	(7) Blaine Co., Ok @ 7950'	(8) Eddy Co., N.M. @ 11,400'	(9) Canadian Co., Tx @ 11,000'	(10) Cimarron Co., Ok @ 5600'
Fresh Water	(-) 1.40	Plugged	Plugged	-----	Plugged	Plugged	(-) 4.29	Plugged	(-) 3.88	Plugged
Fresh Water + F.S.	(-) 0.90	Plugged	(-) 3.88	-----	Plugged	(-) 6.73	(-) 1.76	Plugged	(-) 1.84	(-) 1.16
3% HCl	(-) 2.49	(-) 2.46	-----	(-) 1.15	(-) 1.05	-----	(-) 1.24	Plugged	(+) 3.36	(-) 1.96
3% HCl + F.S.	(+) 1.18	(+) 4.97	(-) 1.12	(-) 1.04	(+) 1.42	-----	(+) 1.68	(-) 2.43	(+) 4.42	(+) 0.81
5% HCl + F.S.	(-) 2.56	-----	(+) 1.09		(+) 2.06	-----	(+) 1.54	(-) 2.04	-----	(-) 1.66
7.5% HCl + H.S.	(+) 1.39	-----	(-) 1.50	(-) 2.46	(+) 2.26	(-) 1.69	(-) 2.54	(+) 10.11	-----	(-) 2.86
7.5% HCl + F.S.	(+) 1.74	-----	(+) 2.03	(-) 1.35	(+) 8.54	(+) 1.06	(-) 1.36	(+) 15.42	-----	(-) 2.19
15% HCl	(-) 2.04	-----	-----	-----	(-) 3.64	(+) 1.16	-----	Plugged	(-) 2.68	-----
3% HCl + 0.6% HF	(+) 2.01	(+) 0.85	-----	(+) 1.42	(+) 1.84	(+) 0.85	(-) 1.03	(+) 3.66	(+) 1.42	(+) 0.85
3% HCl + 0.6% HF + F.S.	(+) 5.07	(+) 1.59	(+) 1.08	(+) 2.33	(+) 2.56	(+) 1.46	(+) 1.47	(+) 24.72	(+) 2.44	(+) 1.84
3-6% HCl + 1.2% HF	(+) 1.16	(+) 1.49	(-) 1.20	(+) 2.04	(+) 2.03	(-) 1.21	(+) 1.21	(+) 5.45	(+) 2.60	(+) 1.45
3-6% HCl + 1.2% HF + F.S.	(+) 2.73	(+) 2.68	(+) 2.70	(+) 2.73	(+) 3.65	(+) 2.27	(+) 2.49	(+) 26.43	(+) 5.05	(+) 3.05
KCl Water (1-2%)	(-) 1.04	0	(-) 2.45	(-) 2.22	Plugged	(-) 1.11	Plugged	Plugged	(-) 2.26	(-) 4.20
KCl Water + F.S.	(+) 1.43	(+) 1.04	(-) 1.16	(+) 1.32	(+) 1.50	(-) 0.64	(+) 1.01	(+) 1.06	(-) 2.03	(-) 2.46
Formation Water	(-) 8.56	-----	-----	-----	Plugged	Plugged	(-) 2.87	Plugged	(-) 1.08	-----
Formation Water + F.S.	(-) 6.24	-----	(-) 2.03	-----	(-) 1.86	(-) 2.56	(-) 1.05	(-) 4.64	(+) 2.04	-----
Formation Condensate	(-) 4.04	-----	(-) 23.58	(-) 1.48	-----	Plugged	(-) 3.46	(-) 2.46	(-) 2.72	-----
Acetic Acid (10%)	-----	(-) 1.44	-----	-----	-----	-----	-----	(-) 2.06	-----	-----
3% HCl + 1% KCl + F.S.	-----	(-) 1.08	-----	(-) 1.08	-----	(+) 1.42	-----	Plugged	-----	(+) 1.42
3% HCl + 1% KCl + HS	-----	(-) 1.65	-----	(-) 1.68	-----	(+) 1.01	-----	Plugged	-----	(-) 1.68
12% HCl + 3% HF	Plugged	Plugged	(-) 1.20	-----	(-) 8.45	Plugged	(+) 1.21	Plugged	Plugged	(+) 2.46
12% HCl + 3% HF + F.S.	-----	-----	(+) 3.62	-----	(-) 3.22	(+) 1.53	-----	(-) 2.64	(-) 1.08	(+) 2.38
Low pH 1% KCl + F.S.	-----	-----	-----	(-) 1.27	-----	-----	-----	(-) 0.85	(+) 1.18	(+) 1.04
Diesel	-----	-----	-----	(-) 1.27	-----	-----	-----	-----	-----	-----

concept has been successfully applied as either the entire fluid or as a prepad ahead of a *clean* and highly efficient fluid. With further investigation, it is hoped that fluid design will be concerned not so much with the complexity of keeping certain elements off the reservoir matrix, but, rather with the benefits gained by designing the most "reservoir-improving" fluid system with reference to chemical and physical compatibility in the Morrow, and in any other "problem" sandstones.

REFERENCES

1. Holcomb, David L.: Low Surface Tension Hydrochloric-Hydrofluoric Acid Mixtures in Low Porosity, Low Permeability Sandstones. SPE 5411 presented at the Okla. City SPE Regional Mtg., Okla. City, Okla., Mar. 24-25, 1975.
2. Smith, C.F.; Crowe, C.W.; Nolan, T.J. III: Secondary Deposition of Iron Compounds Following Acidizing Treatments. *Jour. Petr. Tech.*, Sept. 1969, pp. 1121-1129.

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