A NEW CHEMICAL RETARDER FOR ACID SYSTEMS

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INTRODUCTION

Carbonate formations have been treated with acid for many years to increase fracture length and conductivity and, thereby, stimulate production.

Fracture acidizing of carbonate formations, however, requires consideration of several parameters. One important parameter is the distance acid will penetrate the fracture before completely reacting. This distance is referred to as the acid penetration distance.[1,4] Other parameters include dynamic fracture geometry[5,6] and fracture conductivity.[7,8] Although these three parameters are largely controlled by formation properties, they can be strongly influenced by the treating fluids used and the techniques employed to place these fluids.

Acid penetration distances have been increased to various extents with chemically retarded acids, gelled acids, emulsified acids and acid systems composed of hydrochloric, acetic and/or formic acids.

A new chemical retarder has been developed which can be used with emulsified and non-emulsified acids to help increase acid penetration into fractured limestone formations.

The unique chemical retarder is chemically and physically adsorbed on the formation where it slows the reaction rate of acid. Besides retarding the acid-limestone reaction effectively, adsorption also appears strong enough to withstand turbulent flow.

Although a retarder may greatly increase penetration distance, other parameters, such as fracture conductivity, also have to be considered if the retarder is to be used. For example, during a retarded acid treatment inadequate fracture conductivity may result if fracture cooling causes over retardation of the acid near the wellbore.

Placement techniques are in use, however, that could resolve this problem. During treatment, a less retarded acid can be injected before the retarded acid for better conductivity near the wellbore, and the density of preflush can be balanced with the density of partially spent acid for better acid distribution along the fracture face.

This paper will discuss the laboratory evaluation of the new retarder's effect on acid penetration distances and reaction times with non-emulsified and emulsified 15% HCl, 20% HCl, 28% HCl and a 7-1/2% HCl-10% formic acid mixture.

Also to be discussed, are acid placement techniques used recently in twenty one Mexican wells with the new retarder. Results of these techniques thus far are also listed.

LABORATORY EVALUATION

Determining Acid Penetration Distance

Acid penetration distances are based on laboratory measurements using the rotating disc apparatus and procedure.[2] This apparatus is important to simulate dynamic conditions in a fracture. Note: Roberts and Guin[3], Williams and Nierode[4] have shown that mass transport as well as acid reaction rate is important in determining penetration distance in the fracture. That is, a twofold increase in retardation does not necessarily indicate a twofold increase in acid penetration distance.

The rotating disc apparatus and procedure was used to react acid on limestone cores under dynamic conditions at 1000 psi and various temperatures. The reacted acid solutions were then analyzed for calcium concentration to determine the amount of limestone that dissolved in five minutes.

Data showing the amount of limestone dissolved were used in a computer program to determine the reaction rate constant and reaction order.

A second computer program that utilizes these final reaction data, plus hypothetical fracturing treatment data, was used to calculate acid penetration distance. For the fracturing treatment data we assumed a fracture height of 100 ft, width of 0.25-in., pump rate of 20 BPM and zero leakoff. Note that by using zero leakoff, leakoff was eliminated as a variable. As a result, the penetration distance was solely dependent on the reaction rate of the acid solutions.

Data - Retarder's Effect on Penetration Distance

The effect of the new chemical retarder on the penetration distance of 15% HCl is shown in Table 1. Notice that 1.0% (vol %) retarder increased the acid penetration distance by threefold at 200°F and 1.9-fold at 300°F.

TABLE 1—EFFECT OF CHEMICAL RETARDER ON ACID PENETRATION DISTANCE OF 15% HCL

Injection Rate --------------- 20 BPM
Fracture Width --------------- 0.25 in.
Fracture Height -------------- 100 ft
Leakoff ---------------------- 0
Formation -------------------- Bedford Limestone
Reaction Test Procedure ------ Rotating Disc

Formation Temperature (°F)	Acid Penetration Distance - Feet		
	No Retarder	0.15% Retarder	1.0% Retarder
200	128	246	395
250	92	114	180
300	74	86	138

Rotating disc apparatus was also used to conduct similar tests but with 7 1/2% HCl-10% formic acid, which has the same carbonate dissolving capacity as 15% HCl. The effect of chemical retarder on this system is shown in Table 2. Notice in Table 2 that the 1.0% retarder increased the acid penetration distance of 7 1/2% HCl-10% formic acid by 6.7-fold at 200°F and by 2.95-fold at 300°F.

TABLE 2—EFFECT OF CHEMICAL RETARDER ON ACID PENETRATION DISTANCE OF 7½% HCL-10% FORMIC ACID

Injection Rate --------------- 20 BPM
Fracture Width --------------- 0.25 in.
Fracture Height -------------- 100 ft
Leakoff ---------------------- 0
Formation -------------------- Bedford Limestone
Reaction Test Procedure ------ Rotating Disc

Formation Temperature (°F)	Acid Penetration Distance - Feet		
	No Retarder	0.15% Retarder	1.0% Retarder
200	300	940	2010
250	116	264	645
300	76	114	224

By comparing the data in Tables 1 and 2, one can readly see that longer penetration distance is achieved using the new retarder with the HCl-formic acid mixture.

Data - Effect of Variables on Reaction Time

Reaction measurements were also made using static test equipment. Static reaction data are valid for studying the effect of variables (various acid mixture concentrations, non-emulsified vs emulsified acid mixtures, oil producing vs gas producing formations and various single acid concentrations). However, static reaction measurements are not necessarily valid for making direct acid penetration comparisons in fractures.

Tests were conducted at 1500 psi with Bedford limestone cores having a 1 3/4-in. diameter and 2 3/4-in. length. This provided an acid-surface area ratio equivalent to a 0.25-in. fracture.

Cores were pre-heated in kerosene to simulate an oil producing formation; cores were also heated dry (no liquid hydrocarbon) under 1000 psi N_2 pressure to simulate a dry gas producing formation.

A series of tests were performed. Each test was terminated at a different time to find the residual or unreacted acid concentration. The residual acid concentrations were titrated using phenolphthalein indicator and 0.2 normal sodium hydroxide. They were then plotted on graphs as percent residual acid versus time.

Figs. 1, 2, 3, 4 and 5 show this reaction time information. The "reaction time" in the figures is the time required for the acid to react and leave a residual acid concentration of 3.2%. The reaction time is shown at various temperatures when using various concentrations of chemical retarder. All concentrations shown are by volume.

Fig. 1 contains static reaction time data. Shown are the reaction times vs temperatures with 15% HCl. Notice that the data indicate reaction time is almost proportional to retarder concentration. Reaction times at 250°F ranged from 98 min with 0.3% retarder to 230 min with 1.0% retarder.

Fig. 2 shows similar data using 20% HCl. Reaction times at 250°F ranged from 80 min with 0.3% retarder to 110 min with 1.0% retarder.

Fig. 3 shows similar data using 28% HCl. Notice the reaction time is almost proportional to retarder concentrations and decreases rapidly as the temperature is increased. Reaction times at 250°F ranged from about 55 minutes with 0.3% retarder to about 80 min with 1.0% retarder.

Figs. 4, 5 and 6 show data obtained from the static reaction measurement procedure at various temperatures and retarder concentrations when using emulsified 15%, 20% and 28% HCl.

Fig. 4 shows the static reaction time data of emulsified 15% HCl. Reaction times at 250°F range from 65 min with 0.3% retarder to 270 min with 1.0% retarder.

Fig. 5 shows reaction times with emulsified 20% HCl. Reaction times at 250°F range from 55 minutes with 0.3% retarder to 220 min with 1.0% retarder.

Fig. 6 shows reaction times with emulsified 28% HCl. Reaction times at 250°F range from 48 min with 0.5% retarder to 102 min with 1.0% retarder.

Reaction Time With Non-Emulsified and Emulsified HCl-Formic Acid Mixture - Static reaction measurements were conducted to determine the effect of chemical retarder on the reaction time of non-emulsified and emulsified 7-1/2% HCl-10% formic acid when reacted on a simulated oil producing limestone formation. This HCl-formic blend has an acid content equivalent to 15% HCl.

Fig. 7 data indicate that the chemical retarder retards the HCl-formic acid mixture more effectively than an equivalent concentration of HCl (15%). Data also indicate 0.5% chemical retarder retards the HCl-formic acid mixture almost as effectively as 1.0% retarder. However, 0.5% retarder is much more effective than 0.3% retarder. Reaction times using 0.5% chemical retarder ranged from about 1000 minutes at 215°F to 100 min at 350°F.

Fig. 8 shows data from static reaction measurements with emulsified 7-1/2% HCl-10% formic acid.

In comparing the data in Figs. 7 and 8 the emulsified HCl-formic acid mixtures provided longer reaction time than non-emulsified HCl-formic acid at the higher temperature. Reaction times using 0.5% retarder in the emulsified HCl-formic acid mixture ranged from about 1000 min at 215°F to about 160 min at 350°F. An added benefit of the emulsified system, however, might be its higher initial viscosity. This viscosity might provide an advantage by creating a wider fracture and decreasing acid leak-off.

Reaction Times Under Dry Gas Well Conditions - Static reaction measurements were conducted with the chemically retarded 7-1/2% HCl-10% formic acid mixture to determine if the retarder would extend reaction times under conditions simulating a dry gas well. The cores in these tests were pre-heated dry (no contact with liquid hydrocarbon) under 1000 psi N_2 pressure.

Fig. 9 data indicate that 1.0% chemical retarder in 7-1/2% HCl-10% formic acid will provide reaction times that range from 70 min at 200°F to 25 min at 400°F. Retarded 15% HCl provided about the same reaction time as unretarded 15% HCl. It ranged from 11 min at 200°F to about 4 min at 400°F.

OTHER CONSIDERATIONS FOR TREATMENT

The acid penetration distance is one parameter for fracture acidizing carbonate formations we have been considering so far. However, there are other parameters to consider. One of these is fracture conductivity.

Effect of Fracture Cooling on Conductivity

Injecting large volumes of fluids into oil producing formations may result in fracture cooling. This cooling, resulting in a lower temperature than expected at a certain distance from the wellbore, can occur as far as 200-300 ft into the fracture as shown in Table 3.

TABLE 3—FRACTURE COOLING DUE TO FLUID INJECTION

Brine Temperature -------- 75°F
Brine Volume ------------- 30,000 gal
Injection Rate ----------- 20 BPM
Fracture Height ---------- 100 ft
Fracture Width ----------- 0.30 in.
BHST --------------------- 240°F

Distance from Wellbore (ft)	Fracture Temperature (°F)
0	100
100	158
200	193
300	213
400	228
500	240

When the concentration of retarder in the fluid is based on static bottomhole temperature, this cooling may cause excessive acid retardation.

This excessively slow acid reaction in the cooled area may result in such small quantities of rock dissolution that inadequate fracture conductivity is developed. Meanwhile, in the heated area of the fracture the acid will continue to react, creating conductivity farther from the wellbore.

To achieve adequate fracture flow conductivity in the cooled area near the wellbore a stage of less retarded acid, perhaps unretarded acid, equal to about 25 to 35% of the total acid volume, should be pumped initially. The retarded acid could then be pumped to develop fracture flow capacity farther from the wellbore.

Thus, in light of the foregoing, a treatment design should include consideration of acid penetration distance <u>and</u> fracture flow capacity. It should be emphasized that excessive retardation does not prevent the acid from reacting, but extends the reaction over a greater area of rock surface if acid displacement continues.

TREATMENT DESIGN FOR BETTER CONDUCTIVITY

Two techniques have been used to control placement of acid fluids in fracture systems for better distribution and development of fracture conductivity. These techniques involve the control of fluid viscosity and fluid density. The importance of controlling these properties has been previously reported by Broaddus[9] and Fredrickson and Broaddus[10].

Controlling Viscosity

A viscous preflush ahead of a non-viscous acid stage can produce channeling of acid through the viscous preflush and develop extremely high fracture flow capacities. Minimum channeling will occur if the viscous preflush has a viscosity of 100 centipoise. Most effective channeling should occur with viscosities ranging from 800 to 1200 centipoise at bottomhole conditions.

Controlling Density

When treating long sections and using low density preflushes there is a tendency for acid to flow downward and not evenly along fracture faces. This tendency is intensified during injection because the acid density increases as it reacts with the rock.

More even distribution of acid across the fracture face can thus be induced by balancing the density of preflush with the density of partially spent acid.

Fluid Placement

The following sequence of fluid placement should be considered when treating high temperature formations with acid.

(1) Low viscosity preflush (creates the initial fracture)
(2) High viscosity preflush
(3) Unretarded acid
(4) Retarded acid
(5) Non-acid flush

When treating multiple intervals, the same five-step fluid sequence should be used on each interval with a diverting stage between. This approach has been used to treat wells completed in the Cretaceous of Southern Mexico

SUMMARY OF TREATMENTS

Data was obtained from 21 well treating operations conducted in the Cretaceous formation of Southern Mexico. The wells were treated following the basic technique outlined under "Treatment Design for Better Conductivity". One to four zones were treated in each well using emulsified acid or gelled water as the high viscosity fluid and 7 1/2% HCl-10% formic acid or 15% HCl as the retarded acid system.

Data from these 21 treating operations are presented in Table 4.

Jobs 1, 2, and 3 were conducted with emulsified 15% HCl preceding 7 1/2% HCl-10% formic acid with the new chemical retarder. Job 1 was the first actual job conducted with the new chemical retarder: a high concentration was used. This concentration was decreased, however, for jobs 2 and 3. The low increase in production listed in Table 4 for job one, indicates over-retardation may have occurred near the wellbore.

Jobs 4, 5, 6, 7, 8, and 9 were conducted using emulsified 15% HCl ahead of retarded and unretarded stages of 15% HCl.

The remaining jobs were conducted with gelled water as the viscous stage ahead of both acid stages. This was of benefit. The average production increase was 44% greater when the viscous gel, rather than viscous emulsion, preceded the non-viscous acid stages.

Jobs 5, 6, 11, 12, 17, 18 and 20 were conducted by pumping a viscous stage, a stage of unretarded 15% HCl, and then the chemically retarded acid.

Jobs 4, 7, 8, 9, 10, 13, 14, 15, 16, 19, and 21 were conducted by pumping the viscous stage, chemically retarded acid stage and unretarded acid stage in that order.

In comparing jobs 4-21, data indicate that production stimulation was 82% greater when the unretarded acid was pumped ahead of rather than behind the retarded acid. This production increase indicates the unretarded acid was reacting swiftly, creating larger flow capacity near the wellbore. So, fracture flow capacity should be developed near the wellbore prior to the introduction of acid containing the new chemical retarder.

Jobs 10, 18, and 20 were conducted using density controlled stages ahead of the acid stages. These jobs provided 230%, 400% and 540% increase in production, respectively. This is a 390% average increase in production while the average production increase for the other 18 jobs was 169%.

TABLE 4—JOB RESULTS

		Flowing Production (BOPD)		Gas-Oil Ratio
Job No.	Formation Temperature (°F)	Before Treatment	After Treatment	After Treatment
1	245	2700	2900	138
2	245	6000	12169	138
3	245	2300	6853	1300
4	225	863	756	156
5	260	2500	2898	325
6	280	576	1080	994
7	280	2992	3011	214
8	280	0	0	--
9	315	1207	3124	388
10	350	1266	2898	304
11	220	1984	3276	100
12	230	1500	1764	320
13	240	0	0	--
14	245	7610	16543	110
15	250	0	0	--
16	260	1858	3188	298
17	275	6539	7214	234
18	280	1260	5014	500
19	280	2992	3011	214
20	285	756	4057	289
21	290	1512	3232	190

CONCLUSIONS

1. Laboratory data indicate a 1.9 to 3.0-fold increase of the acid penetration distance can be expected when 15% HCl is treated with chemical retarder.

2. Laboratory data indicate a 2.95 to 6.7-fold increase of the acid penetration distance can be expected when the 7-1/2% HCl-10% formic acid mixture is treated with chemical retarder.

3. Laboratory data indicate the chemical retarder retards the reaction of the 7-1/2% HCl-10% formic acid mixture on limestone under simulated dry gas well conditions.

4. Laboratory tests with rotating disc apparatus indicate the chemical retarder effectively retards the acid-limestone reaction under dynamic conditions.

5. Field results indicate the chemical retarder retards the acid-limestone reaction effectively under dynamic conditions in the formation at pump rates up to 30 BPM, the highest pump rate used for the Mexican wells described in this paper.

6. Field results indicate that viscous gel used as a high viscosity preflush provided more effective stimulation than a preflush composed of viscous emulsion.

7. Field results indicate an initial stage of unretarded acid should be followed by a stage of retarded acid. This will achieve adequate fracture flow capacity near the wellbore and improve fracture flow capacity away from the wellbore.

8. Field results indicate stimulation may be even further enhanced by using density controlled stages ahead of the acid.

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TABLE 1—EFFECT OF CHEMICAL RETARDER ON ACID PENETRATION DISTANCE OF 15% HCL

Formation Temp. (°F)	Acid Penetration Distance Ft. No Retarder	0.15% Retarder	1.0% Retarder
200	128	246	395
250	92	114	180
300	74	86	138

TABLE 2—EFFECT OF CHEMICAL RETARDER ON ACID PENETRATION DISTANCE OF 7½% HCL - 10% FORMIC ACID

Formation Temp. (°F)	Acid Penetration Distance Ft. No Retarder	0.15% Retarder	1.0% Retarder
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300	76	114	224

Table 3

TABLE 3—FRACTURE COOLING DUE TO FLUID INJECTION

Brine Volume ---------------------------- 30,000 gal
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Fracture Width ------------------------- 0.30 inch
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Distance from Wellbore (ft)	Fracture Temperature (°F)
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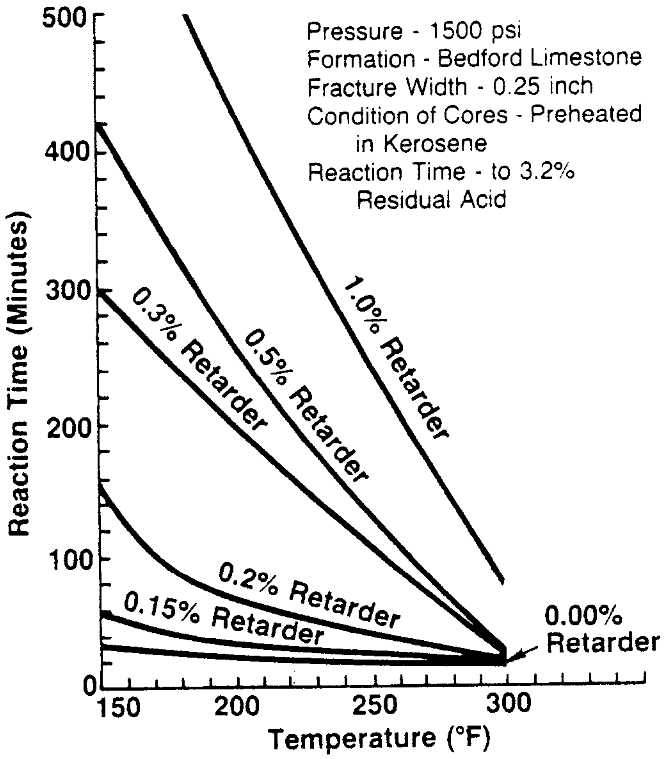

FIGURE 1—REACTION TIMES OF 15% HCL CONTAINING RETARDER

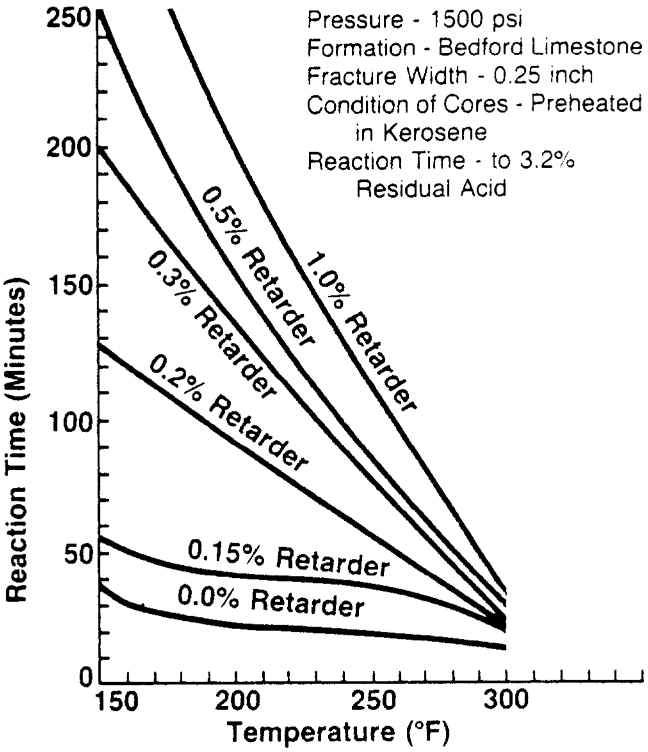

FIGURE 2—REACTION TIMES OF 20% HCL CONTAINING RETARDER

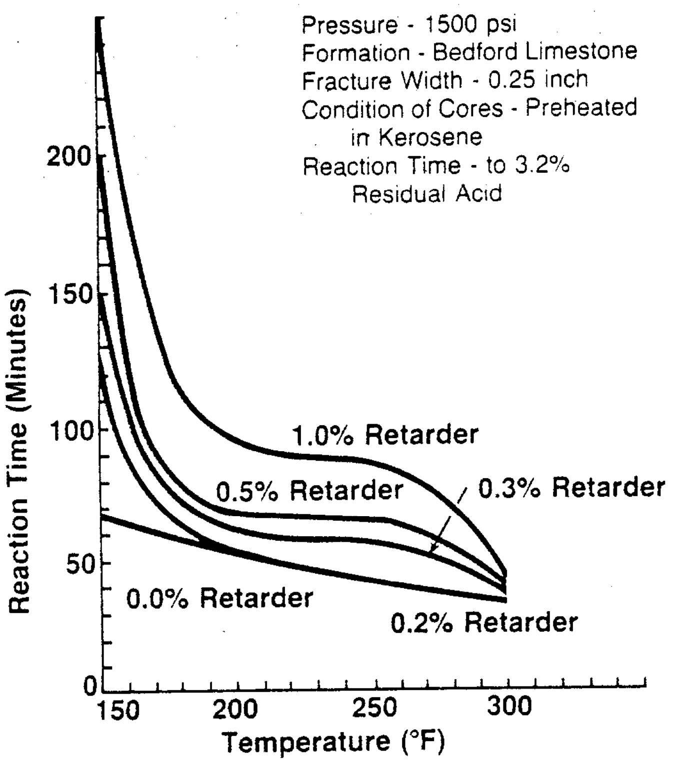

FIGURE 3—REACTION TIMES OF 28% HCL CONTAINING RETARDER

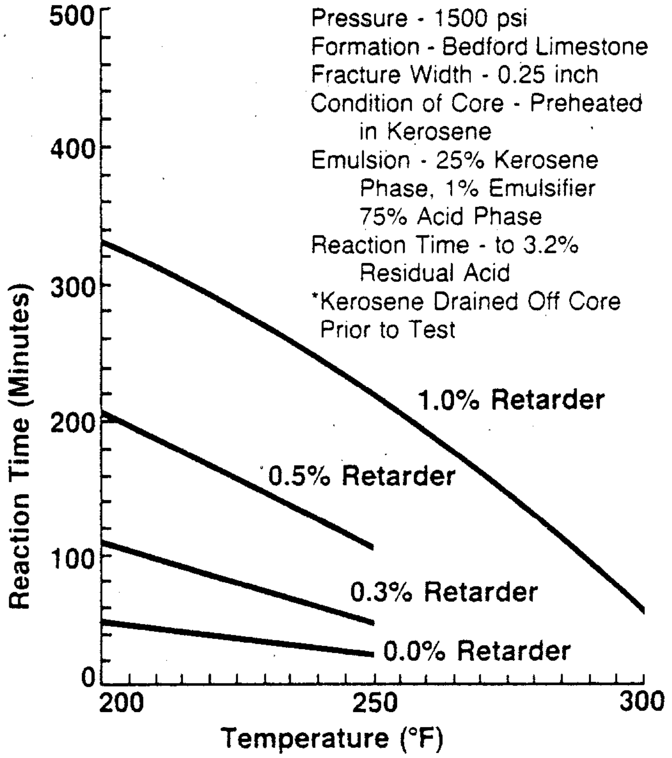

FIGURE 5—REACTION TIMES OF EMULSIFIED 20% HCL CONTAINING RETARDER

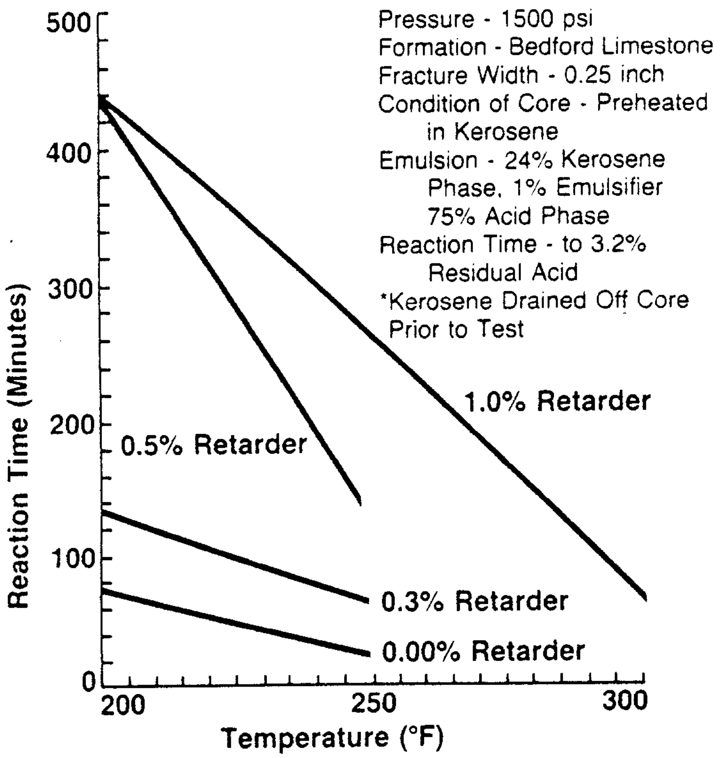

FIGURE 4—REACTION TIMES OF EMULSIFIED 15% HCL CONTAINING RETARDER

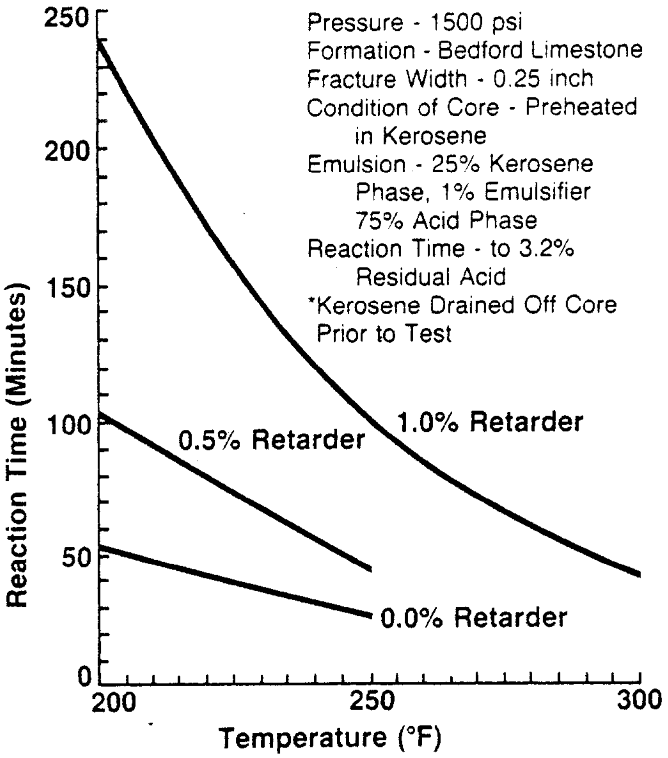

FIGURE 6—REACTION TIMES OF EMULSIFIED 28% HCL CONTAINING RETARDER

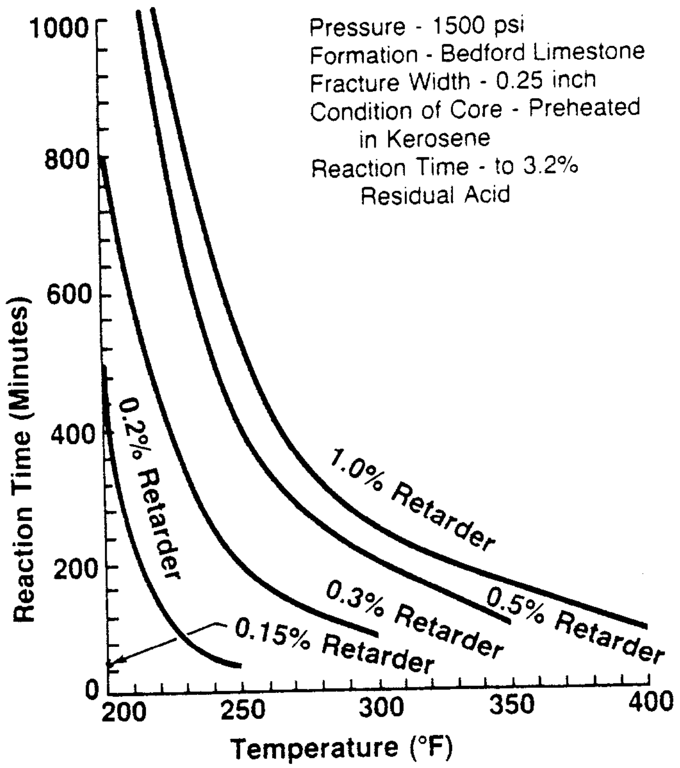

FIGURE 7—REACTION TIMES OF 7½% HCL-10% FORMIC CONTAINING RETARDER

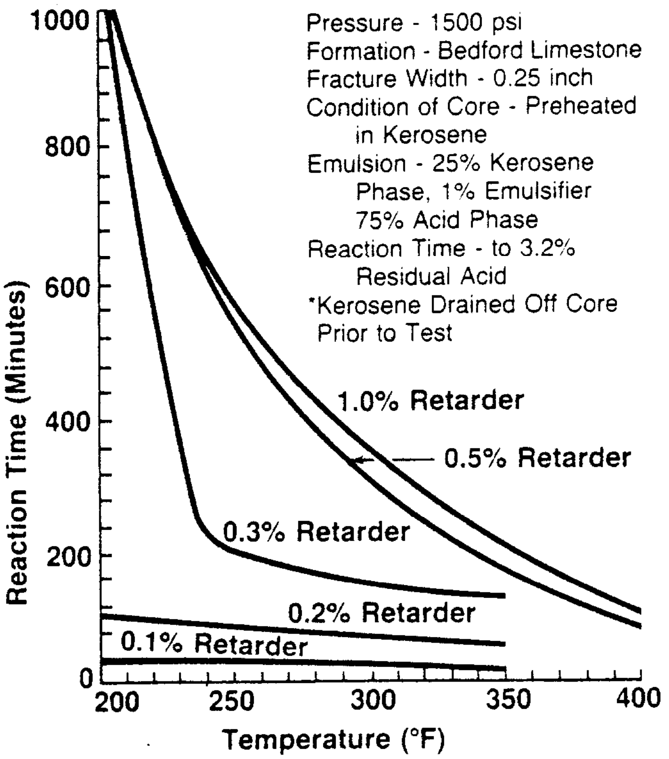

FIGURE 8—REACTION TIMES OF EMULSIFIED 7½% HCL-10% FORMIC CONTAINING RETARDER

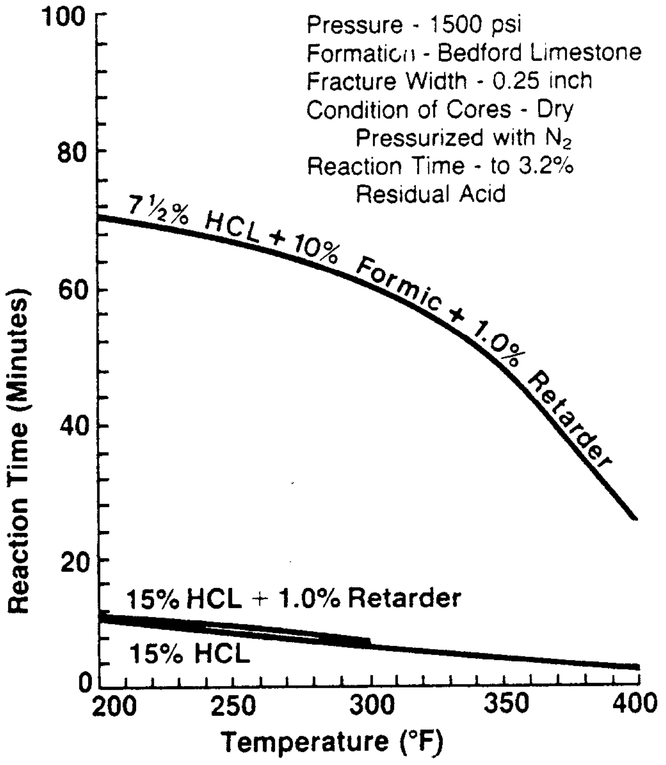

FIGURE 9—REACTION TIME TESTS SIMULATING DRY GAS WELLS