INTERACTIONS BETWEEN FRACTURING FLUID ADDITIVES AND CURRENTLY USED ENZYME BREAKERS

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Abstract

Advances in enzyme technology and its application to hydraulic fracturing have brought enzyme breakers from low-temperature, low-pH applications to being used over a wide range of temperatures, pH's and fluid systems. Their potential as fracturing fluid breakers seems almost limitless as one obstacle after another has been swept away by advances in biotechnology. High-temperature enzymes, high-pH enzymes and controlled release enzymes have contributed to their widespread use as fracturing fluid breakers. Advantages of enzyme breakers over conventional oxidative breakers has been well documented. For example, oxidative breakers have many limitations including interferences and incompatibilities with other fracturing fluid additives.

Enzyme breakers, too, have limitations including interferences and incompatibilities with other additives. Ignorance of these interactions can have dramatic effects on the success of a hydraulic fracturing job. With the new advances in enzyme applications, it is not always easy to keep abreast of the limitations of the new enzyme breakers. Interactions known for other enzymes are often just assumed to apply to new enzyme breakers. This is not always the case. Use of enzyme breakers under more extreme pH and temperature conditions can also cause or magnify interactions. This paper covers interactions between currently used enzyme breakers and fracturing fluid additives including biocides, clay stabilizers, and certain types of resin-coated proppants.

Introduction

For decades enzymes have had limited usefulness as fracturing fluid breakers. The enzyme breakers commonly used for years were only effective under low-pH, low-temperature conditions.[1,2]

In the early 1990s, however, things changed. Over the span of a few years, several new enzyme breakers were introduced. Controlled release enzymes were developed which were effective under conditions where the neat enzyme could not be used [3,4] (in higher pH fluids, for example). New enzymes which were effective at high pH [5,6] with no additional protection were beginning to be applied in borate fluids. Enzyme breakers were even finding application at temperatures previously not thought possible.[7]

Many advantages of enzyme breakers have been claimed, including increased conductivity[8], increased well productivity[9], minimal interference from resin-coated proppants[10], and capacity to break guar polymer long after oxidative breakers have lost their effectiveness.[11]

Along with the increased use of enzyme breakers comes a need for more information on how to use them most effectively. Although seemingly ideal as universal breakers, enzymes do have some limitations.

Enzyme Chemistry & Mechanisms

Enzymes are very efficient protein catalysts.[12] A catalyst enhances the rate of a reaction, but is not changed or consumed by the reaction.[13] After the cleavage of the polymer linkage has occurred, the enzyme is again available to cleave another site. Enzymes' catalysis is more substrate specific than normal catalysts. Enzyme initiated reactions continue at a very rapid rate. Because enzyme breakers work only on specific polymer linkages, they do not generally reduce the effectiveness of additives directly, as oxidative breakers can. If an additive has a significant affinity for amino functionalities or other sites on the enzyme it is theoretically possible that the additive could bind irreversibly to the enzyme and, therefore, not be available to perform. One indication that an additive might have such an affinity for proteins is if it has a significant negative impact on amine-based surfactants or clay stabilizers. If this problem is noticed, interaction between the additive and an enzyme breaker is somewhat likely. Manufacturers of enzyme breakers dilute the enzyme protein in a water solution or on an inert carrier to achieve a specific activity. The neat enzymes are too potent to be used without significant dilution. Because of the small amount of protein actually contained in the enzyme breaker, the protein-additive combination should not significantly affect the additive's performance. The focus, therefore, in studying enzyme breaker/fracturing fluid additive interactions will be primarily on the influence of the additive on the activity of the enzyme.

Because enzymes are proteins, they have different properties and interactions with fracturing fluid additives than oxidative breakers. Proteins are composed of amino acids connected through peptide linkages.[14] The order of the amino acids in this protein chain is called the primary structure. The secondary structure of an enzyme is the coil a protein forms, called an A-helix, as well as variations from this helix due to direct interactions of peptide groups in this chain. Hydrogen bonding between carbonyl and amino groups within the peptide bonds and disulfide bonds contribute to the secondary structure of the protein. Proteins also have a tertiary structure, the way in which the A-helix is twisted and folded due to weak interactions between specific residue side chains (primarily due to hydrogen bonding). The secondary and tertiary structure combine to provide the three-dimensional arrangement of the enzyme and its active site. The configuration of the three dimensional active site determines which substrate(s) the enzyme can bind with and which reactions it can catalyze. If the interactions are causing the secondary and tertiary structure to be sufficiently disrupted, the enzyme cannot function properly. Denaturing an enzyme is disrupting the primary, secondary or tertiary structure of an enzyme so that it can no longer function.

Temperature, pH, salt content and some types of chemicals can influence enzyme activity. Enzymes can be inactivated (or denatured) by irreversible chemical reactions which modify a functional group which is required for the enzyme to function. Normally this modified functional group would be an integral part of the active site on the enzyme. Chemicals which can affect sulfur-containing groups, for example heavy metal ions, can inhibit enzymes. Hg^{2+}, Pb^{2+}, and Cd^{2+} bind to sulfhydryl groups (-SH) and methylthioether groups ($-SCH_3$).[12] Sulfhydryl groups are found in cysteine amino acids and methylthioether groups are found in methionine amino acids. Enzyme active sites frequently contain cysteine.

Enzymes can also be reversibly inhibited. Competitive inhibitors usually resemble the substrate and can combine with the active site. This type of inhibition is more significant as substrate concentration decreases. In other words, initial viscosity degradation may not be significantly changed, but as the concentration of polymer decreases, the competitive inhibitor becomes more effective at tying up the

enzyme. Noncompetitive inhibitors bind to a site other than the active site. They influence the orientation of the active site thereby affecting the enzyme's catalytic ability.

Guar is a nonionic polysaccharide composed of a ß-1,4-linked mannan backbone with D-galactose branches attached via A-1,6 linkages. Oxidative breakers form free radicals which can attack the guar at any oxidizable site whether the reaction results in viscosity degradation or not. Oxidative breakers can also react with other oxidizable substances such as equipment, the formation or other fracturing additives. Enzyme breakers attack specific linkages in the guar polymer. Some fracturing fluid additives can influence enzyme activity by the various mechanisms mentioned above. Variation in fluid formulations and field conditions can possibly produce results different from those expected. It can be difficult to determine which type of inhibition is occurring. Information from research laboratory testing can guide job proposals by pointing out potential incompatibilities, but only pre-job break testing can determine if the combination of fracturing fluid additives, water contaminants and enzyme breakers will produce the desired result. Previous results in the same field should also be considered because effects of formation materials, bottomhole pressure, etc. are difficult to evaluate in a field laboratory before a job.

Some compounds may affect the stability of the enzyme. The rate at which the enzyme works may be influenced by changes a chemical makes which influence the ease at which a substrate, in this case guar, can combine with the enzyme. Chemicals may affect the rate at which the enzyme/substrate complex releases product. Enzymes which have a narrow temperature range can be denatured by extremes of heat. In other words, the effect on the enzyme can be significant enough that the enzyme cannot renature (return to an effective configuration). Some additives can temporarily render an enzyme inactive without denaturing it. An example of this is the pH effect wherein an enzyme can be pumped downhole at a pH where the enzyme demonstrates little activity, but then begins breaking the fluid as its pH changes. This situation has been taken advantage of in the slowly hydrolyzable ester/enzyme combination.[15] One important feature about enzymes is that the loading influences only the rate at which the break occurs, not the final degree of break. Therefore, if some of the enzyme is inactivated and some is still active, the gel will still break but at a slower rate. To achieve the same break time or to ensure some enzyme is still active, enzyme loadings can be increased.

Characteristics of Enzymes Studied

Enzyme Breaker A

Enzyme breaker A is a guar-linkage-specific enzyme which can be used in fluids from pH 3 to pH 11 and at temperatures up to about 300°F.[7,16] This breaker is a specially designed system of two complementary polymer linkage-specific enzymes and is composed of a specific ratio of an endo-1,4-ß-mannosidase and an A-1,6-galactosidase which can obtain a very efficient break for guar-based fluids. In order to prevent potential irreversible inhibition due to interference from other enzymes and thereby achieve the most complete break possible, no significant amounts of other hydrolases are contained in this breaker.

Enzyme Breaker B

Enzyme breaker B is a mixture of hydrolase enzymes effective at low temperatures, not higher than 140°F, and high pH (pH 5 to pH 11).[5] It retains 20% of its activity at pH 11, and thus is not as dependent as other enzymes on formation fluids to lower the pH or higher breaker loadings to compensate for higher pHs. This breaker is also effective on cellulose derivative fluids often used for gravel packing.

Enzyme Breaker C

Enzyme breaker C is a conventional non-isolated, non-purified mixture of various hydrolase enzymes[7]. It is effective at temperatures up to approximately 140°F, and at pH 3 to pH 8. This breaker is typical of the fracturing fluid enzyme breakers used prior to 1990. This breaker is effective on cellulose derivative fluids often used for gravel packing and starches used for fluid loss control.

Interactions between Biocides and Enzyme Breakers

Static Break Test Procedure - Linear Gel

Linear gel was prepared using heavy-duty laboratory stirrer with Tomball tap water and 2% KCl. After gel was fully hydrated and pH was adjusted to 7.0, the fracturing fluid additive was added and stirred 15-30 seconds to disperse. Then the enzyme breaker was added. Tests were run in a 100°F water bath unless otherwise noted. Viscosities were measured using a Fann 35 (R1B1) at 300 RPM. Viscosity of blank (with enzyme breaker alone) and sample containing both enzyme breaker and fluid additive were compared after the specified time interval. Neutral pH was selected because all three enzymes are active at that pH.

Biocide/Enzyme Water Solution Compatibility Test

Another test was run with Enzyme A in water containing normal loadings of enzyme and each biocide. These solutions were left overnight to determine if over a significant period of time the biocides could affect the enzyme's ability to continue breaking the gel. Enzyme A was tested because it has the widest applicability. Enzymes B and C may have produced different results. This enzyme-containing water was then used to attempt hydration of a 40-lb guar/1000-gal gel. A water solution containing enzyme alone will result in slight increase in viscosity for the first 10 minutes and gel degradation thereafter. If the gel viscosity did not begin decreasing within the first 15 to 30 minutes, the biocide was determined to have had negative impact on the enzyme's ability to break the gel. Biocides may take some time to work on bacteria contaminating a frac tank, so it was thought possible that although initial activity may not be retarded and the predicted short-term break might be achieved, the ability of the enzyme to continue breaking gel over a longer period of time may be compromised. Final cleanup of the well may not be as complete as possible. Any effect seen in this test is likely to be more extreme than that which would occur in a fracturing fluid, because the enzyme did not have the stabilizing influence of the guar and other stabilizing additives.

Biocides are an important fracturing fluid additive. Biocides are used to prevent gel biodegradation in frac tanks which is caused by enzymes produced by bacteria.[1] Concern has been generated that biocides might also interfere with enzymes intentionally introduced into the gel as gel breakers.

Biocides are also used to prevent the growth of anaerobic bacteria in the formation. Results of linear break tests are summarized in Table 1. Results of the overnight compatibility tests are found in Table 2. Discussion of the specific biocides follows:

I) Glutaraldehyde-Based Biocide

A glutaraldehyde-based biocide was tested for compatibility with the three enzyme breakers. Glutaraldehyde is a protein crosslinker. It modifies proteins via alkylation of amino and sulfhydryl (or thiol) groups.[17] As mentioned earlier, enzymes are protein-based. Because glutaraldehyde is a protein crosslinker and reacts with amino groups, products with amino functionality such as enzyme breakers, amine-based clay stabilizers or surfactants could potentially interact with the glutaraldehyde-based biocide, thereby reducing either product's effectiveness. Crosslinking a protein may destroy its effectiveness, increase its stability, or reduce accessibility of the substrate to the enzyme (thereby reducing initial activity).[18] Glutaraldehyde did not adversely affect enzyme activity in this test.

It is possible that a glutaraldehyde-based biocide could adversely affect an enzyme breaker's activity if used under conditions different from those tested. The reaction of aldehydes with primary amines is pH dependent and might result in a more significant effect of glutaraldehyde on enzyme breakers at lower pH. The results obtained and outlined in Table 1 and Table 2 demonstrate that glutaraldehyde does not significantly interfere with enzyme breakers under the conditions tested.

II) Isothiazoline-Based Biocide

An isothiazoline-based biocide was also tested for compatibility with the enzyme breakers. It was thought there would be little interference from this biocide because it has been frequently used with enzyme breakers. It acts on the bacterial cell wall not the enzymes produced by the bacteria. The expected results were obtained (Table 1).

III) Thiocyanate-Based Biocide

A thiocyanate-based biocide was tested also. Loadings of this biocide required for fracturing fluid protection are very low. Although it is a very effective biocide, it did not adversely influence the enzyme breakers' activities in this testing (Table 1).

IV) Bromine-Based Biocide

A bromine-based biocide was also tested. The only potentially significant difference in viscosity degradation achieved was for the conventional enzyme, Enzyme C. The increased activity of the enzyme was most likely attributable to the decrease in pH of the gel produced by the biocide. This biocide is primarily recommended for low pH and neutral applications. The overnight water solution compatibility test produced interesting results. It appears that given sufficient time to interact with the enzyme, the biocide can interfere with its activity (Table 2).

When interactions between biocides and enzyme breakers are observed, it should be kept in mind that oxidative breakers can also interact with additives. Oxidative breakers form free radicals which can interact with any available oxidizable substance. Biocides, being more highly reactive than guar, may be preferentially acted upon by the oxidative breakers.

Clay Stabilizers

Static Break Test - Linear Gel

A static break test was run in 40-lb guar gel in 2% KCl, similar to the test run for biocide compatibility. Test results are found in Table 3. Results of a linear hydroxypropyl guar test with no KCl showing the effect of clay stabilizers on ammonium persulfate are included in Table 4 for comparison.

Fann 50 Test

These tests were run at 100°F on a Fann 50 viscometer (R1B1) at 100^{s-1} to compare effect on enzyme A of a tetramethylammonium chloride clay treater versus 2% KCl (Table 5).

Some clay stabilizers include modified polyamines and cationic polymeric clay stabilizers. Clay stabilizers are cationic. The cations are attracted to the cationic exchange sites of the clays and attach to the clays coating them and protecting them from reacting with other ions that may result in swelling or migration. Clay stabilizers adsorb onto silicates and deplete the solution of clay compatibility. A clay treater such as potassium chloride must be used with in addition to a clay stabilizer.[19]

A clay treater does not adsorb onto the formation but remains in solution. Potassium chloride, ammonium chloride and tetramethyl ammonium chloride can be used as clay treaters to prevent the dispersion of clay particles. Enzymes can be sensitive to salts used as clay treaters. Enzyme B demonstrates a 17% decrease in activity with 2% potassium chloride while Enzyme C has a 12% reduction in enzyme activity under the same conditions.[4] Potassium chloride may affect Enzyme A, as seen in the comparison of a Fann 50 test with a clay treater (tetramethylammonium chloride) and a test with potassium chloride. The effect with Enzyme A has not been quantified at this time, but potassium chloride does not appear to cause an extreme decrease in activity with normal loadings.

Some amine-based clay stabilizers have demonstrated the potential to affect enzymes. However, when they do, the stabilizers appear to react with the enzyme causing a delay in break which can often be compensated for by increasing enzyme loading. As long as the enzyme breaker is effective, cleanup will eventually be achieved. Clay stabilizers can also catalyze oxidative breakers at low temperatures. This type of reaction is taken advantage of with the amine-based breaker catalyst currently used to accelerate low-temperature oxidative breaks.[20,21] With oxidative breakers, however, not compensating for increased activity of the breaker in the presence of a clay stabilizer has the potential for causing premature fracturing fluid degradation and failure of the job.

Resin-Coated Proppants

Static Break Test - Linear Gel

Linear gel was prepared using heavy-duty laboratory stirrer with Tomball tap water and 2% KCl. After the gel was fully hydrated, resin-coated sand was added and stirred for five minutes. The enzyme was then added and stirred 15-30 seconds to disperse. Tests were run at 100°F. No activator was added; any alteration of break time from that of the blank was due to the resin-coated proppants. Viscosity was measured at bath temperature using a Fann 35 (R1B1) at 300 RPM. Data can be found in Table 6.

Static Break Test - Crosslinked CMHPG/Zr Fluid

The carboxymethyl hydroxypropyl guar was hydrated in Tomball tap water with 2% KCl. After the gel was hydrated, the pH was adjusted to 5.0. Resin-coated sand was added and stirred for five minutes. pH was checked and adjusted to 5.0, if necessary. Enzyme was added and gel was stirred for another 30 seconds. The test was run at 160°F. Because Enzyme B and Enzyme C are quickly denatured at 160°F, only Enzyme A was used in this test. As shown in Table 7, the break time increased slightly with the resin-coated sand, but this small difference could be due to the pH differences or experimental error. The three phenolic resin-coated proppants tested did not prevent Enzyme A from breaking the gel.

Bonding Strength Test

The bonding strength test was run at 100°F according to API RP 56 showing the effect of enzyme breaker and oxidative breaker on 20/40 curable resin-coated sand (Table 8).

Conductivity Data

Tests were run using a modified API RP 61 procedure to determine long-term (168 hours) fracture conductivity as described by Bilden, et al.[23] The base fluid used was 2% KCl. The test fluid was a 40-lb guar/1000-gal fluid in 2% KCl water with a monoborate crosslinker, buffers and an isothiazoline-based biocide. Testing with a partially cured resin-coated proppant and fluid containing enzyme A showed good regained permeability was achieved (Table 9). Data with 12/20 mesh white sand and the same fluid composition is included for comparison.

A major focus of compatibility testing has been with resin-coated proppants. Phenol-based resin-coated proppants were studied. The resins for these proppants are made by combining phenol with formaldehyde in presence of a catalyst. Usually this reaction is followed by a reaction with hexamethylenetetramine. The degree of completion of this second reaction comprises the difference between curable and pre-cured resins. The effects of these three components on oxidative breakers has been explored, and incompatibility with oxidative breakers has been noted.[10,22] Resin-coated proppants can decrease the effectiveness of oxidative breakers and can cause unpredictable fluid breaks. Use of enzyme breakers, where applicable, has been recommended as one solution to this problem.[9]

A furan resin was also tested for compatibility with enzymes. Furan resins can be made via a reaction between furfuryl alcohol and formaldehyde. Results of the resin-coated proppant compatibility testing can be found in Table 4. Incompatibilities could be due to presence of formaldehyde, bonding of enzyme to reactive furan rings in the resin, or other causes.

Oxidative breakers can also impact upon the compressive strength of curable phenolic resin-coated proppants. Because enzyme breakers work only on the specific polymer linkages the hydrolases attach to and do not catalyze unrelated reactions, one would expect that enzyme breakers do not influence compressive strength of resin-coated proppants. Data to bear this thesis out is found in Table 8.

Phenolic resins used to coat proppant contain compounds which may affect enzymes. Resin-coated proppants can affect fluid pH, thereby influencing enzyme activity. While this pH effect can influence break time, the enzyme still keeps working. One can compensate for known changes in pH by adjusting breaker loading, just as one does to compensate for changes in pH due to effects of field water.

Interactions between resin-coated proppants tested and enzymes appear to be minimal in most cases. Interactions between resin-coated proppants and oxidative breakers not only can be significant, but they can adversely affect both breaker and proppant.[6,10] In many cases, especially with the increased applicability of enzyme breakers allowed to us by advances in biotechnology, the combination of resin-coated proppants and enzyme breakers will produce excellent results.

Conclusions

Short-term break times of the enzymes tested were not adversely affected at neutral pH by any of the biocides tested. The bromine-based biocide decreased the effectiveness of enzyme A when left overnight in a water solution. This may indicate a potential problem for longer break times or impact on continued degradation of the gel (which is one of the advantages of enzyme breakers). The other biocides may adversely affect enzymes under conditions different from those tested. In particular, glutaraldehyde may cause problems at low pH due to possible crosslinking of the enzyme.

Some clay stabilizers can adversely affect enzyme activity. This interaction may also vary dependent on pH. Salt affects enzymes also. These effects can influence break time, but unless they are very significant, they should not affect degree of break. Decreased activity of the breaker can be compensated for by increasing enzyme loadings. If this is not desirable because of fear of premature gel degradation, controlled release enzymes can be used.

Some of the resin-coated sand tested impacted on the activity of enzyme breakers. A significant effect on enzyme activity can be compensated for with larger loadings because enzyme breakers did not affect the resin-coated sand under test conditions. Because of the chemistry and loadings of enzyme involved, it is not likely that enzymes would adversely affect resin-coated proppant's compressive strength under different test conditions either. This differs from oxidative breakers, because oxidative breakers are significantly affected by some resin-coated proppants. Resin-coated proppants can, in turn, be adversely affected by oxidative breakers, especially if loadings are increased to compensate for decreased effectiveness of these breakers.

Interactions attributed to additives can often be explained as effects on the fracturing fluid environment, pH, ionic strength, gel stability effects which do not, in fact, influence the enzymes ability to break the fluid, only the time during which the break occurs. Fluid systems to be pumped should always be tested with all additives. Combinations of additives may produce additional strain on the enzymes which one of the additives alone may not. Also, when enzyme breakers are used at extremes of temperature and pH, some interactions may be magnified.

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Table 1
Biocides
Viscosity (cP) @ 100°F Measured on a Fann 35 (R1B1) @ 511^{s-1}

	Enzyme A (after 2 hours)	Enzyme B (after 2 hours)	Enzyme C (after 4 hours)	pH of blank With Additive
Glutaraldehyde-Based Biocide	5	11	27	Initial pH 8.0 4-hour pH 7.7
Isothiazoline-Based Biocide	6	11	26	Initial pH 8.0 4-hour pH 7.7
Thiocyanate-Based Biocide	5	11	27	Initial pH 8.0 4-hour pH 7.7
Bromine-Based Biocide	7	11	24	Initial pH 8.0 4-hour pH 7.5
Blank-No Biocide	7	11	28	Initial pH 8.0 4 hour pH 7.7

Test conditions: 40-lb guar gel/1000 gal at 100°F.

Table 2
Water Solution Biocide Compatibility Test
Viscosity (cP) Measured on a Fann 35 (R1B1) @ 511^{s-1}

	2-minute Viscosity	5-minute Viscosity	15-minute Viscosity	30-minute Viscosity
Glutaradehyde-based Biocide	10	16	12	8
Thiocyanate-based Biocide	9	13	8	6
Bromine-based Biocide	11	22	28	31
Blank-Enzyme Alone	10	15	13	8

Test Conditions: Water solution at room temperature. Addition of 40-lb/1000-gal loading of guar slurry.

Table 3
Clay Stabilizers/Clay Treaters & Enzymes
Viscosity (cP) @ 2 hours @100°F
Measured on Fann 35 (R1B1) @ 511^{s-1}

Clay Stabilizer/ Clay Treater	Enzyme A	Enzyme B	Enzyme C	pH Readings Range: Initial Through Final
Oxyalkylated Amine Quat. in Methanol	13	11	22	6.9 to 7.0
Quaternized Cocoamine + Surfactant in IPA	7	17	17	6.8 to 7.0
Dicocoamine Quaternary Mixture in IPA	11	17	20	6.9 to 7.0
Cationic Polymer Surfactant in Ethylene Glycol	8	6	18	7.0 to 7.1
Aqueous Soln. of Tetramethyl Ammonium Chloride + Polymers (CLAY TREATER)	8	6	18	7.0 to 7.1
Blend of Quaternary Condensed Alkanoamines in Water	7	27	14	5.9 to 6.0
Blank- 2% KCl	7	7	19	7.0 to 7.1

Test conditions: 40-lb guar gel/1000 gal at 100°F.

Table 4
Clay Stabilizers & Ammonium Persulfate
Viscosity (cP) @ 19 hours @ 80°F
Measured on Fann 35 (R1B1) @ 511^{s-1}

Clay Stabilizer	Viscosity at 19 hours
Oxylated Amine Quat. in Methanol	7
Poly-Quat. - No Hydroxyls	13
Blank-No Clay Stabilizer, Only Ammonium Persulfate	24

Test conditions: 40 lb-HPG/1000 gal at 80°F.

Table 5
Effect of Clay Treater on Enzyme A
Guar/Organoborate Fluid
Viscosity (cP) @ 100°F on a Fann 50 @ $100^{s^{-1}}$

Time Elapsed	2% KCl	Aqueous Solution of Tetramethylammonium Chloride + Polymers
0	347	351
15	355	301
30	338	255
45	324	215
60	297	189
75	269	146
90	248	108
105	210	78
120	181	59
135	152	49
150	119	43
165	101	38
180	87	36
195	70	34
210	64	32
225	50	19

Table 6
20/40 Resin-Coated Sand
Viscosity (cP) @ 100°F Measured on a Fann 35 (R1B1) @ 511^{s-1}

	Enzyme A	Enzyme B	Enzyme C	Final pH
Furan RCP	9	14	18	7.1
Partially Cured Phenolic RCP	9	18	18	7.1 to 7.2
Encapsulated Phenolic RCP	9	9	21	7.3
Curable Phenolic RCP	9	9	20	7.2
Pre-cured Phenolic RCP	8	9	19	7.2
Ottowa	10	10	19	7.2 to 7.3
Blank- No proppant	11	12	20	7.1

Test conditions: 40-lb guar gel/1000 gal at 100°F.

Table 7
20/40 Sand
40-lb CMHPG/Zr Low-pH Fluid at 160°F

	Enzyme A Break Time	Initial pH After Proppant Was Added	pH at Break Time	pH of Fluid Left Overnight (approx. 23 hrs)
Curable Phenolic RCP	Broke at 6 hours to 10 cP	5	5.6	6.6
Pre-cured Phenolic RCP	Broke at 6 hours to 10 cP	5	5.6	6.2
Encapsulated Phenolic RCP	Broke at 6 hours to 5 cP	5	5.1	5.5
Ottawa	Broke at 4.25 hours to 11 cP	5	4.9	5.1
No Proppant	Broke at 4 hours to 9 cP	5	4.8	---

Table 8
Bonding Strength Comparison
20/40 Resin-Coated Proppant/Activator @ 100°F

	Catalyzed Persulfate	Enzyme A	Undamaged Baseline
Stress in PSI Tested Following API RP 56	620	850	850

Table 9
Long-term Conductivity Tests: 168 Hours Shut-in Time

Base Fluid	Breaker	Proppant	Permeability (Darcies)	Regain Permeability (%)
2% KCl	None	16/20 Partially Curable Resin-Coated Proppant	845	100
Guar/Borate Frac. Fluid	2 gpt* Enzyme A	16/20 Partially Curable Resin-Coated Proppant	734	87
2% KCl	None	12/20 White Sand	790	100
Guar/Borate Frac. Fluid	2 gpt Enzyme A	12/20 White Sand	734	88

*gpt = gallons per thousand gallons fluid

Test Conditions:
Leak-off temperature: 150°F
Shut-in temperature: 180°F
Closure stress: 1000 psi