RESIN COATED PROPPANT/FRAC FLUID INTERACTION DEVELOPMENTS

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INTRODUCTION

Since 1987, there have been several papers presented at the Southwest Petroleum Short Course that discussed the use of resin coated proppants in hydraulic fracturing operations. In 1987 proppant selection criteria[1] showed that the resin coated materials had a wide range of application in many types of wells. In 1991, the new resin coated proppants[2] showed the benefits of designing resin coatings to have a minimum long term permeability of 100 Darcys in the operating range of each resin coated product. Over the past year or two, very large jobs have used the resin coated proppants to successfully stimulate all kinds of formations.

With the increased use of resin coated proppants in the industry many more tests have been run on these type of materials. Many chemical interactions of frac fluid chemicals and resin coated proppants have been examined closely. Two basic papers from the service companies[3,4] detailed important effects of the resin coatings on the use of metal ion crosslinkers and persulfate breakers. Also, the effects on pH and compressive strengths were looked at in detail.

In this paper the chemistry of phenolic resins and the most recent test results are presented to find out the effect that resins may have on the various chemicals in commonly used frac fluids, metal ion crosslinkers, persulfate breakers and foam based fluids. Also, the effects of various coatings and chemical combinations on pH and compressive strengths are examined to arrive at ways to improve the resin coated proppant performance in all types of fluids. Enhanced compatibility resin coated products are now available for use where the effects of fluid interaction could be damaging to the results of the fracturing treatments.

Resin coated proppants fall into two basic categories. The first category is that of curable resin coated proppants. These proppants are coated with resin on the outer surface that will cure under bottomhole temperature and pressure to bond the proppant particles together in the fracture. The purpose of this type of proppant is to eliminate flowback, to minimize embedment into the producing formation, and maximize proppant permeability within the fracture. In addition, free fines are eliminated and higher crush resistance is measured with curable resin coated proppant.

The second type of resin coated proppant is often termed "tempered" or "precured". The purpose of the noncurable resin coating on this type of proppant is to add strength to the underlying material so that it may be used in deeper, higher closure stress fractures than would otherwise be possible, in addition to the elimination of free fines. Developments regarding the interactions of both curable and noncurable resin coated proppants will be examined in this paper.

RESIN COATED PROPPANT EFFECTS ON FLUIDS

Both curable and noncurable resin coated proppants can interact with fracturing fluid chemistry. That interaction occurs in four primary areas:

1. Oxidative gel breakers efficiency
2. Crosslinking of gel polymers
3. pH effects - changes in intended pH levels
4. Foamed frac fluid systems

The interactions in each of these areas are discussed, as well as developments in resin coated proppants that address each of these interactions.

RESIN COATED PROPPANT EFFECT ON OXIDATIVE GEL BREAKERS

Recently, compatibility of curable resin coated proppants towards oxidative persulfate breaker systems has caused concern among service companies and proppant suppliers. It seems that some chemical functionality of the curable surface resin causes the proppant to act as a reducing agent, therefore consuming oxidative breaker. Service companies are concerned about the varying amounts required to break fracture stimulation gel systems. To determine the chemical component interfering with the $(S_2O_8)^{2-}$ ion, persulfate demand titrations have been performed with various proppants and chemical species.

It is widely believed that curable resin coated proppants react more with breakers than with noncurable proppants. In a series of tests, an attempt was made to quantify the degree of reactivity one type of proppant showed over the other. As with all titrations repeatability is a key, thus, all weights and volumes were meticulously measured. Resin coated proppant was exposed to a known volume and molarity of ammonium persulfate (a common oxidative breaker) for one hour in a 160° F. bath. In this amount of time a portion of persulfate is consumed by the reaction with resin. It is known that persulfate is not an extremely stable ion, and at higher temperatures this instability is increased. Therefore, controls without proppant were run to determine the percent of persulfate which degraded without interaction with the resin. This effect is shown on the graph in Figure 1. To carry out the titrations, the remaining persulfate was reacted with potassium iodide to yield iodine in a 1:1 ratio. This provides a molecule with a visible endpoint as iodine is titrated against thiosulfate. The volume of thiosulfate required to complete the titration directly corresponds to the amount of persulfate remaining after exposure to resin coated proppant.

In the second series of tests, specific chemical species known to be present in phenolic-formaldehyde resins were introduced to the persulfate system described above. The compounds added separately were phenol, hexamethylenetetramine, and formaldehyde; no proppant was used. With each component 2 moles were added for each mole of persulfate. Low thiosulfate volumes in this test directly corresponds to a competitive reaction between the chemical species and the persulfate ion.

The first series of titrations verified that curable resin coated proppants do, indeed, react with persulfate more than noncurable resin coated proppants, in fact, the curable resin was approximately 6% more reactive. However, the most interesting point is the extent of persulfate degradation without proppant, as seen in the control runs (Figure 2). 50% of the breaker was lost to thermal decay alone in these test conditions.

Of the three previously mentioned leachable chemical species present in phenol-formaldehyde resins that may be responsible for interference with persulfate breakers, phenol is completely unreactive towards persulfate. Hexamethylenetetramine showed slight reactivity towards persulfate - a 7% deviation from the blank. It appears, however, that the real culprit is formaldehyde. Formaldehyde consumed 21% more persulfate than the blank systems. Furthermore, the slight reactivity of hexamethylenetetramine may possibly be explained by noting that hexamethylene-tetramine decomposes to produce ammonia and formaldehyde when exposed to heat.

Knowing that formaldehyde produced by hexamethylenetetramine decomposition is consumed to crosslink phenolic/formaldehyde resins, the lower reactivities seen in noncurable products is probably due to less formaldehyde crosslinker availability, because all the available formaldehyde has been bound up in the resin itself.

RESIN COATED PROPPANT EFFECT ON CROSSLINKING

In a previous investigation into the interactions between curable resin coated proppant and the crosslinkers used in fracturing fluids, Norman, et al[3], showed that resin coated proppant had no effect on a base gel. For systems crosslinked with aluminum and zirconium, they found the chemical effect that curable resin coated proppant had on the crosslinked fluid viscosity can be solved by adjustment of the pH of the fracturing fluid to its originally intended value. In a titanate crosslinked system, it was found that resin dust added to a gel (0.5% wt/vol) decreased gel viscosity. Further, it was found that by increasing the crosslinker concentration, the viscosity was recovered.

Nimerick, et al[4], showed that a titanium crosslinked gel did not achieve designed viscosity in the presence of 8 pounds per gallon curable resin coated proppant at low, neutral, and high pH due to an average of 21% lost crosslinker. They also found that when the surface of curable resin coated proppant removed from a zirconium crosslinked fluid was examined with energy dispersive X-ray, zirconium was found on the resin surface.

Polysaccharide polymers used in fracturing gels (e.g., guar, hydroxypropyl guar, etc.) are primarily crosslinked at hydroxyl sites (Figure 3), forming covalent bonds, with the exception of boron, which forms a complex bond. The phenolic polymer commonly found on curable resin coated proppant also contains hydroxyl sites (Figure 4). Apparently, crosslinkers can bond to these sites as well as to hydroxyl sites on polysaccharide polymers. As a result, at higher proppant concentrations, curable resin coated sand may cause a portion of the crosslinker to be unavailable for reaction with polysaccharides.

In order to minimize the interaction between resin coated proppant and frac gel crosslinkers the proppant manufacturer needs to minimize the surface area of resin exposed to fluid to reduce resin/crosslinker interaction. This can be greatly affected by dust control methods. The manufacturer can utilize chemically neutral additives which are added to the resin coated proppant surface to minimize grain-to-grain friction and thus greatly reduce dust. Careful handling of the resin coated proppant in manufacture, shipping, and transfer can greatly reduce the amount of resin dust present. Additionally, the interaction between noncurable phenolic/formaldehyde resin coated proppant and crosslinkers is almost nonexistent.

RESIN COATED PROPPANT EFFECT ON GEL pH

Although phenolic/formaldehyde resins are far from being strong Lewis acids, in the presence of strong alkaline conditions they may lower a fluid's pH. Leachable phenol was thought to be primarily responsible for this pH change, so it was believed that noncurable proppants, in which phenol is rigidly crosslinked, would have less of an effect on pH than curable proppants. It was also believed that furfuryl alcohol/phenolic resin coated proppants (precured F-A) would have a greater effect on pH than phenolic-formaldehyde proppants due to residual acid catalysts which might remain in the resin. Simple tests were carried out to test these hypothesis.

A 2% KCl solution was adjusted to pH 10 by adding NaOH and further "fine tuning" as needed with fumaric acid. Proppant was added in an 8 pound per gallon concentration. The mixture was stirred at ambient temperature and the pH was monitored with an electronic pH meter.

The results are shown in Figure 5. It was noted that the predicted pH effects were seen. The pH of the control fluid adjusted to pH 10 slowly declined (without proppant present) with time. The pH of the fluid surprisingly declined over the course of 30 minutes to near 8 with noncurable phenolic/formaldehyde resin. The pH declined much more rapidly with curable resin coated proppant, while the pH declined most rapidly and to the lowest level with a noncurable furfuryl alcohol/phenolic resin. These pH effects can be largely overcome with buffered frac fluids.

RESIN COATED PROPPANT EFFECT ON FOAM

In some situations it is preferable to fracture a formation with a foamed fluid system rather than with a crosslinked gel. The foam is generated by a surfactant, and the gas phase is usually carbon dioxide and/or nitrogen. It was found that resin coated proppant could have a detrimental effect on foamed systems by reducing a foam's stability. A great deal of investigation ensued, looking at all aspects of resin coated proppant to determine the cause of foam instability.

Most testing involved the use of high speed benchtop blenders. Fluid containing the appropriate amount of foamer was added to a blender. The blender was run at high speed for approximately 30 seconds. Resin coated proppant in concentrations ranging from 8 to 12 pounds per gallon were added to the blender and the blending continued for another 30 seconds. The foam/proppant mix was then transferred to a graduated cylinder and the foam volume and foam half-life were observed. Many aspects of resin coated proppants were examined in this way.

Resin coated proppants have a very thin surface layer of dust control additive that was described earlier in this paper. It was found that a component of the dust control additives was detrimental to foam. As a result, that component was removed and foam stability was greatly enhanced. Additionally, chemical modifications have been made to the resin coating that can further enhance the foam compatibility of the resin, while non detrimental dust control additives remain in place. A result can be seen in Figure 6.

FLUID EFFECTS ON RESIN COATED PROPPANTS

As fracturing fluids have evolved, the question of the effect of higher pH fracturing fluids on resin coated proppant has come about, since it is known that acidic and neutral pH fluids have no effect on the resins used on resin coated sand. The concern was that high pH fluids could cause the dissolution of the resin coating, resulting in diminished proppant conductivity and flowback control.

In order to determine the effects of high pH fluids on resin coated proppants, a test was devised to expose these proppants to high pH fluids under elevated temperature and pressure, then test the compressive strength of the proppant pack. Additionally, loss on ignition testing was performed to determine the exact amount of resin remaining on the proppant, as compared to before exposure to the high pH fluid. An 8 pound per gallon loading of resin coated proppant was mixed for 15 minutes in a 2% KCl solution which had the pH adjusted to the desired elevated value using sodium hydroxide. After 15 minutes, the slurry was transferred to a special 2 inch diameter cell. The cell was placed in a press and the temperature and pressure increased to 250° F. and 1000 psi for 2 hours. The proppant pack was removed, the compressive strength was measured in much the same manner that cement compressive strength is measured, and the resin loss was determined by loss on ignition techniques.

The results of these tests (see Table 1) show that curable phenolic/formaldehyde resin coated proppants may be used in frac fluids with a pH as high as 12 and noncurable phenolic formaldehyde resin coated proppants may be used in a frac fluid with a pH as high as 12.5. Other resin coated proppant manufacturers products use different resins, therefore, some variation in results in the pH testing is expected since each type of resin gives different results. At least one resin coated proppant manufacturer makes a noncurable resin coated proppant with somewhat different chemistry than a phenolic/formaldehyde resin - that proppant was not tested in high pH conditions, and will probably give different results.

CONCLUSIONS

In the recent past we have seen considerable effort by resin coated proppant manufacturers to address the compatibility issue. In the near future more will be learned about what can be done to make resin coated proppants fully compatible with frac fluids, and manufacturers will use that knowledge to make new products. In the meantime, resin coated proppants will continue to provide flowback control, embedment minimization, fines elimination, and high long term permeability. Resin coated proppants provide an economic, high performance way of stimulating all types of wells and formations, even those where sand and ceramic type proppants were used in the past.

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Table 1
High pH Fluid Effects on Resin Coated Proppant

Curable Double Coated Proppant

Fluid pH	% Resin Lost	% Compressive Strength Lost
12.0	10.7	8.2
12.5	52	100
13.0	>52	100

Noncurable Coated Proppant

Fluid pH	% Resin Lost	% Compressive Strength Lost
12.5	5.3%	N/A

Test Conditions: Proppant at 8 lb. per gal. mixed in fluid for 15 min. Transferred to modified crush cell where press. was increased to 1000 psi and temp. to 250 deg. F. over approx. 30 min. The temp. and press. were held 2 hrs. while fluid leaked off.

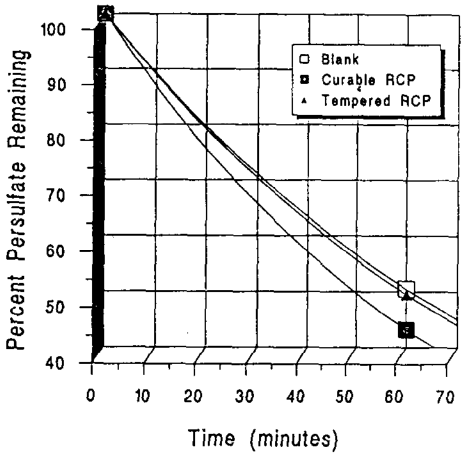

Figure 1 - Breaker compatibility of resin coated proppant

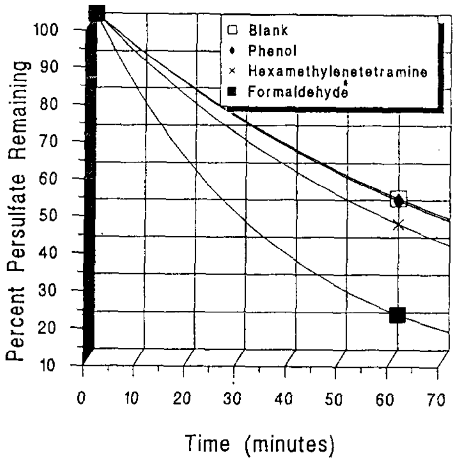

Figure 2 - Compatibility of chemical species

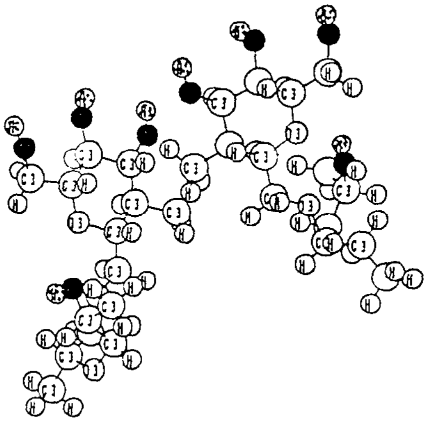

Figure 3 - Three dimensional hydroxypropyl guar polymer with hydroxyl sites highlighted

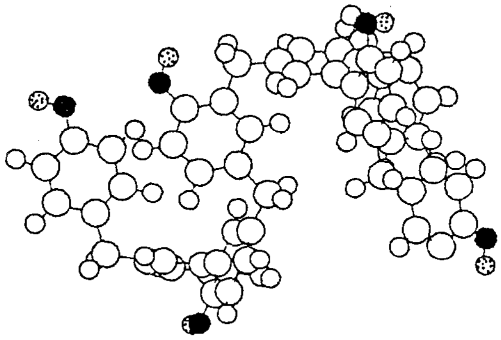

Figure 4 - Three dimensional phenolic formaldehyde resin polymer with hydroxyl sites highlighted

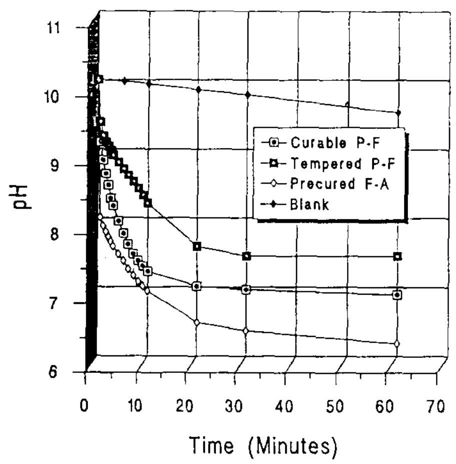

Figure 5 - Effect of resin coated proppant on pH

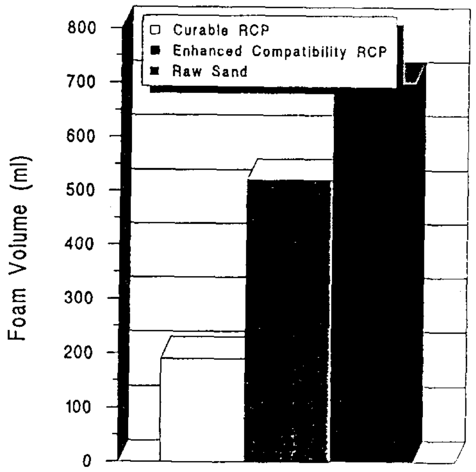

Figure 6 - Effect of an enhanced compatibility curable resin coated proppant on 8 gpt anionic foamer