APPLIED BIOTECHNOLOGICAL ADVANCES FOR THE OIL INDUSTRY

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ABSTRACT

Previous advances in biotechnology have provided significant contributions to the oil and gas industry. Enzymes have been used for many years as low-temperature gel breakers. The previous enzyme products were non-specific mixtures of several different, non-isolated enzymes. Degradation by these systems resulted in the creation of polymeric fragments of widely varying size and damage tendencies. Recent biotechnical research has led to the identification of specific enzyme complexes to effect much improved degradation of polysaccharide polymers. The new technique utilizes substrate-specific enzyme complexes to hydrolyze the polymers to as little residue as possible. Neither the crosslinker type nor the degree of polymer derivatization interfere with the ultimate enzymatic degradation of the polymer.

INTRODUCTION

Enzymes, like all other proteins, consist of long chains of amino acids held together by peptide bonds. Enzymes are present in all biological systems and derived from all natural systems. Degraded enzyme amino acids or reaction products (usable or waste products) are non-toxic and can be readily broken down or absorbed back into nature. Enzyme systems are, therefore, regarded as environmentally friendly.

Enzymes exhibit the unique ability of not changing their structures during the reactions they initiate. They are also known for their tendency to catalyze the initiating reactions at an extraordinary rate. These unique features are components of a property called "turnover number". For instance, one of the selected enzymes (ß-amylase) has a turnover number of 1,100,000. This terminology indicates that one unit of enzyme could turn over or cleave 1,100,000 linkages of substrate per minute. A great many more can be cleaved over the "life-span" of the protein. Conversely, one molecule of ammonium persulfate can only initiate two reactions (only one free radical is released when catalyzed).

ENZYMATIC BREAKER THEORY

1. Guar Enzyme Breaker Mechanism

Guars belong to the family of galactomannans. The proposed structure of guar is said to consist of a linear chain of D-mannose residues (backbone) bonded together by 1,4-ß-glycosidic linkages as shown in Fig. 1. D-galactosyl substituents are attached

through 1,6-α-glycosidic linkages. The galactosyl substituents are randomly arranged along the backbone. The ratio of the galactose and mannose units is believed to be about 1:2.[1]

Galactomannans can be efficiently hydrolyzed by a specific galactomannan enzyme complex, which is a combination of two O-glycosidic hydrolases. Both enzyme cleavage sites are illustrated in Fig.1. The first O-glycosidic hydrolase, α-Galactosidase (also known as Melibiase), is specific for the galactose substituent, hydrolyzing the terminal, non-reducing α-D-galactosides. The second O-glycosidic hydrolase used to degrade the guar molecule is specific for the mannose backbone. This enzyme is called Endo-1,4-ß-mannanase (also known as Mannan endo-1,4-ß-mannosidase), which randomly hydrolyzes the 1,4-ß-D-mannosidic linkages. The selected galactomannan enzymes exhibit properties as outlined in Fig. 4 and 5.

2. Cellulose Enzyme Breaker Mechanism

Cellulose is a linear chain of glucose residues bonded together by 1,4-ß-D-glucosidic linkages.[2] Cellulose can effectively be hydrolyzed by an Endo-O-glucosidic hydrolase, which would yield about 80% monosaccharides and 20% disaccharides. The reaction that takes place is endohydrolysis of 1,4-ß-D-glucosidic linkages in cellulose.
The addition of an Exo-O-glucosidic hydrolase, for instance a ß-D-glucoside glucohydrolase (also known as cellobiase), will hydrolyze the remaining 20% disaccharides into monosaccharides by cleaving the terminal non-reducing ß-D-glucose residues with release of ß-D-glucose. An abbreviated version of this mechanism is illustrated in Fig. 2. The properties of the preferred cellulose-specific enzymes are outlined in Fig. 4 and 5.

3. Starch Enzyme Breaker Mechanism

Non-derivatized or simple starches, commonly used in this industry as fluid loss agents, can be effectively hydrolyzed by several enzymes. The most widely used enzymes are Endo-α-O-glucosidic hydrolases and Exo-α-O-glucosidic hydrolases, such as α-amylase, ß-amylase, and glucoamylase (also known as Exo-1,4-α-glucosidase).

The Endo-α-O-glucosidic hydrolase reacts with the starch by endohydrolyzing the 1,4-α-D-glucosidic linkages in polysaccharides containing three or more 1,4-α-linked D-glucose units. The Exo-α-O glucosidic hydrolases are specific for starches, since they hydrolyze the 1,4-α-D-glucosidic linkages in polysaccharides so as to remove successive maltose units from the non-reducing ends of the chains. Some of the exo-starch enzymes hydrolyze not only terminal 1,4-linked α-D-residues successively from the ends of the chains with the release of ß-D-glucose, but also hydrolyze 1,6-α-D-glucosidic bonds when the next bond in sequence is 1,4.

Combining these specific enzymes together will yield mostly monosaccharides on degradation as illustrated in Fig. 3. The enzymes identified as best for starch degradation exhibit the properties as outlined in Fig. 4 and 5.

These new biotechnological advances have been incorporated into stimulation, completion, and remedial treatments to reduce polymer damage.

STIMULATION TREATMENTS

1. Application

A case study has been conducted on San Andres Formation oil wells (Permian Basin). Conventional high and low pH fracturing fluids, utilizing catalyzed oxidative breakers, have been used for many years to stimulate this low-temperature zone. Lower than expected post-treatment productivity and a rapid rate of decline suggest that the fracture conductivity was less than adequate.

Recent studies have shown that proppant-pack permeability damage may be greater than 50% when such fluids are applied. Furthermore, the addition of highly reactive catalyzed oxidative breakers rapidly degrades the fluid's efficiency and proppant transport capabilities. Such phenomena limit the size of the fracturing treatments, the proppant concentration which may be transported, and ultimately, the proppant volume. The fluid limitations precluded the application of advanced treatment design to improve well productivity.

The introduction of the latest fracturing fluid technologies (high and low pH) has provided the opportunity to improve the treatment design by significantly increasing the proppant concentration and reducing the polymeric damage to the in-situ proppant pack. Laboratory studies have shown that the new biotechnology incorporated into any fracture treatment system provides good fluid efficiency, perfect proppant transport, and up to 97% retained proppant pack permeabilities.[3]

Along with the new biotechnology, resin-coated proppant and forced closure were used to control proppant flowback. Laboratory and field data have also concluded that the new biotechnology exhibits an outstanding and unique compatibility with resin-coated proppants. Conversely, conventional types of oxidizers exhibit a great affinity towards resin and, therefore, minimize the curing and bonding strength of the resin-coated proppant.

In all cases the specific enzymes out-performed the latest and conventional oxidizers and conventional non-specific enzyme technologies, in terms of proppant settling, retained conductivity, and dynamic rheology.

2. Laboratory and Field Data

Both independent laboratory and in-house testing have demonstrated retained permeabilities in excess of 97%.[3] Conductivity data and dynamic rheology measurements also indicate that the crosslinker types (zirconates, titanates, or borates) do not interfere with the clean-up characteristics of the enzyme breakers. The same testing also indicates that the degree of polymerization will not affect the cleanup properties of the enzyme systems (Fig. 6-8).

From 1991-1992, a total of 230 wells, located in the San Andres Formation, were stimulated with the high pH galactomannan enzyme. The results indicate a pre-stimulation production average of 9 BOPD, an offset average of 30 BOPD and a final production average of 120 BOPD. Typical production numbers on 26 wells are shown in Table 1.

WELL COMPLETION AND WORKOVER OPERATIONS

1. Application

Many workover operations require production to be temporarily halted. These situations require the production zone to be isolated in order to prevent damage from leakoff of the heavy brines and fluids used for pressure control. Blocking gels, which prevent this damage by forming a relatively impermeable crosslinked polymer complex across the production formation, are frequently used for this purpose. Although cellulose-based polymers are preferred due to the low residue content, the cellulose-based blocking gel itself can frequently cause damage by leaving polymer residue in the form of a filter cake.

These viscous cellulose-based crosslinked blocking gels normally degrade with little insoluble residue when a sufficient amount of conventional internal breaker is applied. Long-term gel stability precludes the use of conventional internal oxidizing breakers due to the reduction in efficiency of the crosslinked polymer complex.

The new biotechnology advances were applied to this blocking gel system and resulted in extraordinary success. The result is a solids free, non-damaging fluid which is easily recoverable.[4]

2. Laboratory and Field Data

The cleanup properties of the cellulose-blocking gel workover treatment were evaluated through the use of core flow testing, conducted using a Hassler Core Test Cell, according to standard API procedures.[5]

Test results show that the filter cake and gel damage can be completely removed with the specific enzyme complex (Fig. 9). A 98.6% average regained permeability was observed. A second test, using an oxidative treatment, removed a maximum of 80% of the polymeric damage (Fig.10). However, the disadvantages of using oxidizers outweigh the benefits of the polymer removed.

Field tests with this new enzyme-blocking gel combination performed successfully with no detectable damage (initial and final production stayed the same).

REMEDIAL TREATMENTS

1. Application

Polymeric damage to proppant pack and formation permeability can significantly decrease well production. The damage, in many cases, is due to insufficient degradation of drilling, completion, or stimulation fluids and the dynamically formed filter cake on the formation face.[6-8]

Various methods have been used to remove damage in an effort to increase well productivity. Several previous studies describe the application of conventional cleanup treatments.[5,9-11] Historically, treatments for such operations have included either strong acids or oxidizing materials to affect polymer degradations and removal. While the conventional treatments have resulted in some marginal success, the non-specific chemical reactivity of the components has limited their widespread application. Some formations are acid-sensitive. Formation damage can occur from incompatibility with undesirable acid reaction products, and acid contact can cause corrosion of tubular goods. The techniques used previously were not specifically directed to the polymer that caused the damage.

One remedial treatment employs fluoride ions, precipitation inhibitors, and a combination of oxidative salts, including ammonium persulfate and sodium perborate.[9] At low temperatures, an activator is required to initiate the oxidizers. Fluoride ions are extremely reactive with most metal and many nonmetal ions. Free fluoride ions can react with the metals in the tubing forming metal fluoride crystals such as iron fluoride, which is slightly soluble in aqueous solutions. Fluoride ions can also react with calcium ions in the formation forming calcium fluoride, which precipitates in aqueous solutions and can damage the production zone. Another drawback is that oxidizers and acids have a finite effectiveness. They may be consumed in the many different, competing reactions occurring downhole, reducing their availability for polymeric degradation.

Three polymer specific systems (guar, cellulose and starch) have been developed to clean up damage in the formation. The specific systems utilize the new biotechnology for its effectiveness and specificity.

2. Laboratory and Field Data

Guar Damage Removal System

Damage from guar-based fluids most commonly occurs in propped hydraulic fracturing. Therefore, fracture conductivity testing was used to evaluate the improvements provided by the enzyme treatments for guar-based polymers. Fracture conductivity testing was performed using a modified API conductivity test cell and procedures similar to those previously described by Brannon.[11] At completion of the standard conductivity procedures, the guar specific treatment was injected into the damaged pack and shut in for one or two hours at 1000 psi. The treatment fluid was applied in a volume equal to two pore volumes of the clean proppant pack.

After the shut-in period had expired and 2% KCl was again flowed through the proppant pack, the final permeability was measured and a regain permeability calculated. The test results of the guar-based treatment indicates that for the shut-in period of one hour a significant amount of polymer damage can be removed. Longer treatment shut-in periods can provide for complete damage removal as indicated in the tests. The test results also indicate that polymer derivatization or crosslinker type are not a factor for successful cleanup achieved from these specific enzyme combinations (Fig. 6-8).

One field test indicates initial production averages (before remedial treatment) of 60 BOPD to final production averages (after treatment) of 250 BOPD.

Cellulose Damage Removal System

The effectiveness of the cellulose removal treatment was also evaluated through the use of a Hassler Core Test Cell, as mentioned in the workover section, according to standard API procedures.[5] The damage again was completely removed (Fig. 11).

Starch Damage Removal System

Starch damage normally occurs from the filter cakes generated for fluid loss control in drilling, completion, and workover operations. Therefore, test procedures as described by Tjon-Joe-Pin et al. (which simulate typical operations) were used to evaluate the cleanup characteristics of this starch specific enzyme treatment.[12] The test results (Table 2) show that the enzyme system averaged a 90% regained permeability for a 30-minute exposure or shut-in time and an average of 100%

regained permeability for a one-hour exposure time. An oxidizer treatment was also tested and showed a 90% average regained permeability for a one-hour shut-in time. The difference in regained permeability of the enzyme and oxidizer system is not significant, but the advantage of the enzyme system again lies in the specific reaction of the enzyme versus the non-specific reactions of the oxidizer.

Field trials for the starch removal system have yet to be conducted.

CONCLUSION

Laboratory testing has shown that the substrate-specific enzymes reduce the polymer to non-reducible sugars, mostly monosaccharides and disaccharides. The polymer degradation to much smaller fragments has shown significant reduction in damage. Unlike acidic or oxidative processes, the new enzyme systems are non-reactive with anything other than the targeted polymer. Laboratory and field data indicated increased productivity when polymer specific enzyme systems were employed.

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Table 1
Fracture Treatment Case History Production Data
with High pH Enzymatic Breaker

Formation	Before Treatment BOPD	After Treatment BOPD	Offset Ranges BOPD
SAN ANDRES	15	77	20-40
SAN ANDRES	12	130	20-40
SAN ANDRES	10	197	20-40
SAN ANDRES	12	130	20-40
SAN ANDRES	1	51	8-10
SAN ANDRES	NEW	181	20-40
SAN ANDRES	NEW	100	10-20
SAN ANDRES	NEW	27	8-10
SAN ANDRES	NEW	113	8-10
SAN ANDRES	NEW	203	20-40
SAN ANDRES	8	139	20-40
SAN ANDRES	NO DATA	40	8-10
SAN ANDRES	17	66	20-40
SAN ANDRES	NO DATA	143	20-40
SAN ANDRES	ZERO	110	10-20
SAN ANDRES	NO DATA	243	20-40
SAN ANDRES	NO DATA	198	20-40
SAN ANDRES	NO DATA	80	20-40
SAN ANDRES	NO DATA	153	20-40
SAN ANDRES	1-2	35	8-10
SAN ANDRES	ZERO	70	20-30
STRAWN SAND	ZERO	160	20-30
SPRAYBERRY	ZERO	75	20-30
SAN ANDRES	8-10	110	20-40
SAN ANDRES	8-10	200	20-40
SAN ANDRES	6-10	100	20-40

Table 2
Aloxite Disk Filter Cake Damage Removal
Test Results

Breaker	Exposure Time, Minutes	Initial Flow, Seconds	1 minute Spurt Loss (mL)	30 Minutes Fluid Loss (mL)	Return Flow, Seconds	Percent Removal	Remarks
None	60 min	8	4.8	9.6	160	5.0	Large Filter Cake
Enzyme	30 min	9	4.8	9.6	10	90.0	Small Filter Cake
Enzyme	60 min	9	4.8	9.6	9	100	No Filter Cake
Oxidizer	60 min	9	4.8	9.6	10	90.0	Small Filter Cake

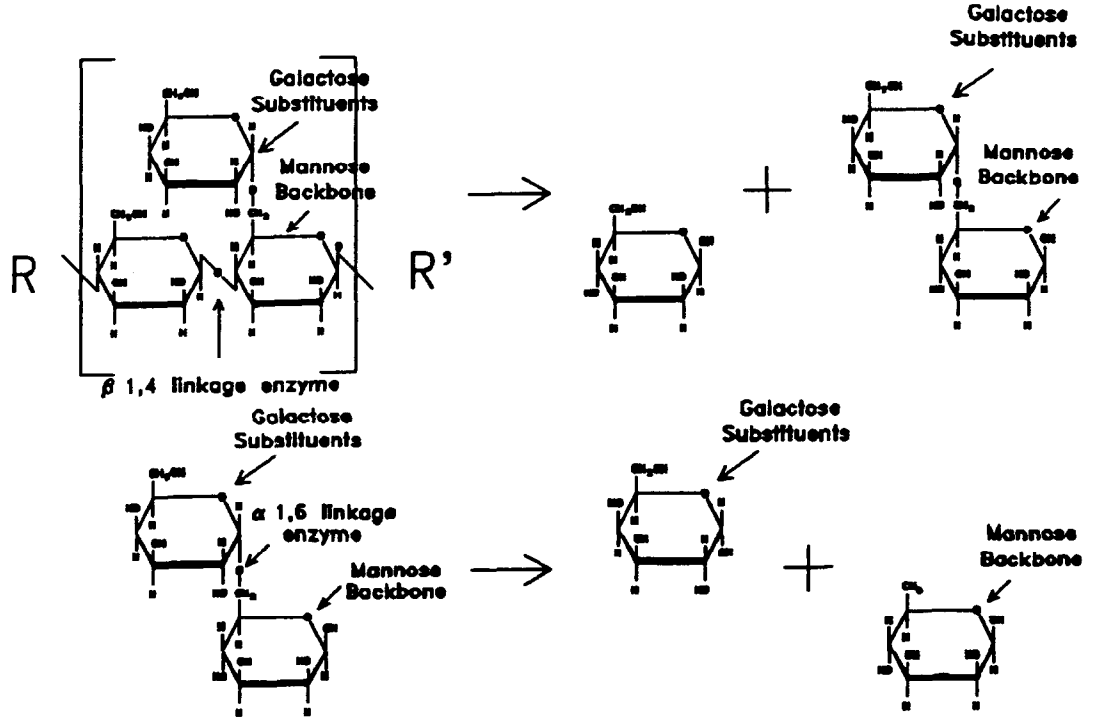


Figure 1 - Guar enzymatic degradation mechanism

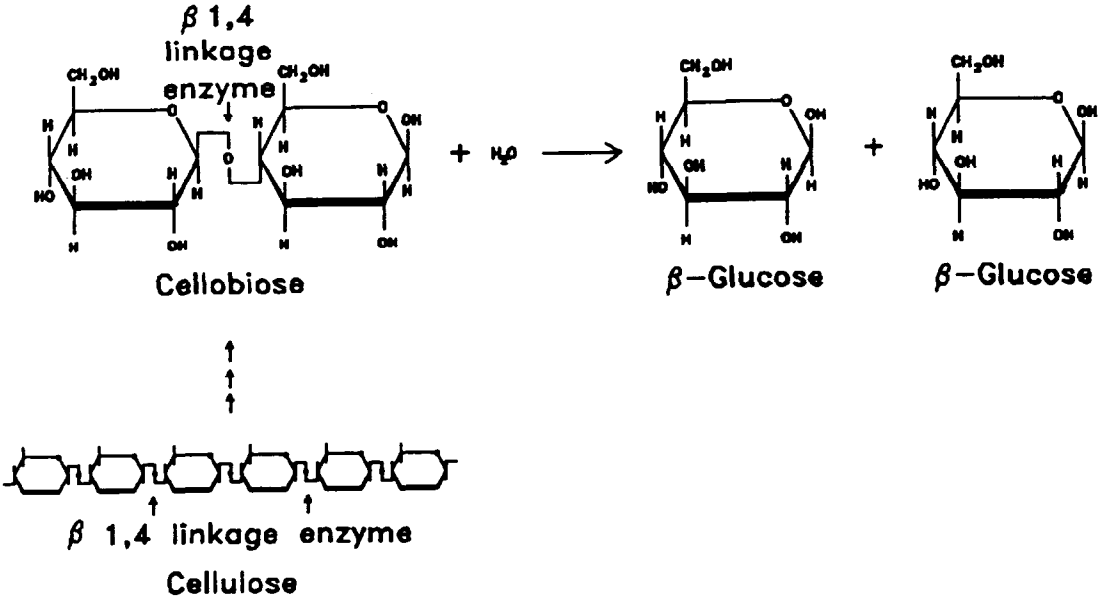


Figure 2 - Cellulose enzymatic degradation mechanism

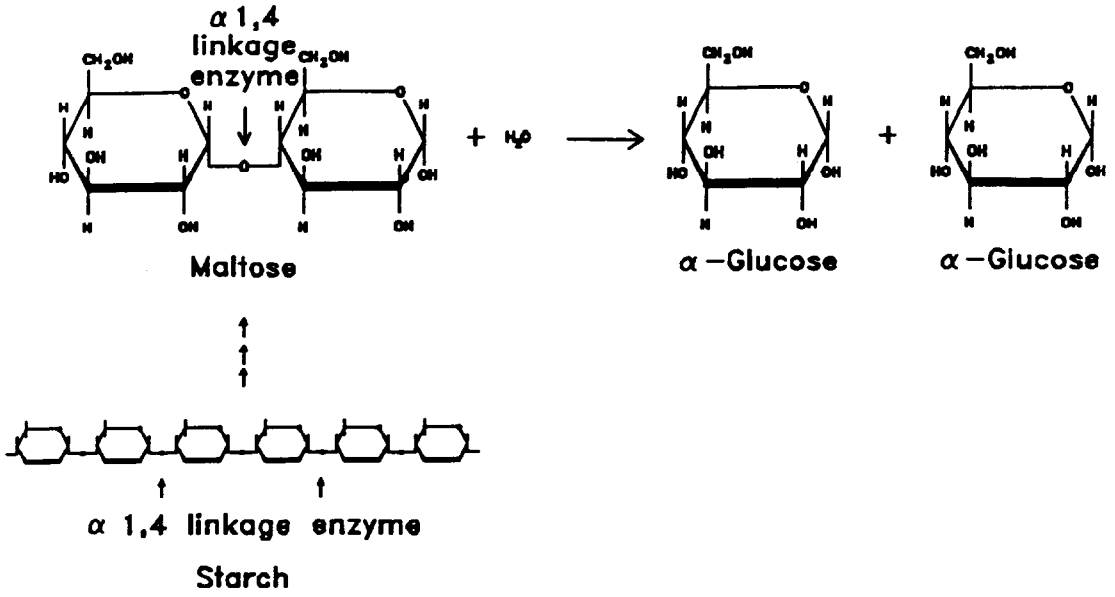


Figure 3 - Starch enzymatic degradation mechanism

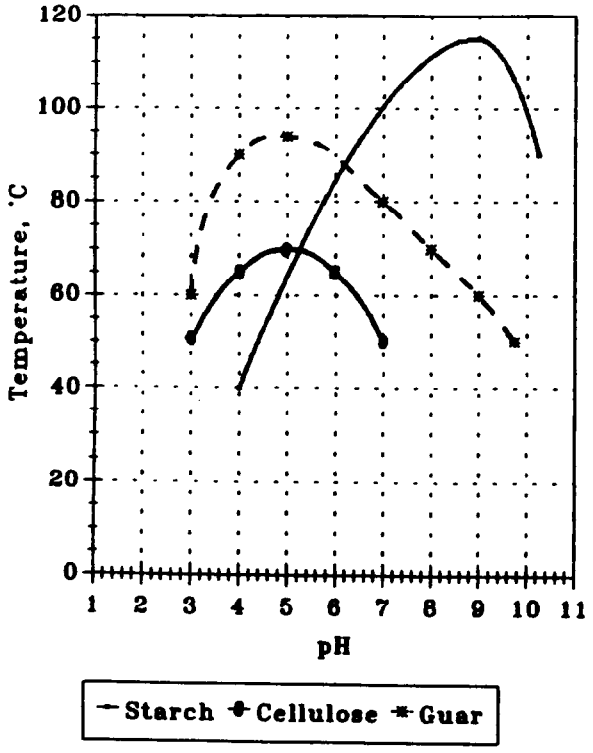


Figure 4 - Enzyme complex fluid pH versus temperature

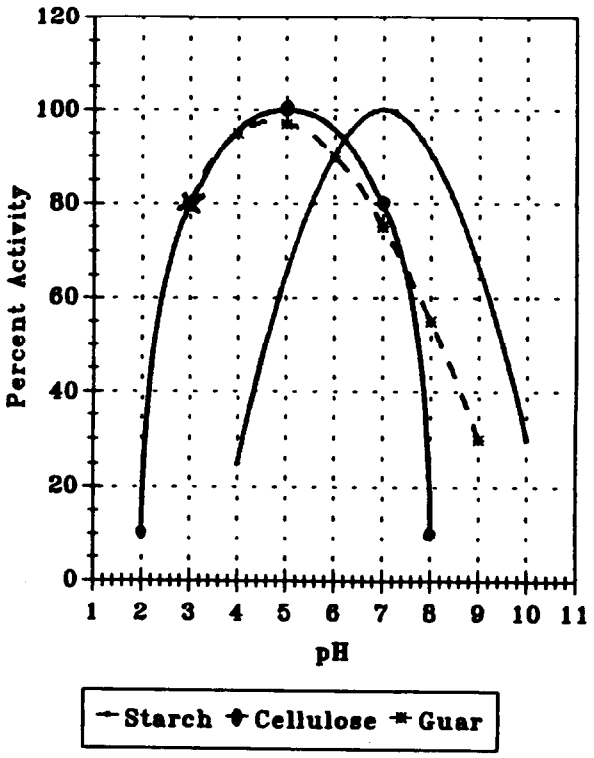
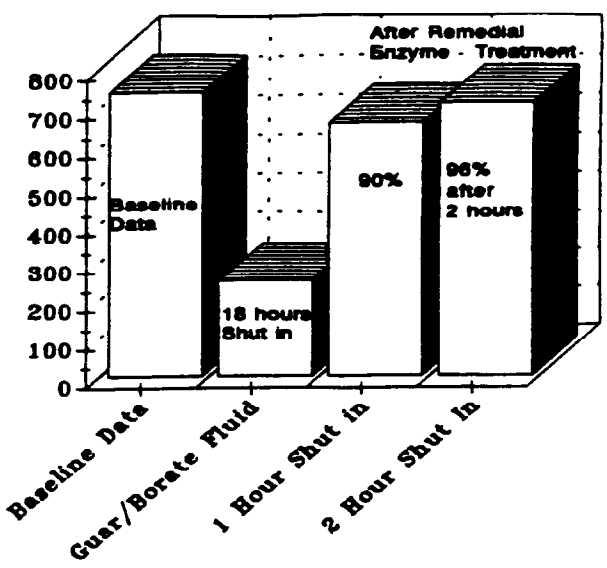
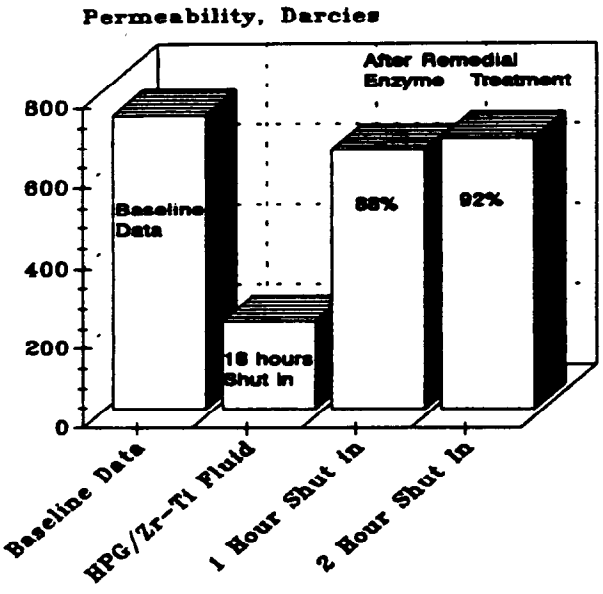


Figure 5 - Enzyme complex fluid pH versus activity



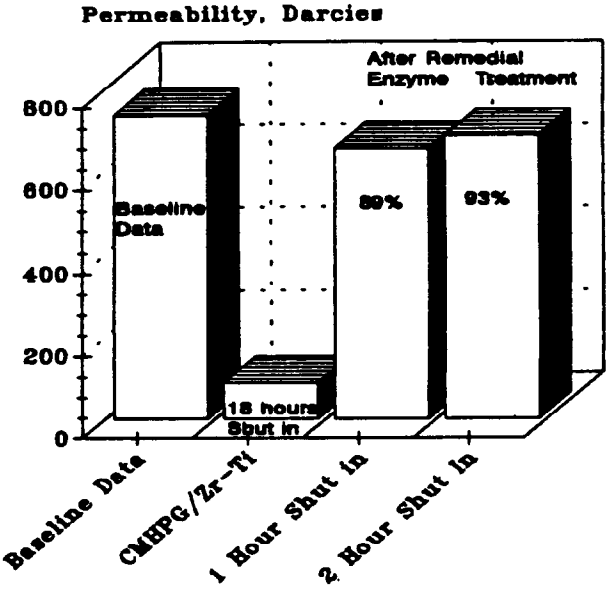
20/40 Interprop Plus at 9.76 kg/m^3
Temperature=180°F Pressure=1000psi

Figure 6 - Regained conductivity tests



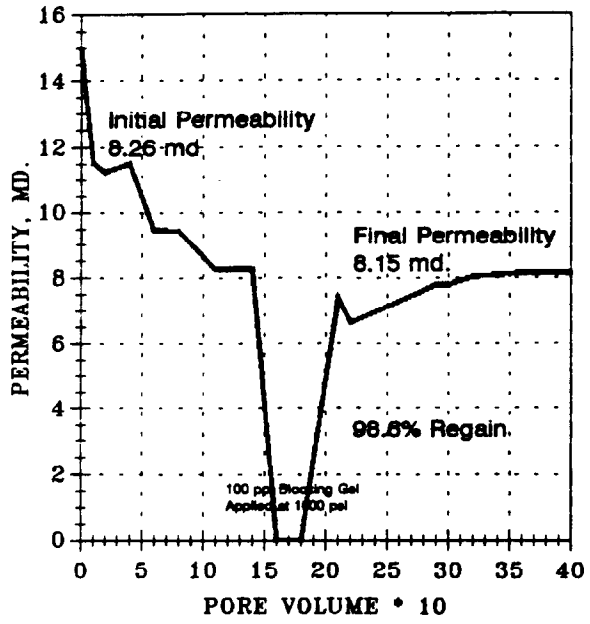
20/40 Interprop Plus at 9.76 kg/m^3
Temperature=180°F Pressure=1000 psi

Figure 7 - Regained conductivity tests



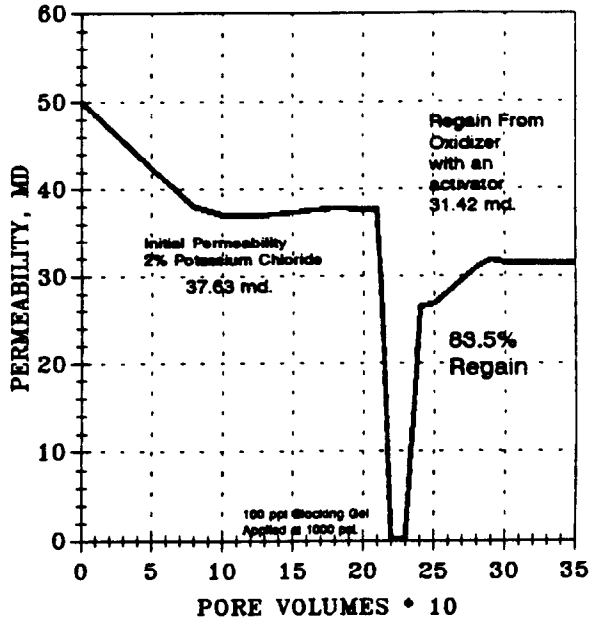
20/40 Interprop Plus at 9.76 kg/m^3
Temperature=180°F Pressure=1000 psi

Figure 8 - Regained conductivity tests



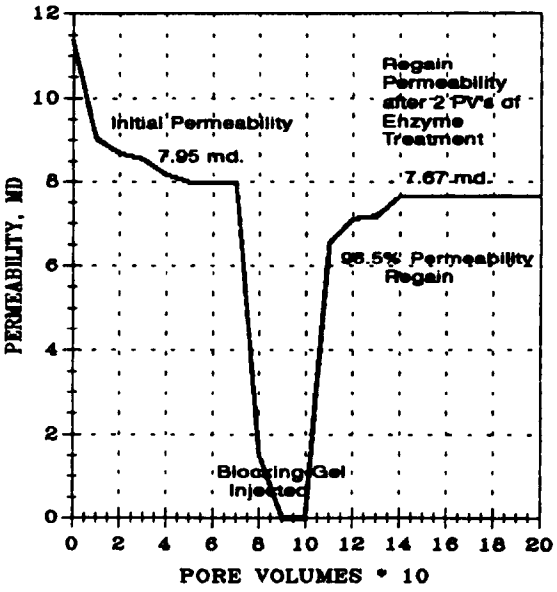
1.17% by Weight Crosslinked Cellulose Gel
Temperature:120°F

Figure 9 - Enzyme blend applied after blocking gel



1.17% by weight Crosslinked Cellulose Gel
Temperature:120°F

Figure 10 - Oxidizer blend applied after blocking gel



0.5% Enzyme Blend in 2% KCl
Temperature 140°F

Figure 11 - Remedial enzyme treatment removal of cellulose