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DEVELOPMENT OF IMPROVED MOBILITY CONTROL
AGENTS FOR SURFACTANT/POLYMER FLOODING

First Annual Report
September 29, 1978 to September 30, 1979

Date Published—May 1980

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Under Contract DE-AC19-78BC00047

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New Mexico Petroleum Recovery Research Center
New Mexico Institute of Mining and Technology
Socorro, New Mexico

U. S. DEPARTMENT OF ENERGY

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AGENTS FOR SURFACTANT/POLYMER FLOODING**

Annual Report
for the Period
September 29, 1978 to September 30, 1979

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I. ABSTRACT

A. OBJECTIVES

The objective of this project is to develop, in the laboratory, improved mobility control agents that will function more effectively in surfactant/polymer flooding. The purpose of Phase 1 of the project was to survey and assess applications data in order to outline problems encountered with currently available mobility control agents used in surfactant/polymer processes.

Phase 2 of the project consists of performing baseline laboratory screening tests on commercially available mobility control agents. For this baseline testing, five different categories of tests are being conducted: (1) basic viscosity and screen factor data, (2) Berea core testing, (3) temperature stability tests, (4) bacterial degradation, and (5) surfactant-polymer interactions. Much of this testing will not be new to those experienced in the use of polymers for mobility control. However, much of the data in the open literature cannot be correlated because different test procedures have been employed. Thus the Phase 2 baseline data will provide a convenient basis for comparison of different polymers at standardized sets of conditions. These screening tests will serve as a measure for judging new or modified polymers that are subsequently developed.

The third phase of the project consists of polymer synthesis in order to determine the relationship between polymer structure and performance. Polymer structure-performance relationships will be generated from a systematic structural modification of the presently available polymer types. These modified polymers will be screened in tests similar to the methods used in the baseline screening; promising candidates will be evaluated in detail.

B. SUMMARY OF PROGRESS

Phase 1: Based on a literature survey and input solicited from industry, academic, and government sources, inadequacies of the currently used mobility control materials were assessed. Results of this input are summarized in this report. The response from the questionnaire form indicates the most serious areas of concern with hydrolyzed polyacrylamides are: (1) shear degradation, (2) viscosity loss in brines, and (3) reaction with divalent ions. Of the deficiencies listed, the least serious was the requirement for filtration. The most serious deficiencies with xanthan gum polysaccharide are: (1) economics (high cost), (2) wellbore plugging, (3) microbial degradation, and (4) filtration requirements. The areas of least concern with xanthan gums are shear degradation and viscosity loss in brines.

Phase 2: During the second quarter of the contract, laboratory investigations were established to permit an evaluation of the polyacrylamides and polysaccharides used in the first seven DOE-sponsored surfactant/polymer field demonstration projects. This baseline screening of commercially available polymers began in January, 1979, and is nearing completion. Rheological measurements and mobility control tests in Berea

cores have been completed on the polymers used in the DOE-sponsored field demonstration projects: Dow Pusher 700, Betz Hi Vis, Nalco Nal-flo, Cyanamid 960S, Kelco Xanflood, and Abbott Xanthan Broth. Similar tests were completed for Pusher 500, Pusher 1000, Amoco Sweepaid 103, and Pfizer Flocon Biopolymer 1035. Shear degradation tests in Berea core plugs have been completed for one acrylamide-type polymer and one xanthan polymer in 0.3% NaCl. Similar tests in 3% NaCl plus 0.3% CaCl_2 are in progress. Viscosity and screen factor data, in selected NaCl and CaCl_2 brines, have been collected for most of the commercially available polymers that may be potentially applicable in surfactant/polymer flooding.

Long-term thermal stability tests with one polyacrylamide polymer and one xanthan polymer have been initiated. Preliminary results are provided in this report; detailed results will be presented in subsequent reports.

Bacterial degradation tests and studies of surfactant-polymer interactions are in progress.

Phase 3: The polymer synthesis phase of the program began on schedule in May, 1979, and is currently in progress. A series of N-alkyl (N-methyl, N-isopropyl, and N-butyl) acrylamide homopolymers and copolymers with acrylic acid has been synthesized. These materials have been characterized and screened in preliminary mechanical degradation tests as well as viscosity tests in brines. Preliminary indications are that these variations of the substituents on the acrylamide nitrogen atom did not substantially change the properties of the parent compound. As expected, increasing the molecular weight (as measured by reduced viscosities) tends to impart increased shear sensitivity. Degree of hydrolysis is also an important parameter that affects performance of the modified polymer; copolymers with a wider range of hydrolysis are being investigated. Additional testing of other polymer systems, including multi-stranded polymers, is planned.

II. INTRODUCTION

A. BACKGROUND

While projections for surfactant/polymer flooding predict a substantial contribution of this process in the area of enhanced oil recovery by 1980-1990, the process at this time is largely developmental. In order for the process to become commercial, both higher oil prices and improved process technology are necessary. This project is concerned with the latter area.

Although a considerable effort is being directed towards the development of improved surfactants or combinations of surfactants, little effort is being expended toward the development of improved polymers. The polymers used in this process today are the same products that were available 10-15 years ago. Therefore, the main goal of this project will be to develop improved polymers that will increase the efficiency of the surfactant/polymer flooding process.

B. SCOPE OF THE PROJECT

The research outlined in this project is applications oriented towards this specific enhanced oil recovery process. Experiments are designed to simulate field conditions as much as possible; however, the results of the tests will be correlated with more fundamental studies that are also being conducted at the New Mexico Petroleum Recovery Research Center. In addition, our efforts are being coordinated with certain academic institutions and major oil company research laboratories where related research is being conducted.

The project has been divided into the following segments:

Phase

- 1 Survey and Assess Applications Data to Outline Problems Encountered with Currently Available Mobility Control Agents
- 2 Obtain Baseline Laboratory Screening Tests on Commercially Available Products
- 3 Generate Structure-Performance Relationships
- 4 Develop Improved Mobility Control Materials

Information in this study regarding the application of mobility control agents includes both laboratory-related and field-developed data pertaining to loss in effectiveness caused by salinity, ionic effects, injectability, temperature, shear, or chemical degradation. Much of the available data regarding mobility control polymers has developed from studies pertaining to improved waterflooding, but the emphasis in this report is on the use of polymers in surfactant/polymer processes. The objective of polymer flooding is to improve the mobility ratio without necessarily making the ratio favorable.¹⁻⁵ However, in surfactant/polymer flooding a favorable mobility ratio, between the polymer drive and the surfactant slug or oil/water bank being displaced, is needed. Deficiencies with conventional polymer flooding will be deficiencies in surfactant/polymer flooding as well. Additionally, with surfactant/polymer flooding, a potential exists for interactions between the two slugs. Consequently, the requirements of the mobility control agents are more demanding in surfactant/polymer flooding than in conventional polymer flooding.⁶⁻¹⁴

The following data regarding problems in the application of mobility control agents were obtained from: (1) surveys of published literature related to polymer flooding and surfactant/polymer flooding, and (2) a questionnaire form that was distributed to many oil industry personnel who are concerned with these enhanced oil recovery processes. The latter input was used to assess the relative importance of deficiencies with the current polymer products.

This report discusses the information obtained in Phase 1, the data obtained in Phase 2, and the Phase 3 testing program that is in progress.

III. PHASE 1: SURVEY OF APPLICATIONS DATA

A. POTENTIAL PROBLEMS WITH CURRENTLY USED POLYMERS.

The level of interest in surfactant and polymer processes is demonstrated by the large number of technical articles that have appeared in the literature in recent years. For example, in a recent bibliography,¹⁵ almost 250 references containing over 80 patents are cited for the period from 1968 to early 1976.

The most commonly used mobility control agents have been water-soluble polymers. Practical application has been limited to two polymer types: partially hydrolyzed polyacrylamides (HPAM) and a polysaccharide called xanthan gum (XG). Chemical structures of these two materials are shown in Figures 1 and 2. Within the permeability ranges typically encountered with surfactant and polymer processes, there is a general agreement that polysaccharides reduce mobility by increasing water viscosity only; whereas, polyacrylamides increase water viscosity and also decrease the relative permeability of the formation to water.^{16,17} For these mechanisms to be operative, it is implied that conditions causing additional complications, such as interactions or physical plugging, are absent. In some cases when permeability of the reservoir is reduced, the polymer concentration necessary to achieve the desired mobility control may be reduced.^{12,18} Therefore, both solution viscosity and relative permeabilities of the reservoir are important in the design of mobility control agents. Once a suitable system has been designed in the laboratory, it is necessary for the system to perform for long periods of time, under reservoir conditions, without undergoing appreciable degradation. Although both types of materials have been successfully used in the field, it is recognized that each suffers limitations that cause process inefficiencies or loss of cost-effectiveness. Some of these potential inadequacies are listed in Table 1. Many of these potential problems were adequately discussed in a recent overview paper on polymer flooding.¹⁸ For completeness of this report, these inadequacies will be reviewed and expanded to encompass the surfactant/polymer process.

1. Economics

With polymer flooding, it is often relatively easy to make an accurate appraisal concerning the economic success of the treatment.¹⁸ However, the complexity of surfactant/polymer flooding makes it very difficult to assess the cost-effectiveness of the polymer only. Common practice is to determine the cost involved to provide a required viscosity or amount of mobility reduction for a specific set of conditions. Because of its lower cost, polyacrylamide is being used in a majority of the field applications; however, it is subject to degradation as discussed below. As will be indicated, the more expensive xanthan gum is not completely satisfactory either.

2. Salinity Effects

In distilled water or very fresh waters, partially hydrolyzed polyacrylamides generate greater viscosities per unit weight than do polysaccharides. As salinity of the solvent is increased, viscosity of the polyacrylamide solution drastically decreases while the polysaccharides are not as adversely affected; therefore in strong brines, the polysaccharides will yield higher viscosities.¹⁶⁻²⁶ Although the magnitude of mobility reduction achieved with acrylamides decreases with water salinity, the effect on mobility control is not as sensitive as the viscosity measurements (partly because adsorption of hydrolyzed polyacrylamides increases with increasing water salinity).^{18,20} Divalent cations, mainly calcium and magnesium, have a more pronounced adverse effect on viscosity and mobility control of HPAM than an equivalent amount of sodium ions.^{24,25} As demonstrated by the data in Table 2, the degree of hydrolysis of HPAM is instrumental in determining the extent of influence exerted by the divalent ions.²⁵ Polyacrylamides commonly used in these processes normally range in hydrolysis from 15 to 35%; the deleterious effects of calcium ion increase as the percent hydrolysis is increased. With strong CaCl_2 brines, highly hydrolyzed (~ 35%) polyacrylamide can react to form a precipitate.

3. Oxygen Degradation

Oxygen dissolved in water promotes chemical degradation in dilute solutions of both HPAM and XG.^{17,26-28} Solutions of HPAM containing dissolved oxygen that were stored at room temperature for 45 days lost about 3% in viscosity, while similar solutions that were aerated daily lost about 13-26% in viscosity after 45 days.²⁸ Oxygen degradation is particularly severe at elevated temperatures.^{26,28} As discussed in the following section, dissolved oxygen adversely affects thermal stability of polymer solutions, which can result in loss of mobility control. Additionally, oxidizable metals and ions (particularly iron) can cause degradation of polymers in aqueous solutions. Degradation caused by oxygen can be minimized by employing an oxygen scavenger, such as sodium hydrosulfite,²⁶ or by using additives such as formaldehyde.²⁶⁻²⁸ With the latter compound, the possibility exists for a crosslinking of polymer molecules to cause a viscosity-building reaction which would be in competition with degradation processes.^{17,28}

4. Thermal Degradation

Short-term tests²⁹ (less than 1 day) indicate that, as temperature increased, viscosities of air-free HPAM solutions decreased at almost the same rate as the solvent; and that thermal decomposition of HPAM occurred at about 275°F. Long-term storage tests²⁶ (> 40 days) have shown that oxygen-free HPAM solutions retained viscosity and screen factor when stored at temperatures up to 140°F. Other tests²⁸ indicated the absence of thermal degradation when HPAM solutions, devoid of oxygen, were stored at 210°F for 6 and 28 days; however, considerable difficulty was encountered in duplicating

results. It is difficult to ensure completely oxygen-free conditions in the laboratory, and apparently only trace amounts of oxygen are necessary to accelerate thermal instability. Certainly, thermal degradation of HPAM solutions is more severe under aerobic conditions. For example, dilute solutions of HPAM, containing dissolved oxygen, lost more than half their original viscosity when stored at 210°F for 5 days.²⁸ These results would indicate that commonly used oxygen scavengers should be effective in aiding the thermal stability of polymers. Also, since oilfield reservoirs are reducing-environments, dissolved oxygen should be rapidly consumed; however, in reservoirs with high bottom-hole temperatures, it is normally prudent to employ additives such as formaldehyde.

In aqueous solutions without chemical additives, xanthan gum experienced severe loss of viscosity when stored at 170°F.¹⁷ Simply scavenging the oxygen did not entirely prevent this degradation. Solutions of XG containing formaldehyde were somewhat effective in maintaining viscosities for up to 32 days at 170°F, but, because of the complexity of the potential reactions, the authors felt that additional work was warranted.

5. Microbial Degradation

Solutions of xanthan gum are highly sensitive to bacterial attack.²⁷ Although few oilfield papers on this subject have been published, tests²⁷ with water from one field indicated that naturally present facultative bacteria caused very rapid degradation of XG solutions in both aerobic and anaerobic media. Under the same conditions, hydrolyzed polyacrylamide did not appear to degrade.²⁷ It is generally accepted that polysaccharides are more susceptible to microbial degradation than are polyacrylamides; however, when data on some of the recent demonstration projects are presented in a later section, it will be observed that microbiological activity increased in the presence of HPAM solutions. Therefore, in addition to the possibility of microbial degradation, conditions may allow the bacteria to increase in population by using the polymer as a nutrient. Excessive bacterial growth can cause wellbore plugging or injectivity problems. Formaldehyde appears to be effective in minimizing microbial degradation of both xanthan gum^{27,30} and HPAM.²⁶

6. Shear Degradation

A number of recent papers have addressed the subject of mechanical degradation of the high molecular weight polymers used in oilfield applications.^{13, 17, 20, 21, 28, 31-41} Smith²⁰ was one of the first investigators to present data that showed the possibility of mechanical degradation of HPAM solutions at very high fluid velocities in consolidated porous material. This mechanical degradation, which adversely affects mobility control properties of the polymer, was especially pronounced in solutions that contained calcium ion.

Hill et al¹⁷ presented laboratory data that confirmed that xanthan gum was more resistant to shear degradation than was HPAM. Xanthan gum solutions would retain their mobility control properties after being exposed to porous media shear rates of $3 \times 10^4 \text{ sec}^{-1}$, but HPAM solutions would start to degrade

at about 500 to 1,000 sec^{-1} . A field test^{32,37} substantiated the laboratory findings that XG is less likely to undergo shear degradation than are HPAM solutions. Therefore, the remainder of the comments in this section will pertain to shear degradation of HPAM.

Jennings et al²¹ reported that screen factor and resistance factor are quite sensitive to mechanical degradation because they are highly dependent on molecular weight distribution and molecular structure; whereas, viscosity loss was not as severe.

Mechanical degradation of polymer solutions can occur in: the surface handling equipment (particularly orifices, restrictions or centrifugal pumps), injection tubing, perforated pipe or slotted liners, gravel packs, the rock matrix in the immediate vicinity of the wellbore, and the reservoir. With proper design of surface and injection facilities, undegraded polymer can normally be delivered to the bottom of the injection well.^{32,34,37} White et al³¹ stressed the importance of preventing shear degradation in the rock matrix near the injector, and suggested injection rate limits to minimize polymer degradation. Perforations, slotted liners, and gravel packs should be designed to minimize mechanical degradation. Open-hole completions should yield less mechanical degradation of polymers than would perforated pipe.⁴⁰ Regarding mechanical degradation in matrix flow, the first inch of rock adjacent to the wellbore is the critical area.^{33,39,40}

Maerker^{33,39} described extensive experimental studies on the mechanical degradation of HPAM solutions. With the exception of very low permeability (<10 md) conditions, percent loss of screen factor was greater than losses in mobility control; viscosity was least affected at any given fluid flux. For permeabilities ranging from 30 md to 1,500 md, high fluxes caused losses in mobility control ranging from about 55% down to 25%. Shear degradation was found to be more severe with larger fluid flux, longer dimensionless flow distances (core length/grain size), lower matrix permeabilities and increased calcium ion present in the fluids.³³ Similar studies in unconsolidated sandpacks showed shear degradation increased with decreasing porosity.³⁹

Gupta and Trushenski¹³ confirmed that shear degradation increases when water salinity increases or permeability of reservoir cores decreases. At a linear flow rate of 200 ft/day through a 29 md core plug, shear degradation resulted in losses in viscosity, screen factor, and mobility control of 2, 14, and 46% respectively. Under similar shear conditions, degradation was greater with higher molecular weight HPAM polymers. As suggested by previous investigators, these authors definitely feel that loss in polymer effectiveness due to shear should be determined from subsequent mobility control tests rather than from screen factor or viscosity measurements. For field applications, these mobility control tests should utilize reservoir core and field waters, and should be conducted at velocities that are expected at the area of fluid entry into the formation.

HPAM solutions, sheared through small diameter tubes, retained their ability to reduce permeability of porous media.³⁸ The manner in which the shearing takes place (capillary tube flow, high speed blenders or dispersators, or high rate flow in porous media) has a substantial effect on the magnitude of losses observed in viscosity, screen factor, and mobility control.^{17,34,39}

Field tests^{32,34,37} describe the extent of mechanical degradation and degree of loss in mobility control during injection of HPAM solutions. Based on an injectivity study, HPAM solution lost about 50% in mobility control in one high rate (shear rate $\sim 5,400 \text{ sec}^{-1}$) test through perforations.^{32,37} In

another test,³⁴ HPAM solutions were injected into a well at various rates and samples of injected polymer were backflowed out of the well. Samples of HPAM produced back out of the formation indicated a 47% loss in mobility control caused by shear degradation, which compared favorably to laboratory estimates⁴⁰ of 50% degradation. This latter test was further complicated because the injected fresh water solution, containing the polymer, dissolved anhydrite out of the formation, which resulted in loss of solution viscosity as a result of the increased calcium ion content. The extent of degradation was directly proportional to the injection rate and to the calcium content.

A polymer flood field test⁴² in Canada provided an opportunity to evaluate the quality of polymer that had been injected, transported through the reservoir, and subsequently detected at the producing wells. Based on samples from three producing wells, losses in screen factor were found to be approximately 50, 62, and 71 percent. Since the polymer had traveled distances of 1,800 ft and had been in the reservoir from 8 to 18 months, both mechanical and chemical degradation could have contributed to the screen factor loss.

7. Injectivity Problems

Although some reduction in injectivity is to be expected with mobility control agents in surfactant/polymer projects, conditions that promote physical plugging of the reservoir or injection wellbore are undesirable. Plugging problems can be traced to material inherently present in the polymer as manufactured, or to undesirable reactions caused by some degradation mechanism, fluid incompatibility, or fluid-reservoir rock interactions. Good quality waters with low levels of suspended solids are necessary to permit preparation of acceptable polymer solutions. Many of the polymers can agglomerate or coagulate finely divided particles into larger clumps of undissolved solids that could easily plug the wellbore injection face. In most cases, it is desirable to adequately filter waters that are to be used for polymer injection processes.

Provided a good quality water has been insured, HPAM solutions normally are not filtered in the field prior to injection. With solid-type polymers, improper drying during manufacture can lead to the presence of microgel particulates. Since these deformable gels are normally undesirable in surfactant/polymer processes, quality control during polymer manufacture is very important.⁴³⁻⁴⁷

With mobility buffers following a surfactant slug, crosslinking of polymer molecules by either chemical additives or in-situ reactions with metal ions should be avoided. However, often it is desirable to precede the surfactant slug with a gelled polymer treatment⁴⁸⁻⁵⁰ to improve vertical permeability stratification.

One of the major problems in the field implementation of xanthan gum is considered to be the extra requirements necessary to prevent wellbore plugging.^{18,51} Plugging observed with XG solutions is largely attributed to three types of particulate matter: denatured proteins, biological cellular debris, and clumps of undissolved polymer aggregates.⁵¹ In a field test described previously,³⁷ appreciable wellbore impairment resulted from the injection of XG solutions. Wellbore plugging caused by XG solutions can be minimized by filtration (normally diatomaceous earth filters),^{37,52} caustic treatment,⁵¹ clay flocculation,⁵³ or enzyme clarification.⁵⁴ As discussed

previously, bactericides are required in XG solutions to control microbiological activity. Some of the recently-developed XG broths or treated xanthan gums may have better injectivity.^{18,30}

One field test reported that inadequate injectivity of HPAM resulted from unhydrated polymer plating out on the formation face.⁵⁵ All injectors were jet-washed with sodium hypochlorite to improve injectivity. Storage tanks were installed to allow complete hydration.

8. Interactions of Polymers and Porous Media

Presently available polymers that are effective as mobility control agents have hydrodynamic sizes such that the polymers may experience difficulty in penetrating low permeability (5-10 md) formations.²⁸ The degree of permeability variation or pore size distribution, as well as the molecular size, will be critical in determining the lower permeability limit for polymers. Chang¹⁸ suggests a lower limit of 20 md (10-20 md in some cases) for polymer flooding. With surfactant/polymer flooding, a slightly lower limit might be possible if the surfactant effectively reduces the waterflood residual oil saturation. A surfactant/polymer field trial is being conducted in the low permeability (8md) Bradford Sand in Pennsylvania.⁵⁶ However, since permeability affects rate of injection, well spacing, and project life, low permeability reservoirs may not be as attractive economically even in cases where fluid injection is not a problem.⁵⁷ Also, extreme variations in permeability can result in early breakthrough of the injected chemicals and loss in recovery efficiency.⁵⁷

Some of the pore space in the reservoir may not be accessible to the larger molecules in the polymer solution.⁵⁸ Whereas adsorption causes the leading edge of a polymer bank to move slower than solution water, this inaccessible pore volume phenomenon causes the polymer slug to travel faster. In surfactant/polymer flooding, this can result in the polymer moving at a faster rate than the surfactant being displaced, and can result in slug breakdown with a resultant loss in effectiveness.¹⁰ Inaccessible pore volume (IPV) is believed to be greater for HPAM than for XG.¹³ Since IPV causes invasion of the surfactant slug by polymer, mobility bank buffer volumes should be increased to compensate for the loss of mobility control.¹⁰ IPV decreases as polymer concentration increases.^{13,59}

Various reservoir minerals can adversely affect the surfactant/polymer process, i.e., clay and gypsum reduced laboratory oil recoveries.⁶⁰ These effects are particularly important with the more ionic HPAM polymers. Also, just as divalent ions dissolved in water have a deleterious effect on polymers, divalent ions in the reservoir can cause significant adsorption or entrapment of polymers. Polymer adsorption on carbonate surfaces is much greater than on sand surfaces.^{20,60-61} Preflushes are often used ahead of the surfactant slug in an attempt to precondition the reservoir for chemical flooding. However, in a polymer flood field test,⁴² a softened water preflush and afterflush was not effective in isolating the polymer from adverse ions in the reservoir. It was speculated that the softened water comingled with the formation brine and also interacted with the carbonate and clay mineral constituents in the formation. Even in cases where the preflush is effective in the portions of the reservoir contacted, improved sweep efficiency of the lower mobility polymer⁶² or mobilization of connate water⁶³ can result in the polymer contacting unfavorable ions in the reservoir.

9. Surfactant-Polymer Interactions

If polymer from the mobility buffer slug invades the surfactant slug, phase instabilities can result.^{10,64} This incompatibility can be controlled by adding oil to the surfactant slug, or by adjustment of the surfactant, cosurfactant, water, or salt concentrations in the slugs.⁶⁴ Polymer retention following a surfactant slug in cores can be much lower than in similar cores that are not treated with surfactant.^{64,65} While it was once felt that the level of polymer adsorption would be a serious problem in surfactant/polymer flooding, data¹⁰ indicate loss of either XG or HPAM will not be a significant factor in field applications.

Salinity of the chemical slugs can affect the oil recovery efficiency and stability of the surfactant and polymer slugs.⁶⁴⁻⁶⁹

Most of the available data on polymers were obtained in water-wet systems. Little data are available concerning wettability effects on polymers. Higher apparent viscosities were needed for adequate mobility control in oil-wet vs water-wet systems which required larger amounts of polymer to achieve equivalent mobility control.⁷⁰ Other tests indicated that wettability did not affect HPAM retention in surfactant/polymer floods in Berea cores.⁷¹

10. Other Potential Problems

Many potential problems were not specifically discussed in this text. These could include: creation of oil emulsions in producing wells, polymer breakthrough into producing wells, productivity problems in producing wells, mechanical or handling problems, non-Newtonian flow behavior, consistency or reproducibility of the polymer, quality control problems, and the extent and rate of hydration on the dissolution of dry polymers.

B. EXPERIENCE WITH POLYMERS IN DOE-SPONSORED FIELD PROJECTS

1. Polymer Flooding

Coalinga Field, California (Shell Oil Company)

Based on injectivity tests,³⁷ xanthan gum is being evaluated to compare a polymer flood with conventional waterflooding in this reservoir. Laboratory filterability tests indicate that enzyme-treated XG solutions should be filtered.⁷² Bacterial growth was observed in XG solutions that were stored for 2-3 days.⁷³ To prevent this bacterial growth from degrading the polymer, a change in bactericide and point of addition was considered. Early attempts with enzyme treatment and filtration of XG with diatomaceous earth were not successful in eliminating injection wellbore impairment. Suction wash samples obtained from the injection face during subsequent water

injection produced quantities of bacteria sufficient to cause wellbore damage.^{72,73}

North Stanley Field, Oklahoma (Kewanee Oil Company)

In the first phase of this project, a one-well mini-test was conducted to evaluate HPAM injection into this mature waterflooded reservoir. Results of the mini-test were:⁷⁴

- (1) Degree of shear degradation was less than anticipated.
- (2) Polymer samples retrieved from the injection well tubing produced screen factors that were comparable to plant samples, which indicated the absence of surface degradation.
- (3) No loss in quality was observed when 2375 B/D HPAM solution passed through a 1-1/2" orifice.
- (4) Polymer solution swabbed back out of the formation and through perforations yielded a 21% loss in screen factor. This loss resulted from dilution by formation water rather than mechanical shear degradation.
- (5) Sodium hydrosulfite proved to be an acceptable oxygen scavenger. Polymer degradation was observed when scavenger was not used.
- (6) At the concentrations of chemicals used, the bactericide did not degrade the polymer.
- (7) Pressure falloff tests before and after the test indicate a reduction in permeability following the polymer treatment.

Prior to the large-scale polymer field trial, a fresh water preflush was injected to minimize formation brine and iron oxide degradation of the polymer. Neither injection nor producing system experienced any major polymer-related problems. The two problems that were anticipated, formation plugging and oil emulsions, did not develop. The cumulative effect of the polymer injection and Channelblock treatments was to reduce the injection rate of 34,600 BWPD at 175 psi prior to the trial to 31,500 BWPD at 345 psi after the polymer injection. All injectors are generally taking less fluid after the polymer injection, and the injection pressure has increased about 50-100 psi depending on the volume of polymer received and the results of the Channelblock treatments. Listed below are some pertinent observations:⁷⁵⁻⁷⁸

- (1) Producing wells that experienced severe fresh water breakthrough also had early breakthrough of polymer. Approximately two years after the polymer injection was initiated, 15% of the injected polymer had been produced at the wells;⁷⁸ more than three-fourths of the polymer was produced from only 6 of the 28 producing wells.
- (2) The higher permeability-capacity suggests more extensive formation parting after the polymer injection.
- (3) In one injector near the injection plant, it was necessary to restrict the rate of polymer injection with a flow regulator coil. Polymer passing through the coil experienced a 12% loss in screen factor as a result of shear degradation.

- (4) The fresh water used for the preflush contained oxygen scavenger to provide an oxygen-free pad ahead of the polymer. Although oxygen content of the source water varied appreciably, the scavenger was generally effective in maintaining an oxygen-free environment throughout the polymer injections.
- (5) A buildup of calcium carbonate scale developed in the polymer handling facilities (feeder, slurry lines, pump, and injection point of oxygen scavenger) during the high polymer concentration portion of the project. Hydrochloric or acetic acids were effective in removing the CaCO_3 buildup. This condition was corrected by adding 4 ppm scale inhibitor to the injection water.
- (6) During warm weather, sulfate-reducing bacteria (SRB) increased dramatically downstream of the oxygen scavenger point of addition.
- (7) During the latter stage of polymer injection, SRB were detected in the producing wells. To date, no corrosion problems were detected that could be attributed to the bacteria.

Storms Pool Unit, Illinois (ERCO)

This project is in the early stages of laboratory evaluation of polymers.⁷⁹

2. Surfactant/Polymer Flooding

Bell Creek Field (Gary Operating Company)

Laboratory tests were initiated to evaluate a soluble oil system (Union Oil Company) and an aqueous surfactant system (Atlantic Richfield Company) for this field. Results of some of these investigations follow.⁸⁰⁻⁸²

Soluble Oil System. Both liquid emulsion HPAM and solid HPAM polymers produced satisfactory performances with the oil external surfactant systems. The presence of polymer in a micellar slug had a negative effect on oil recovery efficiency by causing unfavorable phase relationships. With the soluble oil system that was developed, HPAM did not invade the soluble oil slug enough to damage effectiveness--partly because of the flow characteristics of the polymer and partly because the polymer is insoluble in oil. A sodium silicate preflush provided a favorable salinity and pH for the surfactant and polymer slugs. In some cases, the preflush can increase the volume of reservoir contacted by the surfactant and polymer. A 60% pore volume slug of graded HPAM was found to be optimum for this system.

Aqueous Surfactant System. Injectivity tests were conducted on two XG polymers, and chemical stability tests were conducted on one XG polymer. Because of poor injectivity, higher cost, and a potential for limited

chemical stability, XG was eliminated from further consideration. Two HPAM materials were examined for sensitivity to salinity, calcium ion, chemical stability, shear degradation, and injectivity into sandstone.

Based on these tests, one of the HPAM products was utilized to determine the following design variables: polymer concentration, polymer slug size, and salinity contrast with the surfactant slug. Results indicated it was important for the salinity of the polymer drive to be compatible with the surfactant solution salinity. Increasing the concentration of polymer resulted in lower final oil saturations since the mobility ratio became more favorable; only slight improvement of oil recovery was observed at polymer concentrations in excess of 1,500 ppm. A polymer slug size of 60% pore volume appeared to be adequate and gave results comparable to continuous polymer injection.

Based on the laboratory oil recovery experiments⁸⁰⁻⁸¹ and computer simulations,⁸² the soluble oil process was selected for the field test. This process has been tested at this project in a mini-injectivity test: injection rates exceeded the design criteria, and residual surfactant remaining in the surface injection system caused polymer viscosities to be low. The necessity of thoroughly cleaning the tanks and injection lines of surfactant prior to polymer injection was pointed out, but no mention was made of the possibility of similar effects occurring in the reservoir mixing zone. Based on the results of additional laboratory testing and reservoir computer simulation, a larger-scale test is pending.

Big Muddy Field (Continental Oil Company)

A small pilot test that utilized XG was previously tested with success.⁸³ A large-scale test in this field is planned.⁸⁴ Bacterial degradation of the XG was listed as a potential problem since the XG polymers contain excellent nutrients for the bacteria. Bacterial attack could destroy some of the polymer and cause severe injectivity problems. From an evaluation of bactericides, the most effective treatment was found to be a two-step chlorination-caustic treatment (adjust pH to 12). The producing wells may be squeezed with acrolein for bacterial control. Appropriate steps are being planned to minimize chemical interferences between the surfactant and polymer slugs. Based on laboratory appraisals, HPAM polymer has been selected for the large-scale test.⁸⁵ Selection of polymer will be finalized after a subsequent field injectivity test in this very low permeability reservoir.

Bradford Field (Penn Grade Crude Oil Association)

The surfactant slug (designed by Marathon Oil Company) has been injected into this low permeability sandstone reservoir. Average permeability of the Bradford Third Sand is 8 md. Injection of XG polymer is now in progress.⁸⁶ Polymer of acceptable quality is being delivered to the injection wells.

Delaware-Childers Field (DOE)

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Injections of aqueous surfactant and emulsion HPAM slugs are completed. Mechanical problems were encountered in maintaining proper polymer injection rates. Difficulties were limited to the surface facilities (polymer pump, flow lines, check valves, etc.); no subsurface damage was indicated. Make-up water for the polymer contained oxygen and was handled in an open system. Since no corrosion was indicated (low dissolved iron content) and since the formation temperature was low, no oxygen scavenger was used. A chlorophenolate bactericide at a concentration of 10 ppm was added to the supply water during the polymer injection. The polymer injection was followed by fresh water. The injection rate decrease from 140 B/D during surfactant injection to about 80 B/D during polymer injection was believed to be a result of more viscous fluids.

El Dorado (Cities Service Company)

Two patterns in the El Dorado field are being used to evaluate different types of surfactant slugs.⁸⁹⁻⁹² The South Pattern (Hegberg Lease) will employ a soluble oil-HPAM system (Union Oil Company); whereas, the North Pattern (Chesney Lease) will employ an aqueous surfactant-XG system (Shell Oil Company). Polyacrylamides and biopolymers of several types were subjected to screening tests, which included rheological behavior, solubilization in water, filterability through filter paper, interaction with surfactant solutions, chemical degradation, shear degradation, mobility in cores, plugging tendencies in cores, and adsorption by reservoir rock. Quality control and consistency of the polymers were major concerns. Chlorine gas has been used at this project to control bacteria in the injection water. Since high concentrations of chlorine can cause polymer degradation, bactericides were evaluated that can be compatible with HPAM, XG and chlorine.

South Pattern (Hegberg).

Five liquid-type HPAM products were evaluated; two materials were rejected because they plugged fired Berea cores. Based on performance and economics, an emulsion HPAM product was chosen. Mixing effects between HPAM and soluble oil were investigated; viscosities of polymer diluted with soluble oil were considerably lower than polymer diluted with comparable amounts of fresh water.

North Pattern (Chesney).

Among the XG polymers tested for this pattern were two liquid (aqueous solutions) and one solid-type products. At the same concentrations, the liquid broth products generated slightly higher viscosities. The broth

samples demonstrated better injectability qualities than the solid-type XG product in membrane filter tests, laboratory flow through reservoir cores, and a subsequent field injectivity test. The field test indicated that, because of the shear-thinning nature of the XG solutions, high concentrations of polymer could be pumped with relative ease, and that any wellbore damage caused by the XG material could be successfully treated with acid. Solutions of XG were treated with commercial bactericides or formaldehyde and/or alcalase enzyme. After two weeks of standing, the treated XG solutions maintained their viscosity at about 30 cp; whereas, solutions without biocide or enzyme treatment had decreased in viscosity to about 2 cp.

M-1 Project (Marathon Oil Company)

This commercial-scale project utilized a sulfonated crude oil surfactant followed by graded HPAM solutions.⁹³⁻⁹⁷ The particular HPAM product used was selected on the basis of laboratory core floods, availability, price, and successful utilization in previous field tests. Since excessive hardness ions adversely affect polymer solution properties and can ultimately cause a less efficient oil displacement, the laboratory evaluations used fresh water that was partially zeolite-softened to reduce hardness and lower polymer requirement. In these tests, surfactant/polymer oil recovery was reduced as the core permeability decreased. At various permeabilities, oil recovery was investigated for several different molecular weight HPAM products; better oil recovery was obtained with a higher molecular weight material. In field injectivity tests using wells that were both treated and untreated with surfactant, little difference was noted between the two products; therefore, the higher molecular weight product was selected. Since laboratory displacements do not properly simulate field flow conditions, field designs require about 25% more polymer than that used in most laboratory floods.

Because oxygen can severely degrade polymer solutions, steps included the installation of a nitrogen blanket over the polymer feeder and the introduction of the dry polymer onto a non-turbulent sheet of water for hydration. This sheet of water is sufficiently fast so that all the particles of the dry polymer are wetted to allow for complete hydration. Since it is not possible to always completely exclude atmospheric oxygen from oilfield systems, 200 ppm formaldehyde is to be added to the polymer solution. Formaldehyde also functions as a bactericide.

In the design of field equipment, all line-constrictions or other flow restrictions that could cause abrupt pressure drops and induce polymer shear degradation were eliminated. Based on field flow tests, all lines were sized to minimize mechanical degradation. During the polymer injection, coils of various lengths of copper tubing are used to regulate flow rates.

North Burbank Unit (Phillips Petroleum Company)

A solid-type HPAM product was also used at this project; hence, the precautions mentioned above for the M-1 Project were implemented successfully at the North Burbank Unit.⁹⁸⁻¹⁰² The polymer flow-rate controller was used effectively to adjust rate of flow without shearing the polymer. Average loss in viscosity was 7.7%, while average loss in screen factor was 11%; a screen factor loss of this magnitude corresponded to essentially no change in mobility control properties of the polymer.⁹⁹ A nitrogen blanket was used over the polymer feeder, and sodium hydrosulfite was injected ahead of the feeders. No major problems were encountered with the polymer, but particle size and degree of hydrolysis did vary somewhat from lot to lot.¹⁰⁰

Sulfate-reducing bacterial growth increased during the polymer injection. No increase in corrosion rate was detected. Except for one well, HPAM has been found in produced water from all the production wells. Two years from the initiation of polymer injection, 12.6% of the injected polymer had been produced.¹⁰³ High levels of polymer were associated with known channeling areas. Several injectors were treated with gelled polymer to minimize channeling.

Pressure buildup data indicate that the low injectivity and productivity was due to the viscous fluid flow rather than formation damage.

Wilmington Field (City of Long Beach)

This unconsolidated sandstone reservoir will be pilot-flooded with a micellar solution (developed by Marathon Oil Company) followed by an emulsion HPAM polymer.¹⁰⁴⁻¹⁰⁷

During the early stages of the laboratory core flooding, 100% water-saturated radial sand packs prepared from the Wilmington sand were utilized. A reaction was noted, possibly between the HPAM injected and an unfavorable cation in the sand, which caused a degradation of polymer viscosity. Subsequent tests showed that surfactant slug preceding the polymer slug eliminated most of the unfavorable polymer reaction with the sand. In the initial tests, injectivity problems were noted with a very high molecular weight HPAM product--because of high retention and extremely low mobility, this material had difficulty in propagating through the sand pack. A middle molecular weight HPAM had a favorable retention level and adequate mobility properties; a lower molecular weight HPAM had a low retention but high mobility. All of the polymers were displaced from the packs more efficiently with fresh water than with brine. These results were coupled with a mini-injection field test in which surfactant was followed by several types of polymers at varying concentrations and volumes. This test demonstrated that surfactant and various concentrations of polymer could be injected at acceptable rates and pressures, and resulted in the selection of the middle molecular weight HPAM.

After the mini-test, the injector was backflowed to determine the extent of polymer degradation as a result of injection through a slotted liner. Results indicate the polymer solution had experienced dilution with formation water and had suffered some degree of degradation and/or

adsorption. Degradation could have been caused by aging, mechanical shear, chemical or thermal deterioration. High clay content of the reservoir sand could have contributed to high polymer adsorption. Injectivity decreased about 25% after the mini-test. An emulsion HPAM product has been selected for the main test.

3. Summary of Field Experience

Based on the published information relating to the DOE-sponsored field projects, several problems were mentioned that are common to both HPAM and XG: (1) reduced injectivity, (2) injectability in low permeability reservoirs, (3) surfactant-polymer interactions or phase instabilities, (4) degradation caused by oxygen, (5) quality or consistency of products, and (6) the availability of bactericides that are compatible with polymers. Areas of concern with xanthan gum products also included: (1) degradation caused by bacteria, (2) injection well impairment, and (3) requirements for filtration. Problems with partially hydrolyzed polyacrylamides also include: (1) viscosity loss in brines, (2) sensitivity to hardness ions (calcium and magnesium), (3) requirements for minimizing shear degradation, (4) breakthrough of polymer into producing wells, and (5) increased growth of sulfate-reducing bacteria. The latter area refers to a stimulation of bacterial growth, rather than the familiar degradation in the case of xanthan gum polysaccharides.

C. RESULTS OF INDUSTRY QUESTIONNAIRE

To assess the relative importance of deficiencies with currently available polymers used in surfactant/polymer processes, a questionnaire was distributed to more than 200 oil industry personnel. Input was solicited from oil company, academic, government and supplier sources. More than 75 replies were returned, and the completed questionnaires represented the opinions of almost 100 oil industry people who are concerned with this enhanced oil recovery process. Results of this input are summarized in Tables 3-5. Data presented in these tables are based on the responses from oil company personnel with either field experience or both laboratory and field experience. These results do not differ significantly from the total response to the questionnaire.

As indicated in Table 3, approximately 20 percent of the respondents stated their preference would depend on the particular application, and 3% did not prefer either polymer. With both types of responses, there was a slight preference for the hydrolyzed polyacrylamides over the xanthan gums. The primary reasons for this preference were lower cost required to achieve the desired mobility control in the reservoir and fewer handling problems in the field.

Preferences regarding polymer form are listed in Table 3. If active polymer costs are comparable for the various physical forms, it is obvious that solutions or liquid forms are desirable. Ease of handling was the

primary consideration for the choice of solutions, emulsions, or liquid-type products.

Instructions on the questionnaire were to list the most severe inadequacy as #1, the second most serious as #2, the third most serious as #3, etc. If a polymer was judged to be adequate in a particular aspect, that item was marked "A" for adequate. Entries for each item were averaged so that the most severe inadequacies are denoted by the lowest average rating. The number of adequate ratings for each item is listed in the tables. Inadequacies of HPAM polymers are rated in Table 4. In the opinion of the people who participated in the survey, the most serious areas of concern with hydrolyzed acrylamides are: (1) shear degradation, (2) viscosity loss in brines, and (3) reaction with divalent ions. The least serious of the deficiencies listed was the requirement for filtration. Table 5 indicates that for xanthan gum the most serious inadequacy is: (1) economics (high cost), followed by (2) wellbore plugging, (3) microbial degradation, and (4) filtration requirements. The least serious problems with XG are shear degradation and viscosity loss in brines.

It can be argued that, in some of the areas evaluated, not enough is universally known to make a fair appraisal. However, the results of the survey presented no substantial surprises and are generally in agreement with the information obtained from the published literature. Naturally, the most significant deficiencies in polymers used for surfactant/polymer flooding will depend on the particular field application, but the major inadequacies listed above are those that are currently recognized as being problem areas.

IV. PHASE 2: BASELINE LABORATORY SCREENING OF COMMERCIALY AVAILABLE POLYMERS

Phase 2 of the project consists of obtaining baseline laboratory screening tests with polymers that either have been or are being used on DOE-sponsored field projects. Other polymers have also been evaluated. These screening tests will serve as a measure for judging any improved products that are developed. This work was started in January, 1979, and continues. For the baseline screening data necessary for Phase 2, five different categories of tests are being conducted: (1) rheology, (2) flow categories of tests in Berea cores, (3) temperature stability, (4) bacterial degradation, and (5) surfactant-polymer interactions.

In general, there were no big surprises in the wealth of data which was obtained in these laboratory screening tests. Most of the observed trends have been reported in the literature and are now accepted by knowledgeable workers in the field of polymer flooding. However, this baseline information should be important to future work because new materials can be compared quickly to any of the standard polymers which were tested here under one set of standardized conditions.

A. RHEOLOGICAL PROPERTIES

1. Viscosities and Power Law Parameters

As a prerequisite, an effective mobility control agent must have the ability to thicken water at a low cost or low polymer concentration. Since most of the commercially available polymers exhibit pseudoplastic behavior at typical reservoir flow rates (1-2 ft./day), a portion of the screening involved determining the viscous behavior of polymer solutions at various rates of shear. For this work, a Brookfield Model LVT viscometer with U.L. adapter was used; additional tests with a low shear rheometer and low shear capillary viscometer are planned. All measurements were taken at 25°C. Polymer concentration was 750 mg/l. Viscosities were measured separately in NaCl and CaCl₂ at the following salt concentrations: 0.01%, 0.3%, and 2%. Several polymers were also evaluated in 0.1%, 1%, and 10% brines. A typical plot of viscosity versus shear rate is shown in Figure 3. From these plots, the Power Law parameters can be determined:

$$\tau = K \dot{\gamma}^n$$

where,

τ = shear stress, dynes/cm²

$\dot{\gamma}$ = shear rate, sec⁻¹

K = Consistency Index (dynes/cm²)(sec)ⁿ

n = Flow behavior index, dimensionless

With these log-log plots, n-1 is the slope of the straight line, and K is the intercept where the shear rate is 1 sec⁻¹. The apparent viscosity (μ) for the Power Law fluid is given by: $\mu = \tau / \dot{\gamma} = K(\dot{\gamma})^{n-1}$

For highly pseudoplastic or shear-thinning fluids, n is considerably less than 1. Solutions assume a Newtonian-like character as n approaches unity. Using a best straight-line fit for the Power Law approximation, the parameters K and n were determined for the various polymer solutions. These results are shown in Tables 6-18. Generally, the parameters were determined from data obtained at 1.7 to 73.6 sec⁻¹. A total of 17 acrylamide-type polymers and 10 cellulose-containing polymers were evaluated at several salt concentrations. Although these tests provide a wide spectrum of new baseline data, the main conclusions which can be drawn from the tests are not new. Some of these conclusions are reflected in the answers to the questionnaires which were discussed in Phase 1. However it seems wise to emphasize certain aspects of the polymer solution behavior as brought out in these baseline tests. In general, data in Tables 6-13 for the HPAM show:

- (1) As salt concentration increases, the degree of pseudoplasticity is reduced (n approaches unity with increasing salt content).
- (2) The apparent viscosity falls off drastically as the salinity of the solution is increased (K decreases with increased salt content).
- (3) Calcium chloride has an even more drastic effect than sodium chloride in reducing solution viscosities (K values are lower and values of n are higher at the same weight percent of salt).

The effects of NaCl and CaCl₂ on solution viscosity for these polymers are shown graphically in Figures 4 and 5. The effects mentioned above are particularly severe at low salt concentrations for the acrylamide-type polymers. Conversely, viscosities of the xanthan biopolymers are only slightly reduced with increasing salinity levels. As a result of these effects, the commercial HPAM polymers generate a higher solution viscosity in very fresh waters, but the XG polymers at the same concentration yield higher viscosities in brines. With the xanthan materials, there appears to be some deviation from the Power Law model at shear rates below 10 sec⁻¹. Thus, the parameters K and n were evaluated using viscosity data obtained at shear rates in excess of 10 sec⁻¹. All of the observed effects are widely known and are consistent with previous findings.

2. Effect of Calcium Ion on Polyacrylamide Solution Viscosities.

The loss of polymer effectiveness with salt is well known but there are less data in the literature on the effect of calcium ion on viscosity and we want to include this information in the baseline data. This study is a preliminary attempt to quantify the effect of calcium ions, as compared to sodium ions, on the viscosity of a partially hydrolyzed polyacrylamide solution. The difference between calcium and sodium ions is most apparent at low salinities, e.g., salinities less than 1 or 2 weight percent sodium chloride. Results are reported here for several ionic strengths in the range from $I = 0.0171$ to $I = 0.171$, corresponding to 0.1% to 1.0% (wt/vol) NaCl solutions. At each ionic strength the ratio of calcium to sodium was varied, and the viscosities at each Ca²⁺ to Na⁺ ratio were measured using both Brookfield and capillary techniques.

The results of this study show that, in the range of ionic strengths investigated, drop in viscosity is directly related to the relative calcium ion content (see Figures 7 and 8). Thus, solution viscosity can be predicted from the proportion of calcium in the solution and the viscosity of the same polymer in another solution at the same polymer concentration and the same ionic strength.

a. Experimental Procedures. The polymers used in this study were Calgon 835, a 35% hydrolyzed polyacrylamide of very high molecular weight, and Calgon 825, the same base polymer with 25% hydrolysis. Since the molecular weights are comparable, a study of these polymers will provide a quantitative correlation between carboxyl content and viscosity loss caused by calcium ion. Stock solutions of 1-1/3 times the final concentration of these polymers were mixed and allowed to hydrate for several days before use. Solutions of Calgon 825, which were made up to 1500 ppm, also contained 0.05% NaCl to facilitate handling. All the polymer in each study was from a single batch so that errors due to small polymer concentration differences are minimized.

Salts for this study were NaCl and CaCl₂·2H₂O. Stock solutions of each salt in water were prepared at concentrations equivalent to four times the desired ionic strengths. Seventy-five ml of the polymer solution were added to 25 ml of a mixture of two of the stock salt solutions to give polymer concentrations of 750 ppm or 1500 ppm (for 835 and 825 respectively), a total ionic strength from 0.0171 to 0.171 M and a fraction of calcium ions equal to 0, 0.025, 0.075, 0.15, 0.3, or 1.0. (In the cases where the polymer solution contained NaCl, the maximum fraction of calcium varies with total

ionic strength.) The fraction of calcium ions is calculated from the following formula:

$$X_{Ca} = \frac{M_{Ca}}{M_{Ca} + M_{Na}}$$

where

X_{Ca} = fraction of calcium ions
 M_{Ca} = molar concentration of $CaCl_2 \cdot 2H_2O$
 M_{Na} = molar concentration of NaCl

Note that this is not a true mole fraction because water and polymer concentrations are neglected. The contribution of the polymer to the ionic strength is also neglected in this treatment.

Viscosities were measured for the low concentration solutions using a Brookfield LVT with UL adapter, a Brookfield LVT cone and plate viscometer with an SCP-3 spindle, and a Cannon-Fenske #100 capillary viscometer. Several of the solutions were also measured using a four-bulb Cannon-Ubbelohde 75 viscometer. Viscosities of the more concentrated polymer solutions were measured using two four-bulb Cannon-Ubbelohde viscometers. All viscosities were measured at $25^\circ C \pm 0.1$. Additional low shear measurements will be obtained with a Contraves rheometer.

b. Quantifying the Effect of Calcium Ion on Viscosity. Figure 6 compares the decrease in relative viscosity for 835 at 750 ppm with increasing fraction of calcium for three ionic strengths. As anticipated, higher viscosity is observed at lower ionic strength. The plot also shows that the largest total effect of calcium is at the lowest ionic strength. Figure 7 shows the percentage of the viscosity at $X_{Ca} = 0$ remaining as the fraction of calcium increases. Within the limits of experimental error, data for all three ionic strengths lie on a single line. These data were fitted by least squares to a logarithmic curve (Table 20).

An attempt to repeat these results using 825 at 750 ppm showed that too much uncertainty existed in the experimental data to permit any firm conclusions. Two sources of uncertainty were identified: the accuracy of the Brookfield viscometers and the small differences in viscosity between different solutions. The measurement errors were improved by implementing the four-bulb, variable shear rate viscometers with some sacrifice in analysis time and the ability to obtain low shear rates. Differences in viscosity between solutions was increased by doubling polymer concentration. This necessitated addition of a small amount of NaCl (0.05% by weight) to the polymer solution to reduce viscosity to a point where the solution could be mixed and measured. Thus, readings at $X_{Ca} = 1.0$ were sacrificed. Figure 8 shows that, with these improvements in experimental technique, the results obtained with 835 were corroborated. The equation fitting this line is also given in Table 20. A cursory comparison of these results would seem to indicate a greater effect of calcium ion on 825 than on 835. This may in fact be due to the differences in experimental conditions, especially concentration. This point is currently under investigation.

3. Screen Factor Measurements.

Screen factor is a measure of the viscoelastic property of the polymer solution. Screen factors of the various commercial samples were determined in conventional screen tubes at 25°C. Results in Tables 21 to 24 agree with previous investigations and are presented to provide a basis for comparison of different polymers in standard NaCl and CaCl₂ aqueous solutions. These results can be summarized with the following conclusions:

- (1) Screen factors are higher for the elastic acrylamide-type polymers; screen factors are lower for the more rigid molecular configuration of the xanthan materials.
- (2) Although there was, generally, a loss in screen factor with increasing salinity, the magnitude of reduction was not nearly as great as was observed for viscosities of the same solutions.

The usefulness of the screen factor tests is questioned by some workers in polymer flooding. However, even though it may not be as sensitive to loss of viscous properties with increasing salinity, the screen factor is a good test for detecting changes in molecular weight caused by shear or thermal degradation (see Figures 12-14).

B. MOBILITY CONTROL TESTS IN BEREA CORES

While viscosity and screen factor measurements are useful in screening polymers, flow tests through porous media are normally required to obtain a direct measure of mobility control and the extent of polymer adsorption or retention. In accordance with the terms of the contract, Berea core plugs were used for the porous media studies.

1. Mobility Reduction.

Mobility control tests were performed with 750 mg/l polymer in both 0.1% NaCl and 2% NaCl. A linear frontal advance rate of 1 ft/day was employed for these room-temperature tests in Berea sandstone. Initial permeabilities to water ranged from 350-550 md for the various tests. The initial polymer solutions were filtered through a 325-mesh screen and then pumped through a short Berea core to indicate polymer plugging tendencies. Effluent from the injectivity core was injected through a longer mobility core in order to obtain resistance factor values and polymer retention levels. This sequence of testing may tend to provide lower resistance factors than some of the previously published values; however, we feel this technique provides numbers that are more indicative of the level of mobility control that can be expected in the bulk of the reservoir. Approximately 4 pore volumes of polymer solution were injected; for the most part, the polymer resistance factors had stabilized. After the polymer injection, a

water flush with the same salinity as the polymer solvent was used to generate the post-polymer or residual resistance factors. Since the shear rate during polymer flow through the mobility core cannot be determined precisely, the viscosity of the polymer solution in the core is not accurately known. However, for many of the tests, the resistance factor numbers determined under these conditions are not appreciably different from the viscosity (at the estimated core shear rate) of the effluent from the injectivity core--exceptions are Pusher 1000 and Cyanatrol 960S in both waters, Pusher 700 in 2% NaCl and Abbott Xanthan Broth in 2% NaCl. The resistance factor data shown in Table 25 indicate:

- (1) Several of the hydrolyzed polyacrylamides generate higher resistance factors in the lower salinity water than the same concentrations of the xanthan gum products.
- (2) For the hydrolyzed polyacrylamide solutions, resistance factors are adversely affected by increased salinity.
- (3) In 2% NaCl, the xanthan products are more effective in reducing mobility than are the acrylamide products.

2. Polymer Retention.

Samples collected during the polymer injection and during the following water flush were analyzed for polymer content. From material balance calculations, the amount of polymer retained in the Berea core was determined. Preliminary results, listed in Table 26, indicate a somewhat lower retention for the xanthan products and a greater amount of retention with increased salinity for all types of products.

3. Mechanical Degradation

Shear degradation tests are being conducted in tests similar to the method proposed by Maerker.³³ Polymer solutions are injected through small diameter Berea cores at various flow rates. The extent of induced degradation is measured using a Brookfield model LVT viscometer with U.L. adapter and by a screen viscometer. In addition, these partially degraded solutions are flowed through longer Berea cores at a linear frontal advance rate of 1 ft/day. Mobility reduction (resistance factor) measurements start with the most severely degraded solution first and end with the unsheared polymer solution. Viscosities and screen factors are measured for all effluent samples, and each solution is analyzed for polymer content. In this manner, loss in mobility control can be related to the induced shear conditions. These methods not only permit the screening of mobility control agents, but give a better insight into the loss of mobility control that can be expected under field conditions.

These tests are being conducted with one xanthan product (Abbott) and one hydrolyzed polyacrylamide (Dow Pusher 700). Solvents for the polymers include 0.3% NaCl, and 3% NaCl that contains 0.3% CaCl₂; results with the lower salinity water are presented in this report. As indicated by Figure 9, results obtained with Pusher 700 in 0.3% NaCl appear to agree with previous results presented by Maerker.³³ Concentration of polymer in the present

study was 750 mg/l; the comparative data by Maerker was obtained with 600 mg/l Pusher 700.

Viscosities of the Pusher 700 solutions were measured before and after injection through the shear core plugs. The effect of this induced degradation on the Power Law parameters in Table 27 shows: (1) viscosities are reduced at high flow rates and, (2) the sheared solutions become more Newtonian (Figure 10). The fraction of viscosity retained and the fraction of screen factor remaining after degradation of Pusher 700 are plotted in Figure 11; the loss in screen factor was more severe than the loss in viscosity (at 7.3 sec^{-1}). Results from a similar test with Abbott Xanthan Broth are also plotted on Figure 11; whereas the hydrolyzed polyacrylamide was substantially degraded at high frontal advance rates, viscosity of the xanthan product was not significantly reduced. The loss in mobility control of the acrylamide-containing polymer is shown in Figure 12.

C. THERMAL STABILITY

Both polyacrylamides and biopolymers can be thermally unstable, and this instability is aggravated if the polymer solutions contain oxygen.^{17,26-28} The following procedure is designed to study the long-term effect of elevated temperatures on polymer solution properties. Polymer is mixed in a fresh water (0.1% NaCl) and a brine (1% NaCl), each of these with and without O_2 , and each with and without formaldehyde. Samples are stored at four different temperatures (77°F , 110°F , 150°F , and 200°F). The polymer is prepared according to manufacturer's directions in the desired water with pH adjusted to 7.5. If the sample is to be oxygen-free, it is purged in a glove box with nitrogen that has been treated with 3 scrubbers (a commercial oxy-trap, vanadium (II) chloride, and sodium hydrosulfite) to remove the oxygen. After 4-8 hours, the O_2 is reduced to less than 1 ppb. The samples are then transferred into glass bottles, sealed with polyethylene-lined crown caps, and stored at the desired temperature. If formaldehyde is to be added to an oxygen-free sample, it is added after the oxygen is removed to prevent potential removal of the formaldehyde. Samples are taken every 3-4 days for the first four samples, and once a week thereafter. Brookfield and screen viscosities are measured. Samples are handled in an oxygen-free environment to avoid contaminating the remaining polymer.

Preliminary results in Figures 13 to 15 show: 1) the amount of degradation increases as temperature is increased from 110°F to 200°F , 2) loss in screen factor was greater than the loss in viscosity (at 7.3 sec^{-1}), and 3) removing oxygen from the solutions improves the thermal stability in the temperature range studied. The onset of thermal instability with the purged samples occurred at a lower temperature than expected, and the rate of degradation of the purged samples at elevated temperatures was greater than anticipated; these tests will be repeated. Details of all of the thermal testing will be provided in subsequent reports.

D. BACTERIAL DEGRADATION

The stabilities of polyacrylamide and xanthan gum polysaccharide, in the presence of aerobic and anaerobic microorganisms, are being evaluated by changes in viscosity of polymer solutions with time. The test microbes consist of a mixed population of aerobic bacteria obtained from oilfield water and anaerobic sulfate-reducing bacteria (Desulfovibrio and Desulfotomaculum). These microbes may be able to affect polymer-solution viscosity either by direct enzymatic breakdown and subsequent utilization of the polymer as a carbon source, indirect breakdown resulting from interaction of polymer with a metabolic end product, or as a result of a process whereby recalcitrant molecules are altered by microbial activity. The initial phase of this study will determine only if microbes, such as might be found in oil reservoirs, can effect breakdown of the test polymers.

Two environmental conditions are being compared: an oxidizing environment using an iron-peptone medium with shake cultures for aeration, and a reducing environment established by using a Desulfovibrio growth medium and stationary cultures. The respective media contain the test polymers at a concentration of 1.0 gram per liter. Three parameters for microbial growth in the presence of the polymers will be evaluated:

- (1) respective media with polymers
- (2) respective media with polymers plus 2% NaCl, to simulate a brine
- (3) respective media altered so that the only carbon source provided is the polymer.

The medium is inoculated using actively growing enrichments of aerobic and anaerobic bacteria obtained from oilfield water. One ml of bacterial suspension per 100 ml of medium is used. The cultures are incubated at 32°C, sampled at 7, 14, and 21 days, and the viscosity is determined. Viscosities are compared to blanks that are not inoculated. Growth of the cultures is determined by observation of turbidity, sulfide-production, and microscopic determination of relative cell number. If the polymers are found to inhibit microbial growth, quantitative experimentation will be done to evaluate the degree of toxicity. Results of this testing will be evaluated in subsequent reports.

E. SURFACTANT-POLYMER INTERACTIONS

1. Background

Evaluation of the polymers for micellar/polymer flooding must include consideration of the compatibility of the surfactant and polymer slugs. It is necessary, from the point of view of mobility control, that the surfactant be followed by drive water containing high molecular weight polymers to increase viscosity. The well-established phenomenon of inaccessible pore volume⁵⁸ explains that some of the very large polymer molecules are excluded from the small pores, thus travelling at a faster rate than the rest of the slug. This means that the back of the surfactant slug is mixed with a high concentration of polymer molecules, which may cause adverse changes in the surfactant phase behavior.

Surfactant-polymer interactions have been studied by several different authors. Trushenski^{10,110} did much of the initial work in defining sulfonate-polymer incompatibility (SPI), including phase behavior and core flooding studies. His work included studies of both biopolymer and partially hydrolyzed polyacrylamides with a Mahogany AA sulfonate, isopropyl alcohol, and crude oil. This work showed that invasion of the micellar slug by polymer can result in phase separation and, he postulates, phase trapping. Phase behavior with polymer is shown to be affected by surfactant to cosurfactant ratio, temperature, and salinity. Polymer type and concentration show little effect on phase behavior. Phase separation can be reversed or avoided in this system by increasing temperature, reducing salinity in polymer drive water, increasing cosurfactant concentration or adding oil to the micellar fluid. The point is also made that dilution tests of micellar fluids with polymer drive water are not valid since polymer precedes the remainder of the drive water bank and mixes at nearly full strength with the back of the micellar slug.

Shah et al¹¹¹ report that oil recovery is improved if salinity in the polymer slug is the same as the micellar slug. These tests were performed in high permeability sand packs, and it is not clear whether such results can be extrapolated to low permeability porous media, especially since there are published results that contradict these findings.

Szabo⁶⁵ has looked at phase behavior for several polymers and surfactants. He concludes that the surfactant-rich phase is trapped primarily because it exhibits much higher viscosity than the polymer-rich phase. He suggests that a slug design that equalizes these viscosities would improve recovery results. Salinity reduction in the polymer slug resulted in improved recovery. Results generally were not dependent on the polymer used, with the possible exception of Kelzan MF biopolymer.

An extensive study of the interaction of surfactants and polymers with and without added oil is reported in a master's thesis.¹¹² Tsaur defines a critical electrolyte concentration (CEC) at which phase separation in the presence of polymer is observed to occur for a given mixture of surfactant and cosurfactant in an aqueous system. Typically the CEC is lower than the salinity at which phase separation occurs when no polymer is present. CEC is shown not to vary with polymer type or concentration (within the range of interest for oil recovery systems). Polymer is observed to have less effect in the presence of oil.

Since the major intent of this project is to evaluate polymers, extensive tests of interaction with a variety of surfactant systems are not feasible. It is proposed, therefore, that one or two standard sets of conditions be chosen and that the polymers, commercial and newly synthesized, be compared to results with no polymer in the oil-free system. One possibility is a scan of salinity to determine CEC as defined by Tsaor. Other possibilities include viscosity and interfacial tension measurements at standard conditions.

2. Preliminary Tests

Before a testing program can be finalized, a suitable surfactant system must be found. Ideally this would be a system using a reasonably pure surfactant, as opposed to the very impure petroleum sulfonates likely to be used in actual surfactant/polymer flooding.

Sodium dodecylbenzene sulfonate (SDBS) from several commercial sources has been investigated. These preparations differ in activity, molecular weight and isomer distribution, and nature of contaminants. Tests of these sulfonate products from 0.75% to 5% by weight activity with alcohol cosolvents including sec-butanol, iso-butanol, t-butanol, and iso-amyl and t-amyl alcohols from 1.5% to 4% have so far shown only one combination that separates into two liquid phases at the CEC of the oil-free system. All the other combinations tested so far give phase separation into one liquid and one solid phase (a precipitate of the sulfonate). While this does give a measure of the CEC, it does not permit comparisons of such quantities as viscosity and interfacial tension. Thus, it seems desirable for the model system chosen to be one that separates into liquid phases at the CEC, as would the higher molecular weight petroleum sulfonates.

The one SDBS system that does give the desired phase behavior has been reported previously by Tsaor.¹¹² It consists of 1% Siponate DS-10 and 3% iso-amyl alcohol. Phase volume results at 30°C are shown in Figure 16 as an example of the results anticipated with and without polymer, as the concentration of NaCl increases. Such figures conveniently summarize the relative phase volumes observed and may be made more meaningful by the addition of viscosity, concentration and/or interfacial tension data when they are available. The results in Figure 16 differ somewhat from those of Tsaor; he indicates single phase behavior up to 0.3% NaCl in the presence of 1000 ppm of xanthan gum. In the present study, two phases were observed at 0.1% NaCl with 750 ppm of xanthan gum. Further investigations of the behavior of this system are planned.

One other candidate for the model surfactant system is also under study: a monoethanolamine salt of C₁₂-orthoxylyene sulfonate produced by EXXON. Once again, both liquid-liquid and liquid-solid separations are observed at the CEC, depending on concentration of sulfonate and type and concentration of alcohol. The effect of the oil present on the behavior with polymer will be investigated. Results of these tests, as well as the availability of this product, will determine the feasibility of using this type of sulfonate as the model surfactant for surfactant-polymer interaction characterizations.

F. GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (GPC) is a tool for the determination of distribution of molecular sizes in a polymer sample. With proper calibration procedures, molecular weight distributions can be obtained from these results. GPC procedures are well-established for a wide range of non-ionic polymers in organic solvents. However, these procedures have not proven easily adaptable to the problems of high molecular weight polyelectrolytes that are the polymers of interest for mobility control.

GPC would be an extremely helpful tool for the study of mobility control polymers. It is likely that the distribution of molecular weights is important in determining solution properties. It would be of interest to observe changes in distribution resulting from exposure of solutions to various stresses.

Aqueous Mobile Phase Studies: Since a primary feature of the polymers of interest is their solubility in water, aqueous buffers were first investigated as possible mobile phases. Table 28 lists the solutions investigated, along with intrinsic viscosities of various polymers in these solutions. It should be pointed out that these intrinsic viscosity values are for viscosity results at a shear rate of 100 sec^{-1} . No attempt has been made to extrapolate to zero shear conditions since reliable low shear rate data are not available at this time.

The columns used in this study were DuPont silica size exclusion columns in the 1000 and 4000 Å ranges. In all cases where commercially available Dow Pusher samples and Calgon 800 series polymers were tested, retention beyond the total volume of the column was observed, indicating mixed mode separations. In addition, irreversible column damage as measured by column efficiency was observed when high molecular weight samples were injected onto the column.

Buytenhuys and Van Der Maeden¹¹³ have reported the use of tetramethylammonium hydroxide in aqueous systems to reduce adsorption. This system is being investigated in other laboratories,¹¹⁴ and there are plans to study it here as well.

Dimethyl Sulfoxide (DMSO) Mobile Phase Studies: The high molecular weight, partially hydrolyzed polyacrylamides are soluble in DMSO in their free-acid form. A small amount of water may also be required for solubility. Investigations using DMSO as a mobile phase for GPC with a low molecular weight polymer showed no indication of adsorption or column degradation. Both the DuPont columns and Waters μ -Bondagel E-1000 and E-linear columns were used. However, high molecular weight samples appear to show the same kinds of adsorption and column damage problems as observed in aqueous systems. The varying percentage of water in the DMSO samples and mobile phases interfere with the chromatogram from the differential refractive index detector.

Thus, the problem of GPC with high molecular weight polyelectrolytes remains a difficult and potentially rewarding challenge.

V. PHASE 3: POLYMER SYNTHESIS

As a planned step in developing improved mobility control agents, a number of polymers have been synthesized. These polymers have been subjected to preliminary screening tests in order to correlate performance with the polymer structure. To save a large amount of time that could be consumed by extensively testing every polymer composition synthesized, these preliminary screening tests are quick and simple. The tests are aimed at judging the degree of viscosity which a polymer solution retains when it is subjected to increased shear and/or to increased brine concentration. The extent of shear degradation and viscosity retention in brine are two extremely important properties of polymers used as mobility control agents. The preliminary screening test procedure has been checked with polyacrylamides and partially hydrolyzed polyacrylamides in order to have a verified basis for judging whether or not a given experimental structural modification indeed improves polymer performance. As will be seen subsequently, results of this preliminary screening do correlate with previously known behavior of commercial samples.

Alkyl substituents on the nitrogen atoms of the acrylamide residue, and the degree of hydrolysis are among the major polymer structure variables presently being studied. The correlations achieved now are guiding our further synthetic work aimed at producing polymers having optimum properties for use in enhanced oil recovery. This Phase 3 polymer synthesis work is detailed in the following part of this report.

A. POLYMER SAMPLES FOR LABORATORY SCREENING TESTS

A number of water-soluble polymers have been studied in an effort to find correlations of carboxyl content and substitution to the behavior of polymers with respect to shear and salinity. Acrylamide and N-substituted acrylamide homopolymers, hydrolyzed polyacrylamides, and copolymers of acrylamide and N-substituted acrylamides with acrylic acid comprise the polymer systems investigated to date. The samples consist of polymers and copolymers specifically synthesized for this project and commercial polymers and mobility control agents--in some cases degraded to provide materials of decreased molecular weight.

1. Commercial Polymeric Materials.

The copolymer compositions of commercial mobility control agents were determined by potentiometric titration with standardized base. In the procedure, weighed samples of the polymers were dissolved in distilled water to which 20.00 ml of 0.100 N HCl had been added to neutralize any free base present and to convert the polymer to its acid form. The solutions were then titrated with 25 ml of 0.100 N NaOH to generate a pH-volume curve from which the endpoints are determined as follows:

- (1) the volume, at which the pH = 3.5, is taken as the endpoint for residual HCl.
- (2) the volume, at which the first derivative (dpH/dV) of the titration curve is a maximum, is taken as the polymer carboxyl endpoint.

The percent hydrolysis of the individual samples was determined by the following relationship:

$$\% \text{ hydrolysis (as free acrylic acid units)} = \frac{(A-B)(C)(0.072)}{D}$$

where

- A = ml of base at carboxyl endpoint
- B = ml of base at HCl endpoint
- C = normality of the base (meq/ml)
- D = dry weight of the polymer sample (in g)
- 0.072 = milliequivalent weight of acrylic acid.

The results are contained in Table 29. The carboxyl contents of the synthetic copolymers and the treated commercial products were determined in a similar manner.

A polyacrylamide of molecular weight 5-6 million, obtained from Polysciences, Inc., Warrington, PA, was chosen as the high molecular weight homopolymer model. Samples of Dow Pushers P-500, P-700, and P-1000 and Calgon Polymers 815 and 835 were utilized in the screening process as representative commercial mobility control agents. The commercial polymers were dissolved and re-precipitated prior to testing to insure the removal of impurities. These slightly different hydrolysis values and the reduced specific viscosities are listed in Table 30.

2. Degraded Commercial Polymers.

The polymers initially synthesized are of relatively low molecular weight. To create lower molecular weight counterparts of typical hydrolyzed polyacrylamide mobility control agents for better comparison with low molecular weight synthetic materials, samples of Dow Pushers P-500 and P-1000 and the 5-6 million MW polyacrylamide were placed in solution and sheared in an Oster blender for varying periods of time at constant speed. Solutions subjected to the greatest shear were fractionated¹¹⁵ before re-precipitation to obtain polymers of low molecular weight. Data on these sheared samples are included in Table 31.

3. Synthesized Polymeric Materials.

All polymerizations and copolymerizations were carried out in deaerated, glass-distilled water under a blanket of oxygen-displacing carbon dioxide or dry nitrogen. Reagent grade chemicals were used throughout. Stirring was continuous and temperatures were maintained within $\pm 2^{\circ}\text{C}$. Reactions were terminated and precipitations accomplished with anhydrous methanol, ethanol, or acetone. The synthesis details are contained in Tables 32-35.

B. PRELIMINARY SCREENING TESTS

Polymer samples listed in Table 36 have been evaluated using preliminary screening tests in search of outstanding effects on polymer performance, as measured by viscosity retention when subjected to shear and brine. The effects of varying the substituents on the acrylamide nitrogen atom in polyacrylamides and percent hydrolysis are being investigated. These preliminary screening tests are not to be confused with the baseline laboratory screening reported in Part IV.

1. Experimental

Dilutions of polymer stock solutions were prepared in appropriate waters. Flow time of each solution was determined in a capillary viscometer immersed in a water bath at 25°C. Another portion of each solution was forced once through a screen-shear apparatus by air at 100 psig pressure.

The screen-shear apparatus, shown in Figure 17, is composed of a sampling cylinder and two 3-way valves, a 1/4" diameter 325-mesh screen backed up with a 1/4" diameter 100-mesh screen, and a union connected with 1/4" O.D. tubing. All parts are Monel or 304 or 316 stainless steel. To fill the device, the top valve is opened to a vacuum, and the bottom valve is opened to the polymer reservoir until the cylinder is approximately two-thirds full. Use of a hand operated vacuum bulb keeps fluid flows low enough to minimize polymer shear upon filling. To obtain the sheared sample, the bottom valve is closed, the top valve is opened to a compressed air source, and then the bottom valve is opened to the screens. Pressure adjustments yield various amounts of degradation. We have found that 100 psig is suitable.

Flow times of portions of solutions after shear were determined under the same conditions as before. Thus, for each polymer used, four flow times (which were usually each a mean of three measurements) were determined: in 0.01% NaCl unsheared and sheared, and in 2% NaCl unsheared and sheared.

Copolymers were titrated to a pH of about 9.5 with 0.100 N NaOH before the first dilution was performed in order to place the carboxyl groups of the polymer into the anionic form. A few of the more viscous solutions were subjected to an additional dilution. Polymer concentrations were later corrected for sorbed water, which was determined by mass loss on heating in partial vacuum.

2. Results

Results shown in Tables 37 and 38 and displayed in Figures 18 through 25 have been obtained from a procedure designed as a relatively quick screening in search of gross effects. The fraction of specific viscosity (at 25.0°C) remaining after treatment is used as a measure of polymer performance. Treatments include shearing and/or increasing salinity. Other variables include molecular weight, concentration of polymer, flow rate of

the solution in the capillary viscometer used and thus the shear rate at which viscosities are determined, and the extent of shear (if any) the polymer suffered in preparation. As this experiment was designed to be a relatively quick screening in search of gross effects, molecular weights were usually not determined. The $\log_{10}$ of the reduced viscosity in 0.01% NaCl was chosen as an independent variable in plotting. If an experiment used identical concentrations, identical viscometer shear rates, and polymers identical except for molecular weight, then this function should provide an ordering of polymers by molecular weight. However, this experiment involved various polymers and differing concentrations. Thus, the $\log_{10}$ of the reduced viscosity is viewed as a convenient aid in sorting out data to search for trends in this experiment but is not a direct measure of molecular weight.

For a typical sample, the source of greatest uncertainty is the fraction of sample weight that is sorbed water. This uncertainty, estimated near 4%, affects values obtained for percent hydrolysis, polymer concentration, and reduced viscosity. Fortunately, the test criterion (fraction of specific viscosity retained after treatment) is not affected by this uncertainty.

A key to polymer code numbers is given in Table 36. Experimental results are presented in Tables 37 and 38. In these tables, results for samples of the same polymer type are grouped together. Within each group, results are arranged according to the reduced kinematic viscosity of the "unsheared" sample in 0.01% NaCl. This arrangement facilitates matching the samples with their symbols in Figures 18, 20-22, 24, and 25. The numbers in the last three columns of Table 37 represent the fraction of the untreated polymer's specific kinematic viscosity in NaCl solution exhibited by the treated polymer in NaCl solution ($\eta_{sp} \text{ treated} / \eta_{sp} \text{ untreated}$).

In Figures 18 through 21, $\eta_{sp} \text{ treated} / \eta_{sp} \text{ untreated}$ is plotted vs the log (base 10) of the reduced viscosity of the untreated polymer. Figures 18 and 19 illustrate the results of shearing at constant NaCl concentration (0.01% for Figure 18 and 2% for Figure 19). Figure 20 illustrates the results of a change in NaCl concentration from 0.01% to 2%. The effect of both shear and increased NaCl concentration is illustrated in Figure 21. Since the solvent for the untreated case is chosen to be 0.01% NaCl in Figures 18, 20, and 21 and is 2% NaCl in Figure 19, the horizontal scale is different for Figure 19 than for the other three figures. The vertical scale in Figures 18 and 19 differs from the vertical scales in Figures 20 and 21. Different symbols in Figures 18 through 21 represent different polymers. A key to these is given in Table 39.

Figure 18 indicates that, in 0.01% NaCl, polyacrylamide (unhydrolyzed homopolymer) is more sensitive to shear than the three copolymers under conditions giving the same reduced viscosity when the reduced viscosity is around 20 to 200 dl/g. Figure 19 shows that most, but not all, of this advantage is lost when the NaCl concentration is increased to 2%. At this preliminary stage, the N-substituted polymers seem to fit into the general pattern. However, more data are needed before a final conclusion can be reached.

The copolymers tested are much more sensitive to increased NaCl concentration than the homopolymers tested, as is shown in Figure 20. Also from Figure 20 comes a preliminary indication that poly(acrylamide-co-sodium acrylate) samples exhibiting higher reduced viscosities in 0.01% NaCl tend to be more sensitive to an increase in NaCl concentration than samples of that polymer exhibiting lower reduced viscosities.

For convenience, combined effect of both NaCl and shear is plotted in Figures 21 and 25. Three variables are represented on each plot in Figures 22 through 25. The purpose of the "skyscraper" plotting method employed is to represent THREE variables all in one plot. The log (base 10) of the reduced viscosity of the untreated polymer in NaCl solution is plotted again as the horizontal coordinate. The weight percent hydrolysis is plotted as the vertical coordinate. These are the coordinates at the center of the base of a "skyscraper" symbol. The height of a "skyscraper" represents $\eta_{sp} \text{ treated} / \eta_{sp} \text{ untreated}$. A value of unity for this ratio is scaled at 6.75 units on the vertical coordinate. If all of the specific viscosity were lost, the height would be zero. The height scale and the percent hydrolysis scale both remain unchanged throughout Figures 22 through 25. In Figures 22, 24, and 25, the results at 0.01% NaCl are chosen as the untreated values; whereas in Figure 23, the 2.0% NaCl results are used as the untreated viscosities. Therefore, the horizontal scale in Figure 23 is different from that in the other three figures. In Figures 22 through 25, different polygons at the tops of "skyscrapers" represent different copolymers. Table 40 provides a key to these symbols. Figures 22 through 25 include percent hydrolysis as one of the variables, whereas Figures 18 through 21 do not.

So far, it appears that, for a given polymer, the polymer's sensitivity to shear tends to increase as the reduced viscosity increases beyond a critical value. This effect is expected and can be seen in Figures 18, 19, 22, and 23. This is a preliminary test method which also will be applied to a number of other samples before final conclusions are made. Based on the data available at this time, the following conclusions are drawn:

- (1) Increasing molecular weight tends to impart increasing shear sensitivity to polymers in both concentrations of NaCl solution. Molecular weight distribution is important.
- (2) The degree of hydrolysis is also a factor. The most striking evidence of this so far appears when homopolymers (0% hydrolysis assumed) are compared with copolymers (>15% hydrolysis). At a given reduced viscosity, partially hydrolyzed polymers tend to exhibit greater shear stability than homopolymers; however, the hydrolysis tends to cause greater brine sensitivity. Copolymers having a wider range of percent hydrolysis values will be investigated in the near future.
- (3) Although much of the data on N-alkyl substituted polymers have not been obtained yet, the data thus far imply that the N-alkyl substituted polymers in general seem to conform to the same trends as the parent compounds. As we synthesize and test more N-alkyl substituted polymers, we are filling in the gaps so we will have more polymers of differing molecular weight for N-alkyl substituted compounds.

We have attempted to devise a simple screening process that will enable us to observe structure-utility relationships without having to rely only on extensive and time-consuming core testing. Presently, we are correlating these results to the findings obtained from the Berea core testing, as well as to those from blender shear tests. This comparison will be presented when sufficient data are available from each test.

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TABLE 1

POTENTIAL INADEQUACIES OF EXISTING
MOBILITY CONTROL AGENTS¹⁰⁻⁴⁷

<u>Inadequacy</u>	<u>Polyacrylamide</u>	<u>Xanthan Gum</u>
Economics	Moderate Cost	Higher Cost
Viscosity Loss in Brine	Severe	Slight
Oxygen Degradation	Yes	Yes
Metal Ion Degradation	Yes	Yes
Thermal Degradation	> 250°F	> 160°F
Microbial Degradation	Moderate	Severe
Shear Degradation	Severe	Slight
Reduced Injectivity or Wellbore Impairment	Possible	Possible
Interactions with Porous Media	Possible	Possible
Surfactant-Polymer Interaction	Possible*	Possible*
Filtration Required	No	Yes
Permeability Limitations	> 10-20 md	> 5 md

* Extent of inadequacy would depend on formulation of surfactant slug as well as polymer type.

Other Potential Inadequacies:

- Reactions with Divalent Ions
- Hydrolysis Reactions
- Polymer Retention or Adsorption
- Oil Emulsions
- Producing Well Productivity Problems
- Premature Breakthrough of Polymer in Production Wells
- Handling Problems
- Product Quality Control
- Availability for Commercial-Scale S/P Projects

TABLE 2

BROOKFIELD VISCOSITIES OF HYDROLYZED POLYACRYLAMIDE
IN VARIOUS SOLVENTS

6 RPM (7.3 SEC^{-1}), UL ADAPTER, 25°C , 600 MG/L Polymer²⁵

Percent Hydrolysis	Distilled Water	Percent NaCl			Percent CaCl ₂	
		0.1%	2%	10%	0.1%	2%
0%	1.5	1.6	1.8	1.8	1.9	1.8
15%	246.0*	9.3	2.1	2.1	2.6	1.7
25%	356.0*	14.5	2.6	2.6	2.2	1.3
35%	399.8*	18.4	3.0	2.8	1.8	1.1

* Measured with #1 spindle.

TABLE 3

POLYMER PREFERENCE FOR SURFACTANT/POLYMER FLOODING
 [RESPONSE TO QUESTIONNAIRE FORM]
 RESPONSE FROM OIL COMPANY PERSONNEL WITH FIELD EXPERIENCE

<u>Preference: Polymer Type</u>	<u>Percent</u>
Hydrolyzed Polyacrylamide	41
Xanthan Gum	34
Depends on the Application	22
Neither	3

<u>Preference: Physical Form</u>	<u>Percent</u>
Solution	35
Depends on the Application	19
Emulsion	13.5
Liquid Type	13.5
Powder	11
Bead	5
Solid Type	3

TABLE 4

INADEQUACIES OF PARTIALLY HYDROLYZED POLYACRYLAMIDE FOR SURFACTANT/POLYMER FLOODING
 [RESPONSE TO QUESTIONNAIRE FORM]
 RESPONSE FROM OIL COMPANY PERSONNEL WITH FIELD EXPERIENCE

<u>Rank</u>	<u>Item</u>	<u>Average Numerical Rating</u>	<u>Number of Adequate Ratings</u>
1	Shear Degradation	2.3	1
2	Viscosity Loss in Brines	2.5	0
3	Reaction with Divalent Ions	3.6	0
4	Economics (High Cost)	4.0	6
5	Metal Ion Degradation	4.6	4
6	Oxygen Degradation	4.8	2
7	Use in Low Permeability Formations	5.4	8
8	Surfactant/Polymer Interactions	5.7	10
9	Wellbore Plugging	5.8	12
10	Thermal Degradation	7.3	9
11	Hydrolysis Reaction	8.1	4
12	Microbial Degradation	8.4	17
13	Filtration Requirements	9.3	19

TABLE 5

INADEQUACIES OF XANTHAN GUM FOR SURFACTANT/POLYMER FLOODING
 [RESPONSE TO QUESTIONNAIRE FORM]
 RESPONSE FROM OIL COMPANY PERSONNEL WITH FIELD EXPERIENCE

<u>Rank</u>	<u>Item</u>	<u>Average Numerical Rating</u>	<u>Number of Adequate Ratings</u>
1	Economics (High Cost)	1.5	1
2	Filtration Requirements	3.0	2
3	Wellbore Plugging	3.1	4
4	Microbial Degradation	3.6	2
5	Surfactant-Polymer Interactions	4.9	7
6	Reaction with Divalent Ions	5.1	15
7	Use in Low Permeability Formations	5.4	7
8	Thermal Degradation	5.8	8
9	Oxygen Degradation	5.8	12
10	Metal Ion Degradation	5.9	10
11	Hydrolysis Reaction	6.9	13
12	Viscosity Loss in Brines	7.8	22
13	Shear Degradation	10.8	26

TABLE 6

Effect of Salinity on Power Law Parameters

750 mg/l Polymer, 25°C

Polymers with Acrylamide-Containing Structures

Polymer	Percent Salt	K	n
Betz Hi Vis	0.01% NaCl	201	0.457
	0.1%	46.5	0.674
	0.3%	21.1	0.746
	1%	11.8	0.781
	2%	7.0	0.832
	10%	3.5	0.924
	0.01% CaCl ₂	74.2	0.580
	0.1%	4.2	0.964
	0.3%	*	*
	1%	*	*
	2%	*	*
	10%	*	*

Polymer	Percent Salt	K	n
Cyanamid 960S	0.01% NaCl	323	0.655
	0.1%	100	0.554
	0.3%	34	0.723
	2%	9.6	0.831
	0.01% CaCl ₂	240	0.552
	0.3%	3.1*	0.834
	2%	2.2*	0.873

* Accurate determination not possible because of low fluid viscosities. Solutions approaching Newtonian behavior.

TABLE 7
Effect of Salinity on Power Law Parameters
750 mg/l Polymer, 25°C
Polymers with Acrylamide-Containing Structures

Polymer	Percent Salt	K	n
Dow Pusher 700	0.01% NaCl	159.1	0.488
	0.1%	42.5	0.660
	0.3%	15.7	0.802
	1%	7.1	0.882
	2%	5.3	0.902
	10%	3.4	0.852
	0.01% CaCl ₂	60.4	0.599
	0.1%	5.3	0.893
	0.3%	2.1	0.993
	1%	*	*
	2%	*	*
	10%	*	*

Polymer	Percent Salt	K	n
Nalco Nal-flo	0.01% NaCl	282	0.533
	0.1%	58.4	0.658
	0.3%	19.7	0.800
	1%	8.1	0.897
	2%	5.9	0.905
	10%	5.0	0.901
	0.01% CaCl ₂	122	0.571
	0.1%	5.7	0.897
	0.3%	2.8	0.946
	1%	2.2	0.948
	2%	2.1	0.957
	10%	*	*

* Accurate determination not possible because of low fluid viscosities. Solutions approaching Newtonian behavior.

TABLE 8

Effect of Salinity on Power Law Parameters
 750 mg/l Polymer, 25°C
 Polymers with Acrylamide-Containing Structures

Polymer	Percent Salt	K	n
Dow Pusher 500	0.01% NaCl	112.0	0.597
	0.3%	9.67	0.862
	2%	4.48	0.889
	0.01% CaCl ₂	36.5	0.721
	2%	3.61	0.750

Polymer	Percent Salt	K	n
Dow Pusher 1000	0.01% NaCl	201	0.435
	0.3%	19.2	0.752
	2%	6.95	0.880
	0.01% CaCl ₂	55.9	0.665
	0.3%	7.6	0.867
	2%	4.0	0.930

TABLE 9

Effect of Salinity on Power Law Parameters

750 mg/l Polymer, 25°C

Polymers with Acrylamide-Containing Structures

Polymer	Percent Salt	K	n
Amoco Sweepaid 103	0.01% NaCl	231	0.554
	0.3%	12.1	0.872
	2%	5.0	0.906
	0.01% CaCl ₂	75.2	0.707
	0.3%	4.0	0.925
	2%	2.2	0.963

Polymer	Percent Salt	K	n
Allied Colloids Alcoflood 800	0.01% NaCl	6.45	0.878
	0.3%	2.9*	0.946
	2%	3.3*	0.936
	0.01% CaCl ₂	4.2	0.910
	0.3%	3.4*	0.915
	2%	4.0*	0.894

* Possible anomalies in 0.3% and 2% brines.

TABLE 10

Effect of Salinity on Power Law Parameters
 750 mg/l Polymer, 25°C
 Polymers with Acrylamide-Containing Structures

Polymer	Percent Salt	K	n
Allied Colloids Alcoflood 900	0.01% NaCl	15.5	0.883
	0.3%	2.2*	0.970
	2%	1.9*	0.975
	0.01% CaCl ₂	7.0	0.896
	0.3%	2.1*	0.975
	2%	2.0*	0.983

Polymer	Percent Salt	K	n
Allied Colloids Alcoflood 900L	0.01% NaCl	60.3	0.686
	0.3%	4.6	0.937
	2%	2.4*	0.954
	0.01% CaCl ₂	20.6	0.801
	0.3%	2.9*	0.941
	2%	2.5*	0.943

* Accurate determination not possible because of low fluid viscosities. Solutions approaching Newtonian behavior.

TABLE 11
Effect of Salinity on Power Law Parameters
750 mg/l Polymer, 25°C
Polymers with Acrylamide-Containing Structures

Polymer	Percent Salt	K	n
Allied Colloids Alcoflood 1100	0.01% NaCl	350	0.339
	0.3%	24.4	0.731
	2%	9.6	0.846
	0.01% CaCl ₂	220	0.475
	0.3%	5.0	0.874
	2%	3.7	0.899

Polymer	Percent Salt	K	n
Allied Colloids Alcoflood 1100L	0.01% NaCl	157	0.589
	0.3%	10.7	0.849
	2%	3.7	0.901
	0.01% CaCl ₂	69.5	0.660
	0.3%	3.4	0.927
	2%	2.2	0.982

TABLE 12

Effect of Salinity on Power Law Parameters
 750 mg/l Polymer, 25°C
 Polymers with Acrylamide-Containing Structures

Polymer	Percent Salt	K	n
Allied Colloids Alcoflood 1200	0.01% NaCl	130	0.528
	0.3%	13.6	0.808
	2%	5.5	0.867
	0.01% CaCl ₂	61	0.618
	0.3%	2.5	0.952
	2%	1.7*	0.988

Polymer	Percent Salt	K	n
Allied Colloids Alcoflood 1200L	0.01% NaCl	250	0.465
	0.3%	26.8	0.786
	2%	5.6	0.916
	0.01% CaCl ₂	140	0.562
	0.3%	1.6*	0.974
	2%	1.0*	1.000

* Accurate determination not possible because of low fluid viscosities. Solutions approaching Newtonian behavior.

TABLE 13

Effect of Salinity on Power Law Parameters

750 mg/l Polymer, 25°C

Polymers with Acrylamide-Containing Structures

Polymer	Percent Salt	K	n
CORT N-Hance 315	0.01% NaCl	228	0.508
	0.3%	15.9	0.831
	2%	5.8	0.914
	0.01% CaCl ₂	82.9	0.668
	0.3%	3.2	0.958
	2%	2.4	0.988

Polymer	Percent Salt	K	n
CORT N-Hance 330	0.01% NaCl	445	0.360
	0.3%	79.1	0.553
	2%	13.4	0.799
	0.01% CaCl ₂	215	0.461
	0.3%	9.7	0.771
	2%	3.2	0.939

Polymer	Percent Salt	K	n
CORT N-Hance 335	0.01% NaCl	243	0.464
	0.3%	43.2	0.689
	2%	18.2	0.766
	0.01% CaCl ₂	137	0.562
	0.3%	5.1	0.885
	2%	3.2	0.952

TABLE 14

Effect of Salinity on Power Law Parameters

750 mg/l Polymer, 25°C

Polymers with Cellulose Structures

Polymer	Percent Salt	K	n
Abbott Xanthan Broth*	0.01% NaCl	58.3	0.569
	0.1%	45.2	0.604
	1%	32.8	0.658
	2%	27.8	0.689
	0.01% CaCl ₂	45.0	0.608
	0.1%	31.4	0.663
	1%	26.0	0.694
	2%	27.7	0.710

Polymer	Percent Salt	K	n
Kelco Xanflood*	0.01% NaCl	22.2**	0.770**
	0.3%	20.2	0.736
	2%	18.4	0.754
	0.01% CaCl ₂	22.7	0.700
	0.3%	17.8	0.740
	2%	14.3	0.780

* Deviations from Power Law model at shear rates below 10 sec.⁻¹** Deviations from Power Law model at shear rates below 15 sec.⁻¹
Limited data above 15 sec.⁻¹ causes questionable accuracy.

TABLE 15
Effect of Salinity on Power Law Parameters
750 mg/l Polymer, 25°C
Polymers with Cellulose Structures

Polymer	Percent Salt	K	n
Henkle Galactosol*	0.01% NaCl	3.4	0.978
	0.3%	3.4	0.978
	2%	3.8	0.957
	0.01% CaCl ₂	4.4	0.917
	0.3%	4.4	0.917
	2%	4.1	0.927

Polymer	Percent Salt	K	n
Hercules Natrosol 250 HHR*	0.01% NaCl	4.0	0.949
	0.3%	4.0	0.949
	2%	3.7	0.965
	0.01% CaCl ₂	3.6	0.976
	0.3%	3.7	0.967
	2%	4.1	0.949

* Accurate determination not possible because of low fluid viscosities. Solutions approaching Newtonian behavior.

TABLE 16
Effect of Salinity on Power Law Parameters
750 mg/l Polymer, 25°C
Polymers with Cellulose Structures

Polymer	Percent Salt	K	n
Pfizer Biopolymer 1035	0.01% NaCl	48.1	0.604
	0.3%	43.0	0.620
	2%	31.4	0.666
	0.01% CaCl ₂	39.2	0.624
	0.3%	31.5	0.673
	2%	31.0	0.677

Polymer	Percent Salt	K	n
Stauffer Colloid XHO	0.01% NaCl	19.0	0.928
	0.3%	5.1*	0.948
	2%	3.8*	0.950
	0.01% CaCl ₂	11.7	0.925
	0.3%	4.7*	0.941
	2%	3.7*	0.951

* Accurate determination not possible because of low fluid viscosities. Solutions approaching Newtonian behavior.

TABLE 17
Effect of Salinity on Power Law Parameters
750 mg/l Polymer, 25°C
Polymers with Cellulose Structures

Polymer	Percent Salt	K	n
Stauffer Colloid XHX	0.01% NaCl	13.0	0.931
	0.3%	5.3*	0.936
	2%	4.1*	0.880
	0.01% CaCl ₂	10.0	0.906
	0.3%	4.6*	0.884
	2%	4.0*	0.907

Polymer	Percent Salt	K	n
Stauffer Colloid XH1	0.01% NaCl	6.6	0.919
	0.3%	3.4*	0.919
	2%	3.5*	0.959
	0.01% CaCl ₂	1.9*	0.866
	0.3%	1.9*	0.897
	2%	1.9*	0.948

* Accurate determination not possible because of low fluid viscosities. Possible anomalies.

TABLE 18
Effect of Salinity on Power Law Parameters
750 mg/l Polymer, 25°C
Polymers with Cellulose Structures

Polymer	Percent Salt	K	n
Stauffer Colloid XH2*	0.01% NaCl	2.8	0.926
	0.3%	2.7	0.949
	2%	2.7	0.921
	0.01% CaCl ₂	3.3	0.926
	0.3%	2.2	0.925
	2%	1.9	0.927

Polymer	Percent Salt	K	n
Stauffer Colloid XH3	0.01% NaCl	10.3	0.895
	0.3%	3.9*	0.900
	2%	2.9*	0.913
	0.01% CaCl ₂	7.1	0.914
	0.3%	3.0*	0.912
	2%	2.2*	0.987

* Accurate determination not possible because of low fluid viscosities. Solutions approaching Newtonian Behavior. Possible anomalies.

TABLE 19

Shear Rates of Various Viscosity Measuring Devices

<u>Apparatus</u>	<u>Shear Rate Range, sec⁻¹</u>
Four-Bulb Ubbelohde #75	21 - 985
Four-Bulb Ubbelohde #150	7.4 - 165
Brookfield LVT Cone and Plate with SCP-3 Spindle	1.2 - 230
Brookfield LVT with UL Adapter	0.37 - 73.4
Contraves LS-30	0.017 - 128.5

Note: Rotational viscometers have fixed shear rates at fixed speeds. Shear rates in the Ubbelohde capillary tubes depend on flow times, thus the range of shear rates depends on viscosity.

TABLE 20

Change in Viscosity with Changes in Fraction of Calcium Ion

Polymer	Concentration	Least-Squares Fit*	r^2
835	750 ppm	$\eta_x/\eta_o = 0.347 - 0.132 \ln X_{Ca}$	.98
825	1500 ppm	$\eta_x/\eta_o = 0.247 - 0.163 \ln X_{Ca}$	.98

* η_x = observed viscosity at 100 s^{-1} with $I = \text{constant}$ and $X_{Ca} = x$

η_o = observed viscosity at 100 s^{-1} with $I = \text{constant}$ and $X_{Ca} = 0$

r^2 = coefficient of determination, a measure of the quality of fit of the equation to the data. $r^2 = 1$ is a perfect fit.

TABLE 21

Effect of Salinity on Polymer Screen Factors

Polymers Used on DOE-Sponsored Projects

750 mg/l Polymer, 25°C

Polymer	Lot No.	Percent NaCl					
		0.01%	0.1%	0.3%	1%	2%	10%
Betz Hi Vis	NA	--	23.6	22.7	22.3	21.5	15.2
Cyanamid Cyanatrol 960S	10129-1	35.0	--	24.7	--	23.2	--
Dow Pusher 700	MM060965141	22.8	19.5		17.9	--	18.9
Nalco Nal-flo	G-9110	16.9	16.2	14.6	13.6	13.2	12.5
Abbott Xanthan Broth	05-051-BD	1.7	1.7	1.5	1.6	1.8	1.5
Kelco Xanflood	XFL 14630	2.2	1.6	1.8	1.7	1.6	1.5

Polymer	Lot No.	Percent CaCl ₂					
		0.01%	0.1%	0.3%	1%	2%	10%
Betz Hi Vis	NA	--	15.8	14.3	--	12.7	7.6
Cyanamid Cyanatrol 960S	10129-1	24.6	--	16.4	--	14.8	--
Dow Pusher 700	MM060965141	20.0	11.6	--	8.2	--	12.1
Nalco Nal-flo	G-9110	9.0	9.6	5.9	4.0	4.6	7.5
Abbott Xanthan Broth	05-051-BD	1.9	1.5	1.5	1.4	1.5	1.6
Kelco Xanflood	XFL 14630	1.9	1.8	1.7	1.7	1.7	1.7

TABLE 22

Effect of Salinity on Polymer Screen Factors
 Polymers with Acrylamide-Containing Structure
 750 mg/l Polymer, 25°C

Polymer	Lot No.	Percent NaCl		
		0.01%	0.3%	2%
Allied Colloids Alco Flood 800	BOT 031	12.6	8.6	12.0
Allied Colloids Alco Flood 900	BEX 432	6.7	5.1	3.0
Allied Colloids Alco Flood 900L	EBC 010	11.1	8.5	5.7
Allied Colloids Alco Flood 1100	FAB 094	44.3	27.7	28.6
Allied Colloids Alco Flood 1100L	EBF 101178	17.8	11.7	9.1
Allied Colloids Alco Flood 1200	BOM 976	20.0	17.1	15.1
Allied Colloids Alco Flood 1200L	EBB 016	37.8	17.8	14.1
Amoco Sweepaid 103	6111T	17.1	13.6	12.0
Calgon Polymer 340	13G7B	5.1	3.4	3.0
Calgon Polymer 454	15B5C	7.1	5.4	5.1
Calgon Polymer 815	23D8C	9.4	7.6	6.6
Calgon Polymer 825	04D8B	16.3	12.5	8.5
Calgon Polymer 835	08G8A	24.4	15.8	13.7
CORT N-Hance 315	10011-17-A	21.0	15.0	12.0
CORT N-Hance 330	10011-17-B	58.0*	29.0	24.0
CORT N-Hance 335	10011-17-C	41.0*	31.0	27.0
Dow Pusher 500	MM1034N240	15.6	10.5	8.8
Dow Pusher 1000	MM0923245	33.1	33.6	27.3

* Possible spurious results. Tests will be repeated.

TABLE 23

Effect of Salinity on Polymer Screen Factors
 Polymers with Acrylamide-Containing Structure
 750 mg/l Polymer, 25°C

Polymer	Lot No.	Percent CaCl ₂		
		0.01%	0.3%	2%
Allied Colloids Alco Flood 800	BOT 031	10.9	11.2	13.6
Allied Colloids Alco Flood 900	BEX 432	5.5	5.0	4.8
Allied Colloids Alco Flood 900L	EBC 010	9.5	7.5	7.6
Allied Colloids Alco Flood 1100	FAB 094	30.2	18.3	15.8
Allied Colloids Alco Flood 1100L	EBF 101178	13.5	10.6	8.6
Allied Colloids Alco Flood 1200	BOM 976	16.8	10.1	8.7
Allied Colloids Alco Flood 1200L	EBB 016	27.2	8.6	1.1
Amoco Sweepaid 103	6111T	11.7	9.9	10.0
Calgon Polymer 340	13G7B	4.2	3.5	3.1
Calgon Polymer 454	15B5C	6.5	4.5	4.5
Calgon Polymer 815	23D8C	7.5	5.9	4.9
Calgon Polymer 825	04D8B	13.3	10.2	7.9
Calgon Polymer 835	08G8A	17.1	9.9	7.2
CORT N-Hance 315	10011-17-A	18.0	10.8	10.6
CORT N-Hance 330	10011-17-B	37.0	14.0	16.0
CORT N-Hance 335	10011-17-C	29.0	8.5	7.0
Dow Pusher 500	MM1034N240	12.2	5.6	6.3
Dow Pusher 1000	MM0923245	32.6	25.0	24.5

TABLE 24

Effect of Salinity on Polymer Screen Factors

Polymers with Cellulose Structures

750 mg/l Polymer, 25°C

Polymer	Lot No.	Percent NaCl		
		0.01%	0.3%	2%
Henkel Galactosol	08270A	2.9	3.2	3.6
Hercules Natrosol 250HHR	32639	2.4	2.2	2.2
Pfizer Biopolymer 1035	V-82270	1.9	1.6	1.6
Stauffer Colloid XH0	058H0-180	3.3	2.2	2.0
Stauffer Colloid XHX	048HX-174	3.2	2.4	1.9
Stauffer Colloid XH1	048H1-179	1.9	1.7	1.5
Stauffer Colloid XH2	038H2-161	1.3	1.3	1.2
Stauffer Colloid XH3	067H3-143	1.8	1.5	1.4

Polymer	Lot No.	Percent CaCl ₂		
		0.01%	0.3%	2%
Henkel Galactosol	08270A	2.9	2.8	3.1
Hercules Natrosol 250HHR	32639	2.2	2.4	2.2
Pfizer Biopolymer 1035	V-82270	1.9	1.7	1.7
Stauffer Colloid XH0	058H0-180	2.8	2.0	1.8
Stauffer Colloid XHX	048HX-174	2.8	2.1	1.9
Stauffer Colloid XH1	048H1-179	1.0	1.1	1.1
Stauffer Colloid XH2	038H2-161	1.3	1.3	1.3
Stauffer Colloid XH3	067H3-143	2.7	1.6	1.4

TABLE 25

Resistance Factors in Berea Sandstone
750 mg/l Polymer, Room Temperature, 1 ft./day

Polymer	Supplier	Polymer Resistance Factor		Residual Resistance Factor	
		0.1% NaCl	2% NaCl	0.1% NaCl	2% NaCl
Sweepaid 103	Amoco	19.0	3.5	2.6	1.1
Hi Vis	Betz	19.5	3.9	2.1	1.3
Cyanatrol 960 S	Cyanamid	40.6	10.8	14.8	3.9
Pusher 500	Dow	12.5	3.4	2.7	1.4
Pusher 700	Dow	14.2	7.1	3.3	1.1
Pusher 1000	Dow	34.1	6.4	4.2	1.5
Nal-flo	Nalco	24.4	6.1	2.2	3.2
Xanthan Broth	Abbott	19.5	20.5	1.2	1.2
Xanflood	Kelco	13.5	11.6	5.3	6.7
Biopolymer 1035	Pfizer	14.6	13.6	3.2	2.3
Colloid XHO	Stauffer	6.1	3.4	1.9	1.3

Initial permeability to water for Berea cores: 350-550 md.

TABLE 26

Polymer Retention in Berea Sandstone
 750 mg/l Polymer, Room Temperature, 1 ft/day

Polymer	Supplier	Polymer Retention, lbs/ac.ft.	
		0.1% NaCl	2% NaCl
Sweepaid 103	Amoco	99	147
Hi Vis	Betz	68	130
Cyanatrol 960S	Cyanamid	*	*
Pusher 500	Dow	65	125
Pusher 700	Dow	70	135
Pusher 1000	Dow	107	**
Nal-flo	Nalco	95	149
Xanthan Broth	Abbott	36	77
Xanflood	Kelco	48	75
Biopolymer 1035	Pfizer	41	46
Colloid XHO	Stauffer	33	200

* Analysis in progress

** Spurious result -- test will be repeated

TABLE 27

Effect of Shear Degradation in Berea Cores
on Power Law Parameters

750 mg/l Pusher 700 in 0.3% NaCl

	K	n
Unsheared	13.3	0.816
1000 ft/day	12.1	0.830
2500 ft/day	9.32	0.856
5000 ft/day	6.05	0.903
10,000 ft/day	5.01	0.929
14,300 ft/day	4.41	0.946

TABLE 28

Intrinsic Viscosities (100 sec^{-1} , 25°C)

Polymer	Solvent	pH	$[\eta]_c^*$	r^2	$[\eta]_{\eta_{sp}^n}^{**}$	n	r^2
Dow P-700	1M NaNO_3	7.5	15.3	0.94	16.3	1	0.94
Dow P-700	6% Na_2SO_4	na	19.8	1.0	21.8	1	0.99
Dow P-700	1M NaNO_3	na	10.9	0.5	11.5	1	0.78
Dow P-700	7% NaCl	na	16.8	1.0	18.7	1	0.97
Dow P-700	7.1% Na_2SO_4	7.6	17.7	0.93	18.4 16.6	1 0.65	0.93 0.95
Calgon 835	1M NaNO_3	7.6 6.3			65 66	0.1 0.1	0.5 0.5
Calgon 835 ***	1M NaCl	na	16.1	0.92	16.3 16.6	1 1	0.93 1.0
Calgon 835	.33M Na_2SO_4	na	19		19.0	1	0.99
Calgon 835	.2M HAc/Ac^-	4.0	16.1	0.91	16.0	0.8	0.99
Calgon 835	.025M sorbitol	3.0	12.5	0.77	12.6 15.4	1 0.3	0.77 0.83

* η_{sp}/c vs. c extrapolated to $c = 0$ ** η_{sp}/c vs. η_{sp}^n vs. extrapolated to $\eta_{sp}^n = 0$ *** Leaving out data point at $c = .01199 \text{ g/dl}$

na = not adjusted

TABLE 29

Percent Hydrolysis Values of Commercial Hydrolyzed Polyacrylamides and
Poly(acrylamide-co-acrylic acid)

<u>Sample</u>	<u>% Hydrolysis (or acid)</u>
Amoco Sweepaid 103	28.1
Alcoflood 1100	23.0
Betz Hi-Vis	22.2
Calgon 454	20.3
Calgon 815	24.8
Calgon 825	31.9
Calgon 835	38.9
Dow Pusher P-500	34.7
Dow Pusher P-700	33.3
Dow Pusher P-1000	27.5
Nalco Nal-flo	26.6
Polysciences poly(acrylamide- co-acrylic acid) (low COOH)	9.5
Polysciences poly(acrylamide- co-acrylic acid) (high COOH)	22.8

TABLE 30

Commercial Polymers

Polymer	Sample Number	$\eta_{sp}/c^{a,b}$	% Carboxyl
Pusher P-500	24	129.81 dl/g	36
"	30	156.99	"
Pusher P-700	29	164.58	35
"	35	104.75	"
Pusher P-1000	25	177.22	26
Calgon 815	34	124.16	24
Calgon 835	32	231.40	36
"	33	106.15	"
5-6 x 10 ⁶ mw polyacrylamide	4	129.29	-

- (a) reduced viscosity of unsheared samples in 0.01% NaCl.
- (b) the differences of η_{sp}/c values for samples of Pusher 700 and Calgon 835 are probably attributable to a concentration effect. Concentrations appear in Table 37.

TABLE 31

Commercial Polymers Degraded by Shearing

Polymer	Time Sheared	Sample Number	η_{sp}/c	% Carboxyl
Pusher P-500	12 m	17	128.21 dl/g	35
"	"	28	143.68	"
"	25	16	168.07	37
"	35 ^a	36	140.93	40
"	35 ^b	37	325.37	38
Pusher P-1000	15	18	129.29	26
"	30	19	133.12	26
5-6 x 10 ⁶ mw Polyacrylamide	40	8	6.41	-

(a) second fraction

(b) third and final fraction

TABLE 32

Polyacrylamides

Sample Number	η_{sp}/c	Monomer	Water	Initiator	Activator	Chain Transfer Agent	Temperature	Time	Atmosphere	Reference
5	0.32 dl/g	3.00 g	29 ml	0.0300 g $K_2S_2O_8$	0.0030 g $Na_2S_2O_5$	0.010 ml $HOC_2H_4SH^a$	25°C	60 m	N_2	116
9	6.12	17.23	418	0.0330 $K_2S_2O_8$	1.57 $C_3H_7OH^b$	--	75	120	CO_2	117,118
10	0.75	3.00	28	0.0300 $K_2S_2O_8$	0.0030 $Na_2S_2O_5$	0.005 HOC_2H_4SH	25	60	N_2	116
11	1.50	"	"	"	"	0.003 HOC_2H_4SH	"	"	"	"
14	1.74	"	30	"	"	0.001 HOC_2H_4SH	"	"	"	"
20	15.31	45.40	500 ^c	0.0055 $NaBrO_3$	0.0010 Na_2SO_3	--	"	20	CO_2	117,118
21	32.16	46.49	510 ^c	0.0070 $NaBrO_3$	0.0011 Na_2SO_3	--	"	15	"	"
26	1.12	3.00	32	0.0150 $K_2S_2O_8$	0.0080 $Na_2S_2O_5$	0.040 HOC_2H_4SH	"	60	N_2	116
27	2.87	"	29	"	"	0.020 HOC_2H_4SH	"	"	"	"
31	1.78	"	26	"	"	0.010 HOC_2H_4SH	"	"	"	"

a) 2-mercaptoethanol

b) 2-propanol

c) 0.50 ml concentrated H_2SO_4 added.

TABLE 33

Synthesized Poly(acrylamide-co-acrylic acid)

Sample Number	η_{sp}/c	Percent Carboxyl	Acrylamide	Acrylic Acid	Water	Initiator ^a	Temperature	Time	Atmosphere	References
6	108.98 dl/g	16	20.73 g	2.77 g	250 ml	1.0003 g $K_2S_2O_8$	60°C	5 m	CO_2	119
7	164.27	44	15.40	7.00	240	1.0792 $K_2S_2O_8$	40	10	"	"

a) no activator used.

TABLE 34

Poly(N-methylacrylamides) and Poly(N-methylacrylamide-co-sodium acrylate)

Sample Number	η_{sp}/c	Percent Carboxyl	N-methyl-acrylamide	Acrylic Acid	Water	Initiator	Activator	Temp.	Time	Ref.
2	2.05 dl/g	--	2.13 g	--	20 ml	0.0213 g $K_2S_2O_8$	0.0021 g $Na_2S_2O_5$	25°C	360 m	117
22	2.92 dl/g	--	3.00 g	--	10 ml	0.0150 g $K_2S_2O_8$	0.0075 g $Na_2S_2O_5$	"	18 m	"
23	4.77 dl/g	--	"	--	16 ml	"	"	-04°C	16 m	"
38	3.25 dl/g	--	"	--	8 ml	"	"	-10°C	"	"
39	2.88 dl/g	--	1.89 g	--	10 ml	0.0095 g $(NH_4)_2S_2O_8$	0.0032 g $Na_2S_2O_5$	-04°C	10 m	"
3	37.75 dl/g	51	1.06 g	.91 g	30 ml	0.0196 g $K_2S_2O_8$	0.0020 g $Na_2S_2O_5$	25°C	25 m	"

All reactions run under dry N_2 .

Basic conditions maintained in copolymerization with 0.1N NaOH.

TABLE 35

Poly(N-isopropylacrylamide) and Poly(N-isopropylacrylamide-co-sodium acrylate)

Sample Number	η_{sp}/c	Percent Carboxyl	N-isopropyl-acrylamide	Acrylic Acid	Initiator	Activator	Temp.	Time	Ref.
15	2.28 dl/g	--	3.00 g	--	0.0300 g $K_2S_2O_8$	0.0030 g $Na_2S_2O_5$	25°C	95 m	116
1	3.39 dl/g	33	2.26 g	1.14 g	0.0400 g $K_2S_2O_8$	--	"	60 m	"
12	78.35 dl/g	33	"	"	"	--	"	"	"
13	85.31 dl/g	41	"	"	0.0340 g $K_2S_2O_8$	--	"	"	"

Reaction conditions for copolymers kept basic with 0.1N NaOH

Total amount of water used in each reaction was 30 ml.

All reactions run under dry N_2 atmosphere.

TABLE 36
Key to Polymer Sample Numbers

Sample no.	Polymer	Sample code ^a	Source ^b	Concentration ^c (g/dl)
2	Poly(N-methylacrylamide)	P22	GK	0.0599
3	Poly(N-methylacrylamide-co-sodium acrylate)	M11	GK	0.0578
4	Polyacrylamide	M.W. 5-6,000,000 (av)	Polyosciences, Inc.	0.0653
6	Poly(acrylamide-co-sodium acrylate)	#2	JS	0.0580
7	Poly(acrylamide-co-sodium acrylate)	#3	JS	0.0075
8	Polyacrylamide	2.E6 MW	JS	0.0562
9	Polyacrylamide	1.2E6 MW	JS	0.0575
10	Polyacrylamide	A2	GK	0.2539
11	Polyacrylamide	A3	GK	0.2566
12	Poly(N-isopropylacrylamide-co-sodium acrylate)	M15	GK	0.0571
13	Poly(N-isopropylacrylamide-co-sodium acrylate)	M16	GK	0.0081
14	Polyacrylamide	A4	GK	0.1212
15	Poly(N-isopropylacrylamide)	A8	GK	0.0601
15	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 degraded 25 minutes	Dow; modified by JS	0.0062
17	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 degraded 12 minutes	Dow; modified by JS	0.0028
18	Poly(acrylamide-co-sodium acrylate)	Pusher P-1000 degraded 15 minutes	Dow; modified by JS	0.0127
19	Poly(acrylamide-co-sodium acrylate)	Pusher P-1000 degraded 30 minutes	Dow; modified by JS	0.0138
20	Polyacrylamide	#4, M-bar-sub-V = 3.3E6	JS	0.0591
21	Polyacrylamide	#5, M-bar-sub-V = 2.5E6	JS	0.0874
22	Poly(N-methylacrylamide)	F1	GK	0.0902
23	Poly(N-methylacrylamide)	F2	GK	0.0579
24	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 reprecipitated -- clean	Dow; modified by JS	0.0108
25	Poly(acrylamide-co-sodium acrylate)	Pusher P-1000 reprecipitated -- clean	Dow; modified by JS	0.0108
26	Polyacrylamide	A9	GK	0.1255
27	Polyacrylamide	A11	GK	0.1966
28	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 degraded 12 minutes	Dow; modified by JS	0.0122
29	Poly(acrylamide-co-sodium acrylate)	Pusher P-700 clean	Dow; modified by JS	0.0096
30	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 reprecipitated -- clean	Dow; modified by JS	0.0113
31	Polyacrylamide	A10	GK	0.2457
32	Poly(acrylamide-co-sodium acrylate)	Calgon 835 clean	Calgon; modified by JS	0.0129
33	Poly(acrylamide-co-sodium acrylate)	Calgon 835 clean	Calgon; modified by JS	0.0026
34	Poly(acrylamide-co-sodium acrylate)	Calgon 815 clean	Calgon; modified by JS	0.0094
35	Poly(acrylamide-co-sodium acrylate)	Pusher P-700 clean	Dow; modified by JS	0.0038
36	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 degraded 35 minutes B	Dow; modified by JS	0.0097
37	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 degraded 35 minutes C	Dow; modified by JS	0.0149
38	Poly(N-methylacrylamide)	F4	GK	0.0566
39	Poly(N-methylacrylamide)	F6	GK	0.0799

(a) Each commercial sample was re-precipitated to isolate polymer from the composition.

(b) GK = Gajendra Khune of our research group;
JS = Joel Shepitka of our research group.

(c) Uncertainties in polymer concentrations are estimated at 4% of the stated values.

TABLE 37

Results of Preliminary Screening Laboratory Tests

Sample no.	Polymer	Polymer conc. (g/dl)	Wt % acrylic acid	Specific kinematic viscosities				η_{sp} divided by η_{sp} of unsheared polymer in 0.01% NaCl(aq) solution		
				in 0.01% NaCl(aq)		in 2% NaCl(aq)		in 0.01% NaCl(aq)		in 2% NaCl(aq)
				U*	S*	U*	S*	S*	U*	S*
35	Poly(acrylamide-co-sodium acrylate)	0.0038	35.4	0.398	0.374	0.074	0.051	0.940	0.186	0.128
33	Poly(acrylamide-co-sodium acrylate)	0.0026	35.6	0.276	0.274	0.044	0.036	0.993	0.159	0.130
6	Poly(acrylamide-co-sodium acrylate)	0.0580	15.7	6.321	5.974	0.552	0.515	0.945	0.087	0.081
34	Poly(acrylamide-co-sodium acrylate)	0.0094	23.9	1.167	0.985	0.127	0.099	0.844	0.109	0.085
18	Poly(acrylamide-co-sodium acrylate)	0.0127	25.5	1.642	1.481	0.220	0.181	0.902	0.134	0.110
24	Poly(acrylamide-co-sodium acrylate)	0.0108	35.8	1.402	1.208	0.138	0.124	0.862	0.098	0.088
17	Poly(acrylamide-co-sodium acrylate)	0.0028	34.5	0.359	0.309	0.046	0.037	0.861	0.128	0.103
19	Poly(acrylamide-co-sodium acrylate)	0.0138	25.9	1.837	1.764	0.198	0.177	0.960	0.108	0.096
36	Poly(acrylamide-co-sodium acrylate)	0.0097	40.0	1.367	1.113	0.169	0.135	0.814	0.124	0.099
28	Poly(acrylamide-co-sodium acrylate)	0.0122	34.5	1.753	1.552	0.180	0.147	0.885	0.103	0.084
30	Poly(acrylamide-co-sodium acrylate)	0.0113	35.8	1.774	1.514	0.215	0.148	0.853	0.121	0.083
7	Poly(acrylamide-co-sodium acrylate)	0.0075	44.2	1.232	1.112	0.117	0.096	0.903	0.095	0.078
29	Poly(acrylamide-co-sodium acrylate)	0.0096	35.4	1.580	1.188	0.191	0.148	0.752	0.121	0.094
16	Poly(acrylamide-co-sodium acrylate)	0.0062	36.6	1.042	1.000	0.113	0.106	0.960	0.108	0.102
25	Poly(acrylamide-co-sodium acrylate)	0.0108	25.7	1.914	1.268	0.212	0.164	0.662	0.111	0.086
32	Poly(acrylamide-co-sodium acrylate)	0.0129	35.6	2.985	2.002	0.264	0.215	0.671	0.088	0.072
37	Poly(acrylamide-co-sodium acrylate)	0.0149	37.5	4.848	2.552	0.143	0.154	0.526	0.029	0.032
3	Poly(N-methylacrylamide-co-sodium acrylate)	0.0578	51.3	2.182	2.143	0.188	0.182	0.982	0.086	0.083
12	Poly(N-isopropylacrylamide-co-sodium acrylate)	0.0571	33.0	4.474	4.322	0.464	0.437	0.966	0.104	0.098
13	Poly(N-isopropylacrylamide-co-sodium acrylate)	0.0081	41.2	0.691	0.591	0.100	0.072	0.855	0.145	0.104
10	Polyacrylamide	0.2539	0.0	0.191	0.188	0.200	0.198	0.984	1.047	1.037
26	Polyacrylamide	0.1255	0.0	0.141	0.138	0.145	0.141	0.979	1.028	1.000
11	Polyacrylamide	0.2566	0.0	0.386	0.383	0.405	0.398	0.992	1.048	1.031
14	Polyacrylamide	0.1212	0.0	0.211	0.205	0.222	0.213	0.972	1.052	1.009
31	Polyacrylamide	0.2457	0.0	0.436	0.431	0.472	0.446	0.989	1.083	1.023
27	Polyacrylamide	0.1966	0.0	0.565	0.537	0.591	0.582	0.950	1.046	1.030
8	Polyacrylamide	0.0562	0.0	0.336	0.315	0.297	0.280	0.938	0.884	0.833
9	Polyacrylamide	0.0575	0.0	0.352	0.293	0.373	0.309	0.832	1.060	0.878
4	Polyacrylamide	0.0653	0.0	0.913	0.513	0.793	0.435	0.562	0.869	0.476
20	Polyacrylamide	0.0591	0.0	0.905	0.604	0.965	0.642	0.667	1.066	0.709
21	Polyacrylamide	0.0874	0.0	2.811	1.265	2.937	1.458	0.450	1.045	0.519
2	Poly(N-methylacrylamide)	0.0599	0.0	0.123	0.123	0.129	0.126	1.000	1.049	1.024
22	Poly(N-methylacrylamide)	0.0902	0.0	0.263	0.282	0.266	0.262	1.072	1.011	0.996
39	Poly(N-methylacrylamide)	0.0799	0.0	0.260	0.256	0.269	0.262	0.985	1.035	1.008
38	Poly(N-methylacrylamide)	0.0566	0.0	0.239	0.237	0.251	0.244	0.992	1.050	1.021
23	Poly(N-methylacrylamide)	0.0579	0.0	0.276	0.272	0.267	0.266	0.986	0.967	0.964
15	Poly(N-isopropylacrylamide)	0.0601	0.0	0.173	0.162	0.142	0.134	0.936	0.821	0.775

* U = unsheared; S = sheared

Uncertainties in polymer concentrations and weight % acrylic acid values are estimated at 4% of the stated values. Estimated uncertainties in the next four columns are usually approximately 1% of the stated values.

For samples having specific kinematic viscosities of less than 0.2, percent uncertainty of values in these columns may be estimated by dividing 0.2 by the specific kinematic viscosity.

Uncertainties of values in the last three columns may be estimated at the greater of 0.01 and 0.002 divided by the specific kinematic viscosity of unsheared solution in 0.01% NaCl.

TABLE 38

Results of Preliminary Screening Laboratory Tests

Sample no.	Polymer	Polymer conc. (g/dl)	Wt % acrylic acid	Reduced kinematic viscosities				Log (base 10) of reduced viscosity of unsheared polymer	
				in 0.01% NaCl(aq)		in 2% NaCl(aq)		in 0.01% NaCl(aq)	in 2% NaCl(aq)
				U*	S*	U*	S*		
35	Poly(acrylamide-co-sodium acrylate)	0.0038	35.4	103.70	97.45	19.28	13.29	2.016	1.285
33	Poly(acrylamide-co-sodium acrylate)	0.0026	35.6	107.30	106.52	17.11	14.00	2.031	1.233
6	Poly(acrylamide-co-sodium acrylate)	0.0580	15.7	108.90	102.92	9.51	8.87	2.037	0.978
34	Poly(acrylamide-co-sodium acrylate)	0.0094	23.9	124.04	104.69	13.50	10.52	2.094	1.130
18	Poly(acrylamide-co-sodium acrylate)	0.0127	25.5	128.90	116.26	17.27	14.21	2.110	1.237
24	Poly(acrylamide-co-sodium acrylate)	0.0108	35.8	129.91	111.93	12.79	11.49	2.114	1.107
17	Poly(acrylamide-co-sodium acrylate)	0.0028	34.5	130.24	112.10	16.69	13.42	2.115	1.222
19	Poly(acrylamide-co-sodium acrylate)	0.0138	25.9	132.99	127.71	14.33	12.81	2.124	1.156
36	Poly(acrylamide-co-sodium acrylate)	0.0097	40.0	140.72	114.58	17.40	13.90	2.148	1.240
28	Poly(acrylamide-co-sodium acrylate)	0.0122	34.5	144.15	127.62	14.80	12.09	2.159	1.170
30	Poly(acrylamide-co-sodium acrylate)	0.0113	35.8	156.65	133.69	18.99	13.07	2.195	1.278
7	Poly(acrylamide-co-sodium acrylate)	0.0075	44.2	163.25	147.35	15.50	12.72	2.213	1.190
29	Poly(acrylamide-co-sodium acrylate)	0.0096	35.4	164.67	123.82	19.91	15.43	2.217	1.299
16	Poly(acrylamide-co-sodium acrylate)	0.0062	36.6	168.23	161.45	18.24	17.11	2.226	1.261
25	Poly(acrylamide-co-sodium acrylate)	0.0108	25.7	177.70	117.73	19.68	15.23	2.250	1.294
32	Poly(acrylamide-co-sodium acrylate)	0.0129	35.6	232.09	155.66	20.53	16.72	2.366	1.312
37	Poly(acrylamide-co-sodium acrylate)	0.0149	37.5	325.15	171.16	9.59	10.33	2.512	0.982
3	Poly(N-methylacrylamide-co-sodium acrylate)	0.0578	51.3	37.77	37.10	3.25	3.15	1.577	0.512
12	Poly(N-isopropylacrylamide-co-sodium acrylate)	0.0571	33.0	73.39	75.73	8.13	7.66	1.894	0.910
13	Poly(N-isopropylacrylamide-co-sodium acrylate)	0.0081	41.2	85.80	73.39	12.42	8.94	1.934	1.094
10	Polyacrylamide	0.2539	0.0	0.75	0.74	0.79	0.78	-0.124	-0.104
26	Polyacrylamide	0.1255	0.0	1.12	1.10	1.16	1.12	0.051	0.063
11	Polyacrylamide	0.2566	0.0	1.50	1.49	1.58	1.55	0.177	0.198
14	Polyacrylamide	0.1212	0.0	1.74	1.69	1.83	1.76	0.241	0.263
31	Polyacrylamide	0.2457	0.0	1.77	1.75	1.92	1.82	0.249	0.284
27	Polyacrylamide	0.1966	0.0	2.87	2.73	3.01	2.96	0.458	0.478
8	Polyacrylamide	0.0562	0.0	5.98	5.60	5.28	4.98	0.777	0.723
9	Polyacrylamide	0.0575	0.0	6.12	5.10	6.49	5.37	0.787	0.812
4	Polyacrylamide	0.0653	0.0	13.99	7.86	12.15	6.66	1.146	1.085
20	Polyacrylamide	0.0591	0.0	15.32	10.23	16.34	10.87	1.185	1.213
21	Polyacrylamide	0.0874	0.0	32.15	14.47	33.59	16.67	1.507	1.526
2	Poly(N-methylacrylamide)	0.0599	0.0	2.05	2.05	2.15	2.10	0.313	0.333
22	Poly(N-methylacrylamide)	0.0902	0.0	2.91	3.12	2.95	2.90	0.465	0.469
39	Poly(N-methylacrylamide)	0.0799	0.0	3.25	3.20	3.37	3.28	0.512	0.527
38	Poly(N-methylacrylamide)	0.0566	0.0	4.22	4.19	4.43	4.31	0.625	0.647
23	Poly(N-methylacrylamide)	0.0579	0.0	4.77	4.70	4.61	4.60	0.678	0.664
15	Poly(N-isopropylacrylamide)	0.0601	0.0	2.88	2.70	2.36	2.23	0.459	0.373

* U = unsheared; S = sheared

Uncertainties in polymer concentrations, weight % acrylic acid values, and reduced kinematic viscosities are estimated at 4% to 6% of the stated values. Uncertainties of values in the last two columns may be estimated at 0.02 or 0.03.

TABLE 39

Symbols Used in "2-D" Plots

- ◇ Poly (acrylamide-co-sodium acrylate)
- ▼ Poly (N-methylacrylamide-co-sodium acrylate)
- ▷ Poly (N-isopropylacrylamide-co-sodium-acrylate)
- + Polyacrylamide
- X Poly (N-methylacrylamide)
- Poly (N-isopropylacrylamide)

TABLE 40

Tops of Figures Used in "3-D" Plots

Copolymers:

- ◇ Poly (acrylamide-co-sodium acrylate)
- ▽ Poly (N-methylacrylamide-co-sodium acrylate)
- Poly (N-isopropylacrylamide-co-sodium acrylate)

FIGURE 1
Molecular Structure of Partially Hydrolyzed Polyacrylamides²⁸

FIGURE 2
Structure of Extracellular Polysaccharide of Xanthomonas campestris, According to Jansson et al. (1975).^{108,109}

FIGURE 3

FIGURE 6

COMPARISON OF THE EFFECT OF THE CA ION AT DIFFERENT IONIC STRENGTHS
(CALGON 835-750 PPM AT 25° C)

FIGURE 7

EFFECT OF Ca^{+2} ON CALGON 835 (750 PPM) AT 25° C

FIGURE 8

EFFECT OF Ca^{+2} ON CALGON 825 (1500 PPM)

FIGURE 10

EFFECT OF DEGRADATION IN BEREA CORE ON VISCOSITY OF PUSHER 700

FIGURE 11

SHEAR DEGRADATION AT VARIOUS FRONTAL ADVANCE RATES

FIGURE 12

DEGRADATION OF PUSHER 700 IN 0.3% NACL

FIGURE 13

750 MG/L DOW PUSHER IN AN UNPURGED 0.1% NACL SOLUTION

FIGURE 14

750 MG/L DOW PUSHER 700 IN AN UNPURGED 0.1% NACL SOLUTION

FIGURE 15

750 MG/L DOW PUSHER 700 IN 1.0% NACL AT 150°F

FIGURE 16

SIPONATE DS-10 (1%) & ISOAMYL ALCOHOL (3%) AT 30°C.

FIGURE 17
SCREEN-SHEAR APPARATUS

Figure 18. Effect of shear on specific kinematic viscosity of polymer solutions in 0.01% NaCl (aqueous)

Figure 19. Effect of shear on specific kinematic viscosity of polymer solutions in 2% NaCl (aqueous)

Figure 20. Effect of NaCl on specific kinematic viscosity of unsheared polymer solutions in aqueous NaCl

Figure 21. Effect of both NaCl and shear on specific kinematic viscosity of polymer solutions in aqueous NaCl

Figure 22. Effect of shear on specific kinematic viscosity of polymer solutions in 0.01% NaCl (aqueous)
— COPOLYMERS

Figure 23. Effect of shear on specific kinematic viscosity of polymer solutions in 2% NaCl (aqueous)
 --- COPOLYMERS

Figure 24. Effect of NaCl on specific kinematic viscosity of unsheared polymer solutions in aqueous NaCl
 -- COPOLYMERS

Figure 25. Effect of both NaCl and shear on specific kinematic viscosity of polymer solutions in aqueous NaCl
 -- COPOLYMERS

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