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IMPROVING RESERVOIR CONFORMANCE USING GELLED POLYMER SYSTEMS

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Objectives

The general objectives are to 1) to identify and develop gelled polymer systems which have potential to improve reservoir conformance of fluid displacement processes, 2) to determine the performance of these systems in bulk and in porous media, and 3) to develop methods to predict the capability of these systems to recover oil from petroleum reservoirs.

This work focuses on three types of gel systems - an aqueous polysaccharide (KUSP1) system that gels as a function of pH, the chromium-based system where polyacrylamide and xanthan are crosslinked by Cr(III) and an organic crosslinked system. Development of the KUSP1 system and evaluation and identification of a suitable organic crosslinked system will be done.

The laboratory research is directed at the fundamental understanding of the physics and chemistry of the gelation process in bulk form and in porous media. This knowledge will be used to develop conceptual and mathematical models of the gelation process. Mathematical models will then be extended to predict the performance of gelled polymer treatments in oil reservoirs.

Summary of Technical Progress

Task I : Development and Selection of Gelled Polymer Systems

I.1 Development of KUSP1 and derivatives

One goal was to determine if the polysaccharide which comprises the capsule of *Cellulomonas flavigena* is chemically modified by the alkali used for extraction of the polymer. To that end, the encapsulated cells were extracted with dimethylsulfoxide (DMSO). Polysaccharide was precipitated from the DMSO extracts by the addition of isopropanol. The chemical composition of the polysaccharide prepared in this manner appeared to be identical to that of the alkali-extracted form (KUSP1). However, gels prepared from the polymer extracted with DMSO hold less water. This implied that the in vivo arrangement of the polysaccharide chains was disrupted by dissolution in alkali, and that the polymer renatured in a different form when neutralized.

Carboxymethyl derivatives have been prepared from KUSP1. This was accomplished by treatment of the polysaccharide dissolved in alkali with chloroacetic acid. The acidic ether that was obtained by such treatment was soluble in water. The degree of polymerization has not yet been determined.

I.2 Selection of organic crosslinking system to be investigated

A search of U.S Patents and Society of Petroleum Engineers literature was conducted to identify gel systems applicable to permeability reduction treatments. A draft database containing twenty-six systems was constructed that contains entries for Description, Environmental Acceptability, Temperature Range, Gel Time, Gel Stability, pH Requirement, Composition, Applications and Reference.

Criteria for the selection of an organic gel system were defined. The principal selection criterion dealt with environmental concerns and toxicity of the gel system. This criterion, termed Environmental Acceptance, was difficult to assess in that most gel systems contained chemicals that were considered toxic by some standard. A systematic approach of rating systems for Environmental Acceptance is being considered for further study. Three additional criteria for the selection of a gel system were 1) gel times

on the order of several days to months, 2) wide temperature range with a minimum temperature of 25 °C, and 3) wide pH range that encompassed pH values between 6.0 and 8.0.

Three systems were selected for initial screening experiments. An aqueous system containing sulfonated resorcinol and formaldehyde formed gels as a result of a polycondensation reaction. Using sulfonated resorcinol rather than resorcinol increased the salt tolerance of the system. Sulfonation of the resorcinol was performed prior to the preparation of the gel system. Gel samples were prepared, maintained at 41°F and monitored for pH, viscosity and visual formation of gel. Gel times, as determined from visual observation, were determined for selected concentrations of gel components, selected initial pH values of the gel solution and selected salt concentration and type.

Observed gel times are given in Table 1 as a function of salt concentration obtained for a sulfonated resorcinol-formaldehyde system and for a similar (unsulfonated) resorcinol-formaldehyde system at 25°C. The data show that gel time decreases with increased salt concentration and longer get times were observed for the system prepared with *sulfonated* resorcinol. Gel times for both systems were less sensitive to salt concentration at higher salt content.

Screening experiments for two additional systems were planned. A crosslinked polymer system using organic compounds that contain at least two positively charged nitrogen atoms as the crosslinker will be studied. Examples of the crosslinker are salts of diamines, including alkylene diamines such as propylene diamine. These organic nitrogen compounds will be used to crosslink partially hydrolyzed polyacrylamide.

Initial experiments on an aluminum crosslinked polymer system are also planned. This system was attractive due to its low toxicity level and its similarity to the KUSP1 gel system in that the gelation is triggered by a decrease in pH.

Task II : Physical and Chemical Characterization of Gel Systems

II.1 Rheological Characterization

The development of methods to monitor the gelation process as a function of time using rheometers was initiated. Central to these methods is the use of oscillatory shear where a gel sample is subjected to sinusoidal shear deformation at relatively low shear strain. Result from these types of experiments are commonly reported in graphical form showing the shear storage modulus (G') as a function of time. The storage modulus (sometimes referred to as the dynamic rigidity) is directly proportional to the average energy storage in a cycle of deformation and indicative of the build-up of structure, or gelation. G' is determined from applying the linear theory of viscoelasticity to the oscillatory measurements and, thus, the measurements must conform to the assumptions inherent in the theory. Measurements on a sample that conforms to these assumptions is said to be in the 'Linear ViscoElastic Region' (LVER). Measurements are taken on samples to determine the LVER. Other conditions, in addition to determining the LVER, must be met in the rheometers in order to obtain reliable, reproducible, accurate and precise data. These conditions include 1) gap loading, 2) no slip between sample and platens, and 3) reproducible preparation of gel samples. These factors are being evaluated for the gel systems being studied in this program.

Reproducible preparation of gel samples is inherent in acquiring reliable data. The history of the solutions used to make gel samples is critical for several types of systems. In particular, rheological properties of polyacrylamide solutions change with time due to the disentanglement of polymer molecules. In our systems, several days or weeks may be required after preparation of a stock solution before equilibrium is reached.

The physical characteristics of a gelling solution change significantly from the time of preparation through the development of the gel. The criteria described above must be met throughout the gelation

process. A systematic procedure is being developed to determine optimum conditions for rheological measurements and to assess the integrity of the data.

An example of the age of stock solutions affecting rheological measurements is shown in Figure 1 where the development of storage modulus with time is plotted for samples prepared from stock solutions of selected ages. The storage modulus developed faster for samples prepared from fresher stock solutions. The data show that these stock solutions must be aged for approximately two weeks before reproducible measurements can be obtained. In addition, care must be taken to ensure that biological activity is not degrading the polymers solutions.

II.2 Chemical Reaction Kinetics

A study was initiated to determine the effect of anion type and concentration on the gelation rate of the Cr(III)-polyacrylamide system. The same anion for both the Cr(III) and the added salt will be used. Anions to be studied are chloride, nitrate, perchlorate, sulfate and acetate. Preliminary results have been obtained by monitoring gelation using a microviscometer. Portions of the sample are periodically removed and the viscosity is determined at selected shear rates. The viscosity increased slowly for a period of time followed by a sharp increase indicating gelation. Future work will include gelation monitoring by oscillatory shear measurements.

Task III : Mechanisms of In Situ Gelation

Assembly, testing and calibration of equipment for conducting flow experiments in porous media has begun. Initial flow experiments will be conducted with the KUSP1 system.

Task IV : Mathematical Modelling of Gel Systems

IV.2 Develop of mathematical model(s) of laboratory in situ gelation

Analysis of data collected in our laboratory has demonstrated that many fluid-rock interactions were rate controlled rather than equilibrium processes. For example, the pH of effluent from sandpacks and cores varies with injection rate. Our version of the UTCHEM chemical flooding simulator does not model rate-controlled processes. Work is in progress to develop a simulator that incorporates kinetics of fluid-rock interactions.

A one-dimensional, single-phase, multi-component simulator was developed and tested. Kinetic data for silica dissolution have also been mathematically modelled. Incorporation of the kinetic model into the simulator is presently being addressed.

V.1 Spring 1993 Meeting

A international meeting of people conducting research related to gelled polymer technology was scheduled for the spring of 1993. The purpose of this focused meeting was to enhance the exchange of information between different organizations. This meeting was canceled due to the scheduling of a Society of Petroleum Engineering(SPE) Forum on "Advances in Conformance Control" during August 1993. The SPE forum will accomplish the same purpose proposed for the University of Kansas meeting. Paul Willhite is serving on the Planning Committee for the SPE forum.

Table 1

Effects of Salt Concentration and Sulfonation on Gel Time for a Resorcinol-Formaldehyde System

	Resorcinol-Formaldehyde[*]	*Sulfonated* Resorcinol-Formaldehyde[*]
NaCl Conc. (wt %)	Gel Time (hours)	
0.5	75	1600
1	34	
3	11	
5	8	190
7		64
8	7	50
9		38
10	7	28
13	6	21
15	6	16
20	4	12

* Compositions (wt.%): Resorcinol-Formaldehyde System - 1.23% formaldehyde, 3.0% resorcinol, initial pH of 9.5. Sulfonated Resorcinol-Formaldehyde System - 1.06% formaldehyde, 3.0% resorcinol, initial pH of 9.5; the resorcinol was sulfonated in a preliminary step using an additional 0.614% formaldehyde and 1.72% sodium sulfite (all concentrations based on final gel composition).
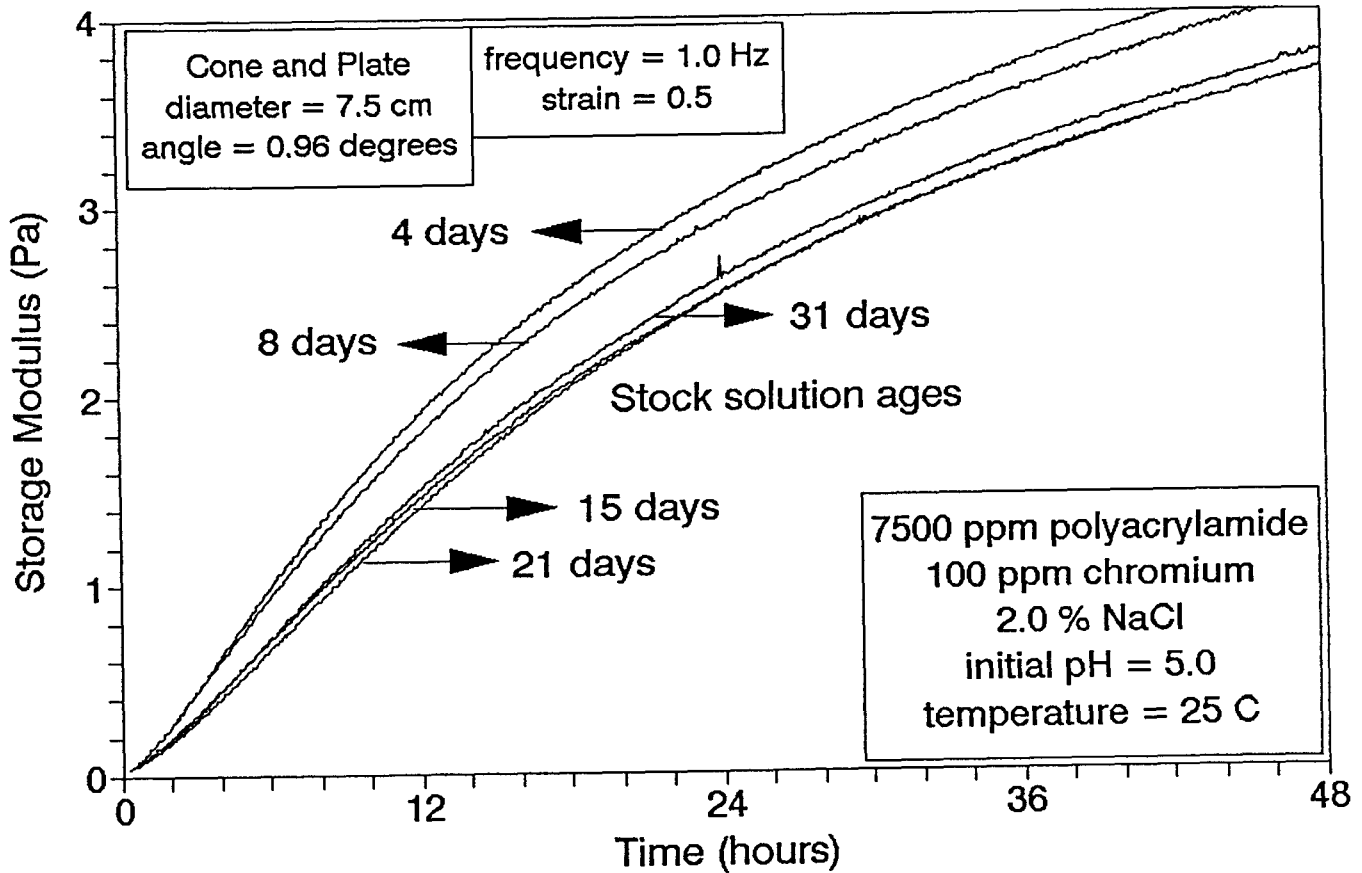
Figure 1: Effect of Stock Solution Age on Development of Storage Modulus for a Polyacrylamide - Cr(III) System