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INCREASED OIL RECOVERY FROM MATURE OIL FIELDS USING GELLED POLYMER TREATMENTS

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Abstract

Gelled polymer treatments are applied to oil reservoirs to increase oil production and to reduce water production by altering the fluid movement within the reservoir. This research program is aimed at reducing barriers to the widespread use of these treatments by developing methods to predict gel behavior during placement in matrix rock and fractures, determining the persistence of permeability reduction after gel placement, and by developing methods to design production well treatments to control water production. This report describes progress of the research conducted during months 13 through 18 of the project.

Procedures were developed to determine the weight-average molecular weight and average size of polyacrylamide samples in aqueous solution. Sample preparation techniques were key to achieving reproducible results. Data on the retention of chromium(III) during flow through dolomite rocks were obtained. Chromium retention was function of the time the solution was in contact with the rock. Approximately half of the chromium from a solution containing 200 ppm Cr(III) was removed from solution in 10 hours of contact with Baker dolomite rock at 25°C. During field application in fractured reservoirs, a portion of the injected gelant leaks from the fracture into the adjoining matrix during placement. We have found that leakoff must occur for a typical gelant system to form a gel in the fracture. Laboratory experiments must be designed to allow for leakoff in order to simulate field conditions.

Introduction

Gelled polymer systems are applied to injection wells in mature oil fields for the purpose of in situ permeability modification to improve volumetric sweep efficiency in displacement processes such as waterflooding. Gelled polymers are also used to treat production wells to reduce water production and operating costs, prolonging the economic life of the wells. While the technology has been applied successfully, there are barriers to widespread utilization. These barriers generally involve a need to develop gel systems that can be used for in-depth treatment of matrix rock and a need for improved understanding of performance in matrix rock and fractures. The research program seeks to diminish these barriers through fundamental studies to predict gel behavior and placement in matrix rock and fractures and to develop a new approach to the control of water production in production wells. The focus of studies for in-depth treatment in injection wells is the role of pre-gel aggregates, which form during the gelation process. The manner in which these aggregates affect gel placement will be mathematically modeled so that designs of treatments can be made more reliable. The application of treatments to injection wells in fractured reservoirs will be investigated by determining the effect of gel dehydration on the performance and persistence of gels that are placed in fractures. The approach to water control in production wells is based on two-phase flow characteristics of gelled polymer systems that are dehydrated in the reservoir rock after placement. Development of successful treatment strategies will provide the means for oil operators to reduce costs, since water production commonly represents a significant portion of oil field operational expenses.

Results and Discussion

Task 1: Investigate In-Depth Treatment of Matrix Rock from Injection Wells

Procedures were developed and applied to measure the molar mass and molar size of polyacrylamide molecules in aqueous samples. Measurements were conducted on Alcoflood 935 polyacrylamide (Ciba Specialty Chemicals) with a multi-angle laser light scattering (MALLS) detector (Dawn EOS, Wyatt Technology). The technique produced weight-averaged molar masses and z-averaged root-mean-square (rms) radii of the polymer.

Sample preparation was key to obtaining reproducible data. Alcoflood 935 is provided in a "dry" microbead form. Samples were dried to constant weight in a vacuum oven to determine the percentage of active polymer which was on the order of 90%. Solutions could then be prepared with accurate polymer concentrations with the dried sample or with an un-dried sample with a known assay. After the polymer was dissolved in water containing 1.0% KCl, the solution was filtered through two 5.0 μm filters, a screen-type filter and a mesh-type filter. All solutions not containing polymer were filtered through a 0.02 μm filter.

The specific refractive index increment (dn/dc) of Alcoflood 935 is a parameter that is required to calculate molar masses and rms radii using the light scattering data. Runs were conducted using an Optilab DSP interferometric refractometer to measure the dn/dc of the Alcoflood 935 polyacrylamide. A dn/dc value of 0.182 mL/g (in 1.0% KCl, 25°C) was determined for both dried and non-dried samples of Alcoflood 935.

Molar masses and rms radii were measured several times for dried and non-dried Alcoflood 935 samples to check the reproducibility of the technique. Results of these measurements are given in Table 1. The average molar mass was 6.87×10^6 daltons and the average rms radius was 241 nm for the dried samples. For the non-dried samples, the average molar mass was 6.40×10^6 daltons and the average rms radius was 231 nm. Differences between the values for the dried and non-dried samples were not considered significant.

Table 1 – Results of laser light scattering experiments.

Dried Alcoflood 935 (Lot 7158V)

Run	1	2	3	4	5
Molar mass (10^6 daltons)	6.87	6.61	7.03	6.98	6.86
RMS radius (nm)	248	226	246	244	239

Non-Dried Alcoflood 935 (Lot 7158V)

Run	1	2	3	4	5	6	7	8
Molar mass (10^6 daltons)	6.42	6.47	6.38	6.52	6.17	6.57	6.41	6.28
RMS radius (nm)	227	234	229	230	227	237	231	230

Work continued on the application of gelled polymer treatments in carbonate rocks. Previous results have shown that the transport of chromium(III) through carbonate rocks is impeded due to the precipitation of chromium from solution. Additional experiments have been conducted to characterize the transport of chromium(III) acetate through Baker dolomite rock samples.

Chromium retention in a dolomite rock was determined under the condition where the chromium acetate solution (200 ppm Cr; 0.0% KCl) was injected continuously at a constant flow rate (0.02 mL/min). Approximately six pore volumes of chromium solution were injected at a rate that gave a residence time of 23 hours. Concentration of chromium in the effluent is shown in Figure 1 as a function of pore volumes injected. Chromium was continuously retained in the dolomite rock as shown by the steady chromium concentration of about 36% of the injected value after 3 pore volumes were injected.

At 6.0 pore volumes injected, the chromium solution resident in the dolomite core was displaced immediately and quickly with water at a flow rate of 1.0 mL/min. The chromium concentration in the effluent increased during the first 0.6 pore volumes of brine injection as shown in Figure 1. The chromium concentration then decreased due to mixing with injected brine. The increase in chromium concentration in the effluent indicated that there was a concentration gradient along the length of the dolomite rock during the previous injection of chromium solution. The chromium concentrations during this time period were related to the time the solution resided in the dolomite rock (residence time). These data are presented later.

Flow experiments were also conducted with shut-in periods to provide long contact times between the injected chromium solutions and the dolomite rock samples. Chromium acetate solutions containing 200 ppm chromium (0.0% KCl) were injected quickly through a dolomite rock sample. Injection was then stopped for a selected time period. This process was repeated for several lengths of shut-in time periods. Chromium concentrations and pH values in the effluent after the shut-in periods are shown in Figure 2. The chromium concentration during the first half pore volume injected represented the chromium concentration that remained in solution after the shut-in time in the rock sample. The data show increased chromium retention with increased contact time. A second series of runs was conducted with the chromium solution containing 1.0% KCl.

Chromium concentrations in the effluent from the flow experiments (both continuous flow and shut-in types) were plotted in Figure 3 as a function of the time the chromium solution resided in the dolomite rock. Agreement between the two types of experiments indicates that retention of chromium was a dependent on the contact time between the dolomite rock and the chromium solution and that flow, at least at low velocities, did not affect retention significantly. This allows retention studies to be conducted by the faster shut-in type of experiments.

Task 2. Investigate Gel Placement and Stability of Gels in Fractured Systems

During the placement of gelant in fractured systems, a portion of the injected gelant leaks from the fracture into the adjoining matrix. The effect of the leakoff on the performance of a chromium acetate-polyacrylamide gel system that is placed in a fracture was investigated. The ability of a gel that has been placed in a fracture to resist failure/rupture when subjected to a pressure gradient was also studied. The failure/rupture experiments were conducted with gels confined in fractures and in lengths of tubing.

The aqueous gel system contained 5000 to 7500ppm Alcoflood polyacrylamide, 417 ppm chromium triacetate and 1% NaCl. The system had a gel time of between 12 and 32 hours depending on the polymer concentration and polymer lot. Three types of fracture models were used for flow experiments: slabs slots and cores. Berea sandstone slabs (10×24×1 inch) were fractured on the 10×1 inch plane in the middle of the 24 inch width. Slots were constructed as a narrow channel between a saw-cut Berea face (1×10 inch) and an acrylic wall. Berea cores were fractured in the middle of the 2×2 inch cross-section and along the length of between 12 to 24 inches. The fracture models were constructed and equipped so that fluids could be injected through the fracture as well as allowing for fluids to leak off into the adjoining matrix.

A series of experiments were conducted in fractured slabs and cores in which gelant was injected into the fracture and allowed to leakoff in the adjoining matrix to depths between 0 and 30 cm.

The gelant was allowed to mature in the model for at least five days. Brine was then injected at the fracture inlet by increasing the brine pressure over time to determine the pressure required to initiate fluid displacement through the fracture. Pressure of the brine as a function of time for Runs 1 and 2 are shown in Figure 4. A minimal pressure on the brine was required to displaced *polymer solution* from the fracture as shown for Run 1. A gel did not formed in the fracture in Run 1 when the gelant was place without leakoff. In Run 2 where the gelant was placed in the fracture with leakoff to a depth of 1 cm, the brine pressure increased to 5.5 psig before displacement of *gel* from the fracture occurred. The pressures required for fluid displacement, or rupture pressures, are given in Table 2 for a series of runs using a range of fracture sizes and depths of leakoff. The results indicate that gelation occurs in the fracture when the gelant was allowed to leakoff into the adjoining matrix to a minimum depth of at least 1 cm. Leakoff probably occurs in most, if not all, field applications. Laboratory experiments that are designed to study the application of gel treatments of fractures must allow for leakoff to simulate field conditions.

Table 2 - Summary of Series 1 experiments for determining the formation and displacement of a gel in a fracture.

Run #	Fracture model and #	Fracture height and length (cm × cm)	Fracture aperture (cm)	Leak off distance (cm)	Shut-in time (days)	Rupture pressure (psig)
1	Slab 1A	2.5 × 25	0.10	0	5	~1
2	Slab 1B	2.5 × 25	0.10	1	5	5.5.
3	Slab 1C	2.5 × 25	0.10	10	5	6.4
4	Slab 2	2.5 × 25	0.030	30	7	12
5	Core 1	5.1 × 30	0.039	2.5*	30	18
6	Core 2	5.1 × 45	0.029	2.5*	7	40
7	Core 3**	5.1 × 61	0.10	2.5*	5	10

* Entire matrix filled with leak-off by injection of about three pore volumes of gelant.
** Gel time of 30 - 32 hours.(Gel time was 12 hours for Runs 1 through 6).

A second series of runs was conducted to determine why the gel did not form in the fracture when the gelant was placed without leakoff. Three runs were conducted with leakoff and three without leakoff. After placement of the gelant, the fractures were shut-in till right before the bulk gel time of the system. The fluid in the fracture was then displaced from the fracture and analyzed for pH value and chromium concentration. The pH of the effluent increased to values around 7, but little difference was observed between the experiments conducted with and without leakoff. Chromium concentrations in the effluent from the runs conducted with leakoff ranged between 70 and 95% of the value of the injected gelant. For runs conducted without leakoff, chromium concentrations of the fluid displaced from the fracture were much lower, between 15 and 40% of the value of the injected gelant. Our results indicate that the loss of chromium from the gelant (when the gelant was placed without leakoff) was responsible for the failure of the gelant to form a gel. We suspect that chromium left the fracture by diffusion into the adjoining matrix. With leakoff, the chromium concentration in the adjoining matrix retards the diffusion from the fracture to the matrix. Simulations of the diffusion of chromium from fractures into adjoining matrix were conducted and the results support our interpretations.

Rupture pressures were determined for gels confined to the fracture models as described above. The process of gel rupture was further investigated for gels confined to transparent tubing. Gelants were prepared and allowed to gel in tubing of various diameters and lengths. Rupture of the gel was conducted by subjecting the gel to brine at increasing pressure. At a threshold or rupture pressure, brine shot through the center of the entire length of gel in less than a second. Rupture pressures for runs conducted in nylon tubing are presented in Figure 5 as a function of the length-to diameter ratio of the confined gel. Although some scatter in the data are observed, the rupture pressure appears to correlate with the length-to diameter ratio. This type of correlation was established earlier with results of similar experiments conducted with polypropylene tubing.

Task 4: Reporting – Data Analysis, Reduction and Correlation & Technology Transfer

Three seminars were presented and four technical papers were published on work performed in this and previous contracts.

Presentations

"A Different Perspective of Disproportionate Permeability Reduction," C.S. McCool, Petroleum Recovery Research Center, New Mexico Tech, Socorro, New Mexico, 2 November 2000.

"Development and Application of Polymer Gels for Water Control," G.P.Willhite, presented at a workshop titled *Gelled Polymers and Their Applications*, Petroleum Technology Transfer Council, Wichita, KS, 6 December 2000.

"Basics of Polymers and Gelled Polymers," C.S. McCool, presented at a workshop titled *Gelled Polymers and Their Applications*, Petroleum Technology Transfer Council, Wichita, KS, 6 December 2000.

Publications

McCool, C.S., Green, D.W., and Willhite, G.P., "Fluid/Rock Interaction Between Xanthan-Chromium(III) Gel Systems and Dolomite Core Material," **15**, *SPE Prod. & Facilitites* (August 2000) 159.

Zou, B., McCool, C.S., Green, D.W., and Willhite, G.P., "Precipitation of Chromium Acetate Solutions", *SPE Journal,* **5** (September 2000) 324.

Zhuang, Y., Pandey, S.N., McCool, C.S. and Willhite, G.P., "Permeability Modification with Sulfomethylated Resorcinol-Formaldehyde Gel System," **3**, *SPE Reservoir Eval. & Eng.* (October 2000) 386.

McCool, C.S., Shaw, A.K., Singh, A., Bhattacharya, S., Green, D.W., and Willhite, G.P "Permeability Reduction by Treatment with KUSP1 Biopolylmer," *SPE Journal,* **5** (December 2000) 371.

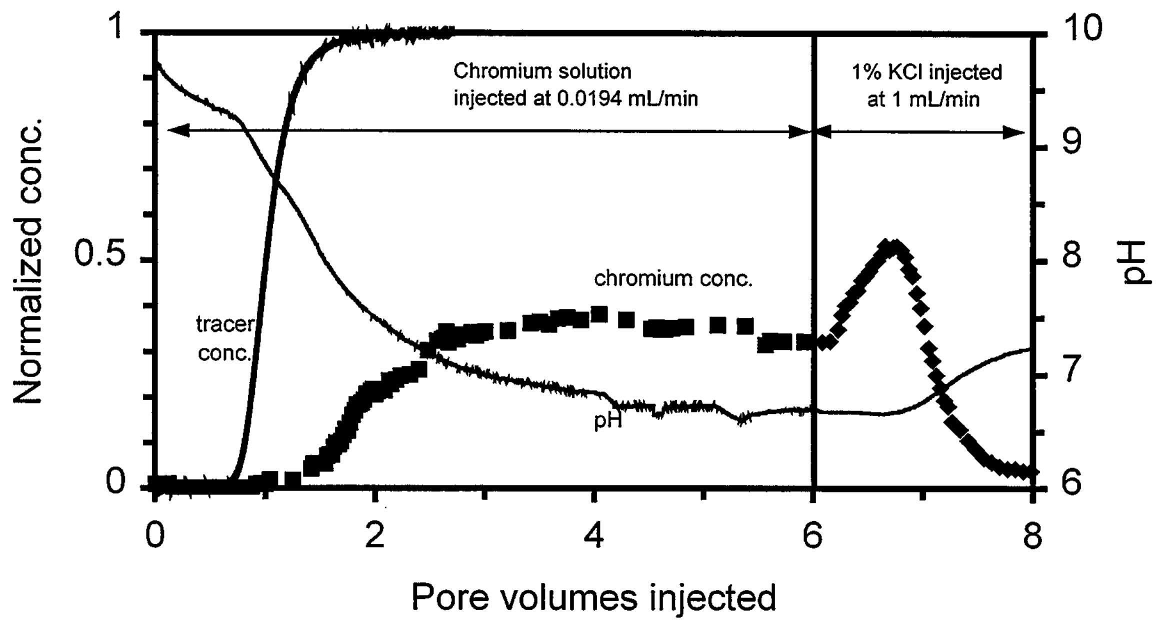

Figure 1 – Results of constant flow rate experiment to determine chromium(III) retention in dolomite rock; Six pore volumes (PV) of chromium acetate solution (200 ppm Cr(III); 0% KCl) injected at 0.0194 mL/min followed by injection of two PV of 1.0% KCl brine injected at 1.0 mL/min; PV of Baker dolomite core was 27.9 mL.

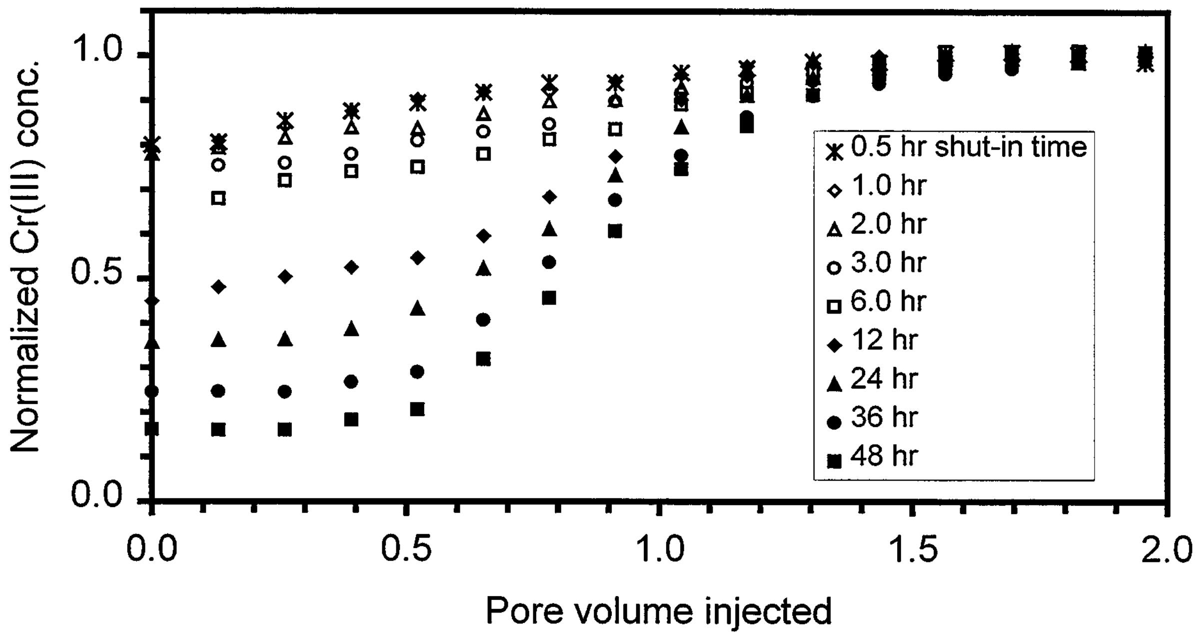

Figure 2 – Results of shut-in type experiment to determine chromium(III) retention in dolomite rock; Chromium acetate solution (200 ppm Cr(III); 0% KCl) was injected quickly at 1.0 mL/min between the indicated shut-in times; PV of Baker dolomite core was 2.8 mL.

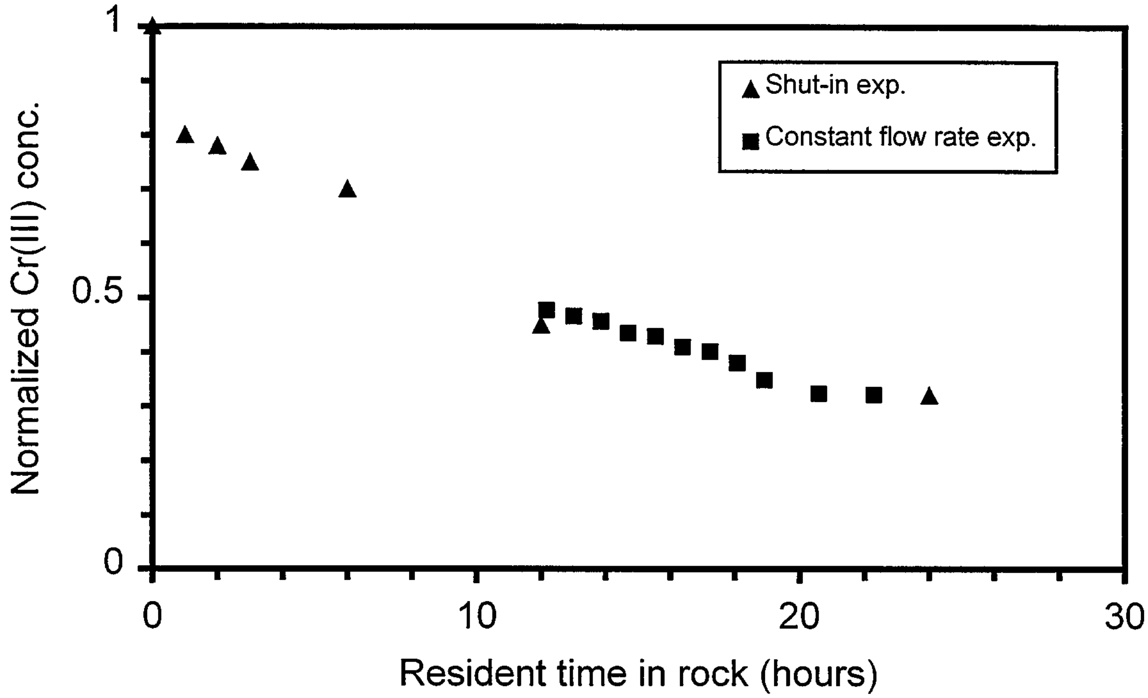

Figure 3 – Fraction of chromium(III) remaining in solution as a function of resident time in Baker dolomite rock.

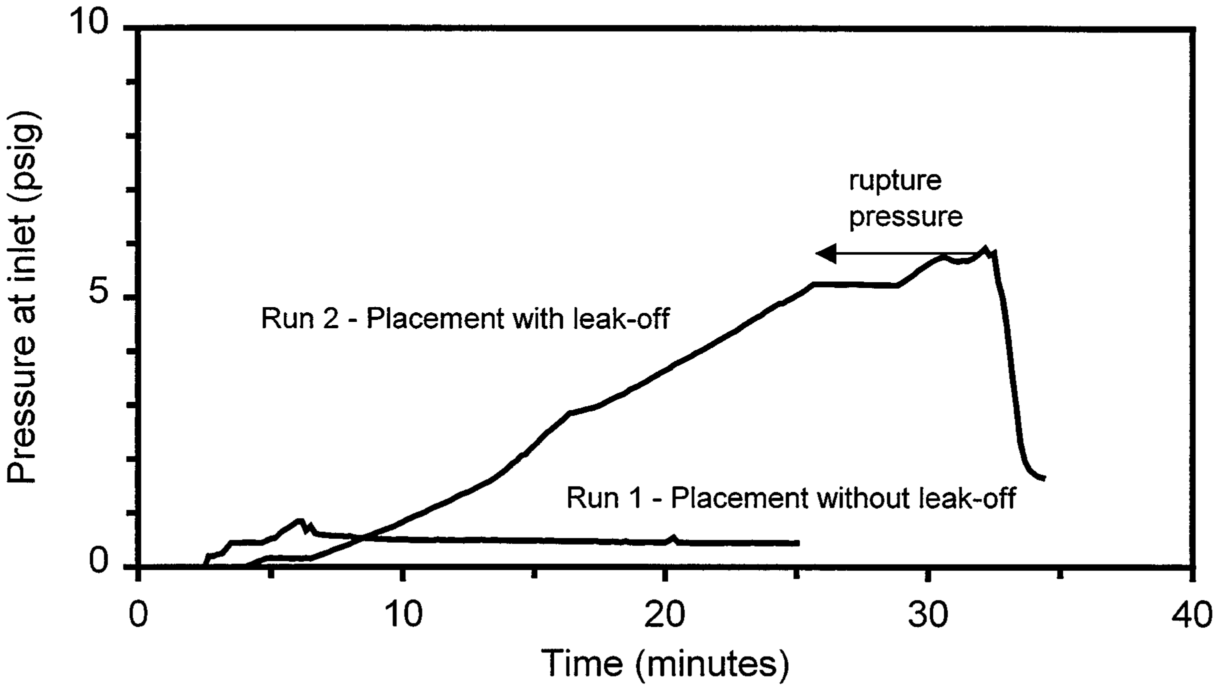

Figure 4 – Pressure of brine at fracture inlet during rupture test.

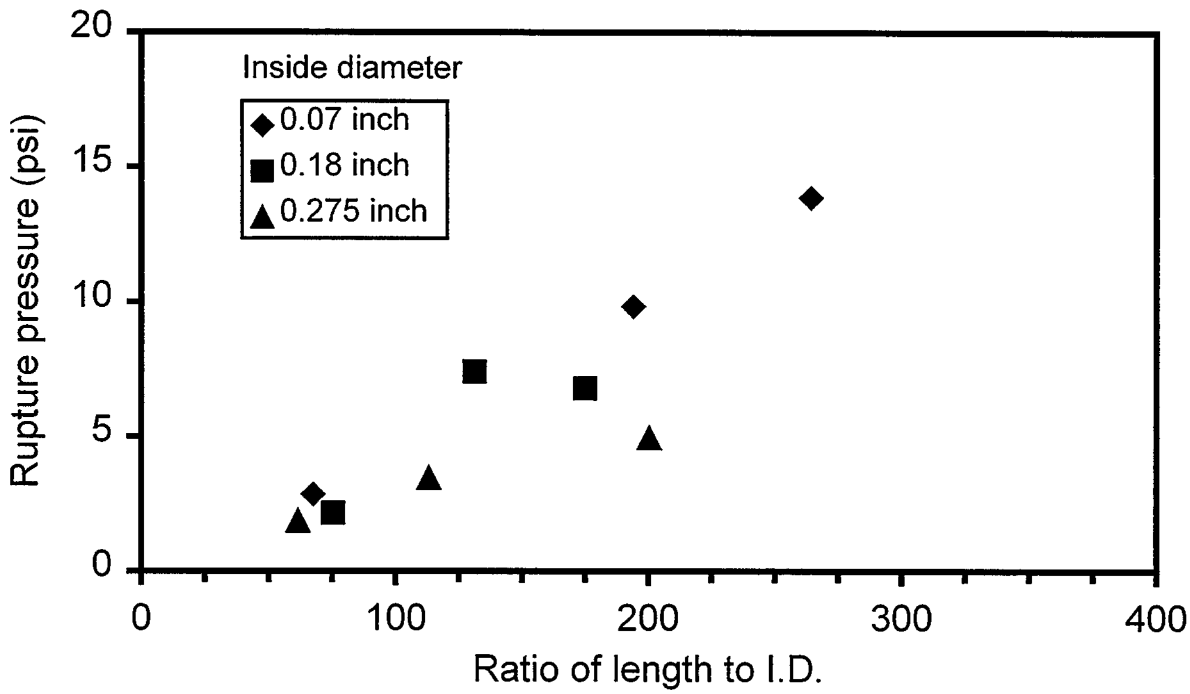

Figure 5 – Correlation of rupture pressure with the ratio of length-to-diameter of the gel.