Effect of Shear on Gelation of Polyacrylamide-Chromium Acetate Gelant in a Circular Tube

BY

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Abstract

This research studies the gelation and flow properties of a partially hydrolyzed polyacrylamide (HPAM)-chromium acetate gel system under shear conditions. Gelation was observed in steady shear on a rheometer and during injection through a 1,031-ft long stainless steel tubing.

Fluid experienced continuously non-uniform shear in the tubing (zero shear at the center and maximum shear at the tube wall) and the shear environment may not be reproduced by rheometers. Both in-line-mixed and preformed gels were injected through the tubing, and gel samples were collected to determine syneresis.

Interesting results were observed due to the non-uniform shear rate distribution in the tube. During injection of in-line-mixed gelant solution, flow resistance developed with length down the tube to a steady resistance value. Shear retarded the gelation process as compared to a quiescent bulk gel. Spaghetti-like gel emerged from the tube, and the low apparent viscosity of the gel in the tube indicated the existence of lubricant solvent between the gel and the tube wall.

During injection of preformed gels, flow resistance at upstream of the tube was higher than that of in-line-mixed gelant. However, it decreased down the tube to steady values that were lower than the steady values measured for in-line-mixed gelant. The effluent gel more easily broke into pieces than the effluent during the injection of in-line-mixed gelant solution.

Effluent samples from both types of flow experiments underwent significant syneresis due to the shear experience in the tube; while bulk-mixed gel samples were stable. Samples placed under constant, steady shear in a rheometer for 10 hours did not form strong gels until the shear was stopped.

This study shows that shear experienced by a gelant during displacement in the reservoir significantly affects the properties of the gel. Results of the study are applicable to gel placement in fractured reservoirs.

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Chapter 1

Introduction

At the early stage of oil production, the oil is driven to the production well by natural reservoir energy provided by fluid and rock expansion and gravity drainage. This stage is called primary production. However, the natural reservoir energy becomes insufficient after a period of production, and only a small part of oil has been produced at that time. So some methods have been developed to enhance the oil recovery, in which waterflooding is the primarily used one. Water is pumped into the reservoir from injection wells to displace the oil out from production wells. This method is very effective in many reservoirs, but is less efficient when water bypasses oil zone through high permeability paths or fractures, which results in early water production and high water oil ratio. This problem is especially severe in naturally fractured reservoirs.

A commonly used method to solve this problem called profile control or profile modification, is to inject in-line-mixed gelant solution or preformed gel into the reservoir to modify the permeability profile. High permeability zones or fractures nearby the injection wells as well as production wells are blocked by the gels (preformed or formed in situ) so that the resistance to water is very high, which forces water to displace the oil in low permeability zones. The volumetric sweep efficiency may be significantly improved.

Before the preformed gel and in-line-mixed gelant solution arrive at their destination, they experience various shear: from the pumps, the lines, the well, and finally the porous media (fractures or high permeability zones). The shear history significantly affects the flow behavior of gel or gelant and the final properties of the gel in the fractures.

Some researchers studied the effect of shear on gelation using rheometers, by observing the change of viscosity with time. Others studied the flow of preformed gel in short tubes and fractures, by observing the pressure-drop data (or resistance factors). However, no work has been done to study the effect of long period of continuous shear on formation of gel. As preformed gel or in-line-mixed gelant solution experiences continuous shear when it flows through the fractures, the behavior is different from that when it experiences shear applied by viscometers for a short period of time (e.g., less than one hour).

The objective of this research is to study the effect of shear on formation and properties of gel in a long circular tube which was used to simulate a long fracture.

Chapter 2

Literature Review

The effect of shear on gelation has been studied by previous researchers for several gelling systems, such as polyacrylamide-chromium (VI), Xanthan-chromium (III), and polyacrylamide-chromium (III). The study is focused on polyacrylamide-chromium (III) gelling system since it is primarily used at present.

This chapter summarizes the results from previous research about the effect of shear on preformed gel as well as on gelation process of polyacrylamide-chromium (III) gelling system. The gelation kinetics of this gelling system has been described in section 2.2 of Cheng's dissertation[13].

2.1 Behavior of preformed gel in fractures (tubes)

Seright et al.[1, 2, 3, 4] studied the behavior of preformed gel in fractures and tubes. They proposed several mechanisms on how the gel performance increased oil production. This section gives a brief review of their research results on preformed gel.

2.1.1 Experimental results

Seright performed experiments of gelants and gels in fractured cores for the first time in lab in 1994[1]. The purpose of the experiments was to examine several factors that could have an important effect on gel placement in fractured system. The gelling system used in the experiments contained 0.5% HPAM (Alcoflood 935), 0.0417% Cr(III) acetate, and 1% NaCl. The gels were 24 to 32 hours old before injection.

Experiments were conducted in fractured Berea sandstone cores at 105ºF (41 ºC). The cylindrical cores were 5.5-inch long with a cross-sectional area of 1.6 in^2. These cores were fractured lengthwise with a core splitter. The two halves of the core were repositioned and cast in epoxy. Figure 2.1 shows the schematic of a fractured core. The results of resistance factors and pressure gradients are shown in Figure 2.2 and Figure 2.3, respectively. The resistance factor was calculated by dividing the pressure drop during gel injection by the pressure drop during water injection before gel placement.

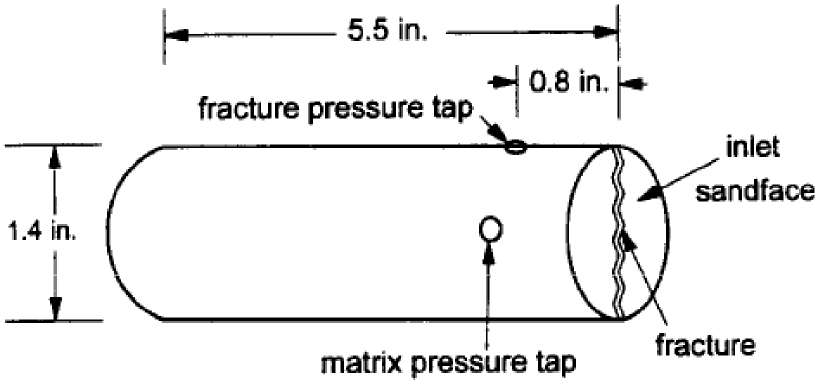

Figure 2.1 Schematic of a fractured core, Seright[1]

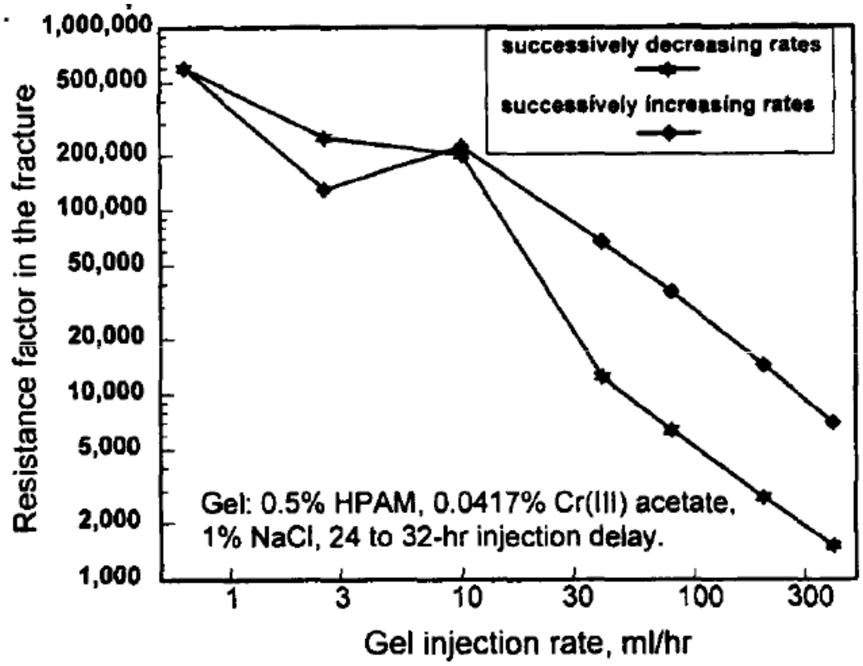

Figure 2.2 Resistance factor in the fracture during placement of a $Cr(OAC)_3$/HPAM gel, Seright[1]

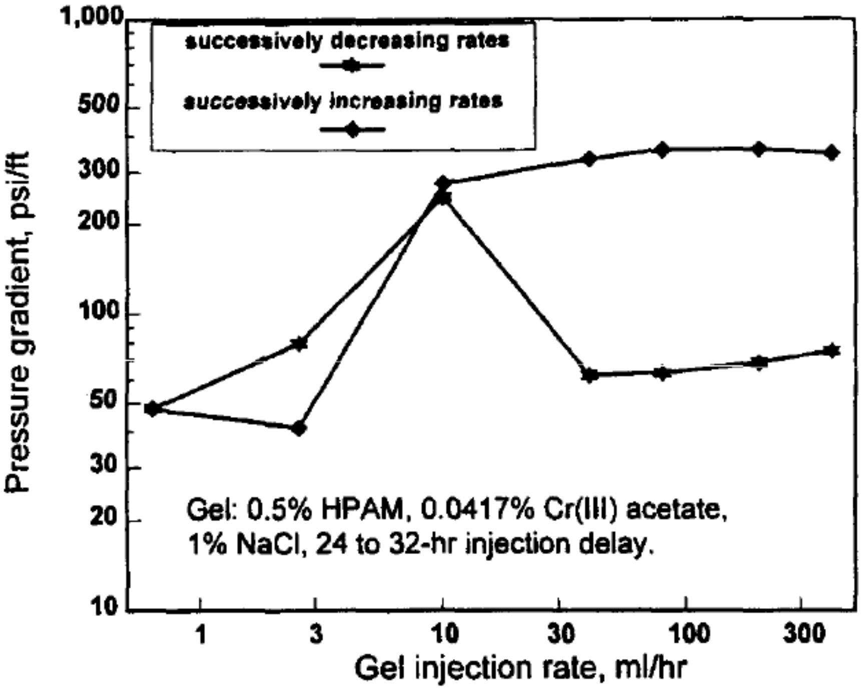

Figure 2.3 Pressure gradient during placement of a $Cr(OAC)_3$/HPAM gel, Seright[1]

Figure 2.2 shows that the resistance factors in the fracture changed in the opposite direction with the change of the gel injection rates. That is, the resistance factor increased with decreasing of injection rate, and it decreased with increasing of injection rate.

Figure 2.3 shows that pressure gradient stabilized at injection rate greater than 30 mL/h. The results indicated that a minimum pressure gradient was necessary to initiate flow of the gel through the fracture, and this pressure gradient was insensitive to the injection rate after initiation of the flow.

Seright performed additional experiments in fractured cores and some experiments in tubes for preformed gel. Results were published in 1996[2]. Fractured Berea sandstone cores with nominal permeability to brine of 650 md were used in those experiments. The cores were 6 in. in lengths and 1.4 in. in diameter, and were fractured lengthwise. Two halves of the core were repositioned and cast in epoxy. One pressure tap was located 90º from the fracture to measure pressure in the porous rock, and another pressure tap was drilled to measure the pressure in the fracture. The fractures were always oriented vertically. The inside diameters of the tubes were 0.009, 0.03, 0.04, 0.079, 0.245, and 0.325 in. All the tubes were 3-ft long except for the 0.03- and 0.325-inch tubes (which were 15 ft in length).

The gel system contained 0.5% HPAM (Allied Colloids Alcoflood 935, weight-average molecular weight Mw ≈ 5×10^6 g/mol, degree of hydrolysis: 5-10%), 0.0417% Cr(OAC)$_3$, and 1% NaCl at pH 6. The gelation time for this formulation was about 5 hours at 105 ºF. All gels were 24 hours old and preformed prior to injection. All experiments were performed at 105 ºF (41 ºC).

The resistance factors in tubes as well as in fractured cores were plotted against superficial velocity in Figure 2.4.

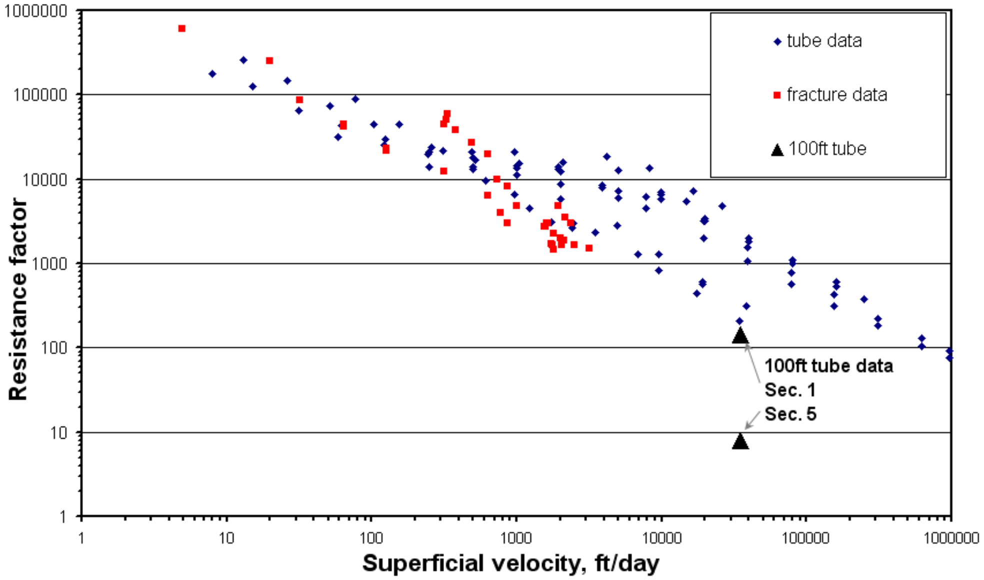

Figure 2.4 Comparison of resistance factors in fractures vs. in tubes, Seright[2]

Figure 2.4 shows that the fracture data were in reasonable agreement with the tube data for superficial velocities less than 2,000 ft/d. Resistance factors are greater than 3,000 at superficial velocities less than 1,000 ft/d.

Seright[2] also performed an experiment using a longer fractured core that was 3.8 ft in length and 2.25 in^2 in cross-section area. Four internal pressure taps were spaced equally along the length of the fracture. The fracture conductivities (the permeability of a fracture times its width) of the five 9-inch fracture sections of the core were 4.2, 5.1, 5.6, 2.8, and 4.6 darcy-ft. The volume associated with the fracture was about 0.8 in^3, and the total core pore volume was 22.9 in^3. The gel system was the same as that mentioned above with age of 24 hours. Figure 2.5 shows the resistance factors in the five core sections as a function of the volume of gel injected.

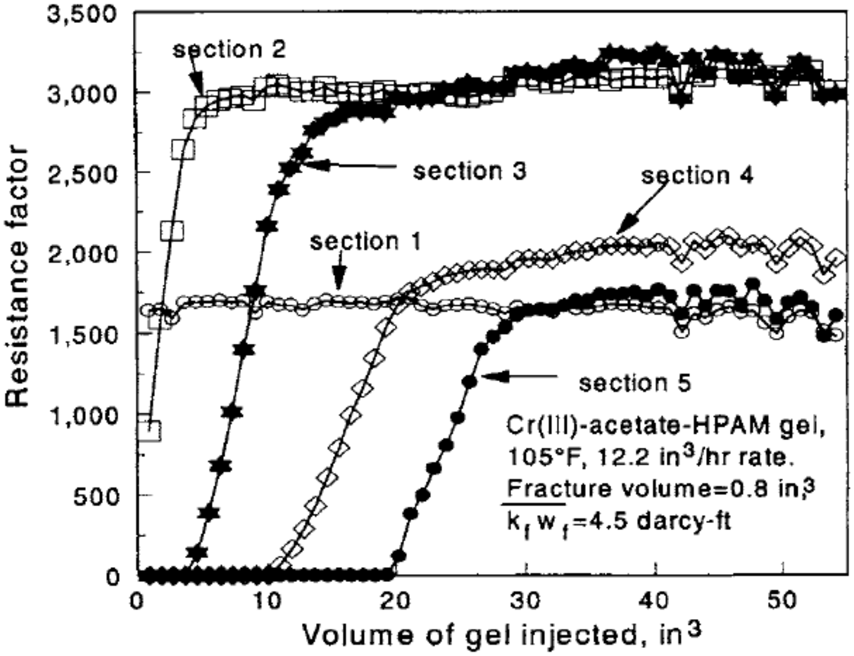

Figure 2.5 Resistance factor vs. volume of gel injected in a fractured core (3.8-ft long), Seright[2]

As can be seen from Figure 2.5, the stabilized resistance factor in all the sections are larger than 1,500. And the resistance factors in sections 1, 4 and 5 are close to each other, but less than those in sections 2 and 3.

Seright also performed experiment of gelants flowing through the fractured cores, but was focusing on the degree of penetration of gel in the fractures. No pressure data or resistance factors of gelants were presented.

Based on his experimental data of preformed gel, Seright[3] concluded that a minimum pressure gradient was necessary to extrude gel through a fracture for a given conductivity. Pressure gradients were insensitive to flow rate after the initiation of flow of the gel[2]. He suggested that a Bingham plastic model (where shear stress is linearly dependent on shear rate after an initial shear stress threshold has been reached) might be appropriate when describing extrusion of gels through fractures.

2.1.2 Interpretation

Seright[3] found out that gels could lose water during extrusion through fractures, and proposed the mechanism of dehydration to interpret the behavior of preformed gel when flowing through fractures. He also studied the mechanism for gel propagation through fractures[4].

Water left the gel and leaked off into the porous rock or flowed through the fracture ahead of the gel, while the crosslinked polymer remained behind in the fracture to propagate at a much slower rate. A filter cake of concentrated gel formed gradually along the length of the fracture because of the high-pressure gradient between the fracture and the adjacent matrix. And the leak-off rate gradually decreased after the gel front passed, and the filter cake become more concentrated on the fracture faces in the upstream sections. However, the pressure gradient required for extrusion did not increase much. For the experiments in tubes, no leak-off was observed.

2.2 Effect of steady shear on gelation

The first part of this section reviews previous experimental results about the effect of steady shear on gelation, and the second part reviews the interpretation from previous researchers.

2.2.1 Experimental results

Stinson[5] studied gelation under shear rates from 0.236 to 11.9 sec^{-1} at temperatures ranging from 24.9 to 25.2 ºC in a cone and plate rheometer. The composition of this gelling system was 3,000 ppm (weight fraction) Superfloc 16 and 25 ppm chromic chloride (8 ppm chromium (III)). Figure 2.6 shows the apparent viscosity with time under different shear rates, where “apparent viscosity” here is the value obtained from viscometer which is the ratio of shear stress to shear rate (dependent on the rate of shear).

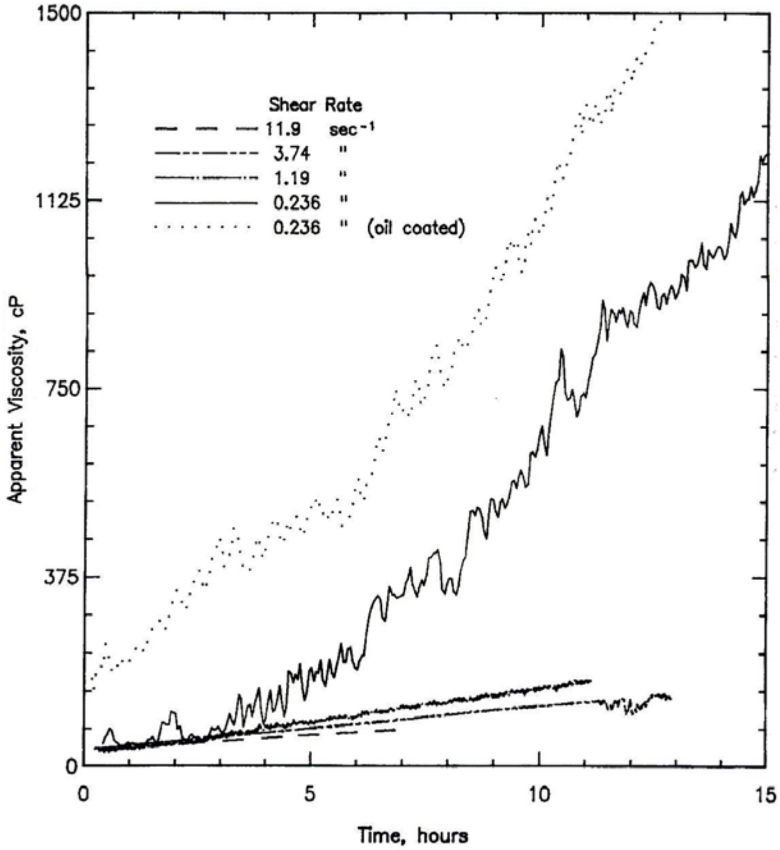

Figure 2.6 Effect of shear on Superfloc 16/chromium (III) gelling solution, Stinson[5]

The apparent viscosity growth was larger with smaller shear rates. For example, after seven hours of gelation the apparent viscosities of the solutions were about 75, 95, 115, and 320 cp for the runs made at shear rates of 11.9, 3.74, 1.19, and 0.236 sec^{-1}, respectively. For the runs made at shear rates of 11.9, 3.74, and 1.19 sec^{-1}, the slope of the gelation curves over the first five hours of the reaction were 6.5, 8.33 and 13 cp/hr, respectively. Hence over the first 5 hours of gelation, the rate of gelation increased with decreasing shear rates, that is, shear retards gelation.

Kote[6] performed steady shear runs on the Superfloc 16 (5,000 ppm)-chromium (III) (27.3 ppm) solution at shear rates of 1.12 sec^{-1} and 2.23 sec^{-1}, using the Weissenberg Rheogoniometer R19. The temperature was controlled at 25 ºC. Figure 2.7 shows the apparent viscosity data with time.

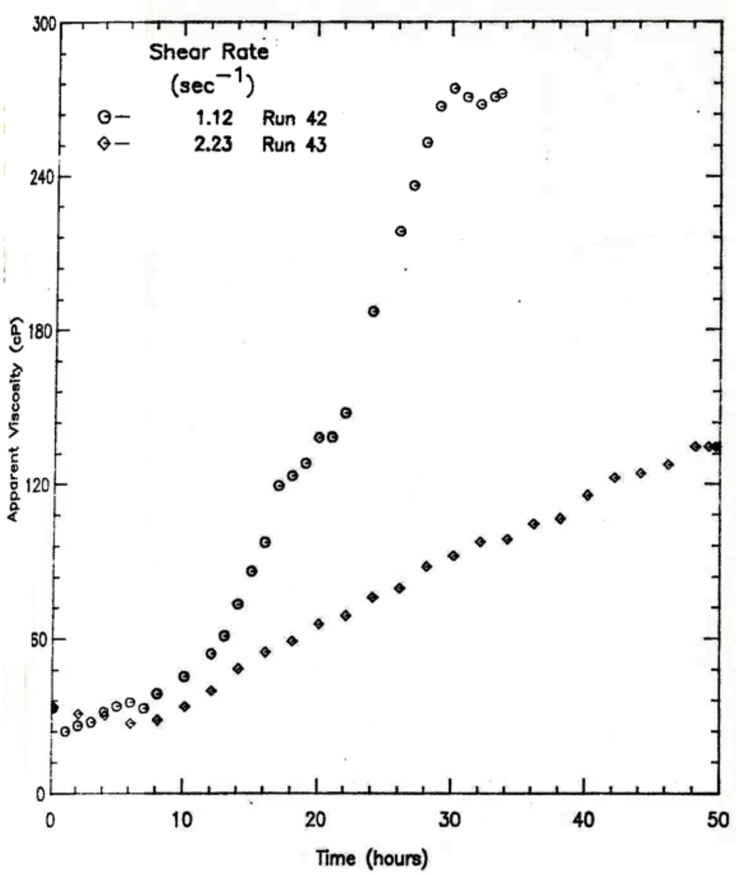

Figure 2.7 Gelation rheograms for Superfloc 16-chromium (III) solution at shear rates of 1.12 sec^{-1} and 2.23 sec^{-1}, Kote[6]

It was observed that at higher shear rates less viscous gels were formed. Initially, the viscosity did not change significantly during a period of time called "induction period". For the gelation at a steady shear of 1.12 sec^{-1}, during the initial 15 hours the viscosity changed linearly with time after an initial induction period. But for the gelation at shear rate of 2.23 sec^{-1}, the viscosity after a short induction period changed linearly with time for the initial 30 hours. It was also observed that the viscosity buildup was steeper at the lower shear rate, which supports the conclusion that more viscous gels were formed at lower shear rates and shear seemed to retard gelation.

Kote[6] also studied the shear effect on the same system using Brookfield Rheolog model LVT. As seen in Figure 2.8 and Figure 2.9, the results showed that the gelation time decreased at higher shear rates, that is, shear enhances gelation. This result is consistent with Aslam's[7] and Huang's[8] results, but contrary to Stinson's result described above.

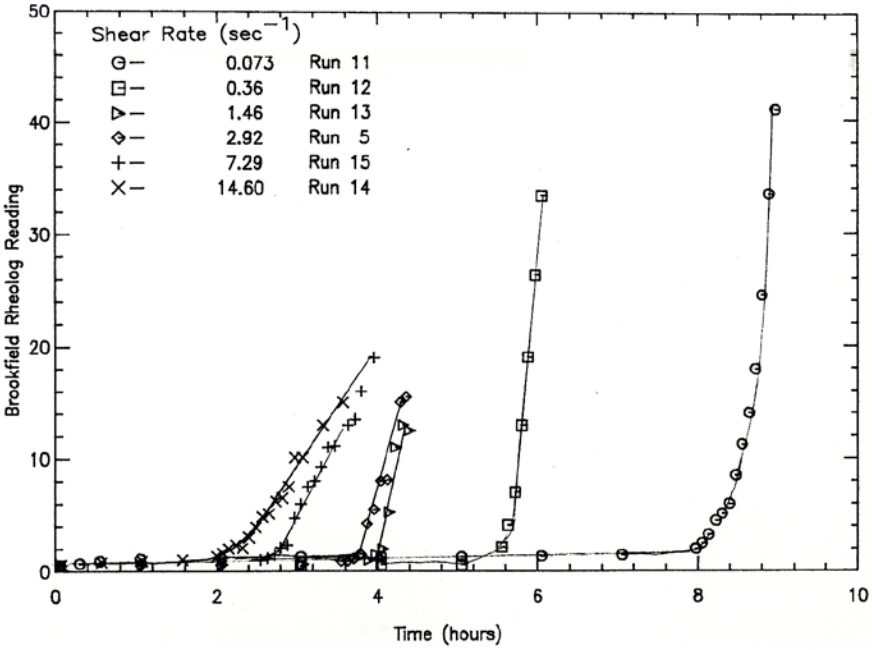

Figure 2.8 Effect of shear rate on Superfloc 16-chromium (III) gelation, Kote[6]

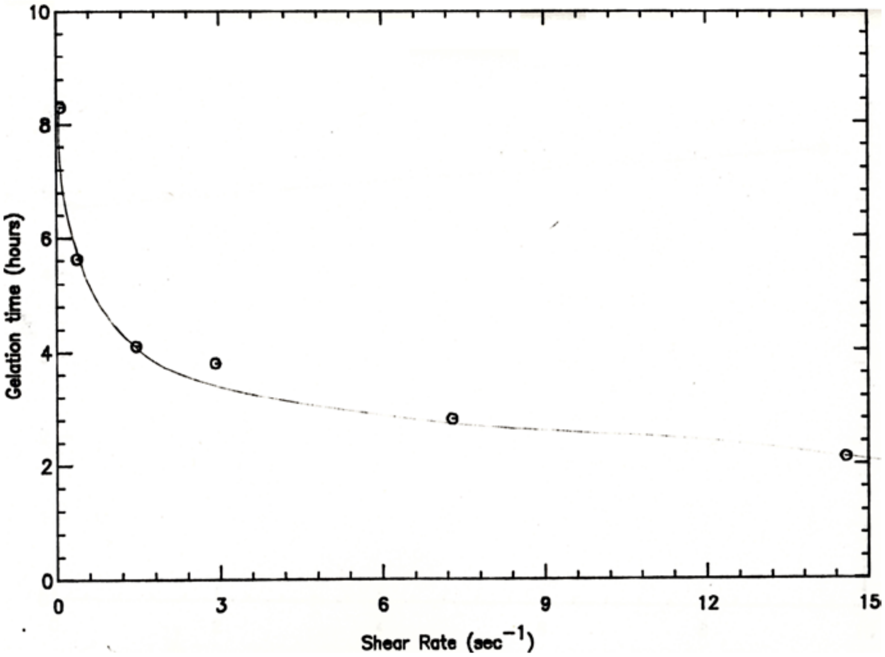

Figure 2.9 Effect of shear rate on gelation time for Superfloc 16-chromium (III), Kote[6]

Bhaskar[9] studied the shear effect on Aldrich polyacrylamide-chromium (III) system, which was named System II in his dissertation, consisting of 2,500-6,000 ppm Aldrich polyacrylamide and 50-150 ppm chromium (III) at pH of 5.0. The results are shown through Figure 2.10 to Figure 2.13.

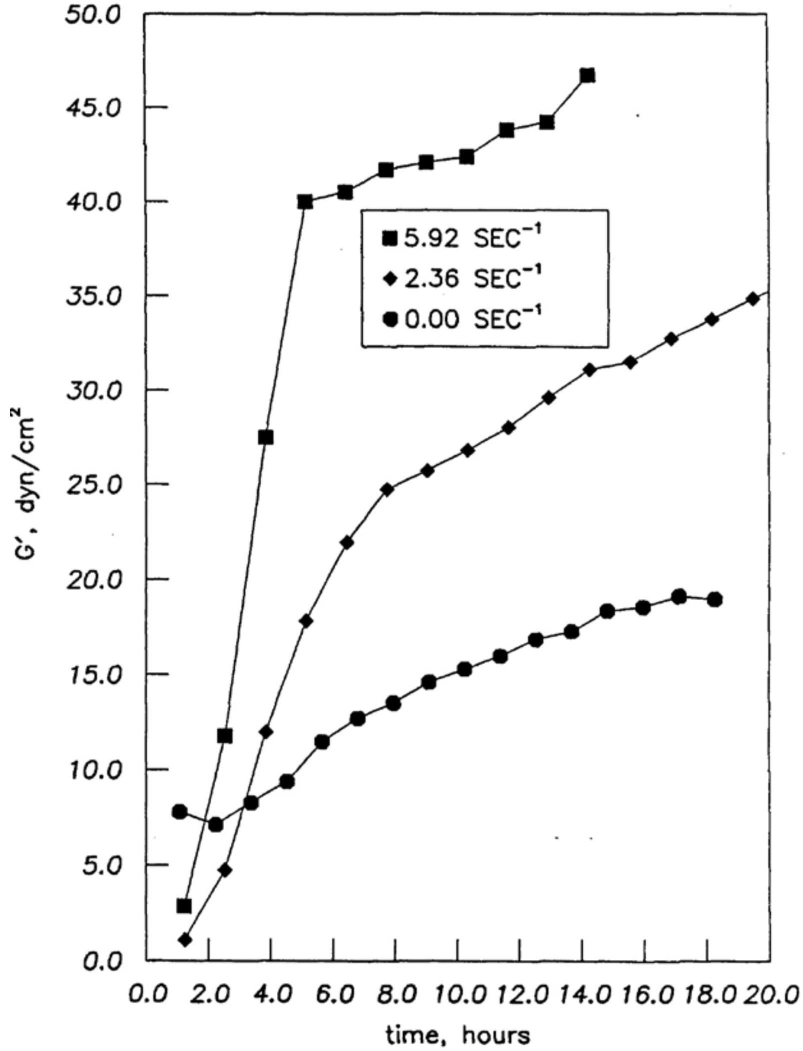

Figure 2.10 Effect of shear on a fast gelling system: 5,000 ppm Aldrich polyacrylamide/100 ppm chromium (III), Bhaskar[9]

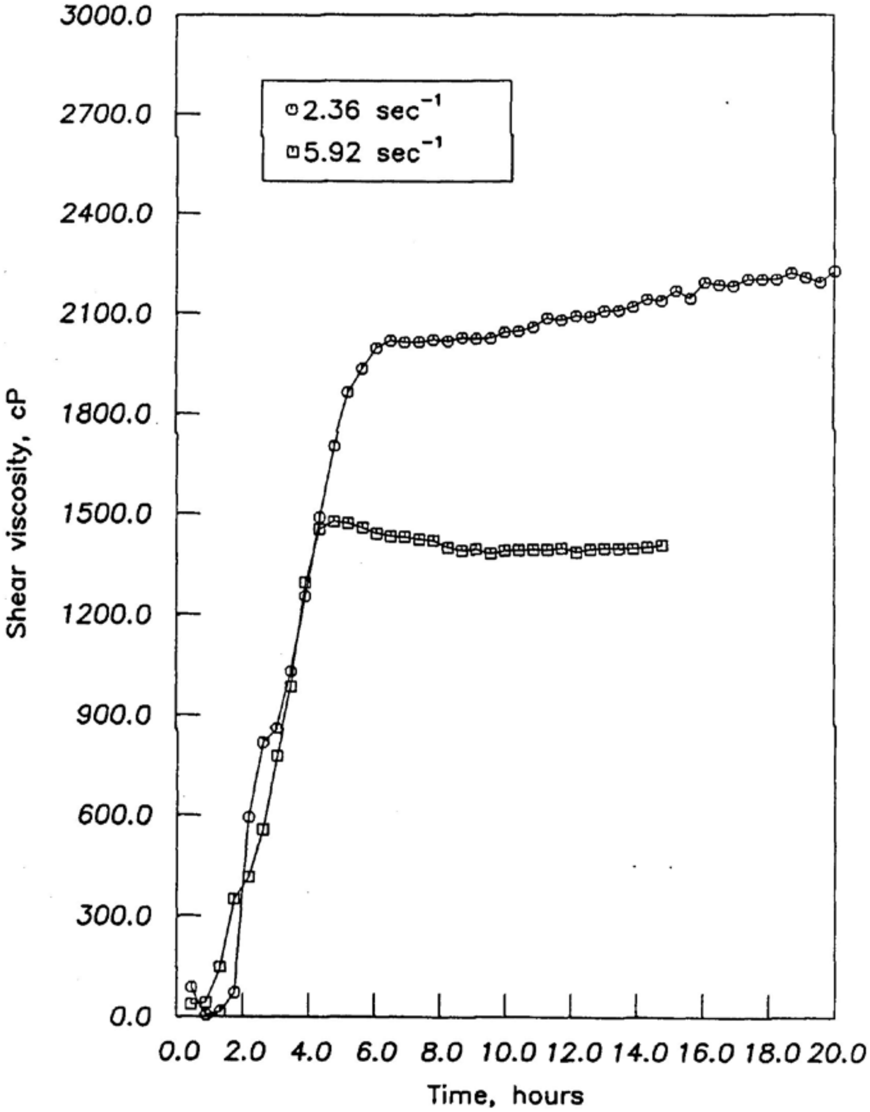

Figure 2.11 Viscosity components of the runs shown in Figure 2.10, Bhaskar[9]

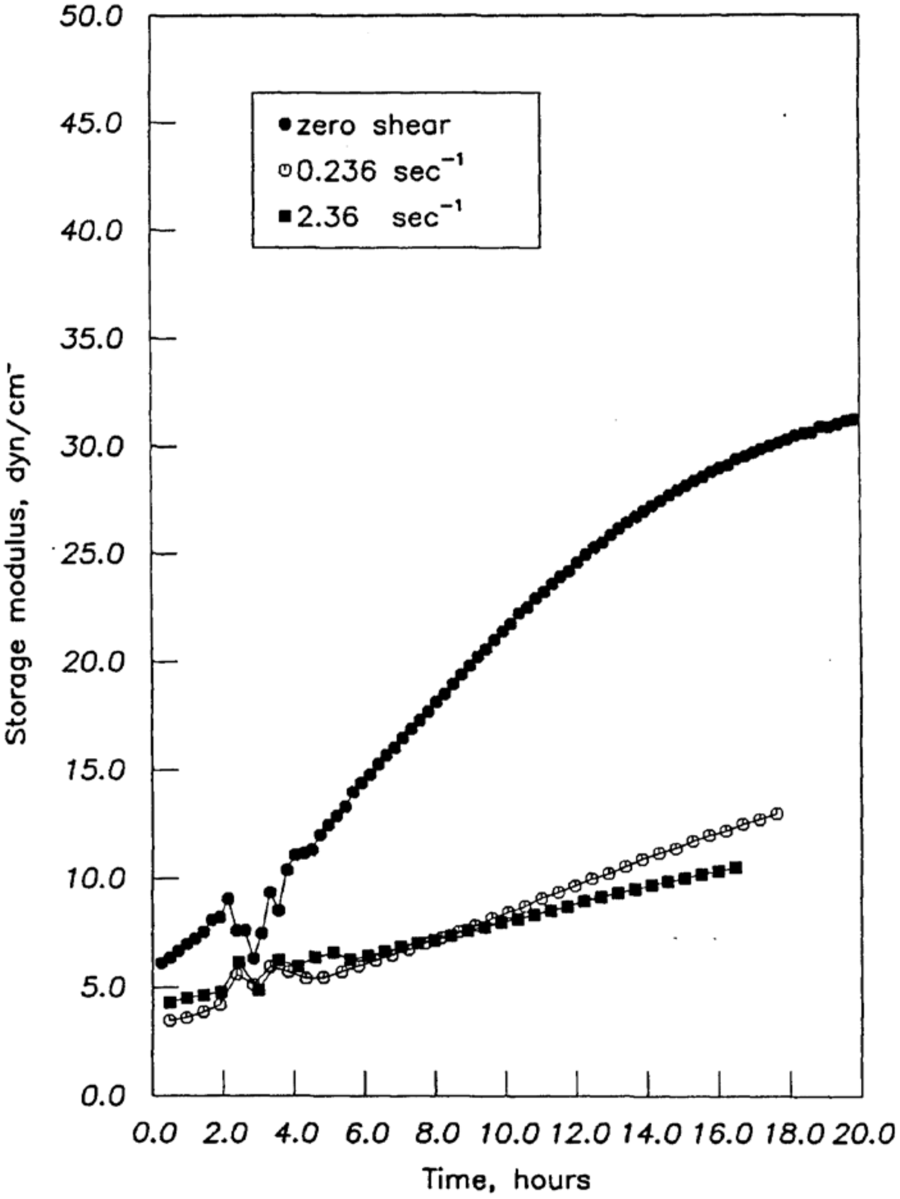

Figure 2.12 Effect of shear on a slower gelling system: 3,000 ppm Aldrich polyacrylamide, 30 ppm chromium (III), Bhaskar[9]

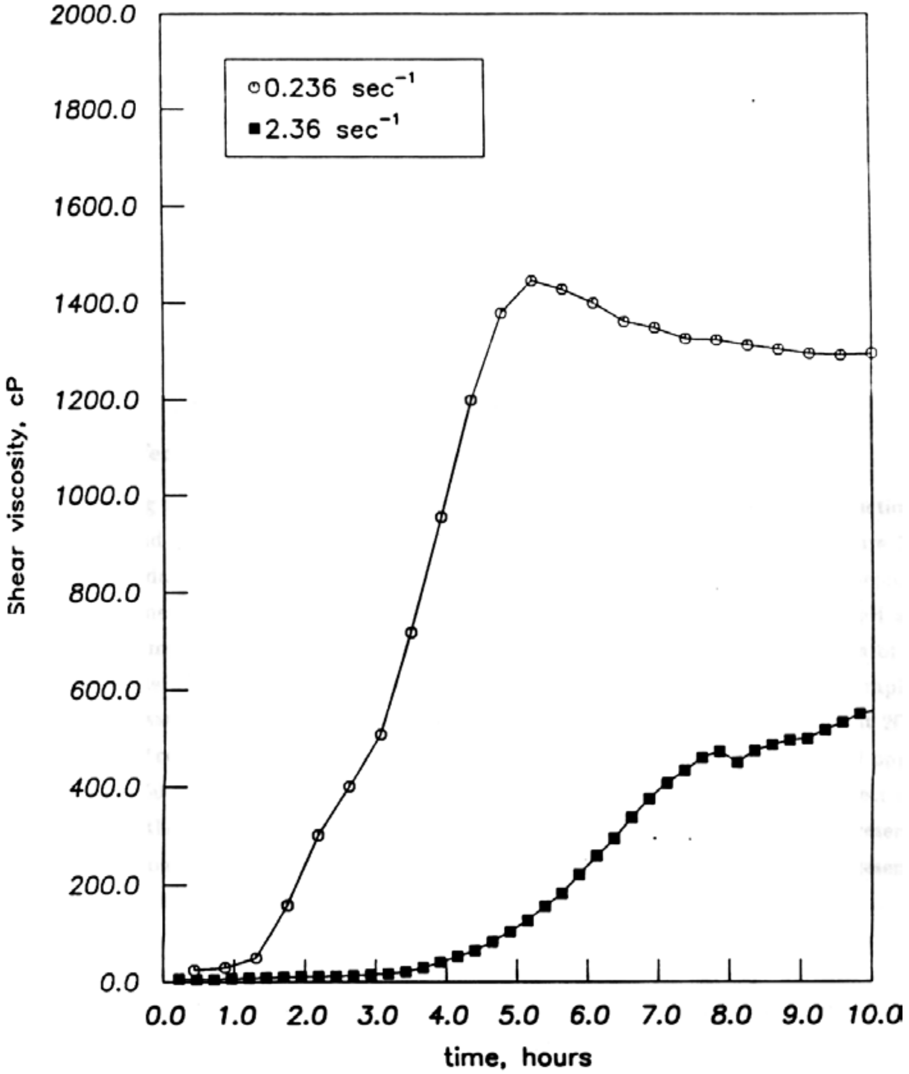

Figure 2.13 Viscosity components of the runs shown in Figure 2.12, Bhaskar[9]

For a comparatively faster gelling system with concentrations of 5,000 ppm polyacrylamide and 100 ppm chromium (III), shear was found to accelerate gelation. This was evident from a faster increase in storage modulus as the shear rate was increased from 0.00 to 5.92 sec^{-1} (Figure 2.10). However, it was not obvious seen from the viscosity data (Figure 2.11). The final shear viscosity decreased with increase in shear rate.

When the concentrations were reduced to 3,000 ppm for polymer and 30 ppm for chromium (III), the trend was reversed. The rate of gelation, as indicated by storage modulus data (Figure 2.12) as well as viscosity data (Figure 2.13), decreased with increase of shear rate. It was concluded that shear accelerated fast gelling systems but retarded the slow gelling ones. It implied that there should be some intermediate concentrations at which shear would have no effect on the rate of gelation. However, the shear applied to the faster gelling system is small (2.36 and 5.92 s^{-1}), hence the acceleration of gelation may be caused by the improvement of mass transfer rate. The detail explanation is given in the next subsection.

Kumar[10] examined the effect of shear rate on gelation of polyacrylamide-chromium (III) system using a Weissenberg R19 and a Bohlin CS rheogoniometer. The experiments were performed using cone-and-plate geometry on the Weissenberg and parallel-plate geometry on the Bohlin. The gel system consisted 7,500 ppm polyacrylamide, 100 ppm $CrCl_3 \bullet 6H_2O$ and 2% NaCl at 25 ºC and initial pH of 5.0. Shear rates ranging from 0.47 to 47.0 sec^{-1} were considered. The rheological property considered for steady shear experiments was the viscosity (labeled as “shear viscosity” in the figures). Gel times were measured using the steep rise in viscosity, the maximum slope in the viscosity-time curve at the indicated shear rate. Figure 2.14

shows typical trends in viscosity behavior over time obtained from Weissenberg R19 at selected shear rates. And Figure 2.15 presents the same data in the first 7 hours for better view.

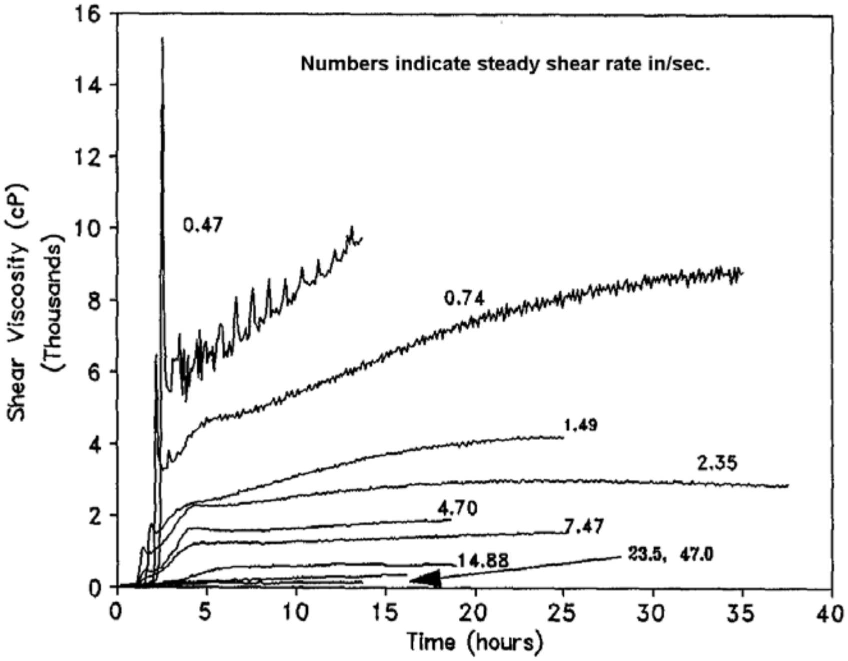

Figure 2.14 Gelation at different shear rates, viscosity behavior over longer periods of time, Kumar[10]

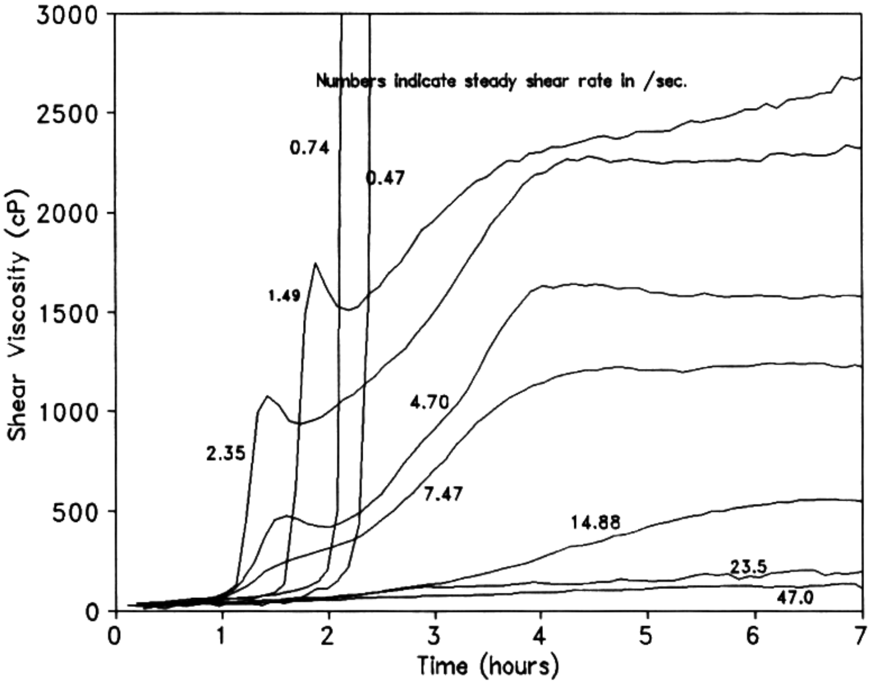

Figure 2.15 Gelation at different shear rates, viscosity behavior over shorter periods of time, Kumar[10]

As can be seen from these two figures, the induction period was observed to be about one hour. After this period, the initial rise in viscosity occurred sooner as the shear rate increased to 2.35 sec^{-1}. For shear rates of 4.70 and 7.47 sec^{-1}, the initial viscosity rise, though not as distinct, occurred at almost the same time as the initial viscosity rise at 2.35 sec^{-1}. The time for the initial viscosity rise increased with an increase in shear rate to 14.88 sec^{-1}. There was no such viscosity rise at higher shear rates, e.g., 23.5 and 47 sec^{-1}. In summary, gel time first decreased and then increased as the shear rate increased. That is, lower shear enhanced gelation while higher shear retarded gelation. Thus, there should be some shear rate at which the gel time dependences on shear rate changes. Possibly the range of shear rates considered in previous studies was not large enough to observe this behavior of viscosity with shear rate. Another result was that the final measured gel viscosities decreased with an increase in shear rate, which was consistent with previous investigations.

Kumar[10] also performed steady shear test on the Bohlin rheometer using parallel plates. Unlike cone-and-plate geometry, the shear rate was not constant throughout the sample when parallel-plate geometry was used. The results are shown in Figure 2.16 and Figure 2.17.

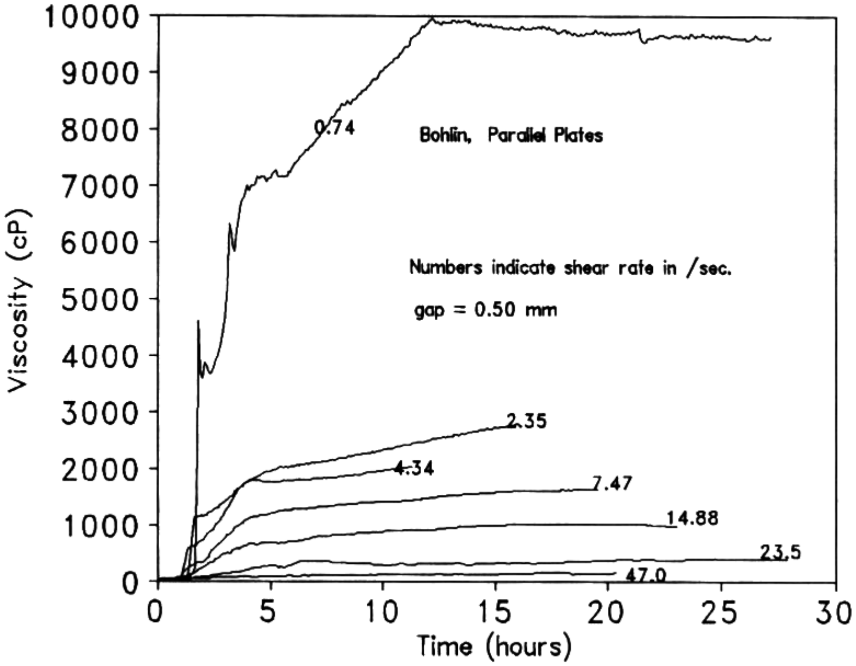

Figure 2.16 Gelation under different shear rates, viscosity variation over long periods of time, Bohlin rheometer, paralle plates, Kumar[10]

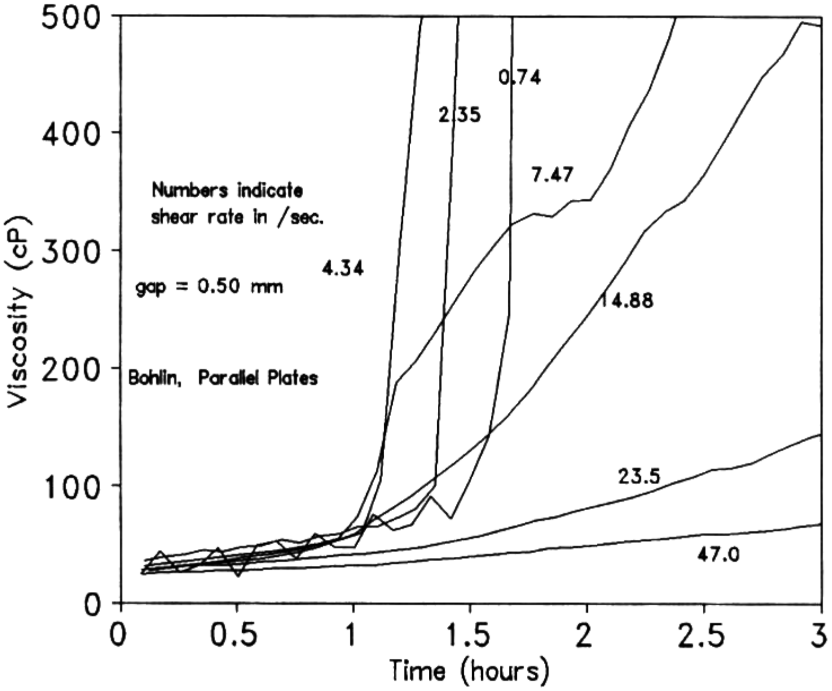

Figure 2.17 Gelation under different shear rates, viscosity variation over shorter periods of time, Bohlin rheometer, parallel plates, Kumar[10]

Similar trends, as seen in data from the Weissenberg, were observed. However, the shear rate at which the reversal in gelation time took place was different. This was understandable because the sample had not been subjected to the same condition.

In summary, previous experimental results showed that steady shear could either enhance or retard the gelation process of a gelling system. And the effect depends on the value of the shear applied on it and also the gelling system itself. The possible interpretation of these results is described in the following part.

2.2.2 Interpretation

The effect of shear on gelation depends on several factors such as the gelling system itself, i.e., types and concentrations of polymer and chromium solutions, and the values of shear as well as the distribution of shear rate. It was concluded by Bhaskar[9] that shear accelerated gelation of faster gelling systems while retarded that of slower gelling ones. For a certain gelling system, Kumar[6] observed that the lower shear rate accelerated gelation while higher shear rate retarded gelation.

Bhaskar[9] stated in the dissertation that the imposed shear affected the rate of crosslinking in two opposing ways: the shear acted to accelerate crosslinking due to improved mass transfer rate, and simultaneously acted to retard gelation due to the scission of the crosslinks.

For the acceleration part, if the buildup of structure is controlled by the collision of the particles (carboxyl groups and chromium crosslinker), the gelation is enhanced by shear. The higher the shear rate, the more particles of proper size and orientation are brought into the gel aggregate zone per time, which makes the gelation faster. For the retardation part, however, the scission forces prevent the crosslinking from formation. Both mechanisms appeared to be active over the entire range of shear rates studied, with the scission mechanism predominant at the higher shear rates.

Kumar[10] tried to interpret the phenomenon of first shortening and then lengthening of induction period as shear rate was increased as following: when the shear rate is increased, more polymer molecules of proper orientation are able to come in contact with one another and the gel time decreases; when the shear rate is further increased, though the molecules are available, disruptive forces are high enough not to allow effective crosslink formation.

Broseta et al.[11] studied the effect of shear sequences representative of those occurring in the filed on two different polyacrylamide-chromium (III) formulations. System A involved a high-molecular-weight polyacrylamide ($M_w=5\times10^6$), which was adapted for plugging fractures; system B involved a low-molecular-weight polyacrylamide ($M_w=2\times10^5$), which was usually employed for plugging porous matrices. The gel properties investigated were the gelation time and final yield stress. System A was strongly shear-thinning, and consisted of 12,000 ppm polyacrylamide, 960 ppm $Cr(OAC)_3$ and brine. System B consisted of 40,000 ppm polyacrylamide, 3,500 ppm $Cr(OAC)_3$ and brine, and displayed a Newtonian rheological behavior up to shear rates in the range of 316 sec^{-1}. The applied shear rates ranged from 1 to 316 sec^{-1} for system A and from 1 to 1000 sec^{-1} for system B. Figure 2.18 shows the results.

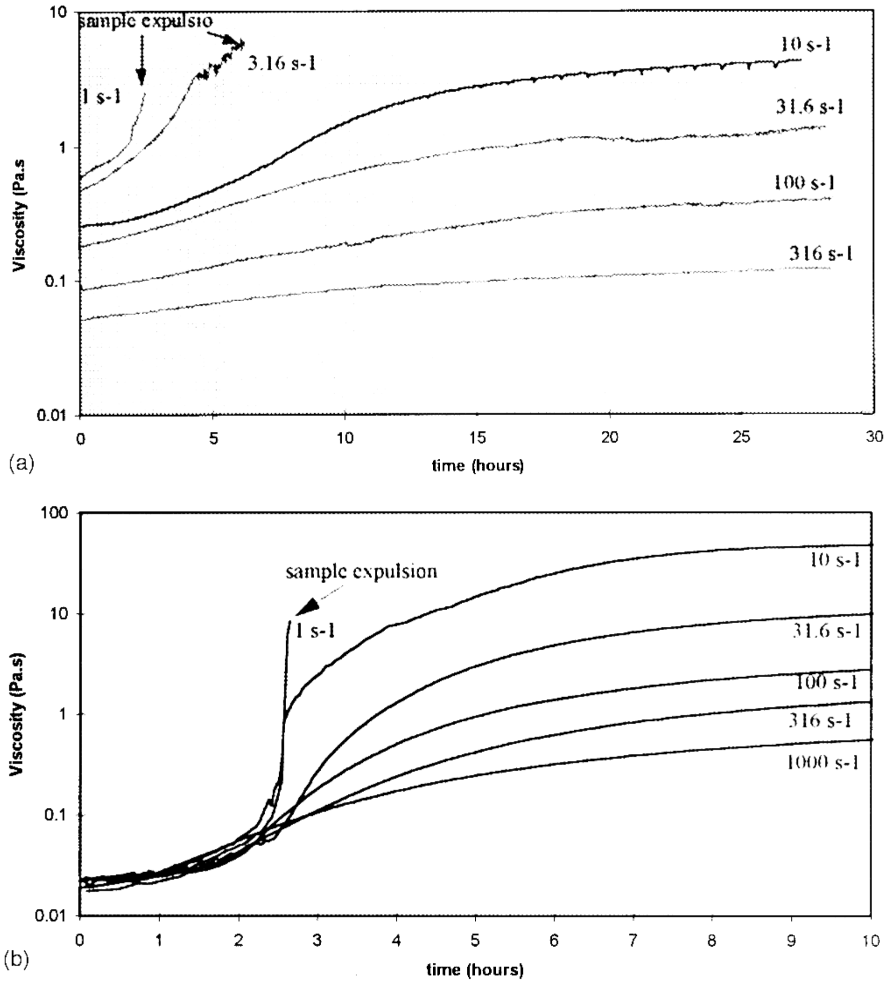

Figure 2.18 (a) Viscosity of system A with time, (b) viscosity of system B with time, Broseta[11]

The viscosity of system B increased very slightly during an induction period of two and a half hours in a manner that did not depend on the applied shear rate. The viscosities then started increasing at a time that was independent of the applied shear rate, but then successively broke away at later times; viscosities deviated sooner at larger shear rate. But the results obtained for system A clearly indicated that shear delayed and limited the increase in the viscosity of gelling solutions. Also, the results for viscosity recovery after cessation of shear showed that the initial shearing had a delaying effect on the viscosity rise. The final gel strength of both systems, evaluated from yield stress measurements, turned out to be independent of the shear rate history.

2.3 Behavior of gel or gelant in a long tube

In 2002, McCool[12] injected in-line-mixed polyacrylamide-chromium (III) gelant solution into a 1,031 ft stainless steel tube to study the effect of continuous shear on gelation. The experiment is labeled as “Run 1” in this thesis. The gelling system he used was 5,000 ppm AF935, 94.8 ppm chromium (III) and 1.0% NaCl at pH of 4.8 (by mixing 7,500 ppm AF935 and 284.4 ppm chromium (III) at flow rate ratio of 2:1). The gel time was 5.5 to 6 hours at 41 ºC, measured using Brookfield viscometer and was defined as the time when the viscosity of the sample became greater than 1,000 cp at 0.3 rpm (shear rate of 3 sec^{-1}). Gel time can also be defined as the time when the storage modulus crosses the value of loss modulus. A good correspondence between the two measurements was observed by Kumar**[10]**. Figure 2.19 shows the sketch of the experimental setup. The 1,031-ft long tube was used to simulate a long fracture, and it was divided into five sections to measure the pressure drop across different parts of it.

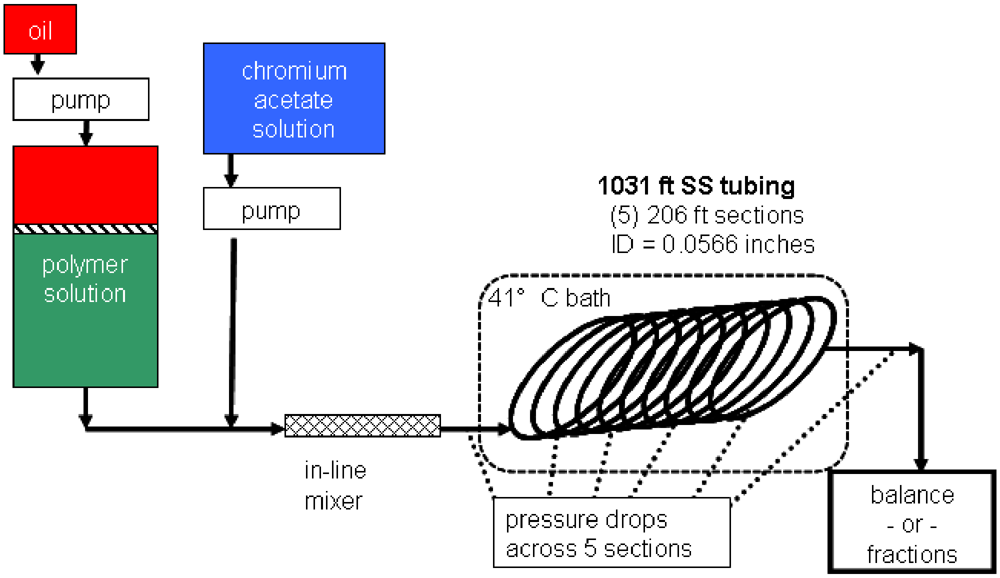

Figure 2.19 Sketch of experimental setup, McCool[12]

McCool found that the effluent emerged from the tube like spaghetti as shown in Figure 2.20. The pressure-drop data are shown in Figure 2.21. The y-axis is the pressure drop across each section or the whole tube. The total flow rate was increased from 0.36 g/min to 0.75 g/min at running time of 72 hours, and then decreased back to 0.36 g/min at running time of 78 hours.

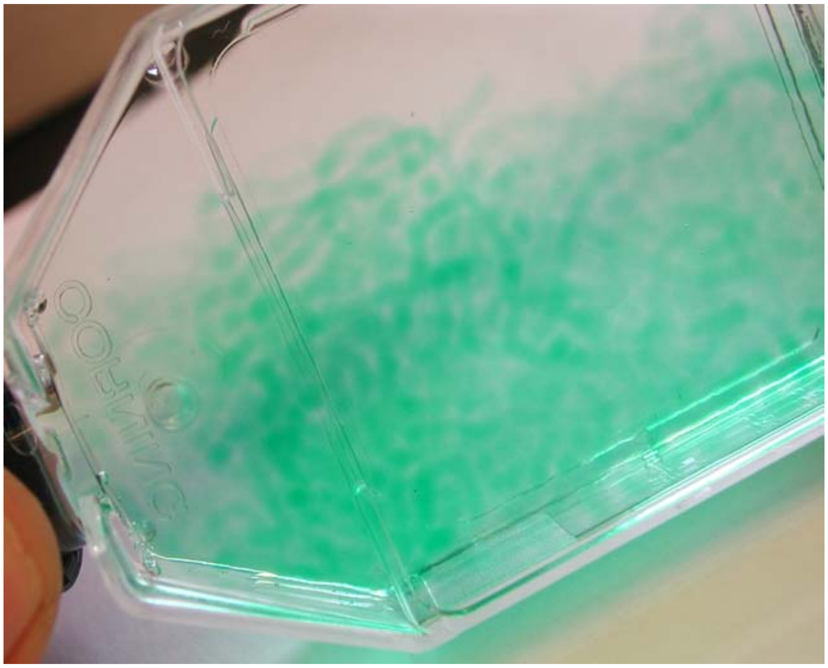

Figure 2.20 Photograph of dyed gel suspended in water; sample produced from tubing during Run 1, McCool

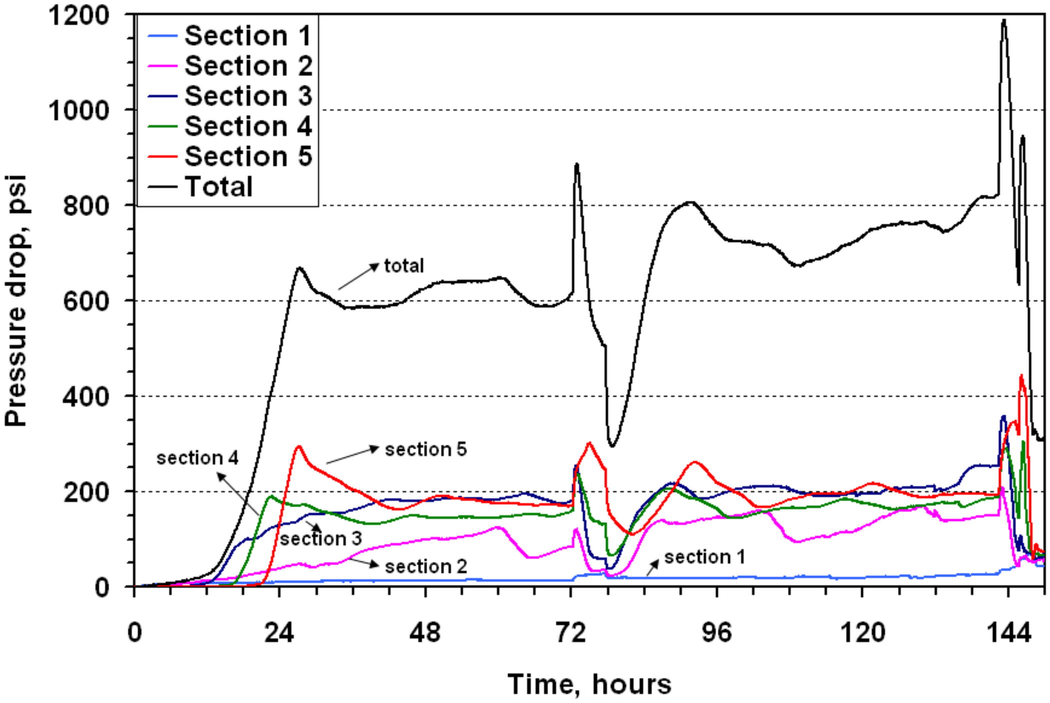

Figure 2.21 Pressure-drop data with time for in-line-mixed gelant solution flowing through a 1,031 ft stainless steel tube, Run 1, McCool[12]

McCool[12] also injected preformed gel into the same setup at flow rate of 0.36 mL/min. The experiment is labeled as "Run 3" in this thesis. The pressure-drop data are shown in Figure 2.22.

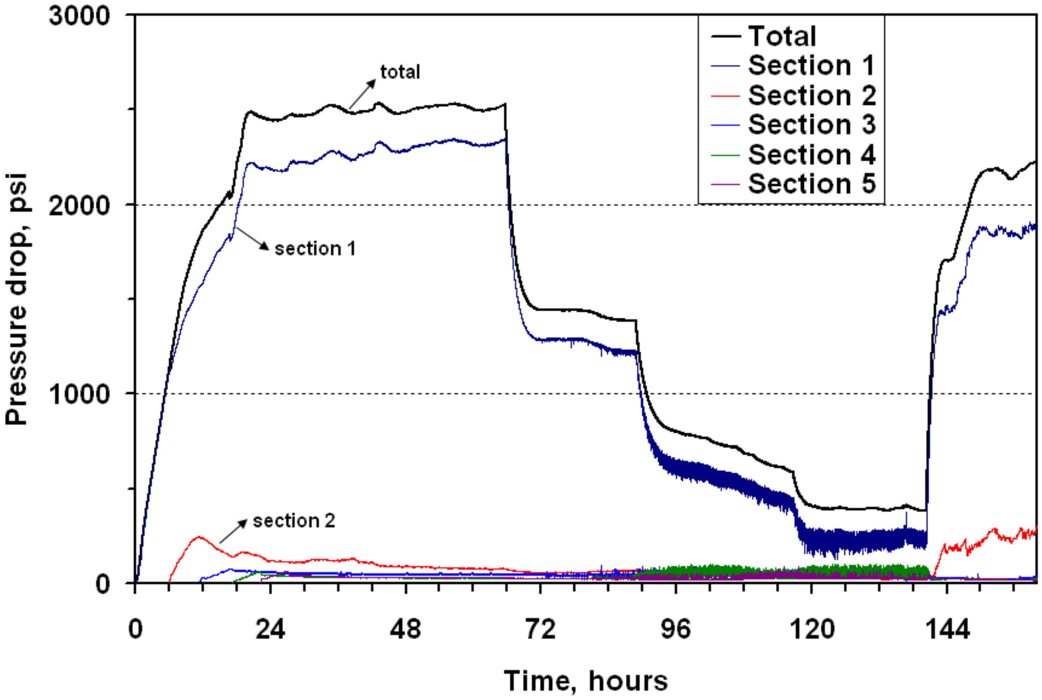

Figure 2.22 Pressure data with time for preformed gel flowing through a 1,031 ft stainless steel tube, Run 3, McCool[12]

McCool calculated the resistance factors from the obtained pressure-drop data, and compared with those from Seright's[2] data. Figure 2.23 shows the results.

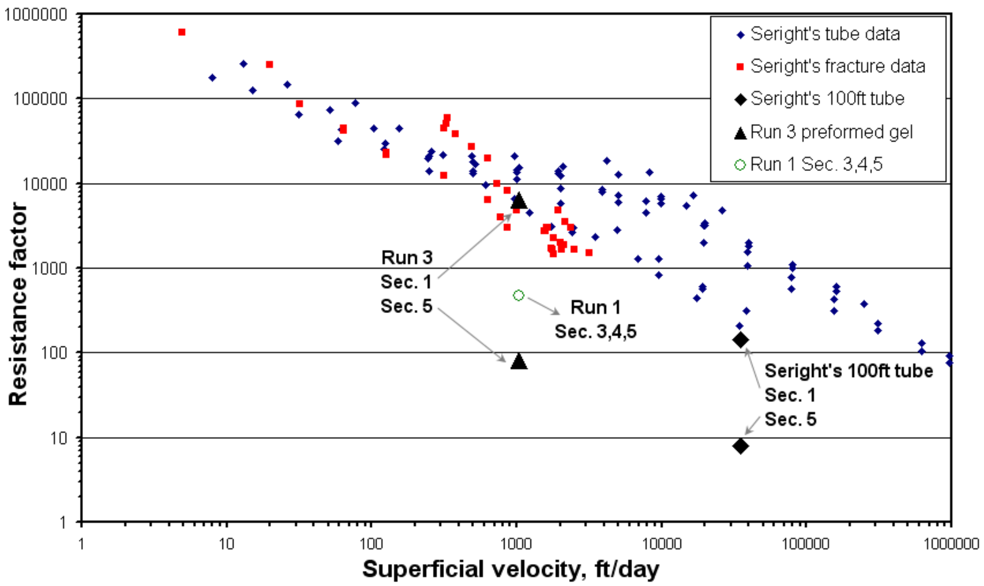

Figure 2.23 Comparison of resistance factors between McCool's results[12] and Seright's results[2]

As can be seen, the resistance factors for in-line-mixed gelant flow were lower than Seright's data from preformed gel flow experiments. And the resistance factors in Section 1 for preformed gel flow in McCool's results were close to those of Seright's data. However, the resistance factors in other sections for preformed gel flow in McCool's results were close to those of in-line-mixed gelant flow, which were lower than Seright's data. Note that Seright's data were from short tubes/fractures, which was comparable to the first section of the tube in McCool's experiments.

The research work of this thesis was finished by June 2005. For literature published afterwards and further analysis of the experimental data, please refer to the paper by McCool et al.[12].

2.4 Summary

Based on the above review, it is proper to state that for a certain system, there should be an equilibrium condition where the applied shear accelerating gelation by improving the mass transfer, to the same extent as retarding gelation due to the scission of crosslinking. The shear rate at this condition can be called a “critical shear”. When the applied shear is smaller than the critical shear, it accelerates the gelation; and when the applied shear is greater than the critical shear, it retards gelation. The value of the critical shear depends on the gelling system itself, i.e., concentrations and pH value, as well as temperature.

This research focuses on the effect of shear on gelation when the gelling system flows through a long circular tube, and to understand the flow behavior. When the gelling system flows through a circular tube, different part of the system experiences different shear. The shear rate is zero at the center of the tube while it is the maximum at the tube wall. As the maximum shear at the tube wall is probably much greater than the critical shear, the critical shear must exist somewhere near the center of the tube. In the zone between the center of the tube and the critical shear, the gelation is accelerated by shear; in the zone between the critical shear and the tube wall, the gelation is retarded by shear. But this result is hard to observe or prove due to the constraints of the current experimental conditions. So this research only considers the “apparent viscosity” of the gelling system. The “apparent viscosity” of the fluid in the tube is calculated according to Darcy’s law, $\mu = \frac{\pi R^2}{1.15716} \frac{k\Delta p}{QL}$, where inner diameter R is in *in.*, the permeability k is in *darcys*, pressure differential Δp is in *psi*, flow rate Q is in cm^3/min, and the length L is in *ft*. The detail of the unit conversion is given in Appendix B.

Chapter 3

Experimental Setup and Procedures

This chapter describes the materials and apparatus used in the experiments, and also describes the procedures for all related experiments.

3.1 Experimental setup

Figure 3.1 shows the sketch of the experimental setup, and a description is included in the following paragraphs.

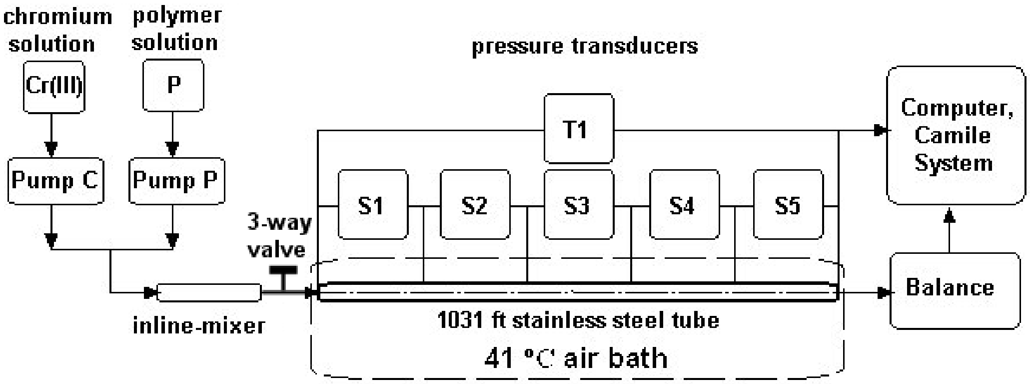

Figure 3.1 Sketch of experimental setup

Two Quizix QL-700 pumps (manufactured by Quizix Incorporated) were used for the experiments. One was used to pump polymer solution, and the other was used to pump chromium solution. One-gallon collapsible containers (from Cole-Parmer Instrument Company) were used as the reservoirs of the solutions in order to minimize evaporation. The two solutions were pumped into an inline-mixer through a Tee-union, and then injected into the 1,031 ft stainless steel tube.

Two types of inline-mixer were used in the experiments. A micro inline-mixer was used at first, for the first two flow experiments of in-line-mixed gelant. After that, a stainless steel tube inline-mixer (OD=3/16 in., 6-in. long, A04669-52) was used.

A three-way valve was used to connect the inline-mixer and the long stainless steel tube. One of the outlets of the three-way valve was used to collect samples from outlet of the inline-mixer.

The 1,031 ft stainless steel tube was divided into five sections in order to obtain pressure-drop data across different segments of the tube. The inner diameter (ID) of the tube was 0.0566 in., and the lengths of the sections were 205 ft for both sections 1 and 2, 206 ft for Section 3, 207 ft for Section 4, and 208 ft for Section 5. The pore volume of the tube was 510 mL. The permeability of the tube was 5.91×10^4 darcys. These data were obtained from experimental results (see Appendix B), and were used for all related calculations throughout this thesis.

Five pressure transducers (S1 to S5, 500 psi) were used to record the pressure drop across each section, and one transducer (T1, 2000 psi) was used to record the total pressure drop across the whole tube. They were all manufactured by Validyne Engineering Corporation, and the accuracy is ± 0.25% of full scale. A pressure calibration system, Mensor PCS 400, was used to calibrate the transducers every time before an experiment was started. The effluent was collected in a flask placed on an analytical balance. The pressure data reading from the transducers and the weight of the effluent reading from the balance were recorded on a computer through Camile 1000 software provided by Camile Products LLC.

The 1,031-ft long stainless steel tube was stored in 41 ºC air bath, while others were under lab room temperature (around 25 ºC). An 18-in. long stainless steel tube (including a three-way valve) was added between the inline-mixer and the 1,031-ft long tube in order to collect samples at the outlet of the inline-mixer.

Density data were obtained from a DMA 4500 Density Meter manufactured by Anton Paar. The pH values were measured using AB15 pH Meter made by Fisher Scientific Company. The viscosities of the solutions were measured using a Brookfield Micro-viscometer (Model LVT). A UV/VIS Spectrometer Lambda20 (Perkin Elmer) was used to analyze the concentration of Cr(III) in the samples.

3.2 General materials used

The polyacrylamide polymer used in the experiments was Alcoflood 935 (AF935) (Lot Number A2247BOV, Ciba Inc., Weight-average molecular weight $Mw \approx 7\times10^6$ g/mol, degree of hydrolysis 10%). The chromium used was chromium triacetate [$Cr(OAC)_3$] liquid solution containing 12.1% chromium (III) (McGean-Rohco Inc., P.N. 35420-NE01, Lot Number 40086816). The sodium chloride was provided by Fisher Scientific Company (Lot Number 984321). Sodium azide (NaN_3), 10 mg/kg was added to prevent biological attack when preparing polymer solutions, and it was prepared from solid sodium azide (Fisher Scientific Company). A deionization system, Water Pro PS (LABCONCO Company), was used to purify water used in the experiments.

All the solutions were prepared by weight. The components of the gelling system chosen for this study were 5,000 ppm AF935 polymer, 100 ppm chromium (III), and 1% NaCl. The gel time was measured using Brookfield viscometer and was defined as the time when the viscosity of the sample became greater than 1,000 cp at 0.3 rpm (shear rate of 3 sec^{-1}). The gel time of bulk-mixed gelant sample, made from freshly prepared chromium (III) solution, was around 5.5 hours at 41 ºC. The preparation of polymer solution, chromium solution and gelling system are described in the following section.

3.3 Experimental procedures

This section describes the procedures of preparation of polymer and chromium solutions as well as the analysis of chromium concentrations of samples. The procedures of other experiments are also described.

3.3.1 Preparation of polymer solutions

In this study, the polymer solutions were prepared based on the following procedures. First, calculation was done to determine the amounts of polymer, sodium chloride, cold water and sodium azide, which were needed to prepare a solution with certain concentration of polymer. A sample calculation is given in Appendix A.

Second, the weighing boat was put on a HM-202 analytical balance (capacity 210 g) to weigh sodium chloride, and the container (Nalgene PMP 1,000 mL) of the solution was put on a top load balance (SC Firebanks, capacity 2 kg) without the cap on.

Third, after the desired amount of sodium chloride had been weighed, it was added into the container followed by proper amount of cold water. Then sodium azide solution was added into the container using transfer pipettes (from Fisher Scientific) to adjust the weight to the desired value.

Fourth, the container with salt solution in it was removed from the balance, and a stir bar was added into it. Then the container was put onto a magnetic stirrer (Corning PC-353), and the stirrer was turned on to dissolve the salt quickly. A vortex should be observed.

Fifth, in the mean time, the desired amount of solid polymer was weighed using a weighing boat on the analytical balance. Then polymer was added slowly to the shoulder of the vortex in the container, trying to avoid formation of polymer agglomerates. After all the polymer was added, the container lid was put on tightly to prevent evaporation. The solution was stirred continuously for 24 hours or longer.

Sixth, the stirrer was turned off after all the polymer particles were dispersed into the solution and no polymer agglomerates was observed. Then polymer solution was filtered with 1-micron glass fiber filter under 15 psi air pressure.

Finally, the polymer solution was ready to use. The pH value and viscosity were measured. Then the solution was stored in a proper environment as desired.

3.3.2 Preparation of chromium solutions

Chromium acetate solution was used to prepare the chromium solutions for the experiments. The chromium acetate solution contains 12.1% chromium (III), so water should be added to dissolve it into the desired concentration. A sample calculation is given in Appendix A.

First, the amounts of chromium acetate and water were calculated. Then the container was weighed, and proper amount of chromium acetate was added into the container by using transfer pipettes. Normally the added amount was not the exact amount planned, so a new calculation should be performed to determine the amount of water needed in order to obtain the desired concentration. Then this amount of water was added to the container. Finally, the container was covered and sealed by the lid, and was shaken by hand for one minute.

3.3.3 Preparation of in-line-mixed gelants or bulk-mixed gel

For flow experiment of in-line-mixed gelants, 10,000 ppm (weight fraction) polymer solution, with 2.0% NaCl, and 200 ppm (weight fraction) chromium (III) solution were mixed through an inline-mixer at flow rate ratio of 1 to 1 at 41ºC. The density of the polymer solution at this temperature was 1.009 g/mL, and that of the chromium solution was 0.997 g/mL (density of water). So the concentrations after mixing should be 5,030 ppm polymer and 99.4 ppm chromium (III).

Bulk-mixed gel samples were prepared by hand-mixing 10,000 ppm polymer solution and 200 ppm chromium (III) solution by weight ratio of 1 to 1. So the concentrations after mixing were 5,000 ppm polymer and 100 ppm chromium (III) in the gelling system. The procedure is described below, and a sample calculation is given in Appendix A.

First, a container for the sample (e.g., a 40-mL vial) was placed on the analytical balance, and the reading of the balance was reset to zero. Then proper amount (e.g., about 10.0 g) of polymer solution was added into the container using a transfer pipette. The weight (mass) of the polymer solution was recorded (e.g., 10.3 g), and the double amount was calculated (i.e., 20.6 g). Then chromium (III) solution was added into the container slowly to reach the desired amount. Finally, the total amount of the sample was recorded (e.g., 20.9 g). And the weight (mass) of chromium (III) solution added was obtained by subtracting the total amount from the mass of the polymer solution (i.e., 20.9 – 10.3 = 10.6 g). If chromium (III) solution added was more than needed, the actual amount of mixed solution would be doubled (10.6 × 2 = 21.2 g) by adding more polymer solution. In this way, the weight ratio of polymer solution to chromium (III) solution could be controlled very close to 1. After the solutions were added in, the container was sealed with closure and shaken by hand for one minute to mix the solutions well. Finally, the pH value was measured and the sample was stored at 41ºC to form a gel.

3.3.4 Analysis of chromium concentration

The chromium concentrations of the samples were measured using Perkin-Elmer Spectrometer Lambda20. The samples were prepared based on the following procedures.

First, the tare weight of the vial and the weight of the sample in the vial were obtained using analytical balance. Second, about 1 mL of each 3% H_2O_2 and 1 molar KOH were added to the sample in the vial (20 mL or 40 mL) to oxidize chromium (III) to chromium (VI) for analysis.

Third, the vial was placed in the aluminum heater block of the Dry Bath Incubator (Fisher Scientific) to help speed up the oxidization and get rid of gas bulbs.

The heater was set at High and the temperature control was set at position 5, which gave temperature of approximately 85 ºC.

Fourth, after one or two hours of heating, when no gas bulbs could be observed, the vial was removed from the heater to cool down. Then water was added and the weight of vial, sample and water was measured again to calculate the dilution factor.

Fifth, the samples might need to be diluted again, because the spectrometer only works well for concentrations of chromium range from 1 to 20 mg/kg. But no heating was required this time.

Finally, the sample was ready for chromate analysis using the spectrometer at wavelength of 375 nm, following the standard measurement procedure. The chromium concentration was calculated based on the measured absorbance and the calibration curve from the standard. Then the multiplication of this value with the relative dilution factor gave the concentration of chromium in the original sample.

3.3.5 Bulk-mixed gelant under constant shear

A Bohlin Rheometer CS (manufactured by the company now called Malvern) was used for the study of bulk-mixed gelant under continuous constant shear. The Bohlin Software CS-10 was used to control the rheometer. A cone 4º/40mm and plate, made of stainless steel, were used, and the gap was set at 150 μm for all the measurements. The temperature was controlled at 41 ºC.

Gelant samples were prepared just before the measurement by hand-mixing 10,000 ppm polymer solution and 200 ppm “well-aged” chromium (III) solution by weight ratio of 1 to 1. The bulk gel time of the samples was 1.5 hours at 41 ºC. The chromium (III) solution is defined as “well-aged” when the gel time of bulk-mixed gelant samples do not change with the age of chromium (III) solution anymore.

After each bulk-mixed gelant sample was prepared, 1.3 mL of the sample was placed onto the plate of the rheometer. Two or three drops of oil (N10, Lot Number 8901) were added around the cone to prevent vaporization of the sample. Then the rheometer was turned on, and the sample was sheared at constant shear rate of 110 s^{-1} for 10 hours. Viscosity data of the sample were calculated and recorded in a data file every one minute.

After 10 hours, the rheometer was stopped, and the cone was lifted up slowly to observe the adherence of gel on the cone or plate. The cone and plate were cleaned and ready for the next measurement.

3.3.6 Flow of in-line-mixed gelant through stainless steel tube

The experimental setup is shown in Figure 3.1. Before starting each experiment, the tube was cleaned and pacified using 6 M HNO_3. Then it was flushed with a large amount of water. The pressure transducers were flushed with water and calibrated.

After injection of in-line-mixed gelant solution, the pumps were flushed with water. Then water was pumped into the stainless steel tube to displace the gelant or gel. The tube was flushed with a large amount of water until the pressure drop leveled off. Then solution of 3% H_2O_2 and 1 M KOH, mixed by volume ratio of 1 to 1, was pumped through the inline-mixer and the tube to break any left gel. Finally, large amount of water was pumped to flush the inline-mixer and the tube.

The polymer solution used was 10,000 ppm AF935 with 2% NaCl, and the chromium solution was chromic acetate containing 200 ppm Cr(III). The flow rate ratio of the two solutions was 1 to 1. All the experiments were performed at 41 ºC.

3.3.7 Flow of preformed gel through stainless steel tube

The experimental setup for flow of preformed gel was similar to the setup for flow of in-line-mixed gelant solution, except a stainless steel transfer cylinder was used as the reservoir of preformed gel. No inline-mixer was used for this experiment.

The total length of the transfer cylinder was 24 in., and the length excluding inlet and outlet end plates is 22.5 in. The inner diameter was 3.75 in. The length of the piston inside the cylinder is 1.75 in. So the volume capacity of this transfer cylinder was 229 in^3 which is about 3,756 mL.

Dyed water containing 25.43 mg/kg methylene blue was pumped into the cylinder to displace water at the other side of the piston, and the flow rate at the outlet was measured. This experiment showed that the piston was leak free and moved smoothly. Some dyed water was pumped into the cylinder to reduce the volume capacity for preformed gel. Then the transfer cylinder was placed in the 41 ºC air bath.

Before the start of the experiment, the 1,031 ft stainless steel tube was cleaned and pacified using 6 molar/L HNO_3. Then it was flushed with large amount of water. The pressure transducers were flushed with water and calibrated. The flow experiment was started by pumping dyed water into the transfer cylinder at the desired flow rate to displace the preformed gel.

After injection of preformed gel, the system was cleaned following the same procedure as for in-line-mixed gelant flow experiments.

3.3.8 Syneresis study

When gel sample experiences shear, syneresis (expulsion of solvent from gel) occurs. The procedure of separation of solvent from gel is described here. First, the weight (mass) of the effluent sample together with the vial was measured using the analytical balance. The weight of the effluent sample itself was recorded when it was collected.

Second, a Buchner funnel (Coors, model 42-T, with diameter of the hole of 0.0410 in. or 0.1 cm) was placed on a 100 mL beaker (Pyrex No. 1000) and the weight of both were measured together using the analytical balance.

Third, the effluent sample (solvent and gel), was removed from the vial onto the Buchner funnel. The funnel and the beaker were rotated together gently for 1 to 2 minutes to help the separation of solvent from gel.

Fourth, when no more solvent came out, the gel on the funnel was transferred to a new vial with known weight for later analysis. The weight of the funnel and the beaker was measured again. Subtracting this value from the dry weight (the second step) gave the amount of solvent separated from the effluent sample. The percentage of the separated solvent was calculated by dividing the weight of the separated solvent by the weight of the effluent sample before separation.

Fifth, the solvent separated from the gel/solvent mixture was transferred to a new vial with known weight, for later analysis of chromium and polymer concentrations. Weights of the separated gel with vial and the solvent with vial were measured. There was always some loss of sample during these procedures, e.g., solvent left in the funnel, hence the total amount of solvent and gel in the new vials was less than that of the effluent sample before separation. But this did not affect the calculations.

Chapter 4

Properties of Bulk-Mixed Gelant

This chapter studies the properties of bulk-mixed gelant samples: effect of age of chromium (III) solution on gel times, and the behavior under continuous constant shear. The experimental procedures were described in Chapter 3.

4.1 Effect of age of chromium (III) solution

During the flow experiments, it was found out that the age of chromium solution affects the gel time. The "age" means the period that the solution was stored after being prepared. The gelling system used for gel time measurement was prepared by hand-mixing 10,000 ppm Alcoflood 935, 2.0% NaCl, with 200 ppm chromium (III) solution by weight ratio of 1 to 1.

Two sets of data were obtained. 200 ppm chromium (III) solution was stored at room temperature (24-26 ºC) for one set, and stored in 41 ºC oven for the other set. At a certain age, the chromium (III) solution was hand-mixed with 10,000 ppm polymer solution by weight ratio of 1 to 1 to make gel samples, and the gel time was measured at 41 ºC using Brookfield viscometer. The gel time with different age of chromium (III) solution is shown in Table 4.1 and Figure 4.1.

Table 4.1 Effect of age of chromium solution on gel time

Age of Cr(III) solution at 24-26 ºC (days)	0	1	2	4	7	11	13	17	36	83
Gel time (hours)	5.5	4.75	4.25	3.25	2.6	2.25	2	1.75	1.5	1.5
Age of Cr(III) solution at 41 ºC (days)	0	1	2	3	4	6	7	10	17	22
Gel time (hours)	5.75	3	2	1.75	1.6	1.5	1.5	1.4	1.4	1.5

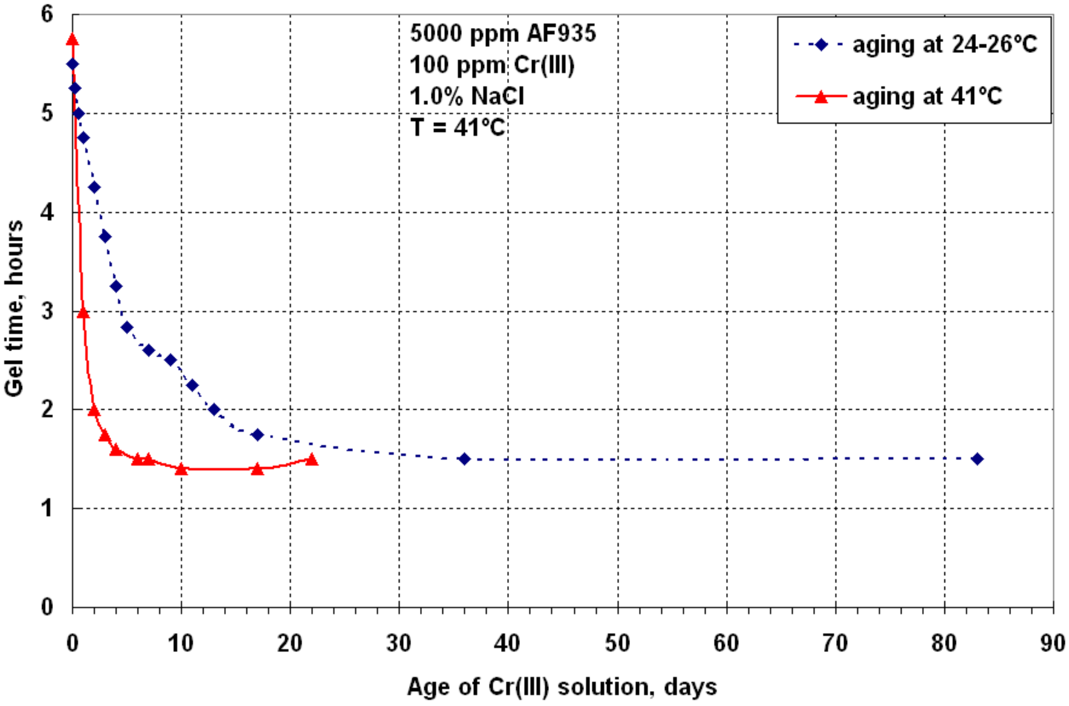

Figure 4.1 Effect of age of chromium (III) solution on gelation (gel time)

As can be seen, the older the chromium (III) solution, the shorter gel time for the bulk-mixed gelant samples. Gel time approaches a limit of 1.5 hours at 41 ºC as the chromium (III) becomes older than a certain age. And it reached the limit faster when the chromium (III) solution was stored at higher temperature, for example, 10 days at

41 ºC, and 40 days at 25 ºC. When the gel time of bulk-mixed gelant samples do not change with the age of chromium (III) solution anymore, the chromium (III) solution is defined as “well-aged”. The bulk gel time for the hand mixed samples prepared from well-aged chromium (III) solution was about 1.5 hours.

The mechanism behind the “aging” of chromium (III) solution might be the condensation of chromium (III) carboxylates[14]. The composition of chromium (III) acetate is complex, and one of the compounds, $[Cr(H_2O)_6](O_2CCH_3)_3$, is unstable under ambient conditions, even at room temperature. Neutral species can be formed with terminal H_2O being substituted by charged bridging ligands. Elimination of acetic acid and water molecules causes the condensation of the chromium (III) centers and the formation of polynuclear systems.

4.2 Effect of continuous constant shear

The procedures of corresponding experiments were described in Chapter 3. This section presents the viscosity data and describes the observation of adherence of gel on cone or plate.

4.2.1 Viscosity data

Figure 4.2 shows the measured viscosity data for measurements of 10 bulk-mixed gelant samples in the first 10 hours. Good reproducibility is observed.

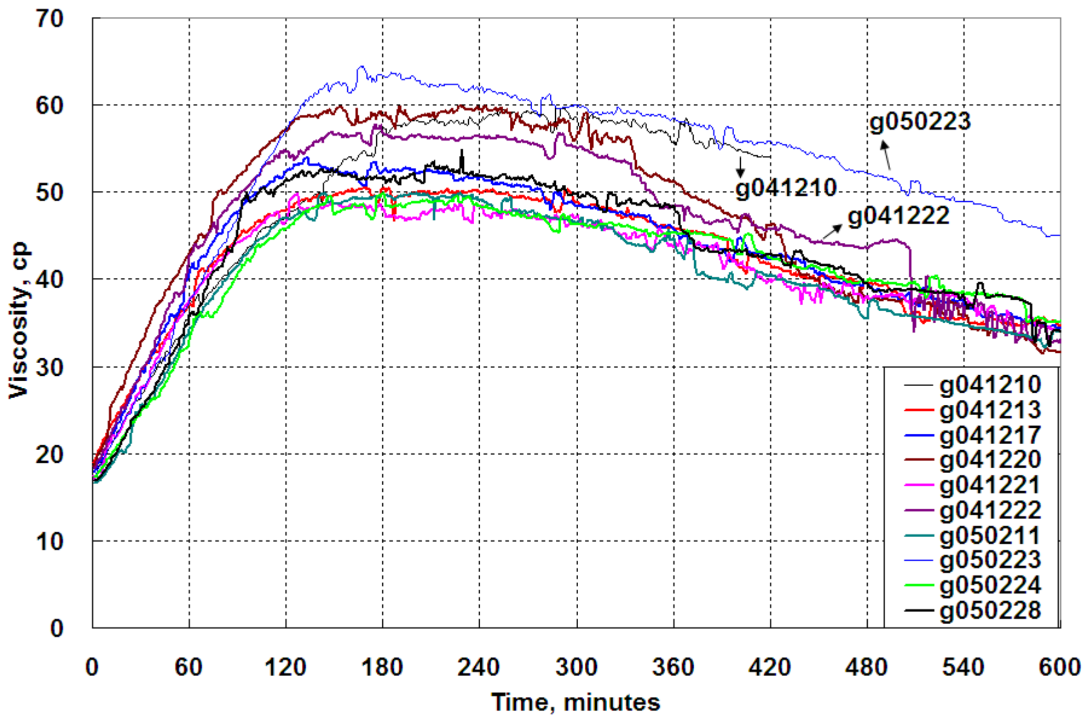

Figure 4.2 Viscosity of bulk-mixed gelant at 41 ºC under shear rate of 110 s^{-1}

All the experiments show similar behavior of the viscosity of bulk-mixed gelant samples sheared at constant rate of 110 s^{-1}. The initial viscosity was about 18 cp, which was the viscosity of polymer solution (without crosslink) at the same shear rate. The viscosity increased in the first two hours, then it leveled off for about three hours, and finally it decreased.

No sharp increase, as observed in the procedure of measuring gel time, occurred in these experiments at constant shear. The maximum apparent viscosity was only about 60 cp at shear rate of 110 s^{-1}. Furthermore, the time needed to reach the maximum viscosity, 2 hours, was longer than the gel time which was 1.5 hours. The results indicated that the constant shear of 110 s^{-1} retarded gelation.

The viscosity increased at first because the rate of crosslinking due to gelation was faster than the rate of scission of crosslink due to the high shear rate. That is, the formation of gel dominated in the first two hours, which led to the increase of the viscosity. After two hours, gelation slowed down, and the rate of crosslinking became equivalent to the rate of scission of crosslink. Thus the viscosity did not change much during that time. As the amount of free carboxyl groups and the crosslinker (chromium (III) acetate) became less and less, the rate of crosslinking became slower and slower. Then the scission of crosslink became dominate, which led to the decrease of the viscosity. Furthermore, some solution might be expelled out from the gel and form a lubricant layer between the gel and the surface of the rheometer (hence reduced the shear stress).

After each experiment, the viscosity of the sample was only about 30 cp at shear rate of 110 s^{-1}, but the structure of gel was formed which provided elasticity of the sample. Figure 4.3 demonstrates this statement for sample g050223. However, the gel was not as strong as those formed after experiencing smaller shear (based on the observation that the gel broke under gravity more easily than those formed under smaller shear).

Figure 4.3 Elasticity of sample g050223 after sheared at a constant rate of 110 s^{-1} for 10 hours at 41 ºC

4.2.2 Adhesion of gel on plate

The bulk-mixed gelant was confined between a rotative cone and stationary plate. After each experiment, the cone was lifted up slowly to observe the adhesion of gel on either cone or plate. Initially, the gel adhered to the cone due to interface tension till the cone was about 0.5 cm away from the plate. Then gel fell down to the plate due to gravity. The plate was removed from the apparatus and leaned on the table, as shown in Figure 4.4. The liquid and most of the gel was observed to slip down from the plate, and only a few drops of liquid stayed on it due to surface friction.

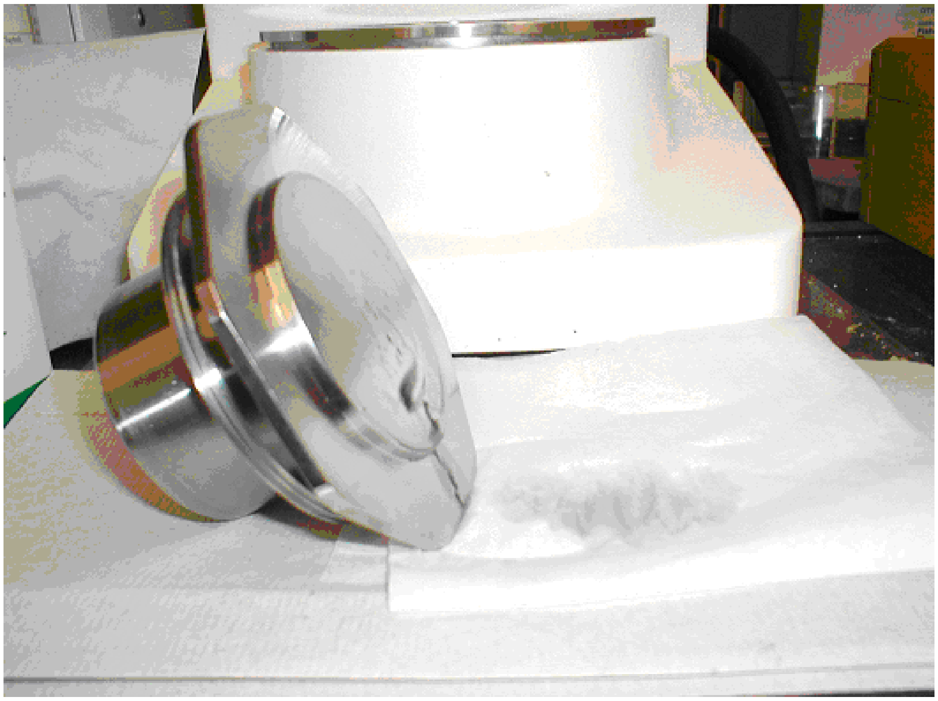

Figure 4.4 No gel adhered on the plate for sample g041220

These result indicated that the gel which was formed under constant shear rate of 110 s^{-1} at 41 ºC could not adhere on the solid stainless steel surface. One possible reason was that some solvent was expelled out due to the shear, and formed a lubricant layer between the gel and the stainless steel surface, which prevented the adhesion on the surface.

When the shear was stopped or reduced to a lower value after the 10-hour experiment, a stronger gel formed and adhered on both the cone and the plate. Figure 4.5 shows the result for sample g050228, which was placed on the plate under no shear for 14 hours after experiencing 10 hours of shear at rate of 110 s^{-1}. But the gel was not as strong as that formed under no shear. The result indicated that shear prevented the formation of gel, but the gelation continued after the shear was released.

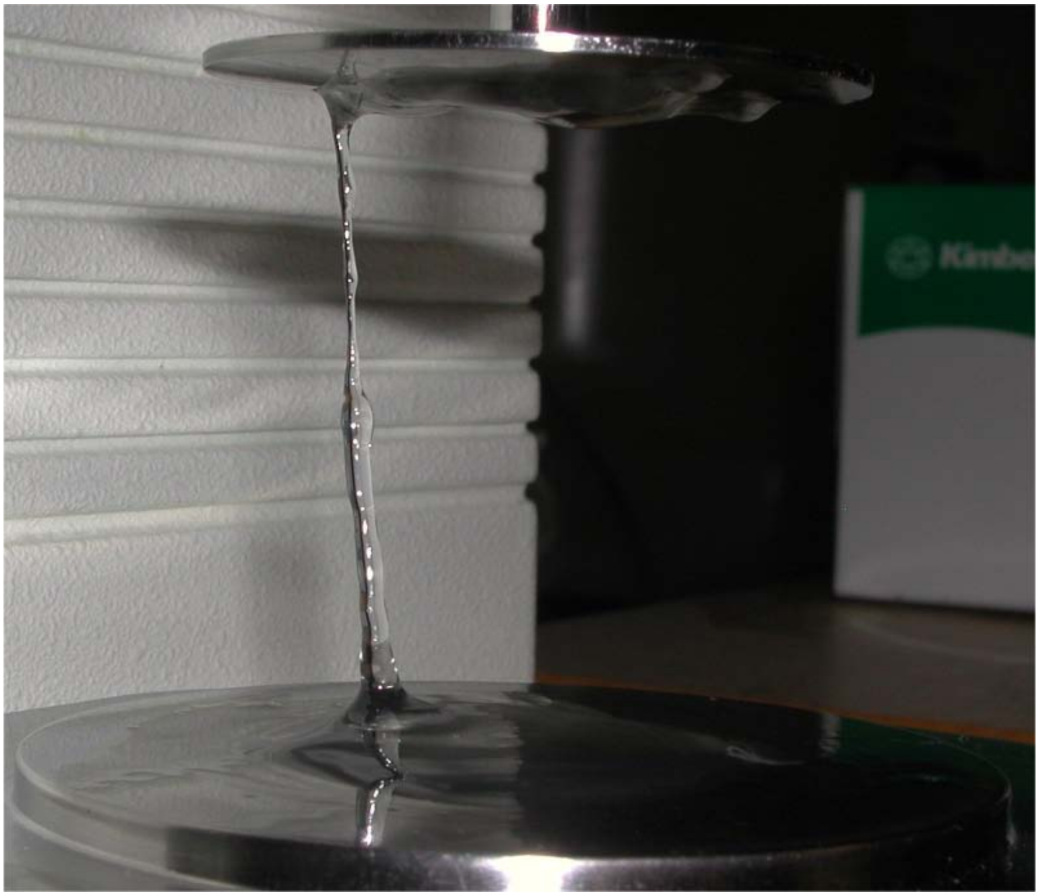

Figure 4.5 Gel adhered on both the cone and the plate for sample g050228

4.3 Summary

Bulk-mixed gelant samples have different gel time if prepared with different age of chromium (III) solution. Hence, the chromium (III) solution should be prepared at proper time for each experiment. In order to avoid this effect, well-aged chromium

(III) solution should be used.

The viscosity of bulk-mixed gelant samples when sheared at a constant shear rate of 110 s^{-1}, increases in the first two hours, then it levels off for about three hours, and eventually it starts decreasing. The maximum apparent viscosity at this shear rate is about 60 cp.

The results indicate that shear prevents formation of gel, but gelation continues after the shear is released. The gel that is formed at a constant shear rate of 110 s^{-1} cannot adhere on either the cone or the plate. But after the shear is stopped or reduced, a stronger gel forms and adheres on both the cone and the plate (as shown in Figure 4.5). The result is comparable to that obtained in flow experiments of in-line-mixed gelant solution in the stainless steel tube (discussed in Chapter 5).

Chapter 5

Flow of In-Line-Mixed Gelant Solution through Stainless Steel Tube

This chapter presents the results obtained from flow experiments of in-line-mixed gelant solution through the stainless steel tube. In the stainless steel tube, the fluid experiences a wide range of shear rates, i.e., zero shear at the center of the tube, and maximum shear at the tube wall. This shear environment cannot be reproduced by any rheometers.

5.1 Experimental results

The experimental procedures were described in Chapter 3. Both pressure data and calculated apparent viscosity data are plotted in this thesis. In the figures of pressure data, labels “S1” to “S5” represent pressure drops across Section 1 to Section 5, respectively. Label “T1” represents the total pressure drop across the whole tube. Label “Sum” represents the calculated summation of S1 to S5, in order to compare with the recorded T1. The small difference between T1 and Sum is due to the shift of zero reading from any of the five transducers. The pressure data were adjusted by zero reading at no flow condition before each experiment.

In the figure of apparent viscosity data, labels "V1" to "V5" represent apparent viscosities in Section 1 to Section 5, respectively. Label "Vt" represents the average apparent viscosity in the whole tube, calculated using the total pressure drop T1. The apparent viscosity is calculated from the pressure data using Darcy's law: $\upsilon = \frac{k\Delta p}{\mu L}$, which gives $\mu = \frac{\pi R^2}{1.15716}\frac{k\Delta p}{QL}$, where inner diameter (2*R*) is 0.0566 *in*., permeability *k* is 5.91×10^4 *darcys*, pressure drop Δp is in *psi*, flow rate *Q* is in *cm*^{3}*/min,* and the length *L* is in *ft*. These parameters were calculated based on experimental data from flow of water in the tube. The detail is given in Appendix B.

The parameters of the experiments of gelant flow are summarized in Table 5.1.

Table 5.1 Parameters of experiments of gelant flow

Run No.	**Age of Cr(III) solution**	**Bulk gel time (hours)**	**Avg. velocity (ft/day)**	**Flow rate (mL/min)**	**Injection time period (hours)**
1*	Fresh at 0 and 55.6 hours	5.7	1,031	0.35	72
1b	Fresh (2 hours)	N/A	1,048/2,096	0.36/0.72	152
1c	5 days	3.0	1,048/2,096	0.36/0.72	317
2	Fresh every 24 hours	5.5	1,048	0.36	149
2b	Fresh (1 hour)	5.5 - 6	1,048	0.36	24
4	Well-aged	1.5	4,948	1.70	9
5	Well-aged	1.5	4,948	1.70	60

1*: performed by McCool in 2002

5.1.1 Experiment Run 1b

This experiment was started on 03/12/2004, the objective of which was to reproduce McCool's[12] experiment Run 1. A micro inline-mixer was used this time.

The polymer solution was prepared and stored at room temperature. The chromium solution was prepared two hours before the start of this experiment. Thirty minutes after the chromium solution was prepared, the Quizix pumps were flushed with chromium solution and polymer solution, respectively, at flow rates of 1.0 mL/min each. 35 minutes later, a sample was collected from the outlet of the inline-mixer using a three-way valve. The gel time of this sample was not measured at that time.

Finally, the three-way valve was switched to the inlet of the stainless steel tube. The flow experiment of in-line-mixed gelant through the tube was started. The flow rates of both pumps were controlled at 0.18 mL/min, which gave a total flow rate of 0.36 mL/min. Then flow rate was doubled (to 0.72 mL/min in total) at running time of 72 hours in order to observe the effect of flow rate change on pressure behavior. Five hours later, the total flow rate was reduced back to 0.36 mL/min. At running time about 144 hours, the flow rate was doubled again (to 0.72 mL/min), and double once again (to 1.44 mL/min) three hours later. Five hours later, the injection was stopped. Then the pumps were flushed with water, and the gelant and gel stayed statically in the tube for about 100 minutes. After that, water was pumped into the tube to displace gelant and gel at total flow rate of 1.0 mL/min.

Similar to McCool's result, the effluent emerged from the tube as spaghetti. Figure 5.1 and Figure 5.2 show the pressure and apparent viscosity data, respectively.

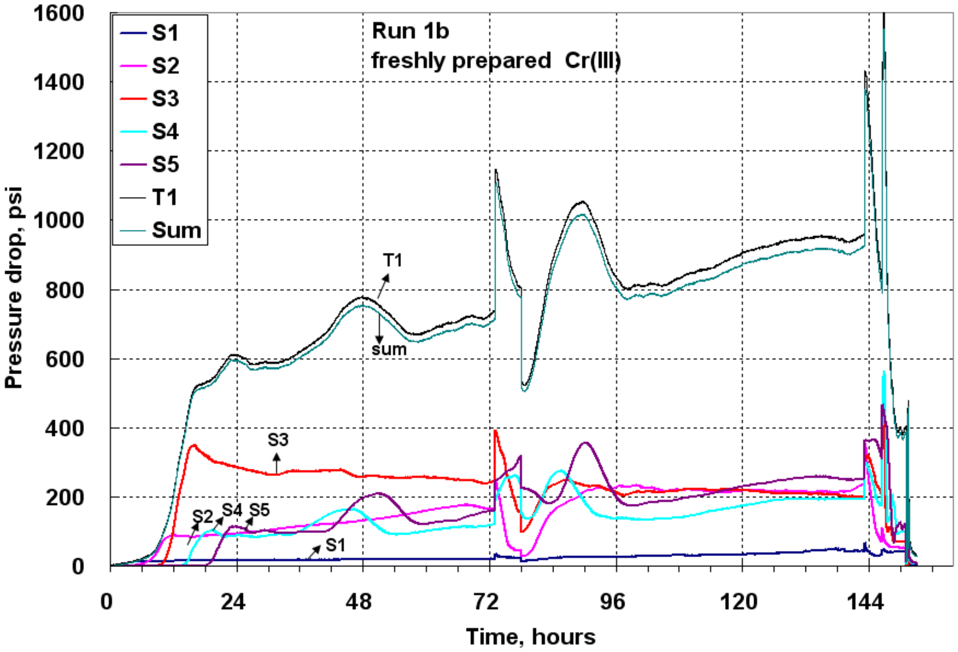

Figure 5.1 Pressure data with time, Run 1b

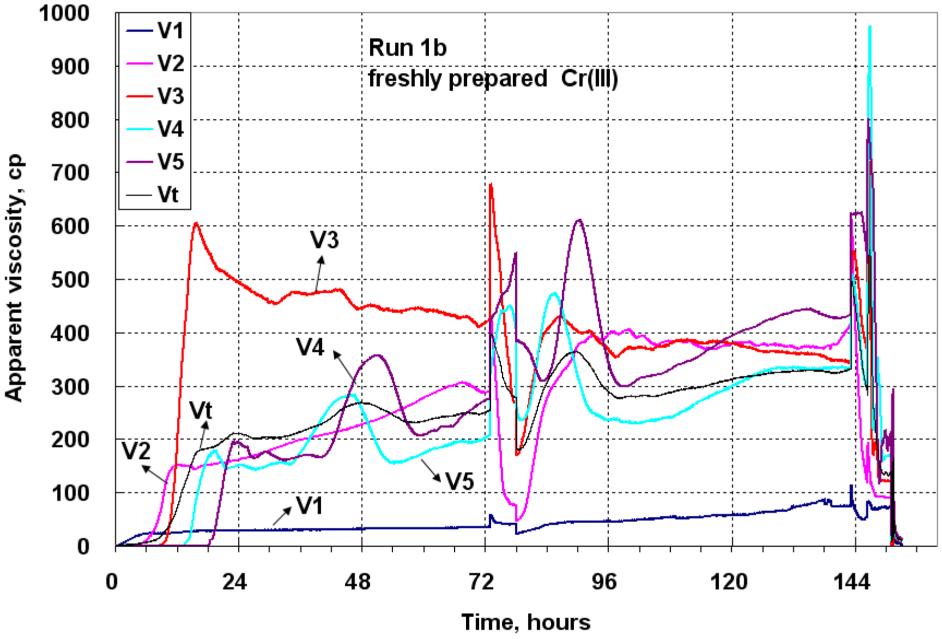

Figure 5.2 Apparent viscosity data with time, Run 1b

Figure 5.1 can be compared with Figure 2.21 (Run 1, McCool's data). For convenience, these two figures were plotted again as Figure 5.3 and Figure 5.4, excluding the data of T1 and Sum for better view of S1 to S5. This two figures show similarities between the results of these two experiments.

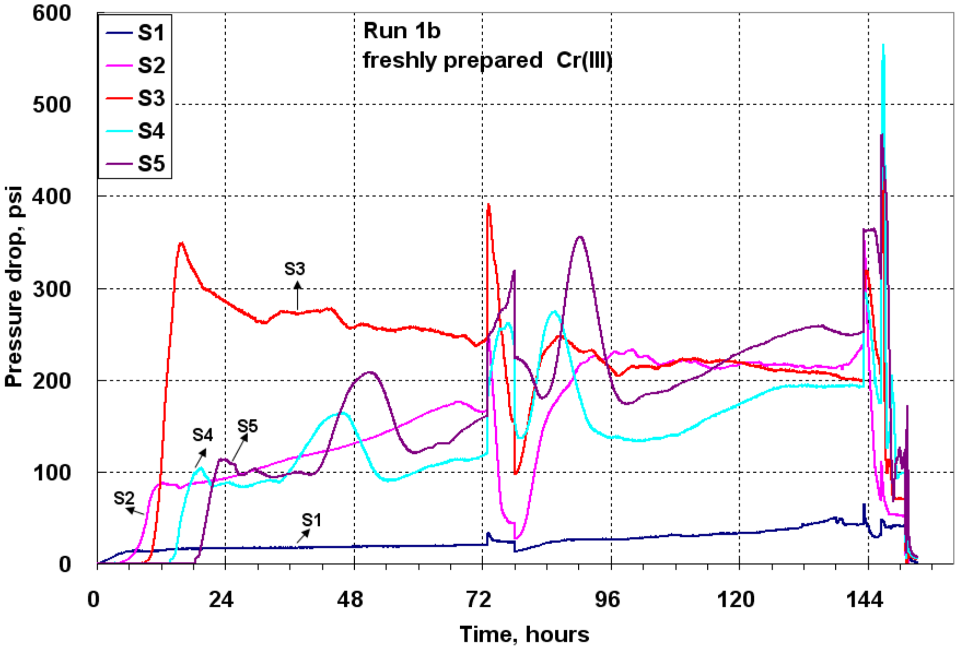

Figure 5.3 Pressure data with time, Run 1b, S1 to S5

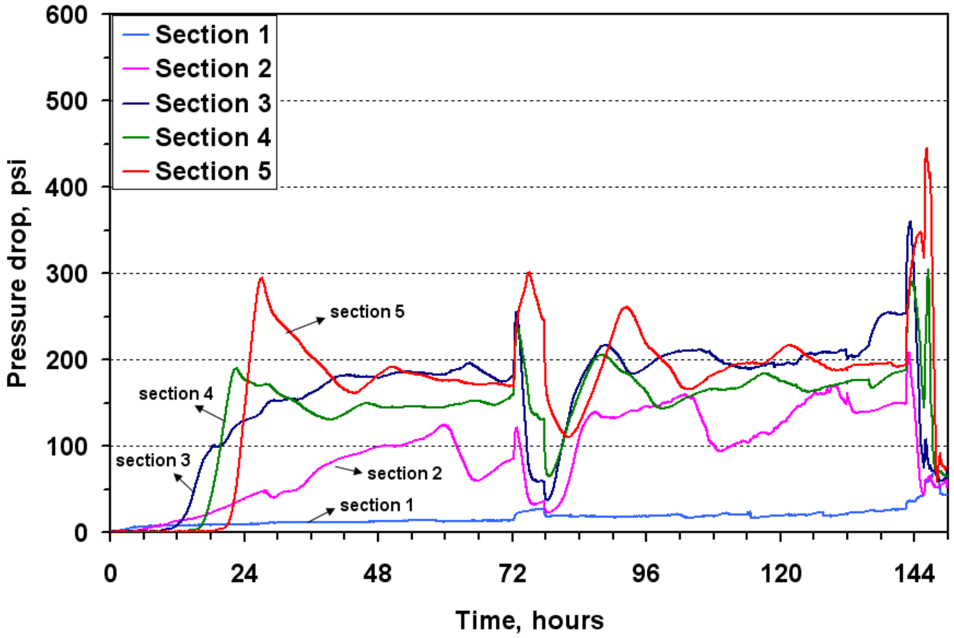

Figure 5.4 Pressure data with time, Run 1, S1 to S5, McCool[12]

First, the overall behavior was very similar between these two experiments. High resistance was observed in both experiments but in different sections. The difference is that the high resistance started in Section 2 in Figure 5.3 (Run 1b), while it started in Section 3 in Figure 5.4 (Run 1).

Second, the pressure data in these two experiments were close, which indicated that the resistance factors were close. The resistance factors were calculated by dividing the pressure drop of gelant flow by the pressure drop of pure water flow at the same flow rate and same temperature.

Third, the effects of the flow rate change are the same. As the flow rate increased, the pressure differential first increased then decreased to even lower than that at lower flow rate.

Fourth, the pressure drops across Section 1 and Section 2 increased continuously after the sections were filled with gelant solution (before changing flow rate). This indicated that the solution in the reservoir was changing with time, which turned out to be the effect of age of chromium solution on gelation (as discussed in Chapter 4).

In summary, McCool’s experiment Run 1 was reproduced successfully. As can be seen from Figure 5.2, the apparent viscosity, less than 500 cp at running time of 24 hours, is lower than the viscosity of preformed gel which is over 1,000 cp.

Figure 5.5 shows the pressure-drop data when water was displacing gelant and gel in the tube. In the first 80 hours, the flow rate was kept constant at 0.36 mL/min. Then it was changed several times to help displace of gel left in the tube. The change of the pressure-drop data at the same flow rate indicated movement of gel slugs in the tube.

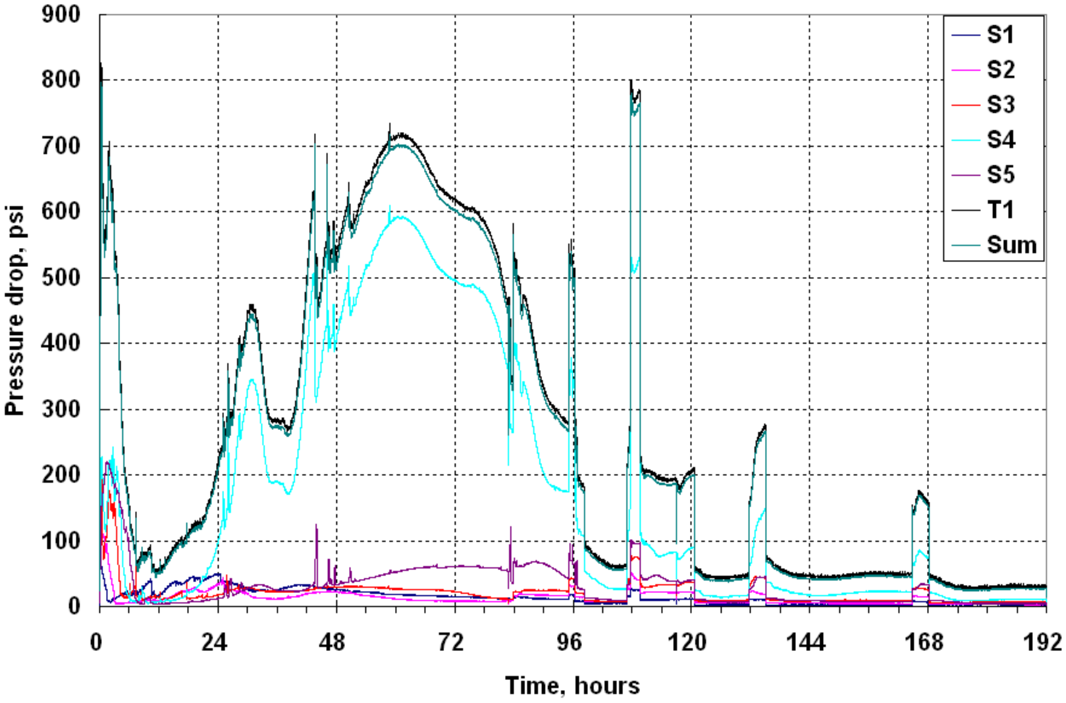

Figure 5.5 Pressure-drop data when water displacing gel, after Run 1b

After the pressure drop of water leveled off, the tube was cleaned by pumping 200 mL mixture of H_2O_2 and KOH into it. It was observed that the effluent was yellow which indicated the existence of chromium (VI) (broken gel, Chromium(III) in the gel was oxidized to Chromium (VI) by H_2O_2), i.e., some gel still adhered on the tube wall after the tube was flushed with large amount of water.

5.1.2 Experiment Run 1c

This experiment was started on 04/22/2004. Based on the results from Run 1b, there was a thought that the age of chromium (III) solution affected the gelation. Thus, for this experiment, the chromium (III) solution was prepared five days before the start of this experiment and stored at room temperature. The polymer solution was 25 days old. The micro inline-mixer was used again this time. Figure 5.6 shows the apparent viscosity data with time (the pressure data is shown in Figure D.1, Appendix D).

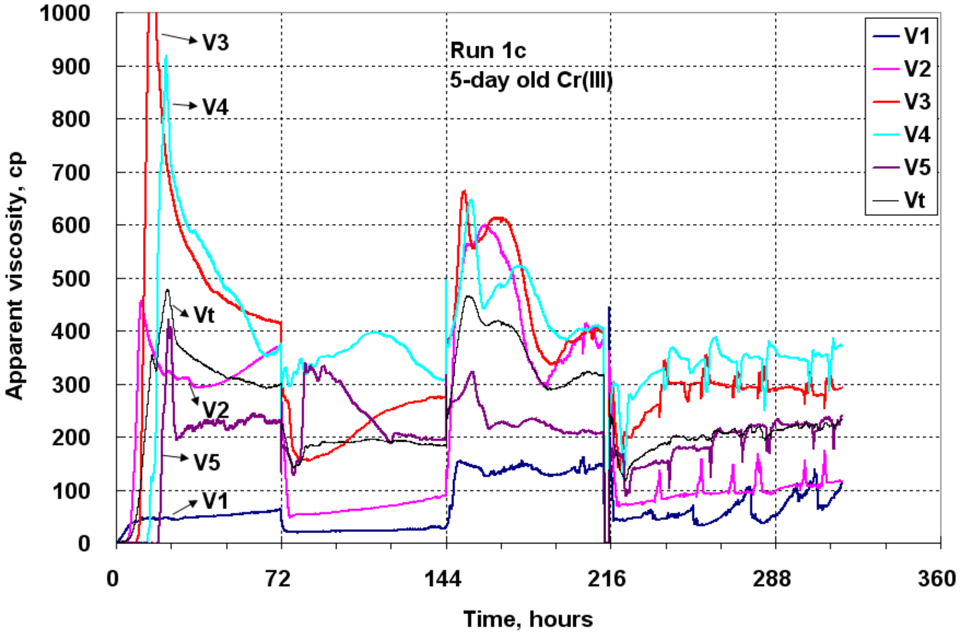

Figure 5.6 Apparent viscosity data with time, Run 1c

During the running time of the first 72 hours, the total flow rate was 0.36 mL/min (0.18 mL/min for each pump). Then the flow rate was doubled to 0.72 mL/min for another 72 hours. At running time of 144 hours, the flow rate was changed back to 0.36 mL/min. At running time of about 213 hours, the pumps stopped working due to electricity outage, and were manually restarted two hours later with the flow rate being changed to 0.72 mL/min again. The experiment was stopped at running time of 317 hours. The gelant and gel stayed in the tube statically for four more hours before water was pumped to displace them.

Figure 5.7 shows the results in the first 72 hours for Figure 5.6. Significant difference can be observed between Figure 5.7 and Figure 5.2 in the first 72 hours..

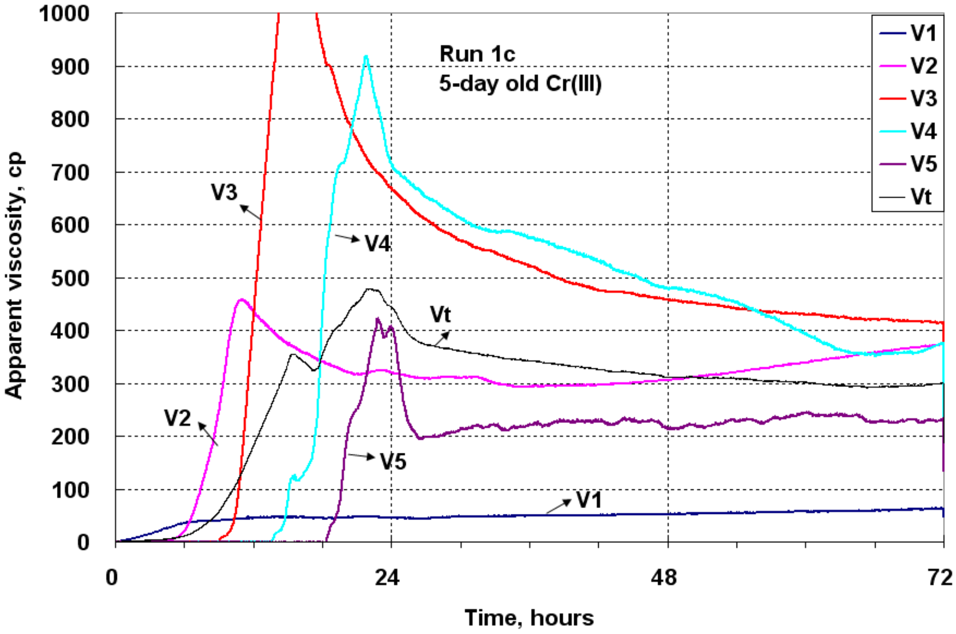

Figure 5.7 Apparent viscosity data with time in the first 72 hours, Run 1c

First, the apparent viscosities (or pressure differentials) in each section for the first 24 hours (one pore volume of injection) were higher than those in Run 1b. This result confirmed the effect of age of chromium (III) solution on gelation. Second, the apparent viscosity in Section 4 was close to that in Section 3 in this experiment, while it was much lower than that in Section 3 in Run 1b.

However, there are similarities between the results of these two experiments. First, the highest resistance occurred both in Section 3 in the two experiments. Second, the apparent viscosities at downstream of the tube were close in both experiments, about 200 cp in Section 5 at running time of 72 hours. Finally, the apparent viscosity in Section 1 increased continuously, which indicated that the effect of age of chromium (III) solution still existed in both experiments.

After the gel stayed in the tube for four hours, water was pumped to displace the gel. The flow rate was first set at 0.72 mL/min but then reduced to 0.36 mL/min two minutes later, due to high pressure differentials in Section 1 and Section 2 (pressure was over the range of the transducers). Figure 5.8 shows the pressure data with time when water displacing gel.

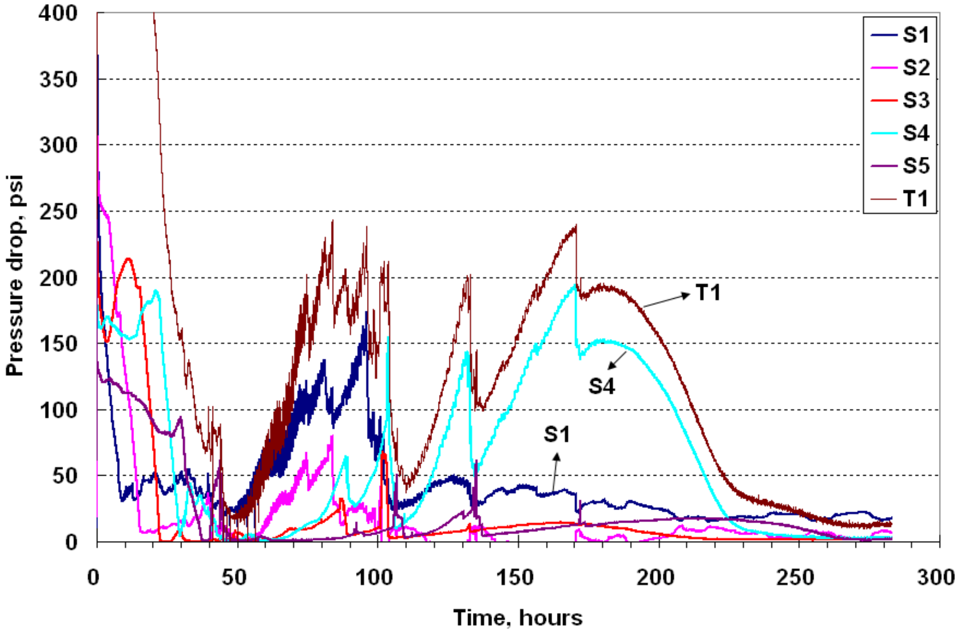

Figure 5.8 Pressure data when water displacing gel after Run 1c

After being flushed with 14 pore volume of water at flow rate of 0.36 mL/min, the flow rate was first increased and then decreased. The pressure differentials of water at different flow rates were obtained in order to calculate residue resistance factors, Frr, which was calculated by dividing the pressure drop of water before cleaning the tube (but after the tube was flushed with large amount of water) by the pressure drop of pure water in the clean tube under the same condition.

Table 5.2 shows the results. Frr(n) represents the residue resistance factor in Section (n), where n is the section number (from 1 to 5). Frrt represents the average residue resistance factor of the whole tube, which was calculated based on the total pressure drop across the whole tube.

Table 5.2 Residual resistance factors at different flow rates after Run 1c

Flow rate (mL/min)	Residual resistance factor (Frr) Frr1	Frr2	Frr3	Frr4	Frr5	Frrt
5.76	5.15	1.04	6.05	9.55	5.38	5.36
11.52	2.15	3.50	4.36	5.99	4.49	4.10
16.00	2.50	2.91	4.27	5.41	3.73	3.81
11.52	1.75	3.47	4.17	5.19	3.69	3.64
5.76	1.88	3.34	4.15	5.13	3.75	3.55
2.88	2.07	3.29	4.20	5.27	3.92	3.43

The Frr's were greater than 1, which indicated that some gel adhered on the tube wall that reduced the effective inner diameter, ID, of the tube. After cleaning the tube, Frr was equal to 1.

By Hagen-Poiseuille equation for laminar and incompressible flow, the flow rate is proportional to the product of pressure drop and ID^4 ($Q = C \cdot \Delta p \cdot R^4$), the effective ID can be estimated from Frr as

$$ID = \left(\frac{1}{Frr}\right)^{\frac{1}{4}} ID_o, \text{ since } Frr = \frac{\Delta p_w}{\Delta p_{wo}} = \left(\frac{R_o}{R}\right)^4 = \left(\frac{ID_o}{ID}\right)^4,$$

where subscript *o* means "original". For example, taking Frr as 4.0, then the effective ID is $ID = \left(\frac{1}{4}\right)^{\frac{1}{4}} ID_o = 0.71 ID_o$, which is about 30% less than the original inner diameter. The thickness of the gel adhered on the tube wall is estimated to be

$$\begin{aligned}\delta &= (ID_o - ID)/2 = (0.15)(ID_o) = (0.15)(0.0566)(in.)\\ &= 0.0085(in.) = 0.026(cm)\end{aligned}$$

At the same flow rate, Frr at later time was less than that at earlier time, which suggested that some gel had been washed out during that period. However, there were still some gel that adhered on the tube wall, which was confirmed when cleaning the tube with H_2O_2 and KOH.

5.1.3 Experiment Run 2

After Run 1c, it was found that the micro inline-mixer couldn’t mix the solutions very well. The viscosity of the effluent came out from the micro inline-mixer, after mixing 10,000 ppm AF935 with water at flow rate ratio of 1 to 1, was not uniform. A stainless steel tube inline-mixer was used in all the experiments performed afterward. The stainless steel tube inline-mixer (A04669-52) was 6 in. long with outer diameter (OD) of 3/16 in.

This experiment was performed on 06/25/2004. The polymer solution was prepared on 06/01/2004. Freshly prepared chromium (III) solution was used, which was about 75 minutes old before being injected into the tube. In order to reduce the effect of age of chromium (III) solution on gelation, the chromium (III) solution was replaced every 24 hours with freshly prepared one. After the pumps were flushed with polymer solution and chromium (III) solution respectively, the solutions were pumped into the inline-mixer, and a gelant sample was collected at the outlet to measure the gel time. The gel time, defined as the time when viscosity is greater than 1,000 cp, was measured to be 5.5 hours at 41 ºC using Brookfield viscometer.

After the sample was collected, the in-line-mixed gelant was injected into the stainless steel tube at total flow rate of 0.36 mL/min (0.18 mL/min for each pump). Figure 5.9 shows the apparent viscosity data with time (pressure data is shown in Figure D.3).

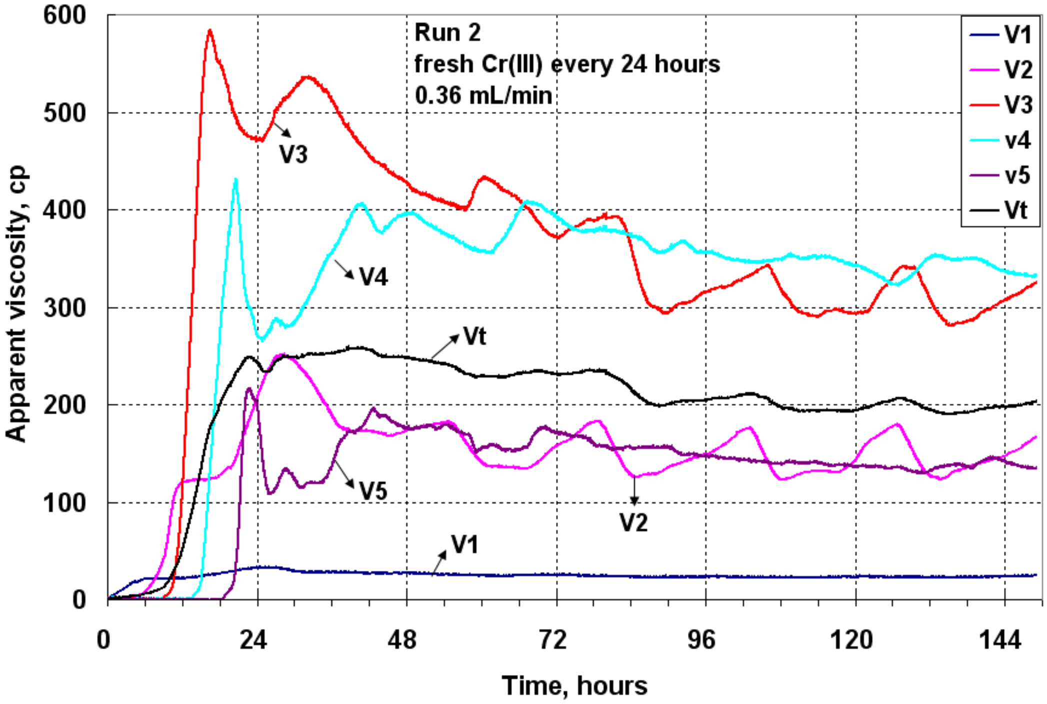

Figure 5.9 Apparent viscosity data with time, Run 2

As can be seen, the behavior in the first 24 hours was similar with those of previous experiments. The major difference was the periodically variation of apparent viscosity data caused by the replacement of chromium (III) solution every 24 hours.

At the end of the experiment, the reservoir of polymer and chromium (III) solutions at the inlets of the pumps were switched to water. By this way, water was pumped to displace gelant and gel in the tube at the same flow rate of 0.36 mL/min without stopping the pumps. Six days later, the flow rate was increased to 14 mL/min to help moving gel that adhered on the tube wall. Flow rate was changed several times till the pressure data at each flow rate leveled off. Then the pressure data at different flow rates were recorded to calculate the residue resistance factors. Table 5.3 shows the results.

Table 5.3 Residual resistance factors at different flow rates after Run 2

Flow rate	**Residual resistance factor (Frr)**					
(mL/min)	**Frr1**	**Frr2**	**Frr3**	**Frr4**	**Frr5**	**Frrt**
2.88	1.09	1.85	1.91	2.93	1.34	1.81
5.76	1.06	1.80	1.87	2.82	1.32	1.77
11.52	1.06	1.81	2.01	2.78	1.32	1.81

Comparing Table 5.3 to Table 5.2, the Frr's after Run 2 were less than those after Run 1c. This was due to the high flow rates when flushing the tube with water, which helped displace more gel out. Taking Frr as 1.8, the effective ID is estimated to be 86% of original ID (ID_o), and the thickness of the gel adhered on the tube wall is 0.0040 inches (0.01 cm).

5.1.4 Experiment Run 2b

The previous experiments indicated that the age of chromium (III) solution affected the gelation process in the tube. So this experiment was performed to demonstrate the effect and was started on 08/04/2004. This time, the gelant solution only flowed through Section 1 of the tube, and effluent samples were collected at the outlet of Section 1 at different time. All the effluent samples experienced the same shear history, and the only difference was the age of the chromium (III) solution when it was pumped into the inline-mixer.

The polymer solution used was prepared 2 days before, and the chromium (III) solution was freshly prepared (60 minutes) before the start of this experiment. Both of the solutions were pumped into the stainless steel inline-mixer at flow rate of 0.18 mL/min, which gave total flow rate of 0.36 mL/min. A sample was collected at the outlet of the inline-mixer at the running time of 0, and the gel time was measured to be between 5.5 to 6 hours. The residence time of gelant in Section 1 is 4.7 hours. Some samples were collected at the outlet of Section 1 after running time of 5 hours. The viscosities of all the samples were measured using Brookfield viscometer at 0.6 RPM at 41 ºC. Figure 5.10 shows the apparent viscosity data with time, and the viscosity data of the effluent samples are shown in Figure 5.11.

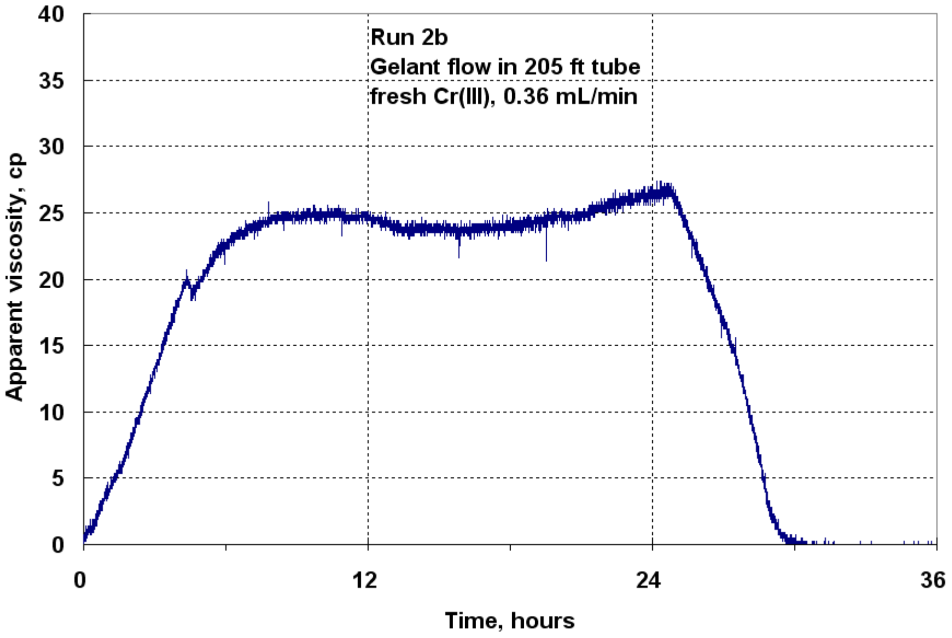

Figure 5.10 Apparent viscosity data with time, Run 2b

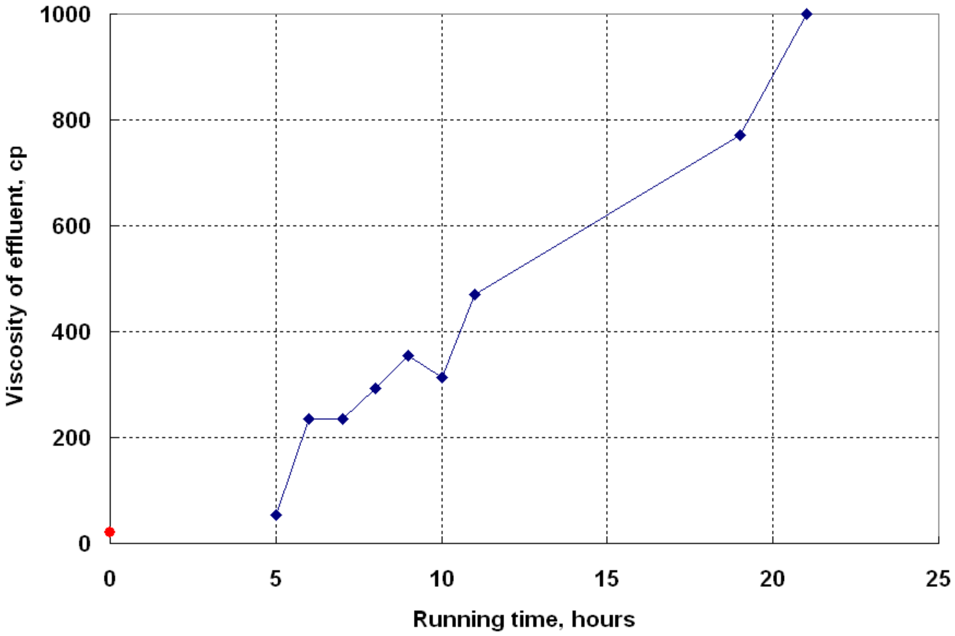

Figure 5.11 Viscosities of effluent samples, Run 2b

As can be seen from Figure 5.11, the viscosity of the effluent samples increased with running time. They were collected at outlet of Section 1 but at different time. This proved that the older the chromium (III) solution, the faster the gelation process. At running time of 21 hours, the viscosity of the effluent was already over 1,000cp. That is, when the chromium (III) solution was 22 hours old, after it was inline-mixed with polymer solution, the gelant took less than 4.7 hours to form a gel, even under shear. This gel time was shorter than the bulk gel time of the samples prepared using fresh chromium (III) solution.

Based on this result, it is necessary to avoid the effect of age of chromium (III) solution on gelation, in order to study the effect of shear when the in-line-mixed gelant flows through the tube. “Well-aged” chromium (III) solutions, as defined in Chapter 4, were used in the experiments performed afterward.

5.1.5 Experiment Run 4

This experiment was performed on 10/29/2004, and well-aged chromium (III) solution was used. The chromium (III) solution had been aging for 11 days in 41 ºC air bath before inline-mixing with polymer solution. The polymer solution was 14 days old.

Since the bulk gel time is only about 1.5 hours for the bulk-mixed gel samples, the residence time in Section 1 should be less than 1.5 hours to avoid formation of gel in Section 1. Total flow rate of 1.70 mL/min was used in this experiment, which gave the residence time of 1.0 hour in each section, and 5 hours for the whole tube. Accordingly, the flow rate was 0.85 mL/min for each solution.

A sample was collected at total flow rate of 1.0 mL/min at the outlet of the inline-mixer, and the measured gel time was between 1.5 to 2 hours. Then the flow rate was changed to 0.85 mL/min for both pumps, and the in-line-mixed gelant solution was pumped into the stainless steel tube. Five hours later, the effluent emerged out of the tube as spaghetti. Another four hours later (running time of nine hours), the total flow rate was changed from 1.70 mL/min to 0.36 mL/min, in order to observe the pressure behavior due to flow rate change.

At running time of 24 hours, the flow rate was changed back to 1.70 mL/min. However, the pressure drop across Section 3 was out of the range of transducer S3. Then the pump for polymer solution stopped automatically due to overpressure. After that, water was pumped into the tube to displace the gel and gelant.

Figure 5.12 shows the pressure data with time. Figure 5.13 and Figure 5.14 show the pressure data and apparent viscosity data in the first 9 hours, respectively. As can be seen, the result is very different from those of previous experiments.

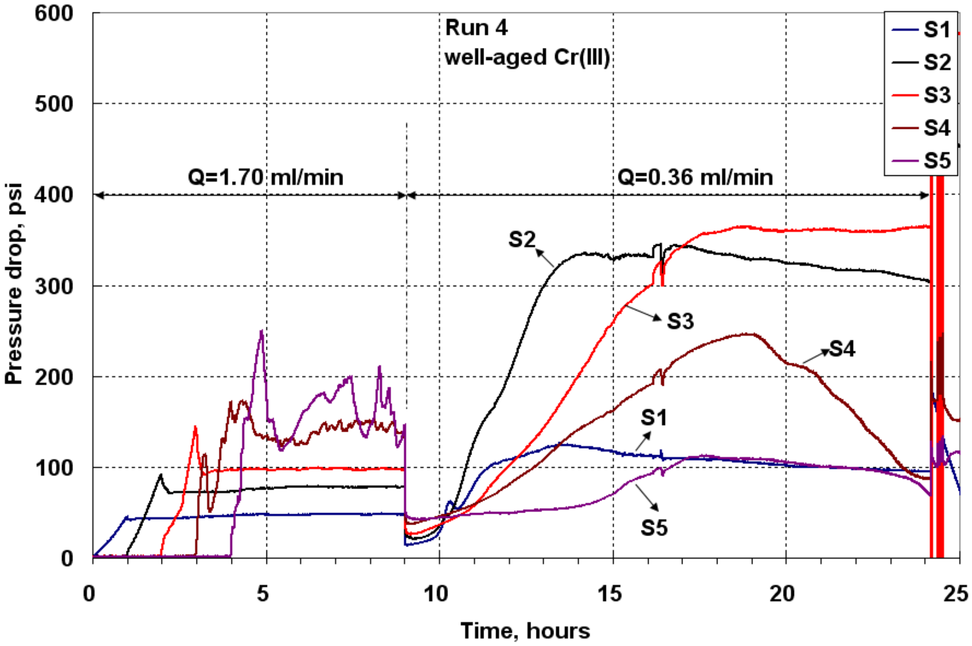

Figure 5.12 Pressure-drop data with time, Run 4

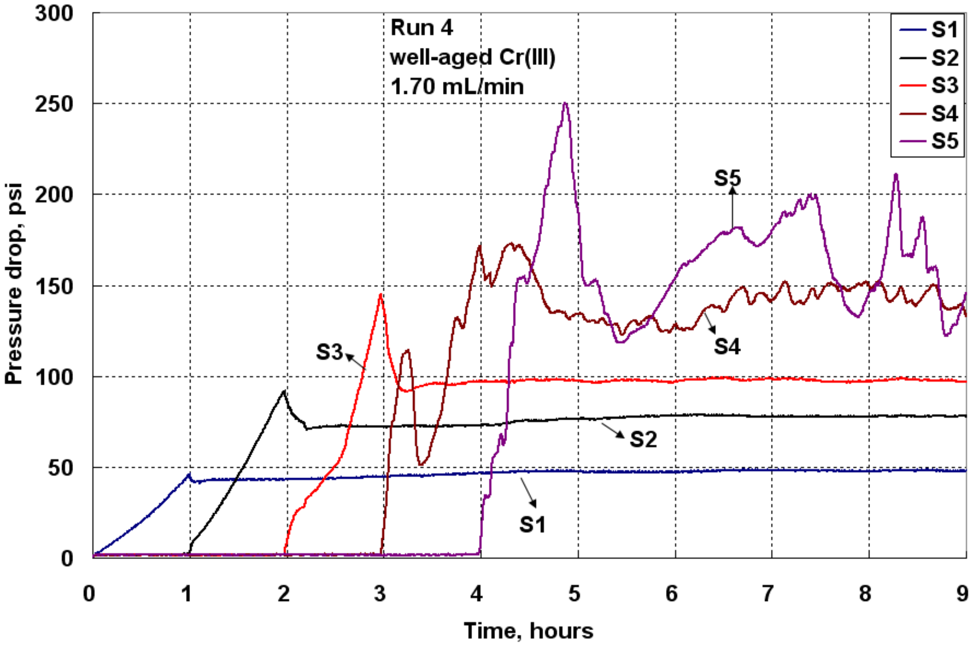

Figure 5.13 Pressure-drop data with time, first 9 hours, Run 4

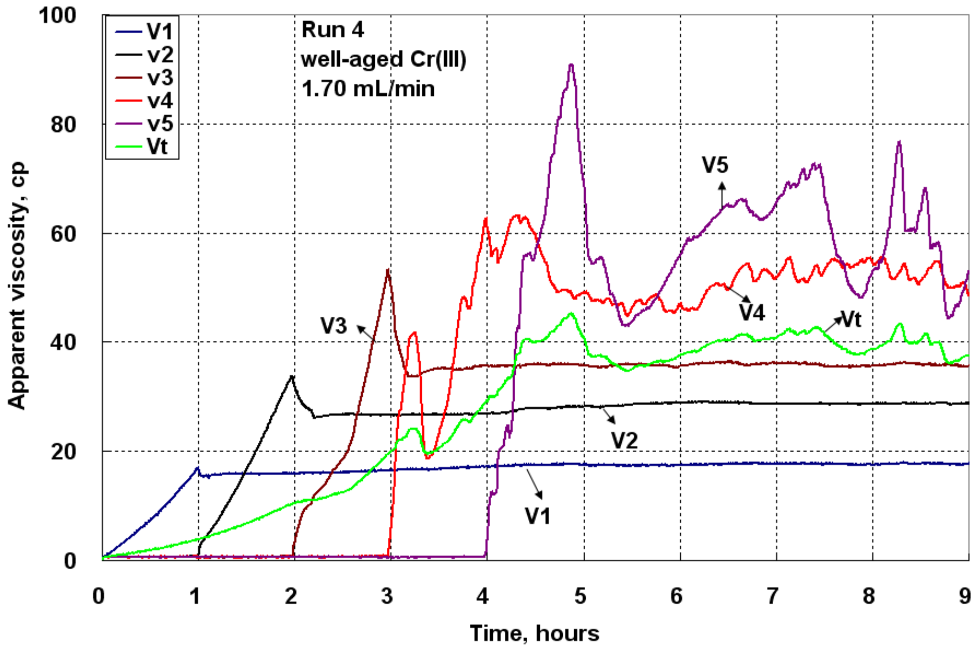

Figure 5.14 Apparent viscosity data with time, Run 4

First, the apparent viscosities in sections 1, 2, and 3 are relatively stable after their spike values. This behavior was expected but had never been observed in previous results. In this experiment, well-aged chromium (III) solution was used, so that the properties of gelant solution at a certain location did not change with time. Hence, after a section was filled with gelant solution, the pressure differential should maintain constant. This was confirmed by the results of this experiment. In previous experiments, the age of chromium (III) solution at a certain location changed with time, which led to the change in the viscosities of the gelant solution with time at that location. The results in this experiments demonstrated that well-aged chromium (III) solution really helped to minimize the effect of age of chromium (III) solution on gelation.

Second, the pressure drop across Section 1 in this experiment at flow rate of 1.70 mL/min, about 50 psi, was higher than those in previous experiments which were about 15 psi at flow rate of 0.36 mL/min. However, the apparent viscosity in Section 1 in this experiment, about 18 cp, was lower than those in previous experiments which were about 24 cp. Well-aged chromium (III) solution reacts faster with polymer solution than freshly prepared chromium (III) solution, so the apparent viscosity in Section 1 in this experiment should be higher than those in previous experiment if they were flowing at the same rate. It was lower, however, due to shear-thinning at the higher flow rate.

Third, the pressure drops across other sections in this experiment were comparable to those in experiments Run 1b, Run 1c and Run 2, which were performed at lower flow rates. This indicated that the pressure gradient did not change much with the change of flow rate. However, the apparent viscosities in this experiment were much lower than those in experiments performed at lower rates, due to the high shear rate which was about 110 s^{-1} at the tube wall. The pressure behavior is interpreted later in this chapter.

Fourth, the maximum apparent viscosity was around 60 cp, except the spike values of Section 5. This was consistent with the results obtained from rheology study discussed in Chapter 4.

After injection of the in-line-mixed gelant solution, water was pumped into the stainless steel tube at flow rate of 0.80 mL/min to displace the gelant and gel. Flow rate was changed several times afterward. Then the residue resistance factors were calculated after the tube was flushed with about 9.6 pore volumes of water. Table 5.4 shows the results.

Table 5.4 Residual resistance factors at different flow rates after Run 4

Flow rate	Residual resistance factor (Frr)					
(mL/min)	Frr1	Frr2	Frr3	Frr4	Frr5	Frrt
4.0	1.27	2.73	1.38	2.05	1.27	1.70
8.0	1.24	2.62	1.35	2.12	1.40	1.73
16.0	1.27	2.52	1.47	1.88	1.51	1.72

As can be seen from Table 5.4, some gel still adhered on the tube wall. The average Frr is close to that shown in Table 5.3 (after Run 2). Taking Frr as 1.7, then the effective ID is estimated to be 88% of original ID, and the thickness of the gel adhered on the tube wall is 0.0035 inches (0.01 cm).

5.1.6 Experiment Run 5

This experiment was performed on 03/04/2005, the objective of which was to confirm the results of Run 4. The chromium (III) solution had been aging for 108 days in 41 ºC air bath before inline-mixing with polymer solution. The polymer solution was also 108 days old. Two bulk-mixed samples were prepared using these two solutions at weight ratio of 1 to 1, and the bulk gel time of them were both 1.75 hours measured by Brookfield viscometer at 40 ºC.

First, the pumps were flushed with chromium (III) solution and polymer solution at flow rate of 0.85 mL/min for 40 minutes, respectively. Then these two solutions were pumped into the stainless stain inline-mixer at the same flow rate, and two samples were collected at the outlet of the inline-mixer. One of the samples was used for gel time measurement under the same condition with those two bulk-mixed samples, which gave the same result of 1.75 hours. The flow rate was checked when collecting these two samples, one gave 1.69 mL/min and one gave 1.70 mL/min, which showed that the pumps were working properly.

After the gel time of the sample had been obtained, the polymer solution and chromium (III) solution were pumped through inline-mixer into the stainless steel tube. The flow rate was still 0.85 mL/min for each solution, which gave the total flow rate of 1.70 mL/min. Samples were collected at the outlet of the tube to check the flow rate, and the results showed that the pumps were working properly all the time. Unlike Run 4, the flow rate was kept constant through out this experiment for 60 hours.

Figure 5.15 shows the pressure-drop data with time, and Figure 5.16 shows the apparent viscosity data. The results in the first 20 hours confirmed those of Run 4. There was slow increase of pressure drop after running time of 20 hours. The reason was that more gel adhered on the tube wall, which slightly reduced the effective inner diameter. The maximum apparent viscosity was about 60 cp except the spike values of sections 4 and 5, which was consistent with the result of Run 4.

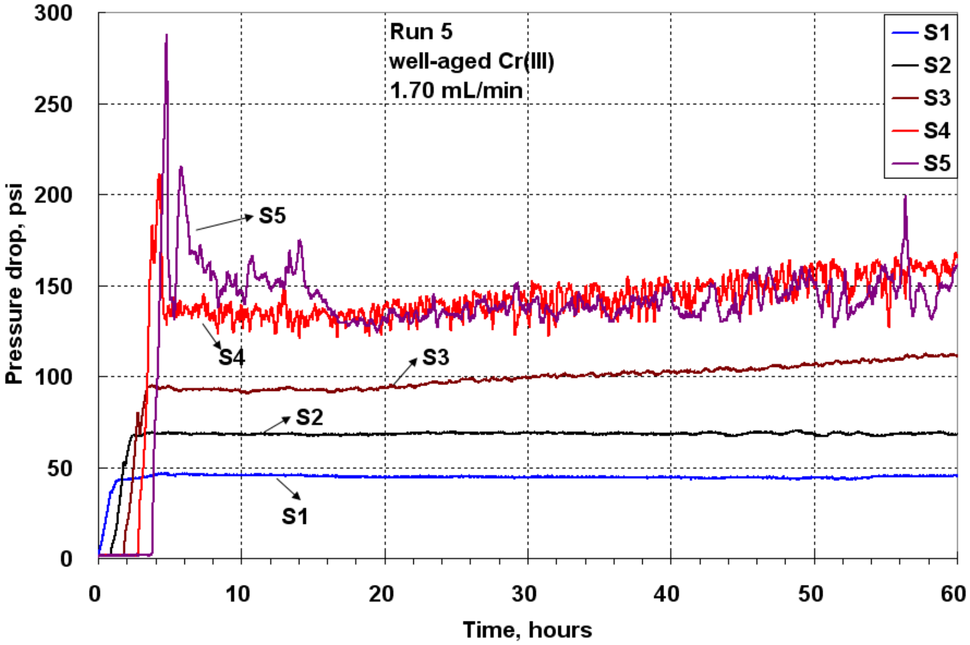

Figure 5.15 Pressure-drop data with time, Run 5

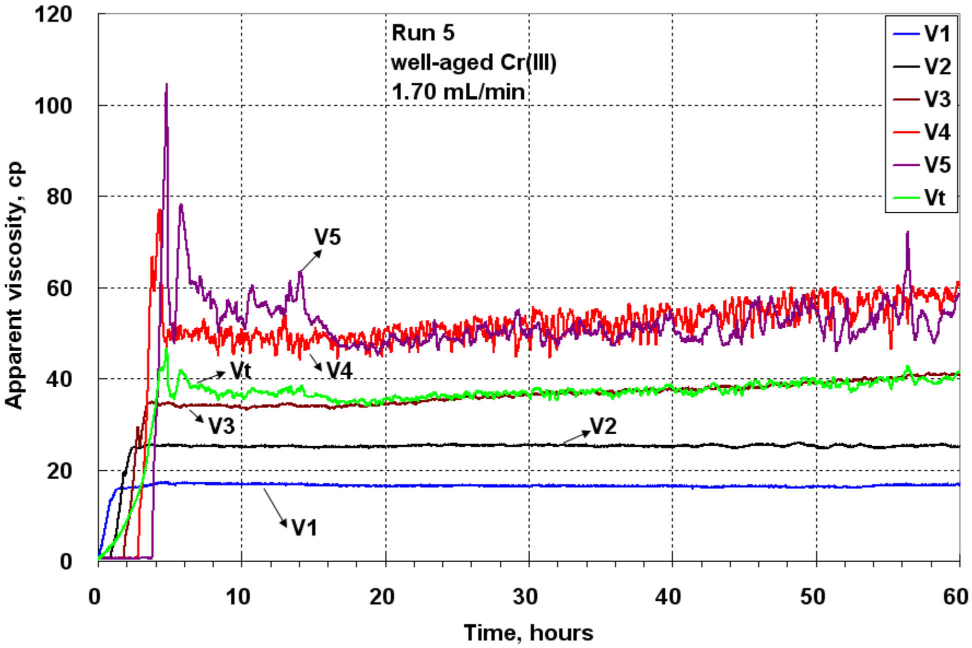

Figure 5.16 Apparent viscosity data with time, Run 5

After injecting in-line-mixed gelant solution for 60 hours, water was pumped into the stainless steel tube at the same flow rate to displace the gelant and gel. Pressure of water through the tube at different flow rates were recorded after the tube was flushed with 15 pore volumes of water. Table 5.5 shows the calculated residual resistance factors.

Table 5.5 Residual resistance factors at different flow rates after Run 5

Flow rate	Residual resistance factor (Frr)					
(mL/min)	Frr1	Frr2	Frr3	Frr4	Frr5	Frrt
4.0	1.18	1.19	1.17	1.47	1.05	1.19
8.0	1.18	1.41	1.11	1.46	1.00	1.15
16.0	1.21	1.13	1.14	1.51	1.04	1.20

The residual resistance factors in Table 5.5 are less than those in previous results because the tube was flushed with more water this time. However, some gel still adhered on the tube wall which was demonstrated by the yellow effluent when cleaning the tube with H_2O_2 and KOH.

5.2 Discussion of the results

Except Run 4 and Run 5, different ages of chromium (III) solutions were used in other experiments, and the results were affected by the aging of chromium (III) solution. So the discussion is only focused on Run 4 and Run 5 in which well-aged chromium (III) solutions were used. Since the results of these two experiments were consistent with each other at the same flow rate, Figure 5.13 and Figure 5.14 were used as representative of the results for both experiments.

5.2.1 Interpretation of flow behavior

The pressure behavior is interpreted as following. First, in-line-mixed gelant solution was pumped into Section 1 to displace water. Gelation occurred very slowly and the viscosity did not change much throughout Section 1, so the gelant flow behaved the same as flow of polymer solution displacing water. The pressure drop across Section 1 increased due to the displacement of low viscosity fluid, i.e., water, by high viscosity fluid, i.e., gelant solution. Figure 5.17 shows the comparison of polymer flow and in-line-mixed gelant flow in Section 1 at the same experimental condition.

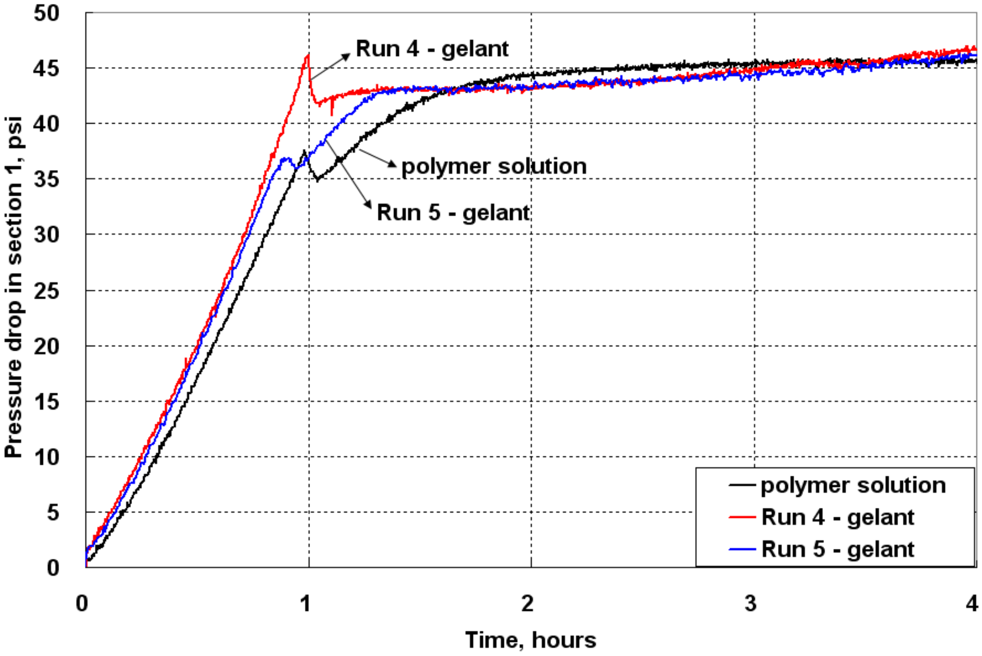

Figure 5.17 Pressure-drop data in Section 1 at 1.70 mL/min at 41ºC

Second, when the gelant solution arrived at inlet of Section 2 to displace water, the pressure drop across Section 2 started increasing. Because the viscosity of gelant increased with time, the increase of pressure differential in Section 2 was faster than that in Section 1. The change of slope of pressure-time curve illustrated the result. As the gelant arrived at the middle part of Section 2, gelant near the center of the tube where shear rate was small, started forming gel. Although gel has not formed near the tube wall due to the high shear rate, the apparent viscosity of the fluid in the tube increased, which led to faster increase of pressure at downstream of Section 2 than that at upstream. After Section 2 was filled with the fluid, the pressure remained constant and was higher than that in Section 1. The behavior in Section 3 was similar with that in Section 2, except that more gel had formed so that the apparent viscosity was higher, leading to higher pressure drop.

When the fluid arrived at Section 4, most gelant had already become gel except a small amount of gelant near the tube wall. The high shear rate near the tube wall prevented formation of strong gel. Some solvent was probably squeezed out from the gelant and acted as a lubricant layer between the fluid and the tube wall, which helped the movement of the fluid in the tube. The pressure drop across Section 4 was not as stable as those in sections 1, 2 and 3. The fluctuation of pressure-drop data indicated the existence of some broken gel slugs in the tube. The pressure behavior in Section 5 was similar with that in Section 4, except the fluctuation was more significant. The average pressure drop was close to that in Section 4.

As mentioned before, some gel adhered on tube wall even after the tube was flushed with large amount of water. The gel may come from the lubricant layer between the fluid and the tube wall. The lubricant layer contains polymer and chromium (III), and gel forms through the adhesion and accumulation of polymer and chromium (III) onto the tube wall.

5.2.2 Resistance factors

The average resistance factors of the gelant flow experiments after one pore volume injection were calculated by dividing the total pressure drop of gelant flow by that of pure water flow at the same rate. The resistance factors in each section were shown in Table 5.6. The results of Run 4 is plotted together with Seright's data[2] from preformed gel experiments in Figure 5.18.

Table 5.6 Resistance factors of in-line-mixed gelant flow experiments

Run No.	Velocity (ft/day)	Resistance factor after one pore volume injection					
		Section 1	Section 2	Section 3	Section 4	Section 5	whole tube
1b	1048	46	253	774	237	303	329
1c	1048	72	500	1042	1118	633	694
2	1048	51	322	736	426	314	381
4	4948	27	44	56	77	109	64
5	4948	26	40	54	77	88	58

Experiments Run 1b, Run 1c, and Run 2 were performed at flow rate of 0.36 mL/min, and the residence time of gelant in the whole tube was 24 hours. Thus the resistance factors were calculated at running time of 24 hours. Experiments Run 4 and Run 5 were performed at flow rate of 1.70 mL/min, and the resistance factors were calculated at running time of 5 hours.

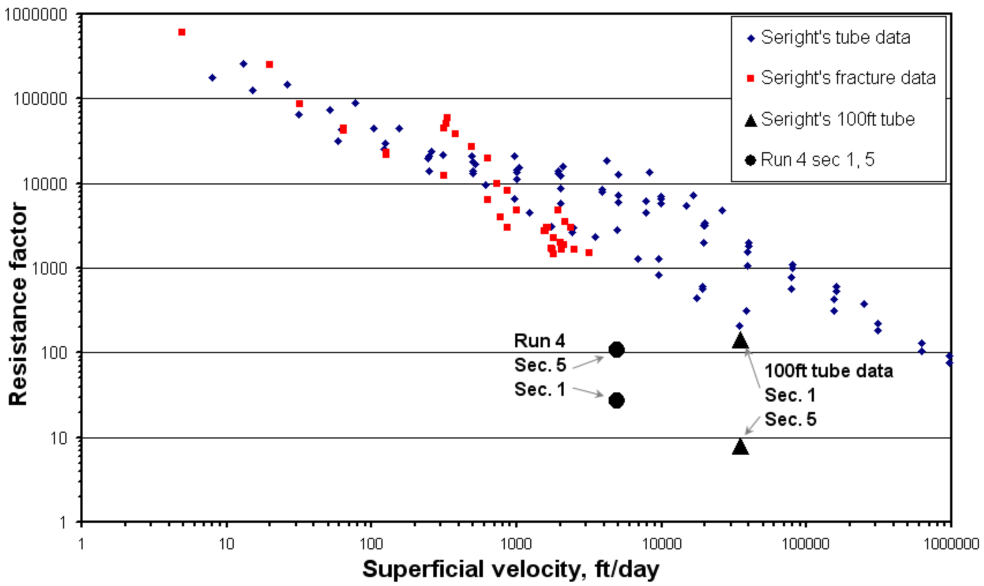

Figure 5.18 Resistance factors of in-line-mixed gelant flow experiment (Run 4) and Seright's data[2] of preformed gel flow

As can be seen, the resistance factors of in-line-mixed gelant flow are lower than those of preformed gel flow at the same superficial velocity. Notice that, Seright only used short tubes and fractures in his experiments (see Chapter 2).

5.3 Summary

Several flow experiments were performed for in-line-mixed gelant solution. It was found that the age of chromium (III) solution affects the gelation. Then well-aged chromium (III) solution was used, in order to study the effect of shear on formation of gel in the tube.

Small shear rate near the center of the tube may accelerate gelation, while high shear rate near the tube wall retards gelation. The gelant flow in Section 1 behaves the same as polymer solution at the same flow condition. The pressure differentials in other sections are higher than that in Section 1 due to the increase of apparent viscosity. A lubricant layer probably exists between the gel and the tube wall which helps the movement of gel in the tube. The resistance factors of in-line-mixed gelant flow in the long tube are lower than those of preformed gel flow in short tubes and fractures.

Chapter 6

Flow of Preformed Gel through Stainless Steel Tube

This chapter describes the experiments and results of preformed gel flow through stainless steel tube, and compares the results with McCool's experiment Run 3.

6.1 Experimental procedures

The common procedures were described in Chapter 3. The volume capacity in the transfer cylinder for preformed gel was prepared as 3,220 mL. The preformed gel was prepared on 04/12/2005 by hand-mixing 1,651.3 g of polymer solution and 1,653.2 g of well-aged $Cr(OAC)_3$ solution. The polymer solution, containing 10,000 ppm AF935 and 2.0% NaCl, was prepared 6 days before, and filtered and placed in the 41 ºC air bath on the day before preparing the preformed gel. The chromium solution, containing 200 ppm chromium (III), had been aging in 41 ºC oven for 14 days. A sample was collected to measure the bulk gel time using a Brookfield viscometer, which gave the gel time of 1.5 hours at 41 ºC. The bulk-mixed solution was placed in the transfer cylinder, and the cylinder was placed back in the 41 ºC air bath.

After 48 hours for gelation, dyed water was pumped into the transfer cylinder at flow rate of 1.70 mL/min to displace the preformed gel. Several samples were collected at the outlet of the cylinder. Then the outlet of the transfer cylinder was connected to the inlet of the 1031 ft tube via 30-in. long stainless steel tubes, which consisted of an 18-in. tube plus a 3-way valve plus another 12-in. tube.

The flow experiment of preformed gel, Run 6, was started on 04/14/2005, when the gel was 49.5 hours of age. Dyed water was pumped at flow rate of 1.70 mL/min to drive the preformed gel into the stainless steel tube. The pressure drop across the transfer cylinder and those across the sections of the tube were recorded using Camile system. The output pressure of the Quizix pump was recorded in another computer which was controlling the pump. During the experiment, some effluent samples were collected in 40-mL vials at different time and stored in 41 ºC oven.

After running time of 30.5 hours, all gel was displaced from the transfer cylinder. Then water was pumped using another Quizix pump into the stainless steel tube to displace gel. After being flushed with large amount of water, the tube was cleaned with 200 mL mixture of H_2O_2 and KOH. The yellow effluent indicated that some gel still adhered on the tube wall.

6.2 Results and discussion

The effluent emerged out of the tube as spaghetti but broke easily by gravity. The results were compared with those from previous experiments of preformed gel and in-line-mixed gelant. Table 6.1 summarizes the parameters of experiments of preformed gel flow.

Table 6.1 Parameters of experiments of preformed gel flow

Run No.	Age of Cr(III) solution	Bulk gel time (hours)	Avg. velocity (ft/day)	Flow rate (mL/min)	Injection time period (hours)
3*	Fresh	5.7	1,030	0.35	72
6	Well-aged	1.5	4,948	1.70	30

3*: performed by McCool in 2002

6.2.1 Results of Run 6

Figure 6.1 shows the pressure-drop data with time. The pressure drop across Section 1 was higher than those across other sections. The pressure drop across Section 2 was close to that across Section 3. The pressure drop across Section 4 was close to that across Section 5.

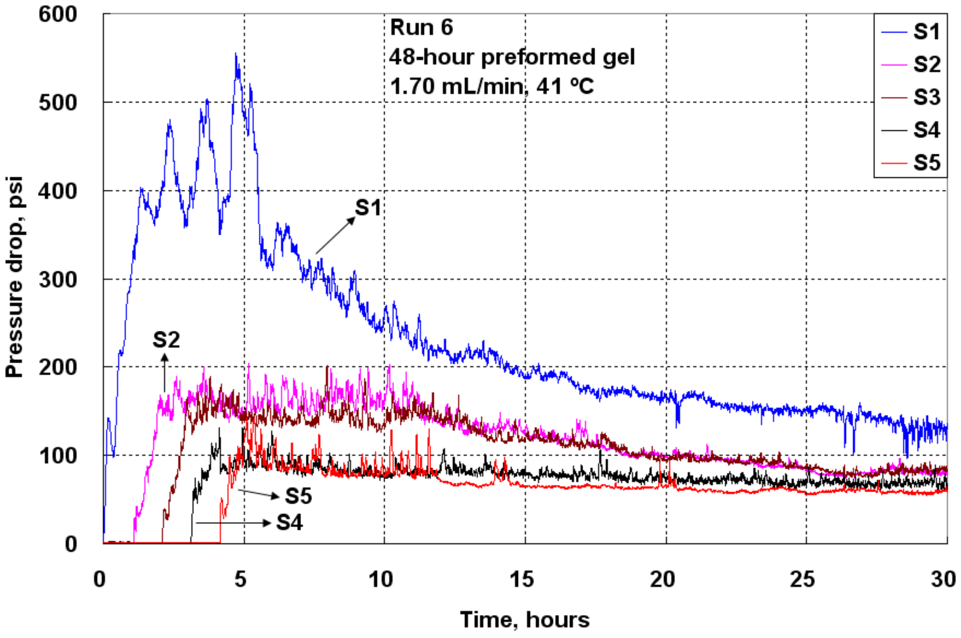

Figure 6.1 Pressure-drop data with time, Run 6

The pressure differentials in all the sections decreased with time after the section was filled with the preformed gel. S1 decreased from about 500 psi to about 133 psi (about 73% decrease), S2 and S3 from about 150 psi to 80 psi (about 47% decrease), S4 from 80 psi to 70 psi (about 13% decrease), and S5 from 80 psi to 60 psi (about 25% decrease).

As time went on, the pressure differential seemed to level off, which indicated that the resistance in each section might become stable after a certain time. Unfortunately, the running time was not long enough to confirm this observation.

Figure 6.2 shows the calculated apparent viscosity in each section at different time. The maximum apparent viscosity, excluding that in Section 1, was around 60 cp. The result was consistent with those obtained from the study of bulk-mixed gelant samples under continuous constant shear (as described in Chapter 4).

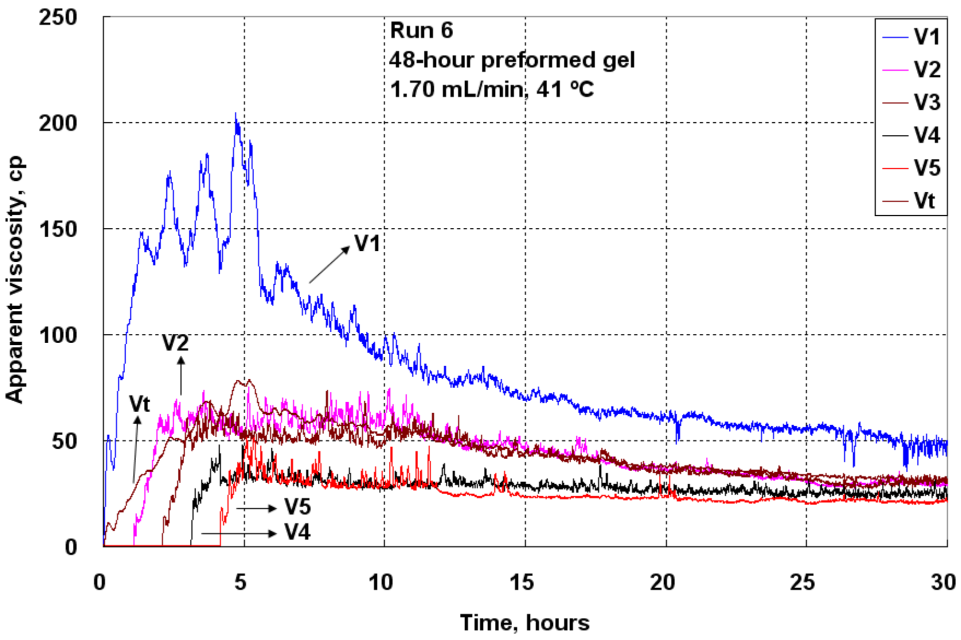

Figure 6.2 Apparent viscosity data with time, Run 6

As mentioned before, there was a 30-inch long tube between the outlet of transfer cylinder and inlet of the 1,031 ft tube. The pressure drop across this short tube was estimated to be between 20 psi and 35 psi.

The resistance factors in all the sections were plotted at different time in Figure 6.3. The resistance factor in the short tube is labeled as “DP”, and estimated using pressure drop of 20 psi for running time of 5 hours and 35 psi for running time of 10 hours. The flow rate of 1.70 mL/min was equivalent to superficial velocity of 4,948 ft/day in the 1,031 ft tube. As can be seen, the resistance factor was higher at upstream of the tube (DP and S1), and lower at downstream of the tube (S4 and S5).

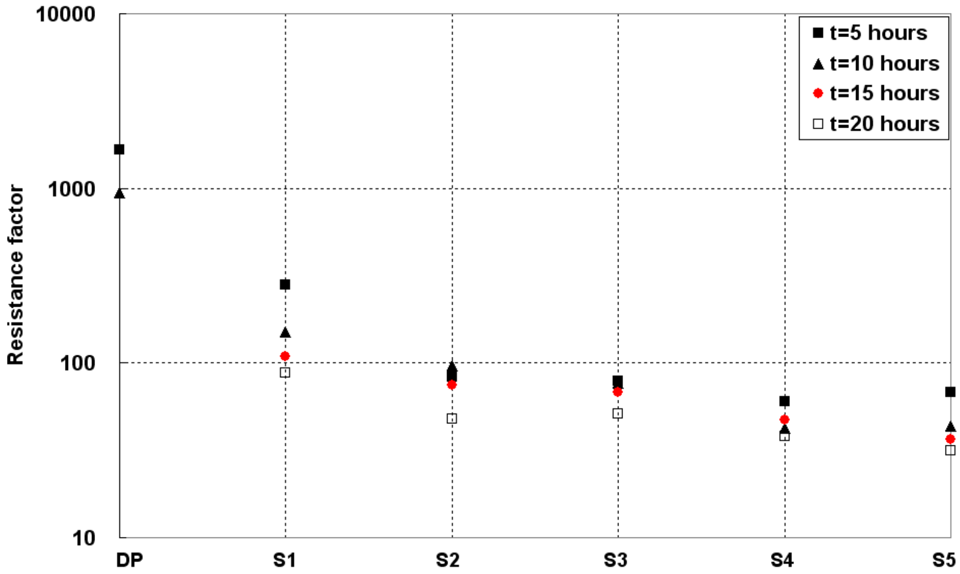

Figure 6.3 Resistance factors at different running time, at superficial velocity of 4,948 ft/day, Run 6

6.2.2 Comparing with Run 3

McCool's experiment of preformed gel, Run 3, used the similar experimental setup but performed at lower flow rate (0.36 mL/min). Details of Run 3 were reviewed in Chapter 2. The pressure-drop data excluding T1 is shown here in Figure 6.4 for convenience (same data as in Figure 2.22 excluding T1). Figure 6.5 shows the apparent viscosity data.

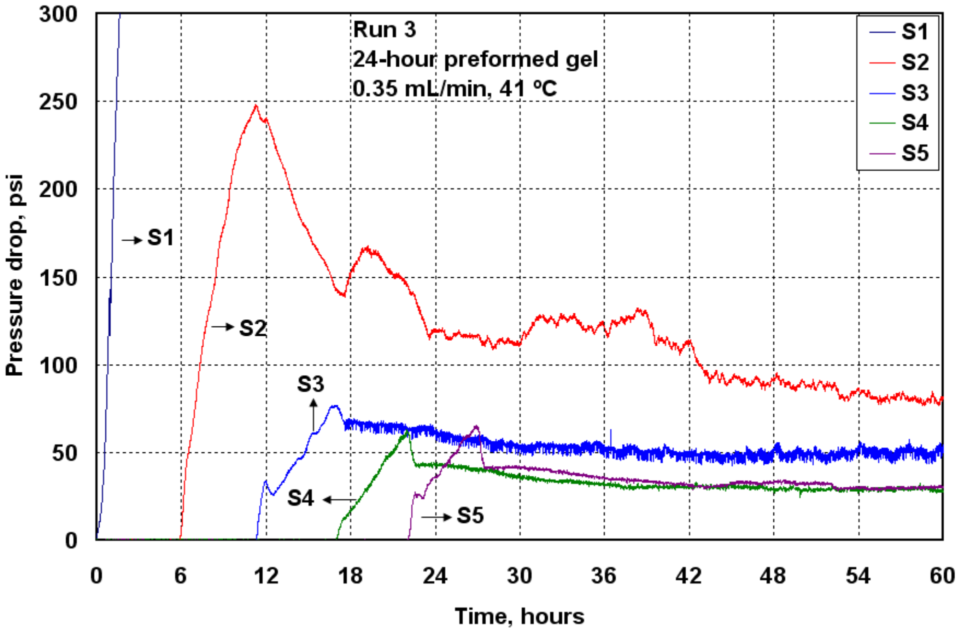

Figure 6.4 Pressure-drop data with time for preformed gel, Run 3, McCool[12]

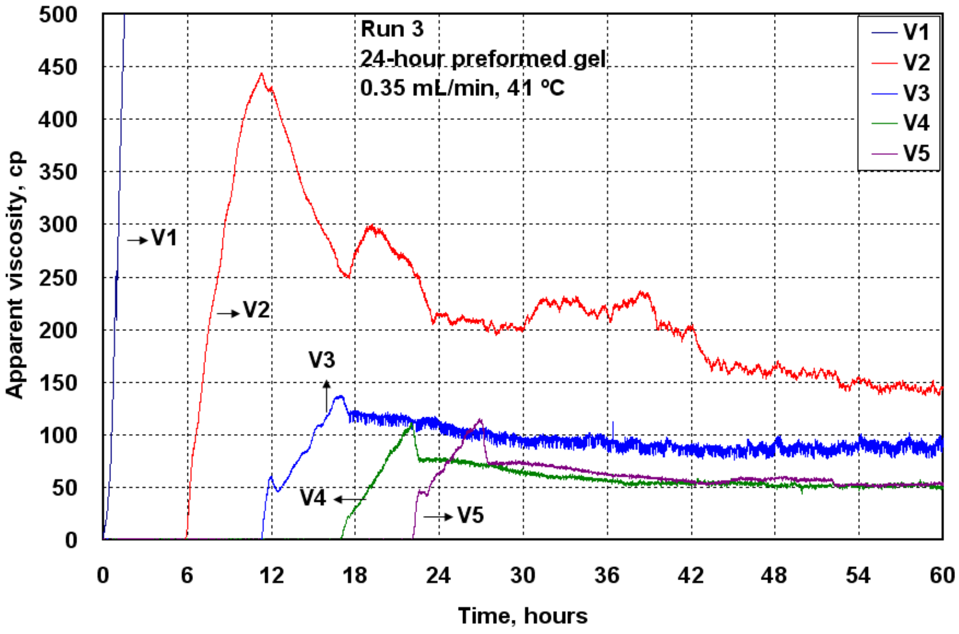

Figure 6.5 Apparent viscosity data with time for preformed gel, Run 3, McCool[12]

The pressure behavior in Run 6 was similar to that in Run 3. The major difference was between the pressure differentials in Section 1 of these two experiments. The pressure drop across section1 in Run 3 did not decrease in the first 60 hours and was much higher than that in Run 6. The difference was due to different flow rates which provided different shear thinning effects. The higher flow rate in Run 6, 1.70 mL/min, provided higher shear to the gel near the tube wall, which led to lower apparent viscosity than that obtained from Run 3 at flow rate of 0.36 mL/min.

The resistance factors in all the sections for Run 3 and Run 6 were estimated at running time of 24 hours, respectively. The results are plotted together with Seright's data in Figure 6.6. DP is estimated using pressure drop of 20 psi.

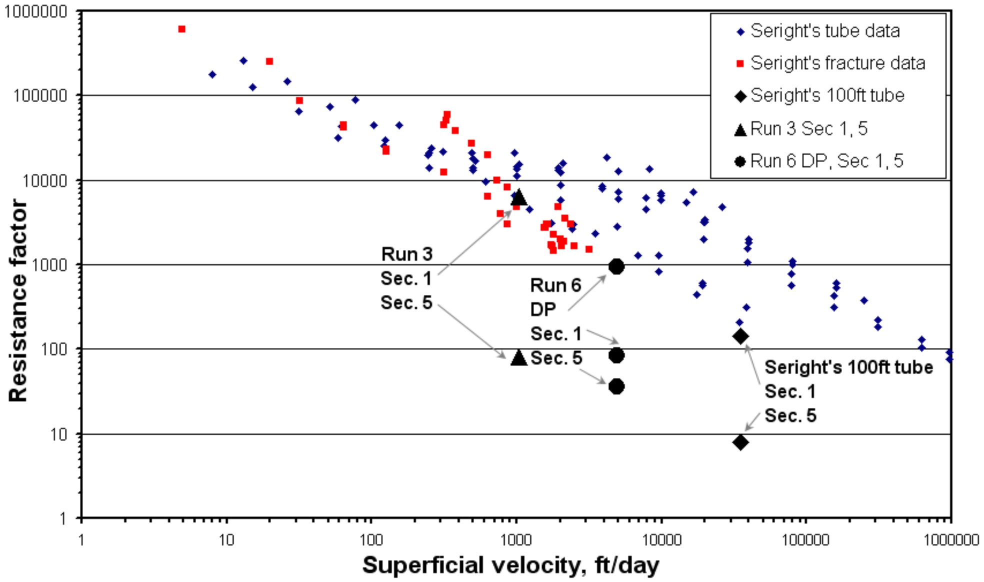

Figure 6.6 Resistance factors of preformed gel

As can be seen, the resistance factors were consistent with Seright's data and

McCool’s data. The resistance factors at downstream of the tube (S5) were much lower than those at upstream (DP in Run 6 or S1 in Seright’s and McCool’s data).

6.2.3 Comparing with in-line-mixed gelant flow

The results of in-line-mixed gelant flow experiments at different flow rates were discussed in Chapter 5. The resistance factors (from Run 4) were consistent with those from experiments of preformed gel flow (Run 6) as shown in Table 6.2 and Figure 6.7.

Table 6.2 Resistance factors of in-line-mixed gelant and preformed gel flow

Run No.	DP	Section 1	Section 2	Section 3	Section 4	Section 5
4	N/A	27	44	56	77	109
5	N/A	26	40	55	77	88
6	945	83	52	58	36	36

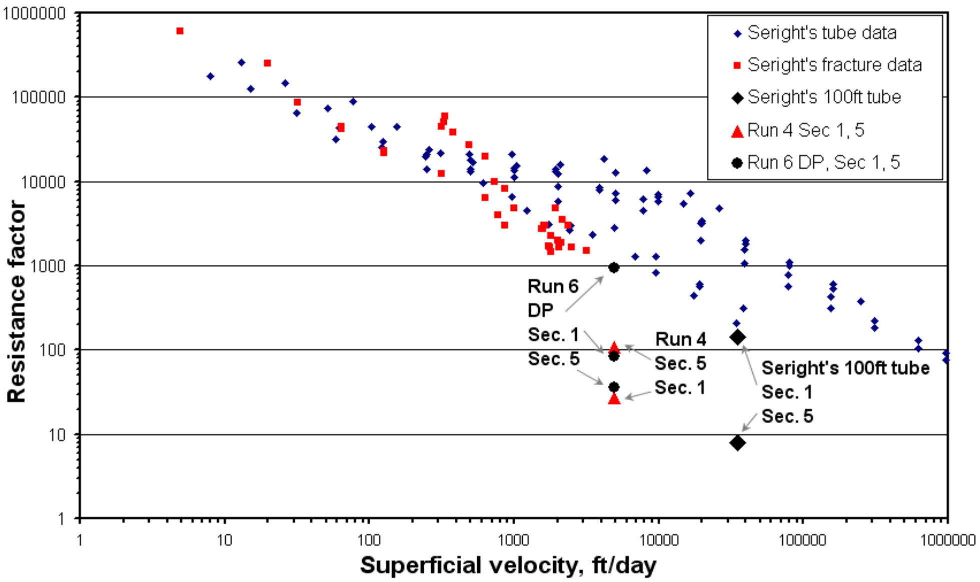

Figure 6.7 Resistance factors of preformed gel and in-line-mixed gelant

As can be seen, the resistance factors for preformed gel at upstream of the tube were greater than those for in-line-mixed gelant. However, at downstream of the tube, the resistance factors for preformed gel were lower than those for in-line-mixed gelant.

Among the in-line-mixed gelant flow experiments, Run 5 was performed under the same flow rate as preformed gel experiment Run 6. So the results are compared between these two experiments.

The apparent viscosity data of Run 5 was plotted in Figure 5.16, which is shown below for convenience.

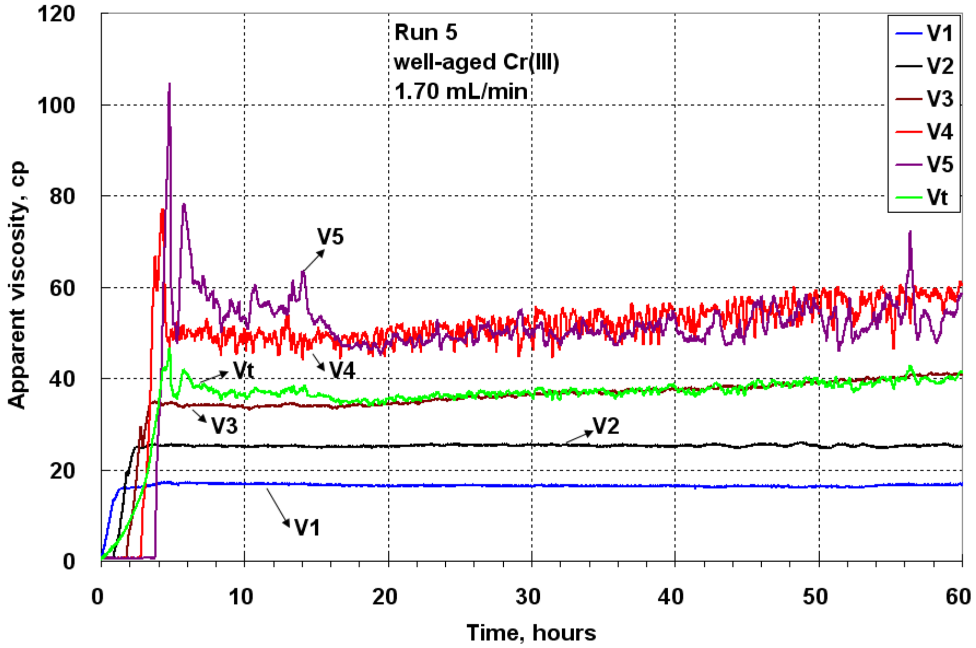

Figure 5.16 Apparent viscosity data with time, Run 5

As can be seen from Figure 6.2 and Figure 5.17, at running time of 24 hours, the apparent viscosity for preformed gel (Run 6) in Section 1 (53.4 cp) was higher than that for in-line-mixed gelant (Run 5) in Section 1 (16.6 cp), but close to those for in-line-mixed gelant in Section 4 (51.7 cp) and Section 5 (49.2 cp). The apparent viscosities in sections 2 and 3 between these two experiments were close (33.3 cp in Section 2 and 37.2 cp in Section 3 for preformed gel, and 25.3 cp in Section 2 and 35.3 cp in Section 3 for in-line-mixed gelant).

For preformed gel, the apparent viscosities at downstream of the tube were 23.3 cp in Section 4 and 22.8 cp in Section 5. For in-line-mixed gelant, the apparent viscosities at downstream of the tube were 51.7 cp in Section 4 and 49.2 cp in Section 5, which were higher than (even doubled) those of preformed gel.

6.2.4 Interpretation of flow behavior

The pressure behavior is interpreted as following based on results of Run 6 shown in Figure 6.1. First, the preformed gel was displaced into Section 1 from transfer cylinder to displace water. The pressure drop across Section 1 started increasing before it was filled with the preformed gel. Then it bounced around 400 psi due to the pressure reading when the preformed gel arrived at the pressure ports. That is, the pressure variation occurred when the preformed gel reached the end of one section, which is also the start of the next section.

After the whole tube was filled with the preformed gel, the pressure drop across

Section 1 started decreasing, because the gel was degraded by shear and some solvent was squeezed out from the gel to form a lubricant layer which helped to reduce the resistance. For in-line-mixed gelant, gel was formed steadily in Section 1 but the leveling off (or slightly decreasing) of apparent viscosity indicated the existence of lubricant layer. For preformed gel, however, the early significant decrease of apparent viscosity indicated broken of the gel. Later on, the slightly decreasing of apparent viscosity (or trend of leveling off) indicated the existence of lubricant layer.

The pressure differentials in other sections behaved similarly as that in Section 1, except with minor variations due to lower apparent viscosities. The pressure-drop data showed that the apparent viscosities of the preformed gel in Section 2 was nearly the same as that in Section 3, and those in sections 4 and 5 were close to each other.

6.3 Summary

Preformed gel was driven through the stainless steel tube to observe the pressure behavior in each section. The result shows that the pressure differential increases before the section is filled with preformed gel, and then decreases afterwards. The preformed gel is degraded by shear, and lubricant layer probably forms to help moving of the preformed gel which reduces the apparent viscosity of the gel.

The resistance factors are consistent with Seright’s and McCool’s data. The comparison between preformed gel and in-line-mixed gelant experiments shows that, the resistance factor of preformed gel flow is higher than that of in-line-mixed gelant flow at the upstream of the tube. At the downstream of the tube, however, the resistance factors of preformed gel flow are lower than that of in-line-mixed gelant flow.

Chapter 7

Observation of Syneresis

This chapter describes the observation of syneresis for bulk-mixed gelant samples as well as samples collected from flow experiments of in-line-mixed gelant and preformed gel.

After the samples were prepared or collected, some of the samples could not adhere on the wall of the vials (observed by placing the vials upset down) due to the expulsion of solvent from the gel. This phenomenon is called “syneresis”. After syneresis was observed for a sample, solvent was separated from the gel at a later time, and the weight percentage of the solvent, i.e., solvent/sample ratio, was calculated. Chromium concentrations of the solvent and separated gel were also measured.

7.1 Results and discussion

Bulk-mixed gel samples were more stable than effluent samples collected from flow experiments of in-line-mixed gelant and preformed gel. Effluent samples did not adhere on the wall of the vials after being collected, and the amount of solvent was measurable in two hours. For bulk-mixed gel samples, however, they were stable for four years without syneresis. The details are described below.

7.1.1 Bulk-mixed gel samples

After hand-mixing, the gelant samples were placed in 41 ºC air bath to gel. Then they were divided into two groups. One group was still kept in the air bath, and the other group was stored under room temperature.

Four samples which were stored under room temperature were still stable as observed on 06/19/2009. They could still adhere on the wall of the vials when placed upside down. They were sample g040820 prepared on 08/20/2004, sample g041020 prepared on 10/20/2004, sample g041021 prepared on 10/21/2004, and g041022 prepared on 10/22/2004. They were stable for more than four years.

Syneresis was observed for four samples after they have being stored under room temperature for about 180 days. They were sample g041019 prepared on 10/19/2004, g041024 prepared on 10/24/2004, g041025 prepared on 10/25/2004, and g041028 prepared on 10/28/2004. Syneresis was observed earlier for some other samples but all samples had been stable for at least 9 days. The syneresis of bulk-mixed gel samples was probably caused by the applied shear every time the vials were turned over. For example, sample g040728 was made on 07/28/2004. It was turned over every two days from 07/30/2004 to 08/08/2004. Then syneresis was observed on 08/10/2004. But it had already been stable for at least 11 days. Samples observed less frequently maintained stable for longer time.

Similar results were observed for samples stored in the 41 ºC air bath. Sample 20050412g07 prepared on 04/12/2005 and sample 20050419g09 prepared on 04/19/2005 were stable as observed on 07/06/2006, for a time period of 450 days. Syneresis was observed for some other samples, but they had been stable for at least 28 days. For example, sample 20050412G01 was prepared on 04/12/2005, and was observed to be stable till 05/10/2005 when syneresis occurred. The other samples in this group maintained stable longer than this sample.

For the bulk-mixed gel samples where syneresis occurred, more solvent came out as time went on, approaching a limit point. Figure 7.1 shows the solvent/sample ratio with time. At the time when syneresis was observed, only a tiny amount of solvent could be separated from gel. However, 23.8% solvent could be separated from gel 276 days after syneresis occurred (age of samples was 283 days), and 22.9% solvent could be separated from gel 707 days after syneresis occurred (age of sample was 721 days). The limit point of solvent/sample ratio seemed to be around 25%.

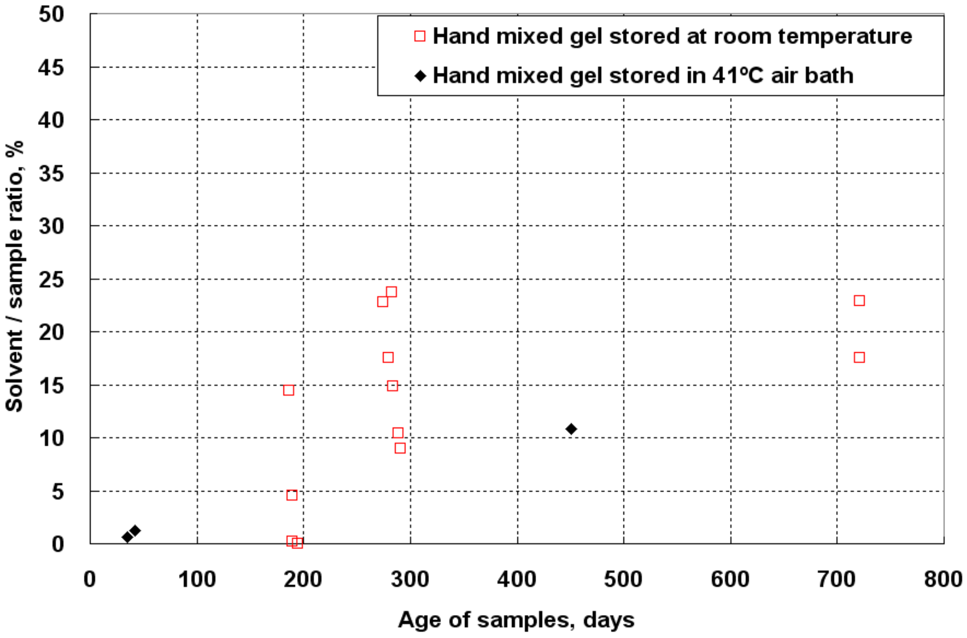

Figure 7.1 Percentage of solvent separated from bulk-mixed gel samples

7.1.2 Effluent from flow experiments

The effluent from flow experiments of in-line-mixed gelant emerged from the tube as spaghetti, which broke easily by gravity. Effluent samples did not adhere on the wall of the vials after being collected, and contracted so quick that the amount of solvent was measurable in two hours. Additional solvent came out as time went on, approaching a limit point. Effluents from flow experiments of preformed gel were similar to those from flow experiments of in-line-mixed gelant. Figure 7.2 shows the solvent/sample ratio with time.

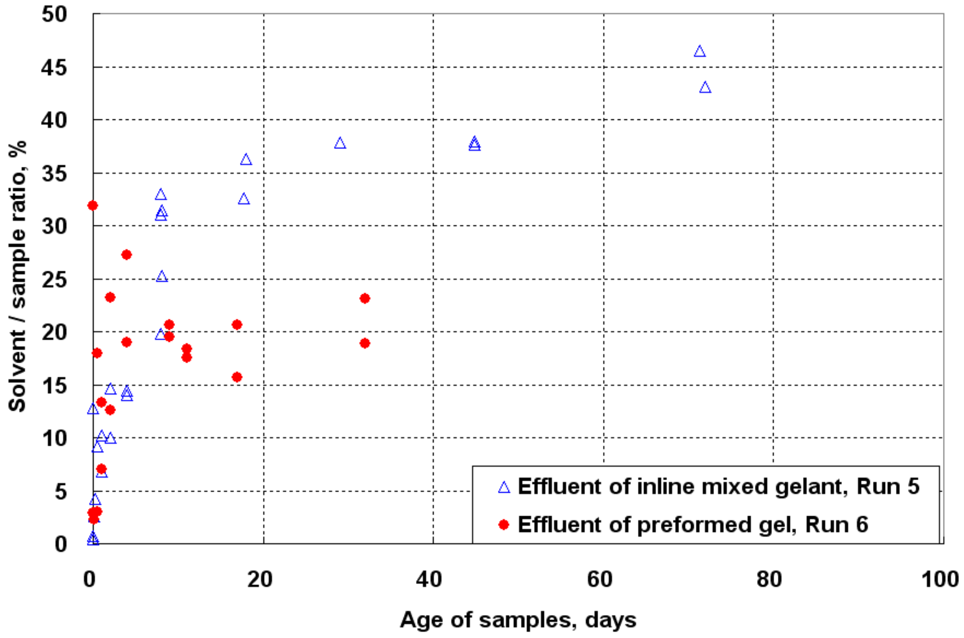

Figure 7.2 Percentage of solvent separated from effluent samples collected from flow experiments of in-line-mixed gelant (Run 5) and preformed gel (Run 6)

The data in Figure 7.2 shows that, at the same time, the percentage of solvent separated from the effluent sample from preformed gel experiment was lower than that of the sample from line mixed gelant experiment. Syneresis was more significant in the in-line-mixed gelant flow experiments than in preformed gel flow experiments.

Figure 7.3 shows more data points, which indicates that the percentage of solvent levels off after a certain time. For example, for effluent samples of in-line-mixed gelant flow experiment (Run 5), the percentage was around 40% at time of 45 days and 490 days.

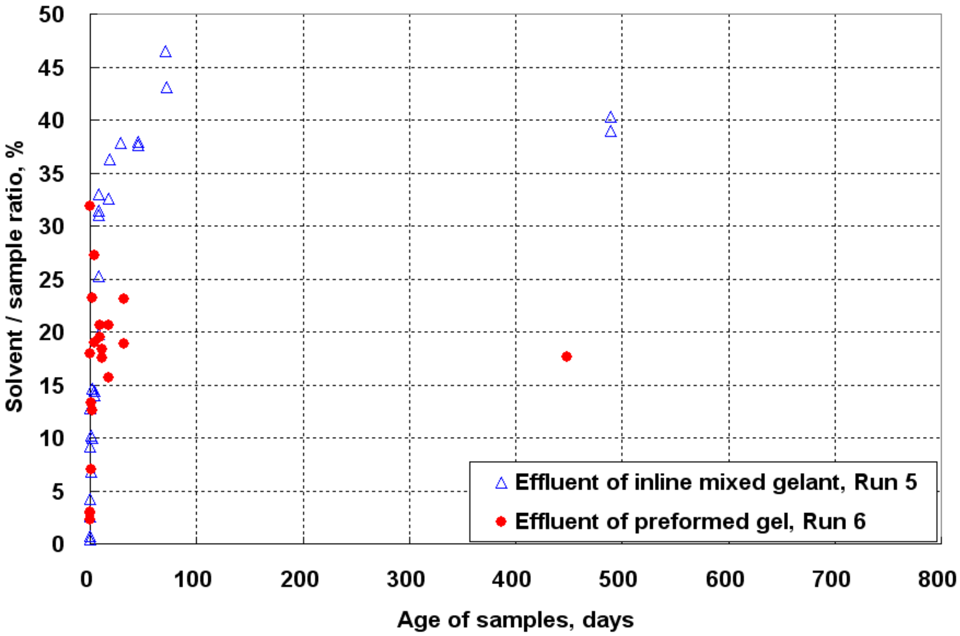

Figure 7.3 Percentage of solvent separated from effluent samples collected from flow experiments of in-line-mixed gelant (Run 5) and preformed gel (Run 6)

7.1.3 Comparing bulk-mixed samples and effluent samples

Data from Figures 7.1 and 7.3 are plotted together in Figure 7.4. As can be seen, syneresis was more significant in effluent samples than that in bulk-mixed samples. Syneresis occurred earlier and quicker in effluent samples than in bulk-mixed samples.

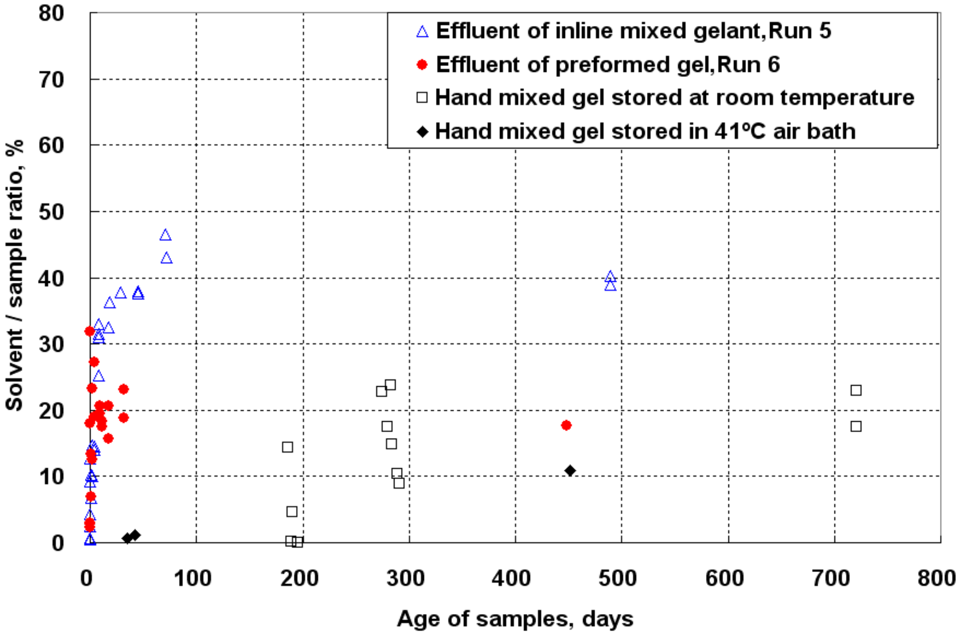

Figure 7.4 Percentage of solvent separated from bulk-mixed gel samples as well as effluent samples

Figure 7.5 shows the variation of the chromium concentration in the separated gel from effluent samples of experiment Run 5. The concentration of chromium in the gel became higher as the sample became older.

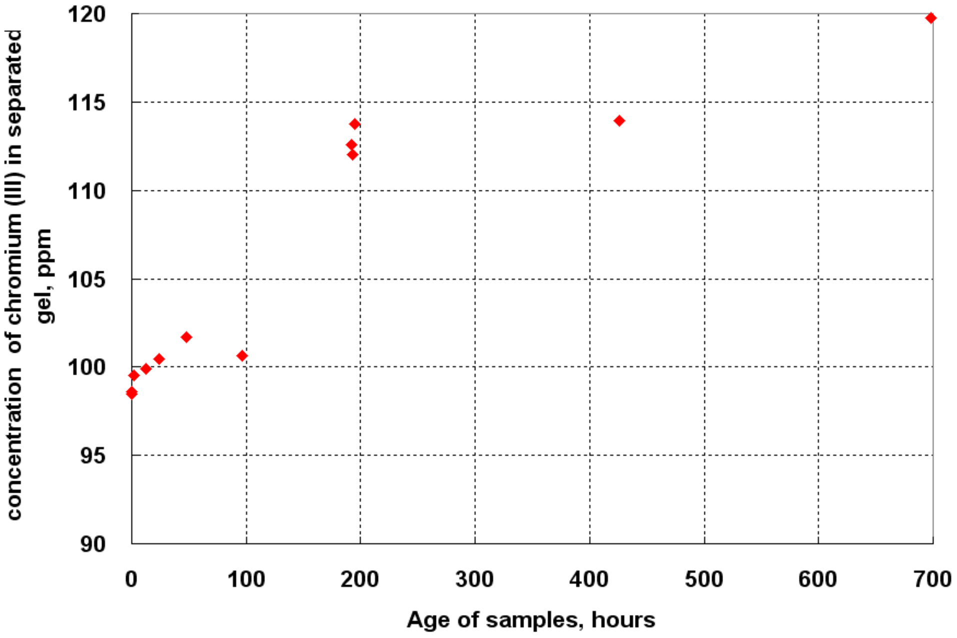

Figure 7.5 Concentration of chromium (III) in separated gel from effluent samples of Run 5

Chromium concentration in solvent was obtained only for samples 20050306G05 and 20050305G03. Gel was separated from sample 20050306G05 at age of 193 hours, and the chromium concentrations in separated gel and solvent were 112 ppm and 72 ppm, respectively. The chromium concentration in this sample before separation was 107 ppm, based on the calculation of material balance. Gel was separated from sample 20050305G03 at age of 698 hours. The chromium concentrations in gel and solvent were 120 ppm and 69 ppm, respectively. The chromium concentration in this sample before separation was 101 ppm, based on calculation of material balance.

7.2 Summary

Syneresis was studied for bulk-mixed gel samples as well as effluent samples from flow experiments of in-line-mixed gelant and preformed gel. The result shows that bulk-mixed gel samples are more stable than the effluent samples. A well-formed gel sample was able to remain stable for at least four years if no shear is applied. Even those contracted samples (due to applied shear when observing syneresis) were stable for at least 9 days. However, the effluent samples, which experienced continuous shear for only 24 hours before being collected, contracted quickly. This indicates that shear induces syneresis.

Once syneresis occurs (for both bulk-mixed gel samples and effluent samples), more solvent comes out as time goes on, till the amount of solvent levels off. And at the same time, the concentration of chromium (III) in the separated gel becomes higher.

Syneresis is more significant in effluent samples collected from in-line-mixed gelant flow experiments than in those collected from preformed gel flow experiments. That is, syneresis occurs more easily in gel samples formed from in-line-mixed gelant under continuous shear than in samples from preformed gel after experiencing continuous shear.

Chapter 8

Conclusions and Recommendations

This chapter describes the conclusions drawn based on the experimental data, and gives some recommendations for further study.

8.1 Conclusions

Effect of shear on formation of gel in a circular tube was studied by performing flow experiments of in-line-mixed gelant as well as preformed gel. The flow experiments were performed in a 1,031 ft stainless steel tube, in which the fluid experiences non-uniform shear, i.e., zero shear in the center and maximum shear at the tube wall. Viscosity behavior of bulk-mixed gel samples under continuous constant shear was also studied by using a Bohlin Rheometer. Some conclusions are drawn from this study as following.

1. For in-line-mixed gelant, the flow resistance (represented as pressure drop or apparent viscosity) first increases as gelation occurs then levels off. The flow resistances in downstream sections are higher than those in upstream sections.
2. For preformed gel, the flow resistances are higher in upstream sections than those in downstream sections. In each section, the flow resistance decreases

after the section is filled with gel.

3. Injection of in-line-mixed gelant produces a more structured gel than preformed gel, which results in higher flow resistances for the in-line-mixed gelant than for the preformed gel in downstream sections.
4. The solvent expelled from the gel forms a lubricant layer near the tube wall in downstream sections for both in-line-mixed and preformed gel flow, which reduces the flow resistance of gel in the tube.
5. Shear during formation of gel and breaking of preformed gel enhances syneresis, while bulk-mixed gel does not undergo syneresis if it experiences no shear.
6. The age of chromium (III) solution affects formation of gel. The gel time is 5.5 hours at 41 ºC for samples prepared by mixing 10,000 ppm polymer solution with 200 ppm freshly prepared chromium (III) solution by weight ratio of 1 to 1. However, the gel time is only 1.5 hours at 41 ºC for the samples prepared by using well-aged chromium (III) solution.

8.2 Recommendations

The in-line-mixed gelant solution experiences non-uniform shear in the stainless steel tube. However, only the apparent viscosity data were used in this study. If the information of shear distribution profile can be used in further study, more useful information may be obtained. For example, if the effluent can be collected in a way such that different parts of the effluent, which have experienced different shear, are collected in different containers. Then the properties of these different parts, such as viscosity and elasticity, will give some information of the gelation under different shear rate.

Another recommendation is to numerically simulate the pressure behavior of in-line-mixed gelant flow in the stainless steel tube. It is a flow problem with special fluid in a circular tube. Some assumptions of the properties of the fluid should be made, and pressure drop across the tube may be computed. The model may consider the effect of lubricant layer between the tube and gel. The results can be compared to those obtained from the experiments.

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Appendix A

Sample Calculations

This appendix provides the sample calculations for preparation of polymer solution, chromium solution, and bulk-mixed gel samples.

A.1 Preparation of polymer solutions

The following calculations apply to 10,000 ppm Alcoflood 935 (AF 935) and 2.0% NaCl.

Desired solution weight : 800 g

Desired polymer weight : 10,000 ppm × 800 g = 8.0 g

Desired NaCl weight : 2.0% × 800 g = 16.0 g

Desired Sodium Azide (NaN_3) : 8.0 g

Desired cold water (deionized) : 800 – 8.0 – 16.0 – 8.0 = 768.0 g

Tare container weight : 119.13 g

Weight of NaCl : 16.0027 g

Container + NaCl + water : 903.40 g

Weight of cold water : 903.40 – 119.13 – 16.0 = 768.27 g

Container + NaCl + water + NaN_3 : 911.12 g

Weight of Sodium Azide : 911.12 – 903.40 = 7.72 g

Weight of AF 935 : 8.0028 g

Total solution weight :

911.12 – 119.13 (container) + 8.0028 (AF 935) = 799.99 g

Polymer concentration : $10^6 \times 8.0028 / 799.99 = 10{,}003.6$ ppm

NaCl concentration : 16.0027 / 799.99 = 2.0 %

A.2 Preparation of chromium solutions

The following calculations apply to 200 ppm chromium (III) solution.

Desired solution weight : 1000 g

Desired chromium (III) : $1000 \times 200 \times 10^{-6} = 0.2$ g

Desired $Cr(OAC)_3$ solution containing 12.1% chromium (III):

0.2 / 12.1% = 1.6529 g

Tare container weight : 68.4923 g

Container with $Cr(OAC)_3$: 70.1496 g

Actual $Cr(OAC)_3$: 70.1496 – 68.4923 = 1.6573 g

Actual chromium (III) : 1.6573 × 12.1% = 0.2005 g

Actual solution weight needed : $0.2005 \times 10^6 / 200 = 1002.5$ g

Weight with added water : 1071.18 g

Actual solution weight : 1071.18 – 68.4923 = 1002.69 g

Chromium (III) concentration : $10^6 \times 0.2005 / 1002.69 = 199.9$ ppm

A.3 Preparation of bulk-mixed gel samples

The following calculations apply to bulk-mixed gel samples containing 5,000 ppm AF935, 100 ppm chromium (III), and 1% NaCl. The polymer solution used contains 10,000 ppm AF935 and 2.0% NaCl, and the chromium solution contains 200 ppm chromium (III).

Desired solution weight : about 20 g

Polymer solution weighed : 10.0122 g

Polymer with chromium (III) : 20.3489 g

Actual chromium (III) solution : 20.3489 – 10.0122 = 10.3367 g

With more polymer solution : 20.6407 g

Actual polymer solution : 20.6407 – 10.3367 = 10.3040 g

Polymer/chromium (III) weight ratio: 10.3040 / 10.3367 = 0.9968

Concentration of AF935 :

$$10.3040 \times 10{,}000 \text{ ppm} / 20.6407 = 4992 \text{ ppm}$$

Concentration of chromium (III) :

$$10.3367 \times 200 \text{ ppm} / 20.6407 = 100.2 \text{ ppm}$$

Appendix B

Flow of Water and Polymer Solution through Stainless Steel Tube

This appendix describes the experiments and results for flow of water and polymer solution through the stainless steel tube. Flow experiment of water was performed to determine the permeability of the tube. Flow experiment of polymer solution was performed to compare the pressure data with those from the experiment of in-line-mixed gelant flow.

B.1 Determine inner diameter and length of the tube

First, the pore volume of each section was obtained by calculating the volume of water in it. The pore volume of Section 1 is V_1=101.42 mL.

Second, the length of Section 1 was estimated by weight methods, assuming the weight distribution was uniform along the whole tube. The weight of the tubing of Section 1, excluding fittings, was 2,964.44 g. And the weight of a 1-ft long tube, with the same material and inner diameter, was 14.46 g. So the length of Section 1 was:

L_1 = 2964.44/14.46 = 205 ft.

This result was confirmed by another estimation method.

Third, the inner diameter of the tubing in Section 1 was calculated by

$$ID_1 = \sqrt{\frac{4V_1}{\pi L_1}} = \sqrt{\frac{(4)(101.42ml)}{\pi(205\,ft)(12in/\,ft)(16.39ml/in^3)}} = 0.0566(in.)\,.$$

Assuming the inner diameter was the same for every section, then ID=0.0566 in. was used to calculate the lengths for other sections.

$L_2 = L_1 \times (V_2/V_1) = (205) \times (101.58/101.42) = 205.3$ ft $\approx$ 205 ft

$L_3 = L_1 \times (V_3/V_1) = (205) \times (101.87/101.42) = 205.9$ ft $\approx$ 206 ft

$L_4 = L_1 \times (V_4/V_1) = (205) \times (102.55/101.42) = 207.3$ ft $\approx$ 207 ft

$L_5 = L_1 \times (V_5/V_1) = (205) \times (102.92/101.42) = 208$ ft

The length of Section 2 was also obtained using the same procedure for L1, and it gave $L_2 = 206$ ft which was pretty close to the one calculated above. So $L_2 = 205$ ft was used for all corresponding calculations. The total length of the whole tube was calculated to be 1,031 ft.

B.2 Flow of water through stainless steel tube

Pressure-drop data across the tube at different flow rates for water flow were recorded. Darcy's law was used to determine the permeability of the tube.

Darcy's law gives the relation between pressure differential and flow velocity as $\upsilon = \frac{k\Delta p}{\mu L}$, where velocity υ is in *cm/s*, viscosity μ is in *cp*, pressure differential Δp is in *atm*, length L is in *cm*, and permeability k is in *darcy*. From this relation, we can get $k = \mu \upsilon \frac{L}{\Delta p} = \mu \frac{Q}{\pi R^2} \frac{L}{\Delta p}$, where flow rate Q is cm^3/s, inner diameter R is in *cm*.

After changing the units (*cm* to *in.* and *ft*, *s* to *min*, and *atm* to *psi*), the formula becomes

$$k[darcy] = [cp]\frac{[cm^3/s]}{[cm^2]}\frac{[cm]}{[atm]} = [cp]\frac{[cm^3/\min]/60}{[in.^2]\times 2.54^2}\frac{[ft]\times 12\times 2.54}{[psi]\times 0.068046}$$

$$= 1.15716[cp]\frac{[cm^3/\min]}{[in.^2]}\frac{[ft]}{[psi]}$$

The ratio $QL/\Delta p$ should be a constant since μ and R are constants, which was confirmed by the straight line obtained by plotting $\Delta p/L$ (pressure gradient) versus Q, as shown in Figure B.1. The ratio $QL/\Delta p$ is the reciprocal of the slope.

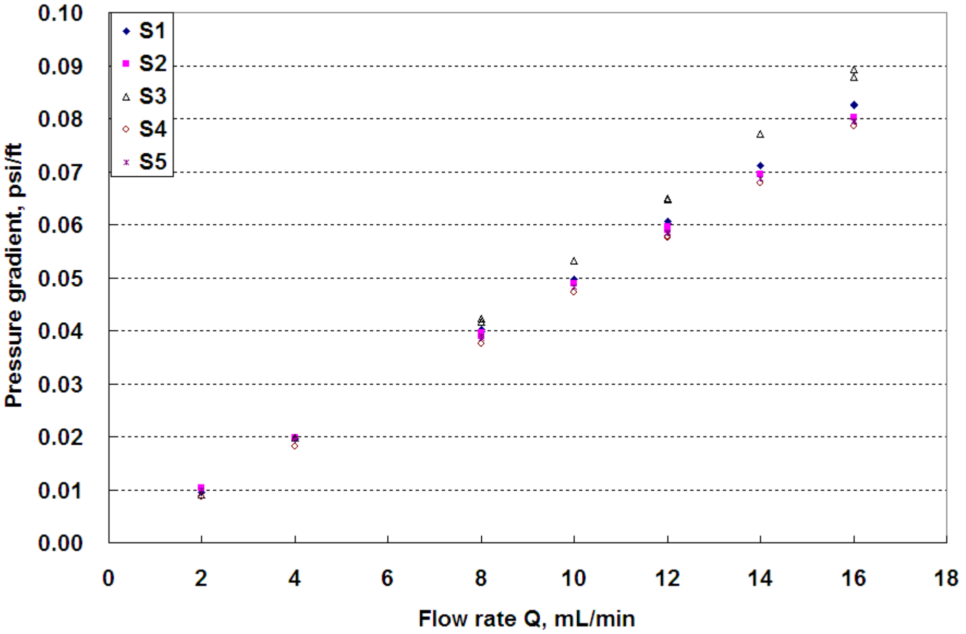

Figure B.1 Pressure gradients at different flow rates, water flow experiment performed on 03/13/2004 at 41 °C

The permeability was calculated for each section, and their average value, 5.91×10^4 darcys, was defined to be the permeability of the whole tube. 0.64 cp was used for the viscosity of water at 41 °C in the calculation.

B.3 Flow of polymer solution through stainless steel tube

Before the gel time, the viscosity of the in-line-mixed gelant solution increases slowly. Thus the gelant in Section 1 should behave similarly with polymer solution under the same condition. An experiment was conducted by in-line-mixing 10,000 ppm polymer solution with water at flow rate of 0.18 mL/min for each fluid.

Figure B.2 shows the result for an experiment E20040312 (performed on 03/12/2004). Figure B.3 shows the apparent viscosity data. The apparent viscosity in Section 1 is plotted in Figure B.4, together with that of in-line-mixed gelant flow experiment Run 1b. As can be seen in Figure B.4, in-line-mixed gelant solution behaves similarly in Section 1 as polymer solution.

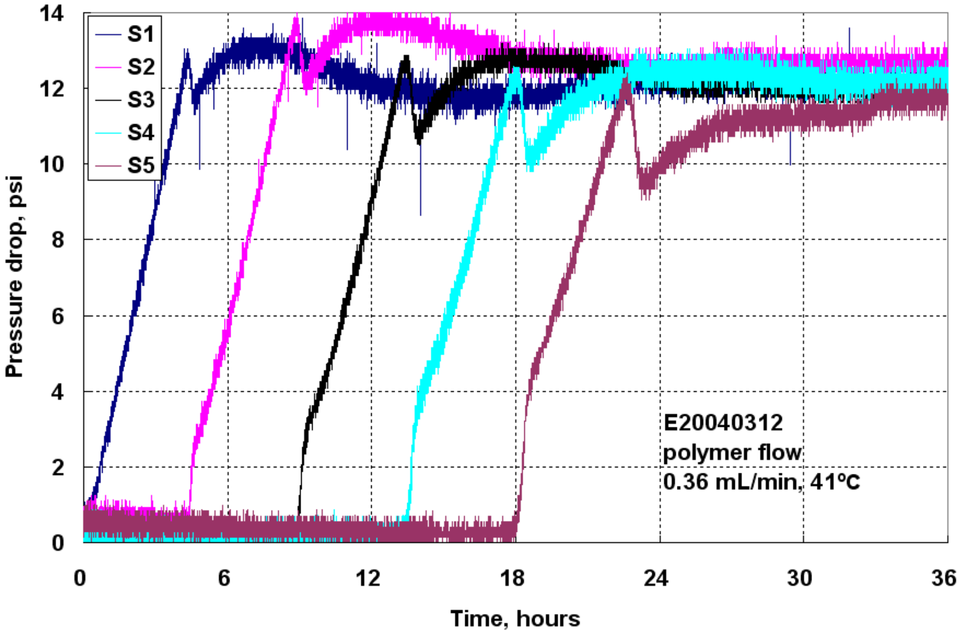

Figure B.2 Pressure-drop data with time for polymer flow experiment E20040312

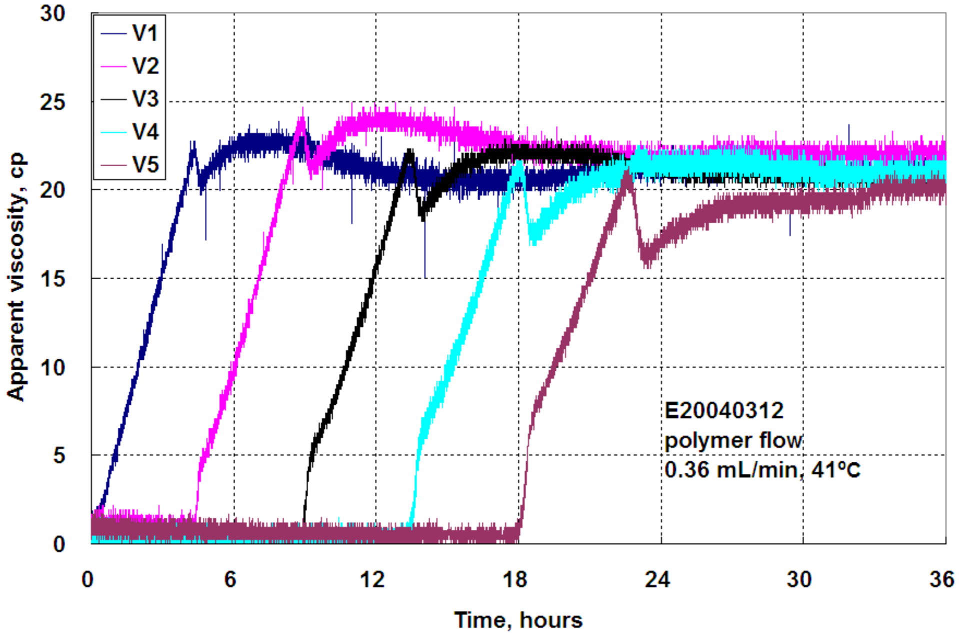

Figure B.3 Apparent viscosity for polymer flow experiment E20040312

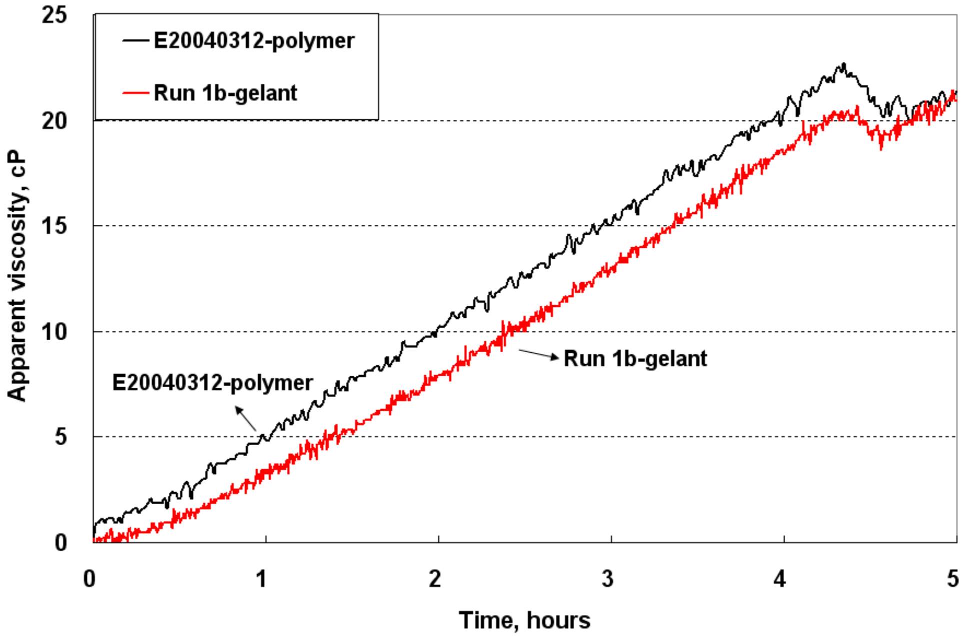

Figure B.4 Apparent viscosity in Section 1 for E20040312 and Run 1b

The pressure differentials of polymer solution at different flow rates were also obtained. Suppose power-law model can be applied for the polymer solution, the power-law index *n* can be obtained by plotting log(Δp) vs. log(Q), which is the slope of the straight line. Figure B.5 shows the result, which gives power-law index of approximately 0.8.

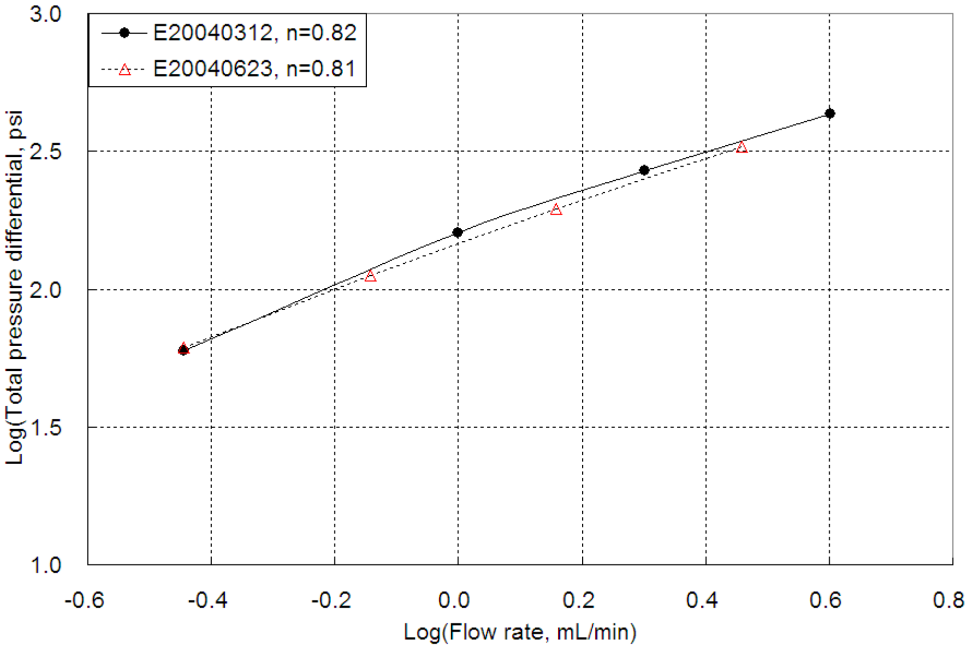

Figure B.4 Calculating power-law index of polymer solution

Appendix C

Estimation of Shear Rate at the Tube Wall

This chapter gives the detail of estimation of shear rate at the tube wall for the in-line-mixed gelant flow experiment at flow rate of 1.70 mL/min. Two methods were used: one used the data from polymer flow experiment, and the other used data from in-line-mixed gelant flow experiment directly.

C.1 Use data from polymer flow experiment

The in-line-mixed gelant in Section 1 is considered to be the same as 5,000 ppm polymer solution. So power-law index of polymer solution was used. The equations used are as following:

Power-law model:

$$\tau_{rx} = m\left|\frac{dv_x}{dr}\right|^{n-1} \cdot \frac{dv_x}{dr} = m\left|\frac{dv_x}{dr}\right|^{n} \tag{1}$$

Calculating shear stress in the tube using pressure gradient:

$$\tau_{rx} = \frac{r}{2}\left(\frac{p_1 - p_2}{x_2 - x_1}\right) = \frac{r}{2}\left(-\frac{dp}{dx}\right) \tag{2}$$

Combine equations (1) and (2) to obtain shear rate:

$$\frac{dv_x}{dr} = \left[\frac{r}{2m}\left(-\frac{dp}{dx}\right)\right]^{\frac{1}{n}} \tag{3}$$

Relationship between pressure gradient and flow rate:

$$Q = \int_0^R 2\pi r v_x dr = \frac{\pi n}{3n+1}\left[\frac{1}{2m}\left(-\frac{dp}{dx}\right)\right]^{\frac{1}{n}} \cdot R^{\frac{3n+1}{n}} \tag{4}$$

Combine equations (2) and (4) to present shear rate in flow rate:

$$\left.\frac{dv_x}{dr}\right|_{r=R} = \frac{Q}{\pi R^3}\frac{3n+1}{n} \tag{5}$$

where Q and R are in unit of cu ft/s and ft, respectively.

The power-law index was n = 0.80, based on the pressure data of polymer flow at different flow rate (see Appendix B).

Therefore, the shear rate at the tube wall at flow rate of 1.70 mL/min was:

$$\left.\frac{dv_x}{dr}\right|_{r=R} = \frac{3(0.8)+1}{0.8}\frac{\left(1.70\frac{mL}{\min}\right)\left(\frac{\min}{60s}\right)\left(\frac{ft^3}{28316.85\ mL}\right)}{\pi\left(\left(\frac{0.0566}{2}in\right)\left(\frac{ft}{12in}\right)\right)^3} = 103(s^{-1})$$

C.2: Use data from in-line-mixed gelant flow experiment

The average pressure drop in Section 1 was about 48 psi for in-line-mixed gelant flow experiment at flow rate of 1.70 mL/min. The apparent viscosity in Section 1 was about 17 cp calculated using Darcy’s law. Equation (6) gives the relationship between apparent viscosity and pressure drop:

$$\tau_{rx} = m\left|\frac{dv_x}{dr}\right|^{n-1} \cdot \frac{dv_x}{dr} = \mu_a\left|\frac{dv_x}{dr}\right| = \frac{\Delta PR}{2L} \tag{6}$$

Hence the shear rate was obtained as:

$$\left|\frac{dv_x}{dr}\right| = \frac{\Delta PR}{2\mu_a L} = \frac{(48\,psi)(6894.757\,pa/psi)(0.0566/2\,inches)}{2(17\,cp)\left(10^{-3}\,pa\cdot s/cp\right)(205\,ft)(12\,inches/ft)}$$

$$=112\left(s^{-1}\right)$$

Based on the above estimations, the shear rate was about 110 s^{-1} at the tube wall at total flow rate of 1.70 mL/min for in-line-mixed gelant flow.

Appendix D

Figures of Pressure Data

This chapter gives the figures of pressure-drop data for experiments discussed in Chapter 5.

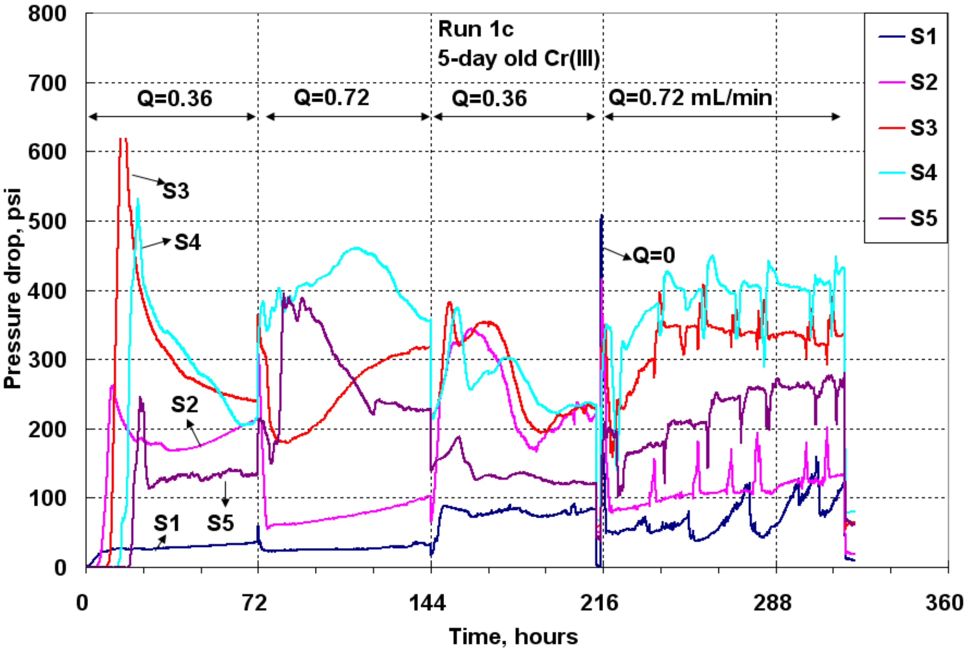

Figure D.1 Pressure-drop data with time, Run 1c

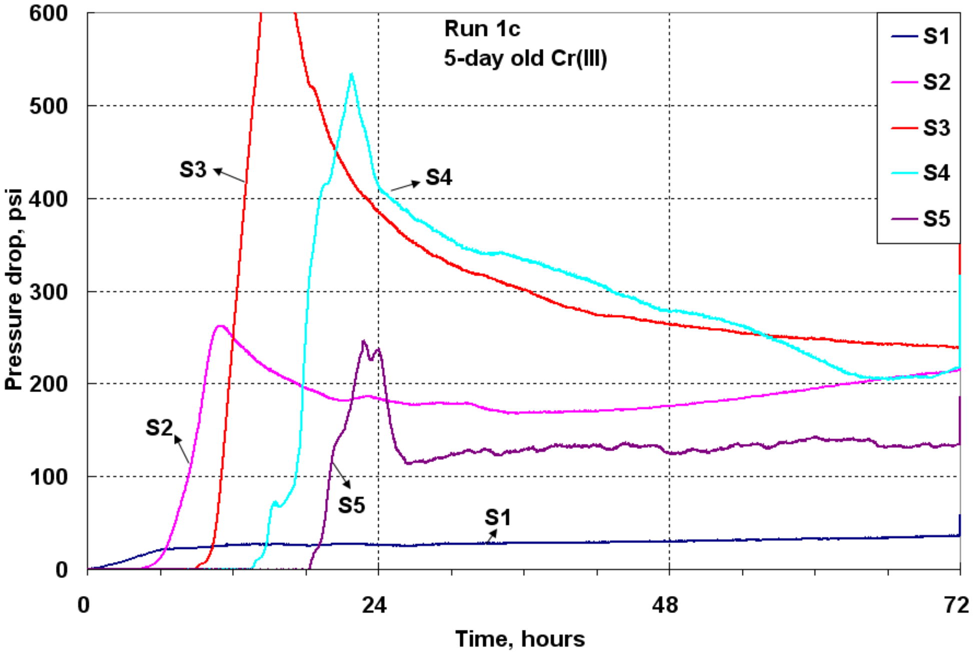

Figure D.2 Pressure-drop data with time in the first 72 hours, Run 1c

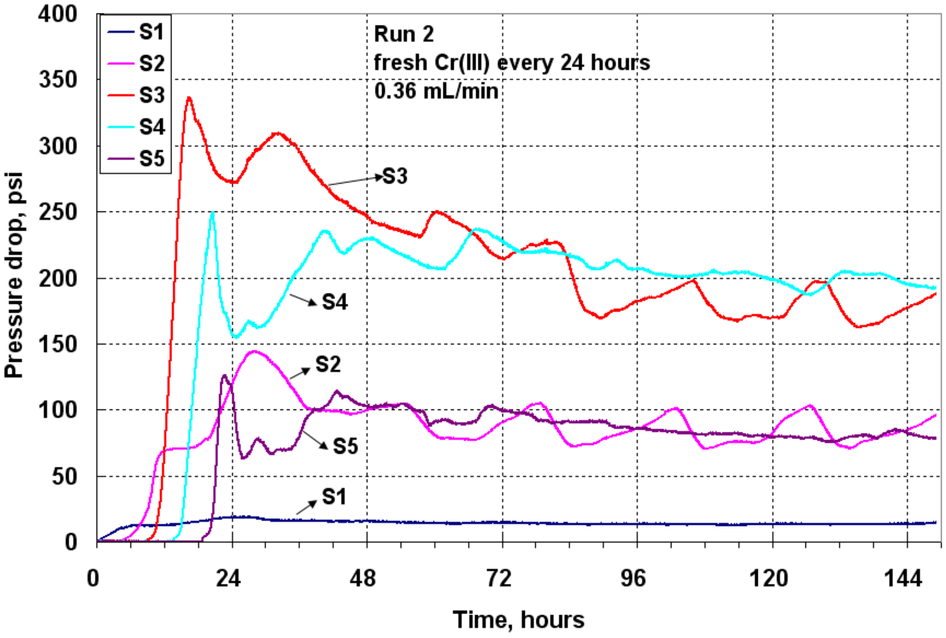

Figure D.3 Pressure-drop data with time, Run 2

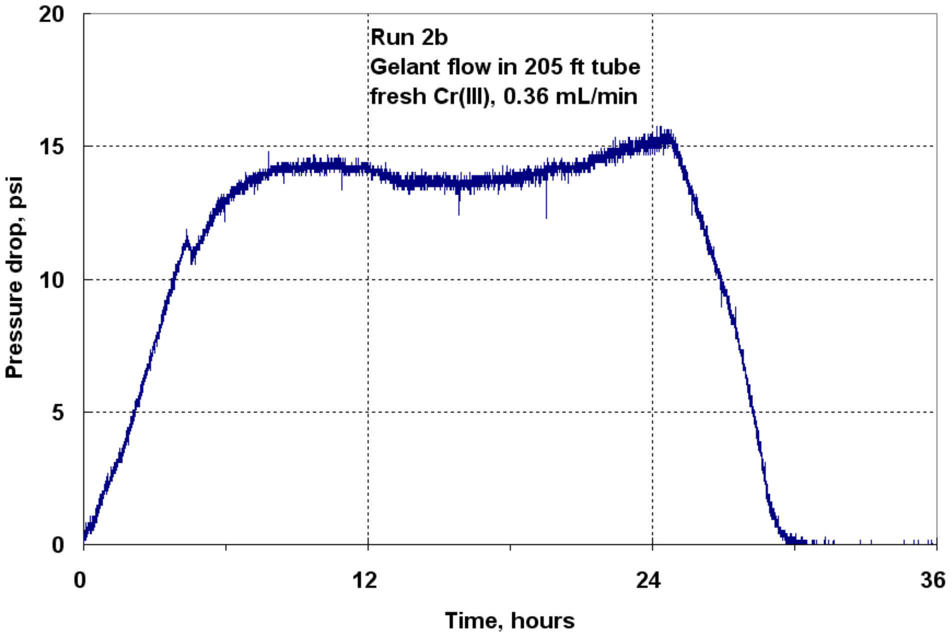

Figure D.4 Pressure-drop data with time, Run 2b