

**CROSSLINKING DRY XANTHAN GUM FOR
PROFILE MODIFICATION IN OIL RESERVOIRS**

Final Report

**By
T.R. French
H.W. Gao
K.M. Bertus**

October 1988

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**IFT Research Institute
National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma**



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**CROSSLINKING DRY XANTHAN GUM FOR PROFILE
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ABSTRACT

When large areas of oil saturation remain unswept in a petroleum reservoir, profile modification is necessary to redirect injected fluids into areas of high oil saturation. Gels made from xanthan biopolymer that is produced and transported to the field site as a liquid broth have been used for profile modification in many field projects.

This report discusses the use, for profile modification treatments, of xanthan biopolymer that is produced and transported in dry, solid form. The report is divided into three sections. Section I covers mixing procedures, section II covers crosslinking procedures, and section III addresses injection strategies.

The effects of reactant concentrations, pH, and salinity on crosslinking were investigated. The optimal conditions for crosslinking the powdered xanthan were identified for gel injection and for in situ gelation. The optimal concentration of polymer was found to be in the 1,400 to 2,000 ppm range. The transition zone from solid to pourable gels occurs at about 20 ppm chromium concentration.

BACKGROUND

The methods used for production of oil from subterranean petroleum reservoirs proceed through a series of sequential operations. When secondary and tertiary recovery methods are applied, sweep efficiency may be adversely affected by reservoir heterogeneities. Although much crude oil may remain within the reservoir, fluid flow can bypass some reservoir zones that contain oil. To reduce the mobility of injected fluids, various thickening agents have been used. These processes usually increase sweep efficiency but do little to improve fluid flow in reservoirs which contain stratified, heterogeneous zones.

When large areas of oil saturation remain unswept, some form of profile modification is needed to direct fluid flow away from the high-permeability

thief zones. Many laboratory and field studies have addressed this problem. Colloidal suspensions, precipitates, emulsions, acrylic/epoxy resins, and gelled polymers are some of the systems that have been reported to provide significant fluid diversion away from thief zones.¹⁻⁸

Much of the previous profile modification work has focused on gelled polymer systems. Gelled polymers can either be formed in situ or prepared on the surface prior to injection. Two types of processes have been used to create crosslinked gels in situ. The first type is based on a controlled release of an ionic crosslinking agent. Examples of this type include the chromium redox process and the high-pH aluminate (AlO_2^-)/ polyacrylamide system.^{1,9-11} The second type involves alternate injection of a polymer slug and a slug containing a crosslinker to build up crosslinked layers of polymer. An example of this type is the aluminum citrate process.² By changing the concentrations of reactants, gel time and gel strength can be controlled.^{2,12-14}

Because of their low cost, much of the early work was done using polyacrylamides. Polyacrylamides are not stable in high salinity reservoirs; hence, biopolymers, which are stable at high salinities, are desirable for use in many reservoirs. Since 1980, many successful field projects have been conducted with xanthan/Cr(III) gels.⁵ These gels are formed by the ionic bonding of Cr(III) at carboxyl groups on the xanthan molecule. Because of the pseudoplasticity of gels, they can be prepared before injection. Gel strength is redeveloped after the gels are injected into formations where the shear force is low. By varying the xanthan and chromium concentrations, gel strength, and to a lesser extent gel time, can be controlled. Biopolymer can also be gelled in situ in reservoirs, particularly with the chromium redox process previously mentioned.

INTRODUCTION

Most of the field projects in which biopolymer gels were used for profile modification were near commercial xanthan production facilities. The xanthan biopolymer was supplied in broth form, typically 5% active. Concentrated broth containing as much as 12% active xanthan gum is also available at a slightly higher cost premium. The use of a dried, essentially 100% active xanthan gum may be less expensive than the use of xanthan gum broth due to

lower freight charges. These transportation charges can be considerable if the profile modification job is located some distance from the broth manufacturing facility. In addition, storage of the xanthan gum prior to or during the job would be easier with dried xanthan gum, particularly in cold weather.¹⁵

Before conducting a field test, procedures for hydrating and crosslinking solid biopolymer must be determined. In addition, it must be determined that there is nothing unique to the dry formulation that would cause injection problems.

This report addresses these areas and is divided into three sections: Section I addresses the mixing procedures, section II addresses crosslinking procedures, and section III addresses strategies for injection. Two synthetic brines that are typical of many midcontinent reservoirs were used for most of the experiments. The dry biopolymer was furnished by a major xanthan manufacturer.

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SECTION I - MIXING PROCEDURES

The properties of polymer solutions prepared in laboratories have been shown to vary widely.¹⁶ These variances result from the use of different blenders, shear rates, additives, blending times, temperatures, and mixing procedures. The following procedure was used (after consultation with the polymer manufacturer) for mixing polymer in water with a Waring blender:

1. Weigh the required amount of makeup water, formaldehyde (biocide), and biopolymer.
2. Autoclave the water to remove dissolved oxygen.
3. Mix the water and formaldehyde slowly, under nitrogen, in a blending jar and adjust pH to between 8.5 and 9.
4. Sift the powdered polymer into the makeup water in the blending jar over a 30-second interval, while stirring at low speed with Variac power at 30% (36 volts).

5. Switch the blender speed to high speed and increase the Variac power to 50% (60 volts).
6. Blend for desired time.
7. Adjust the pH to a desired value.

Mixing raises the temperature of the solution. After cooling, the solution was degassed under vacuum to remove nitrogen.

The optimal blending time was determined from measurements of viscosity and filterability. Viscosity was measured with a Contraves Low Shear 30 viscometer and filterability tests using 6 μm filter paper and 20 psi pressure were performed with the apparatus shown in figure 1. Results of the viscosity measurements and filterability tests are shown in tables 1 and 2 and figures 2, 3, and 4.

TABLE 1. - Viscosity of 2,800 ppm biopolymer (22.4° C, deionized water) after mixing 45, 60, and 75 minutes

Shear rate, sec^{-1}	Viscosity, cP		
	45 min	60 min	75 min
0.0175	1344.6	1165.3	1187.7
0.0323	1338.7	1164.2	1172.3
0.0596	1303.9	1148.5	1159.5
0.110	1249.0	1101.0	1107.0
0.204	1153.2	1021.9	1018.7
0.376	1019.4	910.2	901.5
0.695	850.9	769.3	755.2
1.29	667.7	614.3	599.1
2.37	491.8	464.4	449.4
4.39	345.0	335.3	323.4
8.11	231.0	231.3	223.7
15.0	150.0	155.2	150.0
27.7	95.9	102.3	99.0
37.6	76.5	82.7	80.2

TABLE 2. - Viscosity of 2,800 ppm biopolymer (22.4° C, NBU brine) after mixing 45, 60, and 75 minutes

Shear rate, sec ⁻¹	Viscosity, cP		
	45 min	60 min	75 min
0.0439	9813.7	3836.3	4074.2
0.0596	8553.8	3653.4	3850.3
0.0811	7338.6	3452.1	3621.0
0.1102	6304.3	3196.5	3314.9
0.1498	5399.8	2939.4	3026.8
0.204	4516.9	2626.8	2739.0
0.277	3747.0	2356.6	2439.1
0.376	3094.5	2063.0	2149.7
0.512	2544.3	1785.5	1855.6
0.695	2082.8	1543.3	1590.2
0.945	1687.5	1314.8	1342.7
1.285	1355.6	1106.8	1122.1
1.747	1077.5	915.07	920.7
2.37	858.63	754.22	762.5
3.23	682.17	617.49	627.5
4.39	539.01	501.84	501.8
5.96	424.96	404.72	406.4
8.11	334.34	324.69	325.5
11.02	261.94	259.28	259.3
14.98	204.67	206.19	206.0

The effects of blending time on the viscosity of a 2,800 ppm biopolymer solution in deionized water are given in table 1. The solution viscosity stabilized after 60 minutes of blending. This is consistent with the filterability plots in figure 2. Blending times of 60 minutes and 75 minutes gave almost identical filtration curves. From these results, it was concluded that 60 minutes of blending was sufficient to fully mix and hydrate the polymer in deionized water.

The effect of blending time on the properties of polymer in brine was also determined. The NBU (North Burbank Unit, Osage County, Oklahoma) brine contained 26,160 ppm sodium, 5,525 ppm calcium, 612 ppm magnesium, and 51,906 ppm chloride and is typical of brines in many midcontinent reservoirs. When mixing NBU brine and polymer, the initial pH adjustment recommended by the polymer manufacturer was omitted because at high pH the brine was unstable. The viscosity data in table 2 and the filterability plots in figure 3 indicate that 60 minutes blending time is sufficient to mix polymer solutions in this brine. The viscosity of polymer solutions in brine is roughly three times the viscosity in deionized water. This effect is apparently real and may be due to weak crosslinking that can occur in strong brines.

Filterability tests were also performed on two biopolymer solutions (2,800 ppm) diluted from a more concentrated polymer solution (8,400 ppm in NBU brine). The resulting filterability curves are shown in figure 4 and differ from the curves in figure 3 by about 8%, which is not a significant difference.¹⁴

Based on these experiments, 60 minutes of blending was selected for mixing the polymer solutions used in the experiments described in sections II and III, Crosslinking Procedures and Injection Strategies.

The procedure for mixing polymer with chromium (III) was to add a pH adjusted chromium chloride stock solution to the pH adjusted polymer stock solution. In most cases, the design chromium (III) and polymer concentrations were obtained by mixing equal weights of chromium chloride and polymer stock solutions. Most of the solutions were stirred after addition of chromium chloride stock solution; some solutions were stirred during addition of chromium chloride stock solution; and an in-line mixer was occasionally used.

The procedure for mixing polymer with chromium (VI) and thiourea was similar to that outlined above for chromium (III), except that thiourea stock solution was added to the polymer stock solution before addition of the sodium dichromate stock solution. In-line mixing was not used.

The minor variations in gel mixing procedures outlined above did not appear to affect gel time or gel properties.

SECTION II - CROSSLINKING PROCEDURES

Crosslinking with Chromium Chloride

Bottle tests with two synthetic brines were conducted to determine the optimal conditions for crosslinking the biopolymer with chromium (III). The composition of NBU brine is given in section I. The composition of SHV (Shovel-Tum field, Carter County, Oklahoma) brine is 38,805 ppm sodium, 5,500 ppm calcium, 1,560 ppm magnesium, and 74,135 ppm chloride. Polymer concentrations from 700 to 7,980 ppm and chromium (III) concentrations from 5 to 1,200 ppm were tested. Most published results (for other xanthan polymers) concern gels produced with 800 to 4,000 ppm polymer and 40 to 400 ppm chromium.

The pH value was found to be an important variable. At pH 3, gels were produced, but were extremely unstable. Because of the high ionic strengths of the brines, chromium precipitation was a problem when the pH was raised above 5. (Chromium hydroxide precipitation at lower salinities would not occur until \approx pH 5.7.) The results of experiments performed at pH 4 are given in tables 3 through 7.

Several observations can be made after examination of tables 3 through 7. All gels produced with 700 ppm polymer eventually broke down. Most gels produced with 1,000 ppm polymer broke; however, at chromium concentrations between 50 and 100 ppm, the 1,000 ppm polymer gels were stable (table 4).

Another observation noted was that gels synerese (spontaneous separation of a liquid from a gel due to contraction of the gel) more at elevated temperatures (tables 5 and 6). Even so, the gels were not completely broken at 50° C. At lower chromium levels, stability at 50° C was good. A gel produced with 2,000 ppm polymer and 25 ppm chromium (III) remained stable at 50° C for more than 3 months of observation.

Gelation occurred at chromium (III) concentrations as low as 5 ppm. The transition zone from solid to pourable gel occurred at about 20 ppm chromium (III). See tables 8 and 9.

The viscosity data in table 9 show that both the polymer and the crosslinked polymer are pseudoplastic; thus, it should be possible to make a gel on the surface and inject that gel into a reservoir. Shear thinning would occur as a result of high shear rates that result from pumping and injecting

TABLE 3. - Gel stability, pH 4, NBU brine, 25° C, chromium chloride crosslinker, 8 months

Polymer, ppm	Chromium, ppm						
	100	200	400	600	800	1,000	1,200
7,980	9/10 S ¹	S	S	S	S	S	S
5,000	S	7/8 S	9/10 S	9/10 S	S	9/10 S	S
2,800	S	S	9/10 S	S	S	9/10 S	1/2 S
1,400	S ₂	1/2 S	S	1/2 S	S	S	S
700	B ²	B	B	B	B	B	B

¹Solid gel (for example, 9/10 S = 1/10 water, 9/10 gel).

²Broken gel.

TABLE 4. - Gel stability, pH 4, NBU brine, 25° C, chromium chloride crosslinker, 3 months

Polymer, ppm	Chromium, ppm			
	25	50	75	100
2,000	S ¹	S	9/10 S	9/10 S
1,400	S ₂	7/8 S	S	S
1,000	B ²	1/2 S	S	S

¹Solid gel.

²Broken gel.

TABLE 5. - Gel stability, pH 4, NBU brine, 50° C, chromium chloride crosslinker, 2 months

Polymer, ppm	Chromium, ppm				
	400	600	800	1,000	1,200
2,800	1/2 S ¹	1/2 S	1/2 S	1/2 S	1/2 S
2,000	1/3 S	1/3 S	1/3 S	1/2 S	1/2 S
1,400	1/3 S	1/3 S	1/3 S	1/3 S	1/4 S
1,000	B ²	1/4 S	B	B	B

¹Solid gel.

²Broken gel.

TABLE 6. - Gel stability, pH 4, SHV brine, 25° C, chromium chloride crosslinker, 7 months

Polymer, ppm	Chromium, ppm				
	400	600	800	1,000	1,200
2,800	B	3/4 S	3/4 S	3/4 S	3/4 S
2,000	3/4 S ¹	3/4 S	S	3/4 S	3/4 S
1,400	1/2 S	3/4 S	S	1/2 S	1/2 S
1,000	B ²	1/2 S	B	B	B

¹Solid gel.
²Broken gel.

TABLE 7. - Gel stability, pH 4, SHV brine, 50° C, chromium chloride crosslinker, 2 months

Polymer, ppm	Chromium, ppm				
	400	600	800	1,000	1,200
2,800	1/4 S ¹	1/3 S	1/2 S	1/3 S	1/3 S
2,000	1/3 S	1/2 S	1/2 S	1/2 S	1/2 S
1,400	1/3 S	1/3 S	1/2 S	1/3 S	1/4 S
1,000	1/4 S	3/4 S	B ²	1/3 S	B

¹Solid gel.
²Broken gel.

TABLE 8. - Gel stability, pH 4, NBU brine, 25° C, chromium chloride crosslinkers, 2 months

Polymer, ppm	Chromium, ppm			
	5	10	15	20
2,000	L ¹	P ²	P	9/10 S

¹Gel detectable only through viscosity measurement.
²Pourable gel.

TABLE 9. - Viscosity of 2,000 ppm biopolymer and 2,000 ppm biopolymer chromium chloride gels - pH 4, 22.4° C, cP

Shear rate, sec ⁻¹	Polymer	No visible gel			Pourable gels								Firm gel	
		5 ppm Cr			10 ppm Cr			15 ppm Cr		20 ppm Cr		25 ppm Cr ¹		
		2 day	4 day	8 day	2 day	4 day	8 day	2 day	8 day	2 day	8 day	2 day	6 day	
0.017	919	2936	2913	2809	57705	44820	49302	59386	78061	90013	203,560	-	-	
0.024	934	2891	2797	2764	44236	36268	37917	41489	55639	54677	-	32591	63195	
0.044	928	2587	2492	2474	28846	23122	23122	23493	30854	28623	-	17062	33084	
0.081	885	2213	2140	2140	16657	14726	14283	12996	17341	14363	-	9998	17301	
.277	778	1402	1343	1365	5892	5291	5279	4737	5302	4242	-	3181	4401	
.945	556	767	745	752	2298	1829	2036	1839	1898	1553	-	628	971	
3.23	315	364	360	360	865	754	839	728	761	647	-	-	305	
11.02	22	157	155	155	-	-	-	311	-	-	-	-	(108)	
37.6	66	65	64	64	-	-	-	-	-	-	-	-	-	

¹Firm gel stable more than 3 mo. at 25° and 50° C.

into a petroleum reservoir. When in place, the gel reheals at low shear rates. This process has been successful in many field projects conducted with other biopolymer gels.⁵

Based on the results given in tables 3 through 9, the chromium (III)/polymer gel should contain 1,400 to 2,000 ppm polymer and 5 to 25 ppm chromium (IV) at pH 4. The pH of most midcontinent reservoirs is between 5 and 7. To avoid precipitation problems in a reservoir, pH adjustment with a small slug of polymer is needed before injection of the chromium (III)/polymer gel system. The preferred preflush would consist of a dilute, uncrosslinked, pH adjusted polymer solution that would effectively displace the reservoir brine. The screening tests performed with chromium chloride crosslinker are summarized in table 10.

TABLE 10. - Summary of chromium chloride and dichromate/thiourea crosslinker systems tested

No.	Polymer, ppm	Crosslinker, ppm	pH	Temp., °C	Brine	Condition	Results
<u>CrCl₃</u>							
1.	700 - 7980	100 - 1200	3	25	NBU	anaerobic	All samples gelled, but were unstable.
2.	700 - 7980	100 - 1200	4	25	NBU	anaerobic	All samples gelled within 1 hr. After 1 mo. there was very little change in gel quality. After 8 mo. the most stable gels were obtained at 1,400 and 2,800 ppm polymer and less than 800 ppm Cr.
3.	1000 - 2800	400 - 1200	4	25	SHV	anaerobic	Most stable gels were obtained at 1,400 to 2,000 ppm polymer, 800 Cr.
4.	1000 - 2800	400 - 1200	4	50	NBU	anaerobic	All gels broke or syneresed.
5.	1000 - 2800	400 - 1200	4	50	SHV	anaerobic	All gels broke or syneresed.
6.	1000 - 2000	25 - 100	4	25	NBU	low O ₂	All gelled within 24 hr, except 25/1000 which took 48 hrs. Most stable gels at 1400 and 2000 polymer, 25 ppm. 2000/25 sample not in agreement with repeats.
7.	2000	5 - 20	4	25	NBU	low O ₂	After 2 mo. 5 ppm was a liquid, 10 and 15 were pourable gels, and 20 was a firm gel.
8.	2000	5 - 25	4	25/50	NBU	low O ₂	Transition from pourable gel to firm gel occurred at 20 ppm. 25 ppm sample stable at 50° C.
<u>Dichromate/Thiourea</u>							
1.	1400 - 3400	300 - 1200	4, 5, 6	25	NBU	aerobic and anaerobic	Gel time for all samples was 72 hrs or less. All samples gelled. Higher pH gave lower gelation time.
2.	1000 - 2000	25 - 100	6		NBU	low O ₂	Gel time varied from 7 to 17 days.

Crosslinking with Dichromate/Thiourea

The controlled release of chromium (III) by reduction of sodium dichromate is a procedure that has been used to cause the crosslinking reaction to occur in situ in petroleum reservoirs.^{10-11, 17-18} This process enhances injection into reservoirs and results in deeper penetration because viscosity remains low, for a period of time, even at low shear rates.

The reduction reaction between thiourea and dichromate occurred at a slow rate to produce chromium (III). The slowness of this reaction and subsequent removal of the chromium (III) from solution by the crosslinking reactions were presumed to be the reasons for the absence of precipitation problems in brine at pH 5 and 6 with this crosslinker system.

The biopolymer forms gels with dichromate/thiourea crosslinker. Examination of table 11 reveals stable gels at 1,400 and 2,000 ppm polymer concentrations and 25 to 100 ppm chromium (VI) concentration. This is very similar to the results obtained for similar concentrations of polymer and chromium (III). No samples were prepared containing less than 25 ppm chromium (VI); however, it is expected that gelation would be detected at chromium concentrations as low as 5 ppm.

Gelation time (at 25° C) is given in table 12. All of the samples gelled in 7 to 17 days. Before this system is used in a reservoir, experiments should be performed at the reservoir temperature. Gel time will decrease at higher temperatures and gelation time in porous media appears to occur faster than gelation in a beaker.¹¹

TABLE 11. - Gel stability, pH 6, NBU brine, 25° C, dichromate thiourea crosslinker, 3 months

Polymer, ppm	Chromium, ppm			
	25	50	75	100
2,000	S ¹	S	S	S
1,400	S	1/2 S	3/4 S	S
1,000	B ²	1/2 S	B	3/4 S

¹Solid gel.

²Broken gel.

TABLE 12. - Gel time (days), pH 6, NBU brine, 25° C, dichromate/thiourea crosslinker

Polymer, ppm	Chromium, ppm			
	25	50	75	100
2,000	9	7	7	7
1,400	17	9	9	7
1,000	17	17	9	9

The recommendations for an in situ gelling system are similar to those for the other chromium systems previously described, except that the pH of injected fluids can be higher. Based on the results listed in tables 11 and 12 and the results of experiments with chromium (III) systems, the optimal polymer concentration was found to be between 1,400 and 2,000 ppm, and the optimal chromium (VI) concentration, between 10 and 25 ppm, at pH 6. Table 10 summarizes the experiments conducted with dichromate/thiourea crosslinking systems.

The thiourea concentration in these experiments was always 4 moles of thiourea per mole of dichromate. Stoichiometrically, 6 moles of thiourea are required for each mole of dichromate; however, it has been shown¹⁰ that the rate of reduction (in the presence of polyacrylamide) is:

$$\text{rate (moles/hr)} = k[\text{Cr}_2\text{O}_7^{2-}][\text{NH}_2\text{CSNH}_2][\text{H}^+].$$

Therefore, at a given temperature, gelation rates can be controlled by varying the reducing agent concentration and pH.

Other Crosslinkers

Several other potential crosslinking systems were tested with the biopolymer. The primary purpose of these experiments was to identify crosslinkers that can be used in the pH 6 to 7 range. The results of these experiments are summarized in table 13. No gels were observed in the chromium

chloride/citrate systems made with deionized water. When brine was used, precipitation occurred. No gels were observed in the aluminum/citrate systems. Aluminum chloride (without citrate) did form weak gels. Only high aluminum chloride concentrations at pH 4 were tested. Iron (III) chloride and iron (III) mixed with citrate would not gel when deionized water was used. In brine, precipitation occurred. No gel tests were performed with chrome alum.

Chromium chloride/citrate, aluminum chloride/citrate, iron chloride, and chrome alum all appeared to be unsuitable for use as crosslinking agents in brine. Aluminum chloride appeared to form weak gels on mixing with the polymer and should be tested further.

TABLE 13. - Summary of other crosslinker systems tested

No.	Polymer, ppm	Crosslinker, ppm	pH	Temp., °C	Brine	Condition	Results
<u>CrCl₃/Citrate</u>							
1.	1400	600 - 1200	6, 7	25	DIW ¹	anaerobic	No gels in 6 mo.
2.	1400	600 - 1200	6	25	NBU	anaerobic	Precipitation overnight.
<u>Al Citrate</u>							
1.	700 - 7980	1000 - 1200	3, 4, 7	25	NBU	anaerobic	No gels in 9 mo.
<u>AlCl₃</u>							
1.	2000	1000 - 2000	4	25	NBU	low O ₂	Very weak gel (which formed on mixing)
<u>FeCl₃</u>							
1.	1000 - 2800	100 - 1200	6, 7	25	NBU	anaerobic	Precipitation - no gels in 7 mo.
<u>FeCl₃/citrate</u>							
1.	1400	800 - 1200	6, 7	25	DIW	anaerobic	No gelation in 7 mo.
2.	1000 - 2800	100 - 1200	7, 8	25	NBU	anaerobic	Precipitation, esp. above 200 ppm iron. No gels.
<u>Chrome alum</u>							
1.			7		DIW, NBU		Precipitation, no gel tests.

¹DIW = deionized water.

SECTION III - INJECTION STRATEGIES
Polymer Crosslinked with Chromium Chloride

One property of xanthan polymers and xanthan gels is pseudoplasticity. Shear thinning of the gel permits injection into petroleum reservoirs at normal injection pressures. When in place, the gel reheals at low shear and produces a high-viscosity plug that causes injected fluids to flow into other areas of the reservoir, thereby displacing additional crude oil.

Many successful field projects have shown that xanthan/chromium gels can be injected into petroleum reservoirs. This is undoubtedly due to the high shear that results from pumping large volumes of the gel at high pumping rates. Table 14 gives calculated velocities and shear rates expected in a typical field situation.

Injection Experiment No. 1

Attempted injection of a rubber-like gel through a 15- μ m filter was compared to the injection of polymer. The gel contained 2,000 ppm polymer and 400 ppm chromium. Because of its stiffness, the gel could not be fully characterized, but was shown to be shear thinning. Flow rates and injection pressures are shown in figure 5. The injection of polymer resulted in a steady injection pressure near the value calculated for that flow rate.

TABLE 14. - Frontal advance rate and shear rate for injection at 575 bbl/dy into a 32% porosity, 2 Darcy, 10-ft-thick reservoir zone

Radius, ft	Frontal advance, ft/d	Shear rate, sec ⁻¹
0.29	550	1867
5	32	109
20	8	27.2
30	5	17.0
50	3	10.2
80	2	6.8
160	1	3.4

Injection of gel resulted in high injection pressures which never leveled off. Effluent analysis showed that gel was being filtered from the injected fluid, and it was concluded that a rubber-like gel cannot be injected.

Injection Experiment No. 2

A firm gel containing 25 ppm chromium and 2,000 ppm polymer was injected at 20 ft/d through a 5-cm long, 159-md crushed Berea sandpack. The shear thinning properties of bulk gel are shown in table 9. At shear rates above 3.23 sec^{-1} , gel viscosity was nearly equal to polymer viscosity. At the injection rate of 20 ft/d, the shear rate is about 250 sec^{-1} . Figure 6 shows injection pressure versus the pore volumes injected. Effluent analysis showed that gel was transported through the sandpack; however, the injection pressure never stabilized.

Injection Experiment No. 3

A weak gel containing 20 ppm chromium and 2,000 ppm polymer was injected into a 5-cm long, 2-Darcy crushed Berea sandpack. The same gel was also injected into a 14-Darcy glass beadpack. This was compared with injection of polymer into a 930-md crushed Berea sandpack (see figure 7). The bulk shear thinning properties of the gel are shown in table 9. At the injection rate of 5 ft/d, gel was propagated through the sandpack and glass beadpack; however, pressures did not stabilize, and pressures exceeded the injection pressures for injecting polymer solution many fold.

The results of experiments 2 and 3 are similar to those reported by Willhite¹⁹ when injecting gels produced with a liquid-based biopolymer formulation. Those results are reproduced in figure 8. Even though the gels are shear thinning, it is evidently difficult to obtain steady injection pressures when injecting into porous media at a rate of a few feet per day. The experiments in this report were performed at frontal advance rates of 5 to 100 ft/d; Willhite reported data for 51 and 88 ft/d frontal advance rates.

Injection Experiment No. 4

The final gel-injection experiment was performed with a pourable gel containing 5 ppm chromium and 2,000 ppm polymer. The bulk shear thinning characteristics of the gel are given in table 9. The gel was injected into a

14-Darcy, glass beadpack at three frontal advance rates, beginning with 5 ft/d (see figure 9). Injection pressure increased as in experiments 2 and 3. After the pressure increased to 12 psi, flow was increased 100-fold to 500 ft/d. After a momentary increase to 40 psi, injection pressure fell to 13 psi and then slowly increased for 60 pore volumes. Reducing the injection rate to 31 ft/d caused pressure to drop to 8 psi, which was lower than the maximum injection pressure at 5 ft/d. Injection pressure then began the slow increase typical of experiments 2 and 3.

Frontal advance rates near wellbores can be higher than 500 ft/d,²⁰ and further shearing occurs because of large volumes being pumped through valves and tubing. Evidently, this shear history is necessary to maintain an acceptable injection pressure when injecting gels.

In Situ Gelation

Injection Experiment No. 5

Injection of a delayed crosslinking system is shown in figure 10. The mixture of 1,400 ppm polymer, 25 ppm chromium (see dichromate) and thiourea was easily injected until the onset of gelation. At an injection rate of 5 ft/d, injection pressure was below 1 psi until the onset of gelation at 75 pore volumes (3 days). After gelation, the pressure increased in the same manner as seen previously in experiments 2 through 4.

Gelation occurred faster during the injection than in bottle experiments (see table 10). This effect has been reported previously.¹¹

CONCLUSIONS

1. The xanthan biopolymer studied in this investigation will gel with low levels of chromium (III).
2. The xanthan biopolymer can be injected at flow rates typical of frontal advance rates deep within a petroleum reservoir, without injection problems.
3. When mixed with a delayed crosslinking agent, the polymer can be injected at flow rates typical of frontal advance rates deep within a reservoir.

4. Injectability of a surface-prepared xanthan biopolymer gel is dependent upon the shear history of that gel.
5. Gels produced with dry xanthan biopolymers, which are more convenient to transport and store than liquid (broth) biopolymers, possess the properties for diverting injected fluids into areas of higher oil saturation.
6. The recommended polymer and crosslinker concentrations for surface-prepared gels are 1,400 to 2,000 ppm polymer and 5 to 25 ppm chromium (III).
7. The recommended polymer and crosslinker concentrations for in situ gelation are 1,400 to 2,000 ppm polymer and 10 to 25 ppm chromium (VI).

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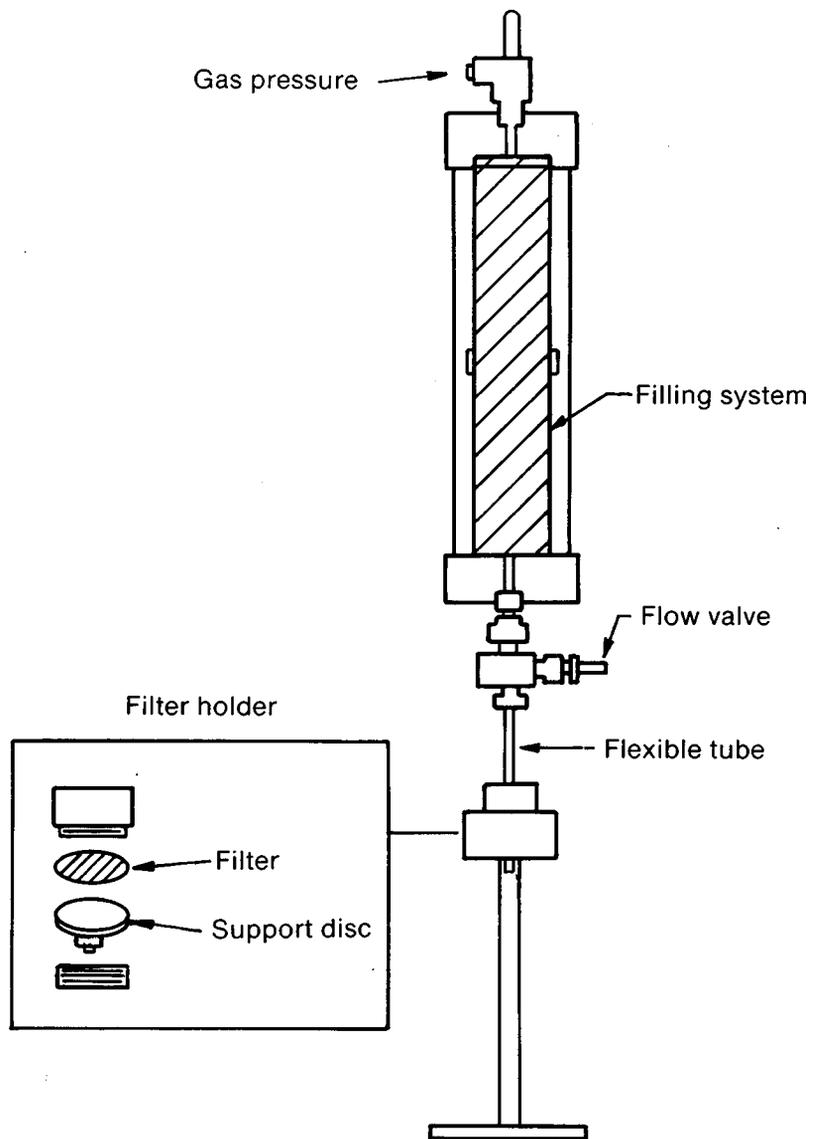


FIGURE 1. - Schematic diagram of filtration apparatus.

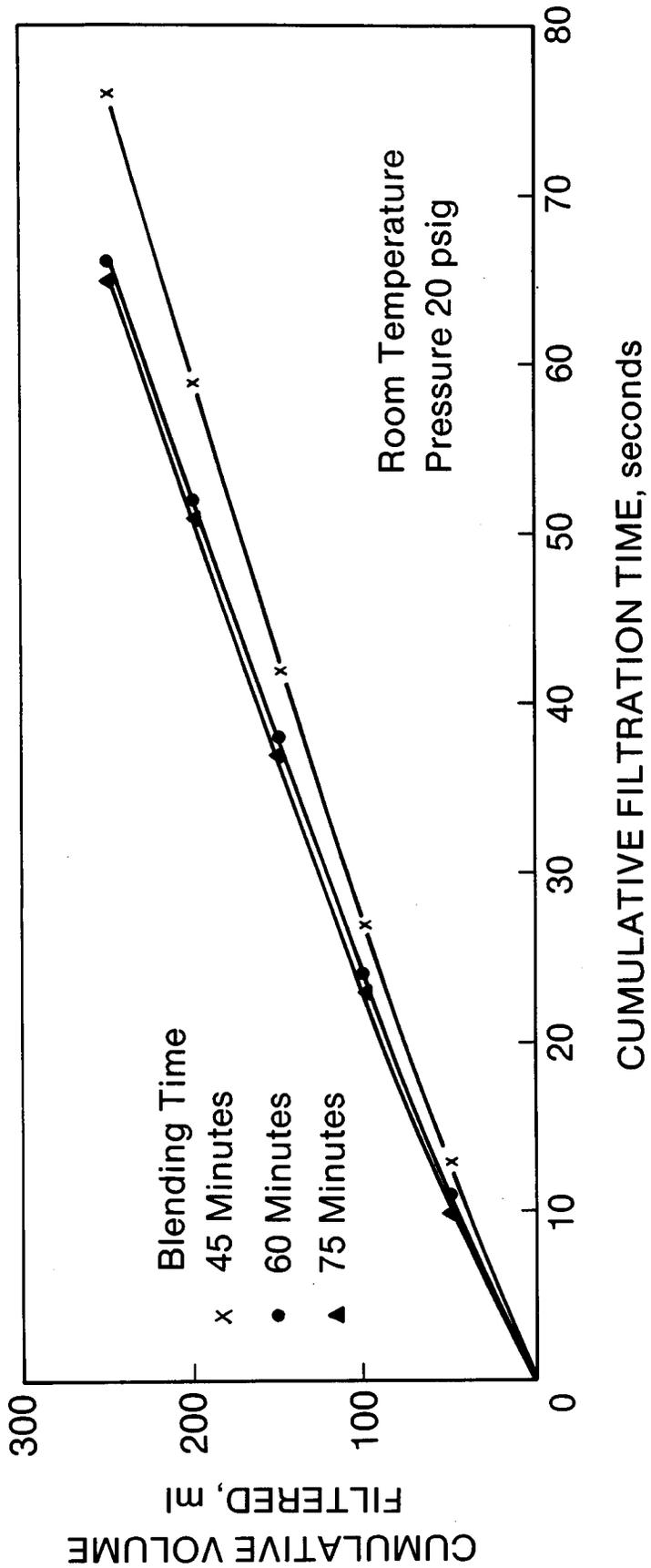


FIGURE 2. - Filtration of 2,800 ppm biopolymer (in deionized water) after mixing 45, 60, and 70 minutes (pH = 7.0).

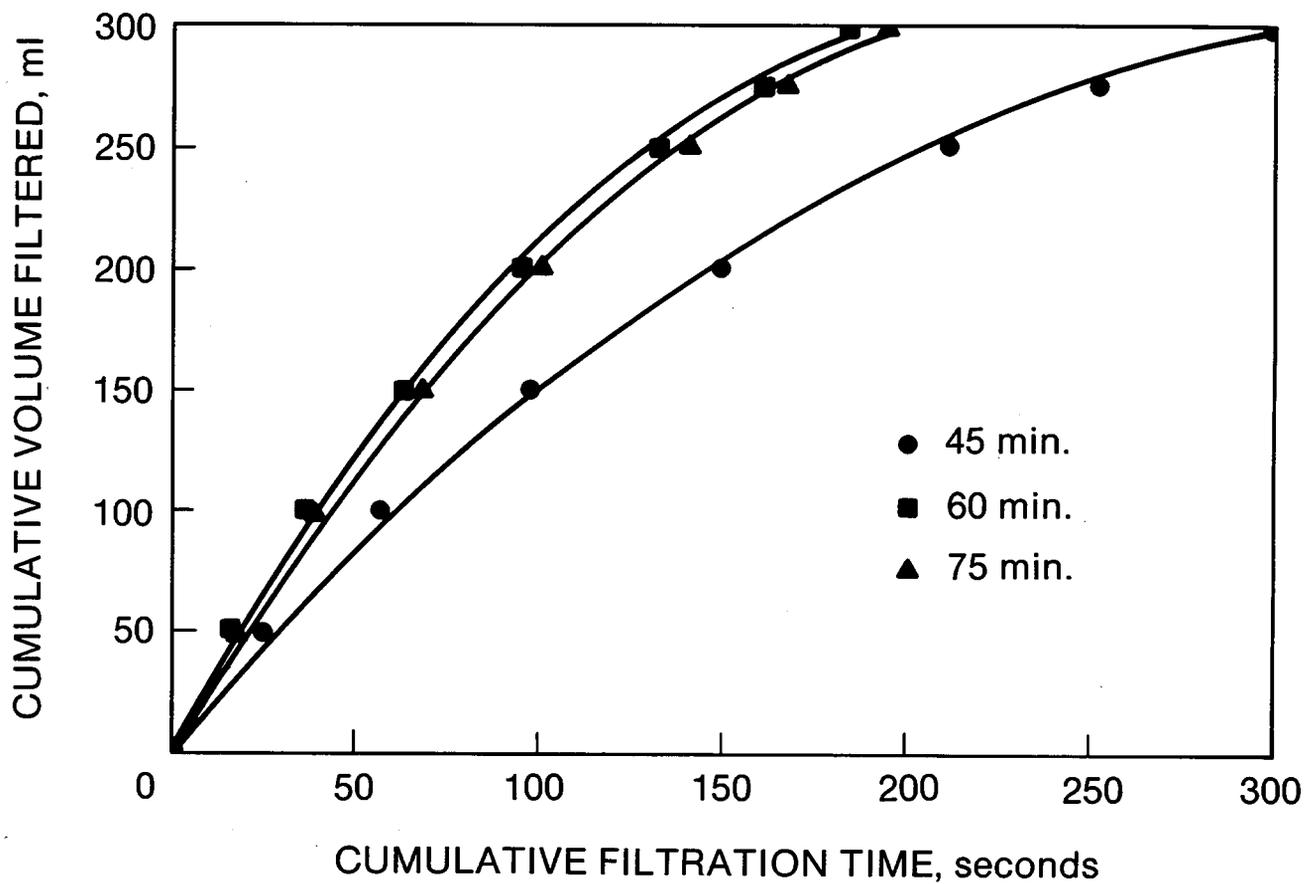


FIGURE 3. - Filtration of 2,800 ppm biopolymer (in NBU brine) after mixing 45, 60, and 70 minutes (pH = 6.8).

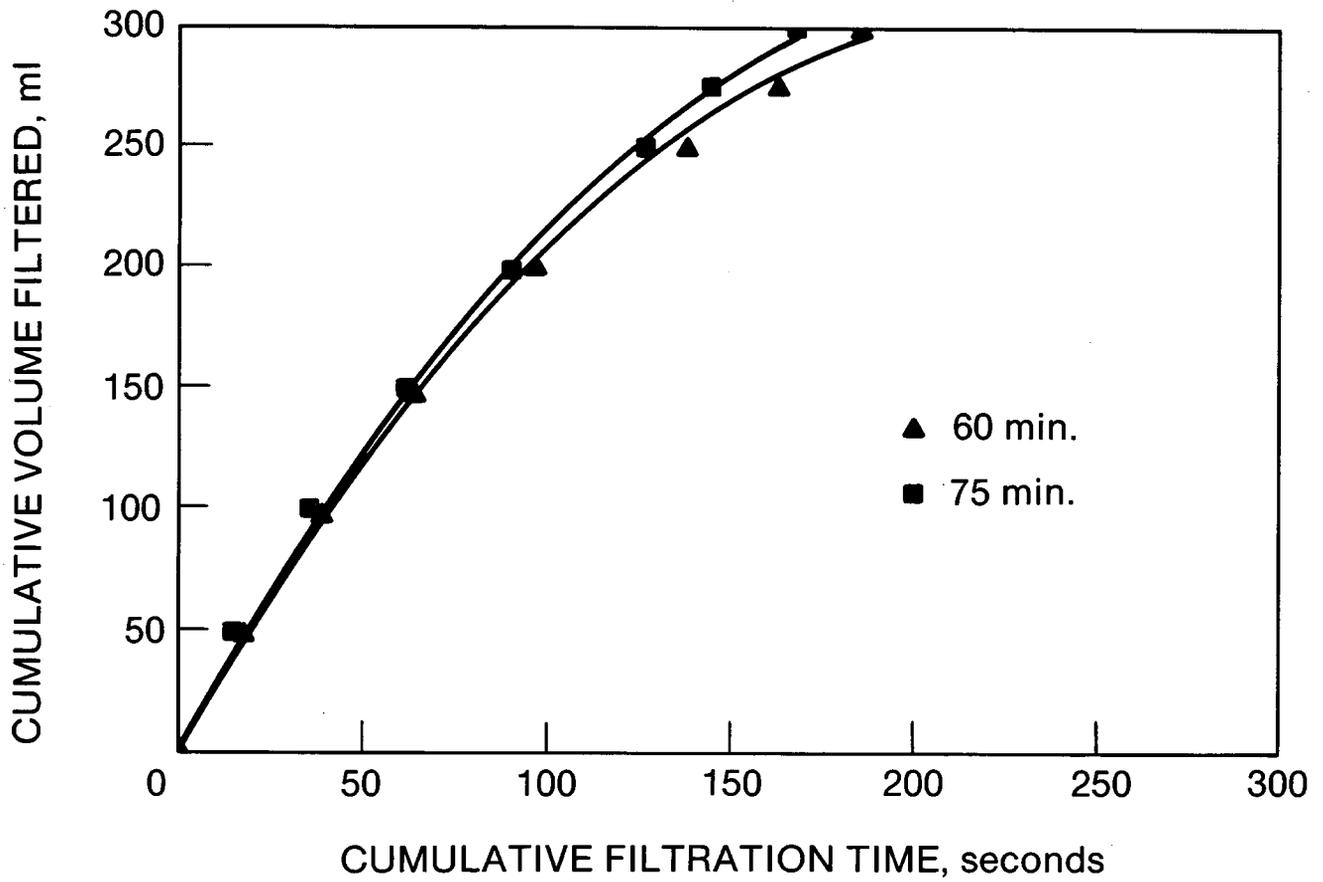


FIGURE 4. - Filtration of 2,800 ppm biopolymer (prepared by dilution of 8,400 ppm biopolymer in NBU brine) after mixing 60 and 75 minutes.

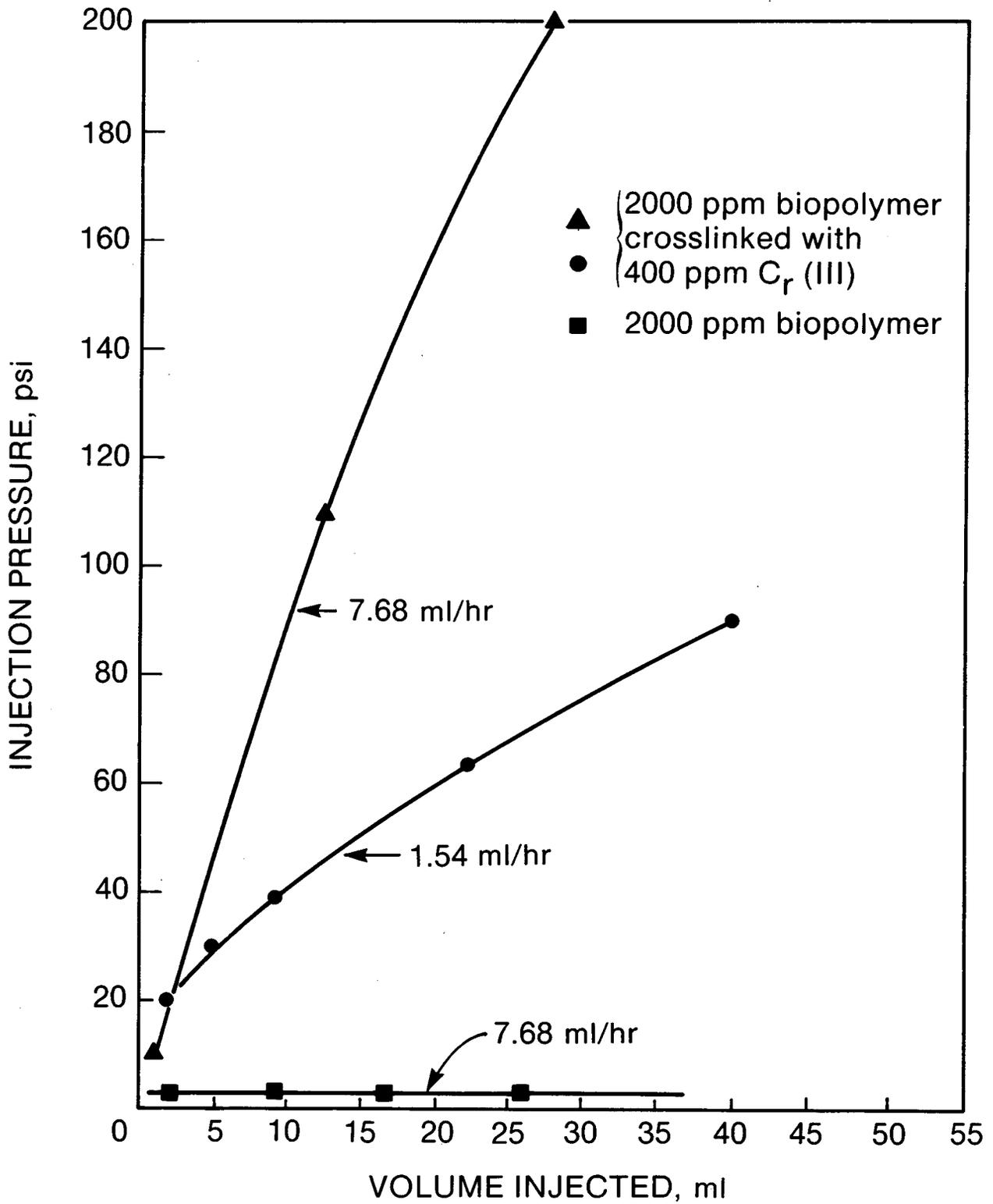


FIGURE 5. - Injection of 2,000 ppm polymer and 2,000 ppm polymer/400 ppm chromium (III) gel through a 15 μ m filter.

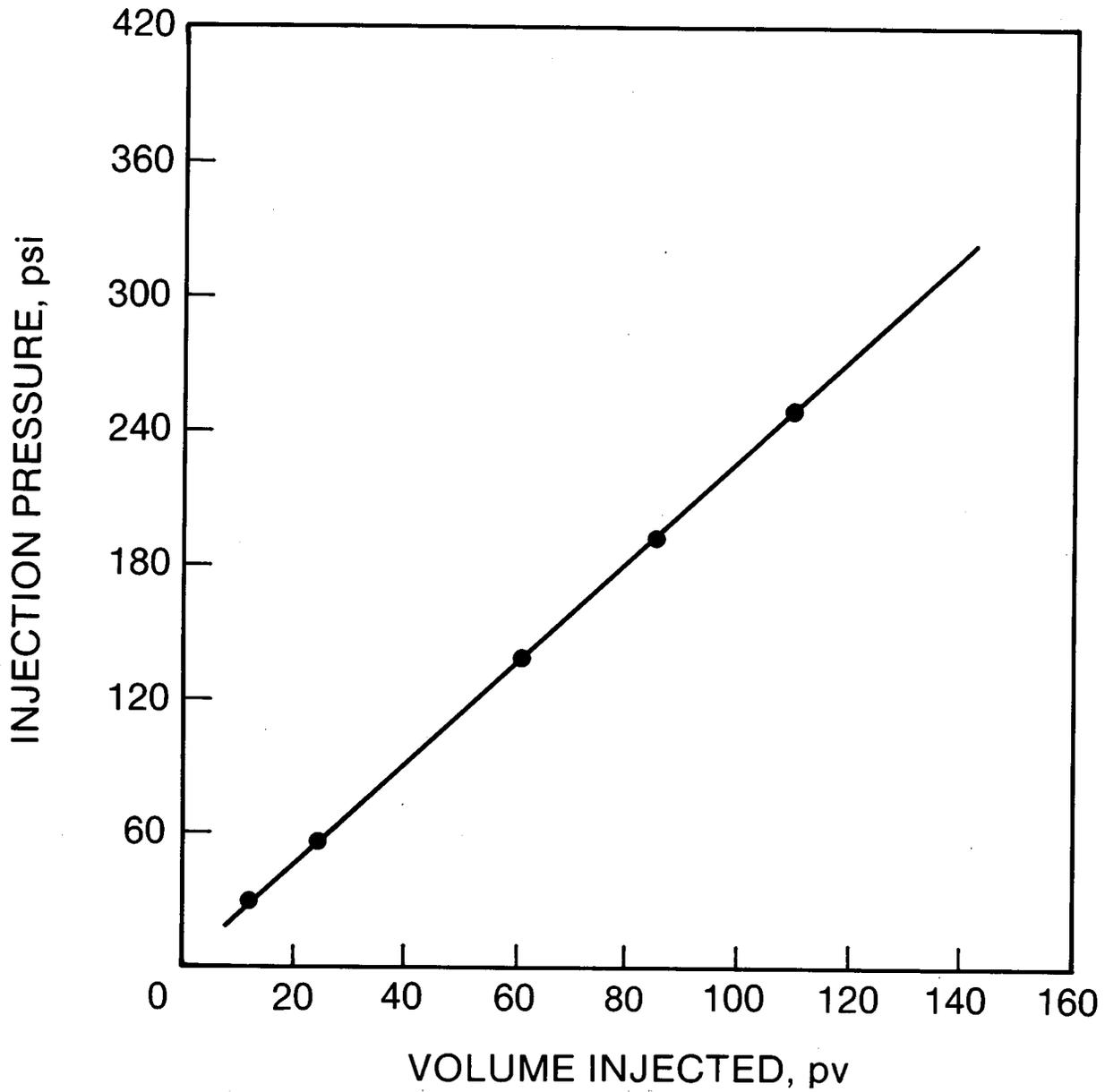


FIGURE 6. - Injection of 2,000 ppm polymer/25 ppm chromium (III) gel into 1.6 Darcy sandpack, 20 ft/d.

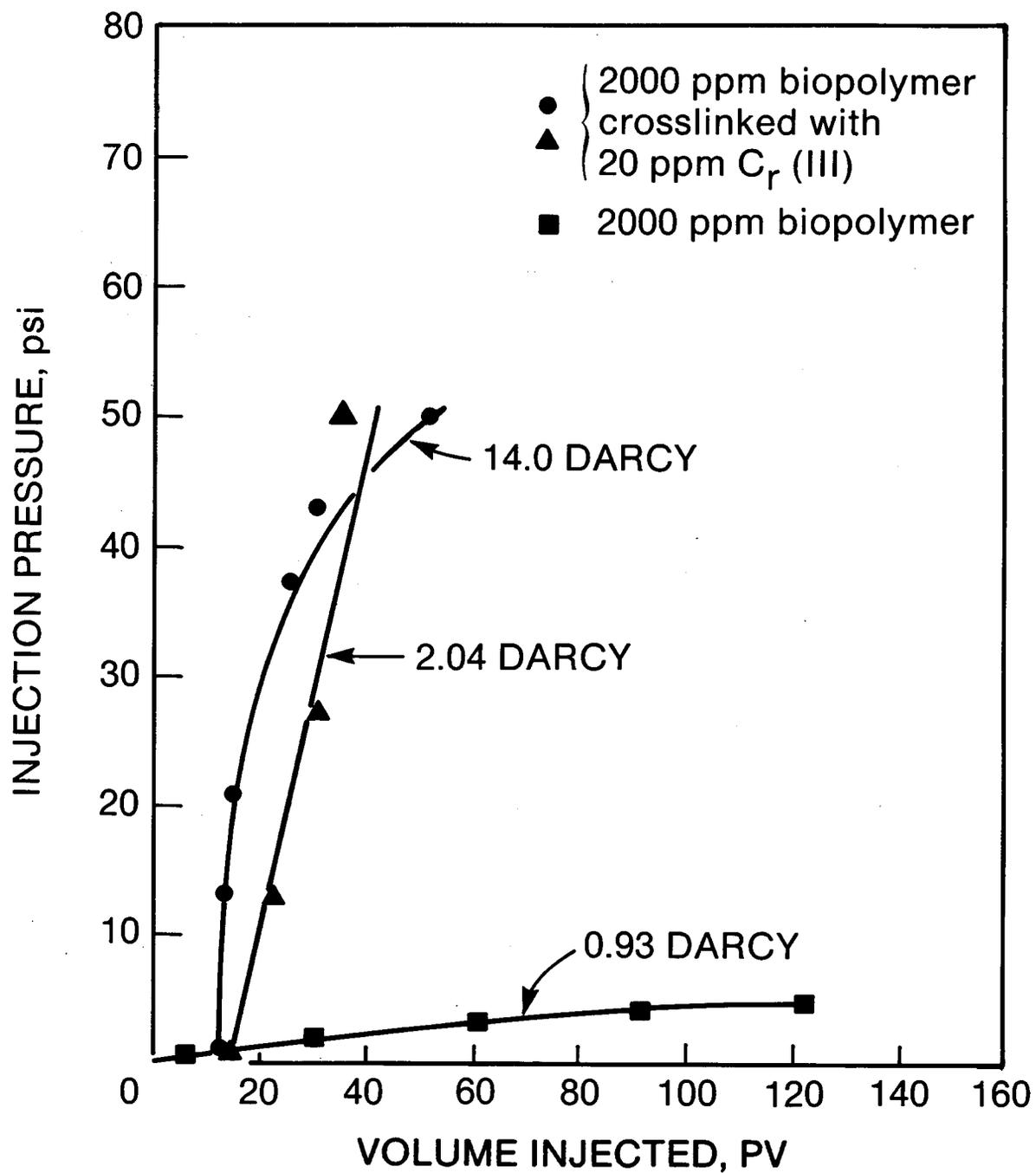


FIGURE 7. - Injection of 2,000 ppm polymer and 2,000 ppm polymer/20 ppm chromium (III) gel into porous media.

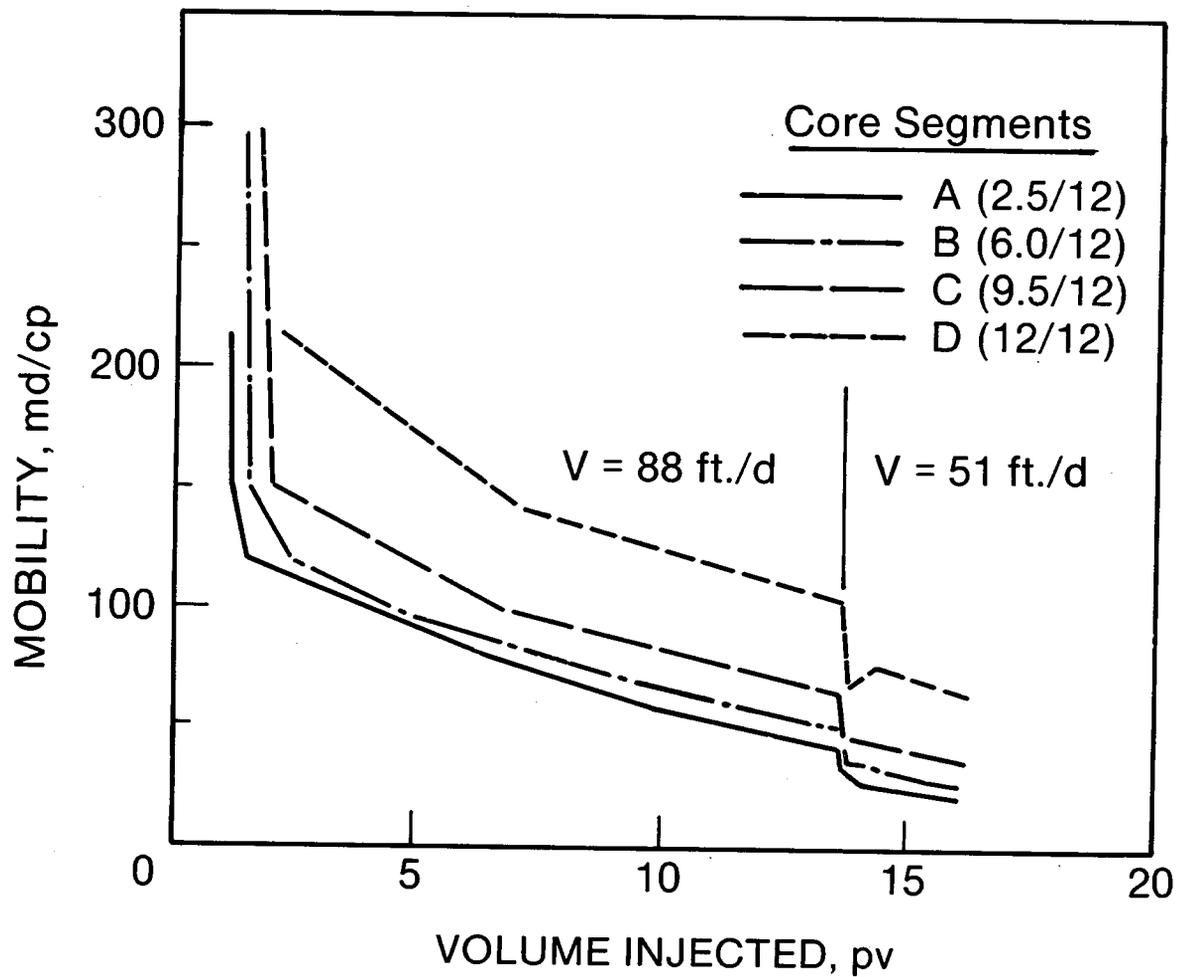


FIGURE 8. - Variation of mobility of Flocon 4800 - Chromium gel during injection into a sandpack at two different rates. (Reproduced from DOE Progress Review Number 6, DOE/BC-86/2).

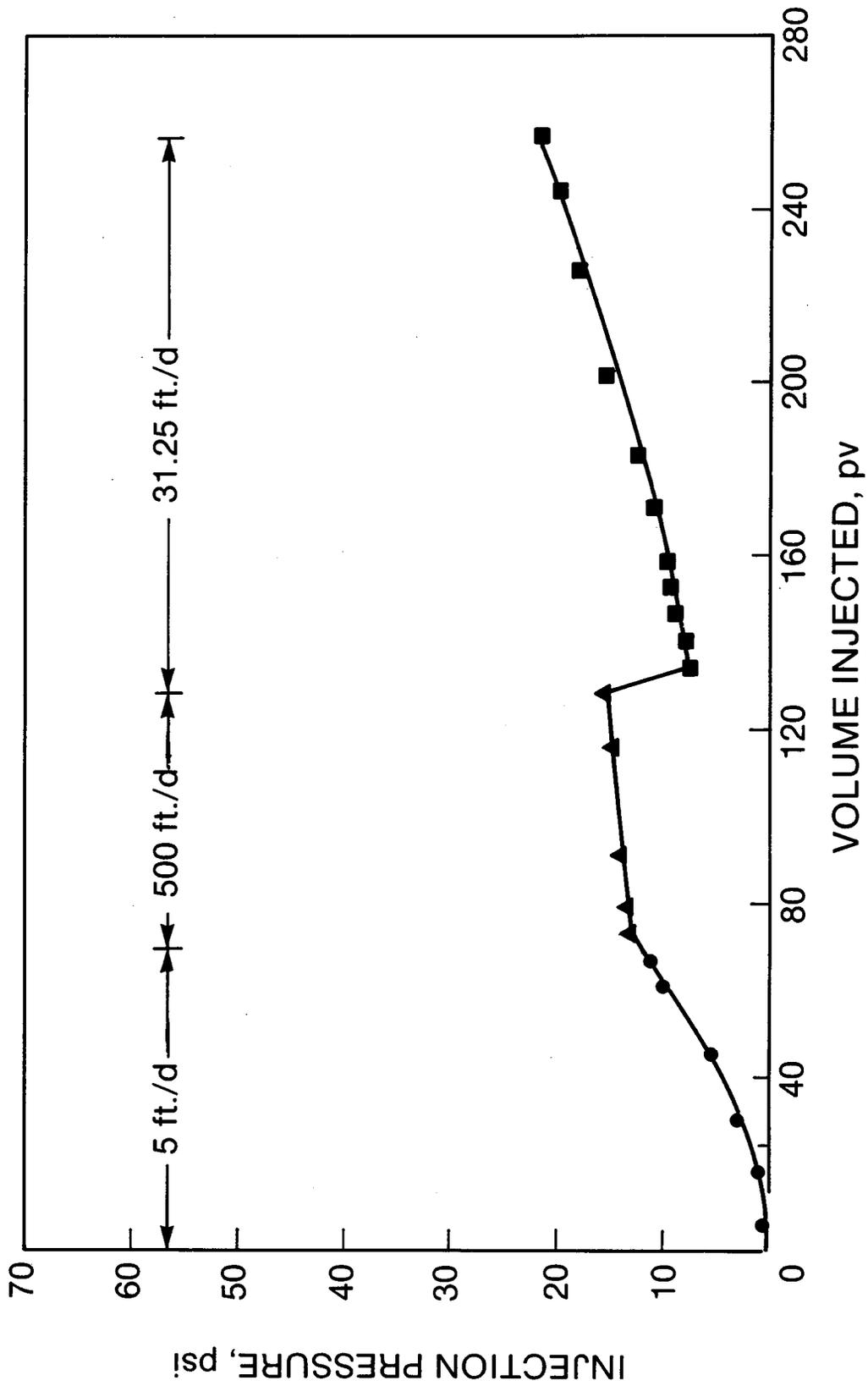


FIGURE 9. - Injection of 2,000 ppm polymer/5 ppm chromium (III) gel into glass beadpack.

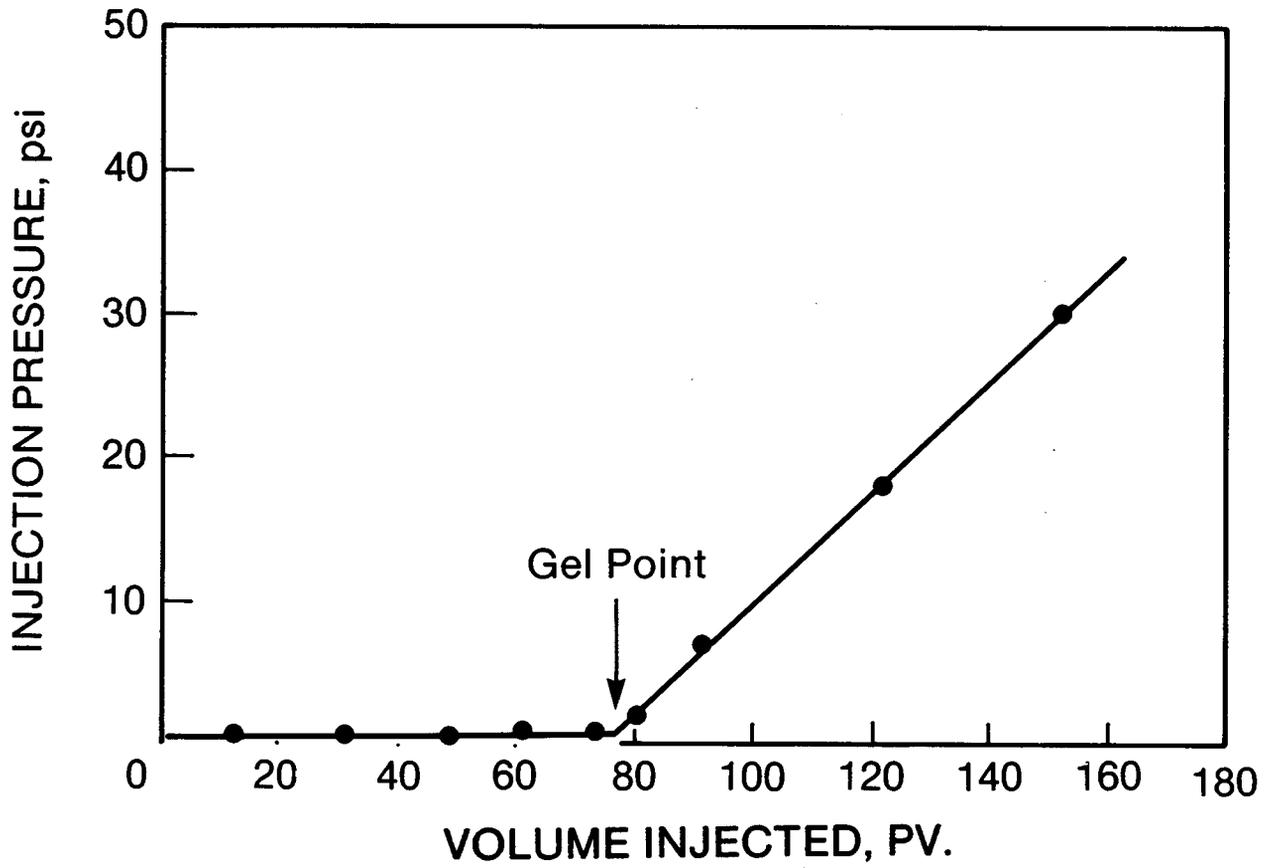


FIGURE 10. - In situ crosslinking of 2,000 ppm polymer with 25 ppm chromium (VI).