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Recommended Practices for Evaluation of Polymers Used in Enhanced Oil Recovery Operations

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RECOMMENDED PRACTICES FOR EVALUATION OF POLYMERS USED IN ENHANCED OIL RECOVERY OPERATIONS

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RECOMMENDED PRACTICES FOR EVALUATION OF POLYMERS USED IN ENHANCED OIL RECOVERY OPERATIONS

FOREWORD

a. These recommended practices were prepared by the Subcommittee on Evaluation of Polymers Used in Enhanced Oil Recovery Operations. This publication is under the administration of the American Petroleum Institute Production Department's Executive Committee on Drilling and Production Practices.

b. The tests recommended herein have been developed to improve polymer quality in field applications. The recommended procedures and conditions have been prepared for use in evaluating and comparing polymer performance under the stated conditions as an aid to selecting materials to be used in enhanced recovery operations. *However, these recommended tests should not be taken as absolute criteria for determining polymer performance under conditions which are characteristic of the downhole environment.* Alternative test procedures are available and are routinely used to meet or exceed recommended practices or performance levels set forth herein.

c. The recommendations presented in this publication are not intended to inhibit the development of new technology, materials improvements, or improved operational procedures. Qualified engineering analysis and judgment will be required for their application to fit a specific situation.

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RECOMMENDED PRACTICES FOR EVALUATION OF POLYMERS USED IN ENHANCED OIL RECOVERY OPERATIONS

SECTION 1
SCOPE

1.1 INTRODUCTION

1.1.1 Water soluble polymers designed for use as mobility control agents in enhanced oil recovery operations and currently available in commercial quantities are mainly of two major types: hydrolyzed polyacrylamides and polysaccharides. Polyacrylamides are synthetic, high molecular weight copolymers and are marketed in a variety of product forms: dry powder, liquid emulsion or dispersion, concentrated solutions, and gels. Polysaccharides produced by fermentation processes (e.g., xanthan and scleroglucan biopolymers) are available as dry powder and liquid broths containing up to 15% active polymer.

1.1.2 These recommended practices have been prepared to provide industry standard procedures and test conditions which can be used to evaluate and compare polymer performance under the stated conditions. *These recommended tests are primarily for qualitative comparison of performance and general screening of water soluble polymers under conditions described herein. This publication does not present recommendations which can be taken as absolute tests for determining polymer performance under conditions which are chracteristic of the downhole environment.* These recommended practices are not intended to obviate the need for applying sound engineering judgment in the selection and application of polymer products for use in enhanced oil recovery operations.

1.1.3 For purposes of these recommended practices, standard brine solutions are stipulated to enable users to evaluate performance of polymers under controlled laboratory conditions. Similar tests may be developed using field brine solutions, but these test results should not be compared with results of tests conducted using the standard brine solutions. These recommended practices are not intended to inhibit users from applying other test procedures or practices to their needs.

SECTION 2
SOLUTION PREPARATION

2.1 INTRODUCTION

2.1.1 General. Special attention to recommended solution preparation and mixing procedures is essential to obtain optimum properties with high molecular weight polymers. Dissolution rates will vary depending on product form and type. Important factors to be considered in preparing solutions are high-shear/low-shear mixing, initial mix concentration, brine composition, pH, activator concentration, and hydration or aging time. Recommended procedures are given in this section for each of the various product forms available. Product manufacturers should be consulted for additional recommendations specific to their products.

2.1.2 Shearing Effects. Some polymers require a short period of high-shear mixing followed by a longer period of low-shear mixing. Hydration times can vary from a few minutes to several hours. Mixing techniques for polysaccharides are different from those used for polyacrylamides. Dried polysaccharides require high-shear mixing, whereas polyacrylamides are degraded by moderate to high shear.

2.1.3 Salinity Effects. As brine salinity increases, both polyacrylamides and polysaccharides become more difficult to hydrate. Solid polysaccharides to be dissolved in high salinity brines can benefit from a fresh water hydration step, i.e., preparation of a fresh water polymer concentrate which is sheared and then diluted with high salinity brine. The higher the salinity and divalent ion content, the more difficult the inversion of polyacrylamide emulsions. Some dry polyacrylamides contain significant amounts of sodium carbonate, which in hard brines may precipitate as calcium carbonate unless the pH is lowered.

2.1.4 Synthetic Brines. Reference should be made to *API RP 45: Recommended Practice for Analysis of Oil-Field Waters,** Second Edition, November 1968 (Reissued July 1981), Section 1.5, "Preparation of Stable Synthetic Brines." For comparisons of polymers, brines may be prepared from sodium chloride alone or from sodium chloride and calcium chloride. Commonly used reference solvents are a "fresh water" containing 1000 ppm NaCl and 100 ppm $CaCl_2$, and a "hard brine" containing 3% NaCl and 0.3% $CaCl_2$ in deionized water. Brine solutions should be freshly prepared. If solutions are to be used for porous media tests, filtration of the brine solution through a 0.22-micron filter is advised.

2.1.5 Concentration Units. Polymer concentrations are commonly expressed as parts per million (ppm). In the recommended laboratory procedures described in this section, *ppm is always used on a weight/weight basis,* i.e., weight of polymer per total weight of solution.

2.2 RECOMMENDED PROCEDURES FOR LABORATORY PREPARATION OF POLYMER SOLUTIONS FROM EMULSION AND DISPERSION GRADE POLYACRYLAMIDE PRODUCTS

2.2.1 General. The term, "liquid polyacrylamide," encompasses products marketed as true aqueous solutions and products which are liquid by virtue of being supplied as emulsions/dispersions in a hydrocarbon continuous phase.

Typically, emulsion/dispersion products are available commercially at concentrations in the range of 25-50 weight percent active polymer either as a water-in-oil emulsion or a dispersion in which the polymer exists as a finely divided suspension in a hydrocarbon continuous phase. General characteristics and handling procedures for emulsion and dispersion products are similar, with both types usually containing surfactant(s) which allow "inversion" and dissolution of the polymer upon contact with water. Additional or even alternative surfactants (activators) may be recommended for efficient inversion in medium to high salinity brines. Polyacrylamide solution concentrates are available commercially at concentrations in the range of 3-20 weight percent active polymer. Before preparing solutions, consult the product manufacturer regarding specified active polymer content and recommendations regarding additional activator.

Products to which activator has been added during manufacture are known as single pack or single component systems. Dual pack or dual component products are also available and involve the polymer concentrate and activator being supplied separately. With this type of product, the activator must be added to the make-up water before the polymer concentrate is added.

Correct preparation of all emulsion/dispersion products requires the application of a brief period of adequately high shear immediately following contact of the product with the brine. Preparation in accordance with this concept allows efficient distribution of discrete polymer particles, promotes rapid hydration, and minimizes possible shear degradation of the hydrated polymer.

In the context of the above, *it is recommended that stock solutions be prepared at a concentration of 0.5% w/w (5000 ppm)* active polymer followed by subsequent dilution to the desired working concentration(s).

2.2.2 Preparation of Solutions (Overhead Stirrer).

2.2.2.1 Apparatus. The following apparatus is required for test solution preparation:

Overhead Stirrer Assembly	Jiffy® mixer, or equivalent caged paddle stirrer or shaft fitted with a two-inch marine blade propeller driven by a stirring motor (Sargent-Welch cone drive variable speed, catalog number OS76445, or equivalent.)

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*Available from American Petroleum Institute, Publications and Distribution Section, 1220 L St., N.W., Washington, D.C. 20005.

Top Loading Laboratory Balance	Sensitivity 0.01 g. Maximum load 2000 g.
Container	16-oz, wide-mouth jar. or 600-mL beaker.
Disposable Plastic Syringe	1mL, 5mL, 10mL
Tumbler	Any device capable of tumbling a 16-oz. jar end-over-end at approximately 30 rpm (usually hand made).

Magnetic Stirrer

Coated Magnetic Stirring Bar

Stopwatch

2.2.2.2 Calculation for Preparing Stock Solution.

1. Using manufacturer's or other data describing the product, calculate the amount of emulsion/dispersion polymer product required to make up the appropriate amount of stock solution.

$$W_{pr} = \frac{W_s \times C_s \times 10^{-4}}{A_{pr}} \quad \text{(2-1)}$$

where:

W_{pr} = weight of polymer product, g.

W_s = weight of stock solution to be made (including additional activator, if any), g.

C_s = concentration of polymer in stock solution, ppm.

A_{pr} = activity of polymer product, weight percent. (*NOTE:* Supplier should specify percent active polymer in the polymer product.)

2. Calculate the amount of makeup water used for the stock solution.

$$W_{bs} = W_s - W_{pr} \quad \text{(2-2)}$$

EXAMPLE: To prepare 400 g of 5000 ppm stock solution using a 30.25% active emulsion/dispersion polymer product, calculate the weight of polymer required using Equation (2-1):

$$W_{pr} = \frac{W_s \times C_s \times 10^{-4}}{A_{pr}} = \frac{400 \times 5000 \times 10^{-4}}{30.25} = 6.61 \text{ g}$$

Then calculate the amount of makeup water using Equation (2-2):

$$W_{bs} = W_s - W_{pr} = 400.00 - 6.61 = 393.39 \text{ g.}$$

2.2.2.3 Mixing Procedure (Overhead Stirrer).

1. Add the calculated amount of makeup water [Equation (2-2)] to a 16-oz, wide-mouth jar.
2. Offset the stirrer slightly from the middle of the jar. Set the speed of the overhead stirrer so that the vortex extends 75% into the solution.
3. If no additional activator is required, proceed to Step 5.
4. If additional activator is required, it should be added to the makeup water by the following recommended procedure:
   a) Determine the amount of additional activator to be added in accordance with the manufacturer's recommendations.
   b) Fill a 1-mL plastic syringe (no needle) with activator and fully discharge the contents to waste.
   c) Fill the syringe, wipe the outside of the syringe with a paper towel, and discharge excess activator until the approximate required amount remains in the syringe. Record gross weight of the syringe plus contents.
   d) Inject the activator *onto the shoulder of the vortex* in one continuous stroke and stir for one minute.
   e) Reweigh the empty syringe to determine the exact weight of activator added.
5. After thoroughly mixing the polymer product to ensure homogeneity, weigh out the required amount of polymer product in the following manner:
   a) Fill a 5-mL or 10-mL plastic syringe (no needle) with polymer product and discharge the contents to waste.
   b) Fill the syringe, wipe the outside of the syringe with a paper towel, and discharge excess polymer product until the approximate required amount remains in the syringe. Record gross weight of the syringe plus contents.
6. Add the product to the brine by the following procedure:
   a) Inject the product *onto the shoulder of the vortex* as rapidly as possible using one continuous stroke. Slow injection, or injection directly onto the wall or impeller, can result in poor dispersion. Stir for five (5) minutes. *NOTE:* It is *not* recommended that the above procedure be used for direct preparation of polymer solutions at concentrations less than 5000 ppm active polymer. To do so may lead to either problems with inversion or excessive mechanical shear of hydrated polymer, depending on the particular activator and brine concentrations.
   b) Set the stirrer speed at 150-250 rpm and continue stirring for two (2) hours. The product should be evenly dispersed.
   c) Reweigh the empty syringe and subtract the syringe weight from gross weight to determine the exact amount of polymer product added.

Recalculate the precise concentration of stock solution.

$$C_s = \frac{W_{pr} \times A_{pr} \times 10^4}{W_{bs} + W_{pr}} \quad \text{(2-3)}$$

where:

C_s = concentration of polymer in stock solution, ppm.

W_{pr} = weight of polymer product added, g.

A_{pr} = activity of polymer product, weight percent.

W_{bs} = weight of makeup water used for the stock solution, including additional activator, if any, g.

EXAMPLE: For a product containing 30.25% active polymer, in which 393.39 g of brine and 6.55 g of product were used:

$$C_s = \frac{W_{pr} \times A_{pr} \times 10^4}{W_{bs} + W_{pr}} = \frac{6.55 \times 30.25 \times 10^4}{393.39 + 6.55} = 4954 \text{ ppm}$$

7. Transfer the 5000 ppm stock solution to a 600-ml beaker and stir gently for 1-2 hours, using the overhead stirrer fitted with a paddle-type impeller (Par. 2.2.2.1) and operating at 150-250 rpm. Additional aging time may be required when using very high salinity brines. Alternatively, transfer the solution to a capped glass jar and tumble end over end for 1-2 hours, using a suitable rotary tumbler.
8. Dilute the aged 5000 ppm stock solution to the desired concentration by addition of the appropriate amount of brine (refer to Par. 2.2.2.4). Mix gently for 10 minutes using a magnetic or overhead stirrer.

2.2.2.4 Calculations for Dilution of Stock Solution.

1. Calculate the weight of stock solution required to make up the desired amount of diluted solution.

$$W_s = \frac{W_d \times C_d}{C_s} \quad \text{(2-4)}$$

where:

W_s = weight of stock solution, g.

W_d = weight of diluted solution to be made, g.

C_d = concentration of polymer in diluted solution, ppm.

C_s = concentration of polymer in stock solution, ppm.

2. Calculate the amount of makeup water required to make the desired amount of diluted solution.

$$W_{bd} = W_d - W_s \quad \text{(2-5)}$$

where:

W_{bd} = weight of makeup water used in the diluted solution, g.

EXAMPLE: To make 400 g of 1000 ppm diluted solution from a 5000 ppm stock solution:

$$W_s = \frac{W_d \times C_d}{C_s} = \frac{400 \times 1000}{5000} = 80 \text{ g}$$

$$W_{bd} = W_d - W_s = 400 - 80 = 320 \text{ g}$$

2.2.3 Recommended Mixing Procedure for Emulsion/Dispersion Polymer Products (Blender Method).

2.2.3.1 Apparatus. The following apparatus is required for test solution preparation:

Blender	No-load speed of approximately 15,500 rpm fitted with 40-oz glass or stainless steel container. (For example, Waring® Blendor™ Model 7011S, or equivalent).
Variable Transformer	0-120 volts (e.g. POWERSTAT® Type L116B, or equivalent).
Top Loading Laboratory Balance	Sensitivity 0.01 g. Maximum load 2,000 g.
Disposable Plastic Syringes	1 mL, 5 mL, 10mL.
Container	16-oz, wide-mouth jar or 600-mL beaker.
Tumbler	Any device capable of tumbling a 16-oz jar end-over-end at approximately 30 rpm (usually hand made).
Overhead Stirrer Assembly	Jiffy® mixer, or equivalent caged paddle stirrer or shaft fitted with a two-inch marine blade propeller driven by a stirring motor (Sargent-Welch cone drive variable speed, catalog number OS76445, or equivalent.)
Magnetic Stirrer	
Coated Magnetic Stirring Bar	
Stopwatch or Timer	

2.2.3.2 Calculations for Preparing Stock Solution. Refer to Par. 2.2.2.2.

2.2.3.3 Mixing Procedure (Blender Method). The following procedure is recommended to mix polymer samples using blender equipment.

1. Connect the blender to the output of a variable transformer.
2. Set the variable transformer to zero volts and blender controls to "LO" and "ON."
3. If no additional activator is required, proceed to Step 5.

4. If additional activator is required, it should be added to the makeup water by the following recommended procedure:
   a) Tare the blender container on a top loading laboratory balance and weigh a sufficient amount of makeup water to make the required stock solution. Replace the container on the blender. Determine the amount of additional activator to be added in accordance with the manufacturer's recommendations.
   b) Fill a 1-mL plastic syringe (no needle) with activator and fully discharge the contents to waste.
   c) Fill the syringe, wipe the outside of the syringe with a paper towel, and discharge excess activator until the approximate required amount remains in the syringe. Weigh and record the gross weight of syringe plus contents.
   d) Set the variable transformer to 50 volts and inject the activator *onto the shoulder of the vortex* in one continuous stroke. Mix briefly and return the transformer to zero volts.
   e) Reweigh the empty syringe to determine the exact weight of activator added.
5. After thoroughly mixing the polymer product to ensure homogeneity, weigh out the required amount of polymer product in the following manner:
   a) Fill a 5-mL or 10-mL plastic syringe (no needle) with polymer product and discharge the contents to waste.
   b) Fill the syringe, wipe the outside of the syringe with a paper towel and discharge excess polymer until the approximate required amount remains in the syringe. Weigh and record the gross weight of syringe plus contents.
6. Add the product to the brine by the following procedure:
   a) Increase the variable transformer to 50 volts; start the stopwatch.
   b) Inject the product *onto the shoulder of the vortex* as rapidly as possible using one continuous stroke. Slow injection, or injection directly onto the wall or impeller can result in poor dispersion. *NOTE:* Use of significantly higher voltages/mixing times can lead to shear degradation of the polymer, particularly when using high salinity brines. It is *not* recommended that the above procedure be used for direct preparation of polymer solutions at concentrations less than 5000 ppm active polymer. To do so may lead to either problems with inversion or excessive mechanical shear of hydrated polymer, depending on the particular activator and brine concentrations.
   c) Increase the voltage to 70 volts for five (5) seconds, then immediately reduce the voltage to zero. The product should be evenly dispersed.
   d) Reweigh the empty syringe and subtract the syringe weight from gross weight to determine the exact amount of polymer product added. Recalculate the precise concentration of stock solution according to Equation (2-3).
7. Follow the procedure in Steps 7 and 8 of Par. 2.2.2.3.

2.3 RECOMMENDED PROCEDURE FOR LABORATORY PREPARATION OF POLYMER SOLUTIONS FROM DRY POLYACRYLAMIDE PRODUCTS.

2.3.1 General. Solutions of polyacrylamide powders are usually prepared as a stock solution (approximately 5000 ppm) and diluted to test concentrations as required. Vigorous agitation is necessary for the initial dispersion of the dry powder. A magnetically driven laboratory stirrer should be adjusted so that the bottom of the water vortex extends 75% into the solution. The dry polymer should be sprinkled uniformly just below the upper curve or shoulder of the vortex within 30 seconds. If dispersion of the polymer is attempted over a longer time span, the higher viscosity resulting from the dissolved polymer may prevent proper wetting. Additionally, adding the dry polymer in a big slug can lead to the formation of "fish eyes." As soon as all of the polymer has been added, adjust the stirrer to a low speed (60-80 rpm) that just keeps the solid particles from settling to the bottom. The lowest possible speed should be used to avoid mechanical degradation of the polymer solution. Continue to stir the solution at low speed for 2 or 3 hours and let it stand overnight. Solutions are then ready for desired dilution by gently mixing the required amount of concentrate and brine solution. Concentrated solutions of polyacrylamide may be stored at laboratory room temperature in brown glass bottles for 2-3 weeks without loss of effectiveness. However, diluted solutions should be prepared the day they are used.

2.3.2 Apparatus. The following apparatus is required for preparation of solutions from polyacrylamide powders:

Overhead Stirrer Assembly	Jiffy® mixer, or equivalent, caged paddle stirrer or shaft fitted with a two-inch marine blade propeller driven by a stirring motor (Sargent-Welch cone drive variable speed, catalog number OS76445, or equivalent.)
Top Loading Laboratory Balance	Sensitivity 0.01 g. Maximum load 2000 g.
Container	16-oz, wide-mouth jar or 600-mL beaker.

Weighing Cups	
Magnetic Stirrer	Coated magnetic stirring bar.
Stopwatch or Timer	

2.3.3 Calculations for Preparing a Stock Solution Using Dry Polyacrylamide Products.

1. Using manufacturers' or other data describing the product, calculate the amount of dry polymer product required to make up the appropriate amount of stock solution. Refer to example calculations shown in Par. 2.2.2.2.

$$W_{pr} = \frac{W_s \times C_s \times 10^{-4}}{A_{pr}} \quad \text{.......................} \quad (2\text{-}1)$$

where:

W_{pr} = weight of polymer product, g.

W_s = weight of stock solution to be made, g.

C_s = concentration of polymer in stock solution, ppm.

A_{pr} = activity of polymer product, weight percent (usually 100%). *NOTE:* Dry polyacrylamide products will gain weight when exposed to the atmosphere, and activity (A_{pr}) may have to be adjusted.

2. Calculate the amount of makeup water required to make the desired amount of stock solution according to Equation (2-2).

2.3.4 Recommended Mixing Procedure for Preparing a 5000 ppm Stock Solution.

1. Weigh calculated amount of dry polymer product in a weighing cup and record weight.
2. Weigh calculated amount of the desired brine into a 16-oz, wide-mouth glass jar. Record weight. Add a 1.5-inch coated magnetic stirring bar to the jar.
3. Using a magnetic stirrer, adjust the vortex to extend 75% into the solution.
4. Sprinkle the polymer on the shoulder of the vortex over a period of 30 seconds. Observe the solution. No large slugs or "fish-eyes" should be present; if present, start over.
5. Stir the solution using a magnetic/overhead stirrer at low speed (60-80 rpm) for 2-3 hours.
6. Allow the solution to sit overnight before diluting to the desired concentration.
7. Check for undissolved particles. If present, start over.

2.3.5 Dilution of Stock Solution. Refer to Par. 2.2.2.3, Step 8.

2.4 RECOMMENDED PROCEDURE FOR LABORATORY PREPARATION OF POLYMER SOLUTIONS FROM POLYACRYLAMIDE SOLUTION CONCENTRATE.

2.4.1 General. Polyacrylamide solution concentrates are highly viscous liquids ranging in polymer content from 3 to 20 weight percent. To prepare dilute solutions in the laboratory, the concentrate must be properly handled and the correct amount added to the makeup water.

2.4.2 Apparatus. The following apparatus is required for preparation of test solutions from polyacrylamide solution concentrate:

Magnetic Stirrer and Coated Stirbar	
Container	16-oz, screw-cap, wide-mouth, (SCWM) glass jar.
Top Loading Laboratory Balance	Sensitivity 0.01 g. Maximum load 2000 g.
Magnetic Stirrer	Coated magnetic stirring bar.
Stopwatch or Timer	

2.4.3 Calculations for Preparing Stock Solutions. Using manufacturer's or other data describing the product, calculate the amount of concentrate required to make up the desired amount of stock solution according to Equation (2-1).

2.4.4 Recommended Mixing Procedure for Preparing Stock Solution.

1. Using syringe, place the amount of desired concentrate into the tared jar on the balance.
2. Add makeup water to final weight to give desired concentration. Refer to Par. 2.2.2.2 and Equation (2-2) for calculation of required makeup water.
3. Flush jar with nitrogen then cap and stir overnight (16 hours) using a magnetic stirrer at a moderate speed (about 50% on most magnetic stirrers).
4. Solution should appear uniform when poured from one container to another. There should be no visible undissolved polymer. If present, start over.

2.4.5 Dilution of Stock Solution. Refer to Par. 2.2.2.3, Step 8.

2.5 RECOMMENDED PROCEDURES FOR LABORATORY PREPARATION OF POLYMER SOLUTIONS FROM POLYACRYLAMIDE GEL PRODUCTS.

2.5.1 General. Polyacrylamide gel products are tough, rubber-like materials that are essentially concentrated solutions of the polymers in water. Active polymer contents are often as high as 30%. To prepare solutions in the laboratory, bulk gel samples must be reduced to small particle size before adding to the makeup water or brine. The product manufacturer can often furnish ground gel in small bead size. It is necessary to adhere closely to the manufacturer's instructions to obtain solutions of acceptable quality. If the strong brine procedure shown in Par. 2.5.4 is used for less saline brines, the time required can be reduced.

2.5.2 Recommended Procedure for Preparing Ground Gel.

2.5.2.1 Apparatus.

Guillotine or heavy duty scissors.

Heavy duty kitchen food grinder.

16-oz, screw-cap, wide-mouth (SCWM) glass jar.

2.5.2.2 Gel Preparation Procedure. Take sample gel cores from the center of the log sample. Cut the gel core sections into cubes (approximately 1 inch) and randomly mix and pass through the food grinder fitted with a die plate having 3/16-inch diameter holes. Store ground gel in the tightly sealed wide-mouth jar to avoid moisture loss.

CAUTION: Protective gloves should be worn while handling polyacrylamide gel products to prevent skin exposure to potentially hazardous materials.

2.5.3 Recommended Mixing Procedure [Stock Solution (Salt Concentrations Lower than Three Percent)].

2.5.3.1 Apparatus. The following apparatus is required for preparation of test solutions from polyacrylamide gel products:

Stirrer	Air or electric, 750 rpm, fitted with two three-blade propellers, each two inches in diameter and spaced approximately two inches apart on the stirrer shaft.
Top Loading Laboratory Balance	Sensitivity 0.01 g. Maximum load 2000 g.
Container	16-oz, SCWM jar.
Tumbler	Any device capable of tumbling a 16-oz jar end-over-end at about 30 rpm (usually homemade).
Strainers	Cylinder approximately 3 inches long by 2 inches diameter fitted with 200-mesh stainless steel screen at one end.

2.5.3.2 Calculations for Preparing Stock Solution.

1. Using manufacturer's or other data describing the product, calculate the amount of polyacrylamide gel product required to make up the appropriate amount of stock solution. Refer to example calculations shown in Par. 2.2.2.2, Equation (2-1).

   NOTE: Supplier should specify the percent of active polymer in the polymer product.

2. Calculate the amount of makeup water required to make the desired amount of stock solution according to Equation (2-2).

2.5.3.3 Mixing Procedure. *CAUTION: Protective gloves should be worn while handling polyacrylamide gel products to prevent skin exposure to potentially hazardous materials.*

1. Place calculated amount of ground gel in a 16-oz, SCWM jar. If ground gel is not available, scissor cut the gel into very small cubes or pieces about 1/8-inch on a side (the smaller the pieces, the faster they dissolve).
2. Add calculated amount of makeup water.
3. Cap bottle and tumble overnight (16 hours) at 30 rpm and 75 F *(24 C)* or above.
4. Remove the solution from the tumbler and stir for 90 minutes at 750 rpm on an air or electric stirrer. Longer or faster stirring can cause shear degradation of the polymer.
5. Solution should appear uniform when poured from one container to another. Solution should be free of partially dissolved and undissolved gels when passed through the 200 mesh screen. If not, start over.

2.5.3.4 Dilution of Stock Solution. Refer to Par. 2.2.2.3, Step 8.

2.5.4 Recommended Mixing Procedure [Stock Solution (Salt Concentrations Higher Than Three Percent)]. The following procedure and apparatus are recommended for dissolution of gel in brines containing high salt concentrations (greater than three percent).

2.5.4.1 Apparatus.

1. One two-liter separatory funnel with a minimum 1/4-inch inside diameter opening at the bottom.
2. One 30-rpm peristaltic pump sized for 0.313-inch inside diameter tubing (Cole-Parmer Masterflex® 7015, or equivalent).
3. Two lengths of 0.313 inch Tygon® tubing (or equivalent), one approximately 30 inches long, the other approximately 12 inches long.
4. Gel polymer dissolving device (refer to Figure 2-1).

Figure 2-2, Sketch A illustrates the initial set up of the equipment. Connect the tubing (approximately 30 inches long) to the bottom of the separatory funnel, insert the discharge end of the tubing through the peristaltic pump head, and install the tubing to allow for return flow to the top of the separatory funnel.

2.5.4.2 Calculations for Preparing Stock Solution. Weigh out polymer and brine in proper quantities for preparing the stock solution (refer to Par. 2.5.3.2).

2.5.4.3 Mixing Procedure.

1. Add the brine to the separatory funnel and start the pump. Check the pump to make sure the speed is 30 rpm and that rotation causes the direction of the flow to match the arrow shown in Figure 2-2, Sketch A (flow toward top of funnel).
2. Add the weighed amount of ground or scissor-cut polymer to the top of the funnel while the pump is running.
3. Observe operation of the pump and movement of the polymer in the separatory funnel for a few minutes to make sure the outlet is not plugged. If the outlet appears to be plugging, pinch the tubing below the outlet several times to start flow of the polymer pieces or reverse the flow for a few seconds.
4. Circulate the polymer and water through the pump for ten hours at which time the polymer solution should be free of distinct pieces of polymer material. The solution should be hydrated and ready to be run through the polymer dissolving device.
5. Stop the pump and connect the discharge end of the tubing to the polymer dissolving device away from the screen end. Connect the shorter piece of tubing (approximately 12 inches long) to the screen end of the dissolving device and insert its discharge end into the separatory funnel top as shown in Figure 2-2, Sketch B.
6. Observe the flow of polymer through the dissolving device. If the tubing between the pump and the dissolving device appears to be ballooning and/or if there is no flow out of the dissolving device, stop the pump immediately, disconnect the device, and continue hydration treatment using Step 4 above.
7. If problems arising from lack of polymer hydration are absent, allow the solution to circulate through the dissolving device for six (6) hours. The solution should be completely homogeneous leaving the tubing at the top of the separatory funnel.
8. Collect the sample of homogenized polymer concentrate solution by placing the discharge end of the tubing into a glass or plastic container and pumping the solution into the container.

2.5.4.4 Dilution of Stock Solution. Refer to Par. 2.2.2.3, Step 8.

2.6 RECOMMENDED PROCEDURE FOR LABORATORY PREPARATION OF POLYMER SOLUTIONS FROM POLYSACCHARIDE PRODUCTS.

2.6.1 General. Polysaccharide is supplied as both dry and liquid material. Dry material is ordinarily used as 100% active. Liquid polysaccharide concentration should be obtained from the manufacturer as there are several different methods for calculating polysaccharide concentration.

2.6.2 Recommended Mixing Procedure.

2.6.2.1 Apparatus.

Blender	Waring® Commercial Blendor™ Model 7011 S, or equivalent, fitted with a 40-oz glass or steel container. No load speed of approximately 15,500 rpm.
Variable Transformer	0-120 volt (e.g., POWERSTAT® Type L116B, or equivalent).
Top Loading Laboratory Balance	Sensitivity 0.01 g. Maximum load 2000 g.
Stopwatch or Timer	

2.6.2.2 Calculations for Preparing a Stock Solution Using Liquid or Dry Polysaccharide Products.

1. Using manufacturer's or other data describing the product, calculate the amount of polymer product required to make up the appropriate amount of stock solution. Refer to example calculations shown in Par. 2.2.2.2, Equation (2-1).
2. Calculate the amount of makeup water required to make the desired amount of stock solution according to Equation (2-2).

2.6.2.3 Mixing Procedure for Dry Polysaccharides*

1. Sift dry xanthan gum into the makeup water in the blending jar, while stirring at high speed with rheostat at approximately 40% (44-45 volts).
2. Mix two minutes at 40% power.
3. Mix three minutes at 60% power.
4. Mix two minutes at 80% power.

   NOTE: This procedure applies specifically to dry xanthan gum polysaccharides and may or may not be applicable to other dry polysaccharide products. Consult the manufacturers of other dry polysaccharide products for their recommended mixing procedure.

2.6.2.4 Mixing Procedure for Liquid Polysaccharides. Add the calculated amount of liquid polymer to the calculated amount of makeup water in the blender jar. Mix two minutes in the blender at 50 volts.

2.6.2.5 Dilution of Stock Solution. Dilute as desired and mix one minute in the blender at 50 volts.

**NOTE:* Solution temperature will be raised by the procedure. Cool the solution to 77 F *(25 C)* before subsequent testing to improve test precision and reproducibility.

2.6.2.6 Preservation of Xanthan Gum and Other Polysaccharide Solutions. If the solution is to be retained, a suitable biocide should be added. For xanthan gum solutions being retained at room temperature, 2500 ppm formaldehyde is usually sufficient. Manufacturer should be consulted for further recommendations.

2.7 RECOMMENDED PROCEDURE FOR LABORATORY PREPARATION OF POLYMER SOLUTIONS FROM SYNTHETIC LATEX POLYMERS.

2.7.1 General. The term, "latex polymer," encompasses high molecular weight acrylate copolymers containing carboxylic acid groups and formulated as an aqueous latex product. Solutions are prepared by diluting the product (active polymer content is specified by supplier) with water and neutralizing with caustic to yield the desired concentration. *A 20,000 ppm stock solution is recommended for latex polymers.*

2.7.2 Components for Preparation of 20,000 ppm Stock Solution.

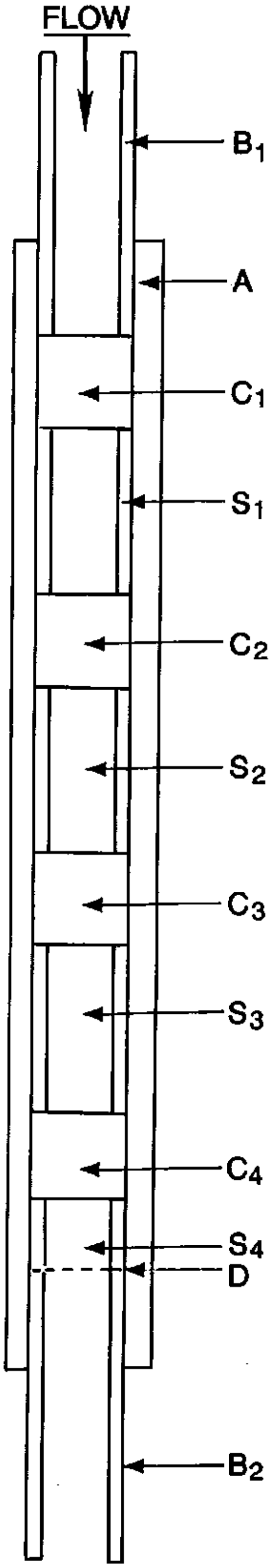
8.25 g polymer (21% active)
87.10 g water
4.65 g sodium hydroxide (10% aq.).

NOTE: The 20,000 ppm activity of the polymer solution is due to addition of the sodium to the polymer molecule as neutralization proceeds.

2.7.3 Mixing Procedure for Preparing a 20,000 ppm Stock Solution.

1. Dilute latex product with the calculated amount of water and mix gently.
2. Add the calculated amount of NaOH solution to the diluted latex.
3. For quantities of one liter or less of stock solution, it is convenient to measure the materials into a glass jar, cap the jar, and shake it vigorously by hand for a minute or so until the liquid changes from a milky fluid to a viscous transparent solution.
4. Allow the 20,000 ppm polymer solution to age for 2 hours to attain maximum clarity and viscosity.
5. If brine is used to dilute the latex to the 2% solids level prior to neutralization with the NaOH solution and a precipitate is noted, the latex should be stabilized with Aerosol® A103, or equivalent, based on the concentration of 0.4 grams of surfactant per 100 grams of latex polymer on an "as is" basis.

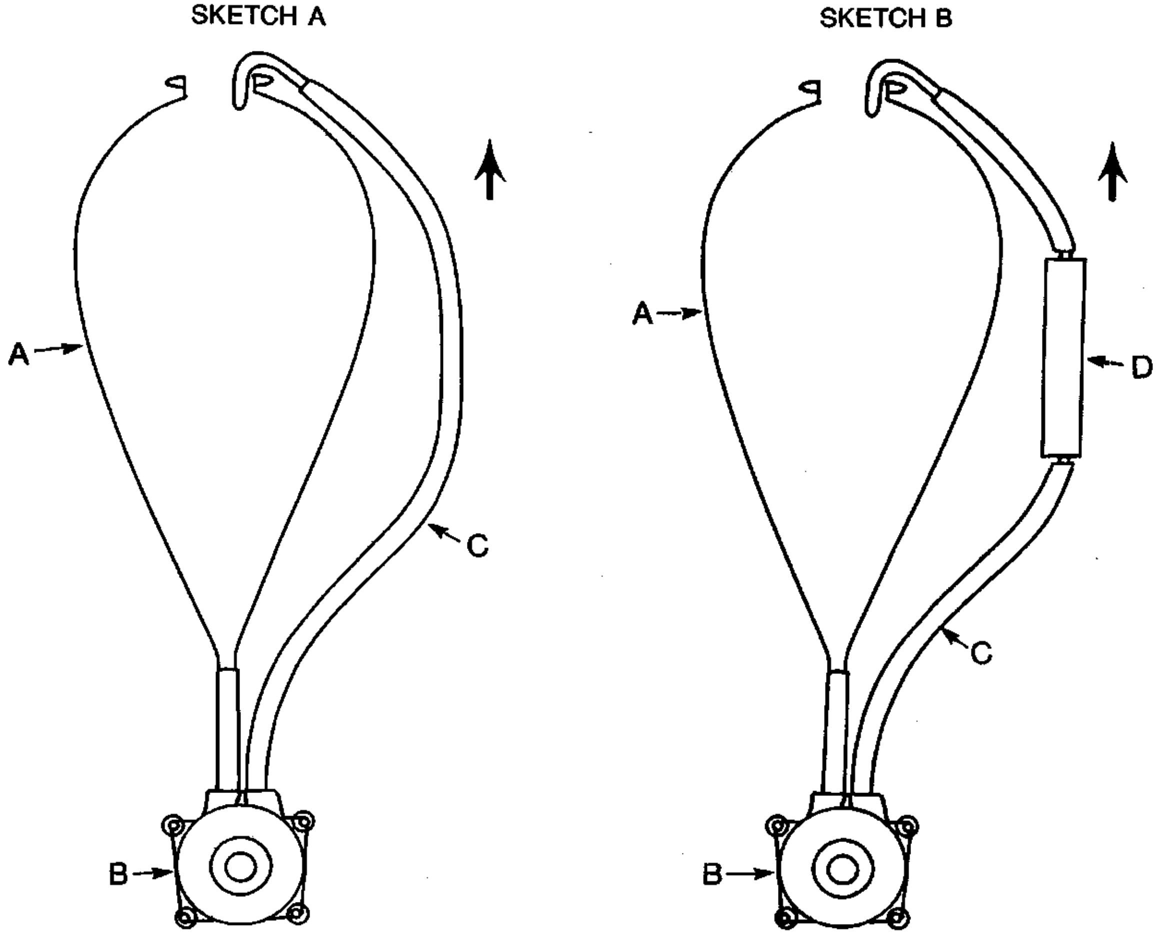
2.7.4 Dilution of Stock Solution. Refer to Par. 2.2.2.3, Step 8.



LEGEND:

A - ACRYLIC TUBE, 3/4" OD, 1/2" ID, 6" LENGTH.
B - ACRYLIC TUBE, 1/2" OD, 3/8" ID,
6" LENGTH CUT INTO 6 PIECES;
B_1 AND B_2: 1 1/2" END PIECES,
S_1, S_2, S_3: 7/8" SPACERS, AND
S_4: 3/8" SPACER.
C - ACRYLIC ROD, 1/2" OD, 2" LENGTH
CUT INTO 4 PIECES, EACH 1/2" LONG.
C_1 - BORED WITH FIVE SPACED 1/8" HOLES.
C_2 - BORED WITH SEVEN SPACED 7/64" HOLES.
C_3 - BORED WITH NINE SPACED 3/32" HOLES.
C_4 - BORED WITH ELEVEN SPACED 5/64" HOLES.
D - STAINLESS STEEL SCREEN, 100 MESH,
1/2" DIAMETER.

FIGURE 2-1
EXAMPLE GEL POLYMER DISSOLVING DEVICE



LEGEND:

A - TWO-LITER SEPARATORY FUNNEL.
B - PERISTALTIC PUMP WITH 30 RPM SYNCHRONOUS MOTOR, COLE-PARMER MASTERFLEX® MODEL 7015, OR EQUIVALENT.
C - TYGON® TUBING, 0.313" ID, OR EQUIVALENT.
D - GEL POLYMER DISSOLVING DEVICE.

FIGURE 2-2
EXAMPLE GEL POLYMER EQUIPMENT

APPENDIX TO SECTION 2
NOMENCLATURE

A_{pr} = activity of polymer product, weight percent. *(NOTE:* Supplier should specify percent active polymer in the polymer product.)

C_d = concentration of polymer in the diluted solution, ppm.

C_s = concentration of polymer in the stock solution, ppm.

W_{bd} = weight of makeup water used in the diluted solution, g.

W_{bs} = weight of makeup water used in the stock solution, including additional activator, if any, g.

W_d = weight of diluted solution, g.

W_{pr} = weight of polymer product, g.

W_s = weight of stock solution, g.

SECTION 3
POLYMER SOLUTION RHEOLOGY AND FLOW THROUGH POROUS MEDIA

3.1 INTRODUCTION

3.1.1 General. This section describes procedures that allow a direct comparison of enhanced oil recovery polymers in a variety of standard tests. The recommended procedures for the viscometric tests are not designed to give information on a particular field water for a specific reservoir application. However, from these procedures, comparable products can be selected for additional site-specific testing, such as further viscometric tests and flow tests through reservoir core samples. The purpose of this section is to provide standard test procedures, including rheometry and flow through porous media, to permit comparison of different polymers. The recommended viscometric tests are designed to assess the effects of: 1) shear rate, 2) temperature, 3) salinity and hardness, 4) pH, and 5) polymer concentration on solution viscosity. Some simple rheological models are reviewed as well as methods for estimating intrinsic viscosity and viscosity-average molecular weight. Sufficient background information is given to enable a better understanding of the rheological behavior of polymers used in enhanced oil recovery applications*. Procedures are described for the measurement of mobility and permeability reduction obtained with polymer solutions in both linear and radial cores.

3.2 EQUIPMENT FOR VISCOMETRIC TESTS

3.2.1 General. The type of equipment required for measurement of viscosity of polymer solutions will vary depending on the intended use of the test results. For monitoring field polymer projects, instruments that are rugged and relatively inexpensive are necessary. For careful research work in the laboratory, instruments that are more accurate or more sophisticated are often required. To operate research-grade rheometers, the manufacturer's instructions should be followed. Procedures are given herein for some of the more common and simpler equipment used for viscosity measurements. Certain advantages associated with several commercial instruments are highlighted in Table 3.1.

3.2.2 Field Monitoring. Viscosities of polymer solutions prepared for injection in the field are monitored as a control measure. Polymer solutions are sampled according to the procedures outlined in Par. 6.4. Using a 4-speed (or 8-speed, if available) Brookfield® Synchro-Lectric Viscometer (or equivalent), the solution viscosity is measured with the Ultra Low (UL) Adapter at a given temperature ±2 F *(±1.1 C)*. If readings for the injected fluid exceed the maximum dial reading of 100, dilution is required. If the dial reading is less than 10, the accuracy of the measurement is poor. If dilution is necessary, the final solution weight for a given amount of field solution sample can be calculated by the following formula:

Dilution Factor x Weight of Sample = Final Wt. . . . (3-1)

The desired amounts of solution and water are mixed by *gentle* shaking or with a magnetic stirrer. The solution viscosity of the field sample or the diluted sample is measured at 6 rpm and at one other speed, preferably one which keeps the scale reading between 10 and 90.

TABLE 3.1
VISCOSITY MEASURING INSTRUMENTS

NOTE: Viscometers suitable for drilling fluid measurements may not be suitable for use in testing enhanced oil recovery polymers.

Brookfield® Synchro-Lectric Model LVF (4-speed), Model LVT (8-speed), or Models LVTDV-I or LVTDV-II (Digital), Model HATD (8-speed), all with Ultra Low (UL) and Small Sample Adapters

Advantages

Convenient to use.

Rugged construction.

Can be portable.

Contraves® LS-30*

Advantages

Accuracy.

Reasonable range of shear rates, especially low shear — even for low viscosity fluids.

Relatively easy to use.

Haake RV-20

Advantages

Accuracy.

Lower shear rate than comparably priced equipment.

Broad temperature control.

Computer control, easy to use.

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* *All text references for Section 3 can be found in Appendix to Section 3.*

* *A fixed-amplitude, oscillatory drive is available as an option for linear viscoelastic measurements.*

TABLE 3.1 (Continued)

Rheological instruments that measure properties in addition to viscosity (normal stresses and/or dynamic viscoelastic properties).

Haake RV-100/CV-100*

Advantages

Accuracy.

Reasonable range of shear rates, but not quite as low as Contraves® for low viscosity fluids.

Good temperature control, higher operating temperature than Contraves®.

Rheotech International VER**

Advantages

Accuracy.

Broad range of shear rates and frequencies.

Good temperature control.

Computer control, easy to use.

Rheometrics Fluids Rheometer Model RFR-7800**

Advantages

Accuracy.

Broad range of shear rates.

Choice of test geometries and transducers.

Easier to use and analyze data than some other instruments.

Broad temperature range — options to provide wider range than Contraves® or Haake.

Microprocessor-based system for operational control and data analysis.

Rheometrics Mechanical Spectrometer RMS-705F*

Advantages

Accuracy.

Better suited for low shear rate range than Fluids Rheometer.

Very broad range of shear rates and frequencies.

Good temperature control over a wide range of temperatures.

Microprocessor-based system.

Rheometrics Fluids Spectrometer RFS-8400*

Advantages

Specifications and features similar to the Fluids Rheometer, except for normal force measurements.

Uses a force-rebalance transducer (instead of the XYZ-force transducer used in the older RFR-7800 and RMS-705F models) to reduce electronic drift during measurements.

Microprocessor-controlled operation.

Rheometrics Mechanical Spectrometer RMS-800FL*

Advantages

Improved version of RMS-705F, especially for normal stress measurements; among state-of-the-art instruments for rheological characterization of fluids.

Features and specifications similar to (or better than) the previous model.

Uses a force-rebalance transducer.

Weissenberg Rheogoniometer™*

Advantages

Accuracy.

Very broad range of shear rates and frequencies.

Good temperature control.

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* *A variable-frequency, variable-amplitude assembly is available as an option. Utilizes an air bearing on the CV-100 option.*

** *Utilizes an air bearing.*

3.2.3 Comparative Testing of Polymers. In order to evaluate a polymer as a potential candidate for a polymer flood, the rheological behavior of the polymer in solution should be measured under a variety of conditions. Viscosity measurements should be made using the 8-speed Brookfield® Synchro-Lectric Viscometer and the UL Adapter, or equivalent, at a minimum of 4 shear rates, if possible. Measurements should begin at the lowest rpm (shear rate) and work upward. Such measurements will yield information about the shear dependence of the polymer viscosity under a given set of conditions (refer to Par. 3.4.1). Recommended conditions for measuring solution viscosity are shown in Pars. 3.4.1 through 3.4.5.

3.2.4 Research Work. Laboratory research work often requires greater accuracy than is necessary for other tests. Depending on the primary research needs, the viscosity measuring instruments (refer to Table 3.1) should be carefully selected for use in this testing.

3.3 MEASUREMENT OF RHEOLOGICAL PROPERTIES

3.3.1 Dissolution of Polymers. Prepare polymer solution in the desired brine system according to applicable recommended procedures shown in Section 2. Prepare at least 100 g of this solution.

3.3.2 Measurement With Brookfield® Synchro-Lectric Viscometer. The procedures that follow apply to the Brookfield® Synchro-Lectric Model LVF (4-speed), Model LVT (8-speed), Model LVTDV (8-speed, digital readout), and Model HATD (8-speed) viscometers. Since the Model LVTD does not have a clutch, readings may be obtained without turning the motor off. All future references to use of a clutch pertain only to Brookfield Models LVF and LVT. The calibration of the Brookfield viscometer should be checked at suitable intervals by the use of standard viscosity fluids. Viscosity oils conforming to *ASTM Designation D 446-74*[6] should be used to check this equipment. If equivalent viscometers are used, refer to the equipment manufacturer for operating and calibration instructions.

3.3.2.1 Apparatus.

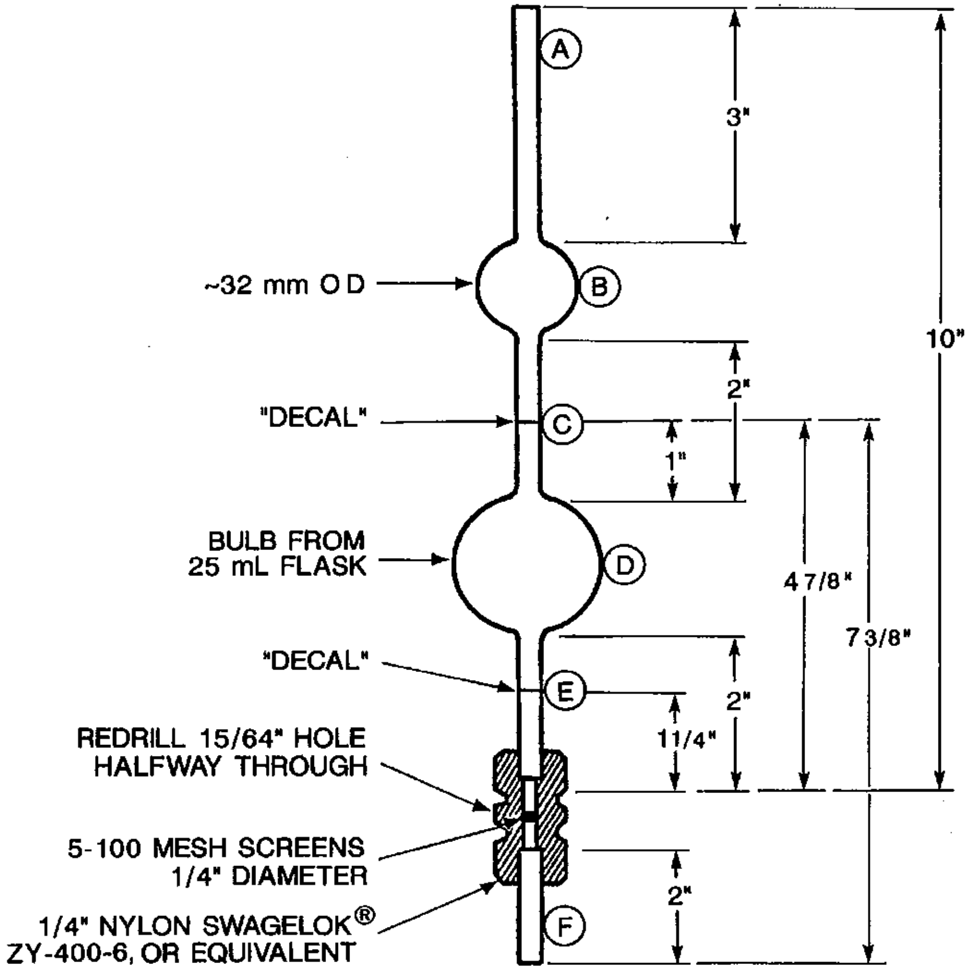
1. Brookfield® Synchro-Lectric LV Series Viscometer.
2. Standard viscosity fluids.
3. UL Adapter (open cup).
4. Constant temperature bath.
5. 25-mL graduated cylinder.

3.3.2.2 Procedures.

1. Lift the lower shaft of the instrument and attach the spindle nut. After attaching the adapter body, place the hook on the UL spindle through the eyelet of the spindle nut.
2. Transfer 16 mL of the polymer solution to be measured into the UL adapter cup. Some cup designs may require different volumes. Refer to the manufacturer's operating instructions for specific information on equipment volume requirements.
3. With the spindle held at an angle, slowly immerse the spindle into the polymer solution. This procedure will ensure that air is not trapped beneath the spindle.
4. Attach the cup to the main adapter body.
5. Set the speed desired on the speed selector knob. Start at the lowest rotational speed and work upward. Although not absolutely necessary, speeds should be changed while the motor is running and the clutch is depressed.
6. Immerse the cup into the constant temperature bath up to the main adapter and start rotation of the spindle by depressing the clutch, turning on the motor, and releasing the clutch.
7. Allow the temperature to equilibrate in the cup for at least 10 minutes at 100 F *(37.8 C)* or longer at higher temperatures.
8. To take a reading on the scale, depress the clutch and turn the motor off with the pointer in view.
9. Record the rotational speed and the dial reading.
10. Obtain a second reading by turning on the motor with the clutch still depressed, releasing the clutch, waiting for the pointer to stabilize, and repeating Step 8. Obtain as many check readings as necessary.
11. With the motor on and clutch depressed, increase the rotational speed to the next higher value, and repeat Steps 8 through 10. The time required for the dial to stabilize depends on the rotational speed; at speeds less than 6 rpm, it may take at least the time required for 3 to 4 revolutions of the dial, while at higher speeds only about 30 seconds may be required.
12. The viscosity of the solution in centipoise (cP) or millipascal second (mPa·s) is determined by using the conversion factors shown in Table 3.2.
13. Calibration of the instrument should be checked on a regular basis with the standard viscosity fluids described in Par. 3.3.5.

3.3.3 Measurement of Screen Factor. This measurement is related to the viscoelastic nature[2] of solutions of some synthetic polymers such as polyacrylamides and is most affected by the larger polymer molecules.

3.3.3.1 Apparatus. Screen factor bulbs[3] (screen factor apparatus, refer to Figure 3-1) are commercially available. This equipment is sometimes called a screen viscometer; however, it does not measure viscosity. The equipment is more properly called a screen factor apparatus (refer to Figure 3-1).



ALL TUBING 6.3 mm OD

FIGURE 3-1
SCREEN FACTOR APPARATUS

TABLE 3.2
CONVERSION FACTORS FOR BROOKFIELD® SYNCHRO-LECTRIC VISCOMETER
[Ultra Low (UL) Adapter]

	Nominal Shear Rate, sec^{-1}			
RPM	Closed Cup	Open Cup (Plastic Cap)	Viscocity Range, cP	Multiply Reading by
0.3	0.4	0.3	0-2000	20.0
0.6	0.7	0.7	0-1000	10.0
1.5	1.8	1.7	0-400	4.0
3.0	3.7	3.3	0-200	2.0
6.0	7.3	6.6	0-100	1.0
12.0	14.7	13.2	0-50	0.5
30.0	36.7	32.9	0-20	0.2*
60.0	73.4	65.8	0-10	0.1**

* *Deduct 0.1 from reading before multiplying to correct for windage.*
** *Deduct 0.4 from reading before multiplying to correct for windage.*

3.3.3.2 Procedure.

1. Set up the screen factor apparatus with a clamp attached to a ring stand. Check from more than one angle to be certain that the apparatus is perfectly vertical.
2. Filter all samples through a 325-mesh stainless steel screen to remove any particles which might clog the apparatus and give erroneous results.
3. Equilibrate samples in a water bath at the appropriate temperature [usually 77 F, *(25 C)*].
4. With the screens attached, place approximately 40 mL of the solution to be measured into the top bulb, B, using a syringe without needle. Release a little of the solution to fill the attached section. An alternate procedure is to invert the screen factor apparatus, immerse tube A into the liquid, and apply suction to tube F. The purpose of this procedure is to avoid the possibility of mechanical degradation by *not* drawing the sample through the screen assembly.
5. Remove any air which may be trapped in the screens by gently tapping and/or blowing some solution through the screens. No air bubbles should be present in either the solution or the screens during the measurement.
6. Allow the solution to run freely. Begin timing when the meniscus passes the first timing mark, C, and stop when it passes the second timing mark, E. Record times for both the solvent and the polymer solution. Calculate screen factor from:

$$\text{Screen Factor} = \text{Solution Time}/\text{Solvent Time} \quad \text{.......(3-2)}$$

7. Thoroughly flush both the bulb and screen assembly with distilled water until original solvent time is obtained. It should not be necessary to remove screens from the assembly to clean, but occasionally it may be necessary to clean the screens with citric acid (0.5 percent). Thoroughly rinse with distilled water. Bleach can be used to clear the screens, but may have undesirable results such as pitting and film formation. Do not mix citric acid and bleach.
8. Solvent time (where the solvent is usually water or brine) should be about 5.5 to 8 seconds. Since it is difficult to reproduce these short times exactly, the average of 3 to 10 runs should be used in Equation (3-2).
9. For improved accuracy, the average of 2 or 3 tests with polymer solution can be used. The screen factor measurement for a given polymer solution may vary among different instruments. In order to obtain comparable results in different laboratories, the instruments should be carefully selected.

3.3.4 Measurement of Viscosity With Capillary Viscometer.

3.3.4.1 General. In a rigorous sense, the use of gravity-type capillary viscometers is limited to polymer solutions that do not deviate much from Newtonian behavior. The shear rates in the capillary are not accurately known and some representative value is usually computed. Nevertheless, procedures are given for the more common capillary viscometers which are used because of their low cost and convenience.

For steady, isothermal, laminar flow of an incompressible Newtonian liquid in a tube, the coefficient of viscosity, μ, may be determined by the Hagen-Poiseuille equation[4]:

$$\mu = \frac{\Delta p \pi r^4 t}{8VL} \quad \text{............................ (3-3)}$$

where:

t is the time required for volume V of liquid to flow through a capillary tube of length, L, and radius, r, under an applied pressure, Δp.

Indirect measurements are usually made in which the viscosity of a liquid is determined relative to that of another liquid whose viscosity has been obtained by an absolute method. In a simple, capillary-bulb viscometer (such as shown in Figure 3-2), the pressure differential causing flow through the capillary is due to gravity and is given by the product of the difference in height (h) of the liquid levels in the two tubes, the acceleration of gravity (g), and the density of the liquid. Assuming quasi-steady state flow, Equation (3-3) can be arranged to:

$$\mu_1 = \left(\frac{hg\pi r^4}{8VL}\right)\rho_1 t_1 \quad \text{...................... (3-4)}$$

The subscript, 1, in Equation (3-4) refers to the first or reference fluid. If the same volume of a second liquid is placed in the same capillary viscometer, then:

$$\mu_2 = \left(\frac{hg\pi r^4}{8VL}\right)\rho_2 t_2 \quad \text{...................... (3-5)}$$

The subscript, 2, in Equation (3-5) refers to the second fluid. The ratio of Equations (3-5) and (3-4) yields:

$$\mu_2 = \mu_1 \frac{\rho_2 t_2}{\rho_1 t_1} \quad \text{...................... (3-6)}$$

From measurements of the densities and flow times of the two liquids, viscosity of the second fluid can be calculated when viscosity of the first liquid is known. Either water or a suitable viscosity standard may be used as the reference liquid. In the case of non-Newtonian fluids, the use of the Hagen-Poiseuille equation provides an apparent shear viscosity, η, at some average shear rate. Since the pressure gradient is not constant during the measurement, unsteady-state conditions prevail, as opposed to the steady-state flow conditions assumed in Equation (3-3). As a result, Equation (3-6) and the measurements are only valid within a specified range of flow times (200-1000 seconds for the Cannon-Fenske routine viscometers). Therefore, this efflux time technique does not permit a precise characterization of the shear-dependent viscosity function for polymeric liquids. Shear rates during flow measurements in the capillary viscometers are generally high, in excess of 100 $sec.^{-1}$ However, this procedure is simple to use and is adequate as a qualitative comparison test in some instances. The procedures will be summarized since detailed methods of testing in capillary viscometers are available in *ASTM D445* and *ASTM D446*.[5,6]

3.3.4.2 Cannon-Fenske Routine Viscometer: Apparatus and Procedures. Cannon-Fenske routine viscometers are often used for a qualitative comparison of viscosities of polymer solutions. The following procedures are recommended for use of this equipment.

1. Select a clean, dry viscometer (refer to Figure 3-2) which will give a minimum flow time of 200 seconds. For dilute polymer solutions, a size 100 or 150 may be acceptable.
2. To introduce a sample, invert the viscometer, immerse tube A into the liquid and apply suction to tube G which causes the sample to rise to etched line E. Turn the viscometer to the normal position and wipe tube A clean.
3. Insert the viscometer into a holder and place in a constant temperature bath. Allow 10 minutes for the viscometer to reach equilibrium at 100 F *(37.8 C)* or longer at higher temperatures.
4. With the viscometer aligned vertically, apply suction to tube A and bring the sample into bulb B, a short distance above mark C.
5. The efflux time is obtained by allowing the sample to flow freely and measuring the time for the meniscus to pass from C to E. If this time is less than 200 seconds, select a smaller size capillary viscometer.
6. Check the efflux time by repeating Steps 4 and 5.
7. The kinematic viscosity (in centistokes) is calculated by multiplying the efflux time (in seconds) by the viscometer constant. Multiply this value by the density of the solution (in g/mL) to obtain viscosity in cP or mPa.s.

3.3.4.3 Cannon-Ubbelohde Four-Bulb Shear Dilution Viscometer: Apparatus and Procedures. Cannon-Ubbelohde four-bulb viscometers permit dilution of the polymer solution within the viscometer and provide estimates of viscosities at approximate shear rates that are dependent on bulb size. The following procedure is recommended for use of this equipment (refer to Figure 3-3):

1. Select a clean, dry viscometer (Figure 3-3) which will give a flow time greater than 200 seconds for the lowest viscosity fluid.
2. Pipette 10 mL of polymer solution through tube G into the lower reservoir H of the viscometer.
3. Using a self-aligning holder, place the viscometer in a constant temperature bath. Vertically align the viscometer.
4. Allow the sample to come to bath temperature; 10 minutes at 100 F *(37.8 C)* or 20 minutes at 200 F *(93.3 C)*. Allow 1 additional minute for each 10 F *(5.6 C)* above 100 F *(37.8 C)*.
5. Place a finger over tube B and apply suction to tube A until the liquid reaches the center of bulb C. Remove suction from tube A. Remove finger from tube B and immediately place it over tube A until the sample drops away from the lower end of the capillary into bulb F. Then remove finger again and measure the efflux time for each bulb.
6. To measure the efflux time, allow the liquid sample to flow freely down past etch mark D. Measure the time required for the meniscus to pass from etch mark D to etch mark E, to the nearest 0.1 second.
7. Without recharging the viscometer, check determinations by repeating Steps 5 and 6.
8. Calculate the kinematic viscosity of the sample by multiplying the efflux time by the viscometer constant.
9. Calculate the shear rate at the wall for each bulb by dividing the shear rate constant by the flow time in seconds.
10. Dilute the sample by adding a measured quantity of solvent from a pipette directly into the lower reservoir of the viscometer. Mix the original sample and solvent by applying slight pressure to tube B several times and shaking the viscometer.
11. Repeat Steps 4 through 9. Additional dilution may be made, if necessary.

3.3.5 Calibration of Viscometers. Viscometers can be ordered with calibration constants provided by the supplier, or such constants can be independently determined by the use of standard viscosity fluids conforming to *ASTM D 445-79*[5] (check latest revision).

3.3.6 Procedures For Other Viscometers. As stated in Par. 3.2.4, a number of high-quality instruments are available to generate accurate rheological data for

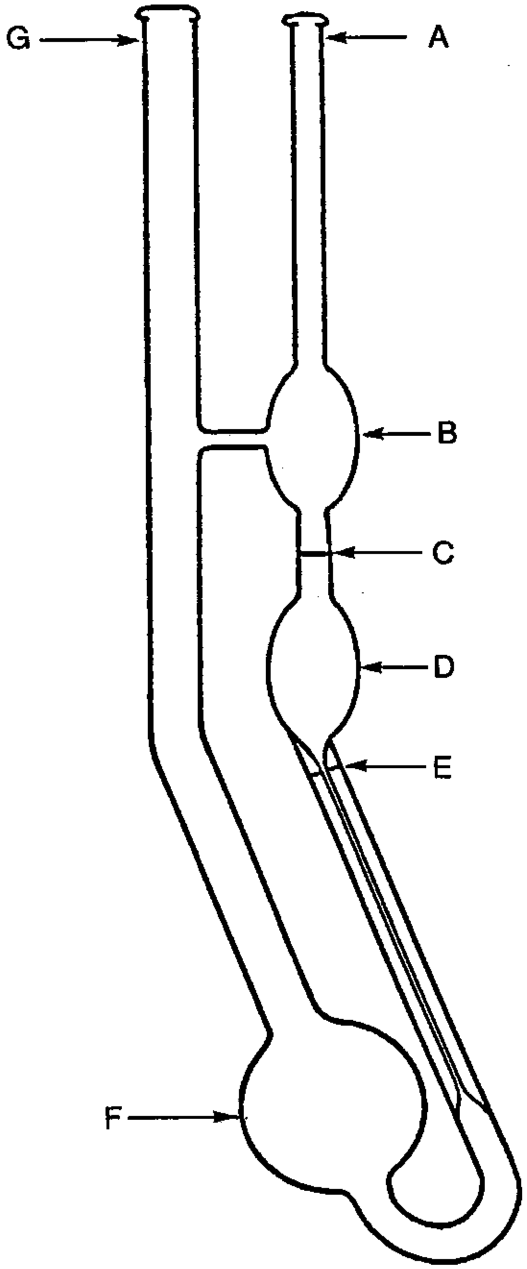


FIGURE 3-2
CANNON-FENSKE ROUTINE VISCOMETER

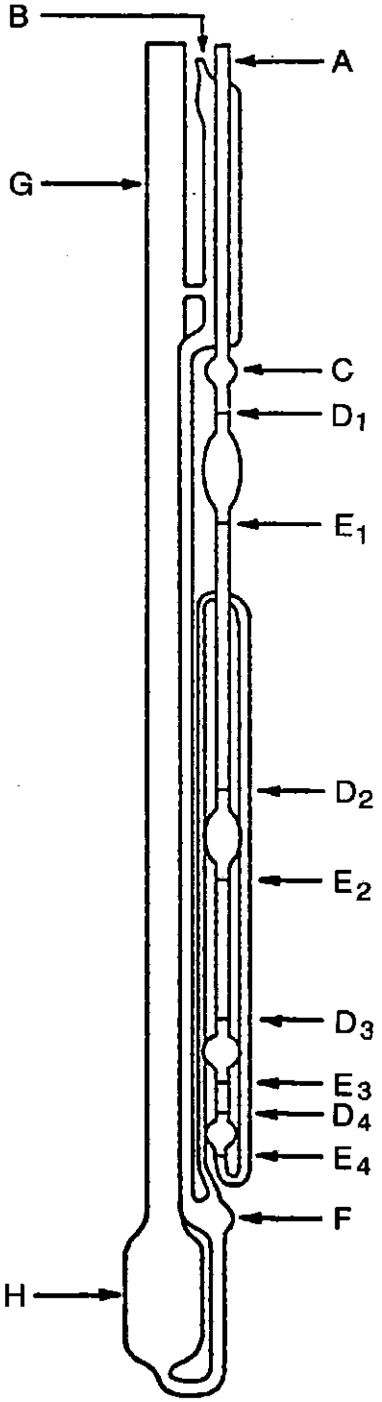


FIGURE 3-3
CANNON-UBBELOHDE DILUTION VISCOMETER

research applications. Since the needs and requirements of various laboratories differ, there is no single rheometer to be recommended. References 9 and 10 provide detailed reviews on measurement of various rheological properties of non-Newtonian fluids and therefore, procedures will not be discussed here for these more sophisticated instruments.

3.4 MEASUREMENTS OF POLYMERS AFFECTED BY FIELD PARAMETERS

3.4.1 General. Because polymers with different molecular weights, ionic charge, or molecular structure are available, preliminary laboratory tests are used to compare products under standardized test conditions. This section provides the recommended procedures for tests that consider the effect of shear rate, temperature, salinity, hardness, pH, and active polymer concentration. From this type of data, comparable polymer products can be selected for additional site-specific tests and ultimately for subsequent core testing. As a precaution, the possibility of short-term polymer degradation should be considered at elevated temperatures and for certain pH conditions.

3.4.2 Dependence of Viscosity on Shear Rate: Apparatus and Procedure.

Apparatus: Equivalent to or more accurate than 8-speed Brookfield® Synchro-Lectric Viscometer with UL Adapter.

Brine: Appropriate to conditions that apply.

Polymer Concentration: Appropriate to conditions that apply.

Temperature: Appropriate to conditions that apply.

Procedure:

1. Measure the viscosity of the polymer solution at a minimum of 5 shear rates. Start at the lowest shear rate and work upward.
2. From the data obtained, plot viscosity versus shear rate. Specify the polymer concentration, water, pH, and temperature of the test.

3.4.3 Viscosity as a Function of Temperature: Apparatus and Procedure.

Apparatus: Equivalent to or more accurate than 8-speed Brookfield® Synchro-Lectric Viscometer with UL Adapter.

Brine: 1000 ppm NaCl and 100 ppm anhydrous $CaCl_2$ (0.1% NaCl and 0.01% $CaCl_2$).

Polymer Concentration: 750 ppm.

Temperatures: 77 F, 122 F, 167 F, 194 F *(25 C, 50 C, 75 C, 90 C).*

Procedure:

1. Measure the viscosity of the polymer solution at two or more shear rates. Start at the lowest shear rate and work upward.
2. Plot the data obtained as measured viscosity versus temperature for each shear rate.

3.4.4 Effects of Salinity and Hardness on Viscosity: Apparatus and Procedure.

Apparatus: Equivalent to or more accurate than 8-speed Brookfield® Synchro-Lectric Viscometer with UL Adapter.

Brines: 0.1, 0.3, 1.0, and 10% NaCl.
0.01, 0.03, 0.1, and 1% $CaCl_2$ (anhydrous)
(Brines containing both NaCl and $CaCl_2$ in ratios of 10 to 1, respectively.)

Polymer Concentration: 750 ppm.

Temperature: 77 F *(25 C).*

Procedure:

1. Measure the viscosities of the polymer solutions at several shear rates. Start with the lowest shear rate and work upward.
2. Plot the data as viscosity [measured at 6 rpm or 7.3 sec^{-1} or other shear rate(s)], versus salt concentration.

3.4.5 Effects of pH on Viscosity: Apparatus and Procedure.

Apparatus: Equivalent to or more accurate than 8-speed Brookfield® Synchro-Lectric Viscometer with UL Adapter.

Brine: 0.1% NaCl and 0.01% anhydrous $CaCl_2$ (1000 ppm NaCl and 100 ppm $CaCl_2$).

Polymer Concentration: 750 ppm.

Temperature: 77 F *(25 C).*

Solution pH: 4, 6, 8, 10, 12.

Reagents: Dilute hydrochloric acid, dilute sodium hydroxide.

Procedure:

1. Adjust the pH of a 1000 ppm polymer solution to the desired value.
2. Dilute to 750 ppm using the brine solution described above.
3. Check the pH of the diluted polymer solution. Adjust if necessary.
4. Measure the viscosity for at least two shear rates of the solutions at each pH level. Measurements should be performed the same day the pH is altered.
5. Plot the data as viscosity versus pH at each shear rate.

3.4.6 Relationship of Polymer Concentration and Viscosity: Apparatus and Procedure.

Apparatus: Equivalent to or more accurate than 8-speed Brookfield® Synchro-Lectric Viscometer with UL Adapter.

Waters: Fresh — 1000 ppm NaCl and 100 ppm $CaCl_2$ (anhydrous).
Brine — 30,000 ppm NaCl and 3000 ppm $CaCl_2$ (anhydrous).

Polymer Concentrations: 250, 500, 750, 1000, 2000, 3000 ppm.

Temperature: 77 F *(25 C)*.

Procedure:

1. Prepare a polymer solution as described in Section 2 at an active concentration of 5000 ppm using the type of water (brine or fresh) under investigation. Dilute the 5000 ppm solution to the desired concentration using the water under investigation.
2. Measure the viscosity at two or more shear rates.
3. Repeat for each of the polymer test concentrations.
4. Present data as a table or plot of viscosity versus polymer concentration for each shear rate.

3.5 INTRINSIC VISCOSITIES[7]

3.5.1 General. As will be discussed in Par. 3.5.5, the intrinsic viscosity of a polymer solution, $[\eta]$, may be used as an indirect indicator of polymer molecular weight for homologous linear polymers. In order to determine $[\eta]$, it is necessary to measure viscosities of a series of polymer solutions at various polymer concentrations in a selected brine solvent. From these viscosities, specific (η_{sp}) and relative (η_r) viscosities are calculated: (η_{sp}) = (η/η_s)-1 and (η_r) = η/η_s; where η_s is the solvent viscosity, and η is the viscosity of the polymer solution, preferably measured at a very low shear rate. Values of η_{sp}/c and (ln η_r)/c are plotted as functions of polymer concentration, and separate straight lines are extrapolated to zero concentrations to obtain $[\eta]$. The y-intercept at $c = 0$ is the intrinsic viscosity estimate, $[\eta]$, in units of inverse concentration.

3.5.2 Materials and Apparatus.

Apparatus: A rheometer capable of measuring low viscosities at low shear rates is preferred (refer to Par. 3.2).

Brine : 3% NaCl.

Polymer Concentrations: Nominally 1000, 750, 500, 400, 300, 200, and 150 ppm.

Temperature: 77 F *(25 C)*.

3.5.3 Procedure With Low Shear Viscometer.

1. Prepare a series of dilutions of the polymer of interest in 3% NaCl brine. Polymer concentration may range from approximately 150-1000 ppm (0.015 to about 0.1 g/dL).
2. Measure viscosities as a function of shear rate for each of these solutions and for the brine alone.
3. Using the very low or zero-shear-rate viscosities of the polymer solutions, calculate specific (η_{sp}) and relative (η_r) viscosities at the same shear rate.
4. Plot values of η_{sp}/c and (ln η_r)/c as functions of polymer concentration, c. Fit to separate straight lines and extrapolate to a polymer concentration, c, equal to zero. As mentioned above, the y-intercept at $c = 0$ is the intrinsic viscosity estimate, $[\eta]$, in units of inverse concentration. Usually concentrations are reported as g/dL and the intrinsics as dL/g, but other units may occasionally be found in the literature.
5. The question of what concentration is "low enough" is one that must be considered on a case-by-case basis. Higher molecular weight, a greater degree of ionic character of the polymer, and lower salinity of the water can all increase solution viscosities at a given polymer concentration. In these cases, obtaining data at lower concentrations is necessary for accurate determination of $[\eta]$.

3.5.4 Procedure With Capillary Bulb Viscometer. A less precise approach is to obtain the viscosities with a capillary viscometer, such as the Ubbelohde dilution viscometer, or equivalent. If the viscosities of the polymer solutions are very weak functions of shear rate, a reasonable estimate of intrinsic viscosity can be obtained. However, if the viscosities of the polymer solutions are affected by shear rate, the data obtained will be questionable since the shear rates and, hence, the viscosities will vary depending on the capillary flow times. For such solutions, extrapolation of viscosities obtained at high shear rates to the zero-shear region is not appropriate.

3.5.5 Estimates of Viscosity-Average Molecular Weight. For linear polymers, intrinsic viscosity is a relative measure of average polymer molecular weight. For a given polymer and solvent, $[\eta]$ increases as molecular weight increases. Intrinsic viscosity is a characteristic of the polymer sample, solvent, and temperature. With a series of samples of the same polymer, but of different molecular weights in a given solvent at a constant temperature, the following relation is usually applied:[7]

$$[\eta] = K' M^a \qquad (3\text{-}7)$$

where:

K′ and a are empirical constants known as the Mark-Houwink constants.

These constants may be determined by measuring the intrinsic viscosities of a homologous series of samples of a linear polymer for which the molecular weights, M, have been measured by another method, for example, osmotic pressure, light scattering, or sedimentation. Values of the Mark-Houwink constants (refer to Table 3.3) have been reported for laboratory synthesized polyacrylamide polymers in 3% NaCl at 77 F *(25 C)*.[8] Values for xanthan polysaccharides have also been reported and are shown in Table 3.4.[17, 18]

If the degree of hydrolysis and intrinsic viscosity of the acrylamide polymer are known, the constants in Table 3.3 can be used to estimate viscosity-average molecular weight from Equation (3-7). Mark-Houwink constants for xanthan gum polysaccharides are dependent on degree of pyruvate side-chain substitution. The level of substitution should be provided by the xanthan supplier.

TABLE 3.3
MARK-HOUWINK CONSTANTS FOR PARTIALLY HYDROLYZED POLYACRYLAMIDES[8]

% Hydrolysis	K′	a
0	7.19×10^{-5}	0.770
12	6.25×10^{-5}	0.810
20	6.3×10^{-5}	0.825
31.5	6.75×10^{-5}	0.830
40	7.1×10^{-5}	0.833

Solvent: 3% NaCl

TABLE 3.4
MARK-HOUWINK CONSTANTS FOR XANTHAN POLYSACCHARIDES[17, 18]

% Pyruvate Substitution	K′	a	Solvent
90-100	6.3×10^{-5}	0.93	0.5% NaCl
30-40	1.9×10^{-5}	0.96	4.4% NaCl

3.6 RHEOLOGICAL MODELS

3.6.1 General. Numerous mathematical models have been proposed in the literature to describe the force-deformation rate characteristics of fluid-like materials. These models can be broadly categorized under: 1) time-independent behavior, and 2) time-dependent behavior. Examples of time-dependent materials are thixotropic substances which show a decrease in viscosity with time and rheopectic substances which show an increase in viscosity with time, upon application of a constant shear stress. Models describing the complex rheological behavior of these substances are limited in scope and application, and will not be considered in the remainder of this text. The following discussion will apply to time-independent behavior only.

3.6.2 Newtonian Fluids. Newtonian fluids are purely viscous fluids for which the shear stress varies directly with the rate of shear, in accordance with Newton's law of viscosity:

$$\Upsilon = \mu\dot{\gamma} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3-9)}$$

where:

Υ is the shear stress, μ is the Newtonian viscosity, and $\dot{\gamma}$ is the rate of shear.

Examples of Newtonian fluids are water and most crude oils. Any material that does not obey Newton's law of viscosity may be regarded as *non-Newtonian.* Materials of this type (e.g., polymer solutions) are usually characterized by a shear-dependent viscosity function; some non-Newtonian fluids (e.g., drilling fluids) may also exhibit a solid-like yield stress. For such materials, the *apparent* viscosity at a given shear rate is:

$$\eta = \frac{\Upsilon}{\dot{\gamma}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3-10)}$$

The term *"apparent"* is used for the viscosity because it can only be given at a specified shear rate. Several simple, purely-viscous, non-Newtonian models are briefly reviewed in the paragraphs that follow.

3.6.3 Power-Law Model. The Power-Law or Ostwald-deWaele model is used to describe many pseudoplastic (shear-thinning) or dilatant (shear-thickening) solutions:

$$\Upsilon = K\dot{\gamma}^{n} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3-11)}$$

where:

Υ = shear stress, mPa

K = Consistency Index, mpa·s^{n}.

$\dot{\gamma}$ = shear rate, s^{-1}

n = Power Law or Flow Behavior Index, dimensionless.

Since viscosity is shear stress divided by shear rate, the apparent viscosity of the Power-Law fluid is given by:

$$\eta = K\dot{\gamma}^{n-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3-12)}$$

where:

η is the apparent viscosity in mPa·s or cP.

To determine the Power-Law parameters, K and n, the logarithm of Equation (3-12) is taken:

$$\log \eta = \log K + (n-1) \log \dot{\gamma} \ldots\ldots\ldots\ldots \text{(3-13)}$$

Thus, a plot of viscosity against shear rate on a log-log graph yields (n − 1) as the slope of the straight line and K as the intercept at a shear rate of one sec^{-1}. For pseudoplastic fluids, $n < 1$; for dilatant fluids, $n > 1$. Solutions assume a Newtonian-like character as n approaches unity. For highly pseudoplastic or shear thinning fluids, n is considerably less than 1. Since many polymeric liquids exhibit pseudoplastic behavior over a wide range of shear rates of practical interest, the Power-Law model finds widespread use. While the Power-Law model accurately reflects polymer solution behavior within some range of shear rates, several objections may be raised regarding its general utility.

Most polymer solutions approach Newtonian behavior at extremely low shear rates and at very high shear rates; however, the Power-Law model does not predict this behavior. In fact, the model predicts infinite viscosity as the shear rate approaches zero (refer to Figure 3-4a). Therefore, it is imperative not to extrapolate the Power-Law model beyond its range of applicability (i.e., range of experimental measurements).

3.6.4 Multi-Parameter Models for Enhanced Oil Recovery Polymers. The rheological behavior of water-soluble polymers used in enhanced oil recovery is quite complex. At very low rates of shear, aqueous solutions of these polymers tend to behave as Newtonian fluids; that is, viscosities of the solutions are independent of shear rate. As noted previously, this limiting Newtonian viscosity is referred to as the zero shear viscosity, η_0. At somewhat higher shear rates, the solutions are pseudoplastic or shear thinning so that viscosities decrease as shear rate increases. At much higher shear rates, many polymer solutions experience a second Newtonian region with a viscosity value of η_∞. By using models with three or more parameters, it is possible to portray more accurately the viscosity behavior of polymer solutions covering several orders of magnitude in shear rate. Two such models for polymer solutions are the Ellis equation and the Carreau equation.

3.6.5 Ellis Model. The three-parameter Ellis equation is given by:[9]

$$\frac{\eta_0}{\eta} = 1 + \left(\frac{\tau}{\tau_{1/2}}\right)^{\alpha-1} \quad \text{......................(3-14)}$$

where:

$\tau_{1/2}$ is the shear stress at which the measured viscosity, η, is one-half the zero shear viscosity η_0, and $(\alpha - 1)$ is the slope of log $[(\eta_0/\eta)-1]$ versus log $(\tau/\tau_{1/2})$. The parameter α may be considered equivalent to the reciprocal of the Power-Law parameter, n.

This model is quite flexible in that it includes Newton's Law and the Power-Law as special cases. The Ellis equation has the distinct advantage over the Power-Law model in that a limiting finite viscosity is predicted at very low shear rates (for $\alpha > 1$); however, a limiting viscosity is not predicted at high shear rates (refer to Figure 3-4b).

3.6.6 Carreau Model. The Carreau equation is a four-parameter model that is very useful for dilute solutions of high molecular weight polymers:[9]

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left[1 + (\lambda\dot{\gamma})^2\right]^{(n-1)/2} \quad \text{...................(3-15)}$$

where:

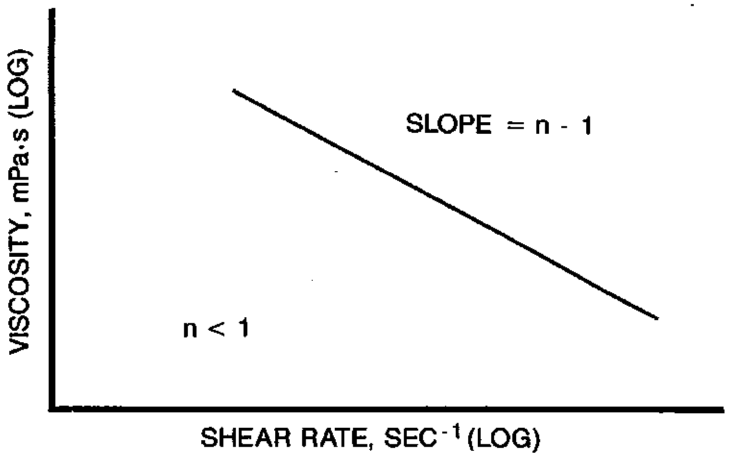
η is the viscosity at shear rate $\dot{\gamma}$; η_0 is the zero shear rate Newtonian viscosity; η_∞ is the high shear rate Newtonian viscosity; (n−1) is the slope of the Power-Law portion of the data; and λ is a time constant that indicates the deviation from the zero shear to the Power-Law region (refer to Figure 3-4c). That is, the Newtonian and pseudoplastic regions of the curve intersect at a shear rate that is approximately $1/\lambda$.

If accurate zero shear viscosities are available, the Carreau model provides a good fit of the viscosity data obtained with polymer solutions of interest in enhanced oil recovery applications. In the absence of high shear Newtonian data, solvent viscosity can be substituted for η_∞ to provide a good approximation. The remaining parameters (λ and n) can then be determined by non-linear, least-squares curve fitting.

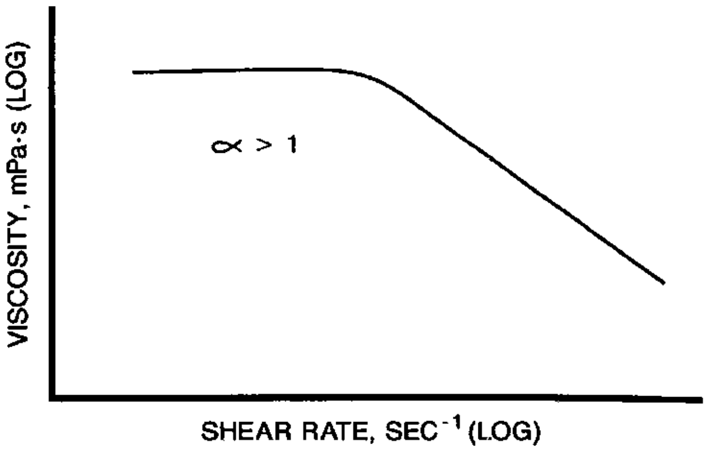
3.6.7 Molecular Models. The previously discussed models, mostly of empirical origin, describe the viscosity behavior of polymer solutions without any consideration of the structure of polymer molecules in solution. A different method of approach that takes into account the structure and configurational statistics of polymer molecules has been adopted by polymer physicists to arrive at the dependence of rheological properties on molecular parameters. Notable contributions in the development of molecular rheological models belong to the works of Debye, Pao, Rouse, Kirkwood and Riseman, Zimm, Williams, Bueche, and Graessley. Discussion of molecular models is beyond the scope of this publication and can be found elsewhere in literature.[10]

3.6.8 Comments on Viscometry. Although the preceding discussion is confined to viscosity characteristics of polymer solutions, other material properties may play an important role in the flow behavior of these solutions in porous media. Many high molecular weight polymers, notably partially hydrolyzed polyacrylamides, possess both viscous and elastic properties. With these viscoelastic fluids, elastic and elongational flow properties can become important at high fluxes in flow through porous media. Once viscoelasticity is encountered, the inelastic rheological models which were discussed are no longer applicable in describing flow of polymers in porous media.

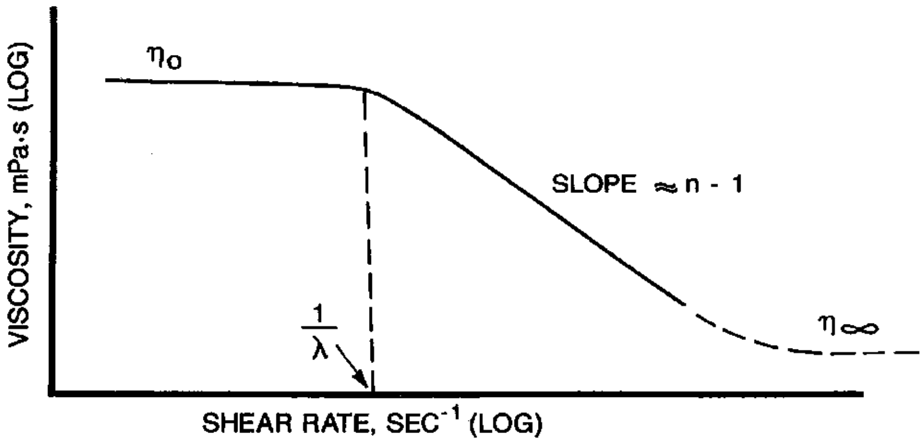
A characteristic material parameter that is commonly used to describe transient flow behavior of such fluids is the relaxation time. Qualitatively, this corresponds to the response time of a material when subjected to a sudden deformation. Experimental measurements of the first normal stress difference as a function of shear rate, using a Rheometrics Mechanical Spectrometer or Weissenberg Rheogoniometer™, or equivalent equipment, allow the calculation of a relaxation time spectrum. However, the time constants from simple shear measurements may not be appropriate for porous media flow because of the elongational nature of the flow field in converging regions near pore constrictions. In spite of these objections, simplified models have been used to provide a theoretical basis for correlating laboratory data on the flow behavior of polymer solutions. Such models may aid in a better understanding of the phenomenological aspects of flow in complex geometries.



a. POWER-LAW MODEL



b. ELLIS MODEL



c. CARREAU MODEL

FIGURE 3-4
RHEOLOGICAL MODELS

3.7 POROUS MEDIA TESTS

3.7.1 General. These recommended test procedures are used to determine the resistance factor and residual resistance factor of polymer solutions in porous media and, hence, the level of mobility reduction achieved. The resistance factor is a measure of the relative mobility of the polymer solution. The residual resistance factor reflects the permanent permeability reduction (refer to Par. 3.7.5.3). This new permeability may be used to estimate the viscosity (from Darcy's equation) of the flowing polymer solution. These tests require pressure and flow rate measurements along the direction of flow under steady state conditions. For constant rate injection in a radial core sample, the flow velocity varies inversely with radial distance. For linear tests, the flow rate can be varied to determine non-Newtonian character of polymer solutions in porous media. However, low flow rates (compared to the mechanical degradation test) are used because interstitial velocities in the bulk of a reservoir may be 1 ft/day or less. To monitor non-Newtonian effects, it is suggested that linear and radial core floods be conducted at several injection rates. Since the polymer solution must first pass through the wellbore region at higher velocities, the preferred procedure is to use polymer solutions that have been prefiltered or pre-sheared through similar porous media (refer to Par. 6.6.3). To simulate field conditions, mobility control tests must utilize polymer solutions that were previously injected through other core samples at high rates representative of specific wellbore conditions. The investigator needs to know which is more important in the comparison of various polymers: detecting mechanical degradation, mobility reduction, permeability reduction, or flowing viscosity of the polymer solution.

3.7.2 Recommended Porous Media. For the purpose of laboratory screening of different polymers for mobility control, it is recommended that Berea sandstone cores be used as standard porous media. This recommendation is prompted by the availability of this material in large quantities. The recommended test procedures will also be the same for evaluating polymer solution flow through other porous media, such as synthetic core materials or reservoir rocks. Core material must be thoroughly cleaned. Procedures for cutting and cleaning cores are described in *API RP 27: Recommended Practice for Determining Permeability of Porous Media* (check latest edition).*

3.7.3 Core Preparation. Berea sandstone cores do not contain oil and are generally available dry. However, the samples will be wetted by the cooling fluid during the core cutting and polishing process. Such wet samples can be dried in an oven at a temperature high enough to remove the coolant but low enough to prevent alteration of clays or other rock materials. A temperature of about 158 F *(70 C)* is recommended. If it is necessary to eliminate certain rock-fluid interactions, fire the Berea sandstone samples at temperatures above 825 F *(440 C)* for more than 3 hours. Firing the core may alter polymer retention.

Reservoir rock samples may require more thorough preparation procedures which include extraction of the interstitial fluids present in the pore space. Extraction and cleaning techniques are discussed in detail in *API RP 40: Recommended Practice for Core Analysis Procedure* (check latest edition).* It suffices to say that a solvent extraction should be performed on the sample to remove all the interstitial fluids. Properly preserved cores may not require extraction.

3.7.4 Core Saturation.

1. The clean, dry core should be weighed and then evacuated to a pressure below 1 mm Hg. Brine is introduced slowly into the evacuated container. Allow brine to imbibe slowly into the core. After the core is covered with brine, vent the container to atmosphere. Allow the core to stand for at least one hour.
2. Remove core from the container and wipe or blot off excess brine. Weigh the core. The difference in weight (saturated minus dry) divided by the brine density is the pore volume of the core.
3. An alternate procedure (which must be used for epoxy-coated cores) is to weigh the dry core in the core holder, saturate the core under vacuum, reweigh the core plus core holder to obtain the weight of brine, and determine pore volume as in Step 2. Corrections should be made for any dead volume in tubing or fittings to avoid erroneously high porosities or pore volumes.
4. With either procedure, it is sometimes desirable (especially for low permeability cores) to displace air in the core with carbon dioxide prior to saturating with brine. Hold 50 psig back pressure on the core during the carbon dioxide displacement. This variation helps ensure that gas is not trapped in the core after brine saturation.

3.7.5 Linear Core Tests.

3.7.5.1 Apparatus. The apparatus for conducting flow tests for polymer evaluation is similar to the apparatus described in *API RP 27: Recommended Practice for Determining Permeability of Porous Media* (check latest edition).* The recommended test apparatus (refer to Figure 3-5) consists of the following components:

1. A device for holding the sample to be tested, i.e., a core holder. The core holder must be designed so that when the sample is properly mounted the entire unit is leak-proof and fluid flow occurs through the sample only. Pressure taps should be provided at the inlet face of the core sample and at least one additional location along the length of the sample. If the pressure at the outlet is not atmospheric (possibly the case if long exit lines or small

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diameter exit lines are used), a pressure tap at the outlet or a differential pressure transducer across the core will be required. Confining the sample may be achieved either by sealing the dry core in epoxy or by mounting the core in a Hassler-type core holder wherein the sample is sealed by the compressive force of a confining fluid acting on a rubber or polytetrafluoroethylene (PTFE) sleeve enclosing the sample. In the latter case, to provide a pressure tap along the length of the sample, it is necessary to have the pressure tap molded in the sleeve. If such a cell is not available, two ordinary cells may be connected in series with an intermediate pressure tap. Even though the solutions used in the flow tests have been previously filtered at high rates, it is possible that some filtration occurs at the inlet face of the core. It is therefore important to have additional pressure taps along the length of the core so that the extent of this filtration can be determined and separated from the phenomena that occur during flow of the polymer solution through the porous medium.

Some brines may corrode metallic surfaces of the equipment in contact with the polymer solution. If this occurs, the resulting iron compounds may interact with the polymer or may precipitate and plug the core inlet. Deaerating the solution may minimize corrosion caused by dissolved oxygen.

2. Devices should be available for measuring the pressure of the flowing fluid at inlet, outlet, and intermediate location(s) along the length of the sample. Such devices, which include manometers, pressure transducers, and pressure transmitters, should have an accuracy of at least 0.1% of the full-scale value of the instrument.

3. Suitable means should be provided to maintain constant pressure at the inlet of the sample or to maintain a constant flow rate through the core. Examples of the former are rodded fluid transfer cells and examples of the latter are positive displacement piston pumps. Suitable chromatography pumps may be used if pulse-free flow is assured and the pump design does not shear degrade the polymer. Provisions should be made for measuring the fluid flow rate.

   The tests should be conducted at a constant temperature. For comparative evaluations or screening tests, a temperature of 77 F ± 1 F *(25 C ± 0.5 C)* is recommended. For tests simulating field conditions, reservoir temperature should be used.

3.7.5.2 Procedures. The following procedures are recommended for linear core tests.

1. The core may be of any regular geometric shape so that the cross-sectional area and the length can be easily and accurately measured. Square or cylindrical cores, 1 to 3 inches (2.54 to 7.62 cm) in diameter and 3 to 6 inches (7.62 to 15.24 cm) in length are recommended.

2. The first step in the flow test is to determine the permeability, k_b, of the selected sample to brine. Permeability between each set of pressure taps as well as over the entire core length should be measured. The core sample should be mounted in the holder and saturated with degassed brine solution. The recommended saturation procedure involves applying a vacuum to the core material prior to saturation. The brine solution composition should be the same as that used for preparing the polymer solutions.

3. Brine from a fluid reservoir is then flowed through the sample at linear velocities of between 0.5 and 2 ft/day. The flow rate(s) and pressure(s) are monitored. When steady-state conditions are reached, i.e., a constant flow rate is attained at a constant pressure differential, the flow rate and pressure differential(s) are noted. The permeability can be calculated using Darcy's equation for horizontal flow of an incompressible fluid. Measurements at three different flow conditions should be obtained so that an average value for permeability can be calculated and so the presence of gas saturation can be detected. For a reliable test, gas must not be present in the core. Gas saturation will manifest itself as higher permeability at higher flow rates.

4. Following the determination of brine permeability, polymer solution should be flowed through the core sample, and the flow rate and pressure at each of the pressure taps noted and recorded. A minimum of 3 flow rates are often used starting at about 10 ft/day, reducing to about 5 ft/day, and finally to about 1 ft/day. For the polymer mobility calculations, low flow velocity, on the order of 1 ft/day, is recommended. Sufficient volume of the polymer solution, more than 2 pore volumes, should be flowed so that steady-state is attained. Failure to attain a stabilized pressure drop is indicative of plugging and polymer mobility data will be of questionable value. During the flow test, the effluent from the core is collected in increments of 0.1 pore volume or in sufficient amounts for viscosity measurements and quantitative analysis.

5. Following polymer flow, sufficient brine is again flowed through the core sample to obtain steady state conditions and determine the post-polymer flow permeability, also called the final or residual brine permeability, k_f.

6. In the case of polymer evaluation in the presence of oil, surfactants, and/or other chemicals, the sequence of fluid injection will be that dictated by the process being evaluated. For field applications, it is important to make these measurements with residual oil in the core.

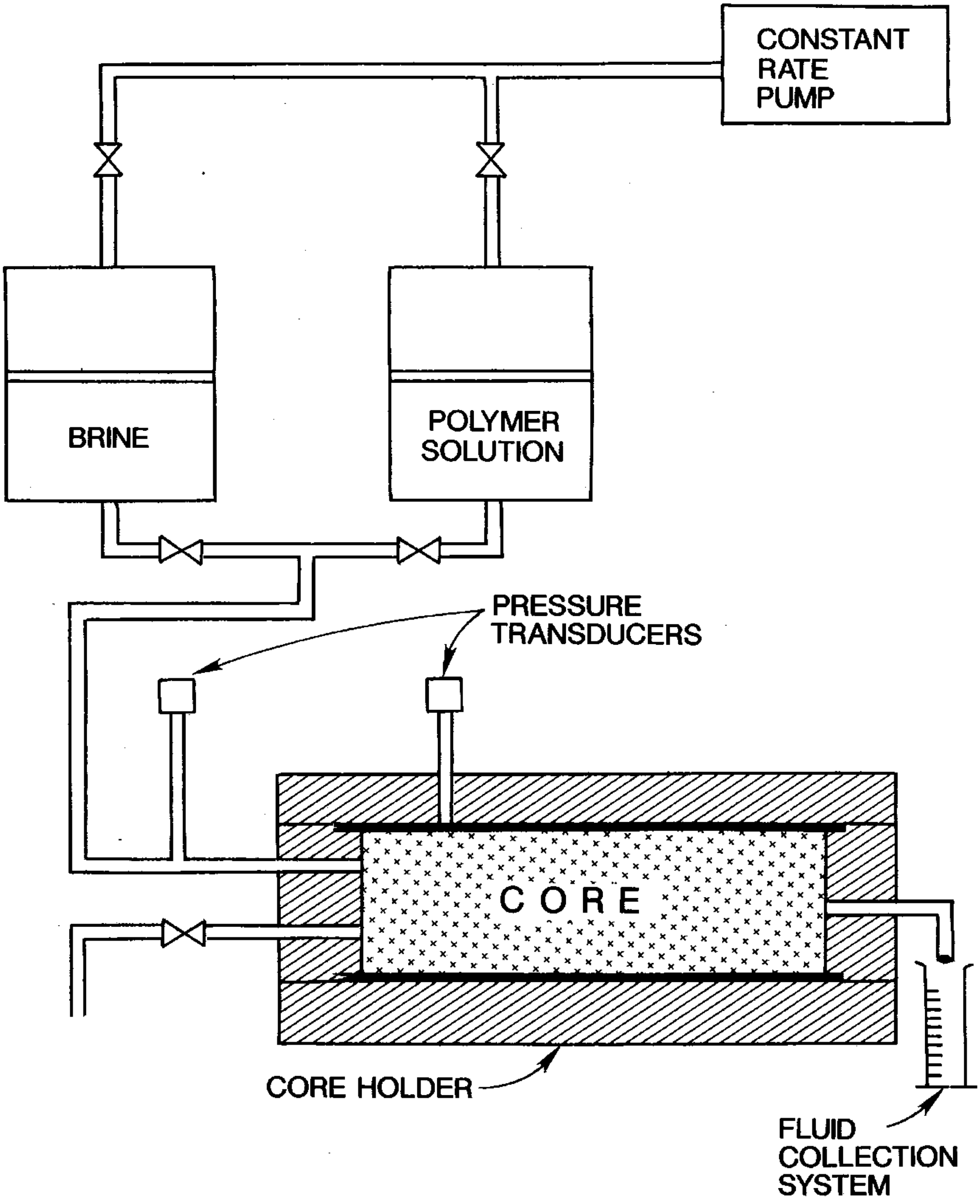

FIGURE 3-5
APPARATUS FOR LINEAR CORE TESTS (SIDE VIEW)

3.7.5.3 Analysis of Data. Darcy's equation for steady flow of an incompressible fluid through a horizontal porous medium can be expressed as:

$$q = \frac{k\,A}{\mu}\,\frac{\triangle P}{L} \quad \text{(3-16)}$$

where:

q = fluid flow rate, cm^3/s.

k = permeability, Darcies.

A = cross-sectional area of porous medium, cm^2.

μ = fluid viscosity, cp.

L = length of porous medium, cm.

$\triangle P$ = pressure drop across length, L, atm.

The area, A, and length(s), L, between successive pressure taps are measured independent of the flow tests. The flow rate, q, and the pressure drop (differences), $\triangle P$, are monitored and recorded during the flow experiments. For a Newtonian fluid, the viscosity, μ, could also be measured separately, but for a non-Newtonian fluid, the fluid mobility, (k/μ), in the porous medium is calculated using Equation (3-16). The subscripts b and p are then used to denote brine (or water) and polymer mobilities, respectively.

The nature of the polymer solution determines the mechanisms by which $(k/\mu)_p$ is altered. For example, xanthan solutions function as mobility control agents primarily by increasing solution viscosity, whereas polyacrylamides achieve the mobility reduction both by reducing the permeability of the porous medium and by increasing fluid viscosity. The viscosity of the effluent from the core tests (at a constant shear rate) is plotted as a function of pore volumes of polymer solution injected. The concentration of polymer in the effluent is also plotted in a similar manner, and these two plots provide an indication of the propagation of the polymer through the core sample.

The following parameters are determined from the measurements obtained during the flow experiments after the flow has stabilized:

1. Brine permeability of sample, k_b
2. Polymer solution mobility,

$$(k/\mu)_p = q_p \left(\frac{L}{A(\triangle P)_p}\right) \quad \text{(3-17)}$$

3. Final brine permeability after polymer flush, k_f
4. Resistance factor, $RF = \frac{(k/\mu)_b}{(k/\mu)_p}$ .... (3-18)
5. Residual resistance factor, $RRF = \frac{(k_b/\mu_b)}{(k_f/\mu_b)}$ ... (3-19)

3.7.6 Radial Core Tests.

3.7.6.1 Apparatus. The apparatus for radial core tests consists of a constant rate injection pump or a constant pressure source, reservoirs for brine and polymer solutions, the core holder, and pressure measuring instruments. An example system is shown in Figure 3-6. Rubber gaskets are used on the top and bottom of the core to prevent fluid from bypassing the core. Pressure on the rubber gaskets can be applied from a nitrogen tank via water. The upper gasket must provide adequate seal around the injection and pressure measuring ports which are located along a single line from the injection port to the radius of the core. Differential pressure transducers can be located between any two ports; however, it is desirable to measure the pressure drop across the entire core radius as well as across a short distance near the injection port. This allows for polymer filtration (face plugging) to be detected. Fluids drain from the outer edge of the core and are collected through a single opening in line with the pressure measuring ports.

3.7.6.2 Procedure. If Berea sandstone is used, suggested dimensions are 2 inches (5.08 cm) thick by 3 inches (7.62 cm) radius. Reservoir cores may be smaller, but the core holder must reflect core dimensions. The center hole is ⅛ inch (0.32 cm) diameter. The following procedure should be used for radial core tests:

1. Load the pre-saturated core into a core holder that contains excess brine. Gravity feed brine through the core holder as upper and lower flanges are secured. Drive brine through the core holder with a constant rate pump or constant pressure source to ensure that all air has been removed. Attach pressure transducers to the core holder pressure taps so that the pressure difference can be measured from the center hole to the outer radius and across two taps near the center port. Pressurize upper and lower rubber gaskets with 200 to 300 psig of nitrogen via the reservoir containing water.
2. Determine core permeability to brine at three different flow rates (q, 2q, and 4q). Permeability should be the same across both sets of pressure taps. If permeabilities are not similar, core heterogeneity is indicated and the core should be discarded. Brine permeability (in Darcies) is calculated using:

$$k_b = \frac{\mu_b\, q_b \left(\ln \frac{r_2}{r_1}\right)}{2\pi h\,(\triangle p)_b} \quad \text{(3-20)}$$

where:

μ_b = brine viscosity, cP.

q_b = constant volumetric flow rate, cm^3/s.

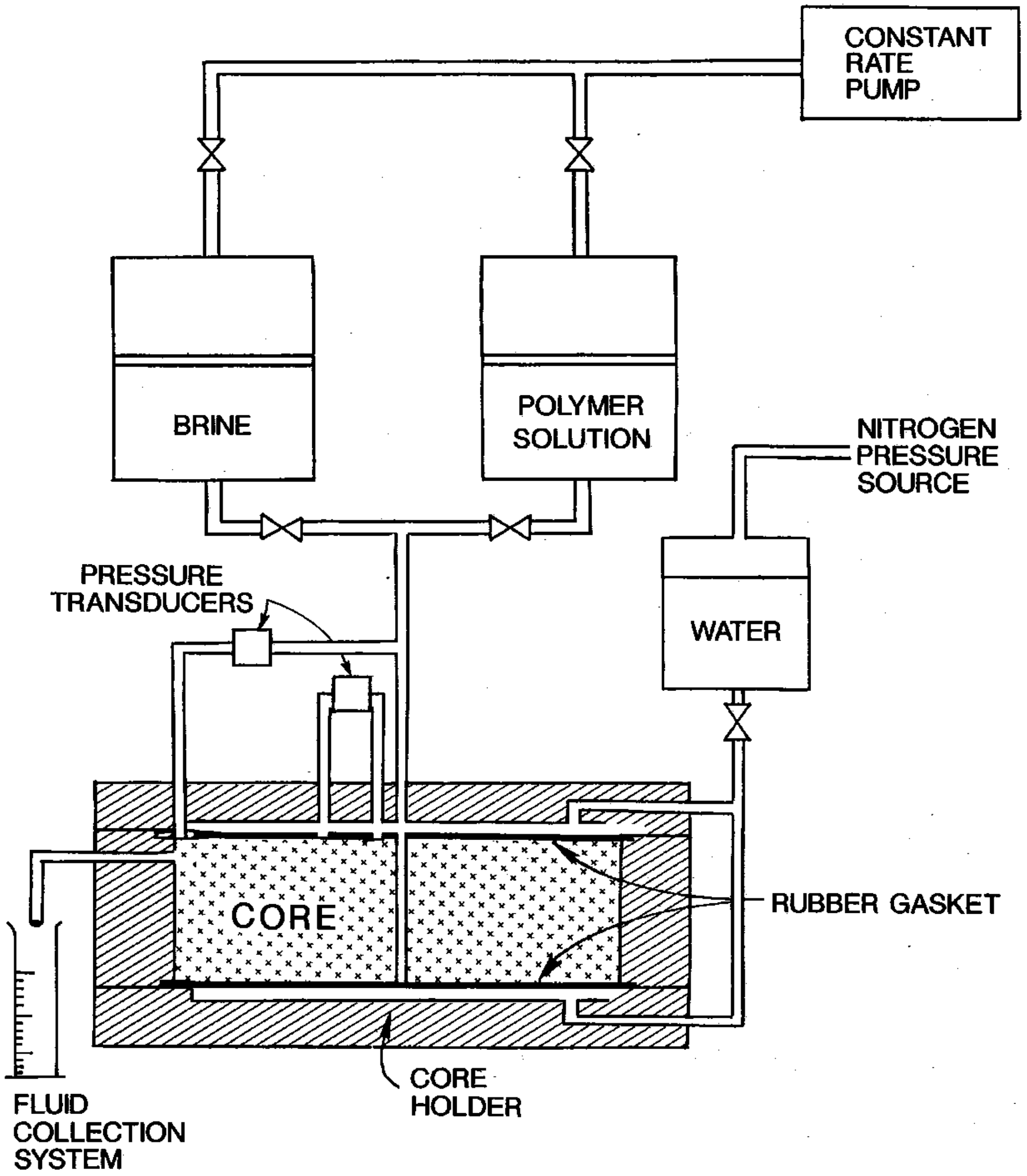

FIGURE 3-6
APPARATUS FOR RADIAL CORE TESTS (SIDE VIEW)

r_2 = radius to the outer pressure port, cm.

r_1 = radius to the inner pressure port or radius of the center hole, cm.

ΔP = pressure drop between ports at radii r_1 and r_2, atm.

h = axial thickness of the core, cm.

3. Flood with polymer solution at the desired rate. Field rates may be from 0.5 to 2 ft/day. At constant q, the frontal advance rate will vary with radius in a radial core flood as $(\phi 2\pi rh)^{-1}$; where: ϕ is the porosity of the core, and r is the appropriate radius. It is convenient to select the frontal advance rate at a radius where half of the pore volume of the core has been flooded. This radius is approximately 70.7% of the radius of the core. Polymer solution injection should continue for at least 2 pore volumes or until flowing mobilities (constant ΔP across each pressure tap) have stabilized. The mobility reduction or resistance factor caused by the polymer solution is determined from these data.
4. Following polymer solution injection, brine is injected for numerous pore volumes at the same constant rate. The flushed permeability, and the permeability reduction caused by the polymer are determined from the pressure response during the post-polymer brine flood.
5. As discussed previously for linear core tests, effluent fluid samples from the radial core can be collected for analysis.

3.7.6.3 Analysis of Data. Data from core tests permit the comparison of different polymers during flow. For proper evaluation, it is necessary to obtain steady-state flow data (resistance factor and residual resistance factor) as a function of temperature, salinity and hardness, and polymer concentration. If a polymer is being considered for a particular reservoir application, the evaluation should simulate reservoir conditions, particularly with regard to the use of actual reservoir rock containing residual oil. Both resistance factor and residual resistance factor are highly dependent on reservoir lithology and pore-size distribution. Also, these data can be highly rate-sensitive.

3.7.6.3.1 Mobility Reduction (Resistance Factor). The resistance factor (RF) is the ratio of brine mobility to polymer solution mobility in the same core. Data must be obtained at constant flow rate after stabilized flow (constant pressure drop between pressure taps) has been achieved. Several resistance factors can be obtained from radial core floods. These factors can be calculated from the injection port to the outer radius of the core:

$$RF = \frac{(k/\mu)_b}{(k/\mu)_p} = \frac{q_b\left[\ln \frac{r_o}{r_w}\right] / 2\,\pi h\,(\Delta P)_b}{q_p\left[\ln \frac{r_o}{r_w}\right] / 2\,\pi h\,(\Delta P)_p} \quad \ldots\ldots (3\text{-}21)$$

where:

$(k/\mu)_b$ = brine mobility.

$(k/\mu)_p$ = polymer solution mobility.

q_p = polymer solution flow rate.

q_b = brine flow rate.

r_o = radius of the core.

r_w = radius of the injection hole in the core.

$(\Delta P)_b$ = pressure drop during flow of brine.

$(\Delta P)_p$ = pressure drop during flow of polymer solution.

The resistance factor can also be calculated across the two ports close to the injection port:

$$RF = \frac{(k/\mu)_b{}^*}{(k/\mu)_p{}^*} = \frac{q_b\left[\ln \frac{r_2}{r_1}\right] / 2\,\pi h\,(\Delta P)_b{}^*}{q_p\left[\ln \frac{r_2}{r_1}\right] / 2\,\pi h\,(\Delta P)_p{}^*} \quad \ldots\ldots (3\text{-}22)$$

where:

$(k/\mu)_p{}^*$ = polymer solution mobility between pressure taps located at r_2 and r_1.

$(k/\mu)_b{}^*$ = brine mobility between pressure taps located at r_2 and r_1.

$(\Delta P)_p{}^*$ = pressure drop during polymer solution flow between pressure taps located at r_2 and r_1.

$(\Delta P)_b{}^*$ = pressure drop during pre-polymer brine flow between pressure taps located at r_2 and r_1.

In the case of homogeneous core material, the brine mobility should be the same across both sets of pressure taps i.e., $(k/\mu)_b = (k/\mu)_b{}^*$. When flooding with polymer solutions that undergo mechanical degradation, cause permeability reduction, and/or are non-Newtonian, $(\Delta P)_p{}^* \neq (\Delta P)_p$ and $(k/\mu)_p{}^* \neq (k/\mu)_p$. The resistance factors obtained for different polymer solutions should be compared as a function of salinity and hardness, polymer concentration, and temperature.

3.7.6.3.2 Permeability Reduction (Residual Resistance Factor). A comparison of the brine permeability of the core before polymer solution flow to that obtained after flow is a measure of the permanent permeability reduction caused by the polymer. Specifically, the residual resistance factor across the entire radius of the core can be calculated as follows:

$$RRF = \frac{(k_b/\mu_b)}{(k_f/\mu_b)} = \frac{q_{bi}\left[\ln \frac{r_o}{r_w}\right] / 2\,\pi h\,(\Delta P)_b}{q_{bf}\left[\ln \frac{r_o}{r_w}\right] / 2\,\pi h\,(\Delta P)_f} \quad \ldots (3\text{-}23)$$

where:

$(\Delta P)_f$ = pressure drop during post-polymer brine flow.

q_{bi} = initial brine flow rate.

q_{bf} = final brine flow rate.

If a permanent permeability reduction does occur, $(\Delta P)_b \neq (\Delta P)_f$. Measurement of permeability across the pressure taps near the injection port gives additional information concerning the nature of the permeability reduction. Data taken here are indicative of near-wellbore permeability reductions that may occur with some polymers. The residual resistance factor will vary depending on salinity and hardness of the water and polymer concentration. Once k_f is determined, it may be used to estimate the flowing viscosity of the polymer solution. This value of permeability is used in the mobility ratio equations to evaluate μ_p.

3.7.6.3.3 Precautions. Due care must be exercised in order to properly evaluate mobility data obtained from radial core tests. The location and arrangement of pressure ports shown in foregoing discussions is only one possible configuration. Depending on information desired, other locations or arrangements may be more suitable. Further, since the frontal advance rate varies inversely with radius, care must be taken when using these data.

3.7.7 Estimating Shear Rates in Cores. Several expressions have been used to estimate the average shear rate during flow of non-Newtonian fluids in porous media. In the most commonly used expression, the porous system is modeled as a bundle of capillary tubes of the same radii and length such that[11]:

$$r = \left[\frac{8k}{\phi}\right]^{1/2} \quad \dots\dots\dots\dots (3\text{-}24)$$

where:

r is the radius of the equivalent capillary, k is the permeability to water before polymer flow, and ϕ is the porosity.

With the shear rate at the wall of the capillary taken as $4\overline{v}/r$ by substituting for the radius and applying a non-Newtonian correction for Power-Law fluids, the shear rate in the porous medium given by Jennings, et al[2] may be modified as:

$$\dot{\gamma}_w = \frac{3n+1}{4n} \cdot \frac{\overline{v}}{\left[\frac{k}{2\phi}\right]^{1/2}} \quad \dots\dots\dots\dots (3.25)$$

where:

$\dot{\gamma}_w$ is the shear rate in $\sec^{-1}$, $\overline{v}$ is the interstitial velocity, defined as $q/A\phi$, and the term $(3n + 1)/4n$ is the Rabinowitsch correction factor. This expression can also be written as:

$$\dot{\gamma}_w = \frac{3n+1}{4n} \cdot \frac{4q}{A\left[8k\phi\right]^{1/2}} \quad \dots\dots\dots\dots (3\text{-}26)$$

where:

A is the cross-sectional area of the core.

At very low flow rates (or shear rates) or for polyacrylamides in strong brines, the non-Newtonian correction can be omitted without serious loss of accuracy.

In the second approach, the tube diameter in the capillary model is replaced by four times the hydraulic radius, and the porous medium is considered as a packed bed of uniform spherical particles.[12] The resulting expression for steady linear flow of a Power-Law fluid is then:

$$\dot{\gamma}_w = \frac{3n+1}{4n} \cdot \frac{12q}{A\left[72Ck\phi\right]^{1/2}} \quad \dots\dots\dots\dots (3\text{-}27)$$

where:

the tortuosity factor, C, is defined as the ratio of the actual flow path length to the length of the porous medium.

For uniform, unconsolidated media, C usually ranges from 2.5 based on the Carman-Kozeny expression to 25/12 based on the Blake-Kozeny expression. Therefore, it is preferable to treat C as an adjustable parameter and determine its "best fit" value for a given porous medium using Newtonian liquids of known viscosity. In the absence of experimental determinations, the generally accepted factor of 25/12 leads to an estimation of shear rate for a Power-Law fluid[13].

$$\dot{\gamma}_w = \frac{3n+1}{4n} \cdot \frac{12q}{A\left[150k\phi\right]^{1/2}} \quad \dots\dots\dots\dots (3\text{-}28)$$

A different approach suggested by McKinley, et al[14] is based on the analogy between laminar flow through a uniform capillary tube and flow through a linear core. The method involves finding a single parameter, α_o, that forces superposition of shear viscosity data from rheological experiments with the apparent viscosity function calculated from linear core floods. The shear rate in the core is given by:

$$\dot{\gamma}_w = \alpha_o \frac{q}{A\sqrt{k\phi}} \quad \dots\dots\dots\dots (3\text{-}29)$$

where:

the dimensionless parameter, α_o, is presumed to be independent of porosity, permeability, and fluid properties and is taken as a constant for a particular type of porous medium, reflecting the pore size distribution and tortuous character of the flow paths. Trial and error calculations are needed to find the optimal value of α_o. Limited data were presented by the authors in support of their model.

In all these expressions, if the flow rate, q, is in units of cm^3/sec and the cross-sectional area, A, is in cm^2, permeability must be in units of cm^2 ($1\ cm^2 \cong 10^{11}$md), and the interstitial velocity, $\overline{v}$, in cm/sec. Porosity, ϕ, Power-Law Flow Behavior Index, n, tortuosity factor, C, and parameter, α_o, are dimensionless.

3.7.8 Stretch Rates in Porous Media. Viscoelastic fluids act like viscous liquids at low rates of deformation and partially like elastic solids at high rates of deformation. When viscoelastic effects are encountered at high flow rates, the capillary model of the porous medium may no longer suffice, and the effects of converging and diverging flow into and out of constrictions must be considered. Under these conditions, the polymer is deformed both by shearing action and by a stretching or elongation in the direction of flow.

In a homogeneous porous medium composed of spherical particles, stretch rate may be approximated for a conically converging section as:[15]

$$\dot{\varepsilon} = \frac{v_2 - v_1}{L_l} \cong \frac{\overline{v}}{\overline{d}_p/2} \cong \frac{2\overline{v}}{\overline{d}_p} \cong \frac{2q}{A\phi\overline{d}_p} \quad \text{.........} (3\text{-}30)$$

where:

$\dot{\varepsilon}$ is a measure of the experimental stretch rate, sec^{-1}; $\overline{v}$ is the interstitial velocity, cm/sec; q is flow rate, cm^3/sec; A is cross-sectional area, cm^2; $\overline{d}_p$ is the average grain diameter, cm; and ϕ is the porosity.

The concept of Deborah Number[16] is often invoked in attempts to correlate the onset of viscoelastic effects (observed as excess pressure drops) during the non-inertial flow of polymer solutions in porous media. In general, the Deborah Number, N_{De}, represents a dimensionless ratio of the time interval required for the fluid to respond to a change in imposed conditions of deformation to the time interval between such changes. For the simple model of an isotropic porous medium in which the flow field in a converging region is dominated by elongational rather than shearing deformation, it is convenient to express the Deborah Number as[15]:

$$N_{De} = \frac{\text{characteristic time of fluid}}{\text{characteristic time of flow}} \cong \frac{\theta}{1/\dot{\varepsilon}} = \theta\dot{\varepsilon} \quad ..(3\text{-}31)$$

where:

θ is the relaxation time of the fluid, sec.
$\dot{\varepsilon}$ is a measure of the experimental stretch rate, sec^{-1}.

Very low Deborah numbers suggest flow conditions under which viscoelastic effects are negligible. The fluid is able to respond to an imposed change in deformation almost instantly and has no memory of its earlier configurations. The deformation history is unimportant under these conditions, and a purely viscous model (e.g., Power-Law) is adequate for flow description.

As the flow rate is increased (higher $\dot{\varepsilon}$ and N_{De}), a point will be reached when the solid-like characteristics of the viscoelastic material will become apparent as a higher than calculated pressure drop. Experimental results are reported[16] which indicate the onset of viscoelastic effects at Deborah numbers of 0.05 to 0.06. The fluids used had a relaxation time of 0.01 second at the deformation rates employed (50 to 100 sec^{-1}). Viscoelastic effects first appeared at a linear frontal advance rate of 60 ft/day in a porous medium having a permeability of 5000 md and at about 20 ft/day for a permeability of 500 md. Despite numerous investigations, data obtained on different porous media using different polymer solutions have failed to show a generalized correlation in terms of Deborah Number alone, when viscoelastic effects are encountered. Much work remains to be done in modelling the quantitative flow behavior of viscoelastic fluids in permeable materials.

To complicate the situation further, higher flow rates and correspondingly higher injection pressures can result in polymer molecules being forced into areas where they previously could not flow. This can cause increased retention in the lower permeability areas which can cause an apparent pseudo-dilatant flow.

APPENDIX TO SECTION 3
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SECTION 4

FILTERABILITY TESTING OF POLYMER SOLUTIONS

4.1 INTRODUCTION

4.1.1 General. Filterability tests using membrane filters can be used to measure variations in solution filterability due to undissolved solids. Factors affecting polymer solution quality are: 1) mix water quality, 2) polymer quality, 3) bacterial contamination, 4) surfactant (or other chemical) compatibility, and 5) mixing and shearing conditions. These recommended tests are reliable as indicators of changes in polymer solution quality or for quality control, but cannot be used routinely to compare different polymers or for predicting reservoir injectivity.

4.1.2 Solution Preparation. Refer to Section 2 for recommended polymer solution preparation procedures.

4.1.3 Filter Media. Some user laboratories report wide permeability variations in filters from batch to batch, especially with filters prepared from mixed cellulose esters (e.g., Millipore®, or equivalent, Amicon®, or equivalent, etc.). Thin (approximately 10 micron) polycarbonate filters (e.g., Nuclepore®, or equivalent) having pores produced by an irradiation-and-etching process are more uniform, as are acrylic copolymer membranes (e.g., Gelman®, Versapor®, or equivalent). Recommendations are to obtain large quantities of one lot of filters, characterize that lot, and replace with new lots that give matching or similar flow times and filter ratios with a standard polymer solution.

4.1.4 Filter Support and Tubing. The design of the filter support has been shown to affect filtration results. This effect may be due to differences in the amount of surface area contacting the membrane. Deformation of the membrane may occur with some types of filter support, resulting in altered filtration rates.

The diameter and length of tubing connecting the fluid reservoir to the filter support can also affect results. For this reason, ¼-inch outside diameter tubing is specified for fluid transfer from the reservoir to the filter. Connections should be chosen so as to minimize flow restrictions. Components should be standardized within the laboratory and comparisons of data from one laboratory to another should consider differences in equipment design.

4.1.5 Evaluation of Results. Since polymer solutions of different types can vary widely in filterabilities, different filter pore sizes may be required, depending on the quality of the fluid. Because of these variations, a generally applicable formula for evaluation is not given, but several alternate data presentations are offered.

4.1.6 Filter Ratio. An indication of fluid quality is provided in terms of a dimensionless ratio, which compares the flow time of an initial or earlier volume to that of a second (later) volume.

4.1.7 Total Volume Filtered. At times it is convenient to compare solutions by measuring total volume filtered. Comparison is valid only if viscosities are the same, or very close to the same.

4.1.8 Filterability Plot. A plot of cumulative volume filtered versus cumulative filtration time will demonstrate relative plugging rates by slope changes. Comparison is valid only if viscosities are the same, or very close to the same.

4.2 PROCEDURES FOR LABORATORY FILTRATION TEST

4.2.1 Procedure with 600-mL Pressurized Reservoir.

4.2.1.1 Apparatus. Figure 4-1 illustrates an example assembled filtration apparatus. Components required for the filterability test are listed below:

Membrane Filter Holder	Equipped to hold 47-mm diameter membrane filters (e.g., Millipore® Swinnex® Disc Filter Holder, Cat. No. SX00-047-00, or equivalent) and with flexible tubing as shown in Figure 4-1.
Solution Pressure Reservoir	Rated at 20 psig working pressure and of at least 600-mL capacity (e.g., Millipore® 600-mL filling system Cat. No. XX11-000-00, or equivalent).
Membrane Filter Support	Stainless steel filter support screen (e.g., Millipore® Cat. No. XX43-047-07, or equivalent).
Filter Forcepts	Smooth tip.
Graduated Cylinders	500-mL
Membrane Filters	47-mm diameter, appropriate pore size, polycarbonate, e.g., Nuclepore® Stock No. 111110 (1 micron), Stock No. 111112 (3 micron), or equivalent. Millipore® MF Type SM (5.0 micron), SS (3.0 micron), RA (1.2 microne), or equivalent.
Nitrogen Cylinder and Regulator	Capable of maintaining a constant pressure of 20 psig (e.g., Air Products Two Stage Regulator, 0-50 psi, Commodity Code Number, E12-4-N1458, or equivalent.)
Stopwatch or Timer	
Flexible Tubing	5-feet long, ¼-inch OD x .062-inch wall nylon tubing to connect solution pressure reservoir to membrane filter holder.

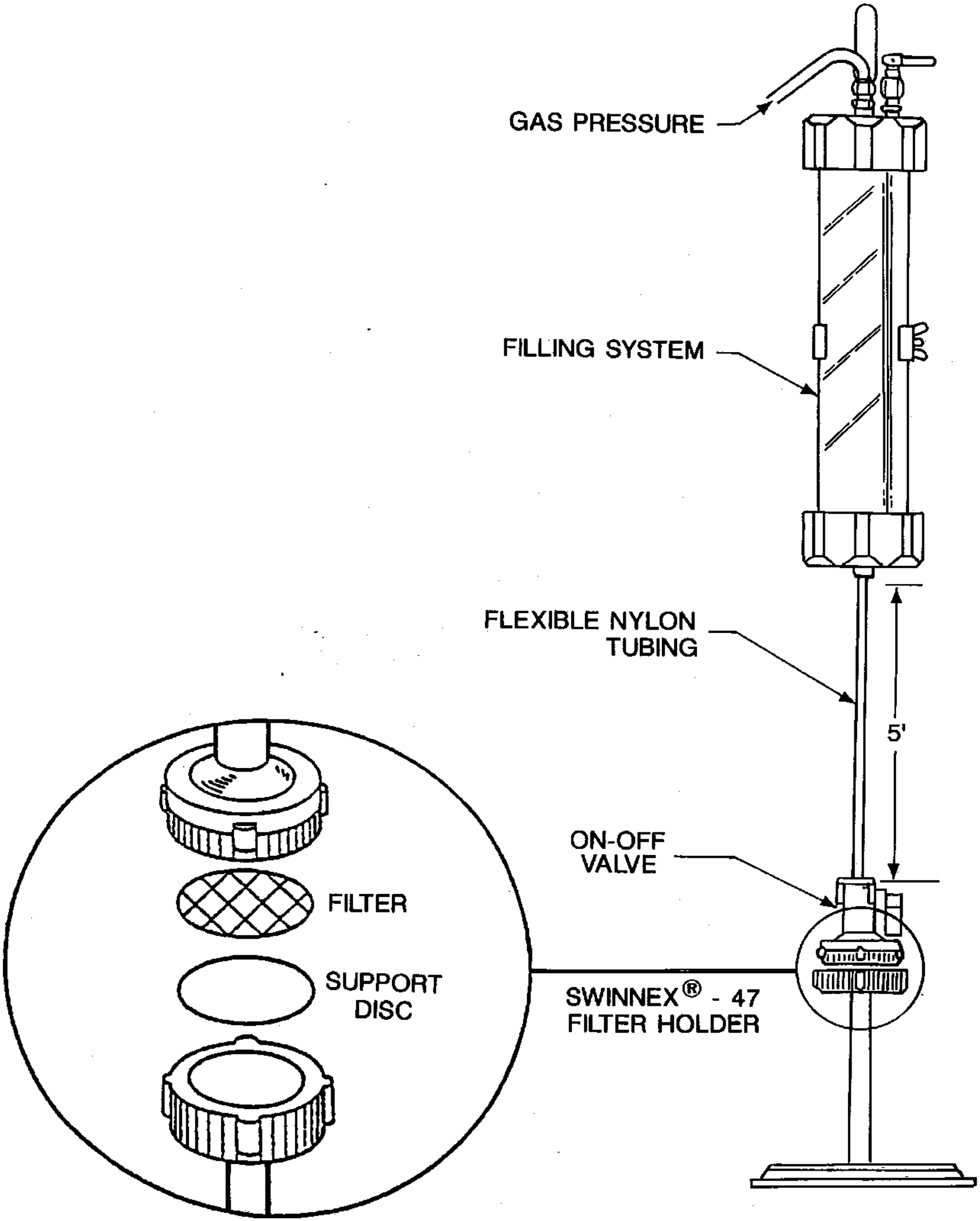

FIGURE 4-1
EXAMPLE FILTRATION APPARATUS,
600-MILLILITER PRESSURIZED RESERVOIR

4.2.1.2 Solution Preparation Procedure. The polymer solution should be prepared as follows:

1. Filterability is determined using standard brine as described in Section 2. Prepare the brine immediately before use and filter through a 0.22 micron filter to remove bacteria, if present.
2. Using the above brine, prepare a 0.5% (5000 ppm) active polymer solution and dilute to 1000 ppm using the procedure recommended in Section 2.
3. Age the solution until hydration is complete, as described in Section 2.
4. Measure viscosity of the fluid, as described in Section 3.

4.2.1.3 Filterability Test Procedure. Test the solution as described below:

1. Prepare the filtration apparatus (refer to Figure 4-1) by placing a suitable pore size membrane filter in the filter holder. For fast filtering solutions, it may be necessary to substitute a smaller size filter to obtain meaningful results. The stainless steel support plate should be placed on the filter holder with the smooth side uppermost. Care should be taken to ensure that the membrane is not wrinkled or creased. *Do not handle the membrane with fingers.*
2. Place 550-600 mL of the previously prepared 1000 ppm polymer solution in the reservoir and attach the top and pressure supply line. Close the exit valve and apply a pressure of 20 psig using the nitrogen regulator.
3. Wet the membrane filter and exclude air from the system.
    a. For 1.0 micron and larger pore sizes this can be done by inverting the filter holder and flowing a small volume (approximately 10 mL) through the filter until air bubbles cease in the effluent.
    b. For filters smaller than 1.0 micron pore size, the filter holder should be filled with solution before assembly in order to exclude air from the system. This procedure requires some practice to achieve consistency.
4. Place a suitable graduated cylinder below the filter outlet. Open the valve at the base of the filter reservoir and simultaneously start the stopwatch. The pressure (20 psig) must remain constant throughout the test.
5. Record cumulative time in seconds for each 50 mL increment filtered. Continue filtering until:
    a. 500 mL have been filtered,
    b. filtration has ceased, or
    c. 600 seconds have elapsed.
6. Examine the membrane filter for tears or other damage, including non-wetted areas of the filter. If damage is found, repeat the run. Record the appearance of material trapped on the filter.
7. Repeat the test on unfiltered solution from the same batch, using a new membrane filter. When comparing xanthan and polyacrylamide solutions, tests should be run on at least two types of membrane filters as described in Par. 4.1.3.
8. Report data as described in Par. 4.4.

4.2.2 Procedure with Five Liter Pressurized Reservoir.

4.2.2.1 Apparatus. The apparatus shown in Figure 4-2 allows filtration of approximately five liters of polymer solution. Pressurization of the vessel forces fluid through the outlet dip-tube and through the connecting line to the filter holder. If the fluid contains particulates, they may settle to the bottom and be left in the vessel. Thus, visual observations and viscosity measurements are also important in evaluation of the fluid. Sustained contact of stainless steel components with high salinity solutions should be avoided due to the possibility of corrosion, which will rapidly and irreversibly alter both polymer solution quality and filterability characteristics. Therefore, tests should be performed as soon as possible after the fluid reservoir is filled. Stainless steel components should be scrupulously cleaned and throughly dried after use. Components of the test apparatus are listed below:

Solution Pressure Reservoir	316 stainless steel, 5-liter dispensing pressure vessel with Cam-Loc™ cover, maximum pressure 100 psig at 250 F *(121 C)*, ¼-inch NPTF elbow fittings for inlet and outlet, ¼-inch NPTF fittings for pressure gauge and relief valve (e.g., Millipore® Corp. XX67-00P-05, or equivalent.)
Vent Relief Valve	100 psig (ASME) (e.g., Millipore® Corp. XX67-00L-24, or equivalent).
Pressure Gauge	60 psig, ¼-inch NPTF male fitting.
Filter Holder	Stainless steel, in-line filter holder with quick releasing wrap-around clamp. ¼-inch NPTF inlet port, ¼-inch, NPTF outlet port.
Pressure Tubing	¼-inch OD x .062-inch wall nylon tubing to connect nitrogen regulator to pressure vessel inlet.
Tubing	¼-inch OD x .062-inch wall nylon flexible tubing, 5-ft long to connect pressure vessel outlet to filter holder. ⅛-inch OD drain tubing, 4 inches long, for filter outlet.

Valves	Two each, one-way stainless steel ball valves for pressure vessel outlet and filter outlet.
Connections	Pipe-to-tubing connectors and 2 Quick-Connect® type connectors, or equivalent, (free flow-through type).
Filter Holder Support	Clamp or support for filter holder.
Filter Forceps	Smooth tip.
Membrane Filters	47-mm diameter, appropriate pore size as stipulated in Par. 4.2.1.
Nitrogen Cylinder and Regulator	Capable of maintaining constant pressure of 20 psig (e.g., Air Products Two-stage Regulator, 0-50 psig, Commodity Code No. E12-4-N1458, or equivalent).
Stopwatch or Timer	

4.2.2.2 Procedure.

1. Before beginning, ascertain that all parts of the apparatus are clean. Be particularly alert for traces of polymer gel or rust. Connect the nitrogen tank, pressure vessel, and membrane holder with tubing and valves. Connect the drain tube.
2. Fill the pressure vessel with test solution. Close and lock the lid. Pressurize to 20 psig with nitrogen.
3. Holding the top half of the filter holder upside down, slowly open the pressure vessel outlet valve and fill the top half of the filter holder with liquid. Close the outlet valve.
4. Close the valve on the bottom half of the filter holder. Transfer the contents of the top half to the bottom half.
5. Place the filter support (smooth side up) on the bottom half of the filter holder, making certain that the support is completely covered with liquid.

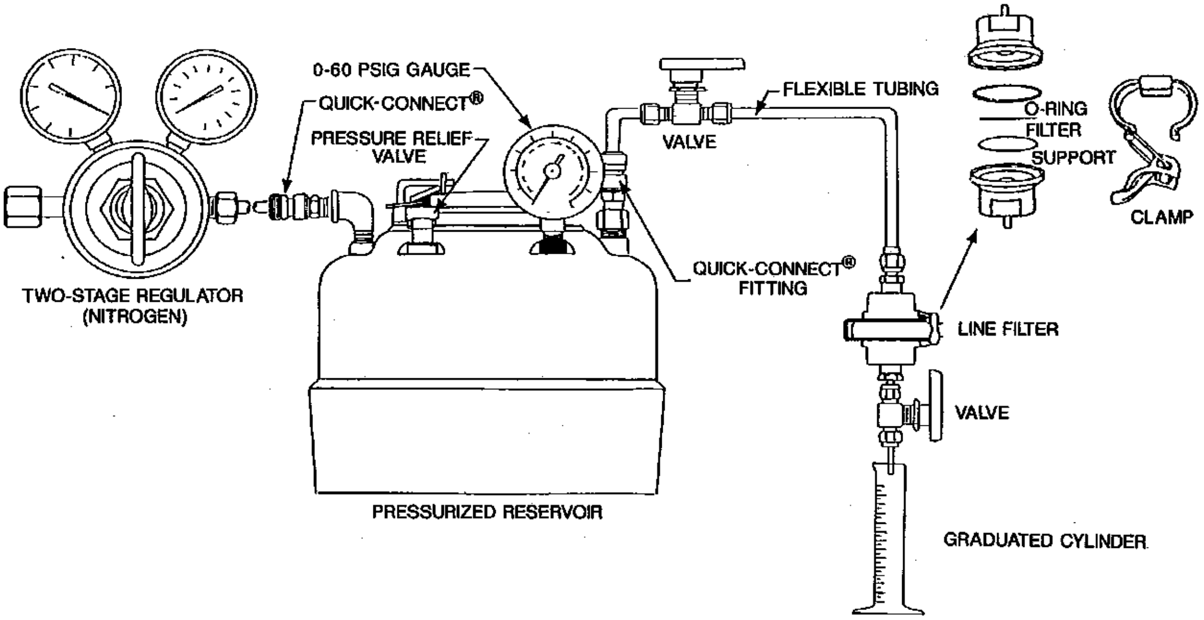

FIGURE 4-2
FILTRATION APPARATUS, 5 LITER PRESSURIZED RESERVOIR (Refer to Par. 4.2.2.1)

6. Center the membrane filter on the support and open the valve to drain some of the liquid until the membrane rests on the support. Close the valve.
7. Place the top half of the holder on the bottom half, being careful not to twist the two sections. Hold both halves firmly, but not tightly.
8. Invert the filter assembly so that the bottom half is on top. Slowly open the pressure vessel outlet valve and allow flowing liquid to expel air and fill the void space. Hold the assembly firmly but loose enough to allow air and excess fluid to escape between the two halves.
9. Close the pressure vessel outlet valve. Fasten the two filter holder halves together with the clamp. Exercise care not to twist the membrane filter.
10. Fasten the filter holder in an upright position and proceed with the filtration procedure as described in Par. 4.2.1.3, Steps 4-8.

4.3 FILTRATION PROCEDURE FOR FIELD APPLICATION

4.3.1 Sample. A 1000 mL sample of the injection fluid taken at the wellhead is required for this test. This sample should be obtained and handled in accordance with recommendations in Section 6.

4.3.2 Sampling Apparatus. Refer to Par. 6.4.

4.3.3 Sample Collection Procedure. Refer to Par. 6.4.

4.3.4 Procedure. High salinity brine can corrode 316 stainless steel in a relatively short time and corrosion products will rapidly and irreversibly alter both polymer solution quality and filterability characteristics. However, an air-free solution tested immediately after sampling should give reproducible filtration results. It is good practice, therefore, to proceed with the filterability test as soon as possible after sampling. Immediately after sampling, proceed with the test as described below:

1. Connect the nitrogen tank, cylinder, and membrane assembly with pressure tubing and valves. This assembly should essentially be the same as shown in Figure 4-1, but the Hoke® sampling cylinder, or equivalent, will be used in place of the Millipore®, or equivalent, filling system cylinder. Refer to Par. 4.2.1.3, Step 1 for cautions in handling of membrane filters.
2. Close the exit valve and apply a pressure of 20 psig using the nitrogen source and regulator.
3. Wet the membrane filter and exclude air from the system.
   a. For 1 micron and larger pore sizes this can be done by inverting the filter holder and flowing a small volume (approximately 10 mL) through the filter until air bubbles cease in the effluent.
   b. For filters smaller than 1.0 micron pore size, the filter holder should be filled with solution before assembly in order to exclude air from the system. This procedure requires some practice to achieve consistency.
4. Place a suitable graduated cylinder below the filter outlet. Open the valve at the base of the filter reservoir and simultaneously start the stopwatch. The pressure (20 psig) must be constant throughout the test.
5. Record cumulative time in seconds for each 50 mL increment filtered. Continue filtering until:
   a. 500 mL have been filtered,
   b. filtration has ceased, or
   c. 600 seconds have elapsed.
6. Examine the membrane filter for tears or other damage, including non-wetted areas of the filter. If damage is found, repeat the run. Record the appearance of material trapped on the filter.
7. Repeat the test using a new membrane filter.
8. Report data as described in Par. 4.4.

4.4 ANALYSIS OF DATA

4.4.1 Method of Analysis. Plots showing cumulative volume filtered can provide useful comparisons of solutions having similar viscosities. However, due to the effect of viscosity on flow rate, the preferred method of data presentation for polymer solutions calls for calculation of a filter ratio, which compares the flow time of an initial or earlier volume to that of an equal later volume. When liquids are very close in initial properties, filtration of large quantities may be necessary to allow differentiation between them. The example shown in Par. 4.4.2 is for relatively low volumes, as described in the preceding procedures.

4.4.2 Example Calculations.

Calculate the filter ratio (FR) as follows:

$$FR_{500} = \frac{t_{500} - t_{400}}{t_{200} - t_{100}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4\text{-}1)$$

where:

t_{500}, t_{400}, t_{200}, and t_{100} are the times, in seconds, required to filter 500, 400, 200, and 100 mL of the solution, respectively.

> *NOTE:* It is often found that the time for the first 50 mL of filtrate will be subject to error. Therefore, it is often more valuable to compare for example: $\frac{t_{500} - t_{400}}{t_{150} - t_{50}}$

4.4.3 Plotting Data. Plot cumulative volume versus cumulative filtration time as shown in Figure 4-3. On the same graph, plot filtration data for the brine used for mixing (makeup water) for comparison.

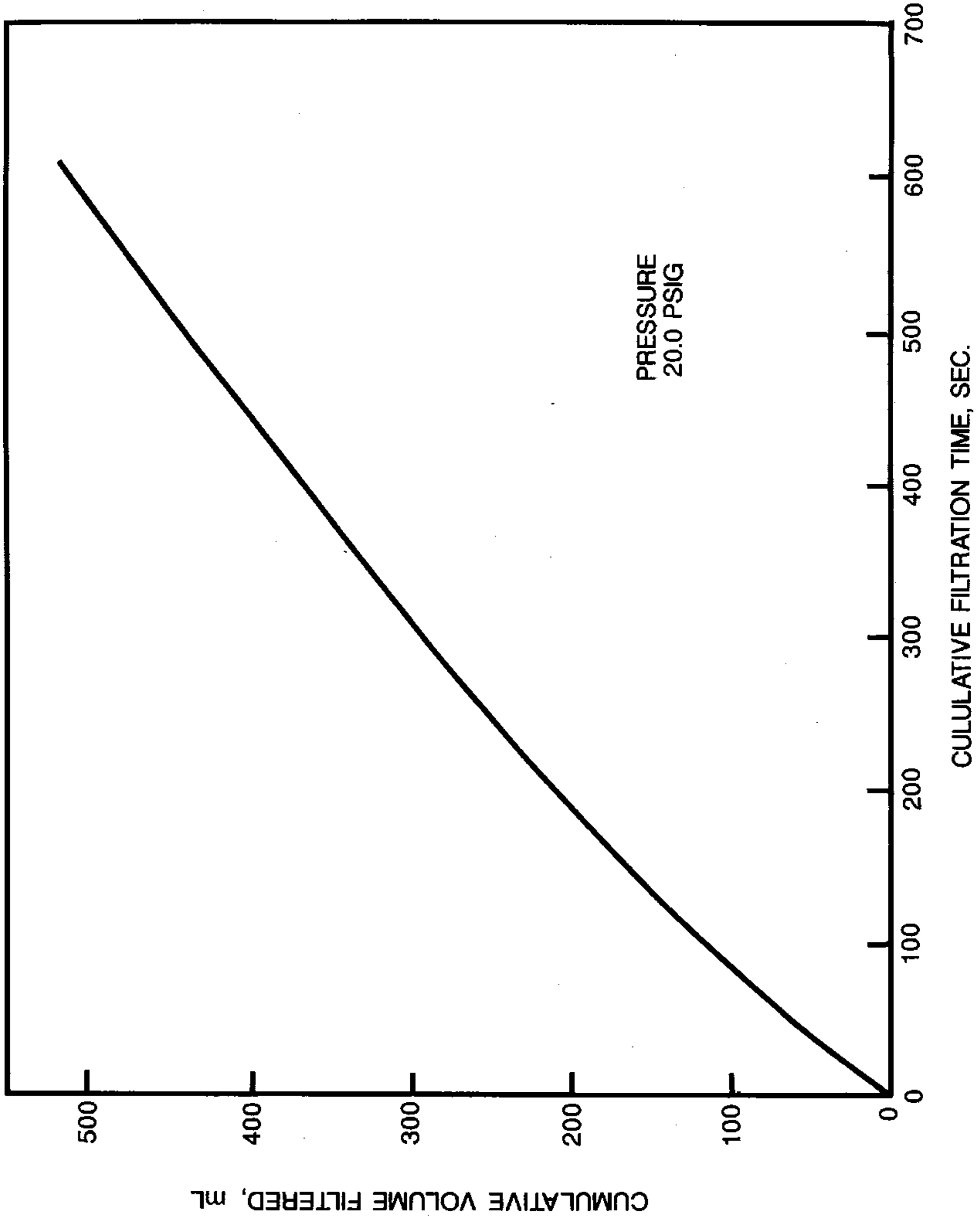

FIGURE 4-3
EXAMPLE FILTERABILITY PLOT

SECTION 5
RECOMMENDED ANALYTICAL PROCEDURES FOR DETERMINING CONCENTRATION OF POLYMERS IN SOLUTION

5.1 INTRODUCTION

5.1.1 General. This section contains recommended methods of analysis for polyacrylamides and polysaccharides. These methods are suitable to analyze for polymers dissolved in synthetic and natural oilfield brines. Presented are four quantitative methods for polyacrylamides and two quantitative methods for polysaccharides; also presented is a qualitative method for polyacrylamides. Only manual methods of analysis are discussed, however; all optical methods presented can be performed using the proper automated analyzer equipment. In this manner, precision is improved. *All analyses presented in this section are designed to yield results in parts per million.*

5.2 METHOD I: MEASUREMENT OF CONCENTRATIONS OF POLYACRYLAMIDES BY THE BLEACH METHOD

5.2.1 General. This method is based on reaction of polyacrylamides with sodium hypochlorite and resultant formation of an insoluble chloramide reaction product. Turbidities of the resulting samples are measured and concentrations are determined by comparisons with standards. The method is discussed in Reference 1 (refer to Appendix A to Section 5). Four versions of the bleach method are presented. The method presented in Par. 5.2.4 is intended for use with samples containing no oil and no colored materials, e.g., certain types of anionic surfactants. The method presented in Par. 5.2.5 is intended for use with samples which originally contain colored materials and/or emulsified oil. The method presented in Par. 5.2.6 is intended for use with solutions containing emulsion polyacrylamides and only those hydrocarbons in which the polymer emulsions were dispersed. In all cases in which the measuring instrument is a colorimeter, final samples for analysis must be free of color and contain no particulate matter. The method presented in Par. 5.2.7 uses a nephelometer as the measuring instrument. This method will tolerate initial low levels of turbidity or color.

5.2.2 Reagents.

1. Acetic acid, glacial.
2. Sodium chloride, reagent grade.
3. Sodium hypochlorite, aqueous solution, 5.25 weight percent (e.g., fresh, commercial-grade Clorox®, or equivalent).

5.2.3 Apparatus.

1. Bausch and Lomb Spectronic® 20 colorimeter, or equivalent instrument, and matched cuvettes.
2. Standard laboratory balance, maximum load 2000 g, sensitivity, 0.01 g.
3. Stopwatch or timer.

5.2.4 Bleach Method For Use With Brine Samples Containing No Oil and No Colored Materials.

5.2.4.1 General. Samples for analysis must be free of oil and colored contaminants. Measurements should be performed on solutions containing 10 to 500 ppm polymer and brine composition must be known.

5.2.4.2 Procedure for Sample Preparation for Measurement of Turbidity.

1. Prepare a solution containing 6 weight percent acetic acid and 20 weight percent of 5.25 weight percent sodium hypochlorite solution. Use distilled water. Shelf life of this solution is approximately two days.

   CAUTION: Add components to water. All operations should be performed in a fume hood to prevent accumulation of hazardous vapors.

2. If polymer samples are known to be more concentrated than 500 ppm, dilute to approximately 250 ppm with brine of the same composition. Record dilution factors for use in later calculations.

$$\text{Dilution Factor} = \frac{\text{weight of diluted sample, g}}{\text{weight of initial sample, g}} \quad \ldots (5\text{-}1)$$

NOTE: Steps 2 through 4 should be completed for all samples to be analyzed before beginning Step 5.

3. Filter 10 g of oil-free, colorless, polymer solution through 5 micron filter membranes. *NOTE:* It has been found that membranes finer than 5 microns can, in some instances, retain polymer. If the samples contain sulfide, refer to Par. 5.2.4.8 before proceeding.
4. Weigh 5.0 g ± 0.03 g of the filtered polymer solution from Step 3 into a clean 4 dram vial (or equivalent container) with cap.
5. Add the sodium hypochlorite plus acetic acid solution from Step 1 to obtain a total weight (sample plus solution) of 9.5 g ± 0.03 g.
6. Cap the container and mix by inverting several times. Do not shake. Shaking can result in flocculation of the reaction product.
7. Transfer the mixture to a sample cuvette and measure the percent transmittance at a wavelength of 470 nm (refer to Par. 5.2.4.3). For each sample, Steps 6 and 7 must be completed within five minutes after completion of Step 5. A standing time of three minutes is recommended. Standing time should be kept as constant as possible.

5.2.4.3 Procedure for Measuring Transmittance.

1. Allow 15 minutes warm-up time for the colorimeter.

2. Set the wavelength to 470 nm.
3. Fill the reference cuvette with distilled water or brine as nearly identical in composition to the sample as possible.
4. Set the instrument to zero percent transmittance.
5. Insert the reference cuvette and set the instrument to 100 percent transmittance.
6. Insert the cuvette containing the sample and record the percent transmittance. Following the measurement, the instrument should be checked with reference solution to ensure against drift.

5.2.4.4 Preparation of the Standard Curve.

1. Prepare a 500 ppm stock solution of the appropriate polymer in brine that is identical in composition to that present in the unknowns. Refer to Section 2 for recommended solution preparation procedures.
2. From the above stock solution, prepare standard solutions by diluting with brine to obtain concentrations of 0 to 500 ppm in 50 ppm increments.
3. Perform Steps 3 through 7 of Par. 5.2.4.2 for the set of standard solutions and record transmittances. Prepare a standard curve of percent transmittance versus polymer concentration.

5.2.4.5 Determination of Sample Concentrations. Sample concentrations are found by direct comparisons of sample transmittances with the standard curve. These comparisons should take into account any dilutions which may have been necessary to reduce the sample concentrations to less than 500 ppm and/or which may have been performed during treatment for sulfide.

Polymer concentration = polymer concentration read from the curve x dilution factor .... (5-2)

5.2.4.6 Interferences. In this test method, the following items will show up as interferences:

1. Oil.
2. Iron sulfide.
3. Any oxidizable material.
4. Any colored material not removed by filtration.

5.2.4.7 Reproducibility. With reasonably clean samples, reproducibility of about 10 percent of the amount of polymer present can be expected.

5.2.4.8 Special Procedures for Samples Containing Sulfide. If sulfide is present, elemental sulfur may form during Step 5 under Par. 5.2.4.2 in the presence of the acidic oxidizing solution. The resulting precipitate is often colloidal and cannot be removed by filtration. When sulfide is present, treat the oil-free, filtered, colorless sample as follows:

1. In a 250-mL beaker, combine 50 g sample and 50 g acetic acid.

   CAUTION: Steps 1 through 3 should be performed in a fume hood to prevent accumulation of hazardous vapors.

2. Boil for 5 minutes.
3. Add 1 g sodium persulfate and boil for an additional 10 minutes.
4. Cool and dilute to 100 g. Proceed with the analysis (refer to Par. 5.2.4.2., Step 5). *NOTE:* In determining concentration of polymer, take into account that the above procedure dilutes the sample by a factor of 2.
5. Steps 1 through 4 must also be applied to solutions prepared for construction of the standard curve.

5.2.5 Bleach Method For Use With Brine Samples Containing Oil or Colored Materials.

5.2.5.1 General. This method is intended for analyses of solutions containing emulsified oil and/or colored materials which are removed with high concentrations of sodium chloride. Colorless surfactants usually have been found not to affect the accuracy of the bleach method of analysis; however, surfactants used in chemical flooding often contain colored impurities. Measurements should be performed on solutions containing 100-250 ppm polymer. If samples contain sulfide, perform Steps 1 through 4, Par. 5.2.4.8.

5.2.5.2 Procedure for Sample Preparation and Measurement of Turbidity.

1. Prepare a solution containing 6 weight percent acetic acid and 20 weight percent of 5.25 weight percent sodium hypochlorite solution. Use distilled water. Shelf life of this solution is approximately two days.

   CAUTION: Add components to water. All operations should be performed in a fume hood to prevent accumulation of hazardous vapors.

2. If polymer samples are known to be more concentrated than 250 ppm, dilute to approximately 125 ppm with brine of the same composition. Record dilution factors for later use in calculations [refer to Equation (5-1)].

   NOTE: Steps 2 through 8 should be completed for all samples to be analyzed before beginning Step 9.

3. Place approximately 15 g of the solution to be analyzed into a one-ounce bottle (or similar container) with cap.

4. Add to the solution approximately 8 g of sodium chloride.
5. Gently agitate the mixture for 5 minutes.
6. Allow the mixture to stand for approximately 30 minutes, then withdraw the clean, oil-free portion of the solution with a hypodermic syringe or other suitable extraction device.
7. Filter the saturated salt solution using a 5 micron membrane filter. If, at this point, the solution is not oil free and colorless, abandon the analysis. If sulfides are present, perform the procedure prescribed in Par. 5.2.4.8.
8. Weigh 5 g ± 0.03 g of the filtered solution from Step 7 into four dram vials (or equivalent containers) with caps.
9. Add the sodium hypochlorite plus acetic acid reagent from Step 1 to obtain a total weight (sample plus reagent) of 9.5 g ± 0.03 g.
10. Mix the solution by inverting the container several times; do not shake. Shaking can result in flocculation of the reaction product.
11. Transfer the mixture to the sample cuvette and measure the percent transmittance at a wavelength of 470 nm. For each sample, Steps 10 and 11 must be completed within 5 minutes after completion of Step 9. A standing time of three minutes is recommended. Standing times should be kept as constant as possible.

5.2.5.3 Procedure for Measuring Transmittances. Refer to Par. 5.2.4.3.

5.2.5.4 Preparation of the Standard Curve.

1. Prepare a 250 ppm stock solution of the appropriate polymer in brine that is identical in composition to that present in the unknowns. Refer to Section 2 for recommended solution preparation procedures.
2. From the above stock, prepare standard solutions by diluting with brine to obtain concentrations of 0 to 250 ppm in 50 ppm increments.
3. Perform Steps 3 through 11 of Par. 5.2.5.2 for the set of standard solutions and record transmittances. Prepare a standard curve of transmittance versus concentration.

5.2.5.5 Determination of Sample Concentrations. If no significant concentration of surfactant was present in the original samples, polymer concentrations are found by direct comparison of the sample transmittances with the standard curve. These comparisons should take into account any dilution(s) which may have been necessary and/or which may have been made during treatment for sulfide.

Polymer concentration = polymer concentration read from the curve x dilution factor .... (5-2)

If no dilutions are made, the dilution factor is 1. If, on the other hand, samples contained surfactant which was precipitated by salt, a correction factor must be applied as follows:

$$C_p = C_p \text{ measured} \times \left[1 - (C_s \times W_s)\right] \quad \text{......(5-3)}$$

where:

C_p = Polymer concentration, ppm.

C_s = Surfactant concentration, meq/mg.

W_s = Milliequivalent weight of surfactant, mg/meq.

5.2.5.6 Interferences and Reproducibility. Interferences and reproducibility are the same as those listed under Pars. 5.2.4.6 and 5.2.4.7.

5.2.6 Bleach Method For Use With Samples of Emulsion Polymer in Brine Containing Only The Hydrocarbons in Which Polymer Was Originally Dispersed.

5.2.6.1 General. This method is intended for use with solutions of emulsion polymer which contain only those hydrocarbons in which the emulsions were dispersed. Measurements should be performed on solutions containing less than 75 ppm polymer.

5.2.6.2 Procedure for Sample Preparation for Measurement of Turbidity.

1. If polymer samples are known to be more concentrated than 75 ppm, dilute with brine of the same composition. Record dilution factor for later use in calculations [refer to Equation (5-1)].
2. Filter samples using 5 micron membrane filter.
3. If samples contain sulfide, refer to Par. 5.2.4.8.
4. Weigh 5 g ± 0.03 g of sample into a 4 dram vial, or equivalent container.

   CAUTION: Perform Steps 5 and 6 in a fume hood to prevent accumulation of hazardous vapors.
5. Add 5 g ± 0.03 g of glacial acetic acid to the vial. ***NOTE:*** If a precipitate forms when acid is added to the brine under study, the 5 g sample in Step 4 should contain sufficient added distilled or deionized water to prevent the precipitation. If this is necessary, the resulting dilution factor should be recorded.
6. Add 1 g sodium hypochlorite reagent (refer to Par. 5.2.4.2, Step 1) and mix by swirling (do not shake). Mix at 5 minute intervals; total mixing time should be 15 minutes (± a few seconds).

7. Transfer the mixtures to sample cuvettes and measure percent transmittances (refer to Par. 5.2.4.3). *NOTE:* Use of as large a cuvette as possible improves accuracy.

5.2.6.3 Preparation of the Standard Curve.

1. Prepare a 500 ppm stock solution of the appropriate polyacrylamide in brine that is identical in composition to that in the unknowns. Refer to Section 2 for recommended solution preparation procedures.
2. From the above stock, prepare standard solutions by diluting with brine to obtain concentrations of 0 to 75 ppm, with minimum increments of 5, 10, 25, 50, and 75 ppm.

   NOTE: If dilution with distilled or deionized water is required in Step 5, Par. 5.2.6.2, the standard polymer solutions should be handled in an identical fashion so that the salinity for all standard solutions is the same as for the unknown samples that are being analyzed.
3. Perform Steps 3 through 7, Par. 5.2.6.2 for the set of standard solutions and record transmittances.
4. Prepare a standard curve of transmittance versus concentration.

5.2.6.4 Determination of Sample Concentrations. Sample concentrations are found by direct comparisons of sample transmittances with the standard curve. These comparisons should take into account any dilutions which may have been necessary and/or which may have been performed during treatment for sulfide.

Polymer concentration = polymer concentration read from the curve x dilution factor .... (5-2)

5.2.6.5 Interferences and Reproducibility. Interferences and reproducibility are the same as those listed in Pars. 5.2.4.6 and 5.2.4.7.

5.2.7 Bleach Method Using Nephelometry Intended For Analysis of Samples of Polyacrylamide in Brine Solutions Which Contain Low Levels of Turbidity or Colored Materials.

5.2.7.1 General. This is a nephelometric method and is intended for analysis of solutions containing 5 to 150 ppm polyacrylamide. It may be used for samples with low levels of initial turbidity or color although this may slightly decrease the accuracy of the method. Some corrosion inhibitors and demulsifiers may interfere with this method. It is usually possible to remove these agents by solvent extraction. If solvent extraction is to be used, efficiency of the solvent for surfactant removal and tendency of the solvent to precipitate the polyacrylamide should be evaluated.

5.2.7.2 Apparatus. One of the following instruments, or equivalent.

1. Hach Ratio Turbidimeter Model 18900.
   Cell: 25 mL
   Range Settings: 0-200 NTU
2. Bausch and Lomb Mini 20™ Nephelometer.
   Cell: 5 mL
   Range Settings: 0-100 NTU
   Wavelength: 470 nm
3. Hach Turbidimeter Model 2100A.
   Cell: 25 mL
   Range Settings: 0-100 NTU

5.2.7.3 Reagents.

1. Sodium hypochlorite, aqueous solution, 5.25 weight percent (e.g., fresh commercial grade Clorox®, or equivalent).
2. Acetic acid, glacial.
3. Distilled water.
4. Concentrated hydrochloric acid.

5.2.7.4 Preparation of Reagents.

1. Add 42 mL concentrated HCl and 286 mL glacial acetic acid to 600 mL distilled water. Mix and dilute with distilled or deionized water to the 1000 mL mark.

   CAUTION: Perform Steps 1 and 2 in a fume hood to prevent accumulation of hazardous vapors. Always add acid to water and wear goggles and gloves to prevent burn injuries in the event of a spill or splashback when handling concentrated acid.
2. To a 500 mL graduated cylinder, add 375 mL distilled water. Add 125 mL sodium hypochlorite reagent bleach and mix. This solution should be kept in a brown bottle and replaced weekly.

5.2.7.5 Procedure for Sample Preparation for Measurement of Turbidity.

1. If necessary, dilute each sample to 25 to 125 ppm using a synthetic version of the sample brine.
2. To a 25 mL stoppered graduated cylinder, add 10 g of the sample to be analyzed. Add 10 g of distilled water and mix.
3. Add 1 g of the acid solution and mix. If turbidity develops, refer to Step 6.
4. Add 1 g of sodium hypochlorite reagent and mix. Allow the sample to stand for 20 minutes.
5. Measure turbidity in NTU.
6. If the sample to be analyzed is turbid or colored, a blank turbidity should be subtracted from the turbidity measured in Step 5. Follow the standard sample analysis procedure (refer to Steps 1 through 5). Add 1 g of distilled water (in place of the sodium hypochlorite reagent), mix, and measure the turbidity.

7. Standards should be analyzed using the same procedure.

5.2.7.6 Preparation of Standards.

1. Duplicate sample brine as closely as possible and prepare a 500 ppm solution of the appropriate polymer in the brine solution. Refer to Section 2 for recommended solution preparation procedures.
2. Using the solution prepared in Step 1, prepare standards by diluting with the sample brine to obtain concentrations of 25 to 150 ppm in 25 ppm increments.

5.2.7.7 Calculations.

1. Prepare a standard curve by plotting turbidity versus known concentration of the standards.
2. Sample concentrations should be determined by direct comparison of sample turbidity (minus the blank, if applicable) with the standard curve. This comparison should take into account any dilutions which may have been necessary to reduce the sample concentrations to 125 ppm or less.
3. The relative precision is about 10%.

5.2.7.8 Interferences.

1. The turbidity developed is a weak function of polymer hydrolysis level and molecular weight. To enhance accuracy, standards should be prepared from the same polymer as the samples.
2. The turbidity developed is also a weak function of the concentration and composition of the brine. Duplicate the field brine as accurately as possible.
3. Some oilfield brines contain oxidizable materials and may require additional bleach to achieve maximum turbidity.
4. Field samples which display significant turbidity due to oil or precipitates should be filtered as follows:
    a. Filter a 30 mL sample of the subject water through a Whatman® #1 filter disk, or equivalent, to remove large particles and oil.
    b. To 20 mL of this solution, add 2 mL acid and mix.
    c. Bubble the sample with nitrogen or air for 10 minutes. Nitrogen is preferred as air oxidizes sulfides to free sulfur.
    d. Gravity filter (optional) through a Gelman® GA-1 five-micron filter, or equivalent. If the filter becomes plugged, then replace. Forcing the solution through the filter can remove polymer.

5.3 METHOD II: MEASUREMENT OF CONCENTRATIONS OF POLYACRYLAMIDE BY THE STARCH IODIDE METHOD

5.3.1 General. This method, which is described in Reference 7 (refer to Appendix A to Section 5), is intended for determining concentrations of water soluble polymers containing pendant primary amide groups, e.g., polyacrylamides. It measures amide groups and, therefore, is sensitive to the level of hydrolysis of the polyacrylamide. The method is suitable for use with polymers in oilfield brines and surface waters. The method is based on the first step of the Hofmann rearrangement of an amide to an amine. The polymer sample is buffered at a pH of 3.5 and the amide is oxidized with bromine water. The excess bromine is reduced with sodium formate solution and the amide oxidation product is allowed to oxidize iodide ion in the presence of linear starch to form the characteristic blue starch iodide complex which is measured spectrophotometrically at a wavelength of 610 nm. Polymer concentrations between 10 and 300 ppm can be determined directly using a 1.0 g sample and comparing absorbances with a standard curve.

5.3.2 Apparatus. The following apparatus is needed to perform this test:

1. Bausch and Lomb Spectronic® 20, or equivalent instrument.
2. Top loading balance (sensitivity 0.01 g), or other appropriate weighing instrument.
3. Whatman® filter paper No. 42, or equivalent.
4. Stopwatch or timer.

5.3.3 Reagents. All reagents should be American Chemical Society reagent grade, unless otherwise noted. References to water indicate distilled or deionized water. The following reagents are needed for this test method:

1. Sodium acetate trihydrate.
2. Hydrated aluminum sulfate.
3. Glacial acetic acid.
4. Bromine water, saturated solution.
5. Sodium formate.
6. Potato starch for iodometry.
7. Cadmium iodide.
8. Polyacrylamide product, either dry, emulsion, or gel.

5.3.4 Preparation of Reagent Solutions.

1. Prepare a buffer solution, pH 3.5. Dissolve 25 g of sodium acetate trihydrate and 0.75 g of hydrated aluminum sulfate in 700 g of water and add 110 g of glacial acetic acid. Adjust the pH to 3.5 with acetic acid and dilute to 1000 g. *NOTE:* Hydrated aluminum sulfate is added to increase the color intensity of the starch-iodide complex.
2. Prepare a 1 weight percent solution of sodium formate in water.
3. To prepare starch-cadmium iodide color reagent, dissolve 11 g of CdI_2 in 400 g of water and boil the

solution for 15 minutes. Dilute to 800 g and slowly add, while stirring, 2.5 g of starch slurried in a small volume of water. Allow the solution to boil gently for 5 minutes; cool and filter with suction through a double thickness of No. 42 Whatman® filter paper, or equivalent. Dilute to 1000 g.

5.3.5 Preparation of the Standard Curve.

1. Prepare a 500 ppm stock solution of the polymer in brine which is identical in composition to that of the sample. Refer to Section 2 for recommended solution preparation procedures. From this stock, prepare standards of 12.5, 25, 50, 100, 150, 200, 250, and 350 ppm. For dilution, use brine identical in composition to that of the sample.
2. Into separate tared 100 mL vessels, weigh 1 g of the samples and 5 g of the buffer solution.
3. Dilute to approximately 35 g and mix each vessel.
4. Add 1 g of bromine water, mix, and allow to stand for exactly 15 minutes.
5. Add 5 g of 1% sodium formate solution and allow to stand for exactly 5 minutes.
6. Add 5 g of starch CdI_2 color reagent, mix, and dilute to 50 g with water.
7. Allow the solutions to stand for 15 minutes to fully develop color. Measure the absorbance of the solutions at a wavelength of 610 nm, having previously set the instrument to zero absorbance using a reagent blank.
8. Prepare a plot of total absorbance versus corresponding polymer concentration.

5.3.6 Determination of Polymer Concentration in Sample.

1. Filter portions of polymer samples using 5 micron filter membranes.
2. Weigh 1 g of oil-free, colorless sample and 5 g of buffer solution into a 100 mL tared vessel. *NOTE before proceeding with Step 2:* If samples are known to contain less than 25 ppm polymer, use a portion larger than 1 g. If samples are known to contain more than 300 ppm, dilute to approximately 200 ppm and record dilution factor [refer to Equation (5-1)].
3. Perform Steps 3 through 7, Par. 5.3.5.
4. To obtain polymer concentrations of samples, compare sample absorbances with the standard curve. If more than 1 g of undiluted sample was used in Step 2, the polymer concentration read from the curve must be divided by the weight of sample used. In the event that dilution was required, calculate polymer concentration using Equation (5-2).

5.3.7 Interferences. The following materials have been found to interfere with this analysis:

1. Oil.
2. Amines.
3. Iodide ion.
4. Heavily colored material.

5.3.8 Accuracy. With clean, oil-free, colorless samples, an accuracy of approximately 10 percent of the amount of polymer present can be expected.

5.4 METHOD III: MEASUREMENT OF CONCENTRATIONS OF POLYSACCHARIDES BY THE PHENOL-SULFURIC ACID METHOD

5.4.1 General. This method is intended for determination of concentrations of polysaccharides in water solutions. The method is suitable for use with both synthetic and oilfield brines. Samples of produced brine may also be analyzed, provided they are free of oil and colored material prior to analysis. The basis of the method is combination of phenol and carbohydrates in an acid environment to form colored reaction products. Therefore, the method does not distinquish between polysaccharide polymers, e.g., xanthan gums, and mono-, di-, tri-, and oligo-saccharides such as glucose, mannose, sucrose, and other polymer degradation products. The phenol-sulfuric acid method may also be used to assay commercial xanthan polymer products, as well as to check carbohydrate levels in injected and produced fluids. Because total carbohydrate content is measured, care must be taken to avoid contaminating samples with threads or lint from clothing or with paper. Samples must be free of colored materials. For precise determination of polymer content, it is necessary to prepare standard solutions from purified xanthan. However, for semi-quantitative analyses or for determining relative polymer concentrations of samples, standards prepared from commercial polymer may be adequate.

5.4.2 Reagents.

1. Concentrated sulfuric acid (AR grade).

   CAUTION: Sulfuric acid is a strong acid. Handle with care using appropriate safety precautions and protective equipment to prevent exposure and injury.

2. Phenol (AR grade).

   CAUTION: Phenol is a strong acid. Handle with care using appropriate safety precautions and protective equipment to prevent exposure and injury.

3. Purified xanthan or commercial xanthan.

5.4.3 Apparatus.

1. Centrifuge tubes, 15 mL, and 7-degree tube holder for acid addition. Refer to Figure 5-1.

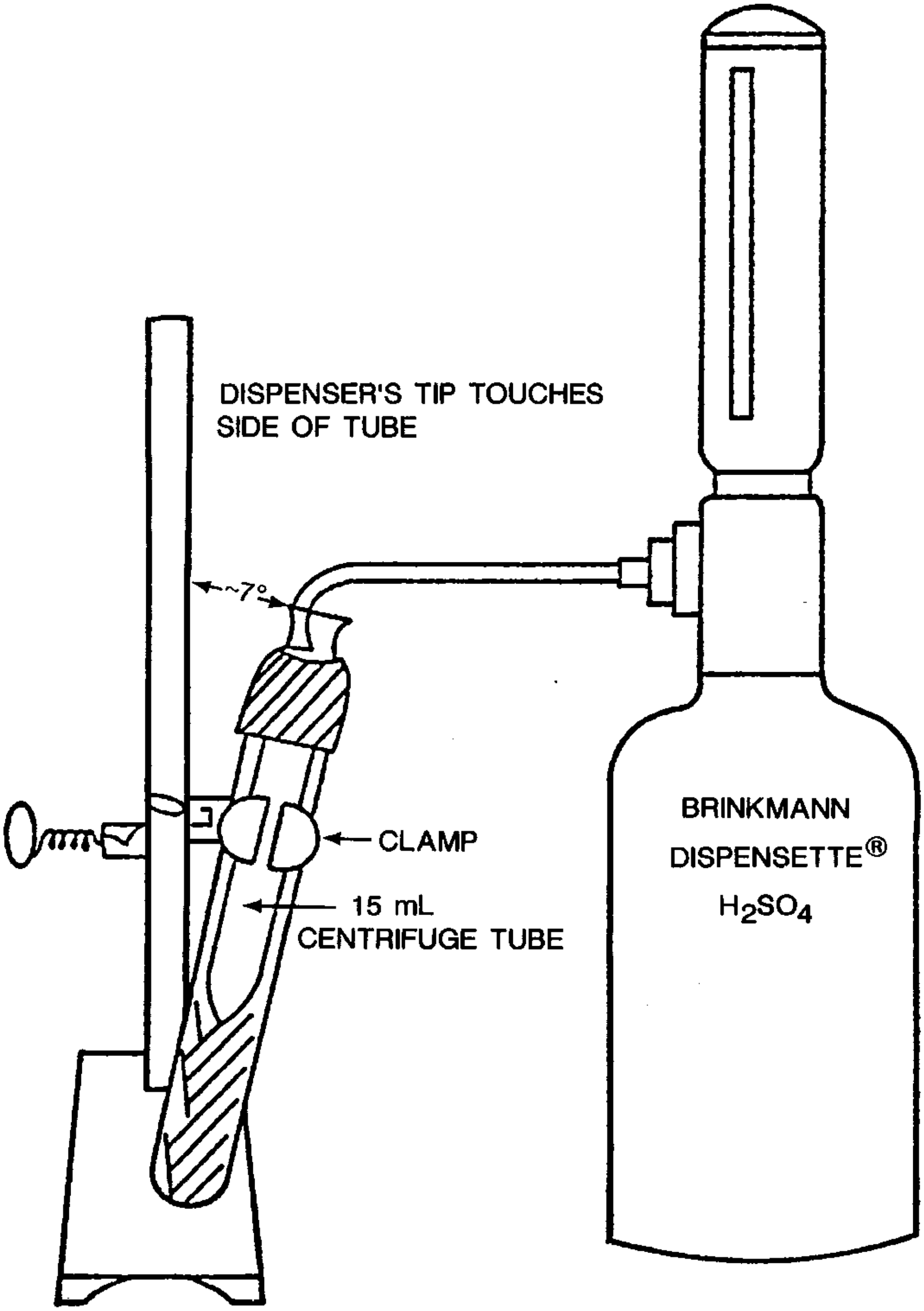

FIGURE 5-1
TUBE HOLDER AND DISPENSER FOR TOTAL CARBOHYDRATE DETERMINATION

2. Refillable volumetric dispenser such as a Brinkman Dispensette®, or equivalent. Refer to Figure 5-1.
3. Colorimeter or spectrophotometer equipped to measure absorbance at 485 nm, e.g., Bausch & Lomb Spectronic® 20, or equivalent.
4. Vortex mixer.
5. Filters.
6. Stopwatch or timer.
7. Analytical balance.

5.4.4 Preparation of Samples.

1. If it is intended to assay commercial polymers, prepare solutions of the appropriate polymers from material in the "as received" condition. Prepare solutions with approximately 100 ppm active ingredient. Record weight used in order to calculate percent polymer in the commercial polymer. Refer to Section 2 for recommended solution preparation procedures.
2. Injection Fluid Samples. If necessary, dilute samples to approximately 100 ppm and record the dilution factor [refer to Equation (5-1)].
3. Produced Fluid Samples. Remove emulsified oil by chloroform or hexane extraction or centrifugation. If surfactant is present, remove by saturating the solution with sodium chloride. Do not dilute until sample is first tested at full strength.
4. Prior to analysis, filter samples using 5 micron membrane filters.

5.4.5 Procedure for Analysis. *NOTE:* A reagent blank is carried through the procedure along with the samples.

1. Prepare a phenol reagent solution by dissolving 5.0 g of phenol in distilled water and diluting to 100 g. This solution is stable at room temperature for about 1 month.
2. Add 1 g of standard xanthan solution, prepared sample, or distilled water blank into a 15 mL centrifuge tube with stopper. Samples should be done in triplicate to ensure reproducibility.
3. Add 1 mL of phenol reagent to each tube. Mix tubes gently on a vortex mixer avoiding excessive splatter.
4. *WARNING: The addition of sulfuric acid to water is an exothermic reaction. Considerable heat may be generated. Appropriate safety precautions should be exercised to prevent spills or burns and to protect personnel who might be exposed.*

   Place the tubes in the 7 degree tube holder fixture and add rapidly 6.0 ml concentrated H_2SO_4 to the surface from a dispenser. Do not vortex mix. (Refer to Figure 5-1). *NOTE:* Tubes must be uniformly positioned and sulfuric acid must be added at the same rate to each tube. Otherwise, significant errors can result.
5. Allow tubes to stand 10 minutes at room temperature. Vortex mix the tubes.
6. Equilibrate the warm tubes in a 77 F *(25 C)* water bath for 15 minutes (± 30 seconds).
7. Read absorbance within 30 seconds at 485 nm with the instrument set at zero absorbance with the reagent blank.

5.4.6 Preparation of Standard Curves.

1. Prepare a 500 ppm stock solution from either purified xanthan or from the appropriate commercial polymer. Refer to Section 2 for recommended solution preparation procedures.
2. By dilution with water of composition identical to that of the samples, prepare standards of 0 to 160 ppm polymer in 20 ppm increments.
3. Perform Steps 2 through 7, Par. 5.4.5.
4. Construct a curve of absorbance versus polymer concentration, ppm.

5.4.7 Determination of Polymer Concentrations.

1. Polymer concentrations of samples can be found by direct comparison of sample absorbances with the standard curve.
2. If dilution is required, calculate polymer concentration using Equation (5-2).

5.4.8 Accuracy. This test method measures total carbohydrates in solution. Therefore, it is sensitive to materials other than polymer. In terms of total carbohydrates, a reproducibility of about 10 percent of the amount present can be achieved.

5.4.9 Interferences.

1. Any stray cellulose fibers.
2. Any colored material and surfactants.
3. Oil.
4. High concentration of aldehydes.

5.4.10 Preparation of Purified Xanthan.

5.4.10.1 Apparatus.

1. Centrifige, e.g., Sorvall Superspeed™ RC 2-B, or equivalent apparatus.
2. Dialysis membranes with 6000-8000 molecular weight cutoff.
3. Lyophilization (freeze dry) bottles.
4. Roll type freezer with self-refrigerated solvent bath, 7 rollers and a freezing capacity for 24 bottles.

5. Lyophilization machine (freeze dryer).

5.4.10.2 Procedure.

1. Prepare an aqueous solution containing 2,000 ppm or less of the desired product.
2. Centrifuge the aqueous solution 1-2 hours at 10,000-12,000 rpm.
3. Separate the aqueous solution from any sediment in the centrifuge tubes and place the aqueous solutions in pre-wet dialysis membranes to remove the undesirable low molecular weight materials. The membrane should be filled to approximately half its capacity and placed in a slow running distilled or deionized water bath over night. The membrane will swell with water as low molecular weight material is removed.
4. After adjustment to pH 7, the aqueous solution should then be placed in lyophilization (freeze dry) bottles in sufficient quantity so that when the bottles are laid on their sides to be frozen, no solution is lost.
5. Place the lyophilization bottles containing solution on their sides in a roller type freezing machine to facilitate even freezing on the bottle sides. Freeze and then freeze dry in a lyophilization (freeze dry) machine overnight.
6. Store the dried, purified polymer in a desiccator. Prior to use, obtain the Karl Fischer water analysis and correct for the amount of water present.

5.5 METHOD IV: MEASUREMENT OF CONCENTRATIONS OF POLYSACCHARIDES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) METHOD

NOTE: The analytical procedures and the equipment specified in this Section are used successfully by knowledgeable practitioners in the industry and were available to the committee in well documented form. It is recognized that there are procedure modifications and comparable equipment currently in use by industry practitioners which can obtain equivalent results. Nothing contained in this publication is intended to prevent a practitioner skilled in the art from using good judgment, experience, and techniques to effect results equivalent or superior to those obtained under procedures contained herein.

5.5.1 General. This procedure measures concentrations of high molecular weight polysaccharides (approximately 1 million molecular weight) in the concentration range of 50-1500 ppm. The procedure uses a size exclusion chromatography technique to separate the macromolecules from smaller components. Elution of the separated components is detected using a differential refractometer. Total polymer concentration is determined by peak integration of the detector response and comparing peak areas of the polymer component to that of polymer standards.

5.5.2 Reagents.

1. Water, HPLC grade.
2. Potassium dihydrogen phosphate, reagent grade.
3. Sodium phosphate (dibasic heptahydrate crystals), reagent grade.

5.5.3 Apparatus.

1. Hewlett-Packard Model 1084B liquid chromatograph, with a Model 79877A differential refractive index detector and Model 79850B LC terminal, or equivalent instrumentation.
2. Waters μ-Bondagel™ Columns E-1000 and E-500, or equivalent.
3. Circulating water bath capable of temperature control within ± 0.2 F (± *0.1 C*).
4. Analytical balance.
5. Filters.

5.5.4 Experimental Procedure for Polysaccharide Analysis by HPLC.

5.5.4.1 Procedure for Solvent Preparation.

1. Weigh 10.08 g of potassium dihydrogen phosphate and 26.80 g of sodium phosphate into a clean, two-liter volumetric flask.
2. Add HPLC grade water to the volumetric flask to form a solution of 2.0 liter volume. Shake the flask until all phosphate particles are dissolved.
3. Filter the solution through a 1.2-micron membrane filter. The solution should then be degassed under vacuum.

5.5.4.2 Column Installation and Preparation Procedure.

1. If a dual pump (solvent gradient) liquid chromatograph is to be used, the second pumping system should be disconnected at the mixing chamber and capped.
2. Install the two columns in the column oven compartment. The columns should be coupled in series with the E-1000 column leading the set. The inlet of the first column should then be connected to the liquid chromatograph sample injection system. The outlet of the second column is connected to the refractive index detector. All connections should be made with low dead volume tubing and fittings.
3. Fill the solvent reservoir with solvent solution (as prepared under Par. 5.5.4.1) and slowly agitate the solvent using a magnetic stirrer. Solvent and column oven temperature should be thermostatically controlled to 95 F ± 18 F *(35 C ± 1.0 C)*. (Most liquid chromatograph systems provide automated control of these variables.)

4. Prime the solvent pump and establish a flow rate of 1.0 mL/minute through the μ-Bondagel™ column, or equivalent equipment. Approximately 50 mL of solvent should be flowed through the column set to purge the original packed solvent (2-propanol) and stabilize the column packing to the solvent solution.

5.5.4.3 Procedure for Sample Injection.

1. Sample injection should be accomplished by a manual sample injection procedure or using a liquid chromatograph system with appropriate automatic sampling capabilities.
2. A manual sample injection scheme requires a six-port injection valve with two ports connected to a 100 microliter sample loop, two ports for inlet and exit of the solvent, one port connected to a LC syringe (500 microliter) and a sampling port. In one position of the injection valve, solvent flows through the sample loop while a sample is withdrawn through the sampling port into the syringe. The injection valve should be rotated to a second position and the sample expelled from the syringe into the sample loop. The injection valve should be returned to the first position to allow the sample to be carried by the solvent to the columns.
3. If the liquid chromatograph system has automatic sampling capabilities, the operator should consult the system reference manual as to the correct sample loading procedure and specifications for the following recommended injection settings: 1) an injection volume of 100 microliters, 2) a time period of 12 minutes for each sample analysis (this is the minimum time required between successive injections), and 3) two injections per sample tested.

5.5.4.4 Procedure for Refractive Index Detector Operation.

1. The reference cell of the differential refractive index detector should be filled with solvent solution as prepared under Par. 5.5.4.1. Care should be exercised to ensure that all air bubbles are purged from the cell.
2. The detector sample and reference cell should be thermostatically controlled to 95 F ± 0.2 F *(35 C ± 0.1 C)* using an external circulating water bath. Allow at least two hours for thermal stabilization.
3. Set the detector attentuation at Refractive Index (RI) x 4 and determine the zero point of the detector. This is the condition of initial equalization of light between the two detecting photocells, which establishes the correct detector baseline. (On the Hewlett-Packard Model 79877A refractive index detector, the zero point is found by rotating the zero adjustment knob continuously in one direction until the zero indicator on the front panel goes completely off. The zero adjustment knob should then be slowly rotated in the opposite direction until the zero indicator begins to light up. This corresponds to the correct zero point setting.) For other detectors, users should consult the equipment reference manual for the specific zero point adjustment procedure.
4. Record for approximately 30 minutes the detector response on the liquid chromatograph terminal plotter or an external chart recorder to determine the stability of the detector baseline. Acceptable baseline drift limits will vary between detectors, and acceptability of these limits is left to the discretion of the user. Baseline drift for the Hewlett-Packard Model 79877A Detector is deemed acceptable if the variance is less than 2-3% of full scale at a recorder attenuation of 8X.
5. The detector is ready for operation when a stable baseline has been established. If a stable baseline cannot be obtained after an extended period of time, consult the troubleshooting procedure in the equipment reference manual. ***NOTE:*** *Excessive baseline drift can commonly be the result of: 1) temperature fluctuation in the detector cell, or 2) incomplete purging of the columns using the new solvent solution.*

5.5.4.5 Procedure for Peak Integration.

1. The refractive index detector response can be integrated by various means, including: 1) manual area integration of the recorder output, 2) analog integration, or 3) analog to digital conversion, followed by digital integration. The latter integration technique has become the preferred method in most HPLC analyses, and is the recommended peak integration technique for this HPLC procedure.
2. To implement the latter peak integration technique, the RI detector should be coupled to an analog to digital conversion unit. This equipment converts the analog detector response to a digital signal. The digital signal is then integrated. Automated HPLC systems employ an on-line minicomputer, interfaced to the analog to digital conversion unit to perform the digital integration. The digital integration is executed by the minicomputer according to pre-programmed integration methods. The two most common pre-programmed integration methods are: 1) the slope sensitivity method, and 2) the area slice method. (The Hewlett-Packard Model 79850B LC terminal has capability for both these peak integration methods plus several others.)
3. If multiple integration methods are available, the area slice method has proven to give better reproducibility at lower polymer concentrations and is the recommended integration method in this HPLC procedure.
4. To specify a particular area slice integration method, users should consult the equipment refer-

ence manual of the HPLC integration system. If the Hewlett-Packard Model 79850B LC terminal is to be used for peak integration, the area slice method is executed as a sequence of time-programmed integrator events. The user must specify times for the start and stop of the area slice integration and the width of the area slice interval. There are also capabilities for baseline manipulation to correct for drift. A baseline extrapolated between two points immediately before and immediately after the elution of the polymer peak is recommended.

5. The area slice integration method should be executed between the analysis times of 2.75 minutes and 5.60 minutes. This corresponds to the elution period of the polymer peak in this HPLC procedure. The resulting area slices are then summed to determine the total area under the polymer peak. *NOTE: Smaller component peaks are eluted at later times, but their respective integration is not within the scope of this recommended procedure.*

5.5.4.6 Preparation of the Standard Curve.

1. Prepare a 1500 ppm standard solution of the respective polysaccharide in brine that is identical in composition to that present in the unknown samples. Refer to Section 2 for recommended solution preparation procedures.

2. Prepare standard solutions of 1000, 750, 500, 250, 100, and 50 ppm polymer concentration by diluting with brine solution in the appropriate proportions.

3. The standard solutions should be analyzed using the HPLC procedure outlined under Par. 5.5.4. Two sample injections should be done for each solution to assess the reproducibility of the analysis.

4. A linear calibration curve should be constructed showing total peak area versus solution concentration using results obtained under Step 3 above. *NOTE: If the calibration curve begins to deviate from linearity at the higher concentrations, this is normally an indication that the sample size is too large. The sample injection volume should be decreased and the standard solutions reanalyzed to obtain a linear calibration curve at all concentrations.*

5.5.4.7 Determination of Unknown Sample Concentrations.

1. The unknown sample(s) should be analyzed using the foregoing HPLC procedure. Two sample injections should be done, and the resulting total peak areas averaged for each sample.

2. Unknown sample concentrations are determined by direct comparison of the total peak areas for each sample with the total peak area versus solution concentration calibration curve.

5.5.4.8 Sensitivity and Reproducibility. Minimum polymer concentration level which can be reliably analyzed is about 50 ppm. Reproducibility of the HPLC method is about ± 10 percent of the total polymer solution concentration.

5.5.4.9 Precautions.

1. Samples containing particulates with sizes in excess of 2 microns should be filtered to avoid possible column plugging.

2. Column efficiency may degenerate if the prepared solvent is allowed to remain in the μ-Bondagel™ columns, or equivalent equipment, during idle periods. The column(s) set should be purged of the prepared solvent using 2-propanol and stored in the 2-propanol for later use.

3. Samples containing more than one polysaccharide or other components of macromolecular size cannot be distinguished using the HPLC procedure.

5.6 METHOD V: MEASUREMENT OF CONCENTRATIONS OF POLYACRYLAMIDES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) METHOD

NOTE: The analytical procedures and the equipment specified in this Section are used successfully by knowledgeable practitioners in the industry and were available to the committee in well documented form. It is recognized that there are procedure modifications and comparable equipment currently in use by industry practitioners which can obtain equivalent results. Nothing contained in this publication is intended to prevent a practitioner skilled in the art from using good judgment, experience, and techniques to effect results equivalent or superior to those obtained under procedures contained herein.

5.6.1 General. This method measures concentration of high molecular weight anionic polymers, including partially hydrolyzed polyacrylamide. The procedure is applicable in the concentration range of 50-800 ppm, with a minimum detectable limit of about 10 ppm. A size exclusion chromatography column is used to separate the polymer from lower molecular weight components. A high sensitivity refractive index detector is used to detect polymer as it elutes from the column. Polymer concentrations are determined by integrating the eluted polymer peak and comparing the results to those of polymer standards.

5.6.2 Reagents.

1. Water, HPLC grade.

2. Sodium sulfate (anhydrous), reagent grade.

3. Tetrahydrofuran, reagent grade.

   CAUTION: Tetrahydrofuran presents an explosion and possible health hazard and should be handled with proper precaution and use of proper personnel protective equipment.

4. Methanol, reagent grade.
5. 50% Sodium hydroxide (NaOH)

5.6.3 Apparatus.

1. Waters Model M6000A LC pump coupled to a Rheodyne 7120 injector with 100 microliter sample loop, or equivalent assembly.
2. Erma® Model ERC-7510, high-sensitivity, refractive-index detector, or equivalent (refer to Par. 5.6.4.10).
3. Nelson Analytical Model 4416 data acquisition system, or equivalent system capable of peak integration.
4. Strip chart recorder, with millivolt sensitivity.
5. 61 cm x 0.7 cm exclusion chromatography column packed with 200 Å Fractosil® glass particles bonded with a Glycophase™ G coating, or equivalent apparatus.

5.6.4 Experimental Procedure for Polyacrylamide Analysis by HPLC.

5.6.4.1 Procedure for Solvent Preparation.

1. Prepare 2 liters of 1.0 M Na_2SO_4 adjusted to pH 7.0 with a dilute NaOH solution. (This is the 2X buffer).
2. Filter this solution through a 0.45 micron HA type Millipore® filter, or equivalent.
3. Dilute 1 liter of the filtered solution in half with one liter of HPLC grade water and check the pH. Readjust to pH 7.0, if necessary. (This is the mobile phase).

5.6.4.2 Column Packing and Conditioning.

1. Columns are dry packed. Approximately 1 g of the 200 Å Fractosil® particles coated with Glycophase™ G, or equivalent, are packed into a 61 cm x 0.7 cm stainless steel column by vibrating the column with an Alltech® column vibrator (Part No. 4012), or equivalent.
2. Repeated additions of packing material into the column should be done 1 g at a time, until packing material completely fills the column.
3. The column is then conditioned by pumping tetrahydrofuran, methanol, and then water through the column in successive steps. At least 250 mL of each solvent should be flushed through the column for proper conditioning. After flushing with water, the column should be opened to check for voids in the packing material. If voids exist, additional packing should be added to fill the column.
4. The water rinsed column should be flushed with at least 250 mL of the prepared solvent (0.5 M Na_2SO_4, pH 7.0) for final conditioning.

5.6.4.3 HPLC System Assembly and Preparation.

1. The HPLC system should be assembled by connecting the pump to the Rheodyne 7120 injector, or equivalent, at the common inlet port for the sampling and flow loops. The outlet port of the injector is then connected to the packed column; the column outlet is connected to the refractive index detector. All connections should be made using low dead volume tubing and fittings.
2. Fill the solvent reservoir for the system with the final solution prepared under Par. 5.6.4.1 and connect the line of tubing from the reservoir to the pump inlet.
3. Prime the solvent pump and establish a flow rate of 2.0 mL/minute. Switch the injector once or twice and purge the 100 microliter sample loop with solvent.
4. Turn on the strip chart recorder at least twenty (20) minutes prior to initiating analysis. The Nelson Analytical Model 4416 data acquisition system (integrator), or equivalent, should be in the correct mode for data acquisition.

5.6.4.4 Procedure for Erma® Model ERC-7510 Refractive Index Detector Operation (refer to Note 1, Par. 5.6.4.10).

1. Adjust the refractive index detector temperature setting to 95 F *(35 C)*. Set the range to ¼ X (refer to Note 2, Par. 5.6.4.10).
2. Flush the reference side of the detector (R/S OUT) for 5-10 minutes at 2.0 mL/minute then return flow to the sample side of the detector (MEAS).
3. Record the detector response on the strip chart recorder for approximately thirty (30) minutes to determine the stability of the detector baseline. If the baseline stability is deemed acceptable, zero the recorder to a reference baseline. *NOTE:* Experience has shown that drift in the detector response may be a result of small air bubbles in the detector. This problem can be avoided by proper degassing of the solvent and, if necessary, the samples.

5.6.4.5 Injection of Samples and Standards.

1. Rinse the injector syringe out several times with the sample to be injected.
2. Rotate the injector to the load position and, using a syringe, flush the injector loop with sample (at least 500 microliters for a 200-microliter loop).
3. Quickly rotate the injector to the inject position.

5.6.4.6 Procedure for Peak Integration.

1. The recommended peak integration procedure is an analog-to-digital conversion of the refractive index detector response, followed by an integration

of the digital signal using the Nelson Analytical Model 4416 data acquisition system, or equivalent.

2. A slope sensitivity method should be used for the digital peak integration. The slope sensitivity threshold should be determined by noting the peak response for the polymer component and adjusting the threshold value to start integration just as the polymer peak begins to elute.

5.6.4.7 Preparation of the Standard Curve.

1. Prepare standard solutions of 50, 100, 200, 400, and 800 ppm polymer in distilled water from the same batch of polymer as that present in the unknown samples (refer to Note 3, Par. 5.6.4.10).
2. Dilute each of the standard solutions prepared in Step 1 in half with an equal volume of the pH 7.0, 2X buffer solution (refer to Note 4, Par. 5.6.4.10).
3. Analyze the resulting 25, 50, 100, 200, and 400 ppm polymer solutions using the procedure outlined in the preceding paragraphs. Two sample injections should be done for each solution to assess reproducibility of the analysis.
4. A standard calibration curve should be constructed of peak area versus polymer concentration from the results under Step 3. This curve should be linear and pass through the origin (refer to Note 5, Par. 5.6.4.10).

5.6.4.8 Determination of Unknown Sample Concentrations.

1. If the unknown samples contain oil, the oil should be allowed to separate from the aqueous layer and then be decanted off (refer to Notes 6 and 7, Par. 5.6.4.10).
2. The unknown samples should be diluted into the 0-400 ppm range. Half the volume of dilution should be supplied by the 1.0 M Na_2SO_4, pH 7.0, 2X buffer (refer to Notes 3 and 4, Par. 5.6.4.10).
3. The diluted samples should be analyzed using the procedure outlined in the preceding paragraphs. Two sample injections should be done for each solution sample and the resulting peak areas averaged for each sample.

5.6.4.9 Sensitivity. Minimum polymer concentration level of detection is about 10 ppm. If levels less than 50 ppm must be routinely determined, a 200 microliter sample loop should be used (refer to Note 4, Par. 5.6.4.10).

5.6.4.10 Notes.

1. In analyzing samples from core studies, a Shimadzu SPD-2A spectrophotometer detector (set at 210 nm), or equivalent, has been used. This equipment has the advantages of equilibrating very quickly and being very stable and very sensitive. With field samples, serious interferences have been noticed with this detector and the refractive index detector (refer to Par. 5.6.4.4) has proven much more reliable.
2. When the system is first set up, overnight flushing is necessary to get the refractive index detector to stabilize on the ¼ X scale. This should be done at 3 to 4 mL/minute and with the detector reference valve in the reference position (R/S OUT).
3. Sample and standard solutions should be *vigorously* stirred for at least 10 minutes to ensure thorough mixing.
4. 2X buffer is used in standard and sample makeup so that their ionic strength will be similar to that of the mobile phase. If 2X buffer is not used in preparation of samples and standards, the chromatograph peaks may tail which makes quantification more difficult. Samples containing very low levels of polymer and/or very high levels of salt can be injected without dilution with 2X buffer. This will allow a detection limit of about 10 ppm.
5. If peaks are not sharp, the column is probably not well packed or a void at the column inlet may exist. If polymer peaks develop a shoulder or become bimodal, the column probably has a void. This can be cured by opening the inlet side of the column and adding sufficient packing material to fill the void.
6. If samples contain particulates, they should be filtered before injection. Use 1.2 micron RA or 3.0 micron SS Millipore® filters, or equivalent, to filter the samples. If the samples are filtered, standards should be filtered. If possible, use a non-glass filter support.
7. If oil containing samples will not separate into two phases, the oil should be removed by extraction with a suitable solvent.

5.7 METHOD VI: DETECTION OF POLYACRYLAMIDES BY FLOCCULATION

5.7.1 General. This test is intended as a qualitative test to determine the presence of polyacrylamides in field samples.

5.7.2 Reagents.

1. Finely divided clay (kaolinite).
2. 1% $CaCl_2$ solution.

5.7.3 Apparatus.

1. 50 mL graduated cylinder.
2. 50 mL bottles.

5.7.4 Procedure.

1. Place 3 g of clay on the bottom of a 50 mL bottle.
2. To the bottle, add about 5 mL of 1% $CaCl_2$ solution and mix to wet the clay particles.

3. Add about 45 mL of sample and invert slowly 3 times. If polymer is present at greater than about 2 ppm, the particles of clay suspension will flocculate and settle to the bottom of the bottle.

5.7.5 Precautions.

1. Almost any finely divided mineral can be used for this test, but a blank containing 2 to 5 ppm polymer should be tested before using it.
2. If no flocculation is observed, it is likely that no polymer is present. However, since many chemicals will flocculate clay, a positive test does not guarantee that polymer is present.

5.7.6 Field Test Kit. A handy portable kit can be made up beforehand using 4 dram glass vials. Add about 2 g of clay to each vial, then cover with 1% $CaCl_2$ solution, cap, and shake. Each vial can then be used to test about 10 mL of sample.

APPENDIX TO SECTION 5
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SECTION 6
RECOMMENDED PRACTICES FOR EVALUATION OF POLYMER SOLUTION STABILITY

6.1 Introduction. Enhanced oil recovery (EOR) polymers are designed to improve the mobility ratio and sweep efficiency of the EOR flood. The ideal polymer will maintain the desired viscosity from the time of mixing at the surface to the end of the EOR project. During the EOR project the polymer solution is subjected to various physical and chemical conditions that may degrade the polymer and decrease solution viscosity and screen factor. Resistance to such degradation is an important property of an EOR polymer. The purpose of this section is to provide a series of recommended standardized procedures for the evaluation of polymer solution resistance to viscosity and screen factor loss. Included are procedures for test solution preparation, solution sampling, long-term elevated temperature stability evaluation, and shear stability evaluation.

6.2 POLYMER SOLUTION PREPARATION

6.2.1 General. To evaluate polymer solution stability under various conditions, an effort must be made to minimize chemical reactions that degrade the polymer. A most devastating reaction is oxidation. Dissolved oxygen with temperature and time will degrade *all* EOR polymers. A little dissolved oxygen plus transition metal oxidation catalysts, such as ferrous or cobaltous ion, will rapidly degrade polymers even at ambient temperatures; such cations should be sequestered or removed from laboratory and field polymer flood waters. In the properly designed field project, chemical scavengers can effectively remove dissolved oxygen. Unfortunately, in laboratory testing such scavengers often cause additional problems. To minimize oxidative degradation during solution stability testing, this section presents physical methods for preparing low oxygen content and anaerobic polymer (Par. 6.5) solutions. The low oxygen procedure is used for additive compatibility tests, whereas, in most cases, the anaerobic procedure is used for longer term stability tests. For realism, test solutions should contain the various chemicals that would be added to a specific polymer flood — biocides, corrosion and scale inhibitors, etc. A procedure is presented to indicate gross incompatibilities among the additives, polymers, and waters.

6.2.2 Apparatus. The following equipment should be used to prepare samples with low level oxygen content:

1. Nitrogen. A low oxygen content nitrogen such as oxygen-free or research grade is used for water purge and maintaining an anaerobic atmosphere in a glove box. Monitor oxygen content of nitrogen sources periodically with an oxygen meter and remove any oxygen by scrubbing the nitrogen through dithionite solution.
2. Oxygen meter for continuous monitoring of the inert chamber. Range 1 to 10,000 ppm. Similar to a Thermox® I by Ametek® (Model TMI control unit), or equivalent.
3. Dissolved oxygen kit for measuring oxygen in polymer and water solutions. This kit should be selected based on the vendor's recommendation for the test range of oxygen content to be measured.
4. Inert atmosphere chamber capable of maintaining 1 ppm or less oxygen content. Types range from glove boxes such as those from Vacuum/Atmosphere or Lab-line® to an I^{2}R glove bag, or equivalent.
5. Magnetic stirrer and coated stir bar.
6. Fritted glass sparging tube.
7. 0.22 micron filtering apparatus.

6.3 PROCEDURES

6.3.1 Low Oxygen Content Sample Preparation.

1. Pour filtered test water into an Erlenmeyer flask to one-half full. Place a fritted glass sparging tube connected to a house grade nitrogen source inside the flask. Stir the water with a magnetic stirrer throughout the purge cycle. Cover the flask opening loosely.
2. Purge water to be used for mixing polymer solutions approximately 30 minutes or until oxygen content is 1 ppm or less. Test dissolved oxygen level. If water contains 1 ppm oxygen or more, continue to purge.
3. If a glove box is used, while water is purging place all necessary equipment for solution preparation inside the inert chamber, i.e., balances, syringes, mixing apparatus, using manufacturer-recommended glove box procedures. Then transfer the uncapped flask containing purged water immediately to the inert atmosphere chamber.
4. Degas a sample of the polymer to be dissolved, in a suitable form and in a suitable vessel, as thoroughly as possible in accordance with supplier's recommendation to minimize oxygen contamination. Close and transfer the sample vessel to the inert atmosphere chamber.
5. If a glove bag is used, transfer all necessary solution preparation equipment including the purged water to the bag and establish an inert atmosphere according to the manufacturer's instructions.
6. In the inert atmosphere, continue water purge with a high purity nitrogen until less than 50 ppb oxygen content is achieved.
7. Dissolve the polymer into the water following recommended polymer solution preparation procedures (refer to Section 2).

6.3.2 Additive Compatibility Studies.

1. Prepare deoxygenated mixing water as described in Par. 6.3.1.
2. Prepare additives at a proper working concentration and in a form which will not introduce extraneous oxygen to the inert atmosphere chamber.
3. Transfer all solution preparation equipment and/or purged water to the inert atmosphere chamber as described in Par. 6.3.1.
4. Conduct a gross compability test of the additives with the water at this time. This test is used to determine if any immediate precipitation or other obvious incompatibilities will occur. Effective concentrations or known interactions which may render chemicals inactive should be specified by the supplier. Using a microliter syringe, add chemicals to the water at desired concentrations. Mix for twenty-four hours with a magnetic stirrer. Check the water for any discoloration, scale, or precipitate. If no obvious incompatibilities are observed, continue to Step 5.
5. Test oxygen content of the purged water. If the oxygen level has not changed appreciably, add chemicals with a microliter syringe to the desired concentrations. It is recommended that the solution not be purged after addition of chemicals.
6. Dissolve the polymer following procedures shown in Section 2. After 24 hours inspect solution for any discoloration, scale, or precipitate.

6.3.3 Serum Bottles.

6.3.3.1 Apparatus. The following apparatus should be used to measure the short-term compatibility of polymer solutions:

1. Borosilicate glass bottles, amber or clear, such as Wheaton® serum bottles, or equivalent. Rubber stoppers and aluminum seals to fit the bottles. Seal crimping tool. These bottles and accessories can be obtained from major scientific supply companies in sizes up to 125 mL.
2. Temperature control device (silicone oil bath, air oven, or drilled metal block) capable of maintaining bottles at the desired temperature, within ± 1.8 F *(±1 C)*.

6.3.3.2 Procedure.

NOTE: The use of serum bottles in this procedure is intended only for compatibility testing at moderate temperature. Sealed glass ampoules may be more appropriate for these tests if higher temperatures are to be used. Refer to the warning statement in Par. 6.5.1.

1. For each set of test conditions (solution composition, temperature), prepare at least ten bottles (for property tests after days 1, 3, 7, 15, 30, 60, 90, 120, 150 and 180). Use larger bottles and/or additional bottles if sufficient aged test solution is required for core testing. In the inert atmosphere chamber, fill the nitrogen-purged bottles with low oxygen content polymer solution (prepared according to Par. 6.3.1), leaving some head space below the bottom of the neck to prevent cracking during subsequent thermal expansion. Crushed core material and/or crude oil may be added to the bottle to more closely simulate field exposure.
2. Place a rubber stopper and aluminum seal on each bottle and crimp the seal.
3. Mark each bottle for identification with a metal tag or use some other appropriate method. Place the bottles in the temperature control device.
4. Remove one or more bottles after the desired test period and cool to ambient temperature. Note any visible changes in the solution (settling of suspended solids, scale formation, color change, gelation, phase separation, syneresis, etc.). Open the bottle. If oxygen content is to be measured, uncap and test the bottle inside a purged glove bag, or equivalent (abnormal oxygen content in one or more bottles may explain any erratic results noted in subsequent tests). Perform the property measurements on the solution as described in other Sections of this publication.

6.4 FIELD SAMPLING OF POLYMER SOLUTIONS

6.4.1 General. Sampling of polymer solutions in the field must be done with care to obtain a representative sample for quality control monitoring and long-term stability testing. Since polymer injection systems are usually operated at high pressures, special procedures must be followed to prevent shear degradation of the polymer during sample collection. This is accomplished by using a high pressure sampling cylinder and controlling the flow rate at the outlet of the cylinder rather than the inlet.

If the sample is for a long-term stability study, further precautions should be taken to avoid oxygen and iron contamination. A cylinder made of stainless steel is resistant to corrosion; however, the inside of the cylinder may be polytetrafluoroethylene (PTFE) or epoxy coated to prevent any iron contamination. Oxygen can be effectively excluded by carefully flushing air from the cylinder with fluid while collecting the sample, and transferring its contents to glass ampoules or vials under an anaerobic atmosphere.

6.4.2 Apparatus. For each sampling point on the polymer injection lines, two full-opening ball valves (½-inch NPT female connections) and a pressure gauge (0 - maximum working pressure) are required. They should be connected to the polymer injection line with ½-inch pipe as shown in Figure 6-1. The pipe stub on valve V2 should point down at a 45° angle from horizontal.

One or more high pressure sampling cylinders are needed to collect samples at locations with the above piping arrangement. A recommended cylinder is Hoke® Model 4HDY150, or equivalent (316SS, 150 mL capacity, 1800 psig MWP). This size is adequate for most purposes. For higher working pressures, cylinders must be special ordered. When working with highly corrosive brines, the inside of the cylinder should be polytetrafluoroethylene (PTFE) or epoxy coated for better chemical resistance.

The recommended sampling apparatus (refer to Figure 6-2) consists of the Hoke® cylinder (or equivalent), an inlet full-opening ball valve (V3), an outlet needle valve (V4), and several Gyrolok® fittings, or equivalent. On valve V3 there is a male elbow and a female adapter for making the connection with the ½-inch pipe stub shown in Figure 6-1. On V4 there is a female connector and a curved piece of tubing for directing the flow when flushing the cylinder. Example Hoke® valves and Gyrolok® fittings are listed below:

Type	Description	Part No.
Ball valve	316SS Kel-F seats, ¼-inch male x ¼-inch NPT female	7115L4Y, or equivalent.
Male elbow	¼-inch tube x ¼-inch NPT	4LM4-316, or equivalent.
Female adapter	¼-inch tube x ½-inch NPT	4AF8-316, or equivalent.
Female connector	¼-inch tube x ¼-inch NPT	4CF4-316, or equivalent.
Needle valve	316SS Kel-F seats, ¼-inch NPT male x ¼-inch male	3752M44, or equivalent.

6.4.3 Cleaning Sampling Cylinders. The frequency and degree of cleaning depends on whether possible contamination (chemical or microbiological) may interfere with the analysis of the sample. During continuous field use, it is not necessary to clean the cylinder between each sample because the cylinder is flushed with fresh solution each time a new sample is collected. Nevertheless, it is advisable to clean the cylinder thoroughly at least once a week. When a sample is kept in the cylinder for several days or longer before testing, clean the cylinder thoroughly before collecting another sample.

Sustained contact of stainless steel components with high salinity solutions should be avoided due to the possibility of corrosion, which will rapidly and irreversibly alter both polymer solution quality and filterability characteristics.

Most of the polymer can be removed from the cylinder by flushing it with hot tap water. However, polyacrylamides leave a film on the walls of the cylinder which does not come off easily. Household bleach is effective in breaking down the polymer, and only a short contact time (5-10 minutes) is required. After cleaning with bleach, rinse the cylinder thoroughly with deionized water (residual bleach may itself degrade polymer in the sample). Dry the cylinder in an oven by flushing dry air or nitrogen through it.

If even small amounts of contamination may be a problem, completely disassemble and clean the sampling apparatus (cylinder and fittings) with soap and hot water. The inside of the cylinder can be cleaned with a small test tube brush. Rinse all the parts with deionized water and dry. The sampling apparatus should then be reassembled.

If microbiological contamination is expected to be a problem or if bioassay samples are being taken, sterilize the sample cylinders. Biodegradation and bioassay sampling are beyond the scope of this publication. Consult the polymer supplier for recommended procedures.

6.4.4 PROCEDURE. ***WARNING:*** *Sampling high pressure lines can be dangerous. Wear safety glasses, goggles, or a face shield for eye protection. Make sure all valves are closed before making or breaking connections.*

1. Determine that valves V2, V3, and V4 (Figures 6-1 and 6-2) are closed.
2. Connect sampling cylinder to pipe stub at valve V2. The cylinder should be oriented about 45° from the vertical with V4 at the top (this facilitates displacement of gas from cylinder).
3. Slowly open V2 and then V3 to the full-open position.
4. Open V4 sufficiently to expel gas in the cylinder and then adjust V4 to obtain a slow steady fluid stream. Maintain this flow rate for sufficient volume to purge all flow lines and fittings. Slow flow rate is extremely important. Minimum sampling time is about 5 minutes.
5. Close V4 first, then V3 and V2.
6. Open V4 slightly to release pressure and then reclose it.
7. Disconnect the cylinder from sampling line.

6.4.5 Sample Disposition. For routine quality control monitoring, drain the sample from the bottom of the cylinder into a sample bottle by fully opening V3 and controlling the flow rate with V4. Measure physical properties of the sample soon after taking the sample because exposure to oxygen in the air may cause rapid changes. If exposure to oxygen is undesirable, such as during long-term polymer stability studies, transfer the sample under an anaerobic atmosphere to glass ampoules or vials that can be tightly sealed. A high quality glove box, or equivalent, is recommended to obtain an atmosphere with very low oxygen concentration.

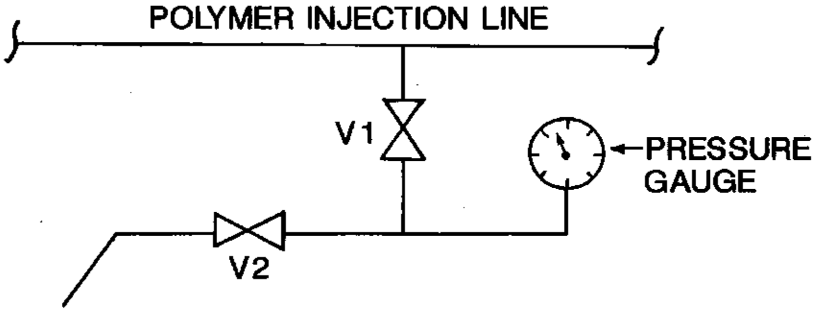


FIGURE 6-1
EXAMPLE PIPING DIAGRAM FOR SAMPLING POINTS

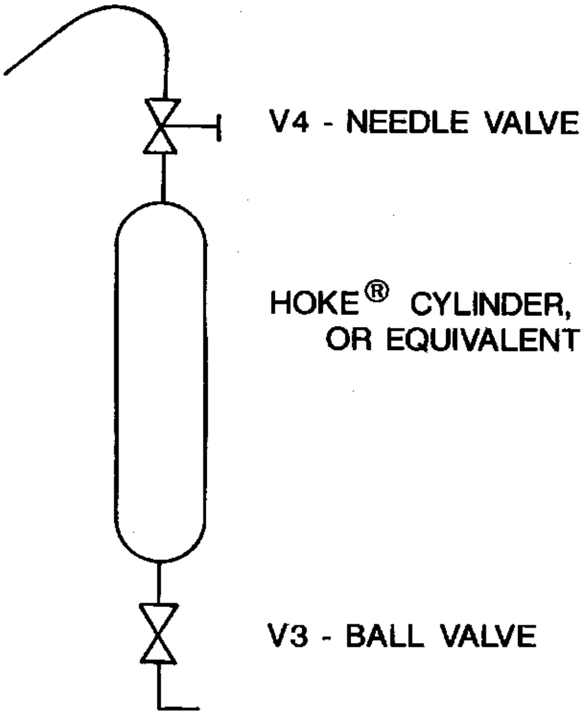


FIGURE 6-2
EXAMPLE OF SAMPLING APPARATUS

6.5 ELEVATED TEMPERATURE STABILITY EVALUATION

6.5.1 Overview. To perform their function in an enhanced oil recovery project, polymer solutions must maintain their properties in the reservoir, under reservoir conditions, for several to many years. This section will deal with the evaluation of long-term polymer solution stability at elevated (reservoir) temperatures. If dissolved oxygen is present at elevated temperature, with or without the presence of heavy metal oxidation catalysts, oxidative degradation of *all* EOR polymers will predominate. To minimize this, extraordinary nonchemical procedures are suggested to remove dissolved oxygen from the polymer solution and to establish an anaerobic system. Two such procedures are presented in the following paragraphs for use depending upon solution oxygen content.

WARNING: The following test procedures involve aqueous polymer solutions sealed in glass vessels that are sometimes heated to temperatures well above the boiling point of water for extended periods of time. At these temperatures, the internal pressure due to vapor pressure of water may be sufficient to rupture the glass vessel if a flaw is present in the glass or if the temperature drifts too high. Precautions must be taken to minimize the chance that the ampoules will rupture. Such precautions include upper temperature limit switches on ovens and oil baths and individual shields to protect the glass ampoules from scratches and impacts. Further precautions must be observed to protect laboratory personnel from flying glass and hot liquids if an explosion does occur. Also, extreme care must be taken to avoid reactions which generate a gas, since the increased gas pressure can rupture the ampoule even at relatively low temperature. Proper safety equipment (safety shields, safety glasses, gloves, etc.) should be used to protect personnel from cuts and burns if an explosion accident happens.

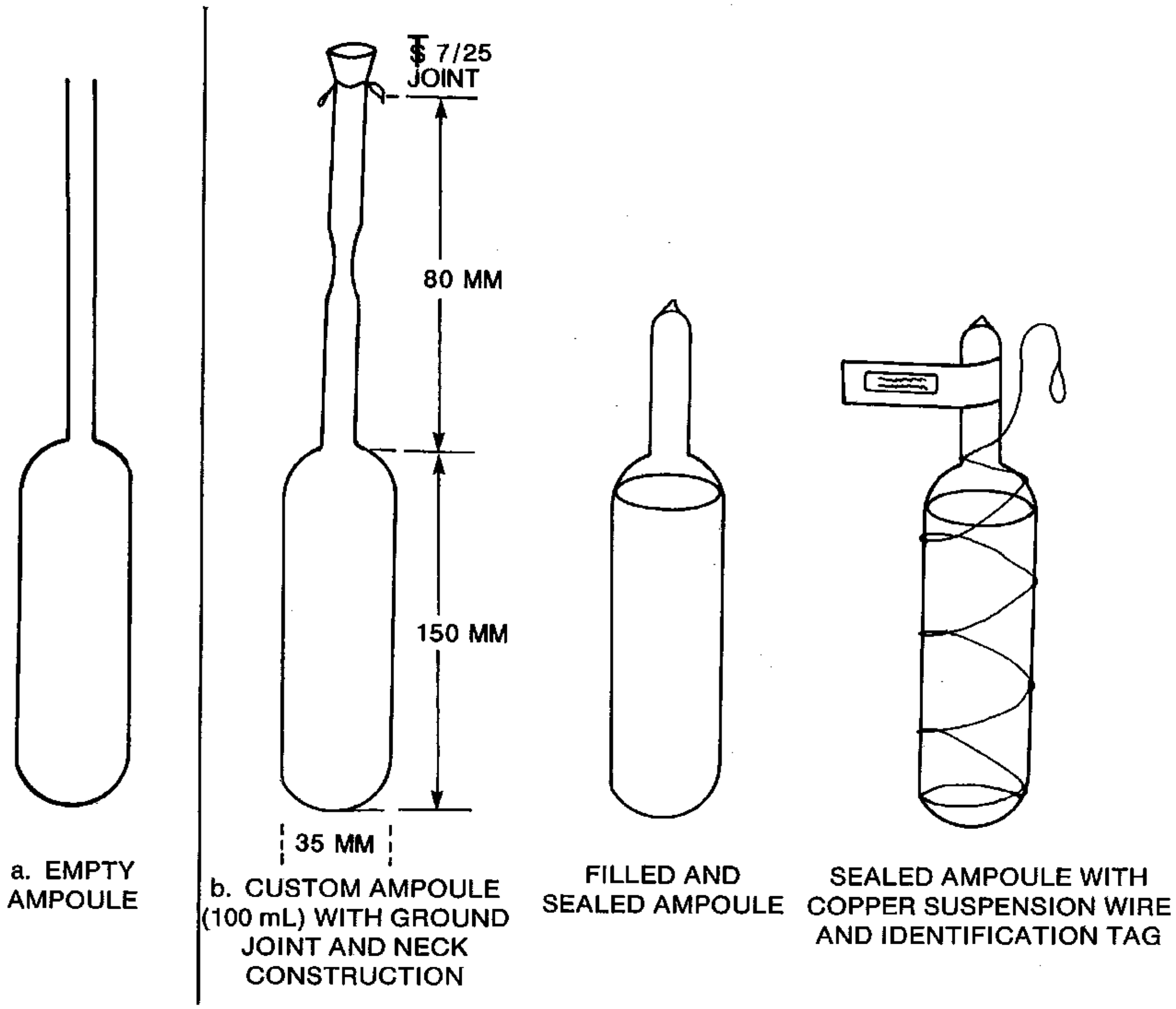
6.5.2 Sealed Glass Ampoules. Closest to anaerobic conditions.

6.5.2.1 Apparatus. The following apparatus should be used to measure the thermal stability of polymer solutions:

1. Borosilicate glass ampoules — Ace Glass Company (Cat. No. A2841-99: 35 mL, or equivalent); Fisher Scientific Company (Cat. No. 10-269-78B: 25 mL; 10-269-78C: 50 mL, or equivalent, refer to Figure 6-3a), or larger capacity custom-made ampoules (refer to Figure 6-3b).
2. Vacuum manifold (refer to Figure 6-4).
3. Nitrogen, oxygen-free or research grade, to purge the vacuum manifold (refer to Par. 6.2.2.1).
4. Propane torch (Bernz-o-matic®, or equivalent) for sealing ampoules.
5. Temperature control device, capable of controlling temperature uniformly within ± 1.8 F *(±1 C)*. All safety precautions appropriate to the particular device must be observed. In all cases, sealed ampoules may be stored in any physical orientation that is convenient. No provision is made here to superimpose periodic motion on the samples.

6.5.2.2 Procedure.

1. For each set of test conditions (solution composition, temperature), at least ten ampoules should be prepared (for property tests after days 1, 3, 7, 15, 30, 60, 90, 120, 150 and 180). Because of the relatively small ampoule volume, additional ampoules should be prepared if sufficient aged solution is required for core testing. Fill the nitrogen-purged ampoules with low oxygen content polymer solution (prepared according to Par. 6.3.1), leaving some head space below the bottom of the neck to prevent cracking during subsequent thermal expansion. Crushed core material and/or crude oil may be added to the ampoule to more closely simulate field exposure, but crude oil may increase gas evolution and the glass breakage potential at elevated temperature.
2. Attach the filled ampoules to the vacuum manifold and evacuate to < 0.1 mm Hg (the ampoules may be cooled in a salt/ice or dry ice/alcohol bath to reduce the vapor pressure of volatile solution ingredients before evacuation; however, do not freeze). The ampoules should be allowed to equilibrate with the 3-liter evacuated reservoir for 2-16 hours, then return the manifold to atmospheric pressure using nitrogen. Repeat the procedure several times to reduce dissolved oxygen content further before sealing. A final 16-hour equilibration period is recommended.
3. While the manifold is under vacuum after final equilibration, apply the torch flame to the ampoule neck 1.5-2.0 inches above the bulb while gently pulling down on the ampoule. Fuse the restriction thus formed and pull the neck apart while continuing to heat to form a uniform bead at the top of the neck. Anneal the neck using luminous flame. Do not allow the solution to contact the hot portion of the ampoule neck. (When flame sealing ampoules, care must be exercised to avoid introducing oxygen into the ampoule. If an opening to the evacuated ampoule is allowed to form during sealing, oxygen may be pulled in from the atmosphere or from the flame itself.)
4. Let the sealed ampoules cool to ambient temperature and attach a copper wire holder and sample tag. Place the ampoules in the temperature control device.
5. Remove one or more ampoules from the temperature control device after the desired aging period and cool to ambient temperature. Note any visible changes in the solution (settling of suspended solids, scale formation, color change, gelation, phase



a. EMPTY AMPOULE

b. CUSTOM AMPOULE (100 mL) WITH GROUND JOINT AND NECK CONSTRUCTION

FILLED AND SEALED AMPOULE

SEALED AMPOULE WITH COPPER SUSPENSION WIRE AND IDENTIFICATION TAG

FIGURE 6-3
BOROSILICATE GLASS AMPOULES

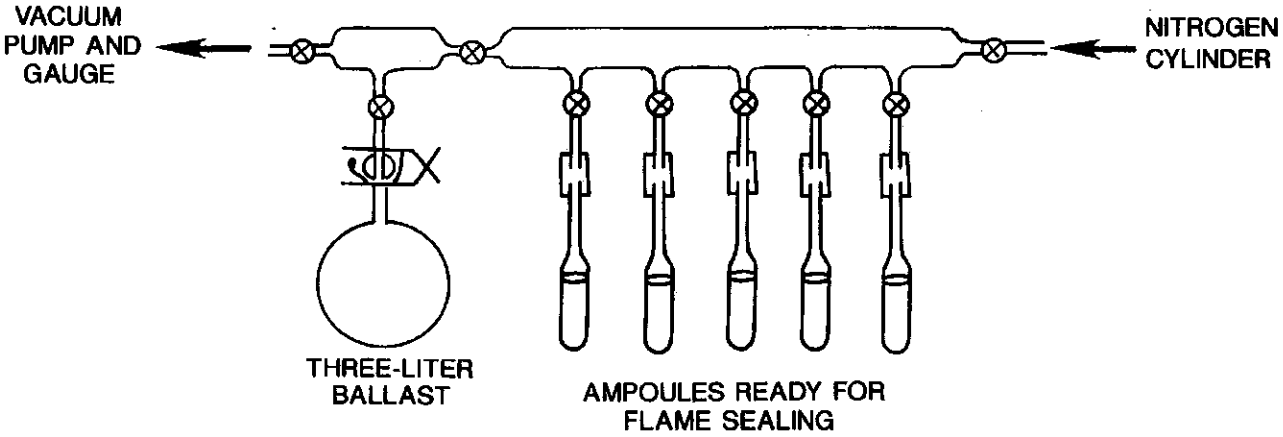


FIGURE 6-4
VACUUM MANIFOLD ARRANGEMENT

separation, syneresis, etc.). Score the neck with a triangular file and break open.

(WARNING: Wear protective gloves to prevent cuts from broken glass!).

If dissolved oxygen content is to be measured, break open and test the ampoule inside a purged glove bag, or equivalent (abnormal oxygen content in one or more ampoules may explain any erratic results noted in subsequent tests). Perform the property measurements on the solution as described in other sections of the recommended procedures.

6.5.3 Data Reporting. Express elevated temperature (thermal) stability of polymer solutions as "percent retained" of the desired property (viscosity, filterability, screen factor, etc.) after a chosen period of elevated temperature exposure. The actual data can also be plotted. The property may be measured initially and finally at room temperature or at the elevated temperature of interest.

6.6 EVALUATION OF SHEAR STABILITY OF POLYMER SOLUTIONS

6.6.1 General. A measurement of the effect of mechanical degradation on a polymer solution is important for determining the correct techniques for preparation, pumping, and handling the solutions in the laboratory and in the field. Two tests that can be done on polymer solutions are a capillary shear test and a core shear test. For the capillary shear test, a prepared polymer solution is pressured through a capillary tube at different flow rates by using varying pressure levels. Shear rates can be calculated by recording fluid flow rates through the measured capillary. In the core shear test, either a Berea sandstone core or a field sample core can be used at the option of the tester. For the Berea sandstone core, a recommended range of permeability is 250-400 md.

It is recommended that the effect of shear degradation on the polymer solution be determined by measuring the solution viscosity and the screen factor before and after the shear test, and also by flowing the initial and degraded solutions through a sandstone core at low flow rates to determine reduction in mobility control (refer to Par. 6.6.3). It is further recommended that the solution viscosity be measured at three or more shear rates using a Brookfield viscometer (UL adapter), or equivalent, or a more precise instrument as described in Section 3.

6.6.2 Capillary Shear Test.

6.6.2.1 Apparatus and Materials.

1. Stainless steel bomb (two to four liter) with top connection to nitrogen supply cylinder and bottom opening with ½-inch MPT (male pipe thread).
2. Fractional diameter tube adapter (e.g., Cajon® SS-4-TA-1-8, or equivalent) to male pipe; ½-inch male pipe to ¼-inch tube with a body orifice of 0.1875 inch.
3. Plug valve (e.g., Nupro® P4T Series, No. SS-4P4T, or equivalent) with ¼-inch Swagelok® inlet and outlet, or equivalent; body orifice of 0.093 inch.
4. Reducer (e.g., Swagelok® SS-100-R-4 or SS-200-R-4, or equivalent) ¼-inch to 1/16-inch or ¼-inch to ⅛-inch. The reducer should be drilled out to allow a 1/16-inch or ⅛-inch tube to pass through.
5. Capillary tubing lengths of known inside diameter and outside diameters of 1/16-inch or ⅛-inch. The ends of the capillaries should be undistorted and filed free of burrs.
6. Nitrogen supply cylinder.
7. Nitrogen pressure regulator (maximum 100 psig).
8. Stop watch or electric timer.
9. Sampling containers 100-300 mL capacity.
10. Balance.
11. Two properly prepared polymer solutions to test at different salinity concentrations. Use 1000 ppm polymer in either 3% NaCl + 0.3% $CaCl_2$ or 0.1% NaCl + 0.01% $CaCl_2$. Optionally, the test may be run in actual field brine using the injection concentration of polymer.

6.6.2.2 Procedure.

1. Connect onto the bottom of the stainless steel bomb items #2, #3, #4, and a capillary tubing length, #5, (in that order) from the list of apparatus and materials (refer to Par. 6.6.2.1 and Fig. 6-5). The capillary tubing should be inserted up into the ¼-inch region of the reducer.
2. After measuring viscosity and screen factor, fill the stainless steel bomb with the prepared polymer solution.
3. Connect the nitrogen supply tank through the pressure regulator to the top of the bomb.
4. Apply 10 psig nitrogen pressure to the bomb.
5. Open the Nupro® valve (or equivalent) completely and sample approximately 100-200 mL of polymer solution into a tared sampling container while measuring the flow time with a stopwatch. The preferred technique is to open the valve and start the flow into a large container before quickly moving the sampling container into the flowing stream, taking the sample, and removing the sampling container before closing the valve. Note sample weight and flow time.
6. Steps (4) and (5) should be repeated at 30, 50, and 100 psig and possibly higher pressures depending upon the capillary used.
7. Solution viscosities and screen factors should be measured on the sheared polymer solutions.

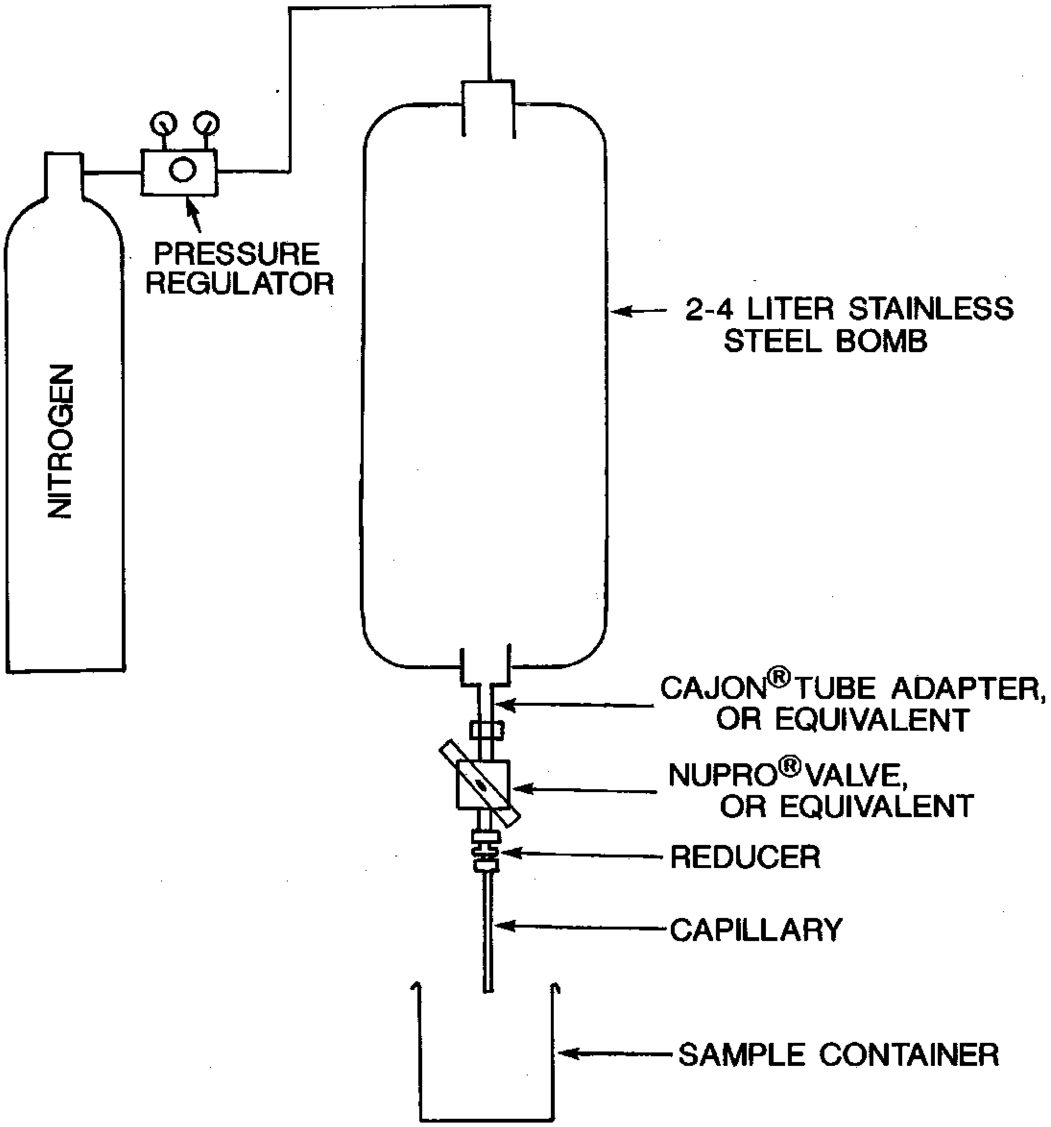


FIGURE 6-5
EXAMPLE OF CAPILLARY SHEAR TEST APPARATUS

6.6.2.3 Calculations and Data Reporting. The following sample data sheet (Figure 6-6) provides an example of data from the test procedures described.

FIGURE 6.6
SAMPLE DATA SHEET

Pressure, psig	Solution Collected, g	Solution Collected, sec	Flow rate, g/sec	Shear* Rate, sec^{-1}	Final Solution Properties: Viscosity, cP	Final Solution Properties: Screen Factor
0 (Initial)	—	—	—	—	6.2	21.0
50	60.4	4.7	12.85	63,900	5.8	13.7
100	73.9	3.3	22.39	111,000	5.1	9.3
150	111.6	3.9	28.62	142,000	4.6	7.0
200	116.2	3.5	33.20	165,000	3.8	5.4

Capillary: OD = .0625 inch, ID = .05 inch, Length = 20 cm

*Shear Rate Calculation:

$$\dot{\gamma} = 4Q/\pi R^3 \qquad (6\text{-}1)$$

where:

$\dot{\gamma}$ = apparent shear rate at capillary wall (without non-Newtonian correction), sec^{-1}

Q = flow rate, cm^3/sec

R = inside radius of capillary, cm

NOTE: This calculation assumes a fluid density of 1.0 gram/cm^3. For most purposes, this approximation is acceptable.

6.6.3 Core Shear Test.

6.6.3.1 Apparatus and Materials.

1. For constant pressure flooding, a stainless steel bomb (2-4 liter capacity) with top connection to a nitrogen supply cylinder and bottom connection through a valve to a core apparatus:
    a. Nitrogen supply cylinder and a pressure regulator for 0-100 psig.
2. For constant rate flooding, a non-pulsating constant rate pump with rate range of 3 to 25 cm^3/minute; if the polymer solution is not to pass through the pump, a two to four liter capacity floating piston or rodded transfer vessel and a reservoir of appropriate displacing fluid to be pumped into the transfer vessel.
3. A suitable core assembly, as needed, to accommodate a core 1-2 inches long and 1 inch in diameter.
4. A suitable pressure measuring device across the core.
5. Collector (preferably a fraction collector) to sample the polymer solution from the core.
6. A Berea sandstone core with 250-400 md permeability or a field sample core.
7. Two brines: 3% NaCl + 0.3% $CaCl_2$; and 0.1% NaCl + 0.01% $CaCl_2$, or a field brine.
8. Polymer solutions with 1000 ppm polymer in each of the brines. For a field sample core, it is optional to use the field brine with the polymer concentration as planned for the field injection.

6.6.3.2 Procedure.

1. Saturate the core with the brine of choice, and determine the core porosity and permeability.
2. Prepare two gallons of polymer solution in the brine and fill the stainless steel bomb, pump, or transfer vessel.
3. Connect the polymer container outlet to the brine saturated core in the core assembly apparatus. (An option is to heat the saturated core to the temperature of the fluid going into an actual reservoir, but the effects of thermal degradation should be considered for the aerobic conditions.)
4. Start the polymer solution injection with a nitrogen pressure of 10 psig or a pump rate of 3 cm^3/minute. Discard the first 50 pore volumes of effluent before measuring the flow rate. Continue solution injection until a constant flow rate or constant pressure drop is obtained, and then collect

sufficient sample to measure the viscosity and screen factor, or to flow through another core. (If a constant flow rate or pressure drop cannot be obtained, this may indicate core face plugging.) .

5. Increase pressure to 20 psig or the flow rate to 6 cm^3/minute, discard the first 30 to 50 pore volumes, continue until constant flow rate or pressure drop is obtained, and collect a sample for measuring viscosity and screen factor.

6. Repeat Step 5 at pressures of 30, 40, 50 and 75 psig or flow rates of 9, 12, 15, 19 cm^3/minute, respectively.

7. Calculate frontal velocity (interstitial velocity) through the core, 800-900 ft/day being a reasonable range for most field applications. Frontal velocity, v, is calculated using the equation:

$$v = q/\phi A \quad \text{(6-2)}$$

where:

v = frontal velocity, ft/day

q = fluid injection rate, ft^3/day

ϕ = porosity fraction

A = core cross-section area, ft^2

A frontal velocity of 300-900 ft/day through a 1-inch diameter core with 0.2 porosity has a volumetric rate, q, of 6.4 to 19.3 cm^3/minute. Thus, for most cases a volumetric throughput rate of 6-20 cm^3/minute is appropriate. Optionally, changes in mobility control performance of sheared solutions can be evaluated using methods in Section 3.

The equation for calculating frontal velocity in units consistent with those used in core flow studies is as follows:

$$v = \frac{7.323\, q}{\phi A} \quad \text{(6-3)}$$

where:

v = frontal velocity, ft/day

q = flow rate, cm^3/minute

A = core cross-section area, in^2

8. Prepare graphs of viscosity and screen factor versus frontal velocity and shear rate. Refer to Section 3 for porous media shear rate calculations.

6.7 Presentation of Results. Polymer solution instability or polymer incompatibility with other chemical components of the solution may be indicated by precipitate formation in the solution. Such evidence need only be noted by a comment. The more likely evidence of partial degradation of the polymer in solution will be indicated by a change in the rheological properties of the solution. It is recommended that the solution viscosity and screen factor before and after test conditions are imposed be recorded in tabular form. (Refer to Fig. 6-7 for an example of a sample data sheet.) Shear rate (or instrument rotation rate) and solution temperature should be recorded as well for each measurement.

FIGURE 6-7
SAMPLE DATA SHEET

Condition	Viscosity @ 77 F (25 C) Brookfield LVT, UL, rpm			Screen Factor @ 77 F (25 C)
	1.5	3	6	
Original	15.0	10.3	8.1	17.2
After:				
(Aging @__F (__C) (for __ days)	11.2	8.9	7.8	8.0
(Capillary Shear) (at __ sec^{-1})				
(Core Shear) (at __ ft/day)				

In addition, it is recommended that the rheological data be presented in graphical form. In the case of long-term stability tests, the graph should represent retention of the measured rheological parameter versus time. Similarly, in the shear stability tests, the graph should represent retention of the measured rheological parameter versus shear rate, γ, or frontal advance rate for the tests. Figures 6-8 and 6-9 present examples of each graph.

If rheological data are obtained from other instruments which provide graphical plots or shear stress versus shear rate, these plots (before and after test conditions) may be presented directly to represent stability of the product.

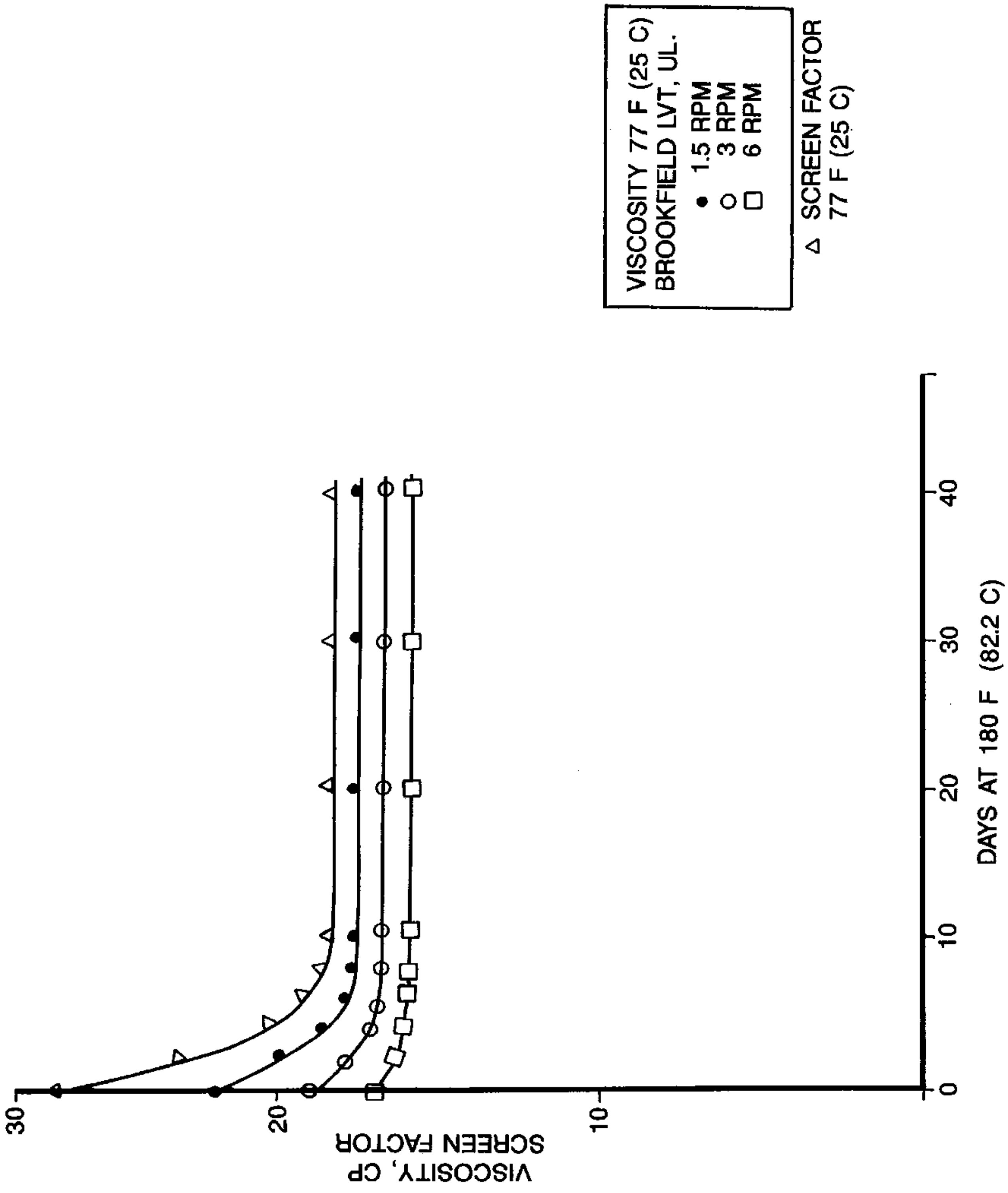


FIGURE 6-8
EXAMPLE OF SAMPLE DEGRADATION PLOT, AGING TEST

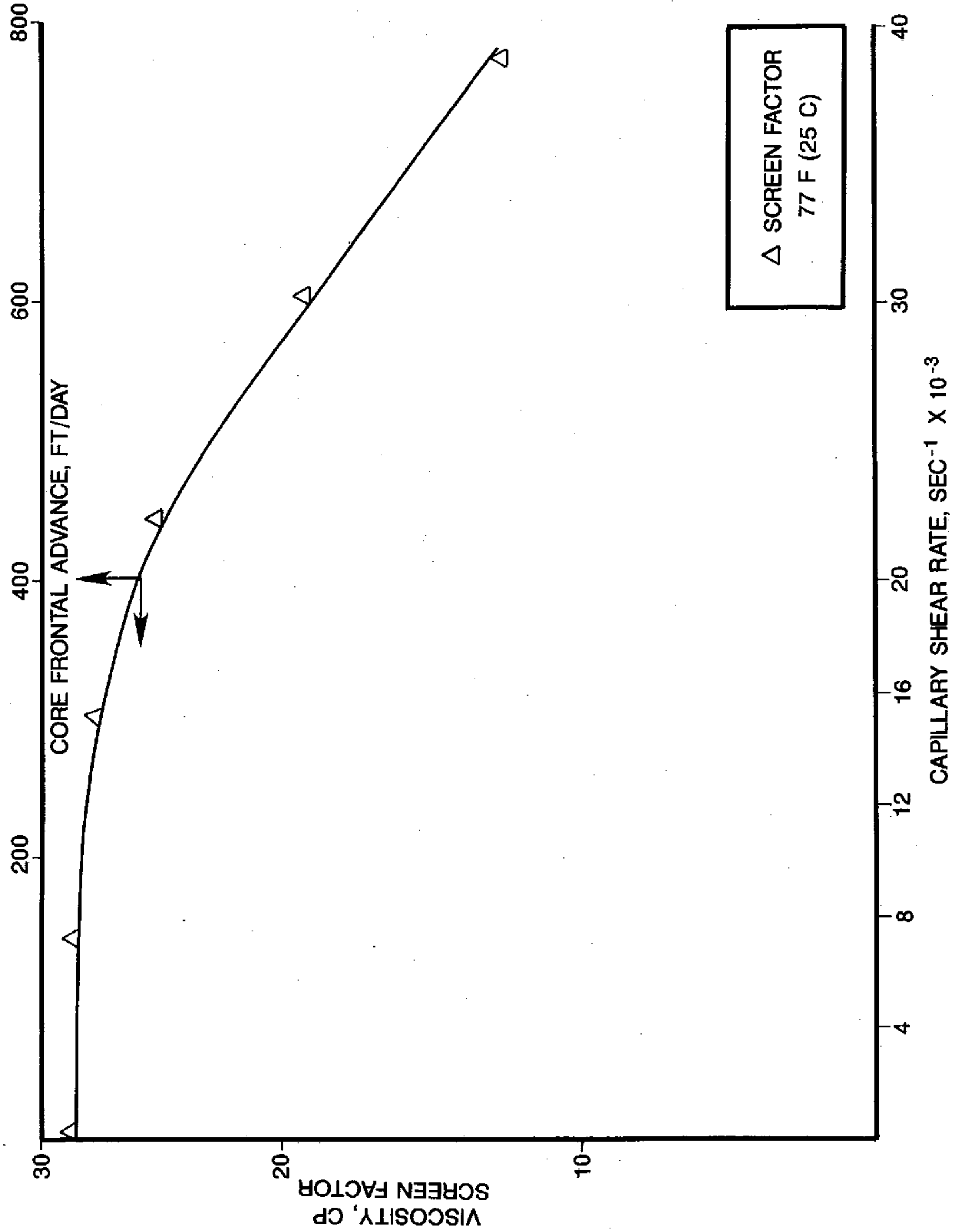


FIGURE 6-9
EXAMPLE OF SAMPLE DEGRADATION PLOT, SHEARING TEST

APPENDIX TO SECTION 6

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SECTION 7
RECOMMENDED PRACTICES FOR EVALUATION OF POLYMER RETENTION

7.1 INTRODUCTION

The purpose of this section is to describe four methods of determining the amount of polymer lost during flow of a water soluble polymer solution through porous media. The four methods are: large slug method, multiple slug retention method, recirculation method, and static method. The relative merits of each are discussed within the portion describing the method.

In any retention method utilizing cores, the data will be only as good as the core material used. Available core logs should be studied to determine the permeability range of the field. The majority of the polymer flow occurs in a higher permeability section of the field, so the cores from the upper half of the permeability range should be chosen. Generally speaking, retention tests are very much a function of the wettability and contamination of the rock surface. Cores which are used for determining the amount of loss of polymer should be drilled with neutral pH drilling fluid not containing water soluble polymers or surfactants, as both of these can occupy sites which would otherwise be occupied by polymer. Cleaning and drying the cores prior to making retention measurements may change the wettability and thereby alter the affinity of the rock surface for the polymer. The best core material to avoid biasing these tests is native state, i.e., drilled with surfactant-free, oil-base drilling fluid which contains no surfactant or water soluble polymer. However, if fresh or native state cores are unavailable and unpreserved cores are used, they should be cleaned and dried. Restoring the cores to field conditions is critical to obtaining representative results.

In the event a nonreservoir porous medium (such as a fired core or Ottawa sand) is being used to select among polymers, it should be uncontaminated by polymer or surfactants and should be as similar as possible from specimen to specimen.

Field brines may be used for the studies but synthetic brines are often preferable because in many cases field brines are unstable and may cause plugging of the cores. If a field brine is used, it should not contain additives such as oxygen scavengers, biocides, or scale inhibitors. The samples should be bubbled with air to precipitate any polysulfide or iron and then filtered through a 0.22-micron filter. *API RP 45: Recommended Practice for Analysis of Oil-Field Waters,** Second Edition, November 1968, (Reissued July 1981), Section 1.5, discusses the preparation of stable synthetic brines. *NOTE:* Some high salinity brines are corrosive to metals (even 316 stainless steel) and care must be used in proper selection of materials for lines, parts, etc., to avoid corrosion products in the test apparatus.

While polymer retention is not a strong function of molecular weight, a very high molecular weight polymer can be too large to propagate through a low permeability core leading to artificially high retention losses.

Prefiltering the polymer through microporous media will remove incompletely solubilized polymer and reduce the chances of face plugging. Any particles removed in the filtration process would not propagate through the reservoir so the filtration should not affect the validity of the determination (refer to Par. 3.7).

7.2 LARGE SLUG RETENTION METHOD

7.2.1 General. The particular method described in this section uses a large slug of polymer containing a nonadsorbing tracer. The amount of polymer retained is determined by examining the differences between the tracer and polymer concentration profiles. Although this method is probably the most rigorous in determining the polymer loss it is also the most time-consuming and probably requires the most analyses. This method also yields the inaccessible pore volume for a particular set of conditions, whereas the others do not.

In this test method a large slug of polymer containing water soluble tracer is injected through the core and displaced by brine. The slug is chosen to be large enough so that the produced concentration will eventually equal the injected concentration. If the injected concentration is not achieved, the loss measured will not be the equilibrium loss for that case. This is important since in the reservoir a large portion of the rock surface will see injected concentration due to the large slug sizes normally used. Unless injected concentrations are achieved, a scaled experiment would have to be used and this is beyond the state-of-the-art at the present time.

Injecting a large volume of polymer plus tracer (such as tritiated water or iodide or thiocyanate ions) does not necessarily lead to the error usually associated in measuring a small difference between large numbers. This is because in this test method the entire amount of polymer that is produced is not taken into consideration. What is examined closely and analyzed is the transition zone at the front of the polymer/tracer bank and the transition zone at the end of the polymer/tracer bank. By examining these two transition zones, the loss can be determined. If the plateau region between the transition zones is large enough, both components will be at their injected concentration. In some instances, this plateau region is a good check on the accuracy of the analytical method in the presence of any interfering material which may be eluted from the core.

7.2.2 Apparatus and Materials.

1. Selected core (refer to Par. 7.1).
2. An appropriate core holder, preferably including at least one pressure tap near the entrance face.

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3. Pressure demodulators, transducers, and strip chart recorder to monitor the pressure drop from the entrance line to each tap and tap-to-exit line. More pressure taps can be used depending on the length of the core and the details of the test design.
4. Constant rate pump.
5. Transfer cylinders.
6. Alternatively, a noncontaminating pump such as Cheminert® Model CP-2, or equivalent, can be used to pump solutions directly without a transfer cell.
7. Heated cabinet to house the cores and holder if reservoir temperature is above room temperature.
8. Fraction collector and suitable test tubes; tubes may be volumetrically calibrated or may be tared if unmarked tubes are used.
9. Filter with small enough pore size to filter out extraneous material but large enough to avoid filtering out polymer (refer to Section 4).

7.2.3 Procedure.

7.2.3.1 Core Preparation.*

1. Measure dimensions of core.
2. Mount core in a holder. If a native state core is to be used, it may be appropriate to skip Steps 3 through 9.
3. Weigh core and holder.
4. Install core and holder in test system.
5. Evacuate core and check for leaks.
6. Measure air permeability of core, if desired.
7. Evacuate core.
8. Again, check for leaks, then saturate with filtered test brine.
9. Reweigh holder and core and calculate pore volume.
10. Inject core with brine and determine brine permeability over all pressure tap intervals.
11. Flood core with a heavy refined oil at a high pressure drop and calculate oil permeability.
12. Replace refined oil with light refined oil and then crude oil, if desired.
13. Flood core with water until residual oil saturation (S_{or}) is established and calculate brine permeability at S_{or}.
14. Maintain brine flow at a low rate until ready for the polymer.

7.2.3.2 Polymer Preparation.

1. Prepare a selected polymer concentrate using standard procedures (refer to Section 2).
2. Dilute polymer stock solution to desired concentrations with filtered test brine.
3. Select tracer to use in polymer (for example, 100 ppm iodide using potassium iodide).
4. After an appropriate mixing time, measure the screen factor and viscosity of the diluted, traced polymer solution (refer to Section 3).
5. Pump the polymer through a selected porous medium for pre-shearing at reservoir determined rate, if desired.
6. Measure and record the flow rate and injection pressure during the shearing process.
7. Remeasure screen factor and viscosity after injecting all polymer through the core and determine the polymer concentration (refer to Section 5).

7.2.3.3 Polymer Injection Procedure.

1. Set pump to correspond to the planned polymer injection rate.
2. Continue pumping brine until pressure stabilizes.
3. Start polymer injection using same pump rate as Step 2.
4. Switch to the higher calibrated transducers if pressures exceed the limits of the low pressure transducers.
5. Collect cuts and mark the test tubes to record events of the fluid and rate changes that occur.
6. Continue injecting polymer until pressure stabilizes (this usually requires several pore volumes for first polymer concentration).
7. Change pump rate if other injection velocities are needed and continue polymer injection until pressure again stabilizes. Continue this sequence until data is collected for the particular polymer concentration.
8. Switch to brine using the same pump rate as the final polymer injection rate. Continue until pressures are stabilized and the presence of polymer is undetectable as determined by polymer flocculation test (refer to Par. 5.7).
9. Have next polymer dilution ready for injection.

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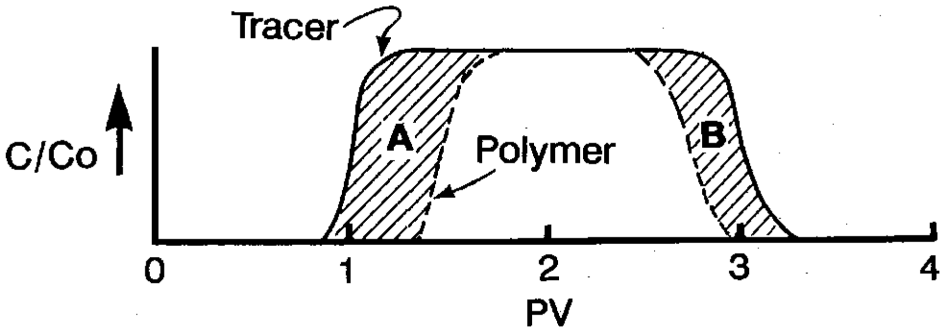
*Refer to *API RP 27: Recommended Practice for Determining Permeability of Porous Media*, and *API RP 40: Recommended Practice for Core-Analysis Procedure*, for detailed recommended core preparation procedures. Available from American Petroleum Institute, Publications and Distribution Section, 1220 L St., N.W., Washington, D.C. 20005.

10. To obtain a retention isotherm, Steps 1-9 can be repeated for any increasing polymer concentrations.

7.2.3.4 Calculation Procedure. After the locations of the transition zones have been determined by analysis and the maximum number of cuts have been analyzed through the transition zones, note the concentration of each component in each of the cuts through the transition zone. There are three cases to consider. In the first case, the polymer curve lags the tracer curve of the first transition zone. In addition, in most instances there is an inaccessible pore volume (IPV) to the polymer molecules and the polymer leads the tracer at the rear transition zone (refer to Figure 7-1 for an example calculation). In Figure 7-2, at the first transition zone, if the polymer leads the tracer it means that the loss of polymer expressed in percent pore volume is less than the inaccessible pore volume. The loss would be the IPV area minus the area between the polymer and the tracer in the front transition zone. In Figure 7-3, at the front transition zone, the polymer and tracer profiles are superimposed. This means that the loss equals the inaccessible pore volume area as determined at the rear transition zone. The integral under the tracer curve in Figures 7-1, 7-2, and 7-3 should equal the number of pore volumes of polymer injected. This calculation provides a consistency check on the core pore volume, cut volumes, and the tracer analysis.

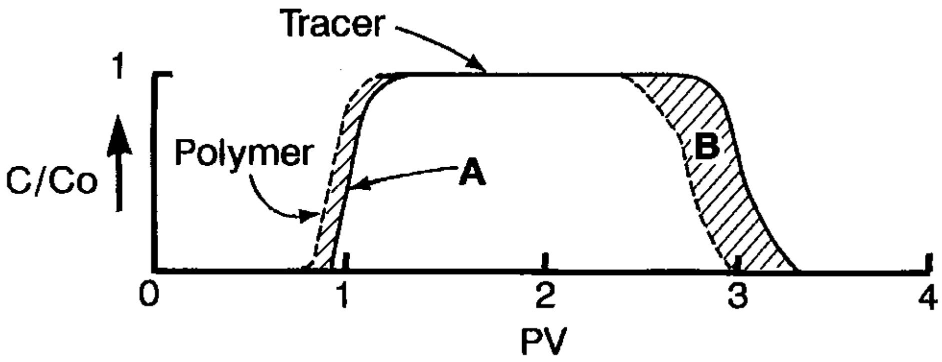


Given: 250 PPM Polymer Solution Injected
Core Porosity = 0.2

Determine Area A = 48% PV From Cut Analysis
Area B = 25% PV From Cut Analysis

At Front Polymer Lags Tracer By 48% PV
At Rear Polymer Leads Tracer By 25% PV
Loss = 48 + 25 = 73% PV
Loss = 250 PPM x .73 = 182 mg/(ℓ of PV) ≅ 100 LBS/ACRE-FT

FIGURE 7-1
EXAMPLE CALCULATION

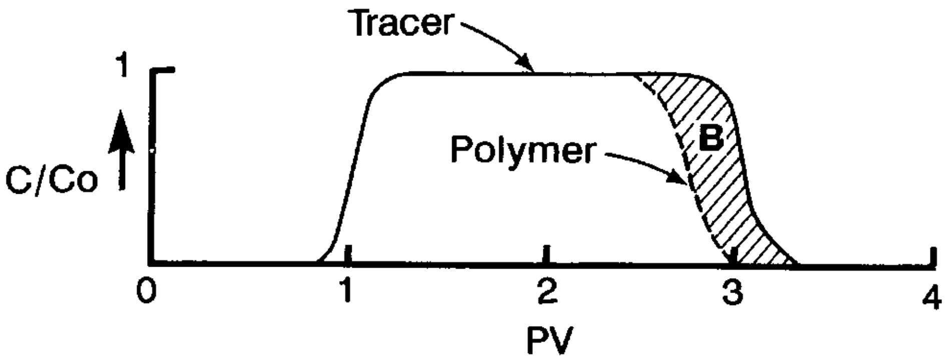


Given: 250 PPM Polymer Solution Injected
Core Porosity = 0.2

Determine Area A = 6% PV From Cut Analysis
Area B = 25% PV From Cut Analysis

At Front Polymer Leads Tracer By 6% PV
At Rear Polymer Leads Tracer by 25% PV
Loss = 25 - 6 = 19% PV
Loss = 250 PPM x .19 = 47.5 mg/(ℓ of PV) ≅ 26 LBS/ACRE-FT

FIGURE 7-2
EXAMPLE CALCULATION



Given: 250 PPM Polymer Solution Injected
Core Porosity = 0.2

Determine Area B = 25% PV From Cut Analysis

At Front Polymer Coincides With Tracer
At Rear Polymer Leads Tracer By 25% PV
Loss = 25% PV
Loss = 250 PPM x .25 = 62.5 mg/(ℓ of PV) ≅ 34 LBS/ACRE-FT

FIGURE 7-3
EXAMPLE CALCULATION

7.3 MULTIPLE SLUG RETENTION METHOD

7.3.1 General. The method described here employs a simple mass balance technique to calculate the polymer retained. In this test method, a slug of known polymer concentration is passed through the core and the effluent is analyzed. The difference in concentration before and after is then used to determine the retention. A second slug of the original solution is injected through the core and the concentration of polymer is determined. This procedure is repeated until the concentration of polymer returned equals the concentration of polymer injected, indicating no more polymer retention is taking place.

7.3.2 Apparatus.

1. Low flow rate (0.02 to 2.0 cm^3 per minute) pump in which the fluid does not contact metal.
2. Pressure sensing device (transducer).
3. Core holder which has limited dead volumes.
4. Brine pump with variable speed.
5. Lines and valves which are set up to minimize dead volumes in which fluids can become lost.
6. Heating cabinet to house the test cores and holder.

7.3.3 Procedure.

1. Determine water permeability, oil relative permeability, and water relative permeability end points according to the procedures outlined in *API RP 27: Recommended Practice for Determining Permeability of Porous Media.**
2. With core at residual oil saturation, introduce the desired concentration of filtered polymer solution to the face of the core.
3. Flow approximately 6 pore volumes of the polymer solution through the core at 1 to 10 ft/day. For a 1-inch diameter by 1-inch long cylindrical plug having a porosity of 20% this corresponds to about 15 mL at a rate of 0.02 to 0.2 cm^3 per minute. Collect all the produced fluid in a tared graduate and record the pressure during the flood. Record the volume of polymer solution produced.
4. Flow approximately 14 pore volumes of brine through the core. The first 2 pore volumes should be pumped at the same rate as the polymer. Flow rate should then be increased as allowed by the pressure. Collect all the produced fluids in the same tared graduate. Record the weight of brine produced. Record pressure during flood. For the core described in Step 3, the brine flush is approximately 35 mL.
5. Analyze polymer in the produced fluids (refer to Section 5).
6. Repeat Steps 2 through 5 to assure the adsorption is satisified.

7.3.4 Calculation Procedure. Calculate the retention for each polymer slug injected as follows:

$$R = 2.72 \frac{(W \times C_i - Y \times C_f)}{V} \quad \text{.................} \quad (7\text{-}1)$$

where:

R = retention, lbs/acre ft.

V = bulk volume of the core, cm^3.

W = weight of polymer injected, g.

C_i = concentration of polymer solution injected, ppm.

Y = weight of fluid produced and analyzed, g.

C_f = concentration of polymer in the produced sample, ppm.

7.4 RECYCLE METHOD

7.4.1 General. The recycle method for measuring dynamic polymer retention is described in this section. In the recycle method, a known concentration of polymer is circulated through a core in a closed loop for a period of time. This method requires that the aqueous volume of the core be known very accurately. Therefore, it is usually used with cleaned and dried cores. This is a disadvantage of the method. If a fresh-state core is utilized then an accurate method of determining the water saturation must be used (such as the use of a non-adsorbing tracer). A simpler alternate, but less accurate, variation of the recycle method is described in Par. 7.4.5.

7.4.2 Apparatus.

1. Suitable core holder such as a Hassler holder, or equivalent.
2. Variable rate pump capable of covering typical reservoir rates of 10 to 0.1 ft/day. Ideally, the polymer solution should not come in contact with metal in the pump. A peristaltic pump will be suitable in most cases.
3. A heated cabinet capable of holding the equipment at reservoir temperature.
4. A stoppered glass container.

7.4.3 Procedure.

1. Select the core (refer to Par. 7.1).
2. Measure the core dimensions.
3. Saturate the core with filtered brine and accurately determine the aqueous volume in the core.

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4. Fill and accurately determine the volume of the associated lines, valves, pumps, etc. For improved accuracy in this test, maximize the core pore volume and minimize the exterior volume.

5. Weigh into the glass container a volume of polymer solution about equal to the pore volume of the core (Step 3) and the lines (Step 4). The concentration of this polymer solution should be accurately known. A nonadsorbing tracer such as sodium iodide can be added to determine any errors due to handling losses or evaporation.

6. Circulate the polymer solution for about 24 hours at rates below that which will cause shear degradation, but sufficient to change out the pore volume of the core at least 10 times. It may be necessary to increase the circulation times for cores having low permeability and/or large pore volume.

7. Disconnect the core from the system and flush with four pore volumes of the test brine into a tared vessel.

8. Accurately weigh the vessel and determine polymer concentration (refer to Section 5).

9. Determine the polymer and tracer concentrations in the glass container (refer to Section 5).

7.4.4 Calculation Procedure. The following equation can be used to calculate polymer retention:

$$R = \left[(M \times C_i) - (M_w + M)C_f - (M_{fl} \times C_{fl})\right] 2.72/V \ldots \text{(7-2)}$$

where:

R = polymer retention, lbs/acre ft.

M = weight of initial polymer solution, g.

C_i = concentration of initial polymer solution, ppm.

C_f = concentration of final polymer solution, ppm.

V = bulk volume of core, cm^3.

M_w = weight of water present in valves, pumps, and lines at start of test, g.

$M_w + M$ = weight of liquid outside of the core, g.

M_{fl} = weight of liquid flushed from the core, g.

C_{fl} = concentration of polymer solution flushed from the core, ppm.

7.4.5 Alternate Recycle Method. The following variation of the recycle method is simpler but is not as accurate because it does not account for the reduced amount of polymer in the core due to inaccessible pore volume. The procedure is essentially the same as shown in Par. 7.4.3, except that Steps 7 and 8 are eliminated.

7.4.5.1 Calculation Procedure for the Alternate Recycle Method. The following equation can be used to calculate polymer retention:

$$R = \left[M \times C_i - (M_w + M + M_{pv})\ C_f\right] 2.72/V \ldots\ldots \text{(7-3)}$$

where:

R = polymer retention, lbs/acre ft.

M = weight of initial polymer solution, g.

C_i = concentration of initial polymer solution, ppm.

M_w = weight of water present in valves, pumps, and lines at start of test, g.

$M_w + M$ = weight of liquid outside the core, g.

M_{pv} = weight of core pore volume saturated with solution, g.

C_f = concentration of final polymer solution, ppm.

V = bulk volume of the core, cm^3.

7.5 STATIC TEST METHOD

7.5.1 General. Static adsorption tests can provide a preliminary screening of polymers. The tests are fairly simple and inexpensive compared to procedures involving flow in cores. It is possible to hold the adsorbent constant for a series of tests thereby isolating the effects of changing properties of the polymer solution. Also, the properties of the adsorbent can be varied in a controlled way, for example, by adding various amounts of clays. Results from these tests may not be representative of field values for several reasons. First, in disaggregating consolidated rock, surfaces are exposed which may not be the same as surfaces of the consolidated rock. This effect should be minimized if the reservoir rock is unconsolidated. Second, the mechanical entrapment component of polymer retention is not measured by the static test. However, it may be used in combination with a flow type retention test to attempt to separate the retention mechanism from adsorption. Third, the wettability of the disaggregated rock may be different from that of the reservoir rock.

7.5.2 Apparatus.

1. Rock crusher (mortar and pestle may be used for small amounts of rock).
2. U. S. A. Sieve Series 50 and 200 mesh screens.
3. Sample splitter.
4. Pyrex® vials, or equivalent.
5. Balance capable of weighing with a precision of 0.01 g.
6. Glass conical filter funnel and 10-micron filter papers.

7.5.3 Procedure.

1. Disaggregate sample of rock.
2. Dry material (in a hood); retain all the sample for sandstones and retain 50-200 mesh particles for carbonates.
3. Wash with appropriate brine solution until the composition of brine remains constant.
4. Dry material (refer to Bush, D. C. and Jenkins, R. E.[15]).
5. Divide the rock material into representative portions with the sample splitter.
6. Tare the vials.
7. Weigh in about 100 grams of solid. (If material quantities are limited, use 15 g.) To reduce the error, minimize the ratio of liquid to solid.
8. Add about 50 grams of polymer solution and reweigh. *NOTE:* If 15 g sample of material is used, add approximately 8 g of polymer solution and reweigh.) If insufficient free liquid results, increase the amount of polymer solution with a known amount. Record all weights.
9. Cap and store containers at representative temperatures for 2 days. Agitate periodically to maintain good contact between liquid and substrate.
10. Separate liquid from solid by centrifuging or by filtering through a 10-micron filter.
11. Determine final concentrations as described in Section 5.
12. Run replicates with adsorbents and samples without adsorbents to ensure against errors.

7.5.4 Calculation Procedure. Adsorption can be calculated using the following equation:

$$A = \frac{W_e(C_i - C_f)}{W_s} \quad \text{(7-4)}$$

where:

A = polymer adsorption, microgram adsorption per gram of solid.

W_s = weight of solid, g.

W_e = weight of polymer solution, g.

C_i = initial polymer concentration, ppm.

C_f = final polymer concentration, ppm.

Dividing the adsorption values calculated using Equation (7-3) by the surface area per unit weight of the solid will express the adsorption on a unit surface area basis.

These results can be expressed in units of pounds adsorbed per acre foot (customarily used in field applications), as follows:

$$A = 2.72\,A\,\rho_g\,(1 - \phi_f) \quad \text{(7-5)}$$

where:

A_f = polymer adsorption, pounds adsorbed per acre foot.

ρ_g = the grain density of the reservoir rock, g/cm^3

ϕ_f = average field porosity.

APPENDIX TO SECTION 7

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