

## MECHANICAL DEGRADATION OF POLYACRYLAMIDES INDUCED BY FLOW THROUGH POROUS MEDIA

by

R. S. Seright and J. M. Maerker

Exxon Production Research Company, Houston, TX 77001  
and

G. Holzwarth

Exxon Corporate Research Laboratory, Linden, NJ 07036

### INTRODUCTION

Mechanical degradation can severely reduce effectiveness of polyacrylamides used in enhanced oil recovery processes. To properly design such processes, petroleum engineers must be able to assess and predict the degree of polymer degradation that will occur under a given set of conditions. This paper describes methods used to assess degradation and factors influencing mechanical degradation. A technique is described whereby polymer molecular weight distributions are determined from sedimentation velocity measurements. Molecular weight distributions of native and degraded polymers are presented and compared with other methods used to assess degradation.

### ASSESSING MECHANICAL DEGRADATION

Mechanical degradation may be assessed by comparing polymer solution properties before and after exposing the polymer to high stresses. There are several properties which may be used to make this comparison. These include viscosity, screen factor, resistance factor, residual resistance factor and molecular weight distributions.

Resistance factor is the most meaningful property to the reservoir engineer. Resistance factor is defined as the ratio of brine mobility in a porous medium to the mobility of the polymer solution. It may be interpreted as the apparent viscosity of a polymer solution. Resistance factors of polyacrylamide solutions are often greater than viscosities. This suggests that polyacrylamides reduce water mobility both by increasing solution viscosity and by reducing effective permeability (1,2). Residual resistance factor is defined as the ratio of brine mobility before polymer injection to the brine mobility after polymer solution has been displaced from the porous medium. For polyacrylamide solutions, residual resistance factors are usually greater than unity.

Core floods are required to determine resistance and residual resistance factors. Since core floods can be time consuming, another method is desired to assess the degree of polymer degradation. Comparison of solution viscosities is an alternative method. However, mechanical degradation often reduces resistance factor much more than it reduces viscosity. Jennings *et al.* (3) suggested that screen factor measurements more closely correlate with resistance factors. Screen factor is measured with a screen viscometer and is defined as the ratio of the time required for a fixed volume of polymer solution to flow through a stack of five, 100-mesh screens to the flow time required for the same volume of brine to pass through the screens. Like resistance factors, screen factors are often larger and more sensitive to mechanical degradation than viscosities. Although screen factors may be measured conveniently and reproducibly, it must be emphasized that correlations between screen factors and resistance factors are empirical. Also, any screen factor-resistance factor correlation is only valid for solutions which have the same salinity, polymer concentration, polymer source and temperature (3).

Molecular weight distributions could provide more quantitative, understandable characterizations of polymers than other methods. Furthermore, they provide a characterization which is independent of solution salinity, polymer concentration and temperature. One would expect the largest polymer molecules to have a great influence on the rheology of a solution in porous media. Also, the largest molecules should be the most susceptible to mechanical degradation (4).

Thus, if molecular weight distribution (particularly the high end of the distribution) could be measured accurately, the behavior of a polyacrylamide solution might be better understood.

### FACTORS INFLUENCING MECHANICAL DEGRADATION

Mechanical degradation has been shown to depend strongly on solution flux, porosity and permeability. It is also slightly dependent on core length (5,6,7). Maerker (5,6) correlated levels of mechanical degradation (screen factors) using the group  $\dot{\epsilon} L_D^{1/3} / \phi^m$  where

$$\dot{\epsilon} = (\text{flux}) / \phi D_p$$

$$D_p = \frac{1-\phi}{\phi} \sqrt{150 k_b / \phi} = \text{average grain diameter}$$

$$L_D = (\text{core length}) / D_p$$

$$\phi = \text{porosity}$$

$$k_b = \text{permeability to brine}$$

$$m = \text{empirical constant dependent on screen factor}$$

Seright (7) correlated degradation with the group  $\text{FLUX} / D_p^2$  where FLUX is the solution flux at the sandface. In the development of these correlations the "dimensionless stretch rate",  $\dot{\epsilon}$ , was assumed to have an important effect on polymer rheology and degradation. For low values of  $\dot{\epsilon}$  the characteristic relaxation time of a polymer solution is short relative to the characteristic time for deformation. This allows adequate time for entangled polymer molecules to relax during the converging-diverging flow through porous media. In this case the solution's viscous nature dominates.

For higher values of  $\dot{\epsilon}$  the characteristic time for deformation in flow through small constrictions may be the same order of magnitude as the polymer relaxation time. In this situation the elastic character creates a dramatically increased resistance to flow. Thus, viscoelasticity causes polyacrylamide resistance factors to increase with increasing  $\dot{\epsilon}$ .

For very high values of  $\dot{\epsilon}$ , stresses become large enough to fragment polymer molecules. This mechanical degradation appears to occur immediately after the polyacrylamide enters a porous medium. Also, an "entrance pressure drop" is observed at the sandface only when degradation takes place (7). Levels of mechanical degradation do not correlate well with  $\dot{\epsilon}$  alone. Empirical terms must be included to obtain the  $\dot{\epsilon} L_D^{1/3} / \phi^m$  and  $\text{FLUX} / D_p^2$  groups which correlate successfully over a wide range of permeability, porosity, solution flux and flow geometry (5,7).

### MOLECULAR WEIGHT DISTRIBUTIONS AND POLYMER DEGRADATION

Molecular weight distributions for many polymers are easily obtained by gel permeation liquid chromatography. However, this method fails for the very high molecular weight polymers used in enhanced oil recovery (8).

Molecular weight distributions of native and degraded polyacrylamides were obtained by band sedimentation of fluorescently-tagged polymer samples. Three commercially available polyacrylamides from three different suppliers were investigated. These were designated Polymers A, B and C. Polymer A is a gel material consisting of 25 percent polymer and 75 percent water; Polymer B is a dry powder; and Polymer C is a water-in-oil emulsion consisting of roughly equal parts of oil, water and polymer. Each of the polymers contains about 30 percent acrylate groups and 70 percent acrylamide groups.

**Experimental Procedure.** Solutions were prepared containing 600 ppm polymer in 3.3 percent brine (3.0% NaCl, 0.3% CaCl<sub>2</sub>, pH 7). Part of each solution was subjected to mechanical degradation by forcing about 700 cm<sup>3</sup> (50 pore volumes) of each polymer solution through a six-inch-long Berea core

(approximately 250 md permeability) at a flux of about 70 ft<sup>3</sup>/ft<sup>2</sup>/d. The rheological properties of the native and mechanically-degraded solutions are listed in Table 1.

The polymers were labeled with a fluorescent dye to allow detection of the various molecular weight fractions after sedimentation. The labeled polymers were prepared by isocyanide coupling of fluoresceinamine to the carboxyl groups of the polymer, essentially as described earlier for xanthan polysaccharides (9,10). The labeling process began using 50 ml of 600 ppm polymer solution which had been dialyzed to 2 mM NaCl, pH 7. To this solution were added 50 ml of 33% dimethyl sulfoxide in H<sub>2</sub>O, 50 μl of acetaldehyde, 50 μl of cyclohexyl isocyanide and 3 ml of dye solution (3 mg 5-amino fluorescein in 3 ml dimethyl sulfoxide). This mixture was allowed to react for 4 hours at room temperature. The labeled polymer was recovered by several cycles of precipitation (ethanol) followed by dialysis against 4% NaCl to remove the last traces of reactants. The extent of dye labeling was found to be about 1% by weight.

Band sedimentation was carried out at 20°C on 4 to 8% NaCl gradients containing 0.04 M phosphate buffer at pH 7. Sedimentation experiments were conducted for 5 ppm and 2.5 ppm starting-zone polymer concentrations. Sedimentation time was 2 to 4 hours at 40,000 rpm in a Beckman L2-65B ultracentrifuge with a SW-40 rotor. The position and shape of the polymer band after centrifugation was determined by displacing the tube contents upward through a flow-cell in a fluorescence spectrophotometer. From the tube and rotor geometry, rotor angular velocity, time of sedimentation, and solution (buffer) viscosity, the distribution in sedimentation coefficient for each sample was determined. No effect of starting-zone polymer concentration was detected. In each run tubes of undegraded polymer were spun at the same time as the corresponding degraded sample.

**Results and Discussion.** Before degradation both Polymer A and Polymer B show roughly similar values of sedimentation coefficient (S), with peaks at 16 to 18 Svedbergs. Weight-averages for S are 20.5 and 19.3 for Polymers A and B, respectively. Both samples show rather broad distributions in S, but Polymer A shows markedly less material of low sedimentation coefficient (S < 10). Polymer A and Polymer B both contain about 12 percent polymer with S > 30.

Polymer C is distinctly different. The value of S at the peak is only 12 Svedbergs. The weight average of S is 14.7, and only 0.8 percent has S > 30.

One can convert the distribution in sedimentation coefficient to a distribution in molecular weight using the Mandelkern-Flory-Scheraga equation

$$M_{S\eta} = \left( \frac{\bar{S} [\eta]^{1/3} \eta_0 N_A}{\beta (1 - \bar{v} \rho)} \right)^{3/2} \quad (1)$$

and the empirical relation

$$M_i = (S_i / K_s)^{1/a_s} \quad (2)$$

where  $M_{S\eta}$  = sedimentation-viscosity average molecular weight

- $\bar{S}$  = average sedimentation coefficient in seconds
- $[\eta]$  = intrinsic viscosity in dl/g
- $\eta_0$  = solvent viscosity in poise
- $N_A$  = Avogadro's number
- $\beta$  =  $2.5 \times 10^6$
- $\bar{v}$  = partial specific volume of polyacrylamide in the solvent
- $\rho$  = solvent density
- $M_i$  = molecular weight of an individual polymer species

- $S_i$  = sedimentation coefficient of an individual polymer species
- $K_s$  = empirical coefficient
- $a_s$  = empirical exponent

A value of 0.52 ml/g was measured for  $\bar{v}$ . Solvent density was 1.03 g/ml. Based on the work of Klein and Conrad (11), a value of 0.39 was used for  $a_s$ . Values for  $[\eta]$  were measured using a Contraves Low Shear 30 viscometer and are listed in Table 1.

Results are shown in Figs. 1, 2 and 3 and Table 1. Two different values of average molecular weight are computed-- $M_{S\eta}$  (using Eq. (1)) and  $M_w$  (the weight-average molecular weight computed from the distributions shown in Figs. 1, 2 and 3). Values calculated with both methods are in reasonable agreement. Average native-polymer molecular weight is largest for Polymer A and smallest for Polymer C. This ranking is retained after the polymers have been mechanically degraded. Viscosities, screen factors and resistance factors reflect differences among the molecular weight distributions. Note that native Polymers A and B exhibit high screen factors and sizeable high molecular weight tails in their distributions. For these polymers, mechanical degradation results in a substantial reduction of screen factors and the high molecular weight tails. Although Polymer C does not have a high screen factor, it is evident that mechanical degradation is still most severe for the largest polymer molecules. For all three cases mechanical degradation results in a narrowing of the distribution, and the concentration of the "peak" species increases. The molecular weight of the peak species is not significantly affected by mechanical degradation.

The data presented here confirm hypotheses that screen factor (SF) is most sensitive to the largest polymer molecules and the largest polymer molecules are most vulnerable to mechanical degradation. A regression may be performed to quantify the relation between screen factor and molecular weight distribution. The parameters listed in Table 2 are results from a non-linear least squares fit of data from Table 1 and Figs. 1, 2 and 3 using the equations

$$SF-1 = K \sum_i N_i M_i^x \quad (3)$$

and

$$\frac{\eta - \eta_0}{\eta_0} = H \sum_i N_i M_i^y \quad (4)$$

where  $N_i$  is the concentration of polymer species  $i$ ,  $M_i$  is the molecular weight of species  $i$  and  $K$ ,  $H$ ,  $x$  and  $y$  are adjustable parameters. Table 2 suggests that screen factor is a rough measure of the third moment of a polyacrylamide molecular weight distribution.

It is somewhat surprising that Polymer C experienced such a large degree of mechanical degradation. Since all three polyacrylamides were subjected to the same shearing conditions, one might expect the molecular weight distribution of Polymer C to be less affected by mechanical degradation. To explain why this did not occur, one may rationalize that Polymers A and B were not sheared long enough to attain equilibrium or limiting molecular weight distributions. However, data presented elsewhere (5,7) suggest that almost all mechanical degradation occurs within a short distance of the point where a polymer enters a porous medium.

An alternative explanation may be that the degree of mechanical degradation is sensitive to the chemical environment (5). Although the solvents were identical, each polymer contains different amounts of catalysts, neutralizing agents and oils as a result of the manufacturing method used. These impurities may affect a polymer's ability to resist mechanical degradation.

A third possible explanation is that differences in the distributions may have resulted from differences in positions of ionized groups within the molecules. Because of different manufacturing processes, it is conceivable that one product may be essentially a block acrylate-acrylamide copolymer while the acrylate groups may be randomly distributed in another polymer product. These differences could also affect a polymer's ability to resist mechanical degradation.

The solid curves in Figs. 1, 2 and 3 represent calculated molecular weight distributions for the degraded polymers. They are based on a simple model which assumes that the probability of a polymer molecule (of molecular weight M) breaking in half is proportional to  $1 - e^{-(M/M_c)}$ , where  $M_c$  is a characteristic molecular weight for the degradation process. After the application of a given level of stress, the new concentration ( $C_{M1}$ ) of a given species is related to the original concentration ( $C_{M0}$ ) by

$$C_{M1} = C_{M0}(e^{-M/M_c}) \quad (5)$$

Concentrations for the highest molecular weight species are calculated first in the model, and the resultant polymer fragments are then added to concentrations of lower molecular weight species. Thus, fragments have an opportunity to break again as the program works its way down the molecular weight distribution. Figs. 1, 2 and 3 illustrate how well this simple model predicts distributions for degraded polymers.  $M_c$  will probably be dependent on flux, temperature, permeability, porosity, brine composition and polymer concentration.

When a reservoir engineer first ponders which polymer product to use during a polymer flood, he usually relies on data supplied by the various polymer manufacturers. Viscosities, screen factors and resistance factors have been used as the bases for comparison. However, availability of molecular weight distributions could improve the selection process since they provide a means of comparison that is independent of polymer concentration, salinity, etc. Although current state of the art allows useful qualitative comparisons, it is anticipated that more experience relating molecular weight distributions with traditional measurements will ultimately permit direct quantitative comparison. Thus, molecular weight distributions may provide a more desirable basis for comparison and could guide polymer chemists in synthesizing polymers that are less susceptible to mechanical degradation.

In summary, molecular weight distributions allow a clearer understanding of mechanical degradation and screen factor measurements, and they allow a greater insight into the rheological behavior of polyacrylamide solutions. Molecular weight distributions could be valuable for comparing polymers for enhanced oil recovery applications.

#### References

1. Pye, D. J., "Improved Secondary Recovery by Control of Water Mobility," J. Pet. Tech. (August, 1964) 911-916.
2. Smith, F. W., "The Behavior of Partially Hydrolyzed Polyacrylamide Solutions in Porous Media," J. Pet. Tech. (February, 1970) 148-156.
3. Jennings, R. R., Rogers, J. H. and West, T. J., "Factors Influencing Mobility Control by Polymer Solutions," J. Pet. Tech. (March, 1971) 391-401.
4. Abdel-Alim, A. H. and Hamielec, A. E., J. Applied Polym. Sci. **17**, 3769-3778 (1973).
5. Maerker, J. M., "Shear Degradation of Partially Hydrolyzed Polyacrylamide Solutions," Soc. Pet. Eng. J. (August, 1975), Vol. 15, 311-322; Trans., AIIME (1975).

6. Maerker, J. M., "Mechanical Degradation of Partially Hydrolyzed Polyacrylamide Solutions in Unconsolidated Porous Media," Soc. Pet. Eng. J. (August, 1976) 172-174.
7. Seright, R. S., "The Effects of Mechanical Degradation and Viscoelastic Behavior on Injectivity of Polyacrylamide Solutions," SPE 9297 presented at the 55th Annual Fall Technical Conference, Dallas, Texas, September 21-24, 1980.
8. Shawki, S. M. and Hamielec, A. E., J. Applied Polym. Sci. **23**, 3323-3339 (1979). See esp. p. 3334.
9. Holzwarth, G., Carbohyd. Res. **66**, 173-186 (1978).
10. DeBelder, A. N. and Wik, K. O., Carbohyd. Res. **44**, 251-257 (1975).
11. Klein, J. and Conrad, K. D., Makromol. Chem. **179**, 1635-38 (1978).

TABLE 1  
PROPERTIES OF NATIVE (N) AND MECHANICALLY  
DEGRADED (D) POLYMER SOLUTIONS

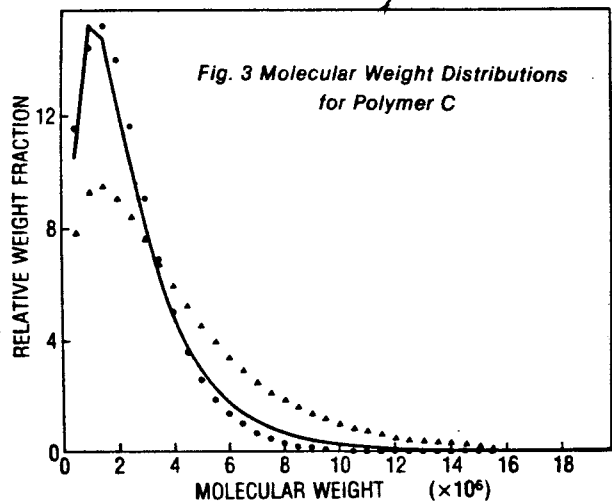
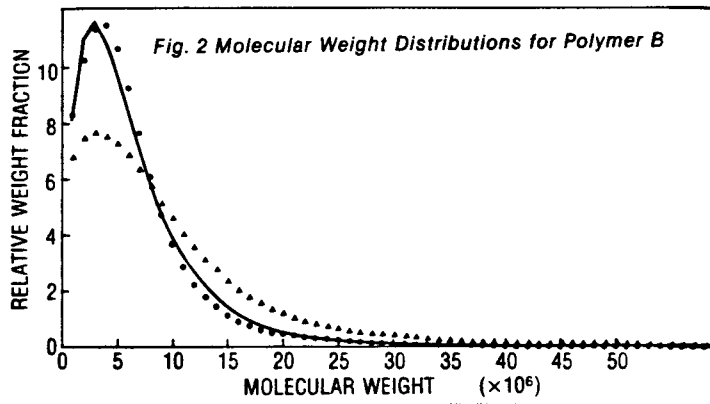
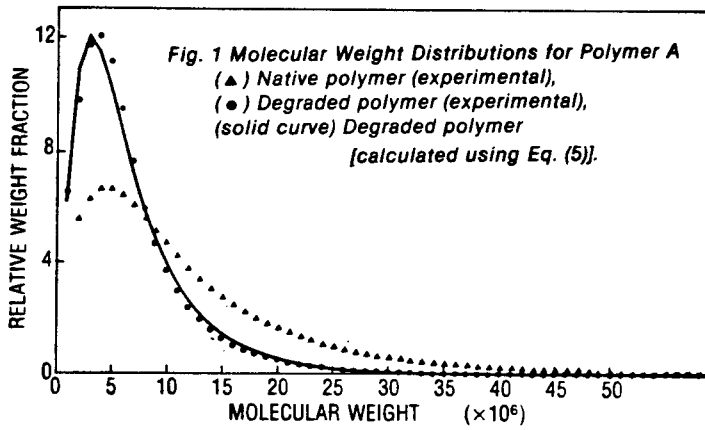
Degradation Conditions	Polymer A		Polymer B		Polymer C	
	N	D	N	D	N	D
Core permeability, md						
	265		240		274	
Core porosity	0.19		0.20		0.20	
Flux, ft <sup>3</sup> /ft <sup>2</sup> /d	73.3		62.5		72.5	
Rheological Properties						
	N	D	N	D	N	D
Viscosity, cp (@ 11 sec <sup>-1</sup> )	5.24	2.98	2.45	2.03	1.61	1.45
Intrinsic viscosity, dl/g	40	22	28	20	12.5	6.8
Screen factor	36.7	6.8	20.8	5.6	7.7	3.1
Resistance factor	--	18.7	--	10.5	--	8.5
Entrance pressure drop, psi	93	--	44	--	46	--
Sedimentation and Molecular Weight Properties of Polymer						
Sed. Coeffic., Svedbergs, (wgt avg)	20.5	18.3	19.3	17.7	14.7	13.8
$M_{s\eta}$ , 10 <sup>6</sup> daltons	6.8	4.3	5.2	3.9	2.3	1.6
$M_w$ , 10 <sup>6</sup> daltons	8.2	5.0	6.6	4.6	2.8	1.8
High M Fraction:						
S > 30	0.13	0.05	0.11	0.04	0.008	0.000
M > 30x10 <sup>6</sup>	0.02	0.00	0.02	0.00	0.00	0.00

FOLD

FOLD

TABLE 2  
PARAMETERS FOR EQUATIONS (3), (4) AND (5)

Parameter	Polymer A	Polymer B	Polymer C
x	3.35	3.59	2.16
K	$1.79 \times 10^{-5}$	$5.11 \times 10^{-6}$	$2.08 \times 10^{-6}$
y	1.38	0.87	0.66
H	$1.25 \times 10^{-3}$	$2.01 \times 10^{-3}$	$2.66 \times 10^{-3}$
$M_c$	$15 \times 10^6$	$20 \times 10^6$	$7 \times 10^6$



FOLD

FOLD