

Formation of Gel - Influence on Flow Behaviour in Porous Media

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ABSTRACT

The rheological behaviour of a xanthan-Cr³⁺ gel system has been studied during gelation. The increase in intrinsic viscosity and Huggins constant as input in a theoretical model was found to match the viscosity increase.

INTRODUCTION

Polymer gels can be an effective method to improve the oil recovery. In stratified reservoirs with large permeability contrasts low sweep efficiency and early water breakthrough are expected. Large volumes of oil are left behind in low permeable and unswept zones. A polymer gel, placed in the water swept zone will reduce the mobility and divert water to the low permeable and oilbearing zones. The most frequently used polymers are hydrolysed polyacrylamides and the biopolymer xanthan. Both polymers can be crosslinked by trivalent cations like Cr³⁺. When the gel is to be placed into the reservoir, it is important to have a good injectivity of the gelant to avoid any front plugging or too early gelation. The gelant solution should therefore have flow properties as the polymer solution during the injection stage and the gelation will take part into the reservoir. The polymers used for IOR properties in North Sea reservoirs must be pseudoplastic and shear stable. This is due to the high injection rates needed and to minimise the pressure increase in the injection zone. This paper will focus on the changes in the rheological properties of a xanthan - Cr³⁺

gel during the formation of aggregates and gel.

THEORY

The viscosity of a polymer solution can be described by the following equation,

$$\eta_{pol} = \eta_s (1 + [\eta]c + k'[\eta]^2 c^2 + \dots) \quad (1)$$

where η_s is the viscosity of the solvent, in this case seawater. The intrinsic viscosity $[\eta]$ is a measure of the size of the polymer molecule and the Huggins constant k' describes the interaction between the polymer molecules. For IOR polymers, k' can be used in the quality control. If k' becomes too high the polymer solution will form aggregates and plugging of the porous media may occur.

Both $[\eta]$ and k' are shear rate dependent and will decrease by increased shear rate, Chauveteau¹. The shear rate dependency for the polymer solution is often described by a Carreau model,

$$\frac{\eta - \eta_\infty}{\eta(\dot{\gamma}=0) - \eta_\infty} = \left\{ 1 + (\lambda \dot{\gamma})^2 \right\}^{(n-1)/2} \quad (2)$$

where λ is a time constant, $\dot{\gamma}$ is the shear rate and n the shear thinning index. At low shear rates, $\dot{\gamma} \ll 1/\lambda$ the viscosity is Newtonian. When $\dot{\gamma} \gg 1/\lambda$ the specific viscosity follows a power law dependency. The time constant λ can be expressed as

$$\lambda = \lambda_0 [\eta] c (1 + k' [\eta] c) \quad (3)$$

by using a rigid dumbbell theory, Bird et al.² The time constant will increase by increasing $[\eta]$ and k' . This means that the Newtonian level will move toward left by increasing $k'[\eta]c$. Notice that the time constant is expressed with the same constants as the viscosity in Eq 1.

The shear thinning index, n , is found to be a function of concentration, Cannella et al.³ Using data from Cannella and this study, it is found that the shear thinning index can be fitted by following expression.

$$n = n_0 + \frac{1 - n_0}{1 - \frac{1}{2}k'[\eta]c} \quad (4)$$

This means that the slope of the viscosity curve will increase by increased concentration, $[\eta]$ and k' and moves asymptotically towards n_0 .

EXPERIMENTAL

Xanthan biopolymer supplied by Statoi Biosentrum, have a broth concentration of 2.12%. A stock solution of 4000 ppm where made in artificial seawater and clarified through Millipore-filters. The crosslinker was Chromium acetate from Aldrich Chemical Company. Samples containing 550 ppm xanthan and 4.0 mM Cr^{3+} , with a volume of 50 ml were prepared and stored at 25°C. Intrinsic viscosity and Huggins constant were measured. The solutions were diluted and viscosity measured on a Contraves LS 30 rheometer at shear rates of 0.11, 0.94, 11 and 95 s^{-1} . Reduced specific viscosity was plotted versus concentration. The intersection at zero concentration gives the intrinsic viscosity and the slope of the curve gives the Huggins constant.

In addition the viscosity of the 550 ppm solution was measured in the shear range 0.1 to 100 s^{-1} . All measurements were conducted as a function of time from mixing to 95 days after mixing. To obtain accurate intrinsic viscosity and Huggins constants can be quite difficult and care has to be taken by calibration and extrapolation of the curves.

RESULTS

Fig. 1 and 2 show the intrinsic viscosity and Huggins constant versus time. It is seen that they increase by increasing time. Both the intrinsic viscosity and Huggins constant are highest at lowest shear rate, which is the reason for the pseudoplastic behaviour for the polymer solution. From these figures, following step reactions in the gelation can be explained.

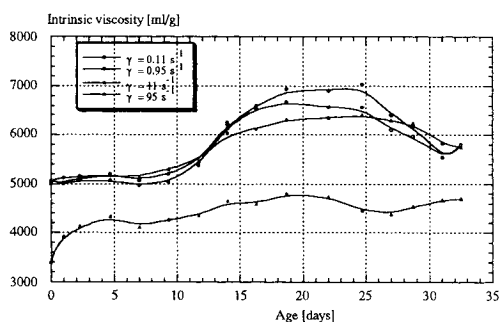


Figure 1. Intrinsic viscosity at different shear rates for a xanthan- Cr^{3+} system.

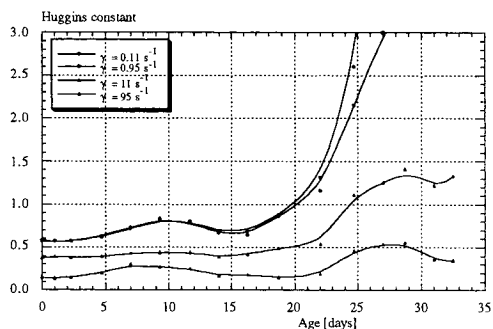


Figure 2. Huggins constant at different shear rates for a xanthan- Cr^{3+} system.

1. There is an increase in k' after about 5 days, from 0.58 to about 0.80. No increase in $[\eta]$ is observed. This is explained by the interaction between the crosslinker and the polymer molecule.

2. After about 12 days an increase in $[\eta]$ is observed and is explained by formation of small crosslinked aggregates. By time, these aggregates increase in size. The k' is fairly stable in this period.

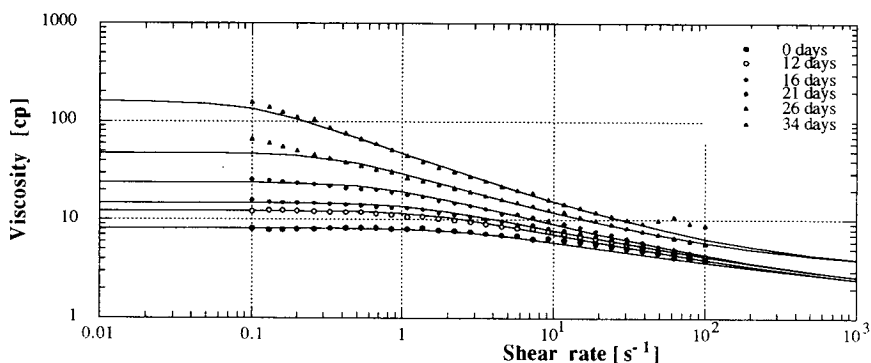


Figure 3. Experimental and theoretical viscosity versus shear rate in a xanthan-Cr³⁺ system.

3. A relative sharp increase in k' is observed at about 20 days. The density of aggregate clusters has increased and they form larger gel aggregates. Visible gel was observed at about 25 days.

Fig. 3 shows the viscosity as a function of shear rate at different age of the gelant. The data points are experimentally values and the lines are theoretical model based on the above equations.

The theoretical model is an extended version of the Carreau model, where the input parameters are the calculated intrinsic viscosity and Huggins constant. The viscosity at zero shear rate is found from Eq. 1. The time constant λ found from Eq. 3 where λ_0 is a fitting parameter. The shear thinning index n is a function of $k'[\eta]c$, equation 4. As shown in fig 1 and 2 there is an increase in k' and $[\eta]$ by time. This increase results in an increase in λ and a decrease in n .

In the Carreau model the viscosity at infinite shear rate is set to the solvent viscosity. Due to the formation of gel the viscosity at high shear rate is higher than the Carreau prediction. In this extended version the infinite gel viscosity is set to three times the solvent viscosity.

In similar experiments the gel solutions have been filtered through porous media. It has been found that the gel solution will plug the filters when the viscosity is about twice the initial polymer viscosity due to the

increased aggregate size. Which in this experiment is about 21 days.

CONCLUSIONS

In the transition from a polymer solution to a gel the rheological behaviour of the solution can be expressed by an extended Carreau model. The viscosity increase is explained by an increase in the intrinsic viscosity and the Huggins constant. Since the time constant increase by increased $k'[\eta]c$, the gel viscosity model moves towards a power law during the gelation.

REFERENCES

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3. Cannella, W.J., Huh, C. and Seright, R.S. "Prediction of Xanthan Rheology in Porous Media" Paper SPE 18089 presented at the 63rd Annual Technical Conference and Exhibition of SPE, Houston TX, October 2-5, 1988