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Permeability Modification Using a Reactive Alkaline-Soluble Biopolymer

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Introduction: Polymer injection has been used in reservoirs to alleviate contrasting permeability zones to enhance oil recovery (EOR). Polymer technology relies mainly on the use of polyacrylamides cross-linked by a hazardous metal or organic. Contemporary polymer plugging has investigated the stimulation of in-situ microorganisms to produce polymers (Jenneman et. al., 2000) and the use of biocatalysts to trigger gelling (Bailey et. al., 2000). The use of biological polymers are advantageous in that they can block high permeability areas, are environmentally friendly, and have potential to form reversible gels without the use of hazardous cross-linkers. Recent efforts have produced a reactive alkaline-soluble biopolymer from *Agrobacterium species* ATCC # 31749 that gels upon decreasing the pH of the polymeric solution. Microbial polymers are of interest due to their potential cost savings, compared to conventional use of synthetic chemical polymers. Numerous microorganisms are known to produce extracellular polysaccharides. One microbiological polymer of interest is curdlan, β - (1, 3) glucan, which has demonstrated gelling properties by a reduction in pH. The focus of this study was to determine the impact an alkaline-soluble biopolymer can have on sandstone permeability.

Materials and Methods: *Agrobacterium sp.* # 31749 (formerly *Alcaligenes faecalis* subsp. *myxogenes*) was obtained from the American Type Culture Collection (ATCC). Curdlan was harvested after 5 days of aerobic incubation in basal fermentation media (previously described by Lee et. al., 1999). Dry biopolymer was resuspended in 0.01 M KOH, 0.10 M KOH, nano pure water, or modified Coleville synthetic brine (CSB). A block heater was used to determine the effect of temperature on biopolymer solubility. A Wells-Brookfield Cone/Plate Viscometer model LVTDV-IIICP (Stoughton, MA) was used to measure viscosity. A Cole Parmer Polystat heated circulating water bath was used to maintain temperature of the viscometer plate. The amount of salt in the modified CSB was varied to determine if salt concentration alters biopolymer gelling. The concentrations of salt tested were 0.0%, 0.7%, 1.5%, 3% and 5% sodium chloride. Dry biopolymer (10% w/v) was added to 0.10M KOH or 0.01M KOH brine. The pH was adjusted using 3M HCl.

Permeability modification was investigated by injecting soluble biopolymer into cylindrical Berea sandstone cores 1 inch in diameter by 6 inch in length and defining the contribution of pH, salt, temperature, and Schuricht crude oil on biopolymer gelation. The average physical characteristics of the cores were as follows: porosity 19.41%; pore volume 12.93 ml; permeability 142 mD. Biopolymer powder (10% w/v) was dissolved in modified CSB with the addition of 0.10M KOH or 0.01M KOH and filtered with 20-25 μ m cellulose papers. Biopolymer

was injected using a stainless steel accumulator (Temco, Tulsa, OK), an Isco syringe pump (Lincoln, NE) and controller at a constant flow of 1.0 ml/min for at least 5-pore volumes. The pressure was recorded with Honeywell pressure transducers (Phoenix, AZ). Cores were shut-in at the desired temperature (23°C or 60°C) for 6-11 days. Core temperature was controlled using a sand-packed heat block. Initially, a hand syringe filled with modified CSB was used to obtain effluent to measure the pH. Flow was established with an Isco pump using modified CSB after the pH decreased below 10.8. Post-injection permeability measurements were calculated for each core. When cores were heated to 60°C, the temperature of the injection brine was maintained using an Omega RTD controller, a variable autotransformer, a 1/8-inch RTD thermocouple, and Barnstead/Thermolyne heat tape. The residual resistance factor (RRF) was calculated for each core according to equation (1):

$$RRF = \frac{K \text{ before treatment}}{K \text{ after treatment}} \quad (1)$$

Where K is the permeability, before treatment is the permeability prior to biopolymer injection, and after treatment is the permeability after biopolymer injection.

Results and Discussion: Initial biopolymer characterization showed that the biopolymer was water-insoluble, but was rendered soluble in 0.01 M KOH. The viscosity of the biopolymer was dependent on the pH of the solution. At an alkaline pH of 11.4, the viscosity of the biopolymer was below 50 cP. The biopolymer formed an opalescent, firm gel when the pH dropped slightly to 10.8. The gel dissolved when the pH decreased to 8, gelation resumed when the pH increased to 10.8. The addition of salt did not affect the ability to form a gel, except the biopolymer was not soluble when 5% sodium chloride was added to the 0.01 M KOH. A stable gel formed in the presence of 0.7, 1.5 and 3.0% sodium chloride. The correlation between viscosity and temperature reflect a reduction of biopolymer viscosity as the temperature increased from 26°C to 96°C (Figure 1).

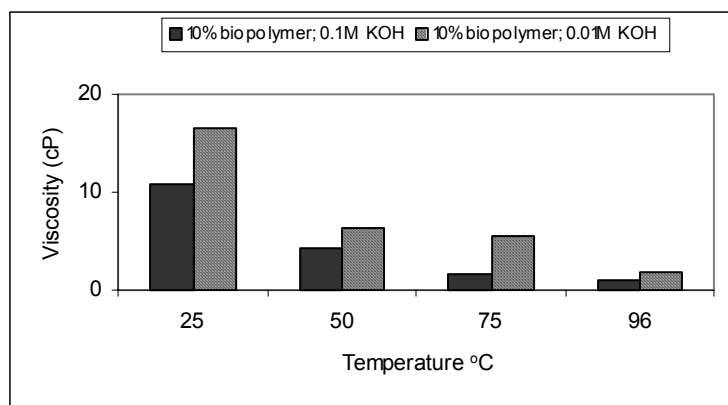


Figure 1. Viscosity of biopolymer solution as a function of temperature.

The results from permeability modifications are displayed in Table I. The permeability increased in the control cores injected with 0.01 M KOH and 0.1M KOH. The pH of the 0.01M KOH control core dropped from 11.93 to 10.68, whereas; the pH of the control core injected with 0.1 M KOH slightly decreased from 12.88 to 12.71. The results indicate that Berea

Table 1. Permeability Modifications.

Core Treatment	pH Change	Pre -injection Permeability (mD)	Post-injection Permeability (mD)	Permeability Reduction (%)	Residual Resistance Factor (RRF)
Control 0.01M KOH	11.93-10.68	122.69	186.80	-52.25	0.66
Control 0.10M KOH	12.88-12.71	129.72	196.54	-51.51	0.66
Biopolymer, ambient	11.45-10.21	112.00	0.32	99.71	350.00
Biopolymer, ambient	11.28-10.04	134.65	0.17	99.87	792.06
Biopolymer, 2% NaCl	12.04-10.67	152.93	64.97	57.52	2.35
Biopolymer, 2% NaCl	12.04-10.46	146.70	5.13	96.50	28.60
Biopolymer, 60°C	11.73- 9.35	167.89	2267.46	-1250.56	0.07
Biopolymer, 60°C	11.73- 9.17	161.94	249.43	-54.03	0.65
Control 0.01 M KOH; Schuricht oil	11.93-10.76	150.20	8.98	94.01	16.72
Biopolymer, ambient; Schuricht oil	11.62-10.59	136.60	6.41	95.31	21.31
Biopolymer, 2% NaCl; Schuricht oil	10.62- 9.85	169.00	0.98	99.42	172.45
Biopolymer 60°C; Schuricht oil	11.65- 9.32	122.60	2.20	98.73	55.73

sandstone could sufficiently buffer 0.01 M KOH brine, but not 0.10 M KOH brine. The pH reduction in the sandstone core was adequate for biopolymer gel formation; therefore, 0.01M KOH was used for further permeability modification experiments.

All sandstone cores injected with biopolymer dissolved in 0.01M KOH showed a reduction in pH within 11 days. The pH of duplicate cores injected with biopolymer and shut-in at ambient conditions decreased from 11.45 to 10.21, and from pH 11.28 to 10.04. The permeability decreased to greater than 99% when biopolymer was injected. The effluent pH also decreased when 2% sodium chloride was added to the alkaline biopolymer although, the permeability reduction was not manifested in duplicate cores. Heating the cores injected with biopolymer resulted in a sharper decrease in the pH. The pH dropped from 11.73 to pH 9.35 and 11.73 to 9.17, however; the permeability increased when the temperature of the core was 60°C. These results correlate with the data described previously about a reduction in biopolymer viscosity at elevated temperatures. All cores saturated with Schuricht crude oil displayed a reduction in pH when 0.01 M KOH was injected. The control core had an initial pH of 11.93 and effluent pH of 10.76. The oil-laden cores which had biopolymer injected, dropped from pH 11.62 to 10.59. The effluent pH of cores with 2% sodium chloride decreased from 10.62 to 9.85, and the pH of the heated cores decreased from 11.65 to 9.32. The post-injection permeability was reduced in all cores saturated with Schuricht crude oil including the control core, which had no biopolymer injected. The permeability decreased 94% in the control core contrary to the increase in permeability increase observed in the control core without oil. Despite the permeability decrease in the Schuricht crude control core, the post-injection permeability of the cores injected with biopolymer were reduced greater than 95%. The magnitude of residual resistance factor (RRF) varied from 0.07 to 792.06. A residual resistance factor of 792.06 was calculated for a core that was injected with biopolymer at ambient conditions. The control cores and cores heated to 60°C had low RRF's; whereas, the cores injected with biopolymer had higher RRF's. Lower RRF's were observed when 2% sodium chloride was added to the brine. The RRF's ranged from 16 to 172 in the cores with Schuricht crude oil. All cores injected with biopolymer showed an increase in the RRF compared to the control cores.

Conclusions: The buffering capacity of sandstone has been demonstrated to reduce the pH of a 0.01M alkaline biopolymer solution sufficiently to cause the biopolymer to form a stable in-situ gel, thus reducing the permeability. This finding could potentially lead to alternate technology for permeability modification and water-cut reduction, thus extending the life of a reservoir and preventing premature abandonment.

References:

- Bailey, S. A., R S. Bryant, and K. E. Duncan. 2000. Use of biocatalysts for triggering biopolymer gelants. 2000 SPE/DOE Improved oil Recovery Symposium, SPE 59305.
- Jenneman, G. E., R. E. Lappan, and R. H. Webb. 2000. Bacterial profile modification with bulk dextran gels produced by the in-situ growth and metabolism of *Leuconostoc* species. 2000 SPE/DOE Improved oil Recovery Symposium, SPE 59307.
- Lee, J. H., M. K. Kim and Y. H. Park. 1999. Optimal pH control of batch processes for production of curdlan by *Agrobacterium* species. J. of Ind. Microbiol. and Biotech. 23: 143-148.

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