

Final Report
DOE SBIR Phase I Project – DE-SC0004194

**Novel Self-Thickening Chemicals for Improved
Conformance Control**

ChemEOR, Inc.

Main Office
841 E San Bernardino Road
Covina, California 91723

Tel: 1-626-966-3808 ext. 155
Fax: 1-877-818-3028

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Executive Summary

The objective of this project is to identify single chemical agents that exhibit a desirable rheological property whereby if such a chemical is dissolved in salt water it increases the solution viscosity significantly with time. We term that behavior as “self-thickening” and have nicknamed this as “T85 technology”. As detailed in the original project proposal, such single chemical products can be applied to advantage as agents for selectively slowing or blocking high flow water channels in subsurface oil reservoirs. The net effect is a decrease in water and an increase in oil flow and production.

The initial testing has focused on five different synthetic co-polymers that have two or more chemical groups. These chemicals were dissolved at a concentration of 2500 ppm into different salt solutions (sodium chloride, potassium chloride, and calcium chloride) that encompass a range of dissolved salt concentrations. For the sodium chloride and potassium chloride solutions the salt concentration ranged from 1 – 5 wt%. The calcium chloride dihydrate sample concentrations ranged from 0.1 – 1 wt%. One set of samples being aged at 25 °C and a second set at 50 °C. Viscosity measurements versus aging time show two of these agents may exhibit apparent self-thickening behavior under certain salinity and temperature conditions. Generally the effect is greater in lower salinity NaCl brines and at 25 C.

Preliminary flow experiments confirm that the aged fluids exhibit increased effective viscosity while flowing through a porous medium (sand pack). These flow tests include the case of the chemical fluid being aged on the bench before injection into a sand pack, and also a second series of sand packs where fresh chemical fluid is injected and allowed to age in-situ.

Thus, the results of the static ageing tests together with the flow tests are a technical validation of the T85 concept.

Introduction

About 80 percent of the total number of U.S. oil wells is now classified as marginal (or “stripper”) wells (U.S.DOE, Reference 1). Tapping into additional oil and gas supplies within the nation's marginal wells for smaller producers can be an important contributor to U.S. energy security (U.S. DOE, Reference 2).

These wells produce oil and gas at the low rates of less than 10 barrels per day of oil or 60,000 cubic feet per day of natural gas, and represent typical operations for many of the small producers in the U.S. Typical operations involve producing and re-injecting large volumes of saline water. Excess water production which, when accompanied by low oil production, results in wells becoming unprofitable to operate and leads to early well abandonment and unrecoverable oil. For crude oil wells nearing the end of their productive lives, Weideman (1996) reports that water can be as much as 98% of the

material brought to the surface. That means, in production wells in a mature waterflood, the amount of water produced can be 10 to 50 bbl for each barrel of crude oil produced (Veil 2003). One of the significant expenses in these operations is the cost of processing the large volumes of water.

One general approach to improve the economics of these mature waterfloods is by so-called “conformance control”. This refers to oil field practices that increase the volume of the reservoir that is contacted by the injected water to sweep additional oil remaining in place. This can be accomplished by injecting a relatively viscous or even gel water-based fluid from the injection or production wells. The fluid treatments are designed to enter preferentially into the more permeable, “watered-out” parts of the reservoir and set up a blocking action. This has the effect of diverting the fluid flow into less permeable portions of the reservoir that contain a higher saturation of remaining crude oil. The net effect is to produce more of the remaining oil and less water.

Our research interest in viscous fluid/gel treatments is focused on developing novel single chemical products we call “T85” that “self-thicken”. These new products will have advantages of relatively low chemical cost and the capability to treat target higher permeability targets to great depth. Another beneficial feature of this product concept is that it could be adapted to preferentially block flow in treated water thief zones both in injection wells and in production wells.

The most common current “bulk” gel technology using in-situ multi-component chemistry (polymer and a cross-linker) has disadvantages such as lack of gelation time control, uncertainty of gelling due to shear degradation, chromatographic fractionation or change of gelant compositions, and dilution by formation water. Other products that have been investigated for this purpose include preformed particle gel – PPG (Coste 2000, Bai 2004), microgels (Chauveteau 2000, Rousseau 2005, Zaitoun 2007), swelling mm-sized polymer grains (e.g., Diamond Seal[®]), and swelling sub-micron-sized polymers (Bright Water[®], Pritchett 2003, Frampton, 2004). These latter products typically have high product cost and/or are not able to treat reservoirs in depth.

The T85 chemistry should also be suitable for water shut-off treatments at production wells. In that case the T85 chemical is a system designed to thicken quickly (within hours) to a gel-like condition. Again, this chemical concept has the distinct advantage that it relies on a single chemical product to create the target in-situ gel to a controlled time and extent versus the conventional “bulk” gel systems that include a multi-component polymer and cross-linker.

The ultimate purpose of the project is to develop, evaluate, qualify, and commercialize self-thickening agents for increasing oil recovery and mitigating water production, thereby extending the life of mature wells. The technical approach for this Phase I laboratory study has been:

- Identify available self-thickening systems that are expected to have desirable physical properties.
- Screening different systems to identify best candidate products for further study

- For these best products demonstrate the desirable self-thickening effect in flow through porous media laboratory experiments.

Yet more detailed laboratory study would have been conducted in a Phase II program to qualify some products for potential commercial deployment. However, this Phase II proposal submitted to DOE was rejected in July of 2011. Because the Phase II proposal was rejected, this Phase I Final Report is required and is being completed written before its November 2011 deadline.

Experimental

Static Ageing Tests

This Phase I, initial testing has focused on several different synthetic co-polymers that have two or more chemical groups. These chemicals were dissolved at a concentration of 2500 ppm into different salt solutions (sodium chloride, potassium chloride, and calcium chloride) that encompass a range of dissolved salt concentrations. For the sodium chloride and potassium chloride solutions the salt concentration ranged from 1 – 5 wt%. The calcium chloride dihydrate sample concentrations ranged from 0.1 – 1 wt%. One set of samples being aged at room temperature, and a second set at 50 °C. Each set includes a sample for each salt composition.

At specified times, sample bottles were selected to have their bulk viscosity measured with a Brookfield viscometer at their ageing temperature. The frequency to re-measure the solution viscosities was designed to be greater near the start of the experiment in case there are any early time fast dynamics.

Flow Tests in Sand Packs

In one series of flow tests aged chemical solutions that exhibit an increase in viscosity with ageing time are injected into sand packs at constant rate and at room temperature. One of these is a solution freshly made, and also for two solutions aged for different lengths of time. The aged solutions have successively higher bulk viscosities with increased ageing time.

The sand packs are Ottawa sand (called F-95 from U.S. Silica – median grain size near 70 mesh), in a SS316 tubing, and has a dimension of 3/16-inch O.D., with an I.D. of 1/4-inch and a total length of 20-inches. The brine permeability is between 5 – 7 Darcies.

The injection pressure is measured for at least several pore volumes injection of the subject chemical solution where there is a steady-state condition. Chemical solution is injected for two different rates. The Resistance Factor (RF) is determined for chemical solution injection at each injection rate. The RF is the increase in injection pressure as compared to brine under the same conditions (i.e. the relative decrease in apparent permeability). This is followed by injecting again the brine solution at two different flow

rates for an extended period of time to determine the Residual Resistance Factor (RRF). Similar to the RF the RRF is the increase in injection pressure as compared to brine under the same conditions (i.e. the relative decrease in apparent permeability).

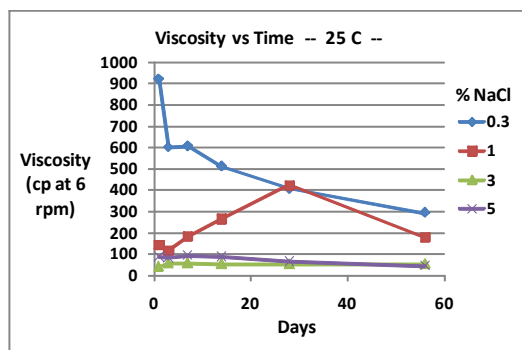
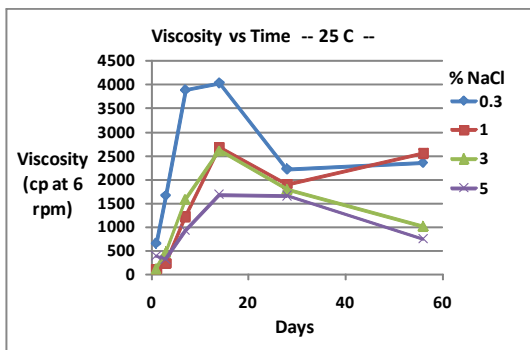
In a second series of sand pack flow tests fresh chemical solution is injected into 3 different sand packs. One sand pack is flushed quickly with brine as a base case. The other two packs are flushed with brine after different lengths of time of aging. The purpose of this test series is to determine the effect of an expected increase in solution viscosity as it ages in-situ. Each pack is restarted with injection of brine at constant rate and the injection pressure is recorded. This pressure is expected to be higher for sand packs with longer aging time, reflecting the in-situ self-thickening effect of the injected chemical solution.

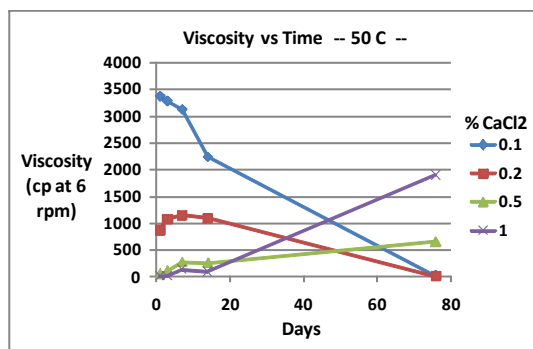
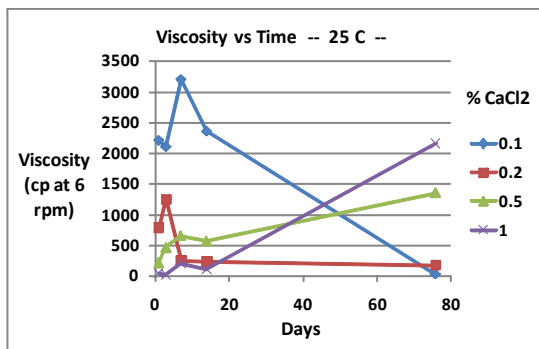
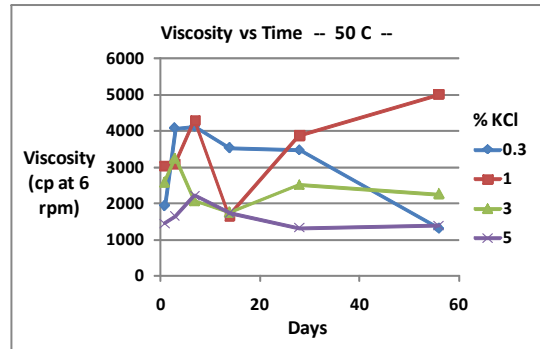
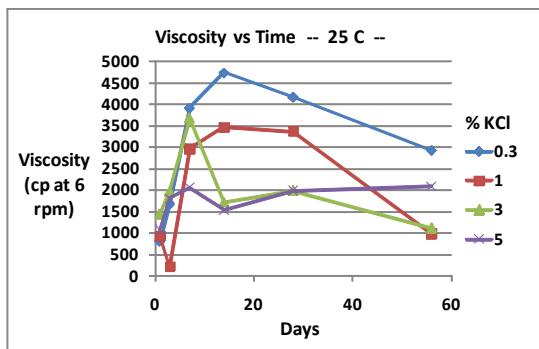
Results and Discussion

Static Ageing Tests

The many figures below summarize the change in the polymer solution viscosity with ageing time. Again, this encompasses a range of brine salinities (sodium, potassium, and calcium chlorides) for several candidate chemistries.

Of the five polymeric-surfactant polyacrylamide modified chemistries investigated in detail, two of them exhibited distinct increases in their solution viscosity versus time under particular process conditions of make-up water salinity and temperature. Data are shown below for the product Polymer 1 examined for its behavior in NaCl, KCl, and CaCl₂ brines at different concentrations. (This same matrix of salinities and temperatures was used to evaluate other candidate polymeric-surfactant compounds).





Figures 1 – 6. Time dependent viscosity behavior of the product Polymer 1 in different brines.

This particular product generally had the most success in exhibiting an increase in the solution viscosity with aging time. Note the viscosity behavior at the combinations of salinity and temperatures of: lower NaCl concentration at 25 C and at 1% KCl at the 50 C aging condition.

A second product that showed good increase in viscosity with time is the Polymer 2. The most interesting behavior found was in synthetic field brine with the composition of:

Concentration (gram/liter)

NaCl	15.4
CaCl ₂ .2H ₂ O	2.54
MgCl ₂ .6H ₂ O	2.1

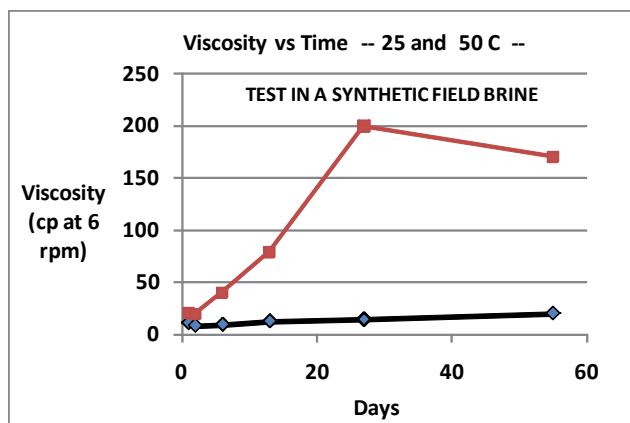
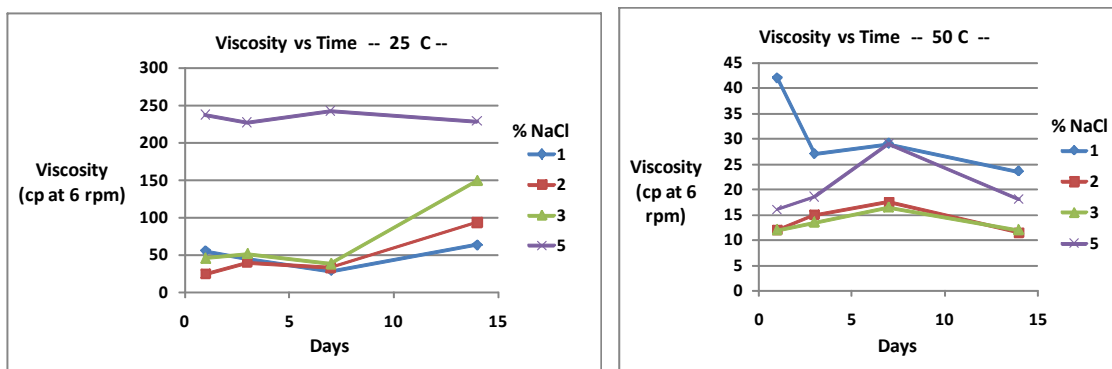


Figure 7. An increase in viscosity with time is seen for the Polymer 2 in the synthetic field brine.

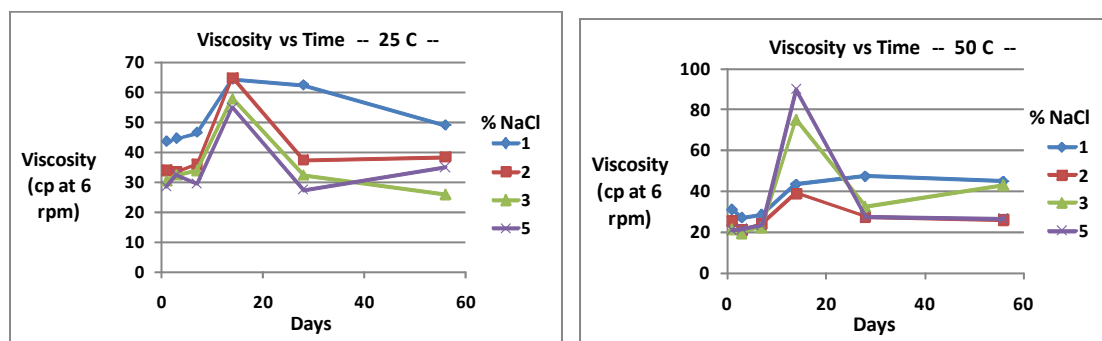
There also are some promising results for this product dissolved in NaCl at 25 C:



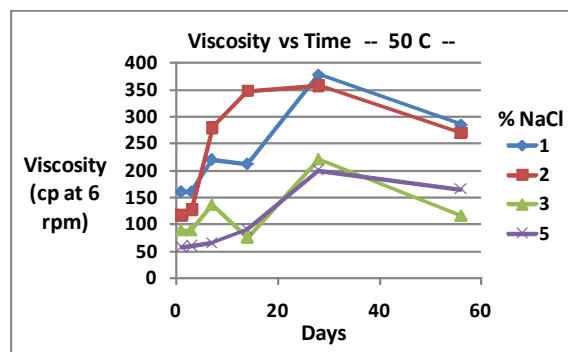
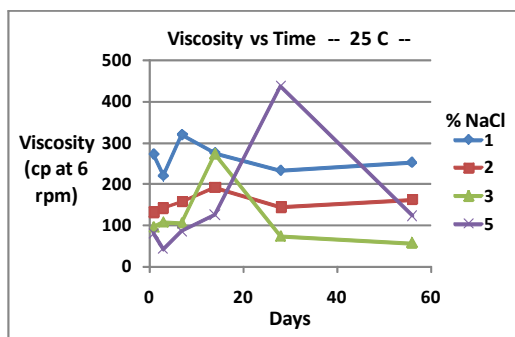
Figures 8 – 9. Solution viscosity versus time in NaCl brines at 25 and 50 C for Polymer 2.

Less favorable response was observed for Polymer 2 in KCl and CaCl₂ brines (data not shown).

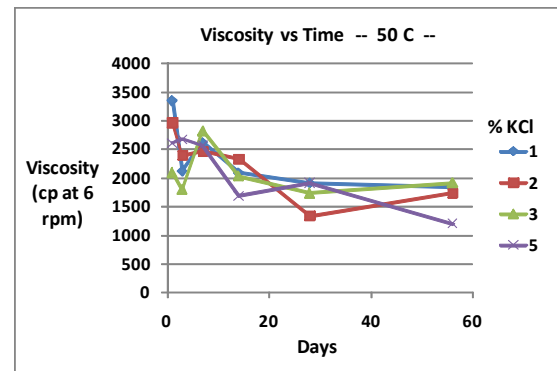
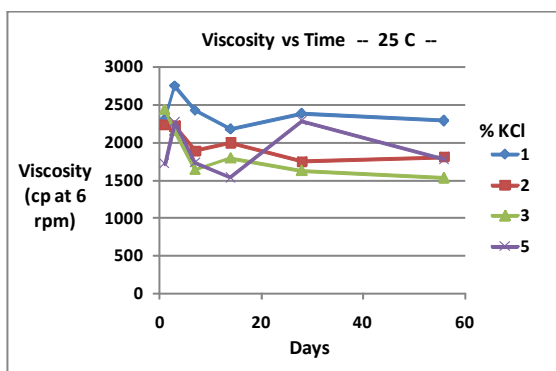
Other products tested did not exhibit a clear trend for increasing viscosity with time. Some selected laboratory data are shown for these other three chemicals, Polymers 3, 4, and 5.



Figures 10 -11. Solution viscosity versus time in NaCl brines at 25 and 50 C for Polymer 3.



Figures 12 – 13. Solution viscosity versus time in NaCl brines at 25 and 50 C for Polymer 4.



Figures 13 – 14. Solution viscosity versus time in KCl brines at 25 and 50 C for Polymer 5.

Polymer 4 perhaps shows a favorable trend of increasing viscosity at lower NaCl salinities when aged at 50 C.

Flow Tests in Sand Packs

Flow Tests - Increased Resistance by Aged T85 Solutions

The next series of experiments demonstrate the capability of a self-thickening solution to exhibit a higher apparent viscosity when in flow through porous media.

First flow test series – aged solutions injected into sand packs

The procedure was to first create three identical sand packs. These use 3/4-inch O.D., 1/4-inch I.D. SS316 pierces of tubing about 20-inches long. These are packed with Ottawa sand of approximately 60-mesh, and have brine permeability of 5 - 6 Darcies. Each of these had injected a series of fluids:

- 1% NaCl brine -- 1 and 2 ml/min
- Aged Polymer 1 2500 ppm in 1% NaCl -- 0.5 ml/min
- Aged Polymer 1 2500 ppm in 1% NaCl -- 0.1 ml/min
- 1% NaCl brine -- 0.5 ml/min
- 1% NaCl brine -- 1 ml/min

The inlet pressure is measured continuously.

The three slim tubes each use a different aged chemical solution as follows:

Tube #1 -- fresh chemical solution -- measured viscosity at 25 C, 8 sec-1 -- 74 cp
 Tube #2 -- aged 7 days -- measured viscosity at 25 C, 8 sec-1 -- 285 cp
 Tube #3 -- aged 13 days -- measured viscosity at 25 C and 8 sec-1 -- 1287 cp

The plot below shows the increase in apparent bulk solution viscosity versus time for the polymeric-surfactant solution used in these sand pack injection tests.

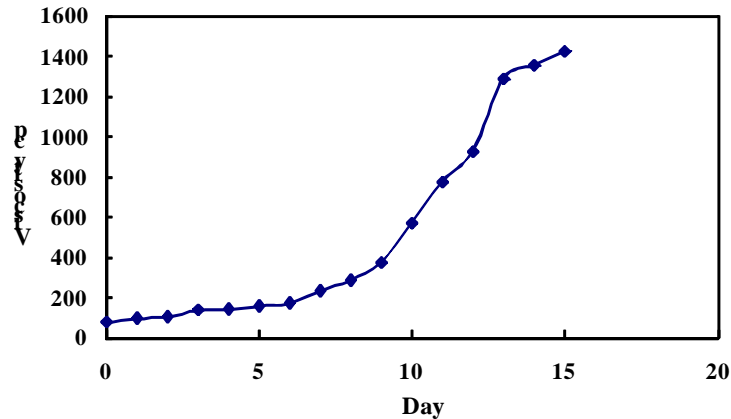


Figure 15. Increase in bulk solution viscosity for 2500 ppm Polymer 1 in 1% NaCl, 25 C.

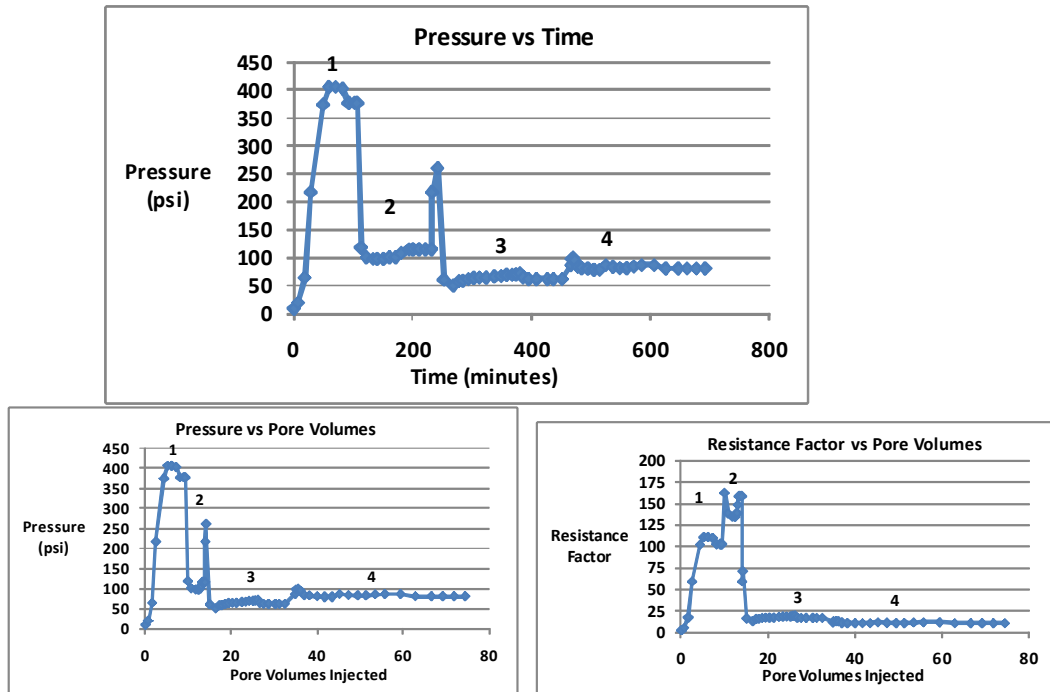
A summary of the first series sand pack flow experiments is given below. This demonstrates the

		Sand Pack 1 Day 0 - Initial Chemical Solution			
Test Sequence	Fluid Viscosity (cp)	Flow (ml/min)	Pressure (psi)	Resistance Factor	
1	76.5	0.5	175	55	
2	76.5	0.1	85	130	
3	1	0.5	45	12	
4	1	1	70	10	
		Sand Pack 2 7 Days aging of chemical solution			
Test Sequence	Fluid Viscosity (cp)	Flow (ml/min)	Pressure (psi)	Resistance Factor	
1	234	0.5	400	120	
2	234	0.1	115	160	
3	1	0.5	65	20	
4	1	1	90	12	
		Sand Pack 3 13 Days aging of chemical solution			
Test Sequence	Fluid Viscosity (cp)	Flow (ml/min)	Pressure (psi)	Resistance Factor	
1	1287	0.5	500	145	
2	1287	0.1	220	325	
3	1	0.5	105	30	
4	1	1	110	15	

injection pressure does increase (and so also the Resistance Factor, RF) with the injection of an aged chemical solution that has a greater measured bulk solution viscosity. Note that the RF

represents the ratio of the injection pressure during chemical injection to the injection pressure that would occur if it was brine injection at the same rate. Another trend is an increase in the Residual Resistance Factor (RRF) after injection of a chemical solution aged longer and having a higher solution viscosity. The RRF represents the ratio of injection pressure when pumping through a brine post-chemical injection to what the injection pressure was with brine initially before any chemical injection at that same flow rate. One more observation is that the RF increases with a decrease in the chemical injection rate; this is consistent with the view that the higher flow rate (higher shear rate) leads to a lower apparent viscosity (shear-thinning behavior).

The details of the results are shown for the Sand Pack #2 as an example of the data collected.



Figures 16 – 18. Inject 2500 ppm Polymer 1 aged 7 days in 1% NaCl, Sand Pack 2, 25 C. The steps denote 1) chemical injection, 0.5 ml/min, 2) chemical injection, 0.1 ml/min, 3) brine injection, 0.5 ml/min, and 4) brine injection, 1 ml/min.

Second flow series – chemical solutions aged in-situ in sand packs

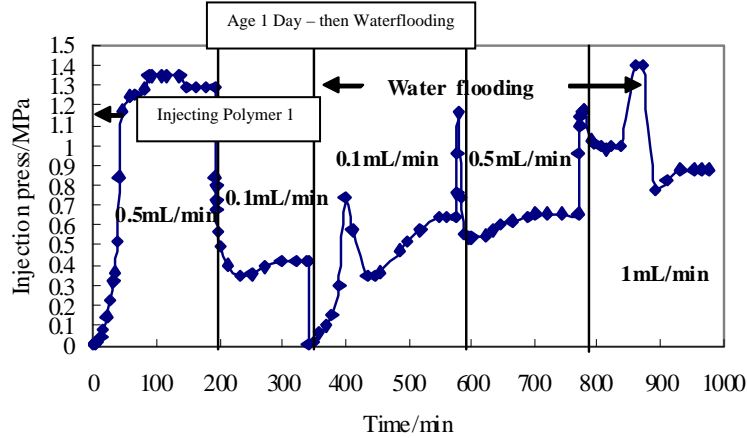
The procedure was to first create another three identical sand packs. These also use 3/4-inch O.D., 1/4-inch I.D. SS316 pierces of tubing about 20-inches long. These are packed with Ottawa sand of approximately 60-mesh, and have brine permeability of 5 - 6 Darcies. Each of these had injected a series of fluids:

- 2500 ppm Polymer 1 in 1% NaCl -- 0.5 and 0.1 ml/min
- Shut-in the pack and allow the chemical solution to age in-situ;

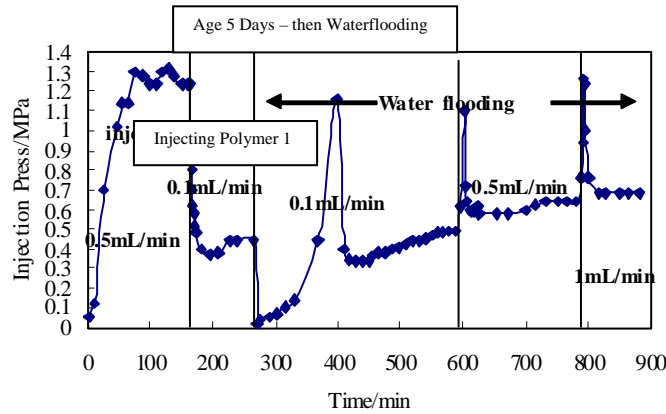
Figure 15 reflects the anticipated bulk solution viscosity increase with time. In-situ ageing times included 1, 5, and 17 days:

- Restart injection with 1% NaCl brine -- 0.1 ml/min
- Continue injection of 1% NaCl brine -- 0.5 and 1 ml/min

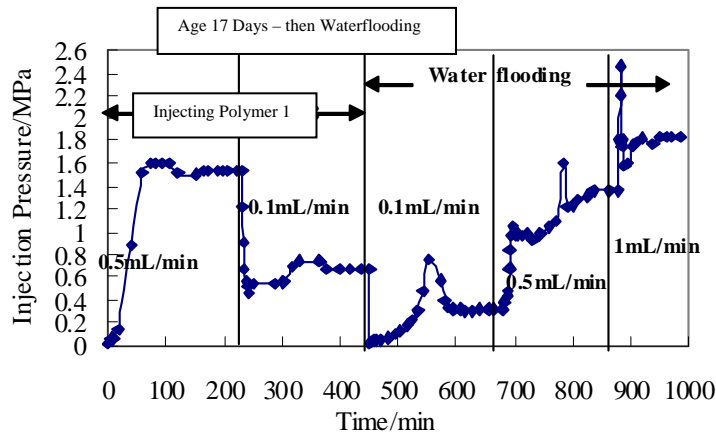
The figures below show the pressure history for these three sand pack experiments #4, #5, and #6.



Pack #4



Pack #5



Pack #6

Figures 19 – 21. Injection of 2500 ppm Polymer 1 in 1% NaCl into different sand packs at 25 C. Pack #4 – aged 1 day; Pack #5 - aged 5 days; Pack #6 - aged 17 days after polymer injection – and before post-flush with 1% NaCl brine.

As expected, the injection pressure is quite similar for the initial chemical solution for all three sand packs. These results then indicate the brine flow resistance after chemical injection increases with additional shut-in aging time of the chemical fluid in a sand pack – especially when comparing the results for the Pack #6 (17 days aging time) versus Pack #4 (1 day ageing time). For example, the inlet pressure (and hence the RRF) is more than twice as high for the Pack #6 and Pack #4 at a flow rate of 0.5 ml/min and 1 ml/min.

An unexpected result is that the injection pressures are similar during the 1% NaCl brine post-flush for the Pack #4 (1 day ageing time) and the Pack #5 (5 days ageing time). The additional ageing time for Pack #5 should have created a significantly greater solution viscosity for the Polymer1 inside that sand pack. The RRF values are roughly the same in each case if comparing the steady-state inlet pressures during the brine injection steps at the same flow rates. One difference is that for the Pack #5 the first pressure spike after injection of brine is considerably higher than that for the Pack #4 higher (1.2 MPa). This would be consistent with the notion of the brine displacing a more viscous in-situ polymer solution.

Conclusions

The laboratory experiments described in this investigation demonstrate the feasibility of developing modified polymer chemistries that exhibit the property of spontaneous “self-thickening” effect when dissolved in the right combination of brine salinity and temperature.

Static ageing experiments show this increase in viscosity can be as much as a ten-fold effect within two months of ageing time.

This increase in bulk viscosity with exposure time also can be seen in sand pack flow tests. In the first flow series, polymer solutions that are fresh and also those that are aged initially are injected into identical sand packs. As expected, the aged solutions having higher bulk viscosity increase the flow resistance more than that when injecting a fresh polymer solution of a lower bulk viscosity.

For the second series of flow tests the same fresh polymer solution is injected into different sand packs with identical properties. The expected trend in pressure response is observed when restarting these sand packs after allowing for different times. This sand packs with longer ageing time and having inferred higher viscosity exhibit greater flow resistance during post-flush brine injection.

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