



**Report on Grimbeek
Chemical Enhanced Oil Recovery Project**

Phases 1–2

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EXECUTIVE SUMMARY

The overall objective the laboratory study is to develop an ACP or ASP formulation and to determine the performance of the formulation for the on-shore Grimbeek reservoir in Argentina. The purpose of Phases 1 and 2 of the laboratory study is to determine the feasibility and favorability of Alkali-Cosolvent-Polymer (ACP) and Alkali-Surfactant-Polymer (ASP) formulations. A formulation with an ultra-low interfacial tension (IFT) is desired for ACP flooding. An ASP flooding process will be considered if an ultra-low IFT cannot be reached with ACP. The results of Phases 1–2 of the laboratory investigation are detailed in this report, which includes polymer rheology and microemulsion phase behavior studies with Grimbeek crude oil conducted at reservoir temperature, 60°C. Future work includes two outcrop corefloods and two reservoir corefloods. The formulations used in the phase behavior experiments excluded polymer, as it was unnecessary in initial IFT studies.

Grimbeek is located at San Jorge's Gulf Basin in Argentina, in the Manantiales Behr area. There is a large volume of oil and natural gas in place (about 900 million bbls) at a reservoir temperature of 60°C. The formation brine salinity is about 21,654 ppm TDS (total dissolved solids) and the reservoir has good permeability. The reservoir rock has been characterized into two types, one with a 2,000 mD average permeability and the other with 200 mD. The porosity is between 25 and 35%.

The Grimbeek oil is medium heavy with an API gravity of 21 and an average viscosity of 120 cP at reservoir conditions produced from the Complejo II of El Trebol formation. The productive sands are found at 1050 m deep, with 50 meters of total thickness, and approximately 10 meters of this are productive. The productive area consists of various stacked layers, each 2-3 meters thick. The original reservoir pressure was around 50 kg/cm². PVT studies showed the crude oil has a bubble pressure around 35 kg/cm². The exploitation is primary production, with a current pressure of 20 kg/cm².

Polymer rheological measurements confirm a polymer concentration range of 2,500-3,000 ppm is required for generating a sufficiently viscous solution at a target viscosity of 50 cP. Polymer compatibility with the formulation will be assessed prior to the corefloods, once the final formulation is established.

Microemulsion phase behavior studies were performed with various cosolvents, surfactants, and surfactant blends using dead Grimbeek crude oil. A robust ACP formulation was not found during the ACP phase behavior study, as the best ACP formulations had only a very narrow ultra-low IFT region that was not adequate. Therefore, ASP formulations were examined and high-performance ASP formulations were identified. **The most favorable ASP formulation consists of 0.2% 2-ethylhexyl-4PO sulfate (2EH4S), 0.2% T-Soft SA-97 (a medium ABS), and 0.5% isobutylalcohol-1PO-5EO (as cosolvent).** This formulation exhibits an ultra-low interfacial tension ($<10^{-3}$ dynes/cm) at the optimal salinity of about 1% Na₂CO₃ (with 30% oil) based on visual observations of the fluids during the pipette tilt technique. Grimbeek oil is an active oil, thus in presence of alkali in-situ soap is produced mainly from acids in the oil. Due to the interactions of the synthetic surfactants in the formulation with the in-situ soap, the solubilization ratio plots may not accurately represent the true solubilization value. The solubilization ratio calculation includes a total surfactant concentration term (Appendix B), which in this case would be the total amount of synthetic surfactant and the amount of in-situ soap produced (that is unknown). The formulation exhibits a good performance in the phase behavior experiments and the favorable properties required for ASP flooding. This ASP formulation is recommended for further testing in corefloods experiments.

During the coreflood experiments, the surfactant retention of anionic surfactants is expected to be lower with ASP relative to SP as the reservoir is a sandstone. In addition, the production of natural soap from the active crude oil at alkaline pH will further help reduce the concentration of synthetic surfactants

required in the formulation and the adsorption of the synthetic anionic surfactants. A reduction in surfactant retention through the use of alkali can have a significant effect on the economics of the project. The results of the coreflood study will be used to determine if further optimization of the formulation is necessary.

RECOMMENDATIONS

A suitable alkali-surfactant-polymer (ASP) formulation has been identified through the initial phases of the laboratory scope. UEORS recommends further testing of the ASP formulation performance in two outcrop and two reservoir corefloods, focusing on a flood design for a low chemical retention. In the first coreflood, we recommend testing the ASP formulation identified in Phase 2, with an emphasis on measuring the oil recovery and surfactant retention.

Based on the results of the first coreflood, another outcrop coreflood will be performed, evaluating chemical retention and surfactant concentration strategies to maximize oil recovery economics. Finally, 2 reservoir corefloods will be conducted to evaluate the formulation performance and flood design in representative reservoir sandstone. The data gathered from these laboratory tasks will be used for modeling and simulation studies, including pilot and field-wide simulations.

SCOPE OF WORK

The scope of work performed for this study is listed below.

Phase 1: Quality Control and Polymer Evaluation

Description: The purpose of this phase is to ensure the quality of crude oil, water, and reservoir cores. Core plugs will be examined so only representative cores are used. Crude oil will be screened for water and contamination. The quality of the injection water will be examined in terms of suspended solids, pH, TDS and limited ionic composition (Ca^{+2} , Mg^{+2} , Na^+ , Cl^- and others not including carbonate ions). Polymer rheology will be examined for the corefloods. Activities/deliverables for this phase includes:

- Brine ion analysis
- Crude oil/water interfacial tension check
- Dewater oil (*added to scope due to quality of oil received*)
- Filter oil (if necessary)
- Polymer rheology to confirm appropriate polymer concentration for corefloods

Phase 2: ACP Formulation Development

Description: The purpose of this phase is to follow up on the ACP formulation developed at UT with favorable characteristics for use in core flooding experiments. ASP will be evaluated if the ACP performance is substandard. A favorable formulation will show ultralow interfacial tension (IFT) between water and oil over a wide range of salinity with an optimum salinity appropriate to injection water compositions, low microemulsion viscosity, orderly phase transition with salinity, aqueous stability in injection brine, proper mobility control characteristics, long term stability at the reservoir condition and economic concentrations of chemicals. Activity of oil in presence of alkali will be evaluated and optimum cosolvent and its concentration will be chosen based on phase behavior pipettes. Compatibility of polymer with the formulation and aqueous stability will also be tested. Activities/deliverables for this phase includes:

- Crude oil activity (natural soap generation) evaluation
- Microemulsion salinity scans and analysis with several formulations in parallel
- Aqueous stability measurements
- Surfactant synthesis of custom chemicals (as needed)

Phase 3: Evaluation of ACP formulation in Outcrop Cores

Description: These tests evaluate the rock-fluid compatibility of ASP/ACP fluids selected for injection. Typically it will involve 2 outcrop corefloods; (1) an initial coreflood to evaluate the effectiveness of the basic formulation and (2) a second outcrop coreflood using a modified/optimized design based on the information gained from the first coreflood. All corefloods will be done in 12" at reservoir temperature and we will measure oil recovery, pressure drop, alkali propagation (in the form of pH), salinity propagation, emulsion production, pressure drop and co-solvent and polymer retentions. Activities/deliverables for this phase includes:

- Microemulsion dilution scan
- Microemulsion rheology evaluation
- Surfactant compatibility with polymer used in coreflood
- Selection of representative outcrop cores
- Restoration of cores to reservoir representative conditions
- 2 corefloods using ASP/ACP formulation & surrogate oil
 - #1 – ASP/ACP oil recovery flood in outcrop rock
 - #2 – ASP/ACP oil recovery flood in outcrop rock for flood design optimization
- Evaluation of surfactant retention using HPLC
- Measurement of saturation and other coreflood results

Phase 4: Evaluation of ACP formulation in Reservoir Cores

Description: These tests evaluate the final recovery from the reservoir cores and the final retention of chemicals. Corefloods will be done in 12" composite cores made from preserved, previously frozen Grimbeek reservoir rock. We will measure oil recovery, pressure drop, alkali propagation (in the form of pH), salinity propagation, emulsion production, pressure drop and surfactant or cosolvent retention. The second coreflood can be used for either optimization purpose or alternative chemical design. Activities/deliverables for this phase includes:

- Core reconditioning by flood with surrogate oil
- 2 corefloods using best formulation
 - #1 – oil recovery flood in reservoir composite core
 - #2 – oil recovery flood in reservoir composite core with polymer flood after waterflood (additional fee applies)
- Evaluation of surfactant retention using HPLC
- Measurement of saturation and other coreflood results

Phase 5: Coreflood History Match and Parameter Development

Description: Laboratory tests, including phase behavior, polymer/microemulsion rheology, and coreflood performance will be modeled using UTCHEM. These mechanistic input parameters will then be translated to CMG-STARs input file to be used for large-scale field simulations. All these parameters will be provided to YPF for use in their in-house simulation studies. We will also provide the base case input file for tracer test simulation in Grimbeek.

PHASE 1.1: QUALITY CONTROL EVALUATION

The objective of the brine quality control investigation is to confirm the composition of brine available for injection for Grimbeek field. The objective of the oil quality control testing is to make sure representative oil is used in the formulation development.

BRINE ANALYSIS

Brine sample before and after water treatment were received in late June 2016 (**Figure 1.1**) for compositional analysis. Samples do not show substantially different ionic compositions. The water samples are also consistent with previous brine analysis (Feb 2010 and Sep 2014 data for Myburg 5). The brine composition as measured for the **after water-treatment sample** will be used for this laboratory study. Its softened version is derived from the original composition by replacing the divalent cations with equivalent sodium ions. The details of the brine composition can be found in **Appendix A**.



Figure 1.1: Brine sample received



Figure 1.2: Crude oil sample received



Figure 1.3: Estimated 20-25% water content in crude oil

CRUDE OIL EVALUATION

About 20 L of crude oil was received in late June 2016 (**Figure 1.2**). The interfacial tension against water was found to be ~ 26 mN/m, a reasonable value that indicates a low probability of contamination. The viscosity of the crude oil received was measured at ~ 415 cP, higher than GBK-663 oil sample at UT of 213 cP, both measured at 60°C. The viscosity of crude oil with 5% toluene was measured at 157 cP (60°C),

higher than the GBK-663 oil + 4% toluene viscosity of ~120 cP. After the initial investigation, it was found that the crude oil sample received has about 20-25% water content as seen in **Figure 1.3**, which explains the high apparent viscosity.

A surrogate oil prepared from dewatered oil with 4% toluene was 126 cP, which falls at about the appropriate viscosity as the UT sample, furthermore it is similar to the live oil viscosity as reported in the PVT report. The choice of surrogate diluent was confirmed in EACN calculation tests. **Figure 1.4** summarizes the EACN study, where the dead crude oil EACN was estimated at 6. The amount of diluent (4% toluene) was calculated based on live oil composition as in the PVT report and the dead oil EACN value.

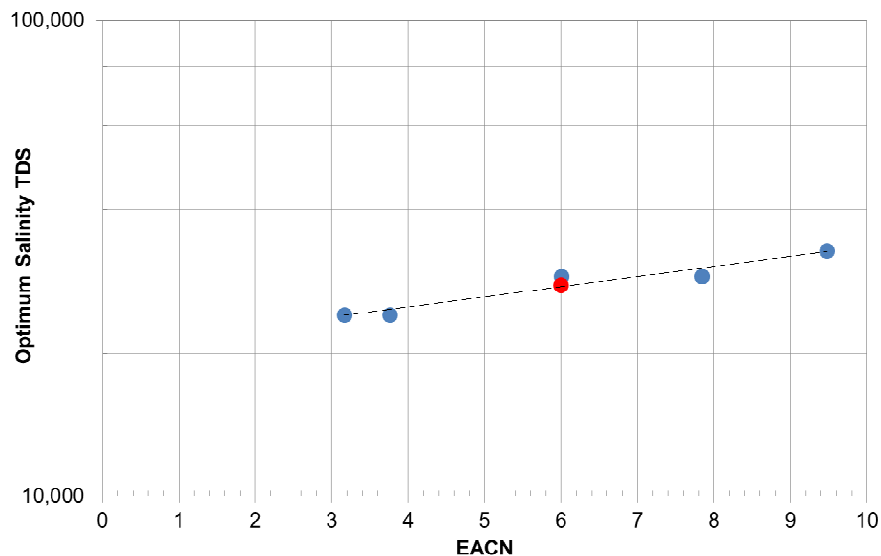


Figure 1.4: Optimal salinity vs EACN for several diluent (blue) and dead crude oil (red)

RESERVOIR CORE

Figure 1.5 shows the twelve core plugs preserved in wax received in late June 2016. The cores should be enough for two reservoir composite cores provided none of the plugs exhibit extreme properties. The cores were kept in the freezer since arrival, and will remain there until just prior to use.



Figure 1.5: Reservoir Core sample as received

PHASE 1.2: POLYMER RHEOLOGY

SAMPLE PREPARATION

The objective of the polymer rheology was to establish if the polymer sample meets the current Grimbeek polymer qualifications for the field. Rheology, filterability, and compatibility were tested at flood conditions. The polymer tested was FP 3630S, a partially hydrolyzed polyacrylamide (HPAM), with comparable performance to the FP 3631 polymer used in the Grimbeek polymer pilot

A parent polymer solution of 5,000 ppm FP 3630S was prepared in softened Grimbeek injection brine (SGIB). Using this parent stock, three dilutions were made to make 1,500 ppm, 2,250 ppm, and 3,000 ppm polymer in SGIB with 0.25% Na_2CO_3 and 1.5% Na_2CO_3 content. The brine compositions were chosen to generate rheological data across varying salinities. Filtration and rheology were performed for each sample.

FILTRATION

The objective of this investigation was to determine if the polymers had appropriate filterability properties. The filterability of the polymer sample was measured via filtration ratio experiments. Details of the filtration procedure is available in the **Appendix C**.

The filtration ratio calculation results are shown in **Table 1.1** where green indicates an acceptable filtration ratio value (a F.R. less than 1.2) and red (if applicable) would indicate that the filtration ratio was greater than 1.2 (i.e. a failed filterability experiment). All polymer solutions showed excellent filtration.

Table 1.1 Filtration Ratio Results

	1,500ppm	2,250ppm	3,000ppm
FP3630S in SGIB + 0.25% Na_2CO_3	0.99	1.02	1.04
FP3630S in SGIB + 1.5% Na_2CO_3	1.04	1.01	1.00

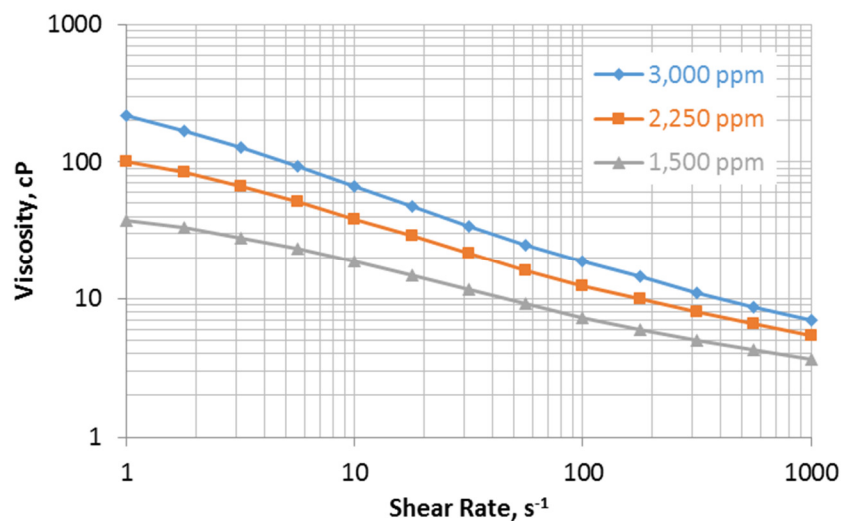


Figure 1.6: FP3630S in SGIB + 0.25% Na_2CO_3 (14,001 ppm TDS) 60°C

RHEOLOGY

Rheological measurements help determine the concentration of polymer needed to obtain a sufficiently viscous solution for stable displacement during the flood. The viscosity was measured of the FP 3630S polymer. **Figures 1.6-1.7** show viscosity versus shear rate curves at multiple concentrations for the estimated Grimbeek coreflood conditions. Typical shear-thinning behavior is observed as expected for HPAM. **Figure 1.8** shows the polymer viscosity versus concentration for FP 3630S. It shows the viscosifying power of FP 3630S in the corresponding injection brine. The values from previous studies at UT were also included. All data presented was for a viscosity at 7.3 s^{-1} shear rate (the approximate condition at the end of chemical flood in $\sim 700 \text{ mD}$ core).

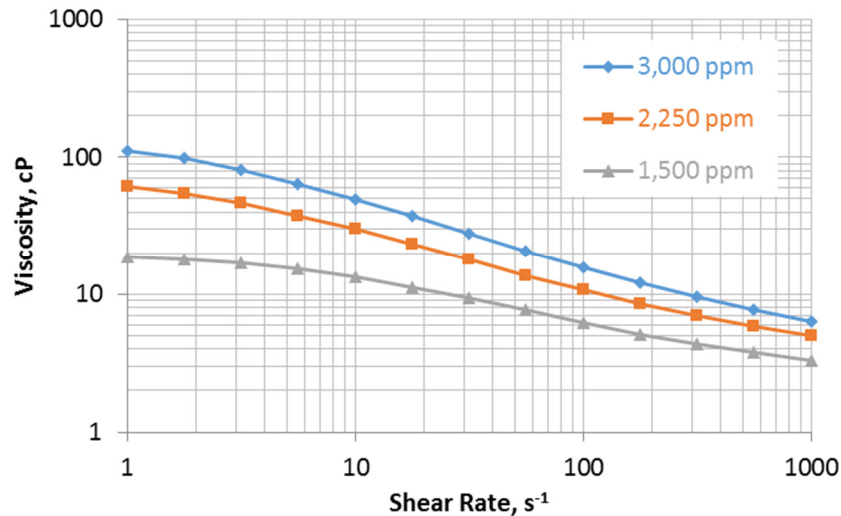


Figure 1.7: FP3630S in SGIB + 1.5% Na_2CO_3 (26,501 ppm TDS) 60°C

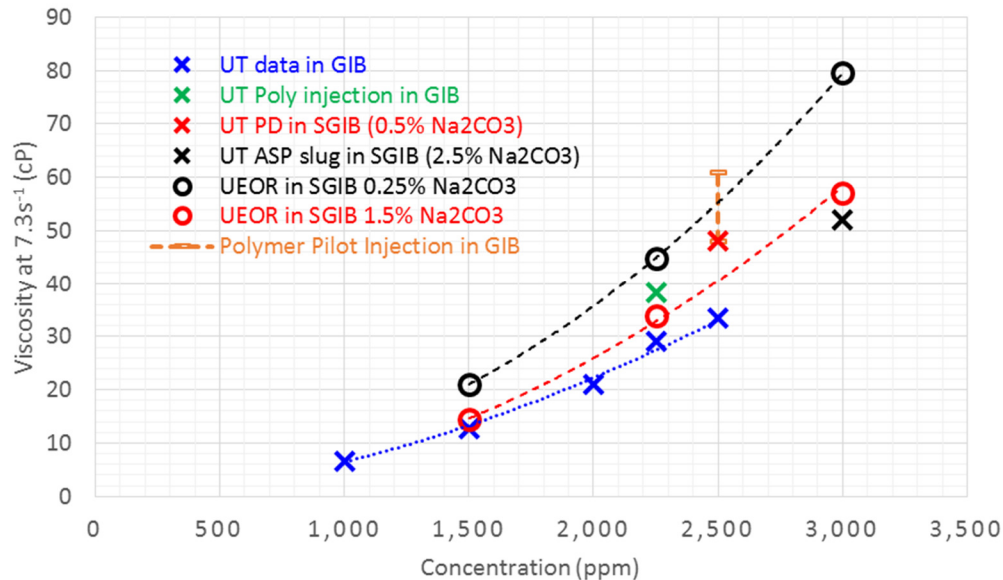


Figure 1.8: FP3630S and FP3631 (pilot) in GIB (hard brine) or SGIB (soft brine) at 60°C with Na_2CO_3 concentration indicated where applicable

According to preliminary studies, it has been estimated that a polymer solution viscosity around 40 cP, at reservoir conditions, will provide mobility control and will be economically appropriate. The SNF company had recommended the evaluation of the FLOPAAM 3630S products with a molecular weight around 20-25 millions. Ongoing polymer injection pilot uses 2,500 ppm FP3631 polymer with available injection brine to make 48–61 cP solution at 60°C. The target viscosity for coreflood tests is set at 50 cP, matching the current injection viscosity. The approximate polymer concentration to reach 50+ cP solution is 3,000 ppm in SGIB with 1.5% Na₂CO₃ content or 2,500 ppm in SGIB with 0.25% Na₂CO₃.

PHASE 1 SUMMARY

Quality of materials received in June 2016 for the study were acceptable and the laboratory tasks could proceed. Rheology measurements were made with FP 3630S polymer at the appropriate coreflood conditions. Good polymer injectivity and transport were observed in previous YPF work with the University of Texas at Austin. It is anticipated that good polymer injectivity and transport will also be observed in during Phase 3 of the laboratory study.

PHASE 2: FORMULATION DEVELOPMENT

The objective of the microemulsion phase behavior study was to develop a high-performing chemical formulation using the Grimbeek crude oil. The formulation should be expected to give low retention, to reduce the interfacial tension to ultra-low values (on the order of 10⁻³ dyne/cm), and to also have adequate aqueous solubility (i.e. it must be a clear homogeneous solution at the injection salinity). Phase behavior salinity scans were used to identify ACP (alkali-cosolvent-polymer) or ASP (alkali-surfactant-polymer) formulations that exhibit the appropriate microemulsion phase transitions and interfacial tension necessary for mobilizing trapped oil in an efficient displacement process. Once formulations were developed with dead oil, surrogate oil (dead oil plus dilutant) was used in formulation optimization. ACP formulations were developed as the first priority of the project, with ASP formulations as a back-up if a high-performing ACP formulation was not found. A description of the phase behavior experiments and equations are in **Appendix B**.

Only commercially available surfactants/cosolvents and those chemicals that can be easily produced in commercial quantities were considered for this project. The selection of chemicals for the Grimbeek reservoir considered several aspects of the project. Early phase behavior scans indicated that the natural soap generated from the active oil showed high hydrophobicity. Therefore, significant hydrophilicity, such as with the addition of EOs (ethylene oxide units) to a surfactant, was necessary to balance the natural, hydrophobic soap. Toluene was added to oil used in phase behavior tests to match the live oil EACN value.

Alkali was included in the ACP and ASP formulation development work. Divalent cations precipitate with alkali, therefore softened injection brine was necessary for ACP and ASP formulation work. The performance of the formulation with hard injection brine will be assessed in the presence of a divalent ion chelating agent.

The moderate temperature of the Grimbeek reservoir gave a wide selection of chemicals, as minimal thermal stability requirements of the chemical components were needed. Sulfate surfactants were used in the formulations based on past performance experience of active oils around 60°C. Sulfonate

surfactants were also considered due to their synergistic and beneficial interactions with sulfate surfactants.

Cosolvents were also incorporated in the formulations, when the performance benefits were clearly identified. Cosolvents were the major component of the ACP formulations, however increasing the hydrophilicity of the nonionic cosolvents is difficult. Phenol type cosolvents were not included in the formulation development work due to environmental restrictions in the reservoir area.

BRINE

The injection brine used for the ASP/ACP phase behavior experiments was SGIB, Soft Grimbeek Injection Brine (unless otherwise explicitly stated). The composition of SGIB was based on ion analysis of actual brine available at the field. The compositions of the brines are available in **Appendix A**.

CRUDE OIL

The Grimbeek crude oil was screened for contamination and basic properties upon arrival. Surrogate oil with 4% toluene as the diluent was used for the most low-pressure phase behavior work. The choice of surrogate diluent was verified in an EACN scan with a preliminary formulation. The surrogate oil composed of 4% by weight toluene in the dead oil gave a comparable viscosity to the live oil as listed in the PVT report. Except when the oil scans were performed, the oil concentration examined during the phase behavior studies was 30% by volume (a WOR, water to oil ratio, of 2.33).

TEMPERATURE

All phase behavior experiments presented in this report occurred at 60°C.

SURFACTANTS, CO-SURFACTANTS, COSOLVENTS, ADDITIVES

The surfactants and cosolvents that were tested during the formulation development are listed in **Table 2.1**. Chemicals from manufacturers Harcros, Sasol, Huntsman, and Shell were included in this study. Over 160 different formulation experiments were completed for this project to date, which are over 1,600 phase behavior pipettes. Concentrations of surfactants and cosolvents are listed in weight percent in the formulations.

The effects of cosolvent on ASP phase behavior were examined in terms of interfacial tension, ultra-low IFT region (robustness), optimal salinity (or optimum), macroemulsion formation/properties, equilibration time, and aqueous stability. The viscosity of the phases, especially microemulsion and macroemulsion phases, were examined qualitatively. The IBA-EO type cosolvents were identified as the most promising based their performance relative to the other cosolvents.

Table 2.1: Chemicals tested during formulation development

Surfactants	Surfactants	Cosolvents
Enordet O332	2EH-10PO-sulfate	IBA-20EO
Enordet J13131	2EH-7PO-sulfate	IBA-10EO
Enordet J071	2EH-4PO-sulfate	IBA-5EO
Enordet J771	2EH-2PO-sulfate	IBA-1PO-5EO
Soloterra H113	2EH-4PO-2EO-sulfate	IBA-1PO-2EO
Soloterra H117	2EH-4PO-7EO-sulfate	IHA-1EO
T-Soft SA-97	2EH-4PO-10EO-sulfate	nBA-3EO
Novel TDA-30	TDA-25PO-40EO-sulfate	DIPA-10EO
Neodol 25-12	C18-25PO-15EO-sulfate	2EH-4PO-2EO
Neodol 25-7	C18-25PO-30EO-sulfate	2EH-4PO-7EO
Neodol 91-8	C18-25PO-40EO-sulfate	TDA-25PO-50EO
IBA-1PO-2EO-sulfate	C18-25PO-45EO-sulfate	
IBA-2PO-sulfate	C18-25PO-60EO-sulfate	
Coco Amido Propyl Betaine	C18-45PO-45EO-sulfate	
TSP-25PO-40EO-sulfate	C24-25PO-46EO-sulfate	

FORMULATION SELECTION AND OPTIMIZATION

ACP Formulations

During the alkali screening test, the Grimbeek oil was determined to be an active oil (an oil that can produce soap in the presence of alkali) as expected. Therefore, ACP type formulations were investigated, where the main source of surfactant comes from the natural soap produced from the oil. Cosolvents are included in the formulations to reduce viscosity, to adjust the optimal salinity, and to balance out the typically hydrophobic soap. ACP formulations, when available, can be an economical choice for some active oils due to lower chemicals costs in some reservoirs.

The alkali included in the formulation provides a source of anions (the alkali) may help to reduce amount of surfactant and cosolvent adsorption on the rock surface. Less adsorption may reduce the concentration of chemicals necessary for the flood. However, divalent cations must be removed from the injection brine (i.e. a soft injection brine is required) due to precipitation in mixtures with alkali.

Several cosolvents (please see **Table 2.1**) were assessed in ACP formulations including the most hydrophilic nonionic cosolvents in our inventory, however these formulations did not adequately balance the hydrophobic soap produced from the oil and therefore did not adequately reduce the IFT. **Figures 2.1-2.2** show the alkali scan for Grimbeek surrogate oil with IBA-ethoxylate cosolvent. Increasing the cosolvent concentration also could not balance the natural soap, it did not give advantageous result either as can be seen in **Figure 2.3**.

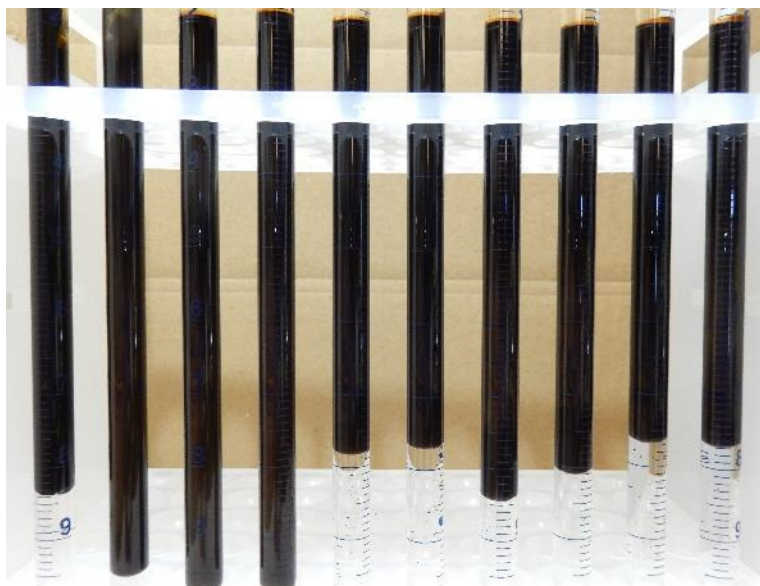


Figure 2.1 Phase behavior of Grimbeek oil (50% oil volume) with 1% IBA-20EO for 0.5-5% Na_2CO_3 in 11.5k ppm SGIB

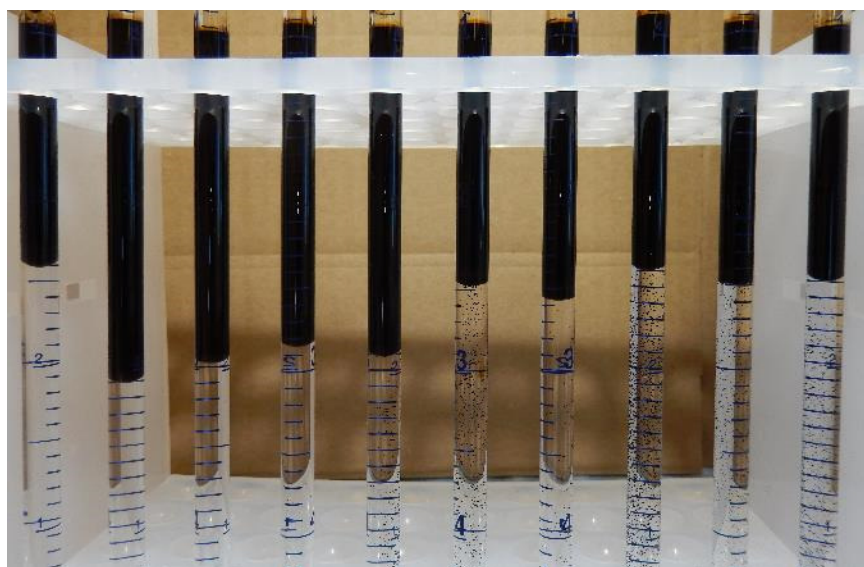


Figure 2.2 Phase behavior of Grimbeek oil (30% oil volume) with 1% IBA-5EO within 0-4.5% Na_2CO_3 concentration range in 11.5k ppm SGIB. Low IFT emulsion not observed.

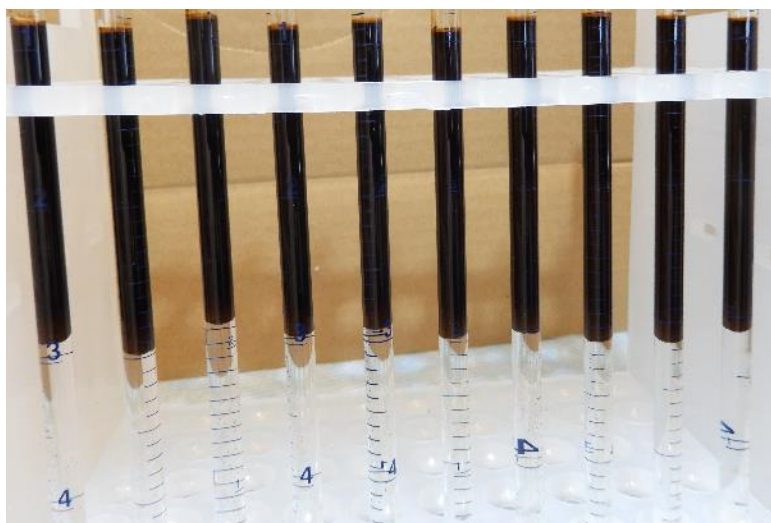


Figure 2.3 IBA-20EO concentration scan (0.75-3%) for Grimbeek oil (30% oil volume) with 0.25% Neodol 25-7 in 11.5k ppm SGIB

ASP Formulation-Recommended Coreflood Formulation

A new class of chemicals, 2-ethyl-hexyl alkoxy sulfates (EH) can either fall into the cosolvent category (due to its small molecule size) or the small surfactant category (due to its anionic group and cost range). These molecules generally do not work well alone, but when used with a larger traditional surfactant or natural soap, they can produce excellent results. These EH chemicals showed good interactions with diluted Grimbeek crude oil (+4% toluene) and alkali, producing ultra-low IFTs. This class of surfactant and its surfactant blends was further investigated.

The ASP formulations also use alkali, sodium carbonate (Na_2CO_3), to create the salinity scan. The injection brine is SGIB due to the precipitation of divalent cations in the presence of alkali. Most of the ASP phase behavior experiments were conducted with Grimbeek surrogate oil (~4% toluene).

Polymer was excluded from most phase behavior development and aqueous stability experiments to allow better mixing and faster equilibration. A set of phase behavior and aqueous stability tests were prepared for the best formulation with polymer. Polymer does not seem to affect the aqueous stability of the formulation. Its effect on the phase behavior is under ongoing observation.

The ASP-266 formulation recommended for Outcrop Coreflood 1 is listed below. It was selected based on the phase behavior results: appropriate optimal salinity and seem to show lower microemulsion viscosity than other candidates. The optimum salinity of this formulation was 1.0% Na_2CO_3 at 30% oil. Qualitatively, the IFT of the formulation was ultra-low at the optimal salinity with surrogate oil. The aqueous stability limit was 54,000 ppm TDS with and without polymer. The design plan for the first coreflood is to inject the slug over optimum salinity, therefore this ASP formulation has adequate excess aqueous stability. The ASP slug salinity selected for Outcrop Coreflood 1 is 1.5% Na_2CO_3 in SGIB (26,500 ppm TDS). The over optimum injection design was selected based on the current waterflood injection of ~11,300 ppm TDS. The salinity of the reservoir is expected to be at similar salinity prior to chemical slug injection. The 1.5% Na_2CO_3 is expected to provide the necessary concentration to reach the optimum salinity during ASP application, both in coreflood and field injection.

The 1.5% Na_2CO_3 injection salinity of ASP-266 formula is a significant improvement from formulation developed in previous YPF project of 2.5% Na_2CO_3 injection salinity. Lower alkali means better

mobility achieved with comparable polymer concentration and lower overall alkali cost. The 0.4% total surfactant and 0.5% cosolvent concentration of the ASP-266 formula are also more economical than previous formulation. Formulation with cosolvent shows orderly phase transition with salinity and lower microemulsion viscosity. The surfactant mixture has better overall performance in orderly phase transition and optimal salinity over individual surfactant and other surfactant ratio. More details on cosolvent and surfactant ratio study can be found in the **Appendix B**.

Outcrop Coreflood 1: ASP-266 Formulation

0.2% 2ethyl-hexyl-4PO-sulfate

0.2% T-Soft SA-97 (neutralized; light ABS)

0.5% IBA-1PO-5EO

1.5% Sodium carbonate in SGIB (~26,500 ppm TDS)

3,000 ppm FP3630S polymer (55–60 cP at 7.3s^{-1})

The ASP-266 formed a distinct Type I microemulsion at the 0.25% Na_2CO_3 concentration for all 10–40% oil. **Figure 2.1** shows the transition of microemulsion from low to high salinity, starting on the left to the right. As the salinity increases, the interface fades (4th tube from left of 40%; 1st–4th tubes of 30%; 2nd–4th tubes of 20%; the first 3 tubes of 10%), until it is hardly noticeable making one continuous Type III microemulsion phase (5th tube of 40% and 30%). The continuous single microemulsion phase suggests a very robust ultra-low IFT microemulsion. The low IFT range observed by visual tilt test inspection is indicated and include some Type I and Type II microemulsion that exhibit low IFT. Any of this phase behavior tube may show ultra-low IFT, but more equilibration time help better identification of the IFT, whether it stays at low IFT or develop to ultra-low IFT range.

Distinct Type II microemulsions were observed at 0.875% and higher Na_2CO_3 for 40% oil and at 1.25% and above for 30% oil. Pipettes with Na_2CO_3 concentration of 2.25% and higher for 20% oil and above 6% for 10% oil are also Type II microemulsion. The solubilization ratio cannot be plotted at this time. This formulation was chosen for further study in the outcrop coreflood based on the ultra-low IFT observed in the study. The phase equilibrium tubes shown in **Figure 2.1** are 5 days old and are equilibrating. Any progress will be monitored.

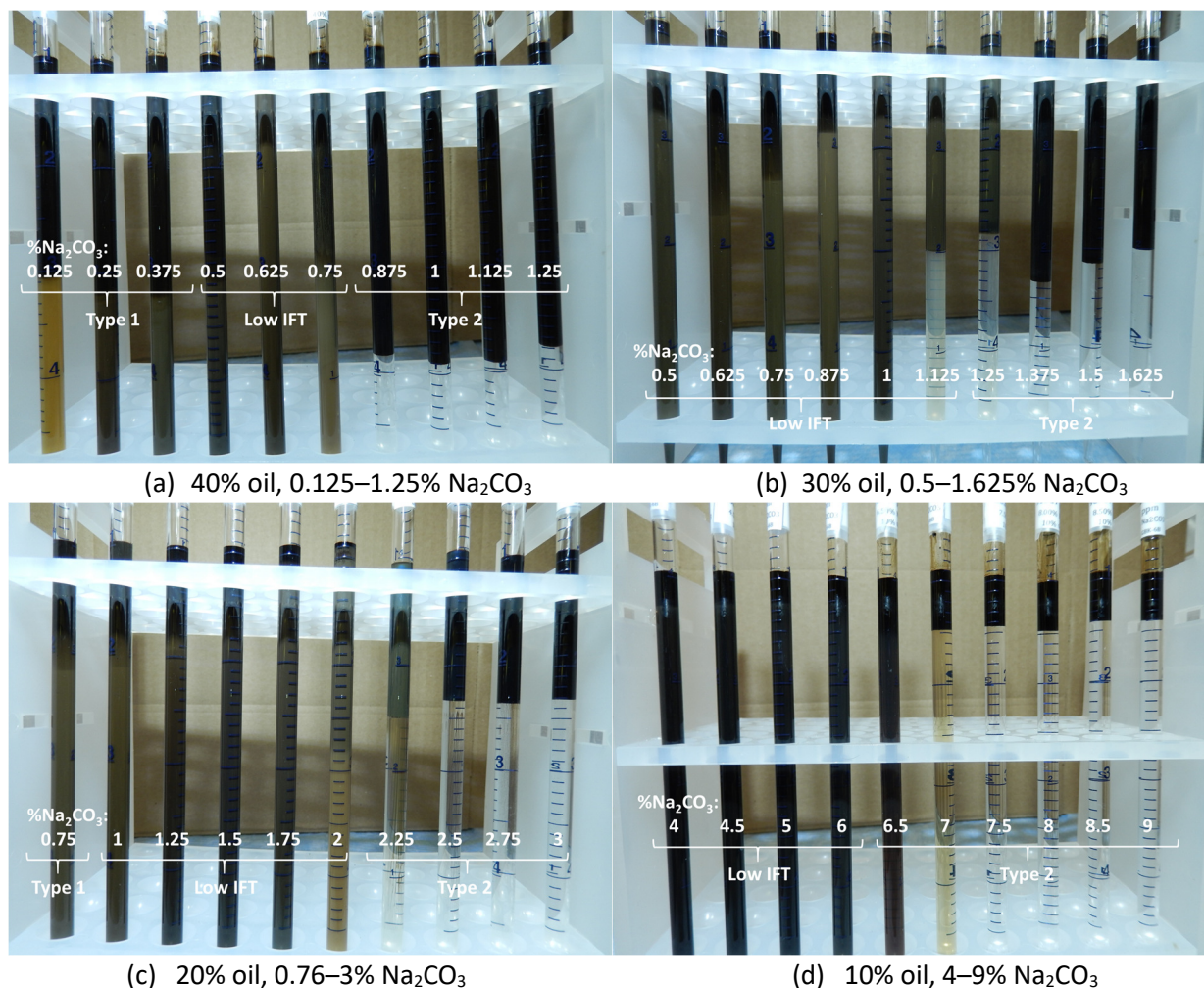


Figure 2.1 Sodium carbonate scan for Grimbeek oil with ASP-266 formulation.

Oil Activity

Since the beginning of this project, the Grimbeek crude oil has been identified as an active oil. Activity scans were completed to plot the shift in the optimal salinity as a function of oil concentration. The activity scans were low-pressure phase behavior salinity scans with 10, 20, 30, and 40% oil (by volume) using the same ASP-266 formulation.

Figure 2.2 shows the activity map for ASP-266 formula. The ASP-266 creates low IFT microemulsion within 0.5–1.125% Na_2CO_3 concentration range at 30 vol% oil. This range is labeled as low IFT range but the IFT may turn out to be ultra-low IFT after further equilibration, which is currently being monitored. The high IFT region (distinct Type II) shifts to 2.25% Na_2CO_3 for 20% oil and considerably higher for 10% oil at 6.5% Na_2CO_3 . This behavior is typical of oil with hydrophobic natural soap.

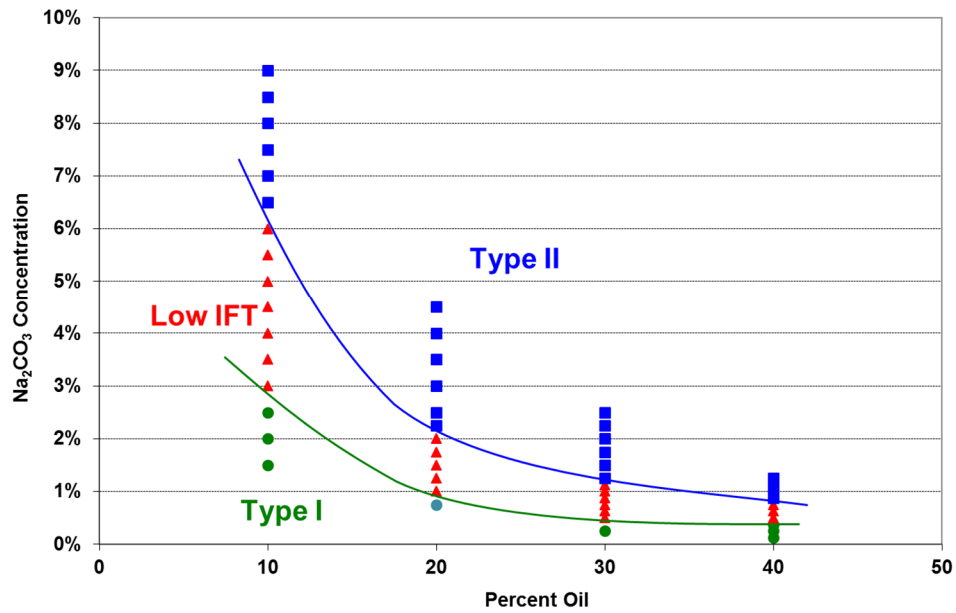


Figure 2.2 Activity map for Grimbeek oil with ASP-266 formulation in SGIB

PHASE 2 SUMMARY

Alkali-surfactant-polymer (ASP) formulations were developed during the low-pressure microemulsion phase behavior study using Grimbeek surrogate oil. These formulations were optimized in terms of surfactant structure, surfactant ratios, cosolvent choice, and surfactant/cosolvent concentration to produce the best performance. The ASP-266 formulation appear to be favorable for coreflood tests.

APPENDICES

APPENDIX A: SYNTHETIC WATER COMPOSITIONS

Table A1: Synthetic water mixtures used in laboratory study

	Produced Brine (GPB)	Injection Brine (GIB)	Soft Injection Brine (SGIB)
Component	ppm	ppm	ppm
Ca ⁺⁺	249	77	0
Mg ⁺⁺	48	23	0
Sr ⁺⁺	0	0	0
K ⁺	n/a	27	27
Na ⁺	8,126	4,022	4,222
HCO ₃ ⁻	287	1,700	1,700
Cl ⁻	12,944	5,430	5,536
SO ₄ ⁼	1	16	16
TDS	21,654	11,295	11,501

GIB was sample after water treatment

APPENDIX B: SURFACTANT PHASE BEHAVIOR

Microemulsion Phase Behavior

Phase behavior experiments were conducted in which the oil was mixed with an aqueous solution consisting of injection brine and the chemical formulation (surfactant(s), cosolvent, and sometimes polymer) in a salinity scan. To prevent evaporation, the components are sealed inside a 5 mL glass pipette and the pipettes are mixed well and equilibrated at reservoir temperature. The pipettes are initially observed visually using the emulsion (tilt) test and then quantitatively using the observed phase volumes after the samples have equilibrated.

The solubilization ratio (σ) is measured quantitatively via changes of the interface levels after a microemulsion is formed. The solubilization ratio of oil (σ_o) is the volume of oil solubilized in the microemulsion (v_o) divided by the volume of surfactant in the microemulsion (v_s) which is assumed to be all the surfactant in the sample. Similarly, the solubilization of water (σ_w) is the volume of water solubilized in the microemulsion (v_w) divided by the volume of surfactant (v_s). Once the microemulsion is equilibrated, the solubilization ratio is related to the interfacial tension (γ) by the Chun Huh equation,

$$\gamma_o = \frac{C}{\sigma_o^2}$$

$$\gamma_w = \frac{C}{\sigma_w^2}$$

$$\sigma_o = \frac{V_o}{V_s}$$

$$\sigma_w = \frac{V_w}{V_s}$$

where γ_o is the interfacial tension of the oil-microemulsion, γ_w is the interfacial tension of the water-microemulsion, and C is a constant that is equal to about 0.3. At the optimal salinity, $\gamma_o = \gamma_w$. Based on the Chun Huh equation, a solubilization ratio of at least 10 is required to obtain an interfacial tension on the order of 10^{-3} dynes/cm, which is the interfacial tension required for chemical EOR. In addition, the formulation must have a reasonable optimum salinity (and alkali concentration), a low IFT (assessed visually), an acceptably low microemulsion viscosity, minimal formation of viscous phases, a fast equilibration time, aqueous stability at the injected slug salinity, and robustness (width of the low IFT region). Each phase behavior experiment is assessed for these criteria.

Cosolvent Effect: ASP-120 vs ASP-183

Experiment ASP-120 includes 0.5% 2EH-4PO sulfate and 1% IBA-1PO-5EO with surrogate oil. The phase behavior scan showed orderly phase transition and more symmetrical solubilization ratio plot than the no-cosolvent formulation counterpart, ASP-183. ASP-183 on has the 0.5% 2EH-4PO sulfate without cosolvent in the formulation. Viscous macroemulsion was also observed in the Type II microemulsion range of the ASP-183 formulation. Although the best formulation is slightly different than the two formulation compared, the benefit of cosolvent in the formulation is identified.

Surfactant Ratio and Total Concentration

Several phase behavior scans in **Table B1** were some examples of surfactant ratio comparison. The optimal salinity and the microemulsion viscosity for the 1:1: surfactant ratio were the best among the others. The effect of surfactant concentration were studied too, and the formula that did not show adverse performance were 0.4% or higher total surfactant concentration. Other comparison was also performed that bring the final choice of cosolvent to IBA-1PO-5EO.

Table B1 Approximate Optimal Condition for ASP Formulations

Formula	T-Soft SA-97	2EH-4PO-SO4	IBA-10EO	Na ₂ CO ₃
ASP-212	0.5%	-	-	1.25%
ASP-183	-	0.5%	-	1%
ASP-237	0.25%	0.25%	0.5%	1.25–1.5%
ASP-220	0.3%	0.2%	0.875%	1.5%
ASP-221	0.375%	0.125%	1.25%	1.5%

APPENDIX C: POLYMER

Filtration Ratio Procedure

The filterability of the polymer sample was measured via filtration ratio experiments. The specified QC criterion is for the filtration ratio to be less than 1.2. The filtration ratio measurement is important as a simple failure indicator. When a filtration ratio of 1.2 or greater is measured, the polymer solution will likely fail to transport properly in a coreflood experiment or in the target reservoir. The filtration ratio is a simple measurement that is conducted on all polymer solutions before use, however coreflood experiments are recommended for polymers that pass the filtration ratio criteria as it is a more stringent test.

After the polymer stock solutions were filtered at 5 µm, the samples were diluted to various concentrations and salinities. The diluted samples were mixed for 2 hours then filtered again under a constant pressure of 15 psi argon through a 1.2 µm nitrocellulose filter, and the filtration ratios were measured.

To measure the filtration ratio, the time was recorded for each 20 mL of polymer that was filtered. Then the filtration ratio (F.R.) was calculated using the following formula

$$F.R. = \frac{T_{V=200ml} - T_{V=180ml}}{T_{V=80ml} - T_{V=60ml}}$$

where T_v is the time for that volume to filter. The filtration ratio is dimensionless. The filtration measurements and filtration ratio calculations are shown in **Table 1.1** where green indicates an acceptable filtration ratio value (a F.R. less than 1.2) and red would indicate that the filtration ratio was greater than 1.2 (i.e. a failed filterability experiment). All polymer solutions showed excellent filtration.