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Professional paper

LABORATORY RESEARCH FOR THE CHEMICAL EOR PROJECTS. CASE STUDY IN SERBIA

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Abstract: During analysis of work process after first chemical EOR project done in Serbia it was observed that our available resources were not used in an optimal way. Some of laboratory tests that were part of standard testing procedures for selection of chemicals gave us little or non-useful information but took a lot of time and resources. This drove us to analyze all our available resources and to develop a process algorithm that will give us best “value for money spent” in terms of time optimization, and developing testing methodology that will utilize equipment that is already available in our laboratory. In a way, entire process was adapted to local conditions – focusing on conditions in Serbian oilfields and chemical selection methods needed for those conditions. The process described here is applied after chemical EOR method selection and it covers all possible combinations: Surfactant, Polymer, SP or ASP EOR. In case that one component is excluded, workflow can be modified with ease.

Keywords: chemical EOR; laboratory tests, polymer surfactant selection, core flood tests

1 INTRODUCTION

There is a greater need to enhance oil recovery from oilfields that are already in production because primary and secondary methods of oil production can only extract a limited portion of the original oil in place (OOIP) and because most large oilfields are in the late stages of production. Cost-effective ways to increase production are required because traditional oil production techniques leave a lot of oil in reservoirs. Chemical enhanced oil recovery (cEOR) techniques are used to accomplish this goal. They involve injecting alkali, surfactant, and polymer either separately or in combination (ASP) into a reservoir to mobilize oil that isn't recoverable using traditional production techniques.

Chemical EOR (cEOR) and ASP techniques have been researched and used in a variety of settings worldwide for many years. The general idea remained the same, but during

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this time considerable progress was made in creating products that can be used in challenging reservoir conditions (high salinity, high temperature, and heavy oil). Soap is created when alkali reacts with organic acids that are found naturally in oil (GAO et al., 1995; MAHDAVI & ZEBARJAD, 2018). This newly formed soap and the injected surfactant work together to modify the wettability of porous environments, reduce interphase tension (IFT) between water and oil, and produce a mobile microemulsion that is aided by a viscous polymer front that follows the surfactant (MOHYALDINN et al., 2019; WANG et al., 2007).

In this paper are presented criteria and methods of selection for surfactants, polymers and alkali for cEOR, evaluating characteristics of SP or ASP mixtures and assessing the effects of field applications.

2 CHEMICAL SELECTION METHODS AND CRITERIA FOR CEOR APPLICATIONS

The first step in preparation for cEOR process is selecting the mixing water. In most cases this is not an issue since cEOR methods are tertiary production methods and it is applied after secondary method – water injection. If water injection is applied on a given field, it means that water injection infrastructure is already in place, pipelines, pumping system, etc. and water source as well, being that a formation water or any other kind. In that case chemicals are simply adapted to the available water because it is most convenient. In Serbia, in most of the oilfields strong aquifer is present, it is providing driving energy for production and because of that it is not necessary apply water injection. This is adding additional burden to cEOR project, not only because of water selection, but because it is putting additional cost for setting up entire injection infrastructure, sometimes influencing profitability of entire project.

In general, there are only two sources of water available: technical – potable water from local aquifer or produced formation water for disposal. Technical water has much better quality than formation water but, often it is not available in large quantities, either because local aquifer cannot produce enough water, or it is used by local community for water supply, and it cannot be used for any other purposes. Produced/formation water is available but regulating standards for disposal water and injection water are different and there are always issues with quality.

In most cases formation water is only one available. Issues that can arise with high oil in water content and suspended particles can be solved with additional filtering unit. If there is high content of sulphide reducing bacteria (SRB) biocide needs to be added in water with sufficient concentration to decrease bacteria content to less than 20 cfu/ml. Biocide needs to be compatible with all the other chemicals that will be used in cEOR project, mainly polymer (SERIGHT and SKJEVRAK, 2015; JOUENNE, KLIMENKO and LEVITT, 2016). Oxygen scavenger can be required as well, if oxygen is present in concentration higher than 46 ppb. The chemical composition of formation water cannot be influenced, such as salinity and ferric ion content, and it will influence polymer selection process.

2.1 Polymer selection and testing

The role of polymer in cEOR is to increase viscosity of displacing fluid and increase displacement of residual oil. There have been experiments with both synthetic and biopolymers, such as partially hydrolyzed polyacrylamide polymer (HPAM) and xanthan. Because of their low cost, wide commercial availability, superior viscosity-enhancing performance, and resistance to microbial degradation, HPAM polymers are currently the most used in polymer flooding. As mentioned previously, polymer is influenced by mixing water. Higher salinity requires higher polymer concentration, presence of Fe ions requires sulfonated polymers and presence of oxygen can cause polymer degradation.

Deciding if polymer is needed and what is target viscosity is done based on mobility ratio (FANCHI, 2010). Mobility ratio is calculated as ratio between oil mobility and water mobility as shown in equation 1.

$$M = \frac{\lambda_o}{\lambda_w} = \frac{\mu_o/k_o}{\mu_w/k_w}$$

Where: λ_{o-w} is oil / water mobility

μ_{o-w} is oil / water viscosity

k_{o-w} is oil / water relative permeability

equation 1.

Ideal case is that M=1 or slightly below, in that case uniform injection front can achieved without viscous fingers breaking through, as it is shown on figure 1. Example of polymer target viscosity calculation is shown in equation 2. Where water viscosity is changed with desired polymer viscosity.

$$\mu_{poly} = \frac{\mu_o \cdot k_w}{k_o \cdot M}$$

example: μ_o = 0,769 cP k_o = 124,42 mD

k_w = 349,83 mD M = 1

Target viscosity: $\mu_{poly} =$ 2,16 cP

equation 2.

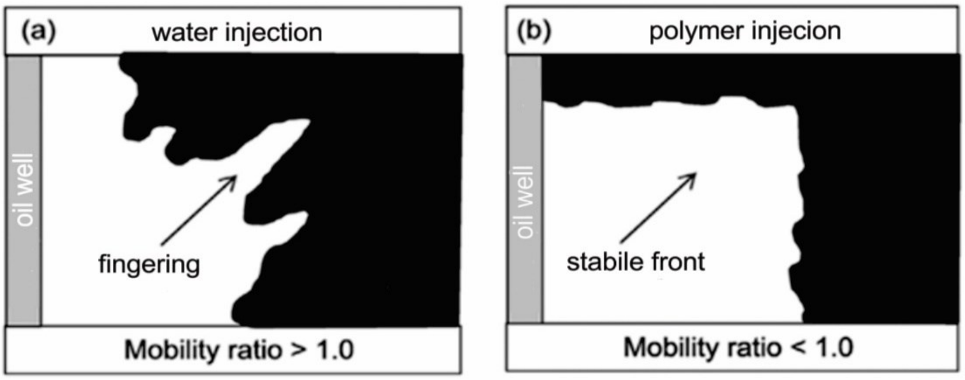


Figure 1 injection front shape (look from above) a) M>1, injection front breaking through forming viscous “fingers” b) M<1 stabile injection front achieved

When selecting polymer, the goal is to get sufficient viscosity with low concentration. Viscosity is influenced by mixing water salinity and by molecular mass of polymer itself (figure 2). The difference in viscosity for the same polymer mixed in formation water and technical water is very high. That’s why, in terms of cost, it is always better if technical water is available. Polymers with higher molecular mass are creating higher viscosity solution for same concentration than ones with lower molecular mass but higher molecular mass means also higher polymer retention and higher injection resistivities so this also must be taken into account during polymer selection process.

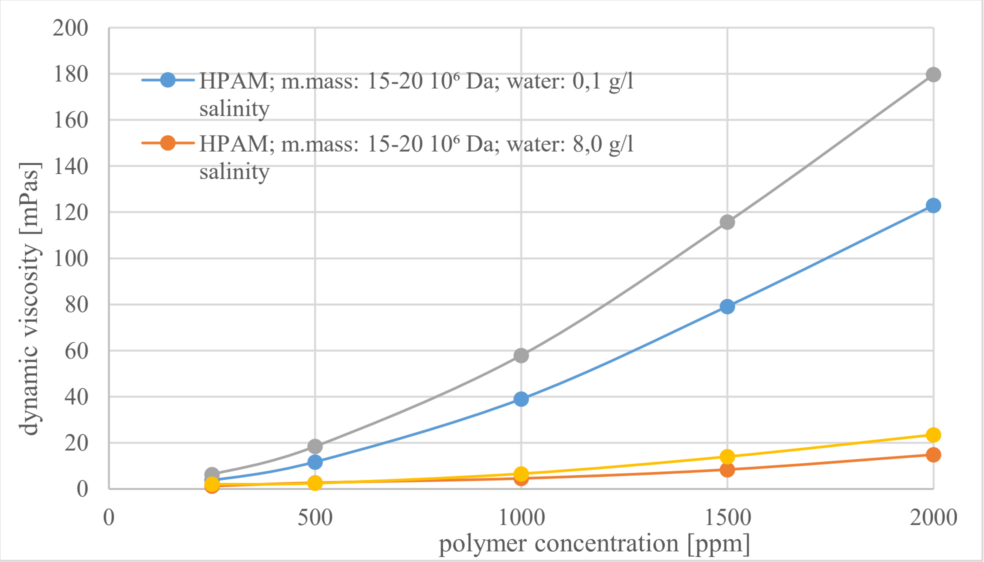


Figure 2 Concentration / viscosity dependence for 2 HPAM polymers with different molecular mass prepared with water with 2 different salinities

Polymer must be stable in time so long-term stability test has to be performed to check if polymer solution will keep desired viscosity in longer period (>30 days). It is good to prepare polymer solution with chosen mixing water, if formation water is used it probably has residual of chemicals used in oil preparation process that can influence mixture. If polymer is stabile in time, polymer selection is confirmed.

2.2 Polymer retention

After the polymer is confirmed, it is necessary to determine technical parameters needed for operation planning: Rf, Rm and RRF. The polymer retention factor (Rf) and parameters that derive form it – resistance modification (Rm) and residual resistance factor (RRF) are calculated from core flood experiment on actual or model reservoir rock, depending on availability. Resistance modification (Rm) is a ration between injection pressure for water and for polymer at same flow rate (FERREIRA & MORENO, 2018). It is calculated from differential pressure during water injection prior to polymer and differential pressure during polymer injection at same flow rate using following formula.

$$Rm = \frac{\Delta P_p}{\Delta P_w{}^{\text{before}}}$$

Where:

ΔP_p Pressure during polymer injection

$\Delta P_w{}^{\text{before}}$ Pressure during water injection before polymer

equation 3.

Residual resistance factor (RFF) is ration between water injection pressure before and after polymer (FERREIRA & MORENO, 2018; THOMAS, A., 2019). It is calculated from differential pressure during water injection before and after polymer is injected through the sample using following formula:

$$RRF = \frac{\Delta P_w{}^{\text{after}}}{\Delta P_w{}^{\text{before}}}$$

Where:

$\Delta P_w{}^{\text{after}}$ Pressure during water injection after polymer

$\Delta P_w{}^{\text{before}}$ Pressure during water injection before polymer

equation 4.

Both parameters are important for planning field operations, Rm for assessment of injection pressure and RRF to assess injectivity of water after polymer, since in practice water is used in the final stage of cEOR as displacement fluid. Both parameters depend on polymer retention, measurement of polymer loss in formation. Adsorption on the surfaces, mechanical entrapment brought on by small passageways in porous media, and hydrodynamic entrapment brought on by high flow rates are the three main causes of polymer retention. The retained polymer lowers the porous media's flow capacity (permeability) by decreasing the flow area. Polymer retention is calculated from data obtained during coreflood test using concentration profile method (AL-HAJRI et al., 2018; SERIGHT, 2016; SORBIE, 2013; THOMAS, A,2019). To do that, polymer is prepared with addition of easy migrating tracer (i.e. solution of KI – potassium iodide). During the first polymer injection on the outlet of core holder tracer appears first and polymer after, that "lag" in polymer appearance is caused by polymer retention. After the first polymer injection, polymer is flushed by long water injection (50-100 pore volumes) or until stabile differential pressure is achieved. The polymer is again injected after flushing. This time polymer is appearing before tracer at the outlet because first to appear at the outlet is the polymer that was retained in pores during first polymer injection. Polymer retention is the difference between polymer appearance first and second polymer appearance in relation to tracer, expressed as mass of polymer per pass of rock. Theoretical curve of tracer and polymer concentration are shown on figure 3.

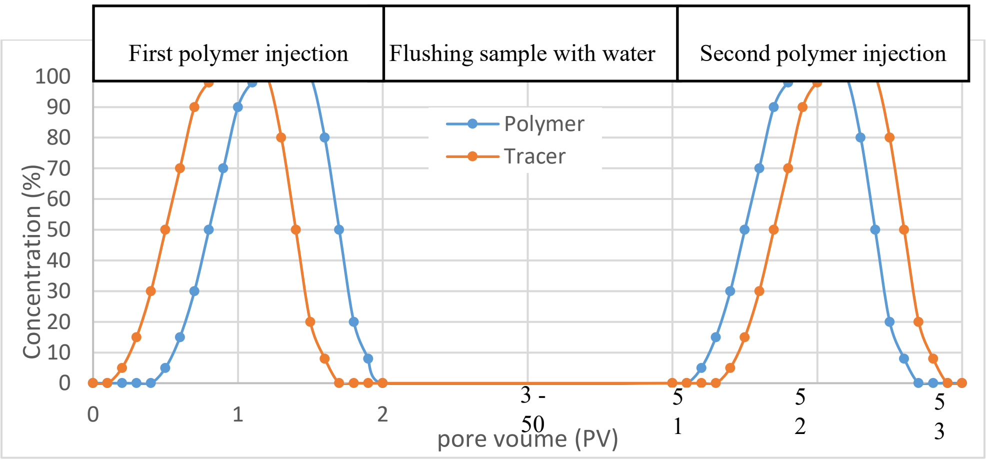


Figure 3 Theoretical curve of tracer and polymer concentration during coreflood test for Rf determination

The concentration of polymer on coreholder outlet during experiment was measured via in-line capillary tube and concentration of tracer was measured from changes in conductivity on the fluid caught at the outlet of coreholder. Method of retention calculation using polymer concentration profile is shown on figure 4 (SAMEER et al., 2018; ILYASOV et al., 2021). Polymer concentration curves for both injection curves are plotted on the same graph, tracer curves should overlap exactly because migration of tracer should be the same. Retention as volume of polymer is calculated as difference between points when polymer is reaching 50% of maximum concentration for first and second polymer injection.

$$R_{(PV)} = PV_{poly1}^{50\%} - PV_{poly2}^{50\%} \qquad \text{equation 5.}$$

From retention expressed as part of pore volume it is possible to calculate retention factor (Rf) using equation 6.

$$Rf = \frac{R_{(PV)} \times PV \times C}{m} \qquad \text{equation 6.}$$

Where:

$R_{(PV)}$	Retention as pore volume
PV	Pore volume (ml)
C	Polymer concentration (ppm)
m	Mass of the rock sample (g)

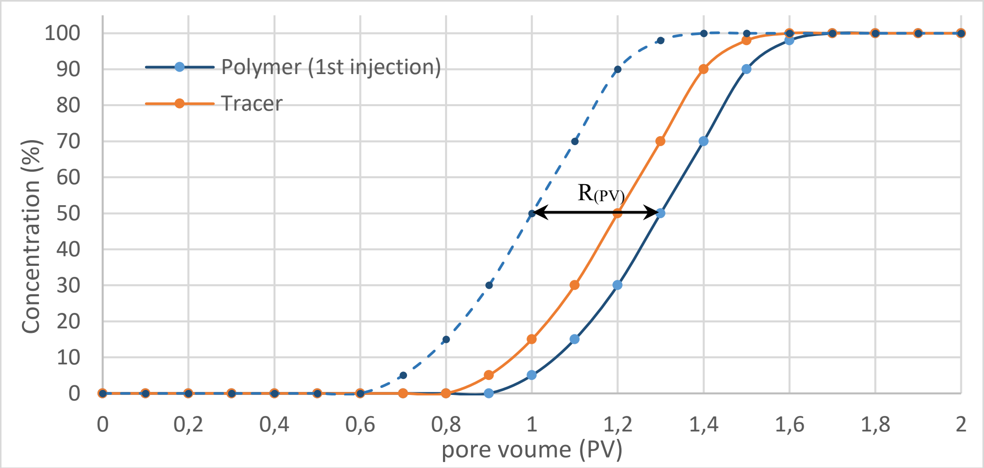


Figure 4 Overlapped curves for Polymer and Tracer concentration for first and second injection - Rf determination using concentration profile method

In case of unsatisfactory results, in terms of resistance modification (Rm), residual resistance factor (RRF) and polymer retention factor (Rf) process of polymer selection is repeated.

2.3 Surfactant selection and testing

Surfactants are surface-active substances with polar (or hydrophilic) head and a nonpolar (hydrophobic) tail, this allows them to have affinity to aqueous and non-aqueous phase due to the amphiphilic nature. All surfactant types can reduce the IFT between the aqueous and oil phase and change environment wettability to more water-wet conditions, but selecting the suitable type of surfactant is very crucial in terms of solubility, thermal and chemical stability, and adsorption of the surfactant under harsh reservoir conditions (BORCHARDt et al., 1985; EFTEKHARI et al., 2015). Generally, surfactants are classified into four main groups: non-ionic anionic, cationic, and zwitterionic or gemini (also known as amphoteric) (GUPTA et al., 2020; MAHBOOB et al., 2022; BERA & MANDAL, 2015; ISAAC et al., 2022). Most commercial surfactants are blend of two or more different types of surfactants regarding type of polar head to decrease adsorption and increase surfactant performance.

The first thing to consider when selecting the surfactant is compatibility with mixing water, it should not form any precipitates or cloudiness / turbidity when solution is prepared. This is important because turbidity of surfactant / water solution can interfere with interphase tension measurement – main parameter for surfactant selection. Interphase or interfacial tension (IFT) is observed on the border between two immiscible liquids that form a surface that behaves like an elastic membrane. IFT is a measure of force needed to change the surface of this “membrane”, unit of measurement is mN/m.

Oil / water tension is dependent on oil and water composition, and it can range from 10 to 30 mN/m. To successfully mobilize trapped oil held in small pores by capillary forces it is necessary to lower interphase tension to a point of forming microemulsion, weather it is Windsor type I microemulsion (oil dispersed in water phase) or Windsor type III microemulsion (microemulsion is separate phase between oil and water). It depends on the oil type, but it is usually achieved when IFT is lowered down to 10-2 – 10-3 mN/m range.

The Surfactant selection process consists of IFT measurement for different surfactant concentrations. If possible, prepare surfactant solution with chosen mixing water. If formation water is used it probably has residual chemicals used in oil preparation process that increase IFT, such as water clarifiers, or can influence surfactant performance. The goal is to determine the minimum achievable IFT value and critical micellar concentration (CMC). CMC is surfactant concentration at which lowest value of IFT is obtained, any increase inf surfactant concentration leading to micelle forming with little or no decrease inf IFT or even mild increase. Typical surfactant selection measurements are shown in figure 5: IFT dependence on concentration for four different surfactants with illustration of how surfactant behaves in solution. Most desirable characteristics for cEOR are observed with surfactant 2, very low IFT values and observed and mild decrease after reaching CMC.

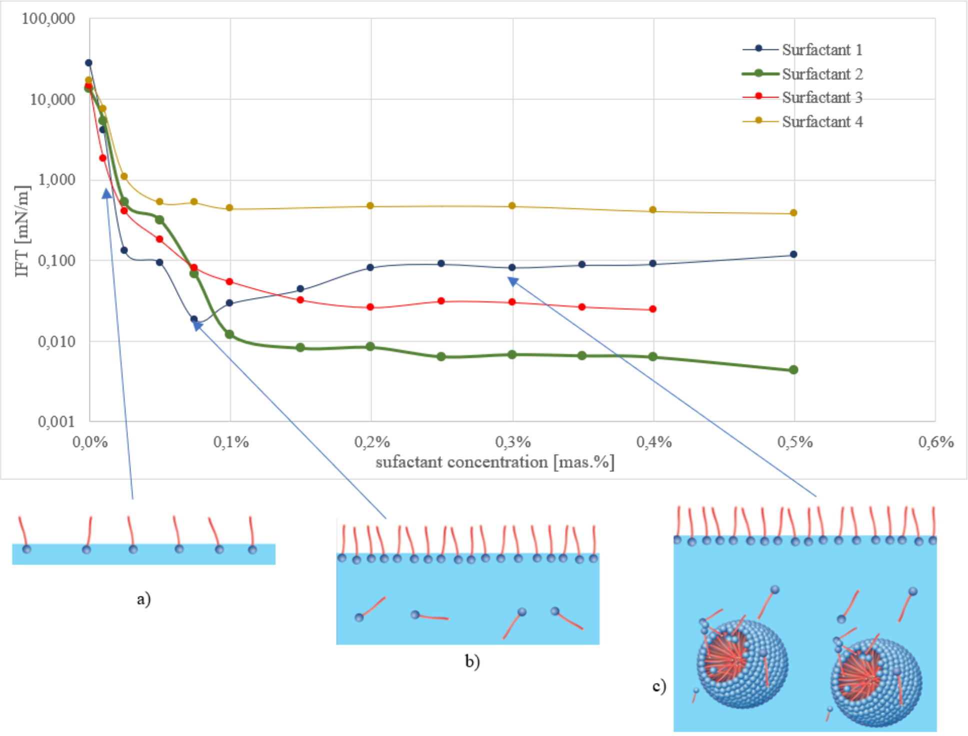


Figure 5 results of IFT measurements for 4 different surfactants, surfactant 2 shows the best characteristics for cEOR. Three different trends are visible on the graph: a) molecules of surfactant are positioning themselves on border between phases, with concentration increase IFT is decreasing b) border between phases is saturated with surfactant, CMC achieved, in most cases this is lowest IFT value c) since border is saturated any increase of surfactant leads to forming of spherical surfactant aggregates – micelle, little or no decrease of IFT, sometimes even increase inf IFT.

Additional benefit that derives from surfactant reaction with reservoir is changing reservoir rock wettability from oil wet to water wet (RATANPARA and KIM, 2023). Changing rock wettability can increase effects of cEOR with oil wet reservoirs (carbonate rich sandstones or limestones) but it is depending on surfactant adsorption on rock surface. Wettability change is important factor for increasing oil recovery since goal is to decrease capillary forces that are trapping the oil in small pores as it is shown by equation for capillary number (equation 7.). Capillary number (Ca) is ratio between viscous forces and capillary forces (GUO, SONG and HILFER, 2020). Higher the capillary number bigger the oil recovery, at Ca values in range 10^{-6} - 10^{-5} mobilization of trapped oil begins and values in range 10^{-3} -10^{-2} marks end of residual oil mobilization. If it is possible to decrease IFT and increase wetting angle at the same time capillary pressure will be lowered even more. Surfactants can change wettability of rock by means of adsorption on rock surface (anionic surfactants) (SUGIHARDJO, 2022) but adsorption is not desirable because it is taking surfactant out of solution. Wettability alteration is more often achieved by smart water injection - water injection with magnesium and sulphate ions (Mg^{+2}, SO_4^{-1}) such as seawater (AHMADI et al., 2020; POPIC et al., 2022).

cEOR projects that include reservoir rock wettability alteration were not done in Serbia so far and this segment will not be discussed in detail any further.

$$Ca = \frac{v \times \mu}{\sigma \times \cos \Theta}$$ equation 7.

Where:

Ca	Capillary number [dimensionless]
v	Darcy velocity [m/s]
μ	Viscosity of displacing phase [Pa·s]
γ	Interphase tension IFT [N/m]
Θ	Wetting angle of liquid

After surfactant selection it is recommended to perform compatibility test with polymer, if polymer is going to be used in cEOR. It is possible that some surfactants can decrease polymer viscosity when added to mixture. Same like with polymer and surfactant, preferably prepare surfactant polymer solution (SP) with chosen mixing water. It is done as form of thermostability test, surfactant polymer mixture is prepared and kept on reservoir temperature for 3 days. Each day viscosity is measured to determine if polymer degradation occurred. It is recommended to do this with various concentration of surfactant. Results with one such test were shown on figure 6 where it is visible that, in case surfactant and polymer are not compatible, polymer degradation is happening within 24 hours after preparation.

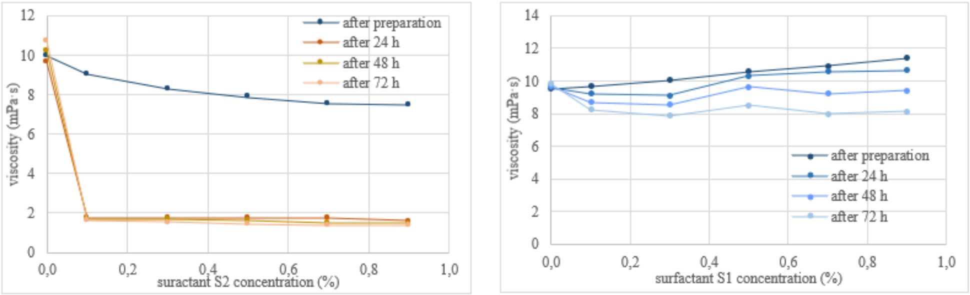


Figure 6 Example of compatibility test with incompatible (left) and compatible (right) SP mixture

In case of unsatisfactory results, in terms of polymer – surfactant compatibility process of surfactant or polymer surfactant selection is repeated.

2.4 Surfactant adsorption test

Surfactant adsorption is a measure of how much surfactant stays trapped on rock particles during injection (GROENENDIJK and VAN WUNNIK, 2021). This value can be significant and impact EOR process at first stages, however adsorption is active until equilibrium is reached between rock and injected solution. In the latter stage, when water is injected to push SP or ASP solution, desorption process will be activated because injected fluid doesn't contain surfactant, and all surfactants will be flushed from rock surface. In this way, the adsorption process acts like surfactant "retarder" since surfactant is not permanently trapped as it is case with polymer. Surfactant adsorption can be measured with static adsorption test or dynamic adsorption test (AL-MURAYRI et al., 2019). Static tests are simpler, and dynamic is more accurate.

Static test is performed by soaking the rock sample in surfactant solution of known concentration for minimum of one week at reservoir temperature (long time is needed since diffusion is only mechanism for surfactant transfer within sample). After soaking time fluid is drained from sample and average concentration of surfactant measured in recovered fluid. Adsorption is calculated through material balance, decrease in mass of surfactant in ratio to mass of rock sample, mg or µg of surfactant per g of rock sample – in units mg/g or µg/g. Surfactant concentration can be measured by High-performance liquid chromatography (HPLC) – direct measurement, changes in IFT measured by spinning drop tensiometer – indirect measurement or Fourier-transform infrared spectroscopy (FTIR) – indirect measurement.

Dynamic adsorption test is performed on similar principle as polymer retention test, using concentration profile. The core sample is saturated with 2% NaCl solution, after saturation phase surfactant mixed in 3% NaCl solution is injected in the core, at least 5 pore volumes to make sure that saturation is reached – adsorption phase. After surfactant solution is injected sample is flushed with 5 pore volumes of 2% NaCl solution – desorption phase. Changes in salinity (NaCl concentration) is used as inert tracer, and it can be measured by changes in conductivity of fluid at outlet. Surfactant concentration at the outlet is monitored by periodical sampling and detection by one of the methods mentioned for static method. The same test can be repeated with surfactant + polymer mixture used, instead of just surfactant – in case that polymer is used in cEOR. Surfactant adsorption is lower in SP mixture (due to polymer retention) in comparing with pure surfactant solution so if both tests are done, we can get clearer information on expected range of surfactant adsorption in reservoir. Theoretical curves of dynamic adsorption test are shown in figure 7.

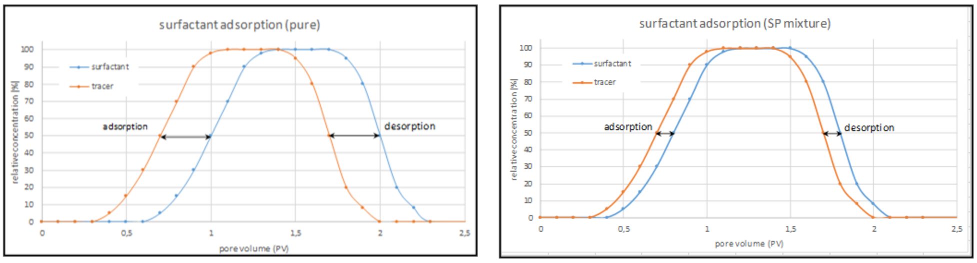


Figure 7 Example of theoretical concentration curves of dynamic adsorption test

Adsorption / desorption is calculated using concentration profile method, with difference in volume at 50% concentration for surfactant and tracer, already described in detail for polymer retention.

Generally, surfactant adsorption is higher than polymer, mainly ionic surfactants, it is also depending on rock surface so higher clay / fines content means more adsorption. In case of unsatisfactory results, if surfactant adsorption is too high the process of surfactant selection is repeated or adding alkali or other "sacrificial" surfactant is considered. Sacrificial surfactants have a role to be adsorbed onto rock surface instead of main one.

2.5 Alkali selection and testing

Basic function of alkali in cEOR is to form surfactant in contact with naphthenic acids that will additionally mobilize trapped oil. This is useful in reservoirs with long distances between injection and production well, to avoid surfactant adsorption to rock before it reaches areas with trapped oil. Condition that alkali can be used in this way is dependent of total acid number (TAN) of oil (measure of how many mg of potassium hydroxide – KOH is needed to neutralize organic acids in 1g of oil). If TAN is above 0,5-0,8 mg KOH/g there is potential of forming sufficient quantities of surfactant. The secondary function of alkali is to decrease adsorption of surfactant (anionic mainly) as "sacrificial" agents – alkali is adsorbed to rock surface instead of surfactant (HAZARIKA and GOGOI, 2019). Most widely used is sodium carbonate (Na2CO3) or, if there is risk of carbonate scale precipitation, monoethanol amine (MEA - C2H7NO). The concentration that is used is usually 1% solution, but it depends on mixing water and surfactant in use, it is necessary for injection mixture to have pH of 8,0-8,5 to form surfactants with naphthenic acids.

When it is put in perspective of local condition, in Serbian oilfields, there is much potential for alkali application on cEOR. TAN measured on oilfields on Serbia varies from 0,03 to 5,16 mg KOH/g so there is potential for use, but lot of commercially available surfactants have pH above 8 so there is no need to add alkali. Major oilfields in Serbia with potential for cEOR are well covered with network of wells so distance between injection and production well is not that big and sweep area can be covered with surfactant without excessive loss. The only potential use is to decrease adsorption of surfactants if it is proven to be too high.

One of biggest disadvantages of alkali use is quantity needed, since concentration of alkali needed is highest comparing to other components in cEOR, surfactant and polymer (in example: alkali concentration of 1%, surfactant 0,3% and polymer 0,1% - real ratio on the ASP flooding project). The biggest logistic challenge is to supply and stock enough alkali, since quantity needed is higher than quantity of surfactant and polymer together and if used it is increasing cost of entire operation.

2.6 Emulsion forming test / bottle test

The bottle test is a fundamental and traditional surfactant selection method. It is carried out to evaluate and compare the quantity, stability, and capacity to form microemulsions. Bottle tests are conducted using reservoir oil that is extracted from the produced fluid purely by heating it without the use of chemicals. A surfactant or an alkali/surfactant mixture made with model or, preferably, real mixing water is used for preparation. Oil and alkali surfactant / surfactant solution were mixed in 1:1 ratio. After turning the bottle upside down continuously by hand for 2 minutes, samples are placed into a thermo regulated oven at formation temperature for a period of 30 days. Samples were removed once daily to determine the type, quantity, and presence of microemulsion. It is widely believed that in surfactant selection process one of the main criteria is type of microemulsion formed with oil and its stability (BERA & MANDAL, 2015; GUO et al., 2012; SALAGER et al., 2013) – Windsor type III microemulsion that is stabile in time at reservoir condition (figure 8).

oil 75 ml, microemulsion 55 ml, water phase 90 ml

oil 30 ml, microemulsion 80 ml, water phase 80 ml

Figure 8 Example of bottle test samples with Windsor type III microemulsion (interphase in the middle)

General criteria are that, when comparing two surfactants, one that has more Windsor type III microemulsion that is more stable in time will perform better in cEOR but in our experience it is not determining factor – some of surfactants that had good results in bottle test didn't perform well in coreflood test and vice versa. Most useful information that can be obtained is viscosity of formed microemulsion. It is possible that microemulsion that is formed has very high viscosity and that it is practically immobile in reservoir conditions. It can lead to reservoir plugging, injectivity issues and many other problems.

For that matter this test can be modified in terms of observation period. Tests are set in same way and as soon as sufficient quantity of microemulsion is formed it can be sampled and viscosity measurement performed at reservoir conditions. It can be surfactant or alkali surfactant exclusion criteria for cEOR implementation – if viscosity of formed microemulsion is too high it cannot be used in cEOR.

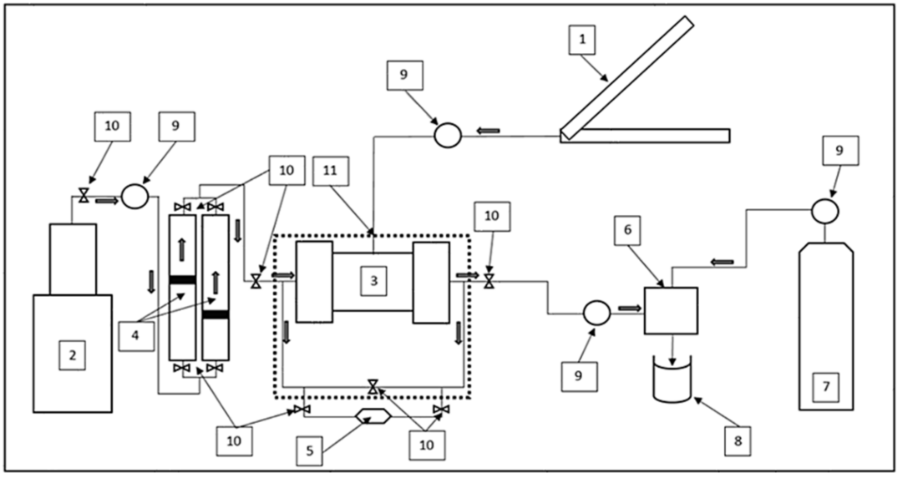
2.7 Salinity test

Salinity influences phase solubility of surfactants, only ionic and amphoteric (zwitterionic or gemini) surfactants, non-ionic surfactants are not influenced. At higher salinity surfactants are highly oil soluble and on lower salinity it is highly water soluble, with amphoteric surfactant this also dependents on pH of solution (HAJIYEV et al., 2023). At optimum salinity surfactant is equally soluble in water and oil and in this way lowest IFT is obtained. This is also influencing microemulsion Windsor type III stability since at optimum salinity IFT at oil-microemulsion and microemulsion water contacts are equal ($\sigma om = \sigma mw$).

As mentioned before, most of the commercial surfactants are blend of two or more different surfactant types so salinity test efficiency depends on selected surfactant blend. It is done when surfactant is already selected and IFT measurements are repeated with selected surfactant at selected concentration with addition of salt (NaCl) in solution in different concentrations. If there is trend of decreasing IFT then optimum salinity is determined though repeated testing, if not – salinity of mixing water is higher than optimum salinity for given surfactant. At projects that were done for Serbian oilfields salinity scan was done but no change in IFT was detected or influence on microemulsion stability was observed so this segment will not be discussed in detail any further.

2.8 Oil recovery coreflood test

Most reliable way to test ability of surfactant or ASP / SP mixtures to mobilize residual oil from porous rock is to perform coreflood tests on rock sample, preferably cut or consolidated (in case of loose or poorly cemented sandstone) from core cut during drilling of oil wells. As criteria to determine selected mixture performance changes in oil recovery factor (ORF) should be used. ORF represents a decrease in residual oil saturation (Soi-Sor) divided by initial oil saturation (Soi). All rock samples must undergo soxhlet extraction using toluene to remove any residual oil or contamination. The test should be done at reservoir temperature and with pressures (pore pressure, overburden pressure) as close to reservoir conditions as possible. As for fluids: reservoir oil extracted from produced fluid only by heating without chemicals should be used, oil should be diluted with petroleum benzine (C7 n and iso alkanes with cyclic HC) to get viscosity at reservoir conditions, modelled formation water should be used as water phase and SP / ASP mixture should be prepared with actual water that will be used during operation. Setup of coreflood system with all necessary elements to perform oil recovery test is shown on figure 9.



1.Hand pump for Overburden (OB) pressure
2.Injection pump
3.Core Holder
4.Floating piston accumulators
5.Differential pressure sensors
6.Back pressure regulator (BPR)
7.Bottle of nitrogen for BPR
8.Fluid collector
9.Manometers
10.Valves
11.Oven

Figure 9 recommended setup of coreflood system

Coreflood experiment was done in as per following steps:

- Injecting the model formation water (MFW) at three flow rates until the differential pressure stabilizes (minimum 1 pore volume), goal is to determine linear permeability for MFW (Kw).

- Injection of oil at a constant flow rate until the differential pressure stabilizes (minimum 3 pore volumes). Fluid at the outlet is sampled and initial water saturation (Swi) is determined by measuring quantity of produced fluid.

- Partial isolation of the core sample on reservoir conditions (aging process) for a period of 72 h. Oil is periodically injected for six hours at the lowest possible flow rate.

- Oil injection at three flow rates until the differential pressure stabilizes (minimum 1 pore volume). Linear effective permeability for oil (Ko@Swi) is determined.

- Injecting MFW at constant flow rate until the differential pressure stabilizes (minimum 3 pore volumes) – pre-flush phase. During injection, fluid at the outlet is continuously sampled, the volume of displaced oil is monitored to determine change in oil recovery factor (ORF1). After stabilizing the differential pressure, the effective permeability for MFW (Kw1@Sor) is determined. 2-3 pore volumes of MFW re injected at an increased flow rate to confirm ORF value. The goal of this stage is to imitate water injection and to remove oil that that ca be produced this way. In this way any additional quantities of oil are produced are result of cEOR.

- Injecting selected ASP / SP mixture or mixtures, amount should correspond to volume planned for field application (usually 0,2-0,5 pore volume) – main treatment phase. Differential pressure should be recorded and the fluid at the outlet is continuously sampled (every 0.2 pore volume). Volume of displaced oil is monitored to determine change in oil recovery factor (ORF2). The goal of this stage is to imitate as accurately as possible planned cEOR operations in the field.

- Injecting MFW at constant flow rate. The MFW is pressed until the differential pressure stabilizes (minimum 3 pore volumes) – post-flush phase. During indentation, the fluid at the outlet is continuously sampled every 0.5 pore volume. Volume of displaced oil is monitored to determine change in oil recovery factor (ORF3). After differential pressure is stabilized, the effective permeability for MFW (Kw2@Sor) is determined. The goal of this stage is to imitate the final cEOR operation when injected chemicals are pushed by water injection.

Examples of this kind of test are shown in figure 10. The results of this test give the most accurate assessment of additional oil that can be produced for cEOR methods. The heterogeneity of reservoir must be taken into account so preferably more than one test should be done with samples of different permeability. From this experiment it is also possible to calculate resistance modification (Rm) and residual resistance factor (RRF), in same way as it’s done in polymer retention test, only difference that results calculated from oil recovery coreflood test are more accurate because residual oil is present in system as it would be in reservoir conditions.

Additional quantities of oil that can be gained are calculated as difference in residual oil saturation (or ORF) after pre-flush and post-flush phase. Satisfactory results are one that indicate that increase in oil production will justify investing in implementation of cEOR methods and it depends on many factors, not just reservoir conditions. This is the main test to assess if selected chemicals can be used. In case of unsatisfactory results in terms of oil recovery or Rm and RRF, surfactant and / or polymer cannot be used in cEOR and selection process is repeated.

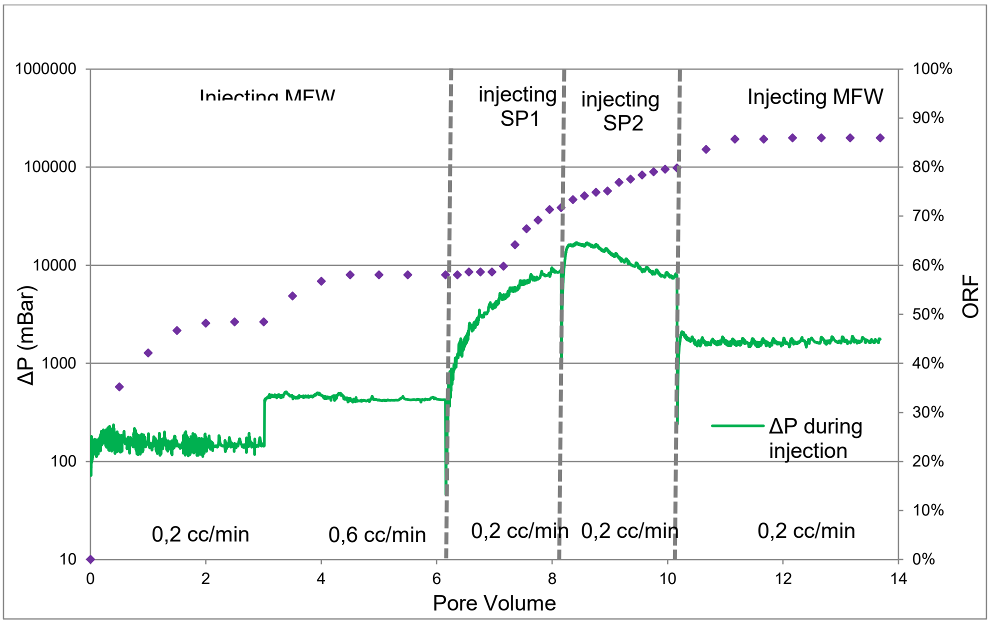


Figure 10 Changes in differential pressure and ORF during injection of SP mixtures. SP1 – mixture prepared with 0,1% surfactant concentration, SP2 – mixture prepared with 0,5% surfactant concentration. Polymer concentration in both cases is the same

3 RECOMMENDED WORKFLOW ALGORITHM

All mentioned tests are important for final decision if certain polymer or surfactant can be used in cEOR but some of tests are longer, more complex and more expensive than others. Our goal was to organize testing procedures in a way that will allow us to do preliminary selection with cheaper and faster tests and to perform more complex and more expensive tests on products that have already passed the first screening methods. The algorithm is shown in figure 11. Our goal was to create universally applicable workflow, regardless of what components of cEOR are used.

Before any laboratory tests it is necessary to select water that will be used for injection. Type of water (formation water or technical), available quantities and quality of water play major role in chemical selection, polymer especially, and even can influence financial aspects of EOR project itself. Selection of polymer and surfactant is done simultaneously, polymer according to target mobility and surfactant according to optimal IFT to concentration ratio.

Next step is to check for surfactant and polymer compatibility at reservoir temperature, followed by bottle test and salinity scan – to check for microemulsion forming and stability. On this step we can consider introducing alkali in mixture, to aid microemulsion stability.

With defined SP/ASP mixture, coreflood tests are performed to assess decrease of oil saturation, retention of polymer and adsorption of surfactant. The methodology of all coreflood tests is designed in the way to deliver maximum information with available equipment. If surfactant adsorption is too high, we consider introducing co-solvent or alkali in mixture.

In organizing process in this way, we can do most of necessary preparation for field test in 6-month period.

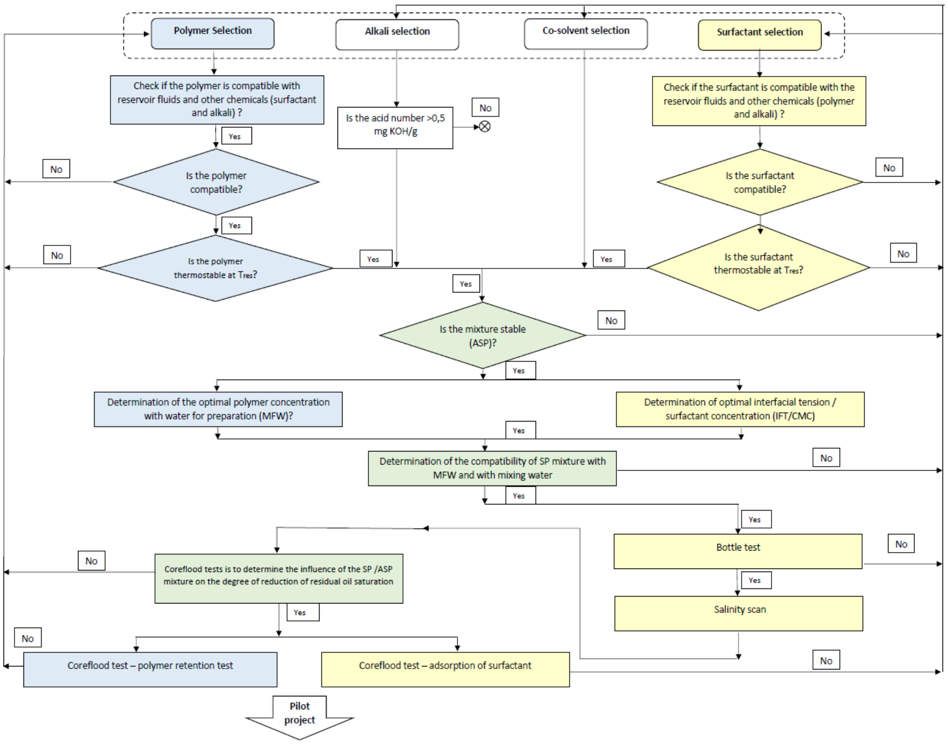


Figure 11 Recommended workflow algorithm for process of chemical components selection for EOR

4 CONCLUSION

When chemical selection process for cEOR is analyzed with respect to local condition we can separate some key points specific to Serbian oilfields.

- Absence of secondary production methods (water injection) and related infrastructure (water treatment units, pipelines, etc.) is putting additional costs on any plan to implement any cEOR method. Because of that, an additional quantity of oil produced by cEOR must be sufficient to justify investing in cEOR.

- Surfactant / polymer compatibility issues are one of biggest problems and this test should be done as soon as possible to avoid unnecessary testing of chemicals.

- Total acid number values of oil in Serbian oilfields are high enough to suggest that alkali should be used but since all major oilfields are evenly covered with production wells there is no need for use of alkali, except as an agent for surfactant adsorption.

- Final and decisive test if selected cEOR mixture will be able to mobilize trapped oil should be done with oil recovery coreflood test done on real rock sample from reservoir. In this way it is possible to imitate injected fluid-oil-rock interaction that takes place in the reservoir and to give clear indication if selected cEOR method is applicable or not.

In current situation, it is important for oil industry in Serbia to move in direction of increasing oil recovery from oilfields that are already in production for some time by chemical or any other EOR method. Developing technical skills and methods to realize this kind of project is one of biggest challenges for our company. All other challenges are available on STC website: Tehnološki izazovi - Naučno-tehnološki centar NIS-Naftagas.

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