ALKALINE-SURFACTANT-POLYMER FLOODING – PRINCIPLES AND APPLICATIONS

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ABSTRACT

About two trillion barrels of oil will remain in the existing reservoirs without implementing enhanced oil recovery. Chemical recovery offers the most obvious and attractive method to recover this oil. Alkaline-Surfactant-Polymer (ASP) is the most promising chemical EOR process due to the synergism of alkaline, surfactant and polymer flooding. In this presentation, we will discuss the following:

- Mechanisms of individual polymer, surfactant and alkaline processes,
- ASP synergistic mechanism,
- Laboratory evaluation procedures,
- Status of ASP application,
- A field case of commercial ASP application,
- Problems with the ASP field application.

INTRODUCTION

With growing global energy demand and depleting reserves, enhanced oil recovery (EOR) from existing or brown fields becomes more and more important for several reasons: 1) the industry cannot guarantee new discoveries; 2) new discoveries most likely lie in offshore, deep offshore, or any difficultly-producing areas; 3) producing unconventional resources would be more expensive than producing from existing brown fields by enhanced oil recovery (EOR) methods. Most of oilfields have been under waterflooding. Among the four EOR methods (gas miscible flooding, chemical, thermal and microbial), chemical EOR method should be easily implemented because minimum facilities are needed to add chemicals in injection water. Among chemical methods, alkaline-surfactant-polymer is the most promising method because it has the synergy of alkaline, surfactant and polymer flooding.

In this paper, we will first discuss the mechanisms of each individual method: polymer, surfactant and alkaline. Then we discuss the ASP synergistic mechanism. The laboratory screening work which is needed for an ASP project is elaborated. The current status of ASP application is reviewed. A field case of commercial ASP application is presented. Finally, problems with the ASP field application are also discussed.

ASP Mechanisms

To discuss ASP mechanisms, we need to first discuss the mechanisms of each individual component of the ASP process, then discuss about the synergy of the ASP process.

Mechanisms of polymer flooding

As we know, the main mechanism of polymer flooding is the increased viscosity of polymer solution so that the mobility ratio of the displacing polymer solution to the displaced fluids ahead is reduced and the viscous fingering is reduced. When the viscous fingering is reduced, the sweep efficiency is improved, as shown in Fig. 1 which compares the sweep efficiency of water flooding and polymer flooding in a 5-spot pattern in a laboratory setup. Clearly, the polymer sweep efficiency is much higher than that in waterflooding. The breakthrough time in waterflooding was 1 hour and 19 minutes, whereas the breakthrough time in polymer flooding was 2 hours and 3 minutes.

The mechanism of increased displacing fluid viscosity can be quantified using the Buckley-Leverett (1942) theory. Fig. 2 shows two fractional flow curves. One is for a waterflooding case with the viscosity ratio of water to oil 0.1. The other one is for a polymer flooding case with the viscosity ratio of polymer to oil 1. From the fractional flow curve, we can estimate the average water saturation at breakthrough by drawing a tangent from the connate water saturation S_{wc} (0.2 in this case) and intersecting the horizontal line of $f_w = 1$, and the corresponding water saturation is the average water saturation. Here f_w is the water cut in the producing fluid. From Fig. 2, the average water saturation in the waterflooding case is 0.58, whereas the average water saturation in the polymer flooding case is 0.76. The difference is 0.18. In other words, by simply increasing the viscosity of displacing fluid, the oil recovery factor can be increased by 18% at breakthrough.

When polymer is injected in vertical heterogeneous layers, crossflow between layers improves polymer allocation in the vertical layers so that the vertical sweep efficiency is improved. This mechanism is detailed in Sorbie (1991).

Another mechanism is related to polymer viscoelastic behavior. The interfacial viscosity between polymer and oil is higher than that between oil and water. The shear stress is proportional to the interfacial viscosity. Due to polymer viscoelastic properties, there is normal stress between oil and polymer solution, in addition to shear stress. Thus polymer exerts a larger pull force on oil droplets or oil films. Therefore, oil can be "pushed and pulled" out of dead-end pores. Thus residual oil saturation is decreased. This mechanism was rarely discussed until recently (Wang et al., 2001; Sheng 2011).

One economic impact of polymer flooding which has been less discussed is the reduced amount of water injected and produced, compared with waterflooding. Because polymer improves the mobility ratio and sweep efficiency, less water is injected and less water is produced. In some situations like an offshore environment and desert area, water and the treatment of water could be costly.

Mechanisms of surfactant flooding

The key mechanism for surfactant floods is the low interfacial-tension (IFT) effect. To discuss this mechanism, we need to first discuss the concept of capillary number versus residual oil saturation. The capillary number, N_c, is defined as

$$N_c = \frac{u\mu}{\sigma}$$

where μ is the displacing fluid, u is the displacing velocity, and σ is the interfacial tension between the displacing fluid and the displaced fluid (oil). Many experimental data show that as the capillary number is increased, the residual oil saturation is decreased, as summarized by Stegemeier (1977) and shown in Fig. 3. When the capillary number is low, the residual oil saturation is not reduced. As the capillary number is increased, the residual saturation is significantly reduced.

Now let us take a look at the capillary number for a typical waterflooding case. Assume that injection velocity is 1 ft/day which is 3.528×10^{-6} m/s, the water viscosity is 1 mPa·s, and the interfacial tension is 30 mN/m, the corresponding capillary number is

$$N_C = \frac{u\mu}{\sigma} = \frac{(3.528 \times 10^{-6}\ \mathrm{m/s})(1\ \mathrm{mPa \cdot s})}{(30\ \mathrm{mN/m})} \approx 10^{-7}$$

To reduce waterflooding residual oil saturation, the capillary number must be higher than the above calculated value. From this figure we can see that if the capillary number is increased by 1000 times, the residual oil saturation is reduced by half.

How can we increase the capillary number? From the above equation, there are three ways: increasing injection fluid velocity u, increasing displacing fluid viscosity μ and reduce the IFT σ. The injection fluid velocity is limited by pump capacity and formation injectivity. Even though the pump capacity is not a problem, if the injection velocity is too high, the injection pressure may be higher than the formation fracture pressure. Increasing injection fluid viscosity is limited at least by economics. For example, increasing polymer solution viscosity needs higher polymer concentration, and polymer is costly. In reality, we could not use a too high polymer concentration owing to a solubility issue. The way left is to reduce IFT. It is known that the interfacial tension between a surfactant solution and oil can be reduced from 20-30 to 10^{-3} mN/m. In other words, by adding surfactants, we can practically increase the capillary number by 1000 times. Other mechanisms are discussed in Sheng (2011)

Mechanisms Of Alkaline Flooding

One obvious mechanism is that a surfactant (called soap to differentiate an injected synthetic surfactant) is generated in situ when an alkaline solution reacts with the acid component in a crude oil. The reaction equation is

$$\mathrm{HA_w + OH^- \rightarrow A^- + H_2O}$$

where HA_w is a pseudo-acid component in aqueous phase, and A^- is the soap component. Simply speaking, this soap functions as a surfactant.

More importantly, when an alkali is added with a surfactant like in an ASP process, alkali can reduce the adsorption of surfactant on the grain surfaces. This makes surfactant work more efficiently and less surfactant is needed. Other mechanisms are summarized by Johnson (1976). These mechanisms include emulsification, oil entrainment, bubble entrapment and wettability reversal.

Synergy In ASP

Olson et al. (1990) reported some incremental oil recovery factors over waterflooding from alkaline flooding, polymer flooding and ASP flooding from laboratory. The recovery factor from surfactant flooding was not available. The recovery factors from alkaline and polymer flooding were 10% and 11.6%, respectively. The sum of these factors was 21.6%, whereas the recovery factor from the ASP was 45.3%. Even we assume the recovery factor from surfactant flooding could be 20%, the sum of the three processes would be 41.6%, still lower than 45.3%. These data clearly demonstrate the synergy from ASP.

One important mechanism is the synergy between in situ generated soap and synthetic surfactant. Generally, the optimum salinity for the soap is unrealistically low, and the optimum salinity for the surfactant is high. When they are function together, the workable salinity range is increased (Nelson et al., 1984).

Sheng (2011) summarized the mechanisms in ASP as follows.

- Increased capillary number effect to reduce residual oil saturation due to low to ultralow IFT.
- Improved macroscopic sweep efficiency due to viscous polymer drive.
- Improved microscopic sweep efficiency and displacement efficiency due to polymer viscoelastic property. Oil in the dead-ends is pulled out, and the oil films on the pore walls are “peeled” off due to the high velocity gradient.
- Emulsification, entrainment and entrapment of oil droplets due to surfactant and alkaline effects.
- Improved sweep efficiency by emulsions.

ASP LABORATORY TESTS

There is no universal formula for ASP flooding or chemical flooding in general. A final chemical formula is always obtained through laboratory using the water and oil which are similar to their actual compositions in the applied field. Minimum laboratory tests include phase behavior test (aqueous stability test, salinity scan and oil scan) and coreflooding test. A typical flow chart of laboratory tests is shown in Fig. 4. It starts with the aqueous stability test to make sure the chemicals when added together can form a clear solution. Then the salinity scan is performed to find the optimum salinity of the system. After that, the oil scan is conducted to check whether the optimum salinity decreases with water-oil-ratio.

Aqueous Stability Test

Injection of a single-phase solution is important because formation of precipitate, liquid crystal, or a second liquid phase can lead to non-uniform distribution of injected material and non-uniform transport owing to phase trapping or different mobilities of coexisting phases. When polymer is added to increase slug viscosity, it is essential to prevent separation into polymer-rich and surfactant-rich phases, which yields highly viscous phases unsuitable for either injection or propagation through the formation. Therefore, we need to first check whether the aqueous solution is transparent without adding oil. The solution should be transparent (clear) up to or higher than the salinity at which you intend to inject the solution. If the solution is hazy or there is any precipitation, chemicals must be re-selected. Such test is aqueous stability test. Generally, the salinity limit in an aqueous stability test is close to the optimum salinity of microemulsion. Fig. 5 shows an example of aqueous stability test.

Salinity Scan

If the solution is clear, add oil in the solution and change salinity. In the pipette tests, the temperature and concentrations of surfactant(s) and cosolvent are fixed while the concentration for the electrolyte is varied between various test tubes. Pressure is assumed to be minor effect, and it is generally at atmospheric. The surfactant solution changes from O/W type of microemulsion, to water and oil bicontinuous microemulsion, to W/O type microemulsion, as the salinity is increased. The test is referred to salinity scan. Fig. 6 is an example of such test. Generally, the water/oil ratio (WOR) in salinity scan is one or a fixed value.

Oil Scan

The optimum salinity for soap is generally lower than that of a synthetic in a practical case. In a real ASP project, a sequence of changes occurs. As the more and more oil recovered, less oil is in the reservoir (water-oil ratio, WOR, increases). Less soap will be generated. Then relatively high percentage of synthetic surfactants is available in the chemical slug. The resulting optimum salinity of the system of soap and synthetic surfactants will be higher. Therefore, it is required that the optimum salinity of the system is required to increase as the water-oil ratio is increased. In an oil scan, we start the test with WOR = 1, then reduce the oil volume so that the WOR is increased up to 10 or 20. Measure the optimum salinity of the system which should increase with WOR or decrease with the percent of oil volume, as shown in Fig. 7. Such a plot is called activity map.

STATUS OF ASP APPLICATIONS

A few field trials in US, Canada and Venezuela were conducted. The former Soviet Union was active in chemical EOR, but the current status is unknown because not many publications in the English literature. Most of the field pilots and commercial applications are in China. Therefore, we will present the status of application in China in this section.

Thirteen field cases (pilots and commercial scale) have been reported from China. Among them, 5 cases are from Daqing. Most of them are in small scale (a few injectors), all in sandstone reservoirs. One Daqing commercial application which started in 2000 had 17 injectors and 27 producers (Li et al., 2003; Wang et al., 2006). This case will be presented in the next Section. Among these 13 tests, the highest reservoir temperature was 86 ^{o}C; in most of the cases, the oil viscosity was 6-13 cP, and 42-70 cP in two cases; the salinity was less than 7,000 ppm (Daqing), except in Zhongyuan 170,000 ppm and 5600 ppm divalent; the well spacing was 50-250 m.

For most of the ASP projects, polymer was injected before and after ASP slugs for conformance control and mobility control. The injection concentrations of alkali, surfactant and polymer in the ASP slugs are shown in Figs. 8-10, respectively. The average injection concentrations of alkali, surfactant and polymer were 1.28%, 0.28% and 0.15%, respectively. Note that only 10 cases had the concentration data available. For the micellar flood or micellar-polymer flood projects in 1980s, the injected surfactant concentration was more than a few percent. In these ASP projects, the surfactant concentrations used is one order of magnitude lower. Several factors contributed to the surfactant deduction. Although some of the factors are not new, these factors have been tested in field practices. These factors are:

- Alkalis can reduce surfactant adsorption significantly;
- Alkalis react with crude oils to generate in situ surfactant (soap);
- Modern surfactants have been improved;
- The synergistic effect of alkaline, surfactant and polymer results in less surfactant required to recover significantly incremental oil.

A FIELD CASE OF COMMERCIAL ASP APPLICATION

This is the Daqing largest ASP project. It is probably the largest ASP project in the world so far. Compared with other small pilots, the formation connectivity was an important factor which affected ASP performance. Emulsion problem was noticed.

Reservoir And Fluid Description

The target layers were PI2^1–3^3. There were 27 producers and 17 injectors drilled in regular 5-spot patterns in the pilot area, as shown in Fig. 11. The distance between injector and producer was 250 m. Some of the reservoir and fluid data are shown in Table 1.

Designed Injection Scheme

The surfactant used is alky benzene sulfonate made in China. Based on experimental work, 0.025–0.3% S + 0.4–1.0% A could make IFT reach 10^{-3} mN/m. The following injection scheme was designed:

1. Preflush polymer slug: 0.0375 PV × 1400 mg/L, viscosity 40 mPa·s.
2. ASP main slug: 0.35 PV, 1% NaOH + 0.2% S + 1650 mg/L P, viscosity 40 mPa·s.
3. 2nd ASP slug: 0.1 PV, 1% NaOH + 0.1% S + 1000 mg/L P, viscosity 35 mPa·s.
4. Polymer drive slugs: 0.1 PV × 1000 mg/L, viscosity 30 mPa·s; 0.1 PV × 630 mg/L, viscosity 15 mPa·s.
5. Water drive until f_w in the central area reaches 98%.

Field Injection Scheme

Waterflooding was started in October 1998, and ended in March 2000 with 0.2002 PV injection. Preflush polymer flood was started in April 2000 and ended in April 2001 (0.128 PV injection). The average polymer concentration was 1538 mg/L with viscosity of 40.9 mPa·s. Injection of the main ASP slug was started on May 1, 2001. By November 2004, 0.354 PV was injected. The average injection concentrations of alkali, surfactant and polymer were 1.02%, 0.201%, and 1407 mg/L, respectively. The wellhead sample viscosity was 30.2 mPa·s, the IFT between the ASP system, and the crude oil was below 10^{-2}. The 2nd ASP slug was started on December 1, 2004.

Field Performance

Fig. 12 shows the injection rate and pressure vs. injection PV in the whole ASP injection area. It shows that as polymer was injected, the injection rate decreased and the injection pressure increased. In the following ASP injection, the injection rate and pressure gradually stabilized. Although the fluid production rate *decreased*, the oil rate increased and the water cut decreased after polymer injection and ASP injection, as shown in Fig. 13.

Fig. 14 shows the well recovery factor during ASP flood vs. formation connectivity for some wells. The connectivity equal to 100% indicates the formation between injector and producer is well connected, 0% not connected. The figure shows that the oil recovered from a production well during ASP flood is directly proportional to the formation connectivity between the producer and the neighboring injectors.

PROBLEMS WITH ASP APPLICATIONS

The problems with ASP applications are chromatographic separation, produced emulsions, formation damage, precipitation and scale.

Chromatographic Separation Of Alkali, Surfactant And Polymer

Fig. 15 is the effluent concentration histories of an ASP slug injection. The vertical axis is the relative concentration of polymer, alkali and surfactant, the effluent concentrations relative to its respective injection concentrations. The horizontal axis is the injection pore volume. This figure shows different effluent histories for the polymer, alkali and surfactant. Here are several observations from this figure. First, their breakthrough times were different. In this case, polymer broke through first, then alkali followed by surfactant. Second, each maximum relative concentration depended on its retention or consumption in the pore medium. The maximum polymer concentration was 1, the maximum alkali concentration was 0.9, and the maximum surfactant concentration was 0.09 in this case. Third, their concentration ratios in the system were constantly changing. In other words, the chemical injection concentrations will not be proportionally decreased.

Precipitation And Scale Problems

In the process of alkaline flooding, alkali reacts with the reservoir rock resulting in the dissolution of some rock materials. The flooding liquid carries the dissolved materials to the production wells. The blending of produced liquid coming from different layers, decrease of pressure, loss of the dissolved gas and decrease of temperature result in precipitation and its deposition on the tubing, surface pipeline and pumps, etc. The deposition can cause downhole severe pipe plugging, tubing plugging and thus break of beam pump rods. Frequent operation failures of the production wells were observed in Daqing chemical flooding projects. In addition to the dissolved rock materials, reactions of alkalis with divalents such as calcium and magnesium lead to the formation of precipitates. The divalents are from mixing with resident brines and ion exchange process.

Formation Damage

Alkaline solutions erode formation rocks and clays. In some cases, the permeability could be increased due to the erosion. In most of cases, permeability is reduced because eroded rocks and clays migrate and block pore throats. And the permeability reduction in low permeability rocks is higher than that in high permeability rocks.

Permeability reduction in alkaline-surfactant is similar to that in alkaline flooding. In such situations, permeability reduction could also be caused by scales and precipitates which are formed through reactions between alkalis and surfactants with rock minerals. In ASP flooding, the formation damage is less than that caused by alkaline flooding alone. The permeability can be recovered in some degree during the post-ASP waterflooding.

Produced Emulsions

Although emulsion can increase sweep efficiency in the reservoir, it can cause difficulties in transportation and oil-water separation. In a Shengli ASP pilot test started in 1992, it was difficult to separate water from oil even the weak alkali Na_2CO_3 was injected. Because it was also difficult to treat produced water, the produced water had to be re-injected in the reservoir.

CONCLUDING REMARKS

ASP is most promising chemical EOR method because it has the synergy of alkaline, surfactant and polymer flooding. It has the highest potential to increase oil recovery. However, some problems like produced emulsion, precipitation and scale are also observed.

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Table 1 – Reservoir and fluid data

ASP area, km^2	2.03
Formation depth (subsea), m	947–1029
Permeability, md	69–673
Average porosity, %	25
Total PV, m^3	3,654,000
Permeability variation coefficient	0.57
Effective thickness, m	7.2
Total thickness, m	10.1
OOIP, ton	2,017,000
Formation temperature, ºC	45
Formation water TDS, mg/L	4144

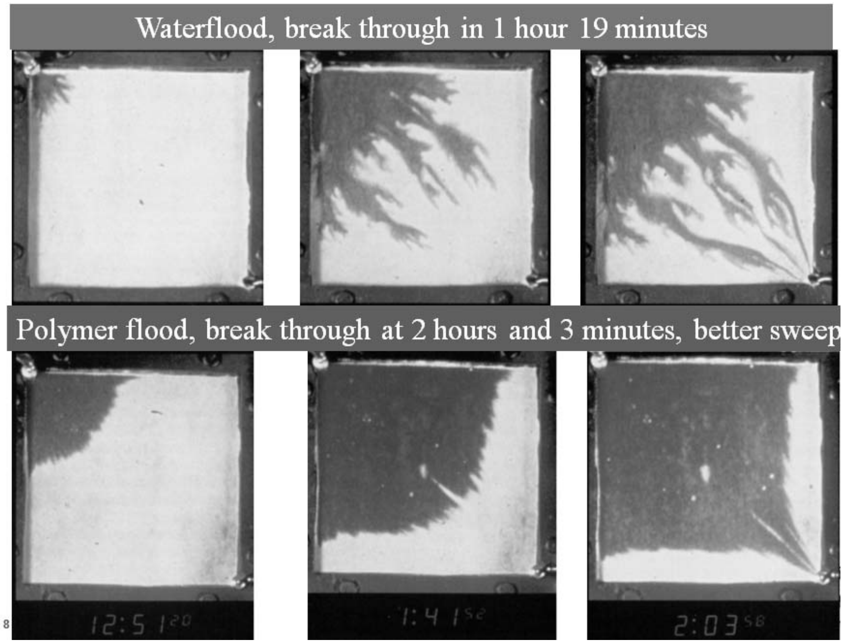

Figure 1 – Comparison of sweep efficiency in water flooding and polymer flooding (Courtesy of Surtek)

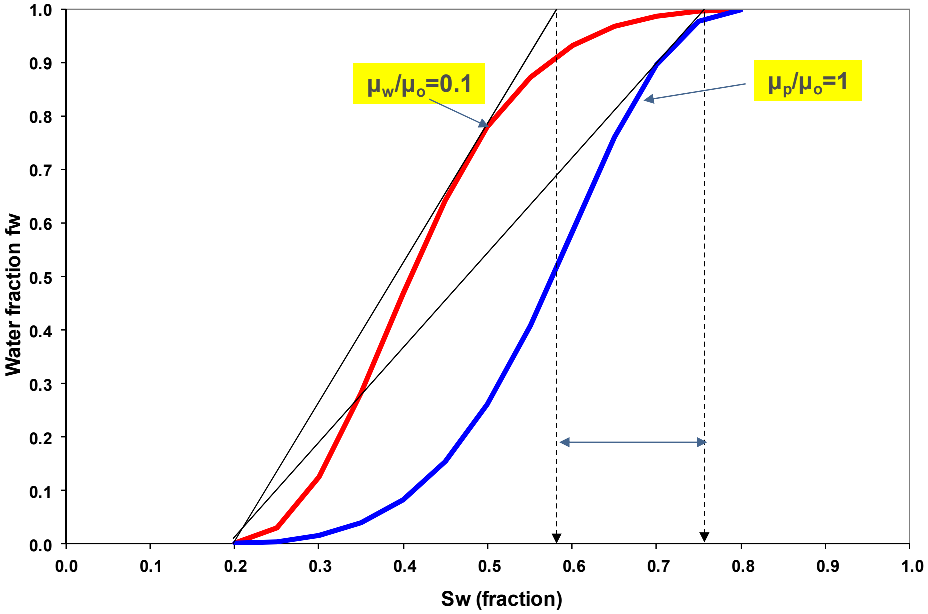

Figure 2 – Effect of viscosity ratio on the fractional flow curve

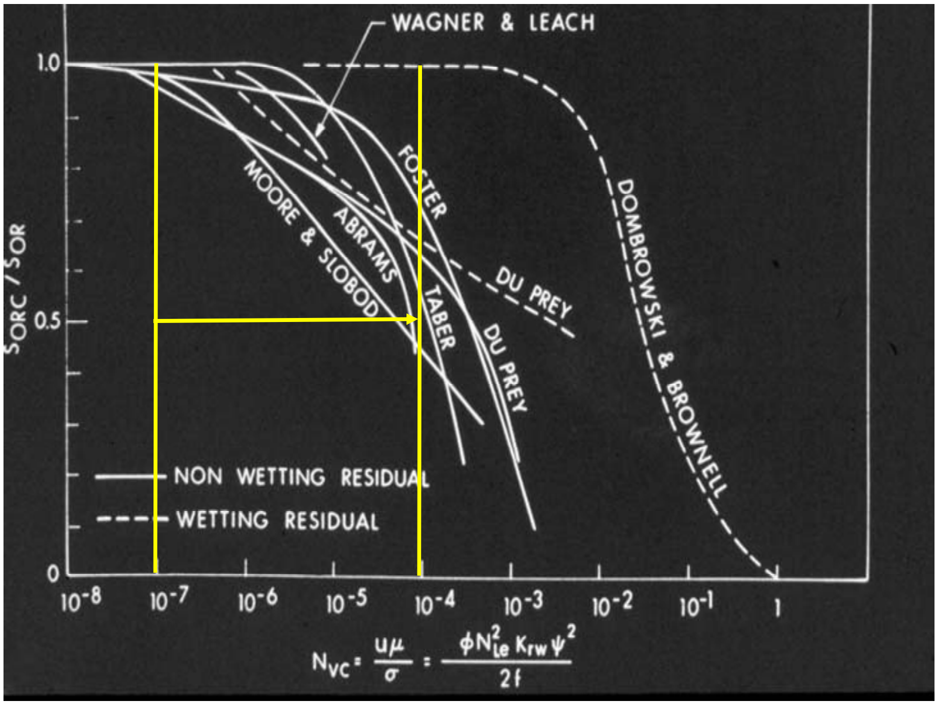

Figure 3 – Average experimental recoveries of residual phases (Stegemeier, 1977)

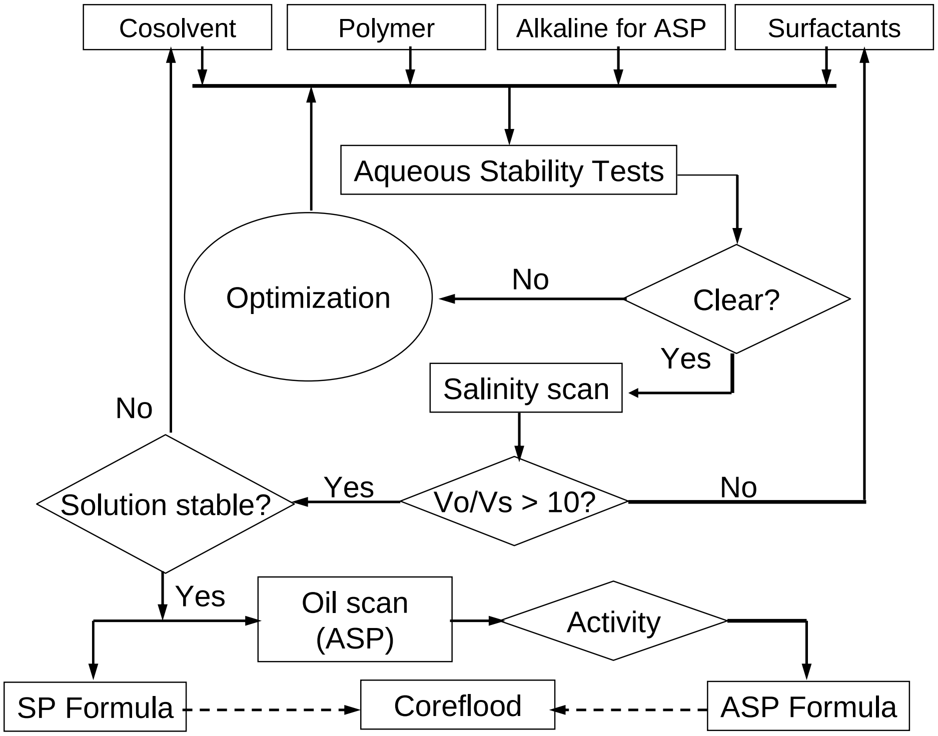

Figure 4 – Flow chart of phase behavior test

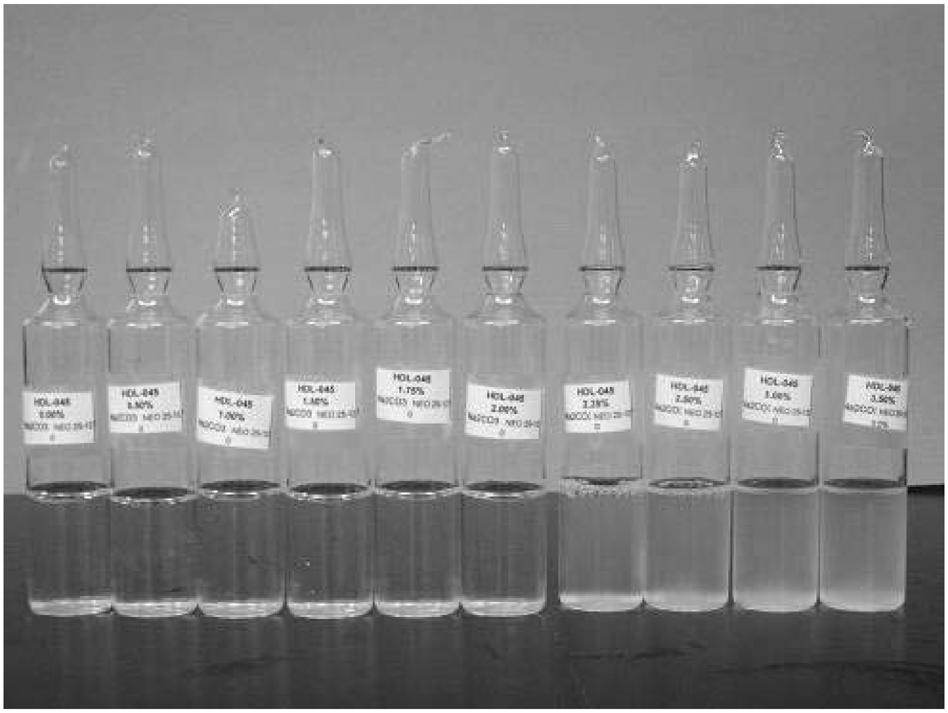

Figure 5 – Photograph of an aqueous stability test

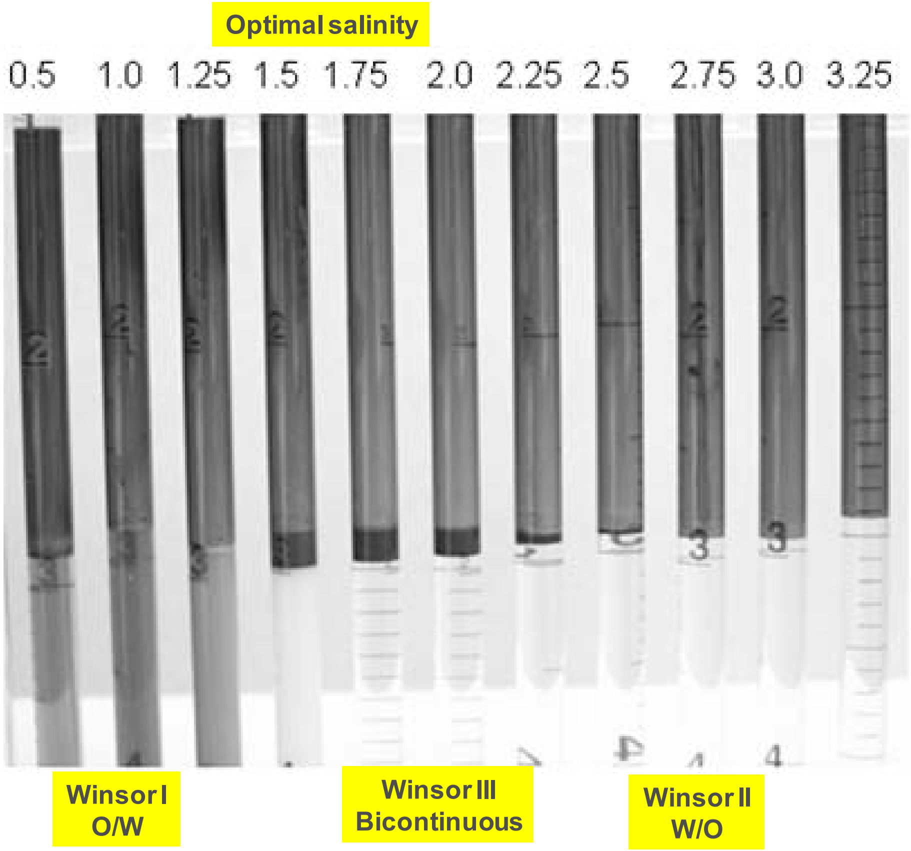

Figure 6 – Photograph of a salinity scan

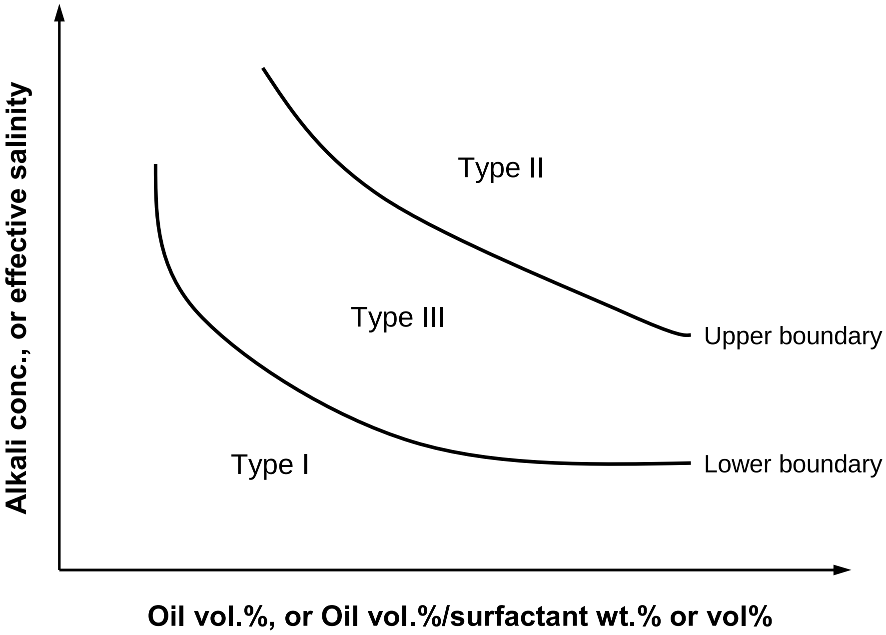

Figure 7 – An activity map generated from a oil scan test

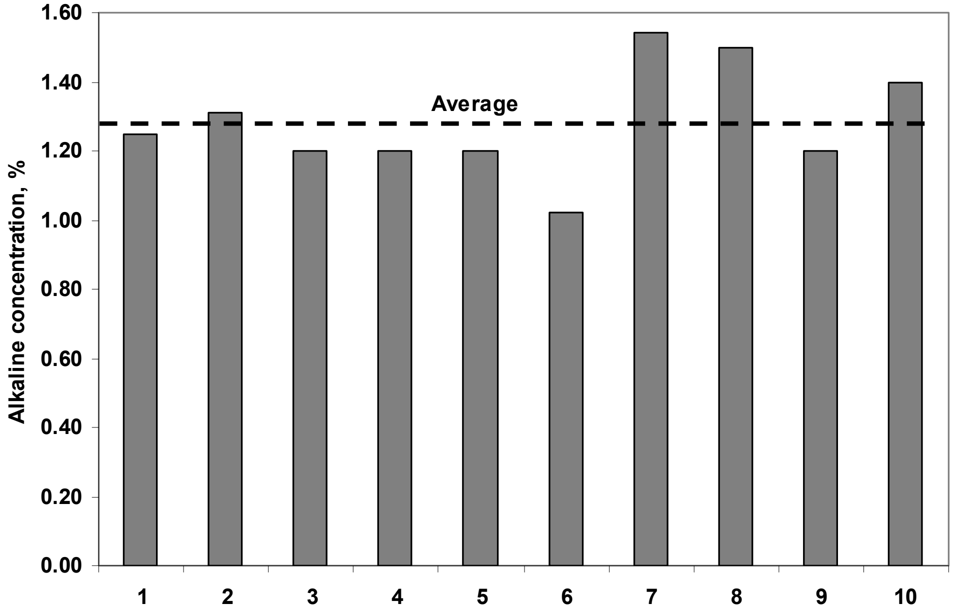

Figure 8 – Injected alkaline concentrations in the field ASP projects

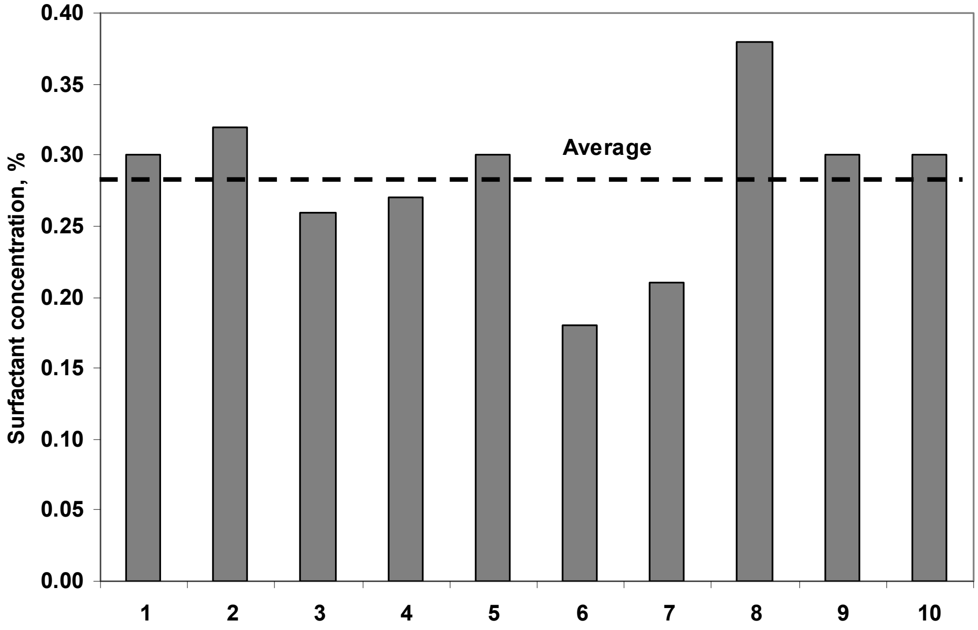

Figure 9 – Injected surfactant concentrations in the field ASP projects

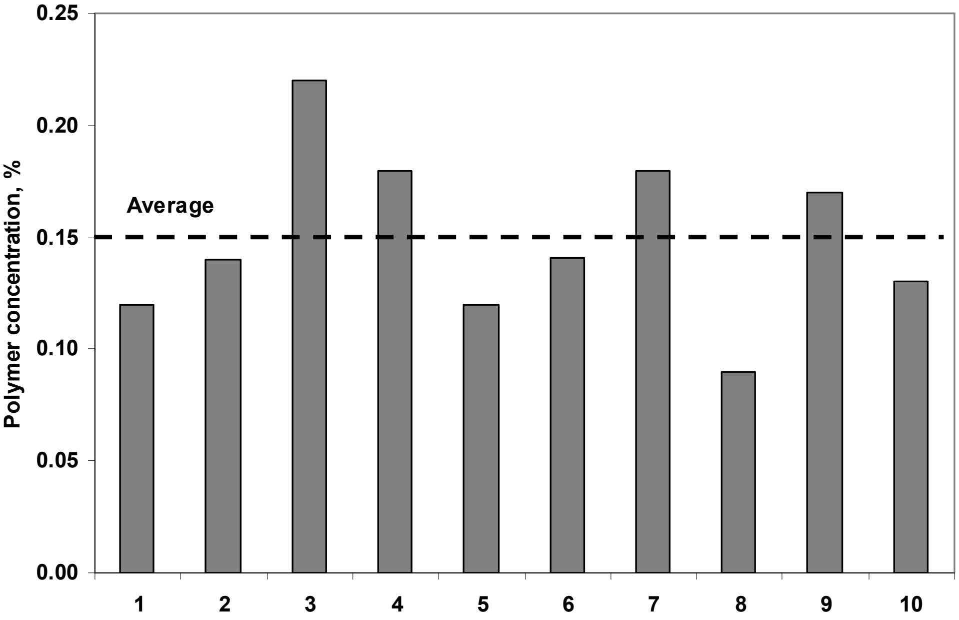

Figure 10 – Injected polymer concentrations in the field ASP projects

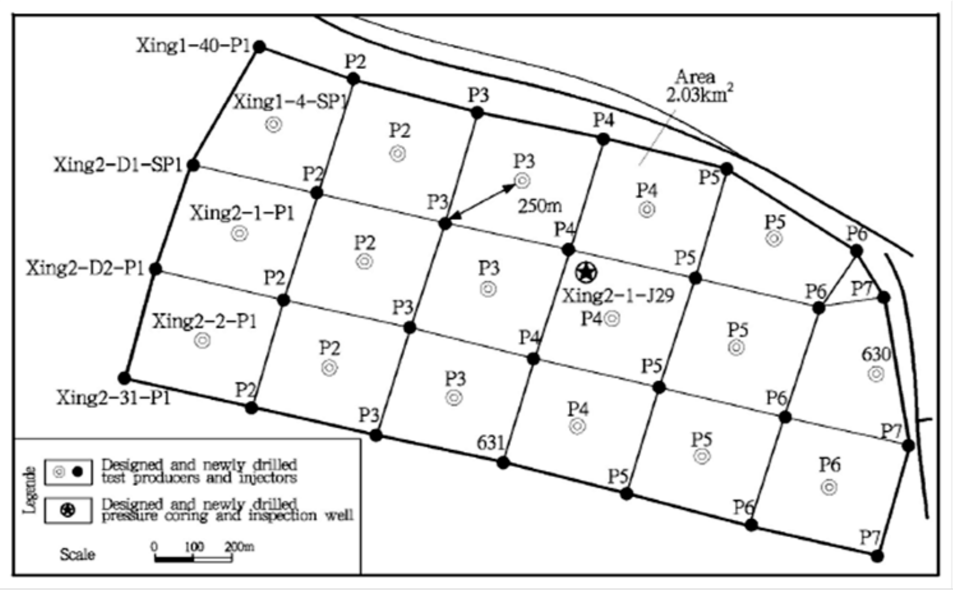

Figure 11 – Well locations in the ASP project

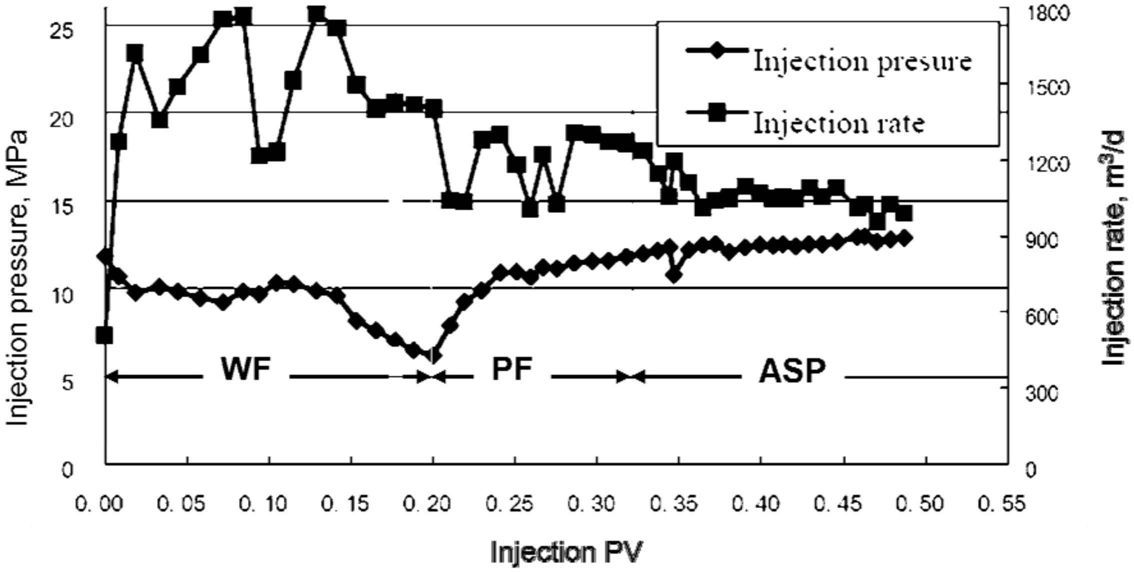

Figure 12 – Injection rate and pressure in the test area vs. injection PV (Wang et al., 2006)

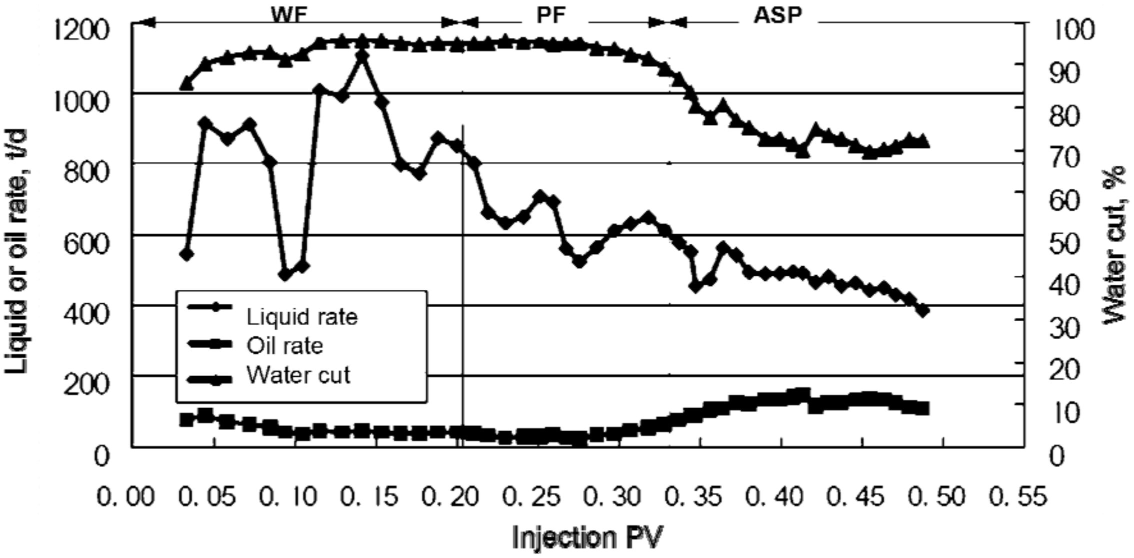

Figure 13 – Production curves for the central area (Wang et al., 2006)

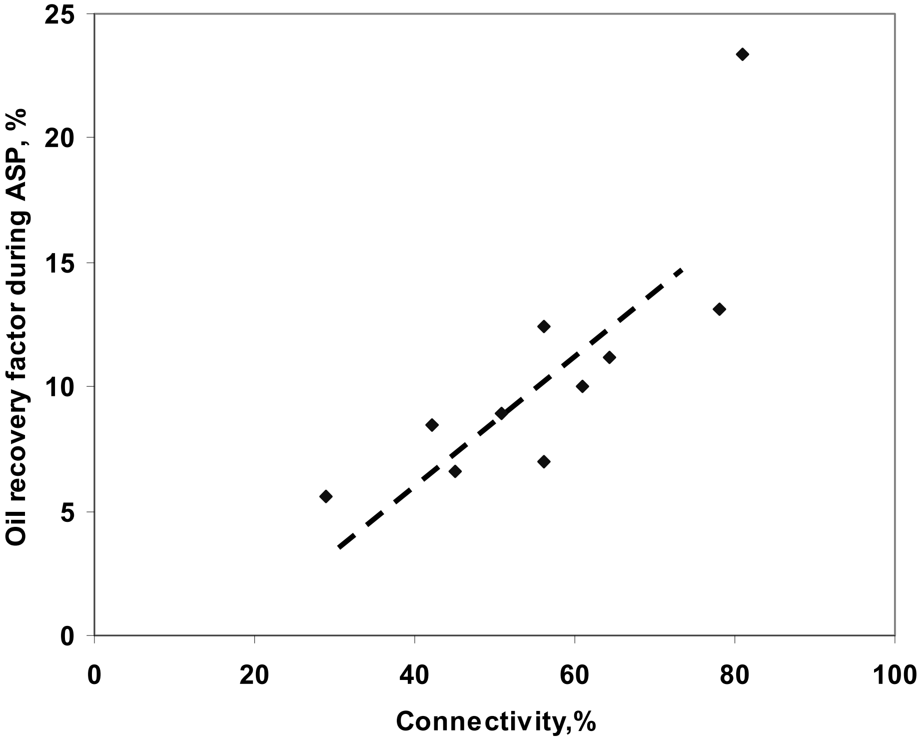

Figure 14 – Oil recovery factor during ASP vs. formation connectivity

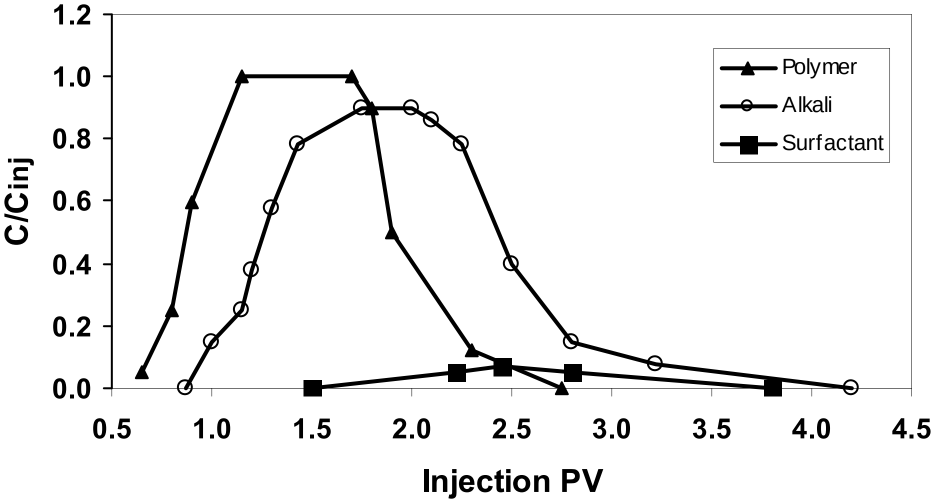

Figure 15 – Effluent concentration histories, 1 – polymer, 2 – alkali, 3 – surfactant (Huang and Yu, 2002)