Chemical flood enhanced oil recovery: a review

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Abstract: Chemical flooding has been found to be one of the major EOR techniques especially for reservoirs where thermal methods are not feasible. The application of chemical flooding is strongly influenced by the current economics, type of reserve oil and crude oil price. In this paper, an up to date status of chemical flooding at the laboratory scale, pilot projects and field applications have been reported. The basic mechanisms of different chemical methods have been discussed including the interactions of different chemicals with the reservoir rocks and fluids. The average recovery of oil after the conventional water flooding is highly encouraging particularly when the demand and price of crude oil is increasing day by day. [Received: February 22, 2013; Accepted: October 4, 2013]

Keywords: enhanced oil recovery; EOR; flooding; alkali; surfactant; polymer; interfacial tension; IFT.

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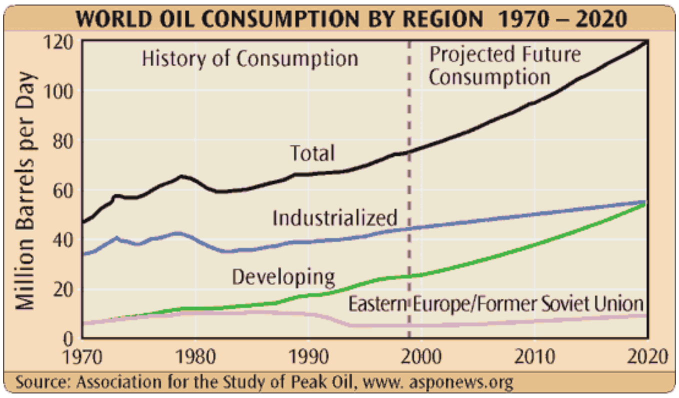
1 Introduction

The oil industry is presently facing pressing challenges to increase well productivity as demand for oil is increasing day by day, particularly in the developed and developing countries. A typical picture of worldwide consumption of oil is shown in Figure 1. It may be found that the rate of increase in consumption is a major issue in the current context. On the other hand, discovery of new oil fields is very limited. Most of the reservoirs are now at matured state with low production rate. Thus, enhanced oil recovery (EOR) projects are strongly influenced by the current economics, type of reserve oil and crude oil price.

Figure 1 Worldwide consumption of oil (see online version for colours)



Typically, two thirds of the original oil in place (OOIP) in a reservoir is not produced and is still pending for recovery by efficient EOR methods. As the displacement of oil by water proceeds, the oil phase eventually disintegrates into blobs of residual oil, which are immobilised in the pores by capillary forces. This entrapped oil can be recovered if the capillary forces, whose strength is set by the oil/water interfacial tension (IFT), are reduced or if the viscous forces increase sufficiently (Larson et al., 1980). The residual oil saturation depends strongly on the microscopic capillary number $Ca = \mu_w v / \sigma_{ow}$, where σ_{ow}, v and μ_w are the oil-water IFT, velocity and water viscosity respectively. The displacement of oil in waterflooding depends on the macroscopic sweep efficiency, which may be increased by improving mobility ratio. Thus the efficient and practical way to increase the capillary number is to reduce the IFT by three to four orders of magnitude and to increase the viscosity displacing fluids.

Most of the oil reservoirs are hardly having uniform porosities and permeabilities. Thus when water or other fluids are injected under pressure, they generally follow the path of least resistance and causes early breakthrough of injected fluids. This leads to by-passing of the trapped oil in the lower permeability zones. However, technically it is possible to improve this recovery efficiency by applying EOR processes. Many EOR techniques are being tried worldwide to mitigate such problems. Chemical flooding is one of the best methods that can be used to recover up to an additional 35% of OOIP. Recently chemical flooding in different modes like injection of polymer, polymer/alkaline, surfactant/polymer and alkaline/surfactant/polymer (ASP) slug are getting importance because of significant potentiality (Wang et al., 2007; Clark et al., 1988; Meyers et al., 1992; Vargo et al., 1999; Demin et al., 1999).

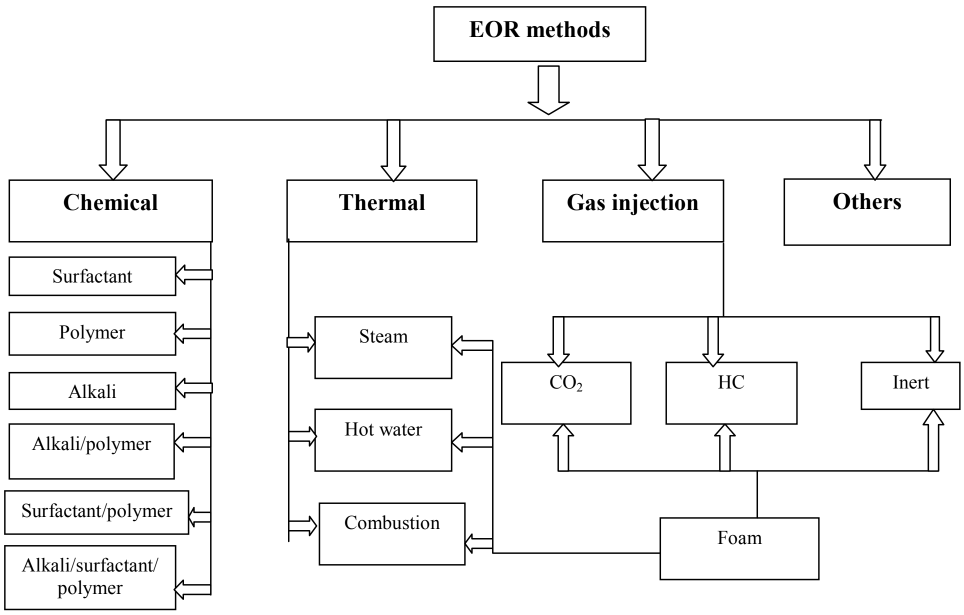
Addition of polymer increases the viscosity of its aqueous phase (Walters and Jones, 1989; Samanta et al., 2010), and decreases the permeability to water so that the mobility of aqueous phase decreases. Thus, the decrease in mobility ratio greatly increase sweep efficiency. Another main accepted mechanism of mobile average remaining oil after water flooding is that there must be a rather large viscous force perpendicular to the oil-water interface to push the average remaining oil. This force must overcome the capillary forces retaining the average remaining oil, move it, mobilise it, and recover it (Guo and Haung, 1990). Alkali reacts with certain crude oil constituents and can lower water crude oil IFT, emulsify oil and water, change rock wettability and solubilise interfacial films, all of which may lead to increased oil recovery (Jenning, 1975;

McCaffery, 1976; Li et al., 2004; Guo et al., 2006). Surfactants are considered as good EOR agents since 1970s (Healy and Reed, 1974) because it can significantly lower the IFTs and alter wetting properties. Displacement by surfactant solutions is one of the important tertiary recovery processes by chemical solutions. The addition of surfactant decreases the IFT between crude oil and formation water, lowers the capillary forces, facilitates oil mobilisation, and enhances oil recovery. In recent years a great progress has been made either in laboratory studies or in pilot tests for alkali/surfactant/polymer (ASP) and surfactant/alkali/polymer (SAP) combination flooding (Zhang et al., 2007; Hou et al., 2005; Daoshan et al., 2004; Thomas and Farouq Ali, 2001; Zerpa et al., 2005; Wang et al., 2011). ASP flooding is a technique which is developed out on the basis of incorporation of mechanisms of alkali flooding, surfactant flooding and polymer flooding (Wang et al., 2007) and oil recovery is enhanced gently by decreasing IFT, increasing capillary number, enhancing microscopic displacing efficiency, improving mobility ration and increasing macroscopic sweep efficiency (Shen and Yu, 2002).

2 Chemical EOR methods

The EOR methods are often classified as shown in Figure 2. The schematic diagram is a simplified- and material-oriented description of several of intensive recovery technologies. One of the greatest advantages of this classification is that the interpretation of each group is apparently transparent and easy to comprehend. The definition of the chemical EOR methods is given as those methods, which are based on injection of chemical compounds. Chemical flooding has been shown to achieve good oil recovery in many successful laboratory tests and several small commercial field projects.

Figure 2 Simplified classification of EOR methods



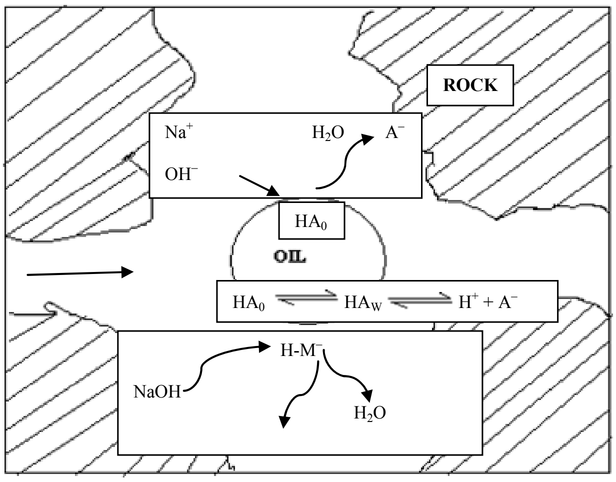
2.1 Alkali flooding

Several mechanisms are proposed for recovery mechanisms by alkali injections (De Zabala et al., 1982; Ramakrishnan and Wasan, 1983). These include emulsification with coalescence, wettability gradients, oil-phase swelling, disruption of rigid films, and low IFTs. The existence of different mechanisms should be attributed to the chemical character of crude oil and the reservoir rock. Different crude oils in different reservoir rock can lead to widely disparate behaviour when they contact under dissimilar environments such as temperature, salinity, hardness concentration, and pH. However, all the researchers agree on the fact that the acidic components in the crude oil are most important factor for alkali flooding. Alkali flooding is a process in which water at pH value of 10–12 is injected to improved recovery (Dokla, 1981). The pH value between 10–12 is obtained at NaOH concentration 0.01 to 1.0 wt% (Samanta et al., 2011a). The effect of alkali solution on oil recovery is partly due to the chemical reactions between the alkali and organic acids that exist in the crude oil. These reactions resulted in the formation of surfactant and emulsification (Langnes et al., 1972); therefore the capillary pressures between the aqueous and oleic phases were reduced oil-water IFT. The reaction is dependent on petroleum acid number and also varied in composition of crude oil (Mayers et al., 1983). The hydroxide ion must react with petroleum acids from the crude oil to form a surfactant. A mechanism is shown in Figure 3. When the aqueous phase and oil phase are in contact, alkaline in the aqueous phase and organic acids, HA in the oil phase migrate into the interface, react and produce surface-active species (petroleum soap). The effect of caustic to the petroleum acids is expressed by the reaction below (Samanta et al., 2011a),

$$HA + OH^- \rightleftharpoons A^- + H_2O \tag{1}$$

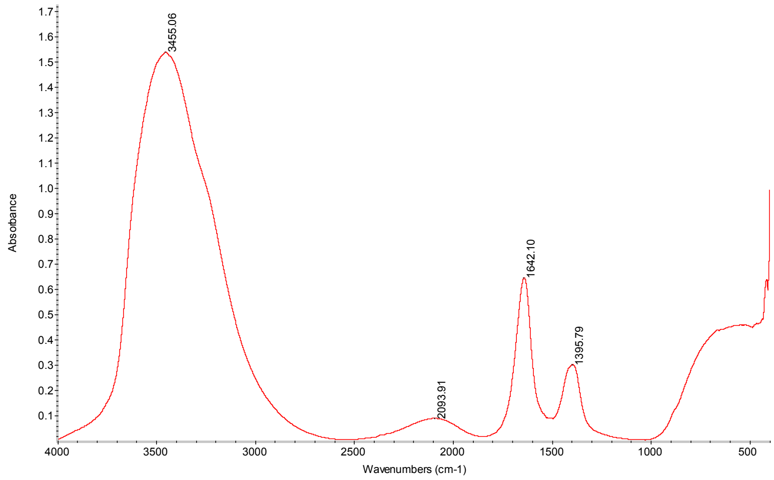
$K = c_A / c_{HA} c_{OH^-}$ is the equilibrium constant. Because this mixed alkaline has buffering ability, c_{OH^-} is a constant. Thus, the ratio of ionised to unionised acids governs the IFT. The IFT is a function of the interfacial ionised acid concentration, which depends chiefly on its rates of production and desorption from the interface (Zhang et al., 2004).

Figure 3 Schematic diagram of alkali-petroleum acid interaction



The presence of acidic groups in crude oil is also supported by the total acid number (0.038 mg KOH/g) of the crude oil. In our earlier work (Samanta, 2011), it has been shown (Figure 4) that IR spectrum of aqueous phase extracted from the mixture of crude oil and NaOH solution reveals the formation petroleum soap with a spectra around 1,650 cm^{-1}.

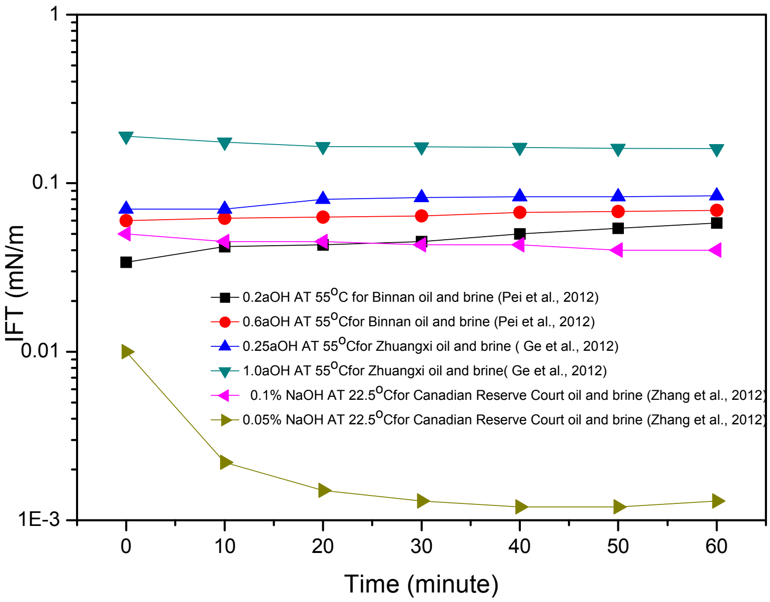
Figure 4 FTIR spectrum of fluid phase after interaction with 1.0% alkali (see online version for colours)



Source: Samanta (2011)

The use of alkaline waterflooding as an EOR process has been studied in the laboratory by many investigators. Atkinson (1927) believed that residual oil is held within the spaces between sand grains by forces of capillary and adhesion in conjunction with oil viscosity and those alkaline solutions overcome these forces to release the oil. Cooke et al. (1974) reported a mechanism by which caustic NaOH could improve water flood oil recovery. They observed that under proper conditions of pH, salinity and temperature, some crude oils and porous media are converted from water-wet to oil wet. Jennings et al. (1974) proposed yet a fourth mechanism by which caustic injection can improve oil recovery. Their laboratory experiments showed that if IFT were low enough, residual oil in a preferentially water-wet core could be emulsified in situ. Symonds et al. (1991) studied caustic flooding for heavy oil recovery. They performed experiments using NaOH as the alkaline agent, and Wainright (408 mPa.s) and Horsfely (18 mPa.s) as crude oils. They examined the effect of injection rate and loss of caustic to the porous medium and found that performance in all cases they had tried was sensitive to injection rate, and loss of caustic to the rock and fluids was significant. Chiwetelu et al. (1994) investigated the feasibility of employing various alkaline agents (NaOH, sodium orthosilicate and sodium metasilicate) to enhance the recovery of specific Saskatchewan heavy oil from the Kindersley region. The dynamic interfacial tension (DIT) of solutions of the alkali in contact with the crude oil was measured for a range of concentrations and temperatures, and the most interfacially active formulations were then tested for their oil recovery efficiencies by conducting oil displacement experiments in unconsolidated linear sand packs at 25°C and 65°C. Some reported data of DIT curves between crude oil and brine have been presented in Figure 5. It has been found that for suitable crude oil alkali can reduce the IFT significantly. Bortolotti et al. (2009) reported that intermittent alkali flooding can significantly enhance oil recovery in oil-wet carbonate reservoirs by reducing the IFT between the reservoir fluids and by reversing the wettability to a more favourable condition. Arhuoma et al. (2009) developed a simulation technique to simulate and match the experimentally measured pressure drop and cumulative oil production during the alkaline flooding processes by incorporating both the measured W/O emulsion viscosity and relative permeability. A comparative picture of oil recovery by surfactant flooding after conventional water flooding at the laboratory scale has been presented in Table 1. The additional recovery after water flooding depends on the type of crude oil, petro-physical properties of core/sandpack and dosing of alkali.

Figure 5 DIT curves between crude oil and brine (see online version for colours)



2.2 Surfactant flooding

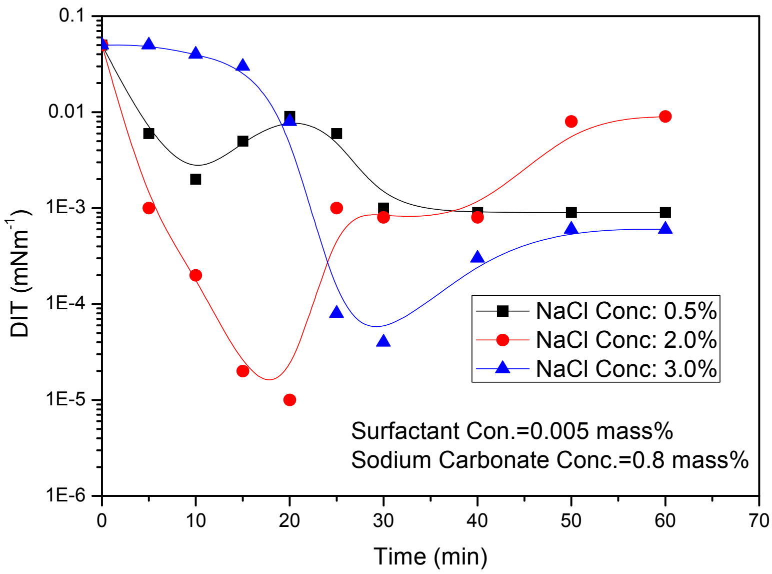
Surface active agents, usually known as surfactants, have at least one hydrophilic and at least one hydrophobic group in the same molecule. Because of this character they can significantly lower the IFTs between crude oil and brine by getting adsorbed on the liquid-liquid interface and alter wetting properties of reservoir rock and fluid. The cost of surfactant is the major limiting factor successful implementation of EOR by surfactant flooding process. George et al. (2008) reported that the alkaline surfactant process co-injects alkali and synthetic surfactant. The alkali generates soap in situ by reaction between the alkali and naphthenic acids in the crude oil. It was recently recognised that the local ratio of soap/surfactant determines the local optimal salinity for minimum IFT.

Table 1 Oil recovery by alkali flooding

References	*Porosity %*	*Permeability mD*	*Initial oil saturation %*	*Crude oil properties*	*Water flooding recovery (%) OOIP*	*Enhanced oil recovery (%) OOIP*
Chiwetelu et al. (1994)	32–33	147,000		Density: 945.1 kg/m^3 at 25°C Viscosity: 474.4 mPa.s at 25°C Acid number: 1.88 mg KOH/g	20	30
Pei et al. (2012)	44.23	2,260	90.05	Density: 947.2 kg/m^3 at 55°C Viscosity: 2,000 mPa.s at 55°C Acid number: 2.69 mg KOH/g	32.24	16.50
Ge et al. (2012)	-	1,580	83.5	Crude oil: Zhuangxi 106 Density: 930.2 kg/m^3 at 50°C Viscosity: 390 mPa.s at 50°C Acid number: 1.0846 mg KOH/g	38.6	12.4
Ge et al. (2012)	-	1,580	85.2	Crude oil: Chenzhuang Density: 977.8 kg/m^3 at 50°C Viscosity: 3,450 mPa.s at 50°C Acid number: 2.018 mg KOH/g	33.7	12.9
Almalik et al. (1997)	33.59	6,000	79.55	API gravity: 30.40°	73.4	13.33
Symonds et al. (1991)	34.5	18,500	87.0	Crude oil: dried Wainright crude Density: 941.3 kg/m^3 at 23°C Viscosity: 408.3 mPa.s at 23°C Acid number: 0.527 mg KOH/g	53.9	7.0
Symonds et al. (1991)	39.2	9,700	85.9	Crude oil: Horsefly crude Density: 886 kg/m^3 at 23°C Viscosity: 18.0 mPa.s at 23°C Acid number: 1.88 mg KOH/g	60.0	12.1
Samanta et al. (2010)	39.6	4,449	79.1	API gravity: 38.86° Viscosity: 119 mPa.s at 30°C Acid number: 0.038 mg of KOH/g	51.5	15.27

The fundamental mechanism for the lowering of DIT between crude oil is very much important while designing an surfactant flooding project. The DIT behaviour is a result of simultaneous adsorption of the added surfactant, ionised acid and unionised acid onto the interface forming a mixed adsorption layer. Typical DIT behaviour between crude oil and surfactant solution at different salinity and 0.8% sodium carbonate concentration as reported by Zhao et al. (2005) is shown in Figure 6.

Figure 6 DIT between crude oil and surfactant solution at different salinity (see online version for colours)



Source: Zhao et al. (2005)

The surfactant is dissolved in either water or oil to form microemulsion (Bera et al., 2011) which in turn forms an oil bank. The formation of oil bank and subsequent maintenance of sweep efficiency and pressure gradient by injection of polymer and chase water increase the oil recovery significantly (Hill et al., 1973; Larson and Hirasaki, 1978; Shah and Schechter, 1977).

The idea of injecting surfactant solution to improve imbibition recovery was proposed for fractured reservoirs (Michels et al., 1996; Miller and Austad, 1996; Austad and Milter, 1997) and carbonaceous oil fields in the USA (Flumerfelt et al., 1993; Spinler et al., 2000; Chen et al., 2000). Other studies as to the effect of surfactant on the capillary imbibition recovery performance basically aimed at identification of the mechanisms involved without considering any particular field (Keijzer and Vries, 1990; Schechter et al., 1994; Cuiec et al., 1994; Babadagli, 1996). In general, the positive effect of lowered IFT on the ultimate recovery due to surfactant addition was observed in these studies.

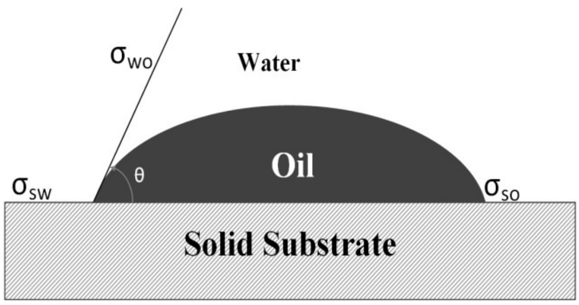
Another important role of surfactant in EOR is the change of wettability of reservoir rock. According to Craig (1971), wettability is defined as “the tendency of one fluid to spread on or adhere to a solid surface in presence of other immiscible fluids”. Wettability of a solid surface relates directly to the solid-fluids and fluid-fluid interactions. The interaction between two immiscible phases implies the interfacial energy. Attraction between the substrates causes lower interfacial energy, and repulsion forces result in higher energy surface. The interfacial forces in a three-phase system relate to one another in a famous equation known as Young's law (Marmur, 1996; Kwok et al., 1998),

$$\cos\theta = \frac{\sigma_{sw} - \sigma_{so}}{\sigma_{wo}} \tag{2}$$

where θ is contact angle and σ values indicate the IFTs between solid-water (σ_{sw}), solid-oil (σ_{so}), and water-oil (σ_{wo}) interfaces.

Figure 7 illustrates the situation how the oil drop will reside on solid surface in presence of another immiscible liquid such as water (Bera et al., 2012a). The Young's equation is valid at equilibrium condition for ideal state of a perfectly smooth, chemically homogeneous, rigid, insoluble, and non-reactive surface. Wettability of reservoir rock has strong effect on distribution, location, and flow of oil and water in reservoir during production (Anderson, 1986; Morrow, 1990). Some special cases a change of wettability from water-wet to oil wet also improve the recovery. A discontinuous non-wetting residual oil is converted to a continuous wetting phase, providing a flow path for what would otherwise be trapped oil. Enhanced oil recoveries by surfactant flooding reported by different authors are shown in Table 2. Similar to alkali flooding additional recovery by surfactant flooding also depends on the quality of crude oil and surfactants used. Salinity plays an important role in reducing the IFT between crude oil and water. At optimal salinity (6 wt% NaCl) the IFT value for crude oil and brine system is near about 7 mN/m which is considerably lower than IFT of crude oil-water system (48 mN/m). The optimal salinity also depends on the nature of crude oil and it varies for different types of crude oils also. Microemulsion reduces IFT significantly up to a range of 10^{-3} mN/m where surfactant can only reduce up to 10^{-1} mN/m.

Figure 7 Illustration of contact angle in three-phase system on solid surface



2.3 Polymer flooding

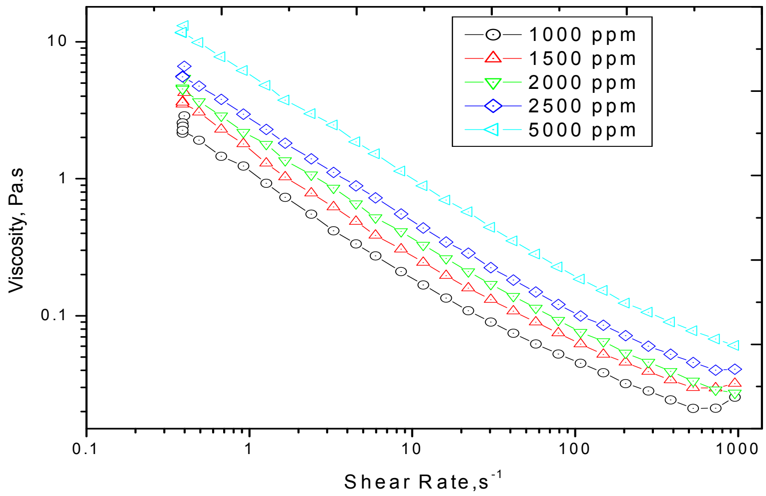
The most widely used chemical method is polymer flooding. Polymer increases the viscosity of the injected water and reduces permeability of the porous media, allowing for an increase in the vertical and areal sweep efficiencies, and consequently, higher oil recovery (Needham and Doe, 1987). The main objective of polymer injection is for mobility control, by reducing the mobility ratio between water and oil. The reduction of the mobility ratio is achieved by increasing the viscosity of the aqueous phase.

Table 2 EOR by surfactant flooding

References	*Porosity %*	*Permeability mD*	*Initial oil saturation %*	*Crude oil properties*	*Water flooding recovery (%) OOIP*	*Enhanced oil recovery (%) OOIP*
Mwangi (2008)	16–17%	40–70	82.5	Viscosity: 12.8 cp at 50°C	32.24	8–15
Aoudia et al. (2010)	13.7–14.6	2.2–2.9		Density: 836.0 kg/m^3 at 65°C Viscosity: < 1 cp at 65°C	40	42
Alagic and Skauge (2010)	22.6–23.2	561–715	76–79	Density: 878.4 at 20°C Viscosity 13.80 cp at 20°C Acid number: 2.84 mg KOH/g	40–60	5–15
Samanta et al. (2011b)	38.665	1234	80.9	API gravity: 38.86° Viscosity: 119 mPa.s at 30°C Acid number: 0.038 mg of KOH/g	52	18

The typical flow curves of aqueous solutions of partially hydrolysed polyacrylamide (PHPA) polymer at different concentrations are shown in Figure 8. The viscosity of solutions increased with increasing polymer concentration as expected. It can be seen from the figure, the viscosities of all samples decreased with the increasing shear rate, suggesting that the aqueous solution of PHPA exhibit non-Newtonian behaviour. This is due to uncoiling and aligning of polymer chains when exposed to shear flow. The zero shear viscosity can be measured by extrapolating the viscosity curve as shear rate approaches to zero. This is the maximum viscosity of the solutions. The behaviours of such fluids which display a decreasing apparent viscosity with increasing shear rate can be characterised as pseudoplastic fluid. This model fairly represents the flow behaviour of polymer at all shear rates except at the very high rates which may exist at the injection well. At these high rates of shear the polymer solution loses its pseudoplastic nature and displays an increasing apparent viscosity with increasing shear rate.

Figure 8 Viscosity of different PHPA solution at 28.5°C (see online version for colours)



Source: Samanta (2011)

Addition of polymer increases the viscosity of aqueous phase, which in turn reduce the mobility of aqueous phase. Unlike the surfactant, the presence of polymer do not decrease residual oil saturation with a few exceptions (Wang et al., 2000), but it greatly increase sweep efficiency. Another main accepted mechanism of mobile residual oil after water flooding is that there must be a rather large viscous force perpendicular to the oil-water interface to push the residual oil. This force must overcome the capillary forces retaining the residual oil, move it, mobilise it, and recover it (Guo and Huang, 1990). Wang (1995) studied the viscoelastic effect of retained polymer molecules in porous media based on the pressure draw-down and buildup process. Wang et al. (2000) put forward the major mechanism of polymer flooding increasing the micro-scale displacement efficiency was that the flow pattern and magnitude of the viscous force parallel to the oil-water interface caused by the flow of viscoelastic fluids in porous media is different to that of Newtonian fluids. Xia et al. (2004) considered that viscoelasticity of polymer solution flow was the main cause of the increase in oil displacement efficiency. Different polymer fluids have quite different elastic properties.

Table 3 Oil recovery by polymer flooding

References	*Porosity %*	*Permeability mD*	*Initial oil saturation %*	*Viscosity of crude oil*	*Water flooding recovery (%) OOIP*	*Enhanced oil recovery (%) OOIP*
Wang and Dong (2007)	35	7.0 μm^2	89	1,450 mPa.s at 22.5°C	35	17 by 0.2% polymer
Asgharik and Nakutnyy (2008)	-	2,100 mD	-	1,450 mPa.s at 25°C	35	19
He et al. (2011)	-	0.1–4.4 μm^2	-	9.5 mPa.s at 45°C	38.2	11.7
Samanta (2011)	37	1,240	80.5–82.7	API gravity: 38.86° Viscosity: 119 mPa.s at 30°C	52	17–19

Yang et al. (2006) found that an incremental recovery over water flooding of more than 20% OOIP can be obtained by injection of high molecular weight, high concentration polymer solution in Daqing field. Two types of polymers, polyacrylamide and polysaccharide, are commonly used in EOR. Polyacrylamides used in polymer EOR processes, normally are PHPAs. Thus, the PHPA is negatively charged, as is the anionic surfactant. Shupe (1981) tested the effect of pH, dissolved oxygen, salinity and hardness on PHPA polymer stability. PHPA has been used in about 95% of the reported polymer tests (Lake, 1989). The commonly used polysaccharide is xanthan gum, which is a bacterial polysaccharide (Walters and Jones, 1989; Mariya et al., 2007). Compared to PHPA, xanthan gum has a more rigid structure and relatively non-ionic. These properties make it relatively insensitive to salinity and hardness. However, it is susceptible to bacterial degradation after it has been injected into the field. Some reported results of polymer flooding are shown in Table 3. Wang and Dong (2007) reported 17% additional recovery by injecting 4.5 pore volume of 0.2% polymer solution. Asgharik and Nakutnyy (2008) performed the polymer flooding experiments in unconsolidated sandpack environment saturated with heavy oil at irreducible water saturation and found more than 19% recovery of OOIP by injecting 1.5 pore volumes of 10,000 ppm polymer solution. He et al. (2011) found 11.7% additional recovery using field cores.

2.4 Alkali-surfactant-polymer enhanced recovery

Currently, ASP is considered as the most promising chemical method in EOR because it integrates the advantages of alkali, surfactant and polymer. In the ASP process, a very low concentration of the surfactant is used to achieve ultra low IFT between the trapped oil and the injection fluid/formation water. The alkali also simultaneously reacts with the acidic components in the crude oil to form additional surfactant *in situ*, thus, continuously providing ultra low IFT and freeing the trapped oil. In the ASP process, polymer is used to increase the viscosity of the injection fluid, to minimise channelling, and provide mobility control. A schematic diagram of ASP flood is shown in Figure 9, which clearly shows the typical stages in an ASP flooding process, namely: a preflush of brine to lower the salinity of the reservoir, an ASP solution used to reduce the IFT between the aqueous and oleic phases, a polymer solution to perform a uniform sweep of the oil and the previous slugs, and chase water to finally drive the oil and the chemicals to the producer wells. Finally water drive is used to move the front towards the producing well. A typical picture showing the oil recovery by water flooding and subsequent ASP flooding is reported in Figure 10.

The oil recovery (N_P) by ASP flooding can be represented by the following equation:

$$N_P = E_D E_A E_{VI}\left(\frac{S_o B_p}{B_o}\right) \tag{3}$$

where E_D is the pore to pore displacement efficiency improved with alkali and surfactant; E_A is the areal displacement efficiency improved with polymer; E_{VI} is the vertical displacement efficiency improved with polymer and $\frac{S_o V_p}{B_o}$ is the stock tank oil saturation.

Table 4 Some reported field data of chemical flood enhanced oil recovery

Ref.	*Field*	*Reservoir rock and fluid properties*	*Methods applied and recovery*
Du et al. (2011)	St. Joseph Field Offshore, Malaysia	P_{av} = 1,000 psia Porosity and permeability-high Medium °API gravity crude oil Lithology-sandstone	Polymer flooding – 13% over secondary recovery ASP flooding – 20% over secondary recovery
Sandoval et al. (2010)	Upper Magadalena Valley, Cambodia Basin	k = 50–200 md φ = 10% Oil viscosity = 10.8 cp at reservoir temperature Lithology-sandstone	Surfactant-polymer – 60% Polymer – 44%
Shutang and Qiang (2010)	Daging Oil Field, China	P_{av} = 12.9 MPa T_{av} = 45°C Well pattern – 5-spot $k = 1{,}120 \times 10^{-3}\ \mu m^2$ Oil viscosity = 10.8 cp Lithology-sandstone	ASP flooding – 20% over water flooding
Jain et al. (2012)	Jhalora Field, Cambay Basin, India	k= 1.9–8.7 Darcy Oil viscosity = 30–50 cp at reservoir temperature Well pattern – inverted five-spot Lithology-sandstone	ASP (pilot) – 23% OOIP
Shehata et al. (2012)	North Africa Field	k = 200–4,000 md φ = 23% μ_{oil} = 12–23 cp P_{av}=2500 psia Lithology-sandstone	Polymer flooding recovery – 3–10% over water flooding
Mogbo (2011)	Niger Delta Offshore, Nigeria	k = 100–6,000 md φ = 39% μ_{oil} = 2–16 cp °API – 16–27 P_{av} = 2,500 psia Lithology-sandstone	Polymer flooding recovery – 7% over water flooding
Pitts et al. (2006)	Tanner Minnelusa Field, WY	k = 200 md φ = 20% μ_{oil} =11 cp °API = 21 Lithology-sandstone	Alkali-polymer – 17% over water flooding ASP – 36% over water flooding

Figure 9 Flow diagram of ASP flooding (see online version for colours)

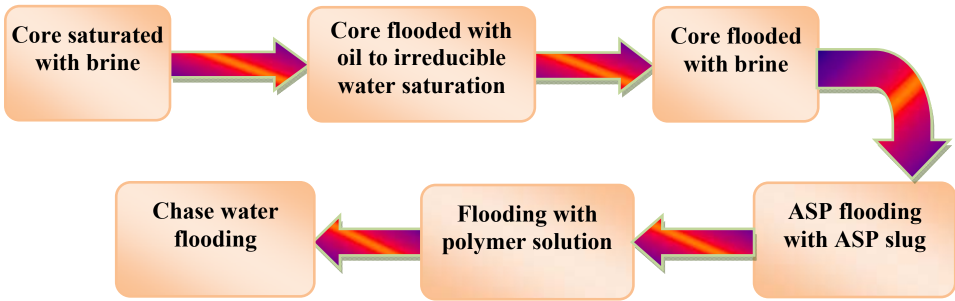
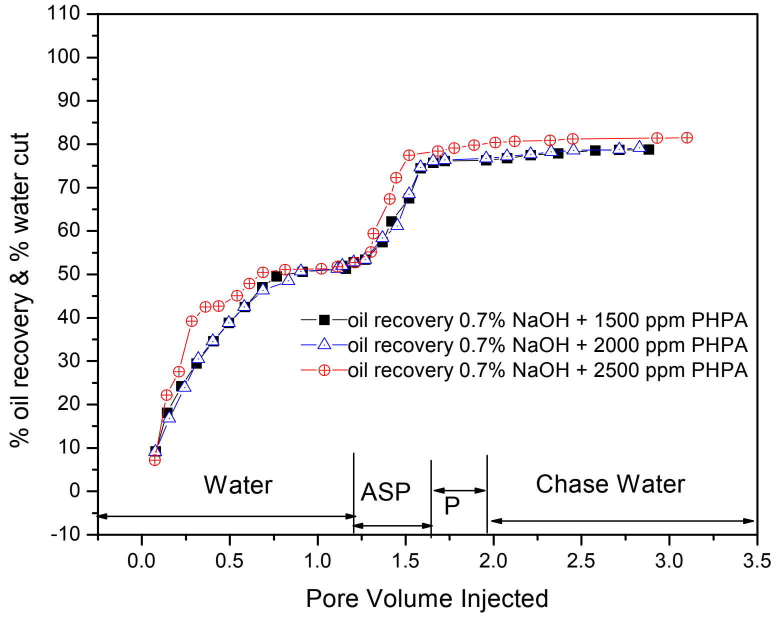


Figure 10 Production performance of alkali-surfactant-polymer flooding (see online version for colours)



Source: Samanta (2011)

2.5 *Microemulsion flooding*

Microemulsions are thermodynamically stable, isotropic dispersions of otherwise immiscible oil and water stabilised by surfactants (and/or cosurfactants) (Kahlweit et al., 1985; Aveyard et al., 1990; Paul and Moulik, 1997).

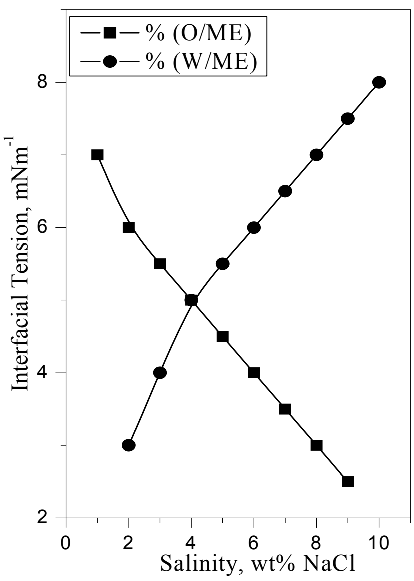
EOR by microemulsion flooding has become more attractive in recent years because of its high level of extraction efficiency (Elraies et al., 2010; Kumar and Mohanty, 2010; Southwick et al., 2010; Santanna et al., 2009). Ultra low IFT IFT can be obtained by creating a middle phase microemulsion using brine, oil, surfactant and cosurfactant. The phase behaviour of surfactant-brine-oil systems is of immense importance for surfactant flooding in EOR due to the well-established relationship between the

IFT and microemulsion phase behaviour (Shah and Schechter, 1977; Abe et al., 1986, 1987; Engelskirchen et al., 2007; Kayalia et al., 2010). The phase behaviour of surfactant/cosurfactant-brine-oil system is one of the key factors in interpreting the performance of chemically EOR by microemulsion process (Healy and Reed, 1974; Healy et al., 1975; Barnes et al., 2008).

Microemulsion flooding is preferred over alkali, surfactant or polymer flooding due to unique physicochemical properties of microemulsions like production of ultra-low IFT, moderate viscosity, good water solubilisation capacity, and nanometer-sized droplets (Shinoda and Lindman, 1987; Friberg and Bothorel, 1987; Holmberg, 1994; Dungan et al., 1997). They are able to reduce IFT up to the magnitude of 10^{-3}–10^{-4} mN/m whereas other surface active agents cannot. It is also advantageous to inject microemulsion slug as displacing fluid due to its higher viscosity than water. Water solubilisation capacity of microemulsion also makes it proper injecting fluid in EOR techniques. Another important property of microemulsion is its droplet size. In particular, the size distribution of microemulsion gives essential information for reasonable understanding of the mechanism governing both the stability and penetration into porous media.

Bera et al. (2012b) investigated the behaviours of microemulsions by measurements of its IFT for microemulsion-oil and microemulsion-water systems. Figure 11 represents the IFTs of excess oil-microemulsion (O/ME) and excess water-microemulsion (W/ME) systems. With increase in salinity the IFT between excess oil and microemulsion phase decreases, while water and microemulsion phase increases. Whenever the middle phase microemulsion is present, both values of IFT are low. The curves for both of the measurements are found to intersect usually at low values of IFT, and the salinity corresponding to this point is termed as the optimal salinity for the surfactant system.

Figure 11 Interfacial tensions of excess W/ME and excess O/ME system for SDS microemulsion system



Source: Bera et al. (2012b)

Bera (2013) showed that the recovery efficiency of microemulsion flooding is more than 29% of OOIP over the conventional water flooding. Several mechanisms such reduction of IFT, emulsification of oil and water, solubilisation of interfacial films, wettability reversal, viscosity improvement, etc., are responsible for the improved oil recovery.

3 Chemical flooding activities in different fields

To enhance the productivities different countries started enhanced recovery techniques by chemical injection. In China, few large-scale successes with polymer flooding and ASP flooding processes have been reported. To date, the PF process has been applied successfully in several major Chinese oil fields such as Daqing and Shengli (Chang et al., 2006). PF alone contributed approximately 250,000 BOPD of production in 2004 from these two fields. Incremental oil recoveries of up to 14% of the OOIP have been obtained in good-quality reservoirs. Seven PF pilot tests were conducted in the Daqing oil field from 1972 through 1998. Continued research and field testing led to fieldwide expansion in 1996. There were 31 commercial-scale PF projects in Daqing in 2004, with 2,427 injection wells and 2,916 production wells. The Tanner field of Wyoming, USA is a sandstone formation containing 21°API gravity crude with a viscosity of 11 cp at a reservoir temperature of 175°F (79°C). The Tanner field ASP flood is very unique in that alkaline-surfactant-polymer injection began after a short water flood when the oil cut was 43%.The project is projected to produce an additional 17% of the OOIP beyond that producible by water injection. The total cost of chemicals, plant and engineering was US $5.85 per incremental barrel of oil recovered. Payout was 2.5 years based on the cost of oil in the period 2000–2005 (Pitts et al., 2006). An ASP flood in the Sho-Vel-Tum field sponsored by the US Department of Energy. This was a small pilot test to prove the feasibility of the ASP process. The well is located in Oklahoma, USA and the reservoir is only 700 feet (214 m) deep making it the shallowest well in the USA where an ASP flood has been initiated. The well has been producing for over 40 years and was producing 4 bbl/day before the ASP project was initiated. The pilot project added 10,444 barrels of incremental oil over a period of 1.3 years (Felber, 2003). Taber South oil filed of Canada was producing 300 bbl/day before the ASP flood. ASP injection started in June 2006. Production increased to 1,502 bbl/day as of December 2007. Oil cuts increased from 1.7% to 7.3% over the same period. Alkali surfactant was implemeted to improve the injectivity of a waterflood located in the Big Sinking Field, Kentucky USA. The reservoir contains 100 million barrels of oil at a depth of 1,150 feet (350 metres) and a bottom hole temperature of 30°C. The economic analysis of the project showed that a 30 barrel (4.8 m^3) increase in injectivity for a mature waterflood with an efficiency of 15:1 (barrels injected/barrel oil produced) would result in a payout of approximately eight months with oil at US $25/bbl (US $4/$m^3$). Alkaline surfactant pilot project was implemented in Angsi field located offshore Terengganu, Malaysia, to evaluate the effectiveness of the alkaline surfactant process in improving oil recovery through the reduction of residual oil saturation. Oil chemical technologies' SS 6-72LV was one the surfactant used in the pilot test. The alkali surfactant solution was injected into Angsi I-68 reservoir as a single well tracer test used to determine the residual oil saturation. The Angsi is the second largest reservoir with the expected recovery factor of 39% of the OOIP (Othman et al., 2007). In India, ONGC has implemented a large scale polymer flood project in Sanand oil field which lies in Ahmedabad-Mehsana block of Cambay Basin in India. Mangala is the largest discovered oil field in the Barmer Basin. Its initial oil production began in September 2009, and implementation of ASP project under process (Pandey, 2010).

However, even with these advantages and the success of many ASP projects, the process is not without problems. One of the major problems in ASP process is the scale formation caused by the reaction between the alkali and concomitant divalent metals cations. The presence of these cations such as calcium and magnesium ions, results in excessive alkali consumption and surfactant precipitation (Mohnot and Chakrabarti, 1987).

4 Conclusions

EOR by chemical flooding is based on two basic mechanisms viz. increase of macroscopic efficiency and increase of microscopic displacement efficiency. Macroscopic efficiency can be improved by polymer injection. Injection of polymer solution increases the viscosity of displacing fluid and reduces the effective permeability to water. Microscopic displacement efficiency can be improved by injection of alkali and surfactant by several mechanism viz., reduction IFT, emulsification of oil and water, solubilisation of interfacial films, wettability reversal, etc.

In the present paper an exclusive literature review on different types of chemical flooding performed at the laboratory scale, pilot project and actual field including every specific mechanism have been reported. Recovery efficiencies of different reported work vary widely as the efficiencies depend on both reservoir fluid and rock properties including reservoir pressure and temperature. Economic performance is dominated by oil price, cost per barrel of injected solution, and duration of chemical injection. Chemical flood oil recoveries have good prospects as most of the reservoirs are getting matured and demand of oil increasing day by day.

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