Understanding the Impact of Chemicals in Produced Water in Enhanced Oil Recovery (EOR) Projects

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Enhanced oil recovery (EOR) is a generic term used for increasing the amounts of crude oil that can be extracted from an oil reservoir or an oilfield. Usually this is done in an effort to increase the output of a matured field where conventional-recovery methods have been exhausted. EOR efforts require strong reservoir characterization techniques i.e. fractured network mapping, permeability distribution through well tests, and permeability upscaling.

Methods used for EOR

Four prevalent methods for EOR are (Bai, 2011):

- Gas injection is the most technically feasible EOR operation at low permeabilities, and is the most widely applied method for light-oil recovery. Methods include, gas flooding, gas injection, use of miscible gases, nitrogen injection, carbon dioxide gas injection and CO_2 flooding.

- Thermal processes are best suited for heavy-oil reservoirs that cannot be produced efficiently from cold flow. Within this steam injection and solar thermal methods are adopted.

- Microbial Enhanced Oil Recovery (MEOR) is a biological based EOR technology where three general strategies exist for the implementation of MEOR: (1) Injection of nutrients to stimulate indigenous microorganisms, (2) Injection of exogenous microorganisms(s) and nutrients, or (3) Injection of ex situ produced products, e.g. biosurfactants. This is the simplest, and most likely for short term success in full field-scale.

- Chemical processes are used for oils that are more viscous than those recovered by gas injection and less viscous than those involving thermal processes. Polymer, alkaline/surfactant/polymer (ASP) and surfactant flooding are included in chemical EOR operations (CEOR).

The application of chemical enhanced oil recovery (CEOR) floods are increasing, see Figure 1. All fields are onshore. Angola operated by TOTAL (Morel et al, 2008) and one or two fields in China have also been initiated for chemical flooding. The use of chemicals is considered most effective; moreover, the use of polymer is one of the most cost-effective methods, based on bench-scale (lab testing) as well as field (Bai, 2012) investigations. For this reason, there has been increasing interest in the use of polymer and hydrolyzed polyacrylamide (HPAM) polymer in particular. Chemical flooding with polymers alone or in combination with surfactants are planned in many new fields also offshore.

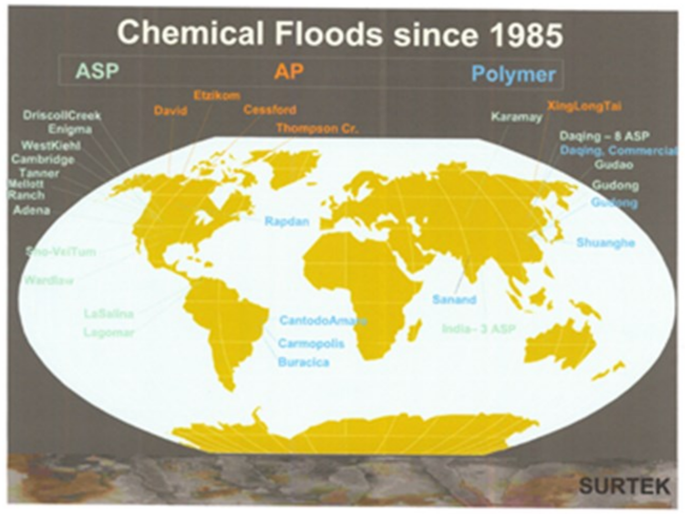

Figure 1. Chemical floods, which according to Surtek (2014) have been implemented since 1985

Environmental properties of most relevant chemicals

Polymer and EOR-surfactants chemical properties challenge the classical risk assessment methods developed for production chemical. First step in risk assessment is HOCNF testing (Harmonised Offshore Notification Format according to requirement from OSPAR 2014). Those ecotoxicological tests are used to classify the chemical in one of the four color categories (Figure 2):

- Not environmental acceptable: Black chemicals are generally not allowed discharged.

- Replacement should be considered: Red chemicals require special approval before use, because they have either a low biodegradation potential, a relatively low biodegradability in combination with high bioaccumulation potential and or notable toxicity.

- Acceptable: Yellow chemicals have no inherent environmentally hazardous properties

- Acceptable: Green chemicals are listed under PLONOR “Pose Little Or NO Risk “ (OSPAR 2012)

EOR chemicals may, however, be biodegraded under environmental conditions given longer time and more inoculum than in the ready biodegradation tests. Anaerobic biodegradation can also occur in the sediments, and since many of these chemicals are likely to adsorb to solids present in the produced water and in the sea, they might very well end in the sediments. Onshore they will usually be eliminated in biological wastewater treatment even if they are not ready biodegradable. However, biological treatment processes are not considered a process which can be implemented offshore. The long retention time needed for the water to be treated in biological processes, results in a footprint and weight which is not available.

PLONOR (Pose Little or No Risk)						
Biodegradability > 60%					Not inherent environmentally hazardous properties	
Biodegradability 20-60%	Need environmental assessment, substitutions should be considered					
Biodegradability < 20%	Should not be discharged					
Octanol-water-partitioning coefficient: 'Pow'	Log Pow > 5		Log Pow 3-5		Log Pow <3	
Effective concentration 50% in mg/L	EC_{50}<10	EC_{50}>10	EC_{50}<10	EC_{50}>10	EC_{50}<10	EC_{50}>10

Figure 2. Color-coded classification for chemicals according to Norwegian and OSPAR regulations. More Complex chemicals are less biodegradable

Topside produced water management issues

Very high concentrations of polymer and surfactants are likely to be found in the back produced water. Typical examples reported from Chinese onshore fields are polymer concentrations in the range of 500 mg/l and surfactant concentrations could be even higher; ~10000 mg/l. It is therefore expected that future regulations could require produced water re-injection (PWRI) with high uptime (80-95 %) of the plant, and that treatment of produced water could be needed in the residual time period before produced water is allowed discharged overboard.

On top of toxicity and environmental issues caused by EOR chemicals, their back production can influence the whole production chain including performance of oil/water/gas separators and the following produced water treatment processes. Problems caused by polymers are expected to be mainly related to an increase in viscosity of the water phase. Moreover, high concentration of back produced polymers can stabilize the oil in water emulsions and cause separation difficulties in many water treatment facilities such as flotation units and hydrocyclones. Polymers are large molecules and they can prevent coalescence of oil droplets as they adsorb at oil droplet interfaces (steric stabilization). Figure 3 shows how polymers influence the coalescence of oil droplets as their concentration increases (Wang et al 2011). It is known that an optimum formulation of EOR surfactants is normally injected to obtain maximum oil recovery. This optimum formulation corresponds to minimum emulsion stability and is anticipated to not to cause any further separation difficulties. However, the back produced fluids

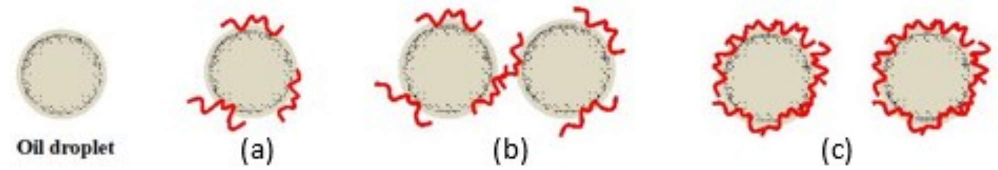

Figure 3. Influence of polymer adsorption on coalescence of oil droplets (a) polymer adsorption at oil droplet surfaces, (b) droplets may flocculate at low polymer concentration, (c) droplets remains apart (very stable emulsions) at high polymer concentration

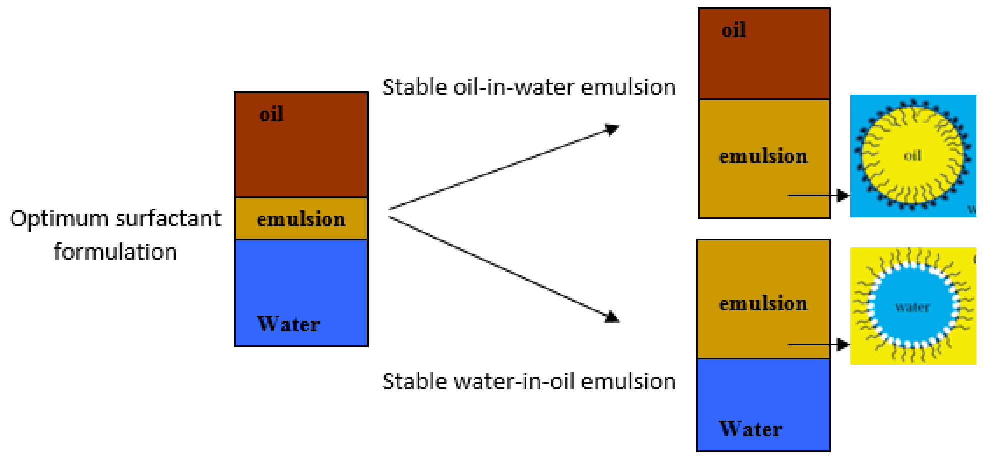

Figure 4. Back produced fluids can easily be shifted from optimum EOR surfactant formulation and both oil-in-water and water-in-oil emulsions may formed

are shifted from the optimum due to many reasons including adsorption of surfactants inside the reservoir, chromatographic effect between the different chemicals injected, salinity gradients, temperature differences and etc (See figure 4). Therefore, stable oil-in-water and water-in-oil emulsions are the main problems caused by EOR surfactants and has been a focus of so many studies during the last years (Argillier et al., 2013 and 2014, Yee et al., 2013, Najamudin et al., 2014).

Furthermore, adsorption of surfactants on gas bubble interfaces can cause foaming problems. Foams take up space in the separation facilities including separators and flotation units and reduce the separation efficiency. Foams can also interrupt the pumping of the fluids at transfer stations and increase the energy consumption of topside processes (Wang et al 2013).

Both polymers and surfactants can influence the performance of filtration facilities and can cause fouling or deformation of droplets in the way that they can pass through the filters and reduce the efficiency of filtration units.

Considering tall these several unique challenges related to separation and produced water treatment as a result of application of EOR chemicals into the oil fields, proper testing is needed in multiple disciplines including separation processes, environmental science and new chemical development to find solutions for encountered difficulties.

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Figure 5. Toxicity testing of whole effluent (here with Skeletonema: marine algae) gives valuable information of environmental risk

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Environmental impact testing

Chemical qualification requires HOCNF information (Harmonised Offshore Notification Format). Detailed requirement are available through OSPAR (2013). OSPAR (2012) has also prepared Guidelines for Risk Based Approach (RBA) to the management of produced water discharges. Whole effluent assessment of treated produced water is a good approach to control if EOR chemicals back produced to the platform has increased the toxicity of produced water.

Produced water treatment testing

In any offshore project who are planning to implement CEOR, environmental impact assessment and produced water treatment testing is likely to be needed. Once a set of chemicals are decided, work needs to

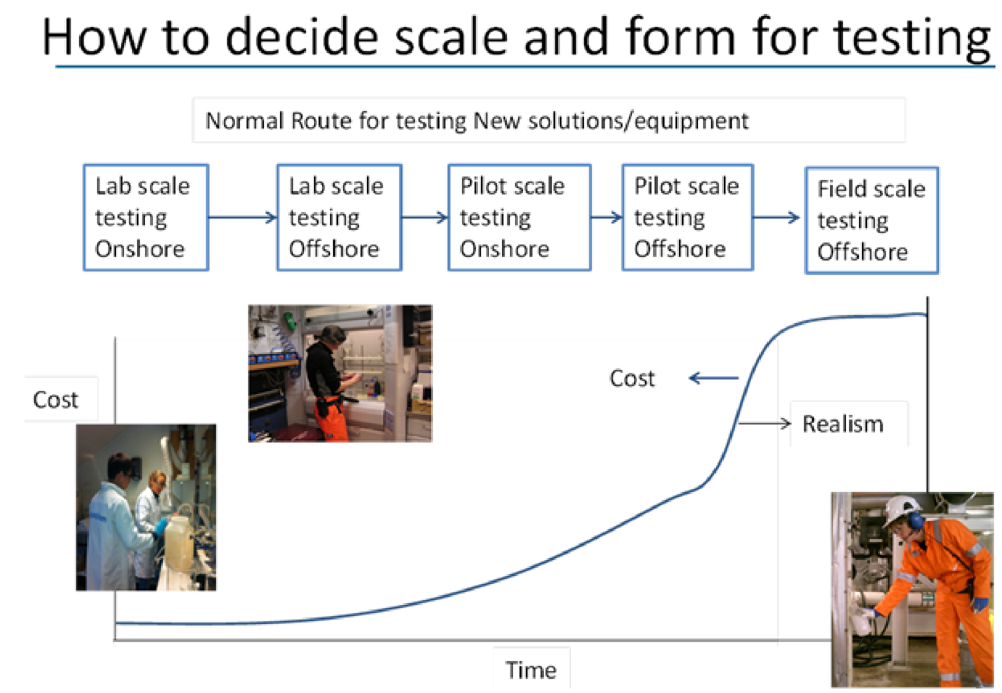

Figure 6. Steps identified for testing the fate of polymers and chemicals used in EOR

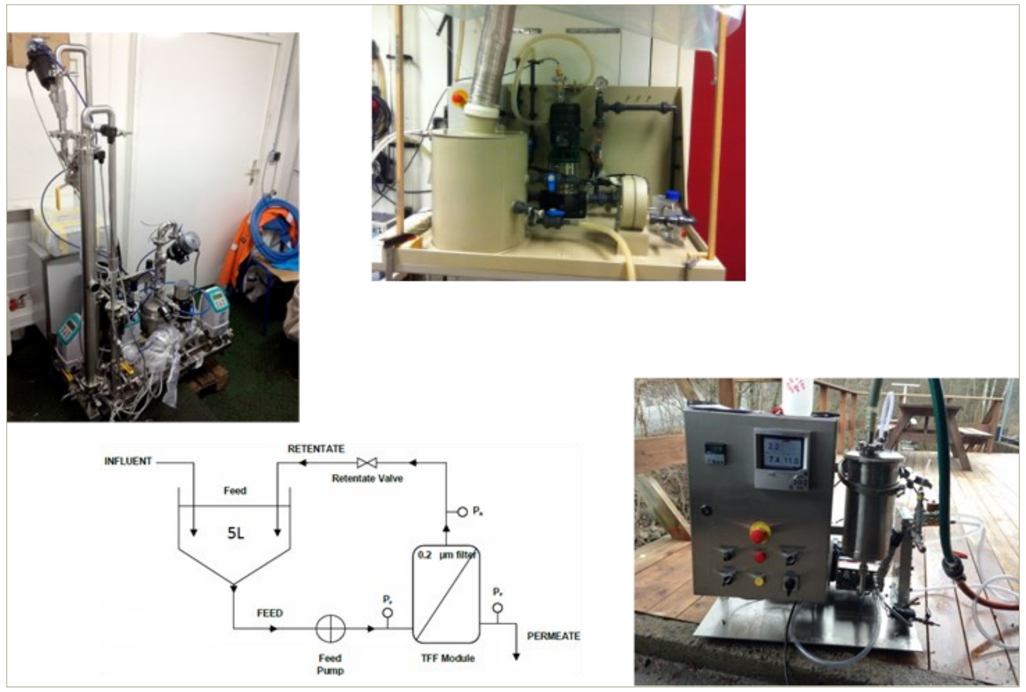

Figure 7. Test skids, including ceramic membranes (CM), Advanced Oxidation, ultrafiltration (UF) and nanofiltration (NF)

start. Normally you would start with desktop studies and literature review to get focused on the critical aspects for the particular project.

“Relevant testing” can mean applying the appropriate conditions that the chemical would experience (real produced water, right temperature and pressure), but also the appropriate scale.

Full-scale testing is the most relevant, but can be either extremely expensive or impossible to perform, or both. The closer one can come to emulating real conditions that the chemicals would experience, the more realistic and relevant the results will be; however, lab studies can be used as a precursor to pilot-scale and then the full-scale testing as suggested by Aquateam COWI (Figure 6). More realistic studies take more time and cost more. However, optimized test conditions can be found on the lab-scale and upgraded to a pilot to provide the information needed. For testing including performance in the separator, using the fresh oil (not exposed to air/oxygen) right pressure and temperature becomes critical.

Ideally, a balance should be struck between the efficacy of the chemical and how environmental friendly it is. Aquateam COWI has been in the vanguard of water treatment testing polymers and different chemicals and their fate in the environment as well as water characterization of produced water and effluent streams. Biodegradability studies of chemicals, including HPAM, have been performed in order to help clients determine the best form of chemical treatments. This helps the oil clients find effective chemicals that are properly treated to allow for a non-toxic effluent. A key part of determining the treatability and biodegradability of the chemicals present in produced water and effluent water streams is characterizing the produced water. Common analyses performed include the following:

- Particle size distribution (PSD) and oil droplet size distribution, gas bubbles distribution using Flow Cytometry, FlowCam, Malvern Mastersizer, nanosizer
- Particle charge by measuring the Zeta potential
- Biodegradation tests both aerobic and anaerobic over extended periods in sea water, fresh water and their sediments.
- Interfacial tension (IFT), viscosity, oil-in water, water-in oil etc. are other relevant parameters.

Additional treatment of produced water to meet discharge permits, could include a number of different approaches, but normally screening appropriate technologies needs to be done. This could include adsorption processes, oxidation, chemical treatment and by using emulsion breakers and flocculants. Figure 7 shows some test skids, applied by Aquateam COWI during such tests.

Due to the prevalent use of polymer and surfactants for EOR as well as the current environmentally conscious mindset surrounding the industry, it is important that treatment of EOR effluent streams and produced water be taken into consideration. Finding the best available technique (BAT) is likely to become a regulating parameter.

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