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OPTIMUM FORMULATION OF ASP FOR INJECTION IN OIL RESERVOIR

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Проведено аналіз оптимального складу інгібіторів корозії ASP для нагнітання у нафтовий пласт. Звертається увага на проблему додавання води в нафтовий резервуар, що є, на думку автора, єдиним методом відновлення тиску в резервуарі.
Ключові слова: інгібітор корозії, нафтовий резервуар, поліакриламід, поверхнево-активні полімери, лужні поверхневі полімери.

Проведен анализ оптимального состава ингибиторов коррозии ASP для нагнетания в нефтяной пласт. Обращается внимание на проблему добавления воды в нефтяной резервуар, что является, по мне нию автора, единственным методом восстановления давления в резервуаре.
Ключевые слова: ингибитор коррозии, масляный резервуар, полиакриламид, поверхностно-активные полимеры, щелочные поверхностные полимеры.

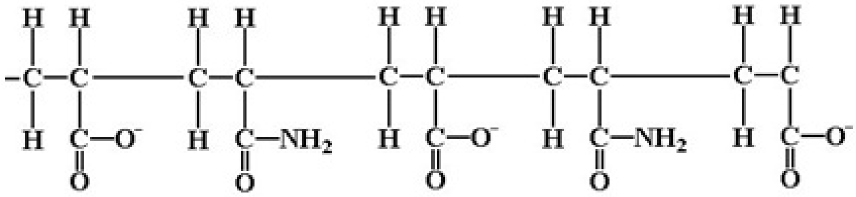
Enhanced Oil Recovery is not a new process and it has been utilized by the Oil and Gas industry for several decades, particularly in the use of water flooding as a secondary recovery measure to ensure maintenance of reservoir pressure.[1] Adding water to an oil reservoir may seem an odd thing to do- anything added to the reservoir should aid in maintaining reservoir pressure, so why add water, as oil and water do not mix? The problem is that most oil reservoirs are solution gas driven, this means that as the oil is produced the reservoir pressure is reduced and the gas that was held in solution is released and expands. This process drives the oil to the producing wells, however the gas is also free to flow and be produced. Once the gas is produced, the reservoir's energy is lost and reservoir pressure is reduced. If this process is the only method of recovery, it will only yield up to 20% of the reservoirs total volume.
Keywords: corrosion inhibitor, oil reservoir, polyacrylamide, surfactant-polymer flooding, alkaline surfactant polymer

Introduction

Water flooding is used in a controlled fashion to maintain and reverse this loss of pressure, and if properly designed can double the recovery values up to 40% [2]. All of this sounds very good and highly feasible, however, there are many obstacles to good recovery rates from water flooding, not least the type of reservoir. Much of the world's oil is held in carbonate reservoirs [3], which are likely to exhibit low porosity and may be highly fractured. These two characteristics, in addition to oil-to-mixed wet rock properties, usually results in low recovery. When Enhanced Oil Recovery (EOR) strategies are pursued, the injected fluids will likely flow through the fracture network, bypassing oil in the rock matrix. The high permeability in the fracture network, and its low equivalent porous volume, result in early breakthrough of the injected fluids. This can result in at least 40% of the assumed recoverable oil reserves remaining in place. This has led to the development of several strategies in Enhanced Oil Recovery; the main methods are listed below. Note that the gas most commonly used is carbon dioxide:

– Water-Alternating-Gas (WAG) Injection;
– Simultaneous Water-and-Gas (SWAG) Injection;
– Foam Assisted Water-Alternating-Gas Injection;
– Hydrocarbon (HC) Miscible Gas Injection;
– Thermal Enhanced Oil Recovery;
– Microbial Enhanced Oil Recovery (MEOR);
– Chemical/Surfactant Enhanced Oil Recovery.

The importance of this 'new' or revisited technology cannot be over emphasized. The high oil price, and its continued stability at these levels [4], has a bearing on the investment strategies in the application of EOR techniques. However, probably more important for Western economies is the ability to achieve more hydrocarbon exploita-



Picture 1

tion from proven reserves in a politically stable environment. The energy crisis for the 'West' is on our doorstep according to many commentators [5].

Chemical EOR

Deployments of chemical EOR were at their most active during the 1980's and peaked, particularly in the United States, around 1986, which was coincident with a high oil price [6]. Usually, these treatments used polymer flooding, the three main treatments which are listed below:

– Polymer Flooding;
– Surfactant - Polymer Flooding;
– Alkali - Surfactant - Polymer Flooding.

Each of these methodologies will now be discussed along with the chemical technologies deployed. There will also be a section on novel and other chemical techniques.

Polymer Flooding

This been the most used EOR chemical method in both sandstone and carbonate reservoirs. Data collected up until 2004 has shown more than 290 polymer field projects had been reported in the literature [3], with more than half of these treatments being conducted in the United States in the 1980's. In the last three years there has again been a dramatic increase in the application of this technology, coincident with an era of high oil prices.

Most of the polymer floods used water-soluble polyacrylamides and biopolymers (polysaccharides and cellulose polymers). The average polymer injection is between 19 and 150 lb./acre-ft., with concentrations ranging from 50 to 3700 ppm, respectively [7]. Historically such treatments gave up to an additional 18% of the recoverable reserves, which is pretty close to target recoveries of 60% if well-planned water flooding has also been used for a period of time. This technology has now been revisited and has become more tailored to the specific reservoir conditions, leading to further increased recoveries of hydrocarbon.

In the last decade much work has been conducted in simulating reservoir conditions in order to accurately assess the realistic outcomes of chemical treatments [8]. This has lead to improved and optimized treatments and a better understanding of the chemical and physical process at work [9].

By far the major polymer used in the chemical EOR are polyacrylamides, a typical structure is shown on picture 1.

Polyacrylamide (PAM) is a long-chain molecule / polymer commonly used to clean wastewater. Historically the primary market for this compound has been municipal wastewater treatment facilities. It makes the fine solids in treated water adhere to one another until they become big enough to settle out or be captured by filters to make sewage sludge. In terms of EOR applications these molecules offer a number of critical properties. The intention of these polymer additives when added to the injection water is to aid the sweep efficiency at the waterfront and ensure more oil is 'pushed' to the producing wells. They do this by creating favorable viscosity conditions and good mobility control. In order for this to occur a number of properties are essential [10]. These are listed below:

– Good water solubility;
– Long term thermal stability;
– Good stability to divalent cations in particular calcium;
– Good resistance to mechanical degradation;
– High injectivity capability;
– Low adsorption characteristics;
– Microbial stability.

Across this range of characteristics, polyacrylamides offer the best fit even although they show some degradation at high temperatures and are subject to precipitation by calcium at high calcium ion concentrations [11]. To overcome these shortcomings many of the manufacturers have engaged in a variety of chemical solutions based around developing a wide range of homologous polymers from a hundreds of different monomers: in particular vinyl, allylic and acryloyl. These result in a wide range of chemistries and structures such as hydrophobic, associative, rod-like, branched, comb, star, zwitterionic, sulfonated, and heat resistant. The polymerisation processes developed using macro-initiators, macro transfer agents, new polymerisation techniques and micellar polymerisation have resulted in new polymers with extremely high molecular weights, HPAM up to 30 millions g/mol and more. In addition to molecular weight, polymer architecture and polymer solution formulations are wide and varied and claimed to fulfill all specific EOR requirements.

The main method of adaption of the polyacrylamide polymer is controlled by selective hydrolysis. Partially hydrolyzed polyacrylamide molecules carry polar amide groups and ionizable carboxyl groups, which impart water solubility to the polymer. The carboxyl groups dissociate and leave negatively charged macro-ions and positively charged counter-ions, leading to polyelectrolyte property in aqueous solution. In comparison with neutral polymers polyelectrolytes gain some advantages, as the solution viscosity is higher than neutral polymers with the same concentration; consequently they present better rheological properties as a thickening agent. As a result of anionic character, partially hydrolyzed polyacrylamide absorbs disperse particles possessing positive charges through ionic attraction and some neutral particles through hydrogen bonding. These properties make it ideal as a pushing fluid additive and profile modifier in Enhanced Oil Recovery applications [12].

Other water-soluble polymers have been used in Enhanced Oil Recovery however they are not as versatile or applicable to as wide a range of conditions as the hydrolyzed polyacrylamides. These include:

– Xanthan gum;
– Guar gum;
– Carboxymethylcellulose (CMC);
– Hydroxyethylcellulose (HEC).

The much higher molecular weights of the polyacrylamides that can now be achieved also aid increased viscosity and sweep efficiency. Typically polyacrylamides can be 13 million molecular weight, as opposed to, 2-3 million for xanthan gum.

Surfactant /Polymer Flooding

Surfactant-polymer flooding, also known as micellar polymer flooding, has been the second most used EOR chemical method in light and medium crude oil reservoirs. However, reported field projects are relatively low in comparison with polymer floods. Although this recovery method has been considered a promising EOR process since the 1970's, the high concentrations and cost of surfactants and co-surfactants combined with the low oil prices until recently, have limited its use.

The most common type of surfactants used in micellar or surfactant polymer floods are petroleum sulphonates and synthetic alkyl sulphonates, which usually require the use of co-surfactants (non-ionic surfactants) or co-solvents, mostly alcohols. These are added to reduce potential surfactant-formation brine incompatibilities and potentially reduce chemical adsorption; in some cases a pre-flush of fresh water has also been used. Again, water-soluble polyacrylamides have been the most common polymer used in these projects with a few cases using biopolymers. In some cases these application have claimed to give significant recoveries [13].

Surfactant-polymer water floods are employed in low permeability reservoirs (0.1 – 100 mD) where it is difficult to inject water. This process can also be employed as a tertiary recovery method where conditions are such that polymer and/or alkali cannot be introduced into the reservoir. This could be the case where the permeability is too low, the temperature is too high, or the salinity is too high to include polymer. This process can also be used where the amount of divalent cations is too high to use alkali (see later section). A surfactant-polymer water flood increases oil recovery by increasing injectivity and lowering interfacial surface tension.

It is the case that surfactants alone have been used in chemical flooding, however, this is seen as a rather expensive option with recoveries being no greater than the combination treatment [14]. The surfactant flooding process suffers from a significant drawback. This is in the sensitiveness of the aqueous surfactant solutions currently being used, to mono-and divalent ions present in the reservoir. Although carbonated water floods have been successful in laboratory studies, the few reported field test statistics indicate that it is not particularly attractive, possibly in view of the extended project life necessitated by the injection of many pore volumes.

In many cases surfactant is added after a polymer flood has been in operation for some time [15]. This is particularly important where decreasing or poor injectivity is observed in the polymer injection wells [16]. As injectivity decreases the recovery rates and benefits from polymer flooding decrease, there is increasing casing damaged caused by high injection pressures.

This has supported further work in recent years in a new high oil price era to examine other potential surfactant additives. Workers have reported results for a number of promising EOR surfactants based upon a fast, low-cost laboratory screening process that is highly effective in selecting the best surfactants to use with different crude oils. Initial selection of surfactants is based upon desirable surfactant structure. Phase behavior screening helps to quickly identify favorable surfactant formulations. Salinity scans are conducted to observe equilibration times, micro-emulsion viscosity, oil and water solubilisation ratios and interfacial tension. Co-surfactants and co-solvents are included to minimize gels, liquid crystals and macro-emulsions and to promote rapid equilibration to low-viscosity micro-emulsions. Branched alcohol propoxy sulfates, internal olefin sulphonates, and branched alpha olefin sulphonates have been identified as good EOR surfactants using this screening process [17. These surfactants are available at low cost and are compatible with both polymers and alkali such as sodium carbonate and thus are good candidates for both surfactant-polymer and alkali-surfactant-polymer EOR processes.

Other workers [18] have examined different types of surfactants for effectiveness in tertiary oil recovery (TOR). The selected surfactant formulations were tested for enhanced oil recovery using core flood tests on Berea sandstones. Effective were low 1-naphthol concentrations dissolved in 1-butanol in alkyl polyglycoside surfactant formulations, which led to significant additional incremental oil recovery (40% TOR) due to dramatic reductions in interfacial tension.

Alkali-Surfactant-Polymer Flooding

Alkaline Surfactant Polymer (ASP) combines the key mechanisms from each of the previous Enhanced Oil Recovery chemical methods. Generally, ASP formulations use moderate pH chemicals such as sodium bicarbonate (NaHCO3) or sodium carbonate (Na2CO3) rather than sodium hydroxide (NaOH) or sodium silicates. Main functions of alkaline additives are to promote crude oil emulsifi-

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cation and increase ionic strength, decreasing interfacial tension (IFT) and regulating phase behavior. The alkaline additives also help to reduce the adsorption of anionic chemical additives by increasing the negative charge density of mineral rocks and at the same time making the rock more water-wet. Thus, the use of alkaline agents contributes to reduce the surfactant concentrations making ASP formulations less costly than conventional surfactant formulations. Again, the most common products that have been used are petroleum sulphonates.

As before, the main function of the surfactants is to reduce interfacial tension between the oil and the injected aqueous formulation. The injected surfactants may sometimes form mixed micelles (at the oil water interface) with in-situ natural surfactants, broadening the alkali concentration range for minimum interfacial tension. On the other hand, the polymer (usually polyacrylamides) is used to reduce water mobility and sweep efficiency by increasing the solution's viscosity and decreasing effective permeability when it is adsorbed onto the formation [19, 20].

Alkaline Surfactant Polymer flooding is an oil recovery method that has traditionally been applied to sandstone reservoirs. However, ASP has also been tested in carbonate formations in the laboratory [21]. The results of this and other studies have shown that the ASP injection slug has to be prepared in softened seawater and be protected with pre and after slugs of softened seawater.

Additionally, recent studies on wettability alteration during surfactant flooding of carbonate minerals showed that commercial anionic surfactants (Alkyl aryl ethoxylated sulphonate and propoxylated sulfates) can change the wettability of calcite surface to intermediate/water-wet conditions [22]. These results suggest that conventional ASP formulations may be used in carbonate reservoirs.

Some Closing Remarks

EOR technologies have demonstrated their capacity to increase oil production and total recovery factors, extending reservoir/asset life, all while being economically viable. High initial capital investments and high marginal costs have limited their widespread application around the world. However, incremental improvements of existing technologies have been achieved in the last decade reducing the cost per barrel of many EOR projects, with CO2 injection (continuous or in water alternating mode) as the best example.

Oil reserves are not expected to be only produced in EOR terms via CO2 injection, either from natural or from industrial sources, other EOR methods including chemical flooding will be considered and deployed.

The maturity of a many fields will require the use of surfactant based recovery methods to recover residual oil in water-flooded reservoirs. Surfactant, alkali and polyacrylamide polymer, have been the most used chemical additives either in combined processes or pure polymer floods. Additionally, the applicability of sodium carbonate and polyacrylamides in carbonate and sandstone reservoir has been proven effective [22, 23].

Although petroleum sulphonates have been the most common surfactant used in micellar or ASP floods [17], the use of non-ionic and cationic surfactants have been evaluated at lab and field scale for carbonate reservoirs [18]. Surfactant injection may be also benefit from the relatively low costs associated with water flooding projects, even more if a water flood is already in place.

Alkali-Surfactant (AS) injection, to improve well injectivity in low permeability formations under water flooding [25] in oil-wet limestone reservoirs [26], has certainly provided new insights useful for chemical floods in carbonate reservoirs.

To the author's knowledge new chemical developments are focused in two major areas:

– Selection of organic compounds with alkaline properties that improve chemical formulations conventionally used in EOR by chemical methods and that reduce, or eliminate, the softening of injection waters due to their high solubility and their capability of sequestering divalent cations.

– New fluid formulations based on new-engineered materials ('Nanomaterials') able to modify, in a controlled way, rock-fluid and fluid-fluid properties and also behave as tailored surfactants improving the flow of oil in the porous media.

Over the last few decades, Enhanced Oil Recovery by gas injection has been the dominant recovery method for crude oil reservoirs, especially in carbonate reservoirs with low permeability/injectivity.

A number of reviews show that EOR chemical methods, particularly in carbonate reservoirs, have made a relatively small contribution in terms of total oil recovered. Further studies are required to improve economic viability of technically proven EOR chemical methods, such as ASP, for their application in other fields including remote and small fields with no short term access to CO_2.

Crude oil reserves, particularly in the US in carbonate reservoirs; can be increased through the application of proven EOR methods, which are increasingly viable from the point of view of their costs and effectiveness.

Chemical methods will benefit greatly from new strategies that reduce the requirements on the specifications of the injection water and use existing infrastructure without much new investment.

All of these factors will present EOR techniques, and particularly chemically supported Enhanced Oil Recovery, as a viable and effective method increasing oil production. The major caveat to all of this will be the future price of crude oil.

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