

Nanoparticles in Chemical Enhanced Oil Recovery

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Nanotechnology in Chemical Enhanced Oil Recovery deals with the application of materials based on nanometer scale to the recovery of difficult-to-access oil from reservoirs. Additional recoveries (after brine flooding) up to 15% of the original oil in place, or higher when combined with smart water or magnetic fields, have been found with formulations consisting of simple nanoparticles in water or brine. The functionalization of nanoparticles and their combination with surfactants and/or polymers take advantage of the synergy of different EOR methods and can lead to higher additional recoveries. The cost, difficulty of preparation, and stability of the formulations are problems that face practical applications.

EO

nano-fluid

core-flooding

1. Introduction

The current global demand for fossil energy sources looks certain to continue for decades to come ^[1]. The need to move towards total independence from crude oil, switching to renewable sources of materials and energy, is undeniable. However, during the time needed to achieve the required technological development, crude oil is a practical necessity. To meet the worldwide needs, taking full advantage of production from current oil fields is therefore essential.

After primary and secondary recovery, the majority of the oil still remains inside the reservoir. Tertiary or enhanced oil recovery (EOR) methods look to recover this oil by the injection of gases, microorganisms, chemicals and/or thermal energy into the reservoir ^[2]. Chemical EOR methods are based on the injection of water combined with low concentrations of added chemicals. Commonly injected substances are surfactants (or alkaline/caustic chemicals that generate surfactants in situ) and polymers. Surfactants reduce the interfacial tension (IFT) between the oil and water. This reduction enhances the mobility of the oil retained in the pores, allowing it to be flushed out of the reservoir. Polymers increase the viscosity of water, thus reducing the difference between water and oil viscosities, leading to a more homogenous displacement. The chemicals can also be used to change the wettability of the rock. It has been shown that EOR methods are effective in recovering the difficult-to-access oil. However, the difference in viscosity between gas and oil in gas flooding, the unpredictable behaviour of microorganisms, the energy cost and risk of thermal methods, the cost of chemicals, the stability of formulations in the presence of salts, among many others, are problems that impede the optimal application of these methods.

2. History

At the beginning of this century, nanotechnology appeared as a new promising means to enhance oil recovery. There are many mechanisms involved when nanoparticles are used in formulations to extract oil [\[3\]](#)[\[4\]](#)[\[5\]](#)[\[6\]](#)[\[7\]](#)[\[8\]](#)[\[9\]](#)[\[10\]](#)[\[11\]](#)[\[12\]](#)[\[13\]](#)[\[14\]](#). Disjoining pressure is considered one of the key mechanisms of nano-EOR, where nanoparticles induce the detachment of oil from the rock surface while allowing the nanofluid to spread further [\[7\]](#). Considerable improvement in oil recovery is usually attributed to wettability alteration effects caused by the nanoparticles, changing in the best case the wettability from strongly oil-wet to strongly water-wet. A synergistic effect in the reduction of IFT has also been shown in surfactant formulations with low concentrations of nanoparticles. Nanoparticles slightly increase the viscosity of the aqueous phase and, combined with polymers, enhance the rheological behaviour of the formulations. Furthermore, the capacity of nanoparticles to reduce oil viscosity and prevent asphaltene precipitation has also been shown. All this translates to successful viscosity control and an increase in the sweep efficiency. There are other advantages associated with nano-EOR. For example, nanomaterials can be used to increase the stability of surfactants and polymers in high-temperature and -salinity conditions. Adsorption of the injection formulation can be reduced by using the surface charge property of nanoparticles. Nanomaterials can also be used to plug some pores and thereby force the oil to exit from adjacent ones which were previously blocked. All these effects are obviously affected by nanoparticle type, size and concentration, and they strongly depend on the types of oil and rock, and reservoir conditions (salinity, temperature, heterogeneity). High nanoparticle concentration or diameter, for instance, can have a negative effect on reservoir permeability due to the blocking of porous media. The promising features of nanotechnology applied to EOR have led to a significant amount of research on this topic [\[3\]](#)[\[4\]](#)[\[5\]](#)[\[6\]](#)[\[7\]](#)[\[8\]](#)[\[9\]](#)[\[10\]](#)[\[11\]](#)[\[12\]](#)[\[13\]](#)[\[14\]](#).

3. Current Status

As core-flooding tests are the most suitable techniques to ensure the efficacy of proposed formulations for EOR, those are likely the most interesting studies from the point of view of application. The analysis of core-flooding tests carried out with nanoparticles, and their combination with other chemicals, may be used to define the current state of this technology.

- The greatest challenge for EOR in general, and for nano-EOR in particular, is the design of a stable formulation at harsh conditions (temperature and salinity) also considering the presence of divalent ions. This is a difficult task common to all EOR methods, but it is likely more difficult in the presence of nanoparticles.
- The simplest and most cost-effective nano-EOR method involves the use of nanofluids consisting only of water or brine and common nanoparticles. Additional oil recoveries achieved with these systems are comparable to those achieved with other EOR methods and justify, in principle, their use to promote oil recovery.
- Even though the number of papers published with simple nanofluids is rather significant, there is not enough information to select the best type and size of nanoparticles according to the application (type of rock, permeability, formation brine, reservoir conditions, etc.). Critically, the number of studies in carbonate rocks is very limited.

- Size and more importantly concentration are key factors that seem to be more critical than the type of nanoparticle for success in practice. The nanofluid concentration must be optimised according to core permeability. Excessive concentration generates aggregation and blocking problems, thus limiting oil extraction and creating pressure problems. Nanoparticle concentration higher than 0.2 wt% is rarely recommended.
- SiO_2 nanoparticles are cost-effective and are consequently the most often proposed for the application. Colloidal are preferred to fumed nanoparticles in order to avoid aggregation problems. Al_2O_3 is sometimes proposed for harsh environments.
- Many experimental studies have confirmed significant adsorption of nanoparticles onto the rock surface during the flooding process. This presents a challenge to nano-EOR due to the associated environmental hazards and operation costs.
- According to several studies, the performance of nanofluids is better when applied as a secondary rather than tertiary EOR method. However, the cost of this injection method is a limiting factor.
- Nanofluid stability is a bottle-neck that sometimes can only be improved using dispersions in alcohols or via the use of different stabilizers.
- Nanoparticles favour disjoining pressure to sweep the oil droplets from rock surfaces. According to the studies presented, the main mechanism is wettability alteration. In certain cases, a reduction in water–oil IFT is also found. However, the addition of a surfactant to the nanofluid drastically enhances this reduction, at the same time as improving or worsening the stability of the nanoparticles.
- To avoid excessive adsorption, cationic surfactants are recommended for carbonate and anionic ones for sandstone rocks. However, a general rule cannot be established regarding the best type of nanoparticles according to surfactant type. More work is required in this line of research.
- Polymers, mixed with nanoparticles or used to functionalise them, are usually employed to improve the stability of nanofluids. Nanoparticles help the polymer to increase aqueous viscosity but also reduce apparent oil viscosity and improve its rheological behaviour.
- The synergy of combining nanoparticles, polymers and surfactants leads to promising formulations for EOR. However, designed formulations are complicated and involve high costs. Moreover, the protocol used to prepare the mixtures, especially in the presence of salts, has to be clearly defined.
- The combination of surface-active ionic liquids with nanoparticles is a niche that must be further explored.
- The flooding equipment used in the tests, as well as the type of core and initial conditions, drastically affect oil recoveries with nanofluids, sometimes leading to very optimistic numbers that should be verified.
- A striking absence of information regarding the costs of nano-EOR methods per incremental bbl, a decisive factor for industrial applications, was noted and needs to be addressed.
- Despite the significant number of laboratory studies carried out, the Technology Readiness Level of nano-EOR is still very low; thus, a lot of effort needs to be made to prove the current system in operational environments.
- In summary, there still exists a need for systematic and rigorous works on EOR with nanoparticles, in order to establish general rules for the best design of nanofluids for practical applications.

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