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Introducing Core-Shell Technology for Conformance Control

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Abstract — Reservoir heterogeneities can severely affect the effectiveness of waterflooding because displacing fluids tend to flow along high-permeability paths and prematurely breakthrough at producing wells. A Proof-of-Concept (PoC) study is presented while discussing the experimental results of a research on “core-shell” technology to improve waterflooding in heterogeneous oil reservoirs. The proposed methodology consists in injecting a water dispersion of nanocapsules after the reservoir has been extensively flushed with water. The nanocapsules are made of a “core” (either polymeric or siliceous materials), protected by a “shell” that can release its content at an appropriate time, which activates through gelation or aggregation thus plugging the high permeability paths. Additional flooding with water provides recovery of bypassed oil. The initial conceptual screening of possible materials was followed by extensive batch and column lab tests. Then, 3D dynamic simulations at reservoir scale were performed to compensate for the temporary lack of pilot tests and/or field applications.

Résumé — Introduction au « core-shell » technologie pour l'amélioration de déplacement d'huile par injection d'eau — Les hétérogénéités de réservoir peuvent gravement affecter l'efficacité de l'injection d'eau parce que les fluides de déplacement ont tendance à couler le long des chemins de haute perméabilité et à parvenir prématurément au puits de production. Une étude de preuve de concept est présentée tout en discutant les résultats expérimentaux d'une recherche sur la technologie « core-shell » pour améliorer l'injection d'eau dans les réservoirs de pétrole hétérogènes. La méthode proposée consiste à injecter une dispersion aqueuse de nanocapsules après que le réservoir ait été abondamment rincé à l'eau. Les nanocapsules sont faites d'un « noyau » (matériaux polymères ou siliceux), protégé par une « coquille » qui peut libérer son contenu à un moment approprié ; ensuite le contenu peut s'activer par gélification ou agrégation ainsi que les chemins de haute perméabilité. Un rinçage supplémentaire avec de l'eau permet une récupération d'huile contournée. La projection conceptuelle initiale de matériaux possibles a été suivie par de nombreux tests de lots et de la colonne de laboratoire. Ensuite, des simulations dynamiques 3D à l'échelle du réservoir ont été effectuées pour compenser le manque temporaire de tests pilotes et/ou applications industrielles.

INTRODUCTION

Scope of Work

Recently, the potential of nanotechnology to transform the design and execution of chemical Enhanced Oil Recovery (EOR) has been disclosed. In this paper we present a Proof-of-Concept (PoC) study about the use of ‘core-shell’ technology for improved waterflooding in heterogeneous oil reservoirs. The developed core-shell technology for improved waterflooding was patented in 2011 (Sangermano *et al.*, 2011, Patent No. MI2010A002412). In essence, “core-shell” technology consists in protecting an active “core” with a “shell” that can release its content at an appropriate time and thus at a precise location. The study comprised an initial conceptual screening of possible materials. Subsequently, a lab testing phase was carried out to confirm the viability of core-shell technology. Micro-size polymeric (for proof of mechanism) and nano-size siliceous (in view of field applications) materials were selected as the core because of their ability to form a gel or to aggregate, respectively. The initial use of a polymeric material (micro) served to determine and better understand the mechanism of the technology given that it is more observable at lab scale than the siliceous material (nano). Specific polymers and siliceous materials (the core) and their respective protecting shield (the shell) were then selected and combined by chemical processing to create a unique ensemble able to remain totally inert during injection and flooding until the shell dissolves releasing its polymeric or siliceous core at the expected time. The chemicals used in this research are environmentally-friendly, cheap and, in the case of the inorganic core, readily available in nano-size, thus making the technology truly deployable for reservoir engineering applications. After, flow tests through sand packs were carried out so as to both confirm injectivity of the nanoparticles water dispersion and the viability of core-shell technology as a means to clog a porous medium. Finally, the durability of the generated core-shell particles under different working conditions (pressure, temperature, shear stresses) was verified.

Eventually, an extensive set of 3D dynamic simulations at reservoir scale were performed to make up for the temporary lack of pilot tests and/or field applications. The expected performance of core-shell technology to enhance the final oil recovery was assessed for different reservoir scenarios. Homogeneous, strongly heterogeneous, layered and fractured oil reservoirs (with oil viscosity ranging between 2 and 10 mPas) were simulated. As expected, the process optimization and the consequent oil recovery factor increase must be evaluated on a case by case basis. However, an optimum for the polymer activation time, injected polymer quantity and injection strategy can generally be identified with a reasonably limited amount of iterations. Reluctant

readers should keep in mind simulations were carried out with the objective to temporarily bridge the gap between lab experiments and field application: the authors are fully aware that pilot tests and/or field applications will eventually confirm the validity of the proposed core-shell technology, and efforts are being made in this direction; however, data is not yet available.

Lastly, authors would like to acknowledge the influence a full economic impact study would have on the further development of the described technology for EOR processes, yet a complete evaluation of the economic feasibility of core-shell technology is out of the scope of this research. However, a rough evaluation of the costs to apply the aforementioned technology was carried out with reasonable preliminary results.

A Concise Account of Polymer-Based Treatments Since the 1960s

Nowadays, the use of polymers in reservoir engineering would seem a commonplace given the large number of papers and studies on the subject. Over the last five decades or so, much has been gained in terms of scientific and technical knowledge, mainly on how to improve oil recovery by flooding the reservoir with water enriched by chemical additives of some sort (Enhanced Oil Recovery or EOR processes), but also on how to reduce the unwanted water in oil- and gas-producing wells (water shut-off interventions). Yet, and despite all the advancing in the laboratory, the question remains: why are there just a few projects involving the use of chemicals, of which polymers are part, still active today? The answer to such question is manifold – ranging from the economical to the environmental, from the theoretical to the practical – and many have attempted, with varying degrees of success, to shed light on the matter.

The following paper seeks to contribute to the existing discussions by readdressing certain issues associated with EOR chemical treatments from a reservoir engineer’s standpoint. It should also be noted a companion paper will deal with water shut-off treatments as, needless to say, controlling water production is still a major challenge for the oil industry, especially in mature fields.

The first step, however, will be to revisit some of the most significant developments in polymer-based EOR techniques as found in the literature from the 1960s onwards. Though out of the scope of this paper, it must be said that already in the 1940s operators had been using several additives for viscous waterflooding, in what can be thought of as the pre-era of chemical flooding in EOR as it is known today (Detling, 1944). The authors also acknowledge that the development of the “bank theory” for alcohol flooding could be considered as the precursor of a range of chemical

flooding processes (Gatlin and Slobod, 1960; Taber *et al.*, 1961; Wachmann, 1964). It should also be pointed out that only recently studies on polymers have been diversified based on their final application. For a long time, research was concerned with the potential use of chemicals at reservoir scale or at well scale indistinguishably.

In 1964, Pye published a paper entitled “Improved Secondary Recovery by Control of Water Mobility” which could be considered as one of the pioneer studies on the use of polymers in EOR. In essence, he argued that if increased water viscosity could be economically realized, marked improvements in areal sweep efficiency would be realized in field operations (Pye, 1964). Laboratory and field experimental data (namely of the Niagara pilot flood and the Texas pilot floods) obtained then led to the conclusion that the use of certain high molecular weight synthetic polymers could decrease water mobility and, by doing so, increase oil recovery. Pye’s work, amongst that of Sandiford (1964), Clay and Menzie (1966), Gogarty (1967), Mungan (1970), Chang (1978) to name but a few, revealed the potentialities of using polymer solutions (specifically acrylamide polymers and copolymers) in EOR processes for the oil producing industry. In layman’s terms, this would become the cornerstone of chemical EOR, and thus the focus of much of the research that was and has been conducted since then. By then, the general consensus amongst all these researchers seemed to be that viscosity increase alone accounted for only a minor part of the improvement in oil recovery resulting from polymer solution floods (Sherborne *et al.*, 1967). Therefore discussions were extended to fluid properties in general: no wonder the often heard phrase “fluid properties and geology determine the technology”, a matter already articulated by Regtien (2010). In fact one study hypothesized that oil recovery could be significantly improved based on the assumption that connate water occupied the smaller and the narrow channels of the formation while oil resided in the larger channels; hence, polymer solutions would preferentially displace oil-filled channels (Mungan, 1969). Even if studies as the aforementioned were promising, the leap from laboratory evidence to certainty on what happens in the field would remain the real challenge.

During the following decade, Needham *et al.* (1974), for instance, studied what was then considered a newly developed process using a combination of water-soluble polymers and multivalent cations (calcium, magnesium, and aluminum citrate) to reduce water mobility; however, large amounts of calcium and magnesium in the brine slug to treat wells is often not advisable because of the incompatibility and precipitation resulting when this brine is mixed with formation waters. Although the results of laboratory experiments showed this process could have applicability in polymer flooding, concerns about what would happen once the polymer system came in contact with the widely varying

conditions of the subsurface (*i.e.*, temperature, the ionic composition of the connate water, pH, presence of either carbon dioxide [CO₂] or hydrogen sulfide [H₂S], absorptivity of rock grains, to name but a few) were latent. On this subject, Lozanski and Martin (1970) had presented, earlier in the decade, the initial results of Canada’s first polymer flood in the Taber South Mannville B oil pool. Broadly speaking, this project had been originally conceived as an alternative to conventional waterflooding. Needless to say, while core flood tests were tagged as successful, certain drawbacks in the field, such as mechanical problems in the injection system, showed the complexities of polymer flooding to actually increase oil recovery. A follow-up study on the Taber South polymer flood by Shaw and Stright (1977) concluded that it was not possible to determine whether or not polymer flood had been successful on the grounds that simulation models could not be used to evaluate the polymer effectiveness because of the difficulty in obtaining a unique history match with unknown polymer quality. In other words, because polymers can degrade under certain conditions, short-time laboratory tests can be misleading; hence, making polymer stability at reservoir conditions (*e.g.* temperature, pH, etc. as mentioned above) essential to EOR applications. Towards this aim, later in the decade, Pledger *et al.* (1979) tested a graft copolymer prepared by polymerizing acrylamide side chains on a starch backbone in order to increase the rheological effectiveness of the polymer. One of the purposes was to show not only that readily available and cheap raw materials could be treated to produce polymers, but that these could also meet the requirements of EOR. Lab-driven success stories would be partly responsible for bringing the boom of activity in EOR techniques which pretty much defined the coming decade.

In 1986, the number of ongoing EOR field projects in the US peaked (512, out of which 206 corresponded to chemical floods, 178 alone to polymers, according to a special report by Moritis in 1998), these were mostly fuelled by the oil-price rise of the 1970s. So work in the labs continued and more evidence that specifically designed polymer systems could actually be a valid alternative for conformance control was being gathered. Among the research of this period, Moradi-Araghi’s *et al.* (1987) explored the suitability of polymers for hostile environments due to the exploitation of deeper and consequently hotter oil bearing formations. Copolymers of acrylamide (Am) and sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS) were evaluated for flooding applications at elevated temperatures (exhibiting stability limits for temperatures lower than 93 °C for application in seawater) yet in spite of the partly positive results no field tests were carried out. The issue with the development of more advanced polymers, such as the above mentioned, was that though they could remove temperature and salinity limitations, their high cost would generally

make them of questionable utility for companies (Needham and Doe, 1987). Paradoxically, though, while investigations were producing functional data on the performance of polymer floods, mostly through coreflood tests, progress in field applications was still far from satisfactory. Field case histories were either not sufficiently complete or extensive to provide solid guidelines for identifying suitable candidates for polymer flooding (Needham and Doe, 1987). And just to make matters worse, the oil price bust later in the decade (world oil price dropped from US\$27 to below US\$10 in 1986) led many companies to abandon marginal and uneconomic projects.

By the mid-1990s, the total number of active US EOR projects had plummeted to 212, out of which chemical floods were only 12 (specifically 11 polymer floods and 1 caustic, alkaline according to a 2010 Moritis special report). From a laboratory perspective, though, the use of polymers still remained a panacea. By now, research was well focused on techniques designed to reduce water production and redistribute waterdrive, either near the wellbore, or deep in the reservoir where chemicals were needed (these techniques also fall within conformance control). Since early on, injection of polymers was tried but proved uneconomical because of the large volumes required to alter reservoir behavior and because polymers tended to get washed out (Borling *et al.*, 1994). Furthermore, even if coreflood tests hinted at reasonably functional polymer treatments, what factors were to determine whether a reservoir would benefit from it? And, once a good candidate had been found, how should the treatment proceed? Via producers or injectors? Sydansk and Moore (1990) offered interesting data on the subject when they analyzed the production responses in Wyoming's Big Horn Basin as a result of the application of acrylamide-polymer/Cr³⁺-carboxylate gels, generally referred to as Conformance-Improvement-Treatment (CIT) gels or gelling polymers. However, it should be noted that the use of Cr³⁺ as the crosslinking agent, though relatively non-toxic, is highly regulated nowadays as reported by Sydansk (2007) (on the issue of inorganic crosslinker toxicity see also El-Karsani *et al.*, 2014). They concluded that as compared to the production-well treatments, the injection-well treatments promoted much larger amounts of incremental oil production and did so in a much more profitable manner (Sydansk and Moore, 1990). Throughout the decade different gel treatments were used in hundreds of wells in China's oil fields with an array of results (Bai *et al.*, 2013; Liu, 1995). An advantage over the previous decade was that a good number of published field results could finally be scrutinized in order to decide whether guidelines to select candidate wells were realistic. To this end, a major survey (information was obtained from over 600 articles and reports) was carried out by Seright and Liang (1994), their review of the petroleum literature was limited to field

applications of gel treatments for water shutoff. Hence, the first step was to make a distinction between polymer flooding and gel treatments, two technologies that, up until then, had generally been lumped together as "polymer-augmented waterflood" (Seright and Liang, 1994). Both processes were intended to improve reservoir sweep efficiency, only that in different ways; in essence, polymer flooding is designed to control mobility for waterflooding whereas gel treatments to reduce excess water production in channeled or fracture-dominated mature reservoirs. The aforementioned review would corroborate how an adequate identification of the source and the nature of the water production problem (a competency of reservoir engineering) improved the success rate of gel treatment applications (Seright and Liang, 1994). More insightful information could be found in the works of Mack and Smith (1994) or Whittington *et al.* (1994), among many others. By this time, it appeared unmistakable that an in-depth understanding of reservoir behavior was the key to selecting the most appropriate EOR method for a given field, thus shifting the attention from the chemist to the reservoir engineer. The big question became not whether, but when, to inject something. Taber *et al.* (1997a, 1997b) proposed screening criteria (mostly stemming from lithological and petrophysical properties), based on both field results and oil recovery mechanisms, to better reservoir management practices. Some of the wide-range recommendations suggested for polymer flooding were: relative to crude oil, gravity > 15° API, viscosity < 150 mPas (preferably < 100 and > 10), composition not critical; for reservoir, oil saturation > 50%, type of formation (lithology) sandstones preferred (but could be used in carbonates), net thickness not critical, average permeability > 10 mD, depth < 9000 ft (about 2750 m), and temperature < 200 °F (about 93 °C) to minimize degradation. At the time of writing, Saleh *et al.* (2014) published a paper in which screening criteria for polymer flooding had been readjusted after a thorough revision of the collected data from EOR projects reported in a survey of the Oil and Gas Journal as well as other publications. In contrast with Taber *et al.*'s recommendations (1997a, 1997b), authors of this recent study suggest the following: gravity > 12° API, viscosity < 5000 mPas, oil saturation > 21%, temperature < 210 °F (about 100 °C) and permeability > 0.6 mD (though the permeability of target zones should be higher than 10 mD as Taber *et al.* (1997a) had previously suggested). Notwithstanding some of the excellent chemical flooding research and development work in laboratories around the world during the 1990s, steam flooding was still the dominant EOR method; moreover, the oil produced by steam flooding far exceeded that from all the other methods combined (Taber *et al.*, 1997b). The use of polymers was once more subject to uncertainties approaching the beginning of a new millennium.

By 2010, it was obvious that polymer-based EOR techniques had been developing somewhat unevenly when compared with other EOR techniques (*e.g.* thermal methods), mostly due to the high costs generally associated with the former (polyacrylamides, for instance, are derived from petroleum products). Furthermore, the significant costs of field tests were surely not encouraging (Kaminsky *et al.*, 2007). This being said, it is also true that chemical EOR processes have a smaller CO₂ footprint because of their lower associated energy requirements when compared to thermal EOR (Raney *et al.*, 2012). El-Karsani *et al.* (2014) have thoroughly documented major developments in polymer systems for both water shutoff and conformance control during the 2000s. Various field results were discussed for both systems; from a polyacrylamide-(PAM-)based thermally stable polymer and an organic crosslinker developed by the *Petróleos de Venezuela S.A. (PDVSA) Research and Development Center* to an in-depth profile modification treatment known as Bright Water[®] (El-Karsani *et al.*, 2014). The latter technology has been tested in different fields with relatively positive results (Mustoni *et al.*, 2010; Ohms *et al.*, 2010; Pritchett *et al.*, 2003). Amongst the conclusions drawn by El-Karsani *et al.* (2014) was that research should be driven towards the use of more environmentally friendly and naturally occurring materials in EOR chemical methods.

The application of such advanced EOR technologies becomes even more pivotal as considerably greater amounts of the world's oil production are currently coming from mature fields (Manrique *et al.*, 2010). To date, the application of EOR methods has produced mixed results based on hundreds of field tests and the oil production by chemical processes accounts for roughly 0.2% of the world oil production, nearly all of it in China and largely by polymer flooding (Farouq Ali, 2013). So, what has truly been learnt over the past decades? Why is it then that every paper discussing polymer-based EOR technologies seems to fall under the so-old-it's-new-again category? Well, for starters, the success of other methods, thermal recovery as already mentioned, have overshadowed that of chemical methods despite the fact that the latter is considered a more mature technology (Manrique *et al.*, 2010, Yerramilli *et al.*, 2013). Another possible explanation for the above may be found by going back to basics, *i.e.* the Darcy equation, as Farouq Ali (2013) has proposed in a recent paper in which it is argued that in thermal processes the oil rate can be increased by orders of magnitude because of the change in oil viscosity (to the extent of considering it “the only variable that can be varied almost without limits [. . .] in the case of viscous oils”) with temperature whereas chemical processes rely on an increase in relative oil permeability for an increase in the oil rate. From this standpoint it would seem that polymer flooding has been primarily designed to improve the mobility ratio, M , *i.e.* the ratio between the mobility of the

displacing and displaced fluid phases (Chang, 1978; Gogarty, 1967; Kumar *et al.*, 2008; Lake, 1987; Pye, 1964) because, as it well known, if M is greater than unity the displacing front becomes unstable (*i.e.*, unfavorable mobility ratio); conversely, a value equal to or less than unity is a favorable mobility ratio and, it goes without saying, the target value (Mungan *et al.*, 1966; Ali and Thomas, 1996; Morelato *et al.*, 2011). However, achieving this in the field has proven more challenging than expected because, as it is known, in many EOR processes there will be more than one displacement front; for example, if multiple slugs of different fluids are injected, the flow behavior of any specific displacement front will be affected not only by the mobilities of the fluids immediately ahead of and behind that front, but also by the mobilities of fluids in regions around the other fronts (Green and Willhite, 1998). Furthermore, all too often, reservoir heterogeneity is what makes EOR so difficult, increasing the mobility ratio has been found to address this issue (Abu-Shiekah *et al.*, 2014). Sound reservoir-engineering practice should try to live side-by-side with uncertainty rather than just try to reduce it, that is, if true progress is intended (as the playwright once said “all progress depends on the unreasonable man”). In fact, proper evaluation of uncertainties in reservoir engineering not only spans a wide variety of topics, but it has also been the focus of a great deal of research from general works (*e.g.* Capen, 1976; McVay and Dossary, 2014) to specific ones (*e.g.* Bryant *et al.*, 2002; Viberti and Verga, 2012).

Recently, among the new possible advancement options Fletcher and Davis (2010) outlined the potential of nanotechnology to transform the design and execution of chemical EOR arguing that through nanotechnology an explicit connection between the disciplined study of fundamental molecular forces and the practical application of petroleum engineering could be made. To this end, the authors believe a conformance improvement flood that combines core-shell technology with traditional oilfield flooding operations could be implemented with subsequent beneficial rates of return. To move forward, a PoC study is often needed to address any unresolved issue still present in the development of existing technologies. Thus, the following conceptual (it bears repeating) screening of possible materials, based on the authors' knowledge as well as past experiences reported in the literature from very different scientific areas, is presented to evaluate the potentiality of core-shell technology.

Why Core-Shell Technology?

In the spirit of all science is a collaboration the following certainly seems worth considering. Recent studies in drug delivery applications have argued that “spatially controlled

drug delivery can be obtained by conjugating drug-encapsulated nanoparticles with targeting ligands, which *could facilitate the preferential delivery of nanotherapeutics to the sites of interest while reducing undesired side effects elsewhere* [emphasis added]” (Swami *et al.*, 2012). In fact, Cocuzza *et al.* (2012) had already anticipated the possibility of applying nanotechnology in the oil industry by developing “smart fluids” for water shutoff and/or improved/enhanced oil recovery amongst its potentialities. Rendered into the reservoir engineer’s lingo as the injection of nanocapsules, of which the core is a polymeric, but not limited to, material that activates through a gelation, protected by a shell that can release its content at both a precise location and an appropriate time (*i.e.*, tunable release). Moreover, if controlled release polymer technology, resulting in the temporal control of drug exposure, has benefited virtually every branch of medicine over the past four decades (Swami *et al.*, 2012), who is to say that an application crossover to the oil industry of this existing technology would not result in the optimization of, for example, ongoing as well as upcoming waterflooding processes to displace additional oil?

From a strictly engineer’s perspective, the coverage and characterization of reservoir heterogeneity should be limited to only those reservoir characteristics, channels and layers for instance, whose effects on flow are critical to the recovery of reservoir hydrocarbons (Alpay, 1972). The natural tendency of the displacing fluid to flow through the higher permeability network or thin layers (also termed thief zones) often implies that preferential paths are followed in the reservoir, causing an early water breakthrough at the producing wells. This can dramatically slow down the oil displacement process from the lower permeability zones of the reservoir and additional oil – if any – can only be produced at the cost of producing large volumes of water too, with serious consequences on the final recovery factor. So far, attempts at reducing water occurrence by means of conformance-improvement treatment systems normally are of a relatively small volume and usually are used to treat the near-wellbore region or a relatively small fracture within the reservoir (Sydansk, 2007; Sydansk and Romero-Zerón, 2011); these local interventions may limit water production to some extent, but they do not truly affect waterflooding at the reservoir scale. One of the problems that could not be overcome and severely limited the extension of the treated reservoir volume is intimately correlated to properties of the injected treatment: the high viscosity of the water enriched with chemicals dramatically reduces the fluid injectivity thus preventing that large quantities can be deployed in a reasonable time span. Furthermore, Bai *et al.* (2007) have pointed out that gel treatments had been used to correct permeability heterogeneity near the wellbore (5-10 m) up to the 1990s, after which and as oilfields began to mature, crossflow in heterogeneous thick zones became an increasingly

influencing factor on oil recovery, thus the attention-shift towards in-depth well treatments. Ideally, a polymer treatment that is injected and adequately positioned in the high permeability channels or layers so as to create barriers for modifying the injected fluid mobility and path could bring considerable advantages in terms of oil recovery. In fact, Seright *et al.* (2012) have argued that in-depth profile modification would work best in the presence of high permeability contrasts. In addition, and since no oil reservoir is perfectly homogeneous, polymer-based treatments should be designed to improve both conformance and sweep efficiency simultaneously. In other words, both “the viscous-fingering-mitigation mobility-ratio mechanism and the permeability-heterogeneity improved-sweep mechanism must be functioning during any given polymer flood” at the same time (Sydansk and Romero-Zerón, 2011). To that end, core-shell technology along with the use of emerging technologies of polymeric nanoparticles could be applied in the design of oil-recovery drive fluids or smart fluids (when appropriate the latter term will be used from now onwards in this paper). Moreover, these smart fluids would fall into the ideal category of combined mechanisms that can contact and mobilize oil in hard-to-reach locations in the time frame of interest.

The key challenge is thus to couple a core able to clog the high permeability reservoir zones or layers and divert waterflooding into the unswept areas to displace more oil with a compatible shell which can somehow dissolve and liberate its reactive content when and where needed. In other words, the possibility to achieve a tunable release of the polymers represents a major improvement in waterflooding. Thermally Activated Particles (TAP), such as the abovementioned Bright Water[®], attempt to address this issue because they are activated by a temperature change which can be predetermined. Because the technology relies on the progressive warming up of the injected water when flowing through the reservoir, it implies that a reliable model of the temperature distribution in the reservoir must be available for design purposes. Furthermore, laboratory tests have shown that there is a strong correlation between TAP viscosity and adsorption, and temperature (Galli *et al.*, 2012). On the same subject, authors of a paper on the use of TAP to improve sweep efficiency at the San Jorge Basin, Argentina, concluded that within reservoir characterization injector-producer temperature profile was key in the ultimate success of TAP treatments (Mustoni *et al.*, 2010). Fethi *et al.* (2010) shyly pointed out that after a planned water injection shut down (due to pump system maintenance) a wellhead pressure increase and a constant decrease of injectivity had been detected during TAP treatment in the a pilot test in Tunisia. El-Karsani *et al.* (2014) have also observed some limitations for the application of TAP, such as: (1) swelled particles will not help in improving the sweep efficiency

much beyond the maximum depth of microparticle propagation; (2) sweep efficiency in the reservoir before the treatment is supposed to be very poor for the process to work well; and (3) the resistance factor of the particles should not exceed that for water and should not increase during microparticle placement (El-Karsani *et al.*, 2014).

Along this line, in the following the results of a fundamental research on core-shell technology to improve water-flooding processes in oil reservoirs are presented and discussed as a springboard towards a not so distant future. The use of said technology would enable delivery of a polymer core to a target location within the reservoir without any interaction occurring during and/or after injection, thus eliminating issues related to injectivity and polymer degradation (Li and Delshad, 2014; Sheng *et al.*, 2015).

1 MATERIALS AND METHODS

1.1 Preliminary Screening

A major concern in field applications is that the two types of polymers typically used in field operations, biopolymers and synthetic polymers, continue to present certain drawbacks. While the former are disfavored because of their sensitivity to water salinity and hardness and due to their sensitivity to mechanical or shear degradation (Seright *et al.*, 2009; Sydansk, 2007; Sydansk and Romero-Zerón, 2011), the latter tend to be disfavored for their sensitivity to microbial attack as well as the common occurrence of fermentation-process-induced cell debris that impairs polymer-solution injection into reservoir matrix (Sydansk, 2007; Sydansk and Romero-Zerón, 2011). However, one of the benefits of applying core-shell technology would be the mitigation of these effects as the core remains protected until reaching the target in the reservoir.

Because areal and vertical sweep efficiencies are in large measure determined by the mobility ratio in the displacement process, which is inversely proportional to the displacing-fluid viscosity (Green and Willhite, 1998), one of the first objectives of the research was to identify a suitable chemical for the core to form an organic or inorganic gel having high viscosity when released into the flooded reservoir. Different cores underwent preliminary selection: metal-organic compounds, in particular metal alkoxides, where the metal was alternatively Si (Silicon), Al (Aluminum), Ti (Titanium) and Zr (Zirconium). The metal-organic compounds were tetramethoxysilane (TMOS), silicon tetrachloride (STC), trimethylmethoxysilane (TMMS), methyltrimethoxysilane (MTMS) and methyltrimethoxysilane (MTES). Especially promising was the TMOS, which is insoluble in water and slightly soluble in oil. However, organic polymeric gels crosslinked with monomers and/or

prepolymers could also be used. Should an organic polymeric gel be used, it must be crosslinked with a monomer and/or prepolymer. Furthermore, starch, an organic compound that has been used in EOR processes in the past was tested as a core (Karmakar and Singh, 1997; Pledger *et al.*, 1979). The term “starch” refers to a polysaccharide consisting of a large number of glucose units joined by glycosidic bonds, *i.e.* $\alpha(1\rightarrow4)$ bonds which make up the amylose component and $\alpha(1\rightarrow6)$ bonds which make up the amylopectin component (or the glucose chains are unbranched in amylose and branched in amylopectin, which occur mixed in starches). Starch is insoluble in water at standard conditions, but begins to gel at 60–80 °C. In contact with water the starch loses its original semi-crystalline structure and water molecules bond to the hydroxyl of the amylose and amylopectin components through hydrogen making the granules swell. Because starch is naturally occurring, it offers significant advantages; of particular interest for the case at hand are: (1) it is undoubtedly environmentally friendly (thus no hazardous chemicals would be injected into the subsoil); (2) large quantities are readily available; and (3) it is low cost. Not surprisingly, starch is the most widely used thickening and gelling agent in the food industry (Sakač *et al.*, 2012).

Recently, Ogolo *et al.* (2012) also evaluated the use of fluid suspensions of nanoparticles based on oxides of aluminum, zinc, magnesium, iron, zirconium, nickel, tin and silicon, exploiting EOR mechanisms as disjoining pressure gradient, interfacial tension reduction, wettability alteration or plugging of pore channels by nanoparticles adsorption. Ogolo *et al.* (2012) demonstrated that aluminum oxide nanofluids tend to reduce oil viscosity, whereas silicon dioxide nanoparticles are able to modify rock wettability and reduce the interfacial tension and the contact angle between oil and water phases. In addition, Miranda *et al.* (2012) evaluated the potentiality of silica nanoparticles as an EOR agent, considering as main advantages: (1) their good stability when suspended in a liquid medium, (2) the easy control of their thermal, mechanical and rheological behavior through the definition of their size and shape; (3) the change of their chemical properties through several possible surface modifications; and (4) their composition compatibility with sandstone, which makes them environmentally friend.

1.2 Selection and Preparation of the Core-Shell Particles

1.2.1 Cores

On the basis of the above mentioned literature, two core substances of different composition and particle size were selected: organic micrometric particles and inorganic nanometric ones. The scope of initially using a micrometric

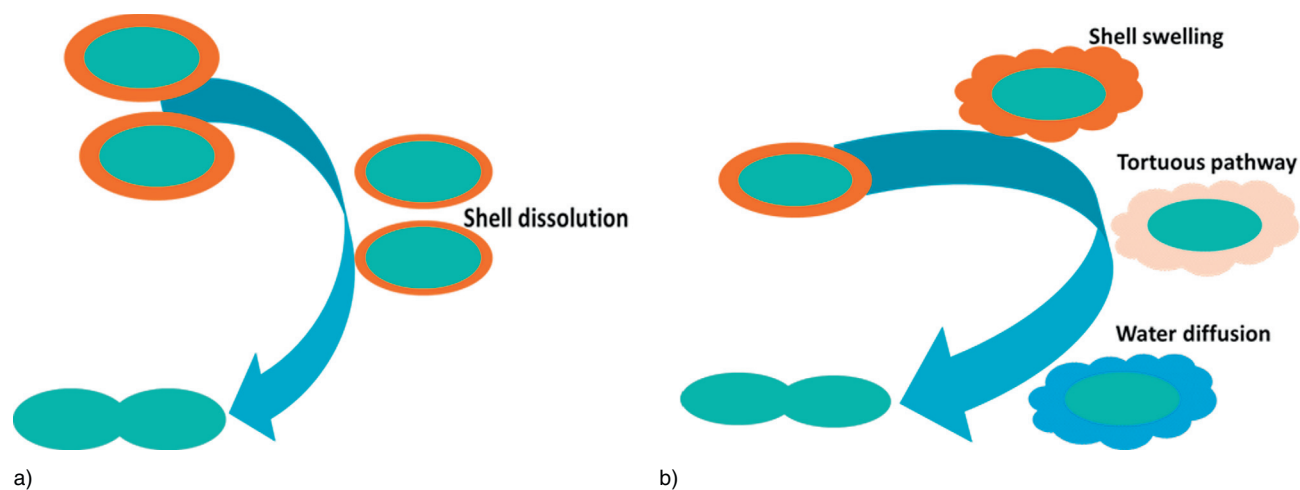


Figure 1

Possible mechanisms for core release by: a) shell dissolution; b) shell swelling.

polymeric particle core substance (specifically homopolysaccharides made of glucose, such as glycogen and starch) was that of exploiting its gelling properties to prove the effectiveness of the mechanism. The formation of a continuous coating, namely the efficiency of the shielding effect of a deposited shell, and its ability to decompose after a fixed time can be easily verified by observing whether a gel is formed or not.

Once the efficiency of the core-shell mechanism was verified using the organic micrometric particles, a siliceous nanometric powder suitable for EOR applications was selected as core substance. Direct visual inspection at the nano scale was impossible, thus the effectiveness of a shell to protect the inorganic core could only be assessed through a dissolution test in a hydrofluoric acid (HF) solution.

1.2.2 Shell

Obviously, the nature of the shell and the process able to create a protecting layer on the core surface depends on the selected core. Generally, shell systems that achieve temporal controlled drug release could be designed in order to delay the drug dissolution or to control the diffusion of the drug out of the device (Uhrich *et al.*, 1999). Polymers employed to delay drug release aim to slow the rate at which the core is exposed to the surrounding aqueous environment and consist in coatings or matrices able to dissolve at a slow rate. In diffusion-controlled release, at the beginning, an insoluble polymer matrix insulates the drug. A prolonged exposition to the surrounding aqueous environment induces a decrease in the barrier properties of the shell and a tortuous pathway develops within it, *e.g.* by swelling, creating voids in which

the drug can slowly diffuse. These two mechanisms can easily be transferred to EOR applications: the former can be exploited for both core types, which are able to act when the polymeric shell dissolves (Fig. 1a), whereas in the latter water can diffuse through the tortuous pathway and react with the core (Fig. 1b). This last principle is not suitable in the case of the inorganic particles for which surface mechanisms must occur.

Shells were selected based on their mass variation (*i.e.*, weight decrease as a consequence of polymer decomposition or weight increase due to water absorption in swelling structures) recorded after water immersion, under critical conditions of high temperature and high water salinity.

Laboratory tests were carried out to evaluate the mass variations of several polymers after immersion in salty water at 80 °C at atmospheric pressure for different times. On the basis of these results, two polymeric systems were chosen as possible candidates for the shell realization. The former, named P1, showed several steps in mass variation, probably due to an erosion/disruption of the polymeric surface: weight losses of 10, 34 and 48% were recorded after 390, 990 and 1992 h, then the mass remained quite constant up to 4000 h. On the other hand, a mass increase was recorded for the second polymer, labeled P2, due to water absorption. An in-oven drying treatment not effective in the removal of the absorbed molecules, confirming that water absorption was irreversible. This demonstrated that the P2 polymer is able to swell when immersed in hot salty water. These two polymers seem to be able to perform a core release at a controlled time according to the above-described mechanisms. Both polymers were thus employed for realizing a shell

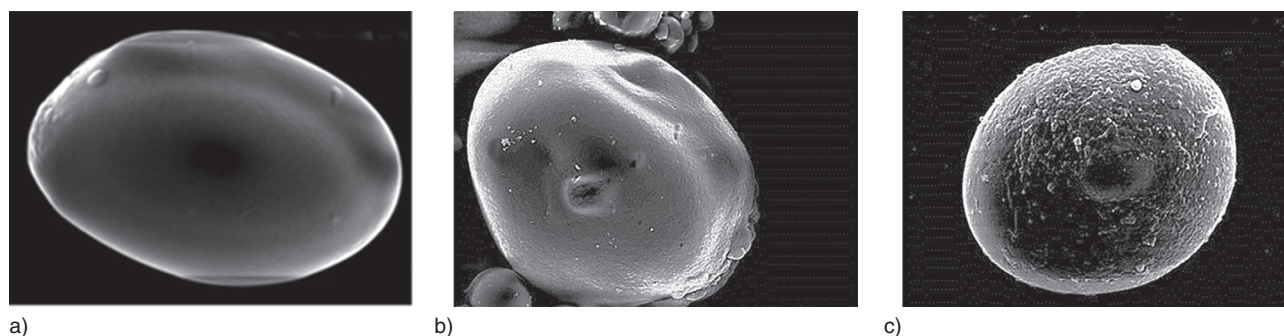


Figure 2

FE-SEM images of organic micro-size core particles: a) before coating deposition; b) coated by P1 shell; c) coated by P2 shell (5.000 \times).

structure on the selected core particles to allow their gelation only after a controlled time.

On the basis of the technical literature, different synthesis routes as a function of shell polymer nature were exploited, evaluating the influence of different process parameters. In the case of the P1 material, a coalescence method was employed for the core-shell preparation, making the droplets of the shell solution to coalesce with the droplets containing the core particles. In particular, core particles were dispersed in the continuous phase, containing distilled water and a stabilizer; part of the Reagent A (pre-polymer) was added to such dispersion and vigorously stirred; at last, the Reagent B (hardener) was dispersed in the remaining part of Reagent A and added to the continuous phase. The mixture was kept at 55 °C under magnetic stirring for about 4 h to promote droplet coalescence and, therefore, shell creation through an *in-situ* polymerization. On the other hand, the P2 material was employed as starting material for the shell production through an emulsion solvent evaporation technique, dissolving it in a suitable solvent and dispersing the core particles in distilled water. The aqueous suspension and the polymeric solution were mixed under vigorous stirring to form a water-in-oil emulsion. This emulsion was then stirred at about 50 °C in order to promote the evaporation of the solvent and the shell deposition on the core surfaces.

The core particles and core-shell systems were characterized by means of an FE-SEM microscope and the relative micrographs are reported in Figure 2. The comparison of the images in Figure 2 shows that, after the above-described procedures, the organic core particles were homogeneously coated by the P1 and P2 materials: corrugations and roughness were observed on their surfaces.

The P1 and P2 coatings were also deposited on the siliceous core particles according to the same preparation methods described above. The FE-SEM images reported in Figure 3 show smooth particle surfaces for the core-shell

system. In order to confirm the presence of the shell, a dissolution test in hydrofluoric acid (HF) was also performed on siliceous powder after coating deposition. The core-shell systems did not undergo any changes thanks to the protective action of the deposited coatings whereas the unprotected inorganic core particles had completely dissolved in the HF solution.

2 RESULTS

2.1 Core-Shell Testing

As already stated, this research was aimed at verifying the feasibility of the application of core-shell technology for improved waterflooding under a reservoir temperature of 80 °C in a salty environment. Preliminary tests were run at atmospheric pressure; a further characterization was carried out evaluating shell decomposition at different pressures (25, 50 and 100 bar) and temperature (120 °C).

Then, a set of column tests through sand packs were performed with both the polymer and silica core-shell particles to both evaluate the effects of mechanical degradation and to assess the ability of the released cores to clog a porous medium. Porous media were lab-scale sand packs, with a diameter of 8 cm and a height of 5 cm, obtained by compacting a common sandstone with mean particle diameters of about 600 μm .

2.1.1 Batch Tests

A set of batch tests were initially performed. Preliminary tests proved that the selected organic particles were able to rapidly (30–40 min) gel at a temperature above 70 °C in salty water. In particular, the salty water employed in the experimental tests was made up of 80% sea water and 20%

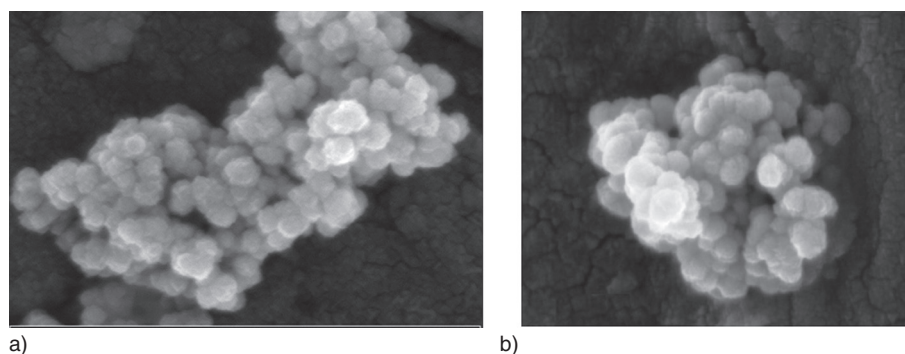


Figure 3

FE-SEM images of nano-size inorganic core particles a) before and b) after shell deposition (500.000 \times).

TABLE 1
Composition of formation water used for testing the materials.

Components	(g/L)	wt.%	ppm
NaCl	38.5136	3.85136	38 514
Na ₂ SO ₄	4.3152	0.43152	4315
CaCl ₂	6.7540	0.67540	1748
MgCl ₂ .6H ₂ O	14.4432	1.44432	14 443
KCl	0.8870	0.08870	887

formation water and thus had a composition similar to that resulting from waterflooding in a real field; the composition of the water used for testing the materials is reported in Table 1.

Dissolution tests of the deposited shells on the organic particles were carried out in salty water at 80 °C under shaking, showing that the organic core particles coated by the P1 shell are able to withstand the test conditions 6 months before their gelation; on the other hand, P2 coatings prevented core reaction with hot salty water for 3 months. When dissolution reached a critical level, water was able to interact with the organic core: solution viscosity increased and gel formation was observed after 2 days.

“Real time” shell dissolution under simulated operating conditions requires several months, being P1 and P2 materials selected for their long-term resistance in water. An accelerated testing method was then set-up in order to allow the evaluation of different parameters in shorter times. Faster polymer degradation can be easily obtained at elevated temperatures (higher than that of the selected operating conditions of 80 °C): in this case, closed Teflon vessels were employed for tests at 120 °C (for these experiments the

working pressure was obtained by heating the mixture, and it corresponded with the vapor pressure of the salty water mixture for the fixed working temperature). As expected, in these conditions the core-shell systems, based on the organic particles, underwent gelation in shorter times, equal to 28 and 12 h for the P1 and P2 coatings, respectively. Furthermore, in the case of the P1 coating, some additional tests were carried out to investigate the role of pressure on shell degradation. Accelerated tests at 120 °C were performed at fixed pressure values of 25, 50 and 100 bar: core gelation occurred after about 26, 23 and 20 h, respectively, thus showing that a pressure increase causes faster shell degradation. At high pressures water uptake took place with higher rates, as demonstrated by Lefebvre *et al.* (2009). This favored degradation and the swelling phenomena of the P1 coating and, consequently, water reacted with the organic core in shorter times.

The release time of the siliceous core particles coated by the P2 shell, measured through accelerated tests, proved equal to that recorded for the polymeric particles. In fact, after 12 h at 120 °C the degraded core-shell particles

completely dissolved in HF solution, confirming the absence of the polymeric coating on the surfaces of the siliceous particles. This suggested the two core/shell systems behaved in the same way, with a release after three months at 80 °C. On the other hand, in the case of the P1 coating a different behavior was observed, with the persistence of the shell even after 185 h at 120 °C, confirming the incompatibility of this core with the diffusion-controlled release mechanism.

2.1.2 Column Tests

Preliminary flow tests of water containing 10 wt.% silica showed plugging of the porous medium. The flow tests through the sand packs were repeated with the coated nanoparticles and no plugging occurred. This is due to the negligible adsorption of nanoparticles, as a consequence of the presence of the coating which implies a relevant decrease of surface forces that generally exist between inorganic particles.

Mechanical degradation of core-shell capsules was assessed after repeated flow through the sandstone porous medium. A core-shell suspension with a solid content of 10 wt.% was circulated in the porous medium five times and then subject to an accelerated degradation test at 120 °C at the vapor pressure of the water mixture for the fixed working temperature, as in the “accelerated tests” described in the previous section. Gelation occurred after 22 h (under the same conditions, degradation of the “as-prepared” core-shell structures took place after 28 h), demonstrating that the shell withstands mechanical stresses but the core release takes place in shorter times.

Finally, a set of flow tests through sand packs were performed with both polymeric and siliceous core-shell particles. In both sets of experiments complete clogging was observed after core activation occurred, therefore very encouraging results were obtained. However, this also posed significant problems with the subsequent experimental part since it would be extremely difficult to monitor the efficiency of the barrier (whether polymer or silica) over months and/or even years under a pressure difference mimicking reservoir conditions. Accordingly, only a pilot test would be able to further address the efficiency of the core-shell technology under field conditions.

2.2 Viscosity Tests

The aqueous suspensions containing 10 wt.% of the polymeric particles or the siliceous powder presented viscosity values that did not differ (or did not significantly) from that of water.

After shell deposition, no changes in viscosity values of the aqueous suspensions containing different core-shell

systems were measured. This implies injectivity is not jeopardized by the presence of chemicals and the same injection rates as in a conventional waterflooding can be assured.

Conversely, after activation, the homopolysaccharide solution underwent a rapid (within hours) viscosity increase on the basis of its concentration, as observed by laboratory tests (Tab. 2 and Fig. 4): the viscosity of the polymeric fluid ranges between 10^5 and 10^6 mPas for initial concentrations of the polymers equal to 10 wt.%.

2.3 Simulation of Polymer Plugging and Performance Using Core-Shell Technology

The main goal of simulations was to investigate the efficiency of the technology as a temporary surrogate of pilot tests and/or field applications, which are yet to be carried out. In fact, despite some limitations inherent to all simulations at reservoir scale (rock and rock-fluid interactions homogeneity, just to name an obvious one), simulations can provide preliminary insight on the effectiveness of a proposed methodology as long as the occurring phenomena are correctly represented. Thus an effort was made to perform simulations which would describe core-shell transport and core release and activation in the reservoir in a meaningful manner. In the absence of a dispersivity coefficient at this stage of the PoC, dispersion was not considered even if the authors are well aware of the impact dispersion might have in flow through reservoirs (*e.g.*, Seright, 1991).

The key point in the application of the core-shell technology is the possibility to block the water flow along the higher permeability network of the reservoir so as to force water into the lower permeability zones, where otherwise the oil would remain unswept. The water blockage is yielded by the activation of the injected chemicals at a given time significantly increasing the viscosity of the advancing water front, thus achieving a reduction of the water mobility in the flooded, thief zones. Further water injection will preferably flow where less resistance is encountered, *i.e.* lower permeability zones flushed by water with unaffected viscosity.

To that end, a thorough analysis of the methods and benefits of core-shell technology in waterflooding operations, by simulating its application to several synthetic but representative reservoir scenarios, was performed. The core-shell particles were injected in the reservoir as a dispersion in water. The efficiency of the plugging effect of the high permeability layers or channels due to the core activation was analyzed in terms of improvement in the oil recovery factor and reduction of water production with respect to a reference do nothing scenario. Then, sensitivity analyses were carried out for the different reservoir scenarios by varying the petrophysical characteristics (the most important of which was the permeability) and fluid properties (the most important of which was the oil viscosity) so as to identify the optimal design

TABLE 2
Gelified starch viscosity (70 °C, 120 min).

Starch-water ratio	Starch concentration by weight (%)	Viscosity (mPas)	
		Rotational speed @ 10 rpm	Rotational speed @ 100 rpm
1:1	50.0	$>6.4 \times 10^6$	Out of range
1:2	33.0	1.4×10^6	9×10^4
1:3	25.0	7.4×10^6	1.3×10^5
1:5	17.0	3×10^5	4.2×10^4
1:7	12.5	1.4×10^5	4.3×10^4
1:10	9.0	5.5×10^4	1.4×10^4
1:20	4.7	1.5×10^4	3.5×10^3
1:50	2.0	1.6×10^2	1.6×10^2
1:100	1.0	17	17

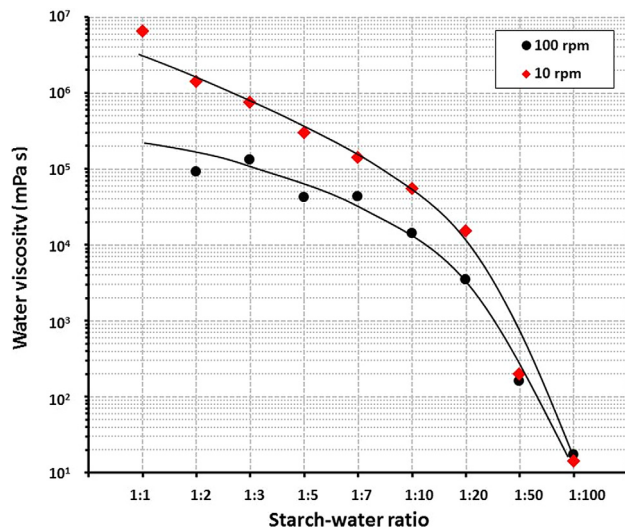


Figure 4
Injection fluid viscosity as a function of polymer concentration.

conditions for the execution of the intervention and to determine the corresponding increments of oil recovery factor that could be achieved.

2.3.1 Set up of the Reservoir Numerical Models and Simulation Constraints

Commercial software was used for simulating the dynamic behavior of reservoirs subject to water and polymer flooding.

Different 3D reservoir numerical models were generated (the areal size of the models ranges between 1 and 3×10^6 ft² and the thickness ranges between 7 and 50 ft).

The core-shell technology was tested both in homogeneous and heterogeneous scenarios, namely in two reservoirs with high permeability layers, in a reservoir with high permeability channels, in a reservoir with a random distribution of high permeability facies, in a heterogeneous reservoir with multiple transmissibility barriers, and a homogeneous reservoir with gravitational segregation. The six reservoir models are presented in Figure 5.

The same basic reservoir properties were assumed for all scenarios. It was assumed that the reservoirs were located at a depth of 2000 m, with an initial pressure of 200 bar and a temperature of 70 °C. Reservoir porosity equal to 20% was assumed for the permeable layers or zones. The Net-to-Gross Ratio (NGR) was set equal to unity. The rock compressibility was set equal to 3×10^{-5} bar⁻¹.

A dead oil was assumed for reducing the reservoir simulation time. With this assumption, the reservoir pressure never reached bubble point during production, thus the oil remained in undersaturated conditions and no free gas was present in the reservoir at all times. The oil density was assumed equal to 30° API and the oil viscosity was varied between 2 and 10 mPas. The water density was assumed equal 1070 kg/m³, the water formation volume factor equal to 1.03 m³_r/m³_{ST} and the water viscosity equal to 0.5 mPas.

The rock absolute permeability was changed in the sensitivity analyses and ranged between 20 and 2000 mD. The permeability anisotropy (vertical permeability divided by horizontal permeability) was varied between 1 (isotropic

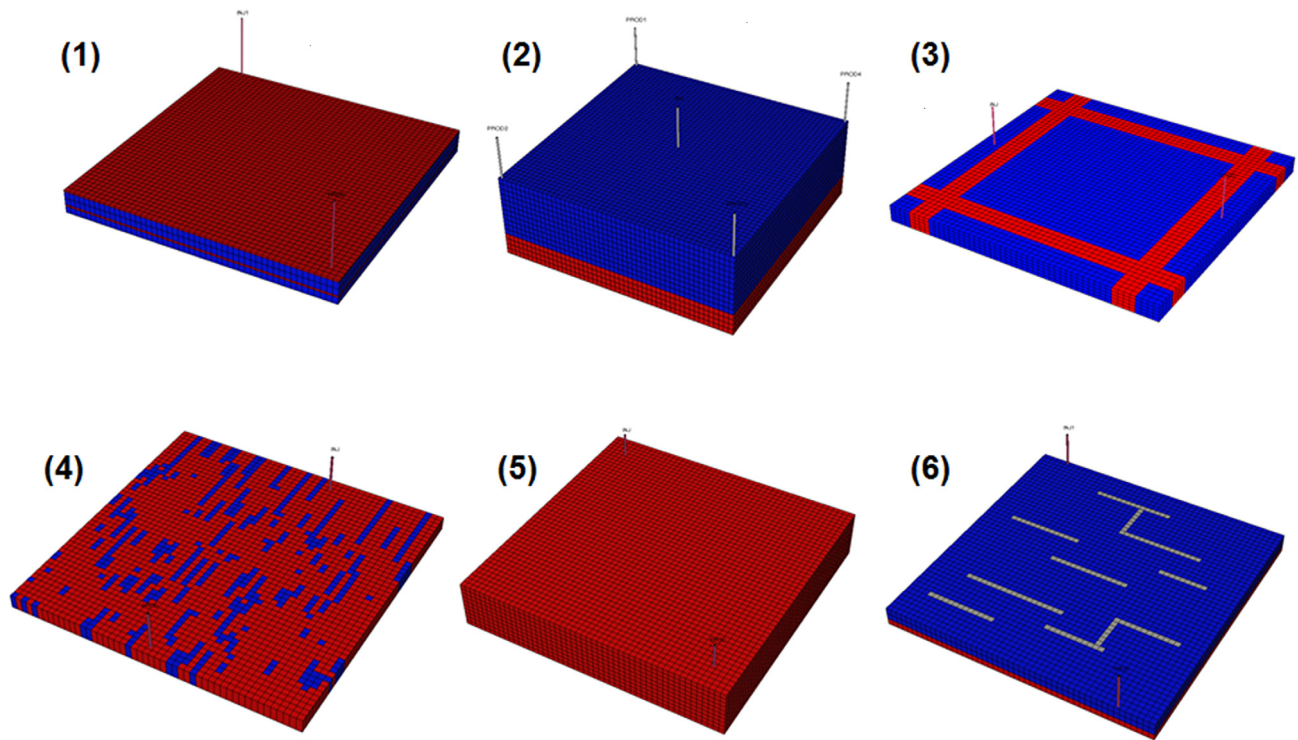


Figure 5

Investigated reservoir scenarios [vertical scale enlarged]: (1) multi-layered reservoir with thief zones; (2) two-layer reservoir with five spot water-flooding; (3) reservoir with high permeability channels; (4) reservoir with random facies distribution with different permeability; (5) thick homogeneous reservoir with occurrence of gravitational segregation; (6) reservoir with multiple faults/flow barrier.

conditions) and 0.01. In addition, the critical water saturation and the residual oil saturation were set equal to 20%.

The core-shell fluid was simulated as a polymer volume concentration in water. Because the polymeric fluid is actually a dispersion of inert nano-capsules, containing the polymers or the siliceous powder, in water, the polymer injection process was simulated as a tracer injected in water with a given concentration. The core-shell fluid density was set equal to the water density (1070 kg/m^3) and the viscosity was set equal to 0.5 mPas because, as it was verified with the lab tests previously reported, the dispersion of inert nano-capsules does not alter significantly the water properties. The effects of polymer adsorption were not considered under the assumption that adsorption would be negligible.

In all the simulated scenarios the polymer injection was scheduled to start at a precise time, when the average field water cut (*i.e.*, the ratio between water production and the total liquid production) reached 0.85. Well constraints were defined for both the injection phase and the production phase. A limit of 240 bar ($120\% p_i$) was set as the maximum

bottom hole pressure at the injection well(s) and a limit of 100 bar was set as the minimum bottom hole pressure at the producing well(s) in all the simulated cases.

In the simulated scenarios the polymer or the silica, protected by the shell and thus inert, was injected in water at the injector well(s) and flowed through the reservoir toward the producing well(s). The delay of the polymer/silica activation with respect to the start of injection was designed based on preliminary sensitivities, carried out for each considered scenario.

In the reservoir model the polymer concentration values were different in each cell of the domain and varied at each time step of the simulation. The polymer injection was simulated adopting short time steps (2.5 days). After reaching the activation time, the water viscosity changed in each cell of the model based on the polymer concentration, according to the adopted law of viscosity increase (Fig. 4). Because laboratory tests showed the increase in viscosity occurred within hours and the adopted time step was set to days, in the model the viscosity increase occurred “instantaneously” once the polymers were activated. The law of viscosity

increase after core activation was set according to the results of the available laboratory experiments; in particular the correlation found for 10 rpm was adopted because fluid velocities in porous media are very low. A polymer concentration threshold was also defined for triggering the activation of the polymers. Preliminary analyses were performed to tune the parameters needed to simulate the *in-situ* generation of the polymer barrier. Based on these analyses, the value of the polymer threshold concentration was set equal to 0.0001 lbs/bblST.

Complete laboratory experiments were available for organic core particles only and, therefore, those results were used in the simulation (the use of other technologies, such as TAP, may very well reveal themselves equally promising notwithstanding). Accordingly, the methodology can be applied to any polymer type by adjusting the viscosity reduction as a function of the concentration. Based on preliminary laboratory experiments viscosity reduction in time due to core degradation was not simulated.

The numerical models were used to evaluate the efficiency of the core-shell technology for different reservoir scenarios and for different injection rates and periods. The simulation of the plugging effects due to polymer injection and activation and the evaluation of the oil recovery factor increment were performed in two different stages. Initially, a reference case was defined for optimizing the injection and production rates during a conventional waterflooding process (or do nothing scenario). Then, sensitivity analyses were carried out for the selected scenarios in order to optimize the polymer intervention by changing the volumes and rates of the injected polymers and the activation time.

The production and injection rates in the do nothing scenarios were calibrated after preliminary simulations in order to optimize the oil recovery factor. As [Thomas et al. \(2002\)](#) state, the rate at which the treatment is placed is one of the more important parameters to consider; indeed, it is really the differential pressure that drives the selectivity of the chemical treatment (which is intimately linked to flow rate).

A voidage replacement ratio equal to unity was adopted to keep reservoir pressure constant. The same production and injection rates were adopted both in the do nothing scenarios and in the corresponding polymer injection scenarios (optimized waterflooding intervention) so as to obtain comparable results. The production rates assigned to the producing well(s) for each scenario varied in the range 300-2000 bblST/day.

In the optimized waterflooding intervention scenarios, a polymer slug (or, at times, repeated polymer slugs) was injected and the polymers activated after a given delay time so as to plug the highly permeable zones in the reservoir. The same rates and pressure constraints adopted in the reference cases were assigned for the production forecast after the polymer placement and activation. The production forecast

duration was set equal to 5 years in order to estimate the impact of the intervention on the recovery factor within a reasonable time frame. The time step length was varied between 2.5 days (early simulation time, after polymer injection) and 30 days (late simulation time).

2.3.2 Simulation Results and Discussions

The simulation results indicated that, when the intervention was properly designed in terms of polymer quantity and concentration, injection schedule and time of activation, the water flow along the high permeability paths was effectively blocked and diverted by the polymer activation, thus significantly increasing oil recovery with respect to the corresponding reference case, in which a conventional waterflooding was applied. It must be pointed out that no evidence of significant bank dispersion during placement neither in the higher permeability layers nor flow blockage in the lower permeability layers or zones was observed. The reasons for this are: once polymer activation time is reached, shell dissolution occurs rapidly (within hours); and, threshold polymer/silica concentration to affect water mobility was not reached in the low permeability zones.

Numerical simulations were also aimed at verifying whether an optimized injection strategy could be established to maximize the sweep efficiency. As expected, the process optimization and the consequent oil recovery factor increase have to be evaluated on a case by case basis because results are affected by petrophysical and fluid properties as well as by the injected polymer quantity and injection strategy. However, simulation results proved that a general workflow for the proper design of a polymer intervention is applicable to all the investigated scenarios.

The time lag of polymer activation can arguably be considered as one of the most important parameters to be optimized because it strongly affects the placement of a barrier. A too short activation delay can lead to clogging of the injection zone, while a too long activation delay can seriously damage the formation around the producer ([Fig. 6](#)). In order to prevent well clogging, the time lag for polymer activation has to be accurately designed for each reservoir scenario and for each combination of reservoir and fluid properties. Therefore, in real field applications, a preliminary tracer test would be recommended for this purpose, so as to reliably set the time lag for core release. A better calibration of the dynamic model based on the tracer production data could also be achieved and the model be used for forecast purposes, but the success of the methodology does not depend on the reliability of the model. In this research, in order to define the activation time for each case, a pilot test was simulated by injecting a small amount of tracer during normal waterflooding operations and by monitoring the tracer concentration at the production well.

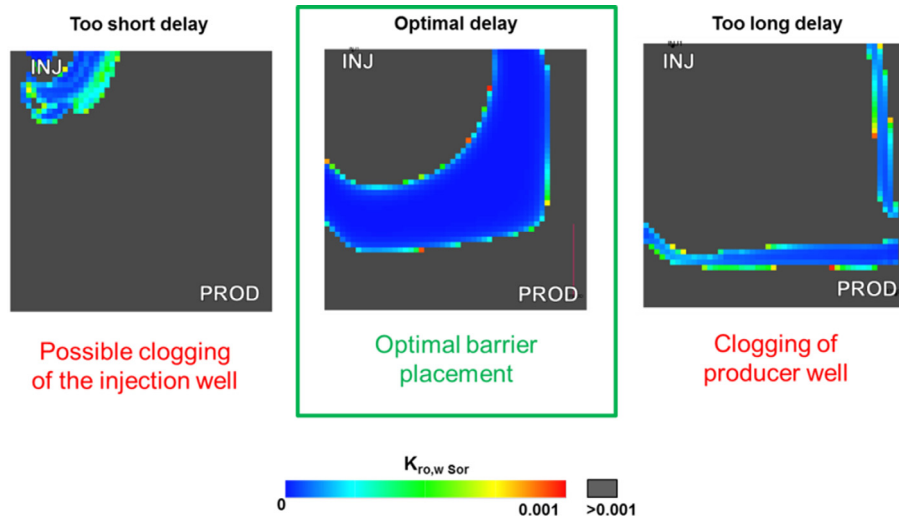


Figure 6
Impact of different polymer activation times on the barrier placement.

In general, it was found that the time lag for polymer activation should be defined as the time preceding breakthrough of the tracer at the producing well. After setting the optimal time lag of polymer activation through execution (and/or simulation) of a tracer test, the amount of injected polymer can be optimized accordingly. Different combinations of time lag of polymer activation and polymer quantity can be found to increase oil recovery, *i.e.* multiple local optima exist in the space of the possible solutions. However, an optimum for the polymer activation time and for the injected polymer quantity can generally be found and the global maximum can be identified with a reasonably limited amount of iterations (by way of example, Figs. 7 and 8 show the results obtained for Scenario 1).

The impact of polymer quantity and concentration and the impact of reservoir and fluid properties on the barrier placement were investigated for each scenario. In relation to polymer quantity, findings show that it affects the extension of the barrier; at the same time, barrier geometry is influenced by the mobility ratio and particularly by the oil viscosity. As for polymer/silica concentration it was found to be the least critical parameter because the same amount of chemicals can be injected with different concentrations by varying the injection time and/or rate. However, it is worth noting that a polymer w/w concentration of 1:10 was optimal in most scenarios (results for Scenario 1 are shown in Fig. 9). As previously mentioned the time lag of polymer activation strongly affects the placement of the barrier; in that regard, besides absolute rock permeability, the polymer

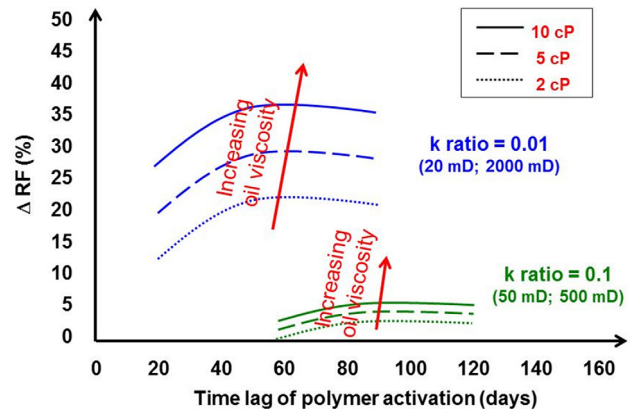


Figure 7
Oil recovery increment as a function of time lag of polymer activation for different oil viscosities and different permeability heterogeneity ratios for Scenario 1.

injected quantity affects the optimal time lag of polymer activation.

Figure 10 shows the progressive oil displacement in the case of a layered reservoir with vertically heterogeneous properties, for a representative combination of reservoir and fluid parameters, after 1, 2, and 5 years from the beginning of the intervention, respectively. The figure shows the

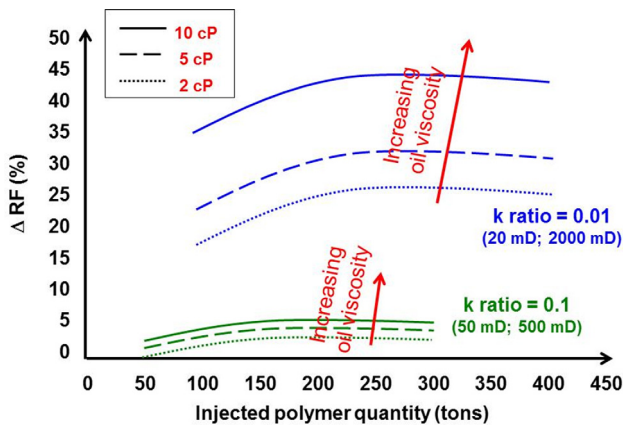


Figure 8

Oil recovery increment as a function of injected polymer quantity for different oil viscosities and different permeability heterogeneity ratios for Scenario 1.

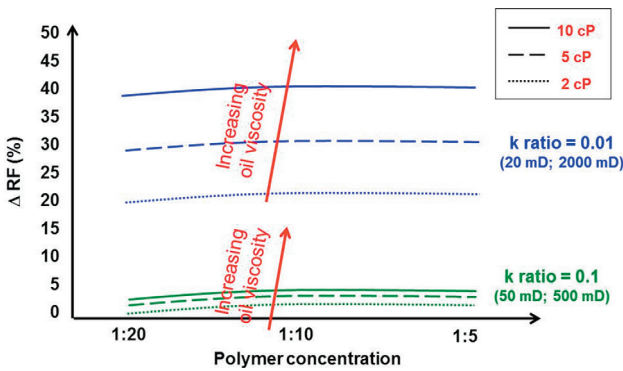


Figure 9

Oil recovery increment as a function of polymer concentration for different oil viscosities and different permeability heterogeneity ratios for Scenario 1.

oil saturation distribution when the smart fluid is injected in comparison with the corresponding do nothing scenario.

Figure 11 shows the evolution in time of the barrier during five simulated years after the intervention. The efficiency of the barrier slightly decreases overtime (years) because continuous injection of water might cause water fingering and local ruptures of the barrier. However, simulation results show that the water flux in the thief zones is still largely prevented and the oil displacement effectively occurs in the main oil bearing layers.

Figures 12-16 give reservoir maps and cross sections with the oil saturation distribution in the investigated scenarios from 2 to 6 with an optimized polymer injection strategy.

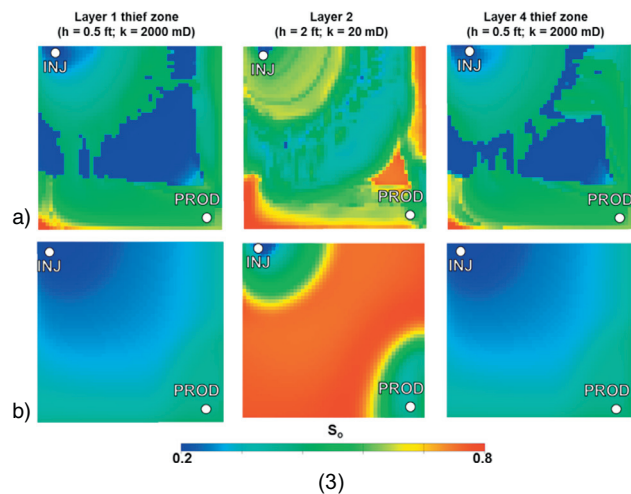
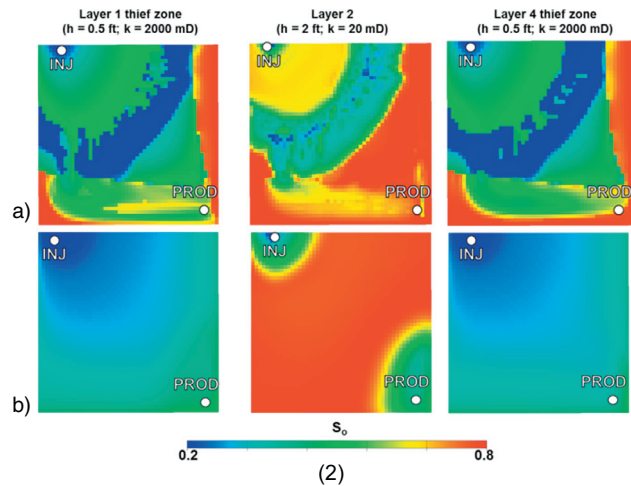
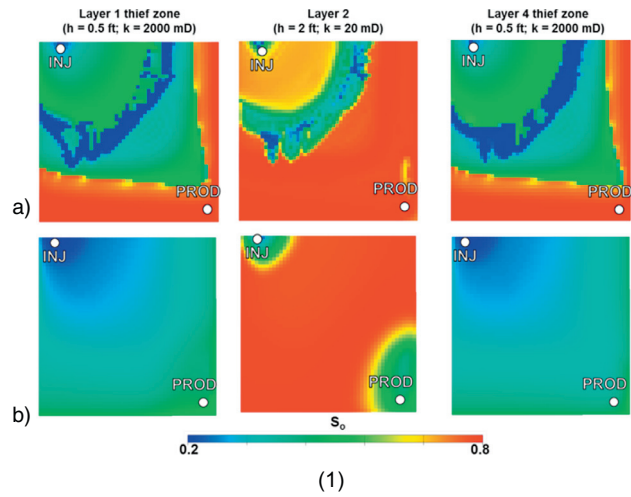


Figure 10

Low and high permeability reservoir layers for case (1) [oil viscosity = 5 mPas; permeability heterogeneity ratio = 0.01; kv/kh = 0.1] with oil saturation distribution in the core-shell injection case a) and do nothing case b) after 1 year (1), 2 years (2) and 5 years (3) from the start of intervention

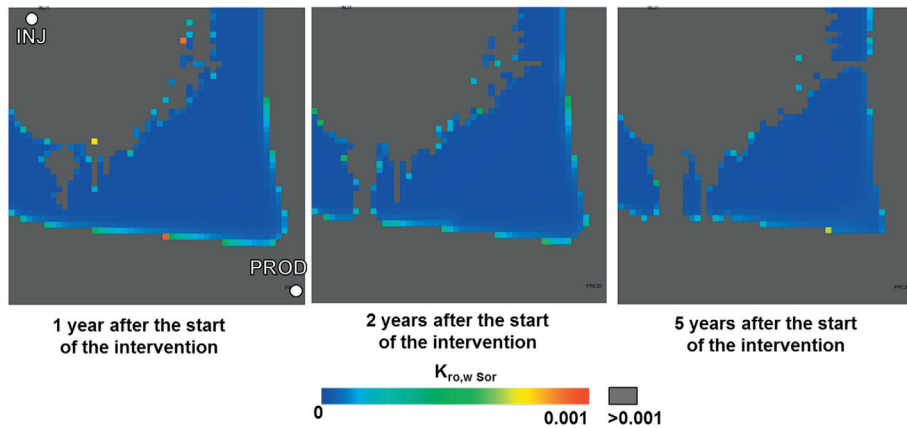


Figure 11

Reservoir cross-section for case (1) [oil viscosity = 5 mPas; permeability heterogeneity ratio = 0.01; kv/kh = 0.1] – Evolution in time of the barrier.

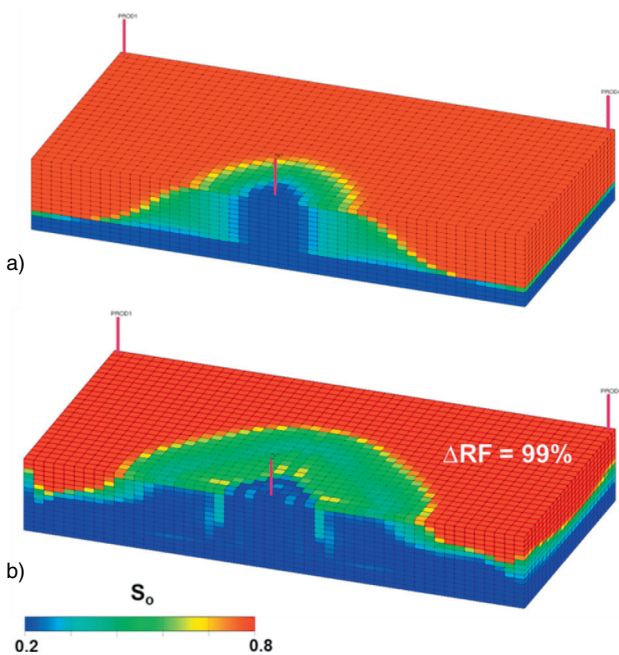


Figure 12

Scenario 2 – Oil saturation distribution after 5 years from the start of intervention: comparison between do nothing case a) and smart fluid injection case b).

The simulation results also showed that the optimal intervention strategy consists in injecting one or more polymer slugs for a given amount of time, followed by water injection as in a typical waterflooding operation. In most cases one single polymer slug proved to be the optimal strategy to maximize oil recovery, but in a few cases the injection of additional slots after the first one was more efficient to optimize the waterflooding pattern.

A full set of sensitivity analyses on reservoir and fluid properties was carried out for the six analyzed scenarios. From the analysis of the simulation results, the oil recovery increments with respect to the reference waterflooding cases varied from 2 to 130%. The overall results of the simulations in terms of oil recovery for both the smart fluid cases and the corresponding do nothing scenarios are shown in Figure 17. As expected, all the simulations showed that the increment of the oil recovery factor with respect to the reference waterflooding case is greater for increasing oil viscosities and decreasing permeability ratios between high permeability zones and low permeability zones, as the benefits of the technique are most evident in extremely adverse cases. However, one should always keep in mind that oil recovery tends to be low in the case of viscous oil. Moreover, conventional wisdom argues that thermal recovery methods are more appropriate for these cases (Taber *et al.*, 1997a); notwithstanding, recent screening criteria reconsiderations have pointed out to the potential of polymer flooding to recover viscous oil (Seright, 2011). Conversely, even a small oil recovery increment for light oil reservoirs can correspond to significant additional oil production.

In addition, the location of the barrier represented by the distribution of the reduced water relative permeabilities is also shown for some representative cases.

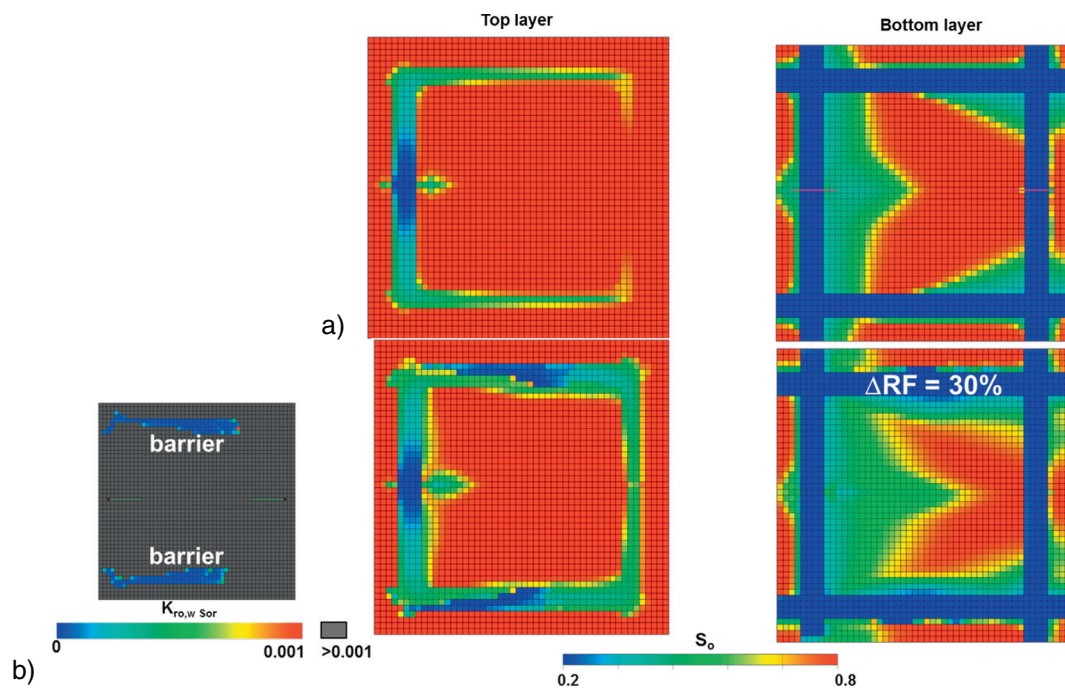


Figure 13

Scenario 3 – Cross-sections with oil saturation distribution after 5 years from the start of intervention: comparison between do nothing case a) and smart fluid injection case b); barrier placement (relative permeability end point at S_{or}).

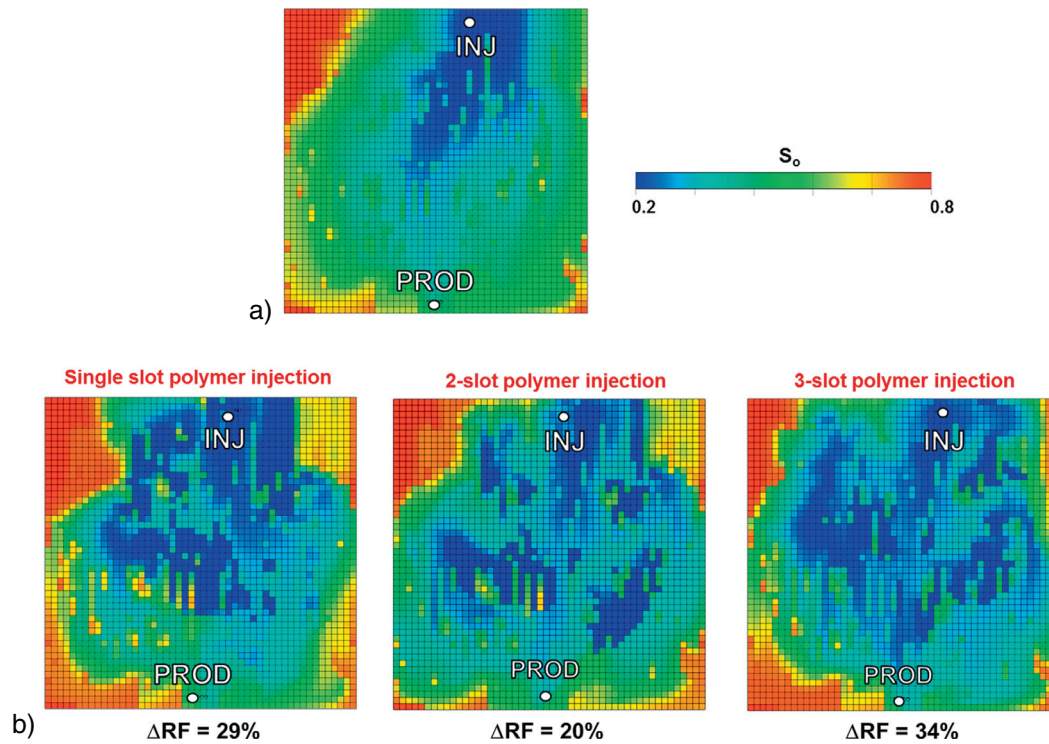


Figure 14

Scenario 4 – Cross-sections with oil saturation distribution after 5 years from the start of intervention: comparison between do nothing case a) and smart fluid injection case b).

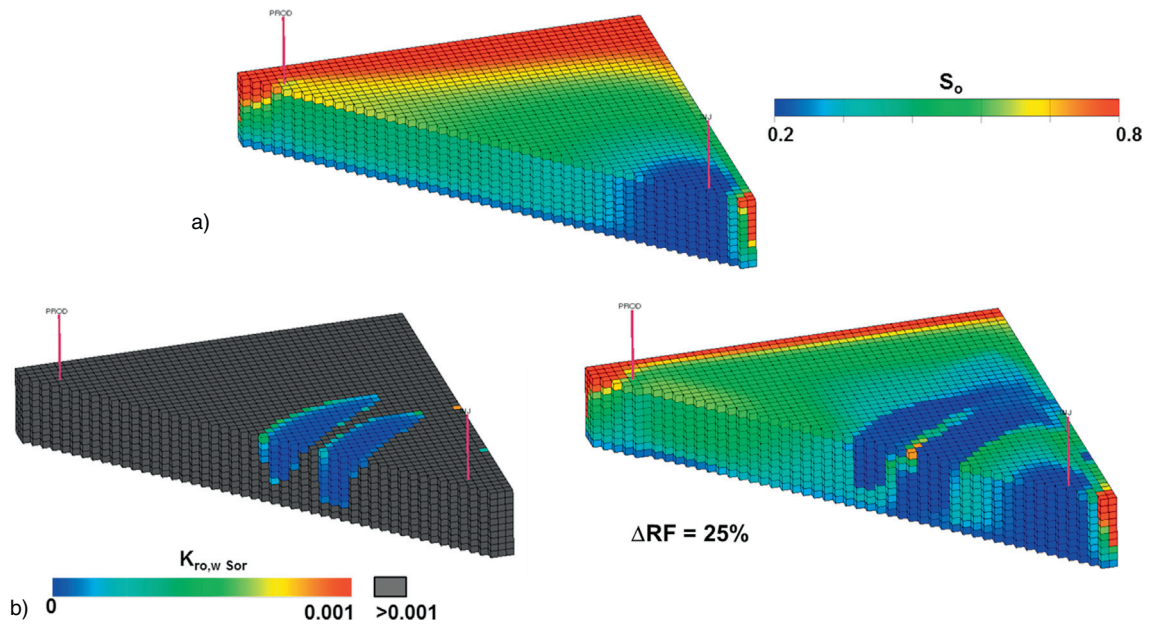


Figure 15

Scenario 5 – Oil saturation distribution after 5 years from the start of intervention: comparison between do nothing case a) and smart fluid injection case b); barrier placement (relative permeability end point at S_{or}).

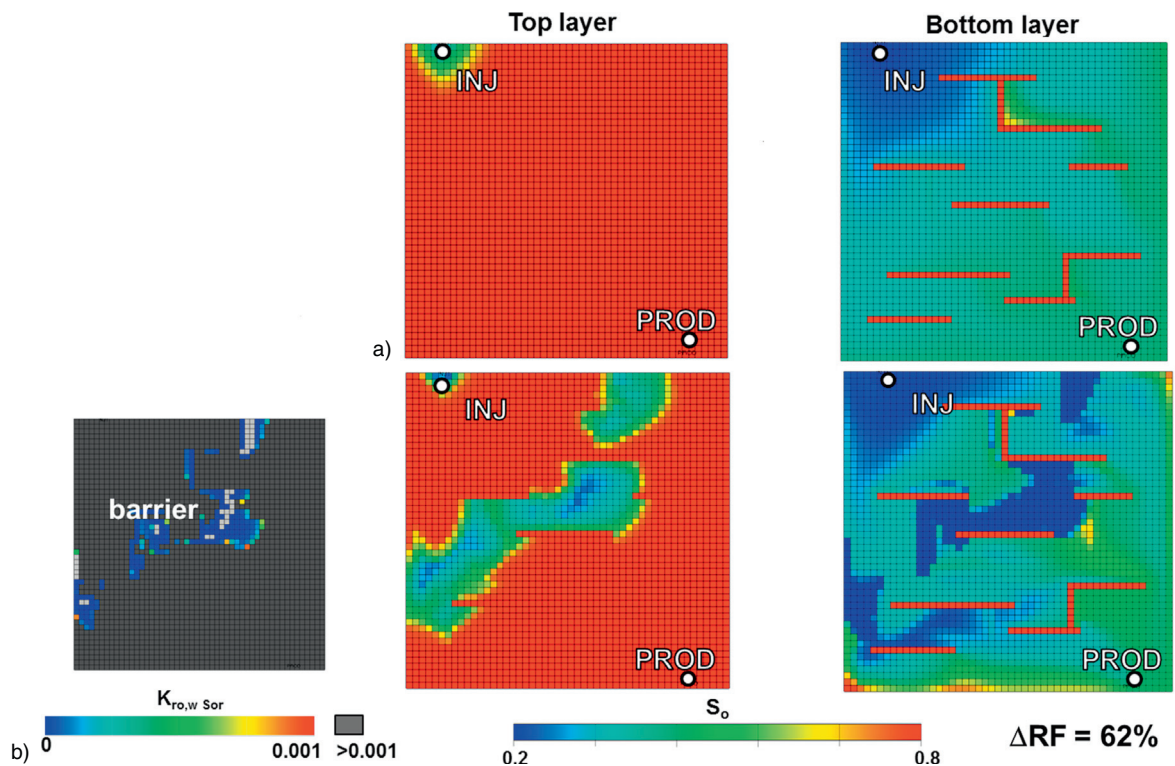


Figure 16

Scenario 6 – Cross-sections with oil saturation distribution after 5 years from the start of intervention: comparison between do nothing case a) and smart fluid injection case b); barrier placement (relative permeability end point at S_{or}).

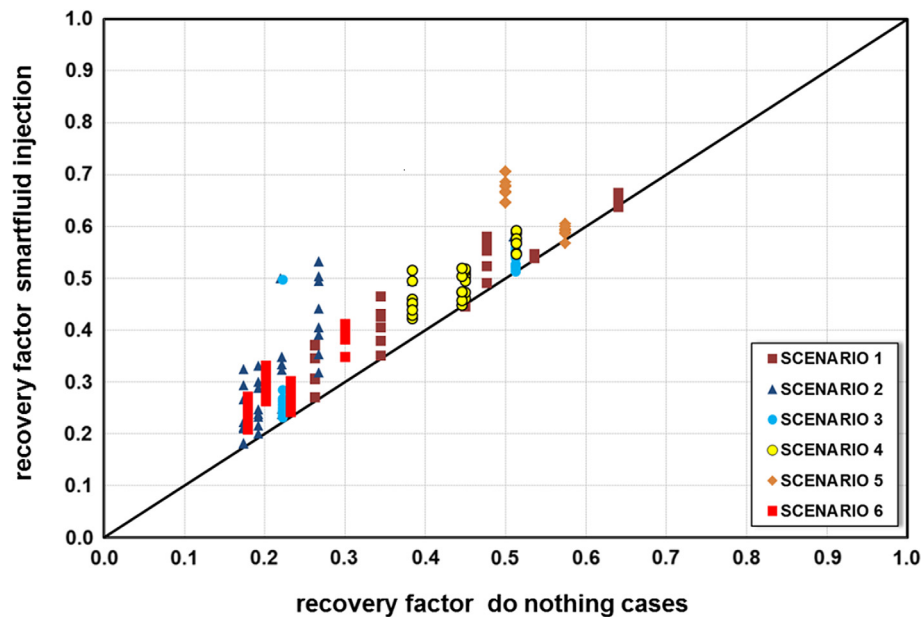


Figure 17

Overall results – Comparison between the recovery factor of smart fluid injection cases and corresponding do nothing scenarios after 5 years from the start of intervention.

CONCLUSION

Core-shell technology, as described and discussed throughout this Proof-of-Concept study, can be highly beneficial to improve the effectiveness of waterflooding interventions when the presence of different permeability zones strongly affects oil displacement. The proposed methodology consists in injecting a water dispersion of nanocapsules after the reservoir has been extensively flushed with water. Specifically, in core-shell particles the “core” is a green, low cost polymeric or siliceous material that activates through gelation, protected by a “shell” that can release its content at a precise time thus location within the reservoir (*i.e.*, tunable release) with subsequent plugging of the high permeability paths. To this end, two mechanisms were considered: shell dissolution and shell swelling. The former could prove particularly convenient for EOR applications. The main advantage of shell dissolution over shell swelling is that both organic and inorganic particles can be used as core types. In shell swelling surface mechanisms cannot occur and therefore inorganic particles are not suitable.

Experimental activities were carried out to select, produce and test, at laboratory level, some core-shell structures with a temporal controlled release in salty water for given reservoir conditions, one of the main being the temperature, set at 80 °C. Additional tests were also carried out at higher temperatures (up to 120 °C) to assess the degradation of the shell

in increasingly severe working conditions. Flow tests through sand packs proved that both the polymeric (specifically homopolysaccharides) and siliceous materials could completely plug the porous media after the cores were released.

The above described preliminary study demonstrated that the release time depends on the complete core-shell system and can be controlled through shell composition, its degradation mechanism and its compatibility with the gelation behavior of the core. Thus, nanocapsules can be designed on the basis of reservoir characteristics suggesting the high versatility of the application of core-shell technology to waterflooding interventions.

Pilot tests and/or field applications are not available at this time. Thus sound reservoir dynamic simulations were the only option to preliminary assess the efficiency of the core-shell technology at the reservoir scale. The results discussed in this paper have shown how a typical waterflooding intervention can be improved by the application of core-shell technology to a wide range of representative reservoir scenarios with petrophysical heterogeneities (layers, channels, barriers). A perk of the presented methodology is that it does not rely on the availability of a dependable dynamic model despite the fact that reservoir simulation can provide reservoir engineers with meaningful insight. In practice this means that for cases in which reservoir simulation is not fully trustworthy, core activation time can be defined by

the results of a tracer test. In addition, nanocapsule concentration is not all that critical provided it remains around 1:10 w/w. The chemicals used in this research are environmentally-friendly, cheap and, in the case of the inorganic core, readily available in nano-size, thus making the technology truly deployable for reservoir engineering applications.

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