Towards In-situ Reservoir Nano-Agents

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ABSTRACT

To test the future reality of having molecular agents in underground oil and gas reservoirs, an experimental research study was initiated to establish transport boundary conditions for nanoparticles in natural porous media; in this case, carbonate reservoir samples from the prolific ARAB-D formation. The study used scaled laboratory core flow tests with inert nanoparticle suspensions as a precursor for the injection of traceable nanoparticles into the reservoir. Overall, the experimental study was designed to generate baseline data for the injection response of nanoparticles in a bi-modal carbonate. It worked to correlate the impact on the rock permeability and the particle transport efficiency in terms of particle size, concentration, and surface chemistry. This paper details visions, procedures, and results from these tests.

Keywords: nanoparticles, nanofluid, pore network, coreflood, upstream E&P.

1 INTRODUCTION

The advent of atom specific sensing and manipulation tools has spurred a widespread interest in nanotechnology with the prospect of re-engineering matter and synthesizing functional systems at the nanoscale. This "thinking outside the box" has spawned applications in biotechnology, medicine, material science, computing, energy, and most recently the upstream sector of oil and gas Exploration and Production (E&P).

The petroleum industry requires strong stable materials suited for use in harsh and corrosive environments. Nanotechnology can provide these and could also provide new tiny metering solutions to address wellbore and reservoir sensing requirements in-situ. Today, complex fluids are being used to enhance oil recovery, limit water production with the oil, and reduce drag and friction forces during drilling. The capabilities become limitless with the possibility of having functionalized molecular agents, or nanomachines, that can illuminate the reservoir and intervene to alter adverse transport conditions.

To the uninformed of the logistics of extraction of hydrocarbon from underground, the oil or gas reservoir may seem to be a giant cavity filled with fluids [1]. As such, oil exploration and production is rendered a matter of locating this cavity and drilling holes through the earth crust and into this embodiment. Unfortunately, the process is not that simple. The reservoir is made of rocks. The hydrocarbons are hosted in the very fine, micron to sub-micron, pores in these rocks. Figure 1 is a plastic cast of a 3-D carbonate pore system. And in order to produce the oil or gas, the pressured fluid has to seep through the pore network and fractures in the rock towards the producing wells. Often times, water is injected underground to aid the flow of hydrocarbon in the porous rock system and help maintain the pressure in the reservoir. The process is known as waterflooding (Figure 2).

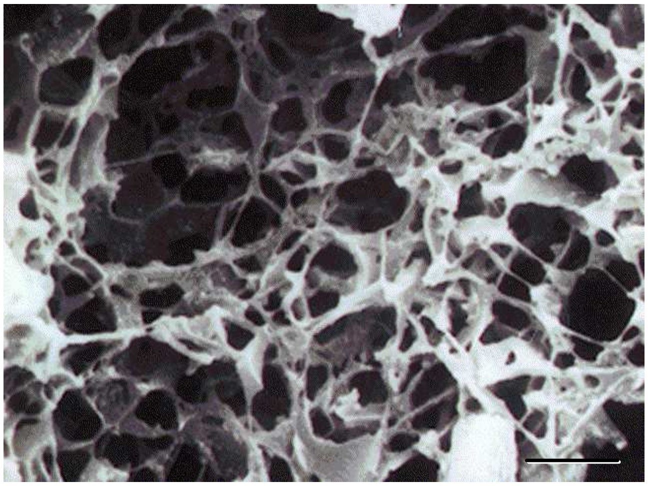

Figure 1: SEM photograph of epoxy pore cast of a carbonate rock. This is created by injecting resin into a rock sample. Once the resin hardens, the rock material is dissolved out to detail the rock pore network system. The scale bar measures 2μm. As such, the majority of the connecting pore throats are sub-micrometer in size. (Adopted with permission from Reference [1].)

It has been stated on munerous occasions the prospect of nano-devices in different areas of upstream E&P from

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[1] After M. Rawlings, "Anatomy of a Patent," *Dimensions*, A Periodical of Saudi Aramco, pp. 25–31, Winter 2007.

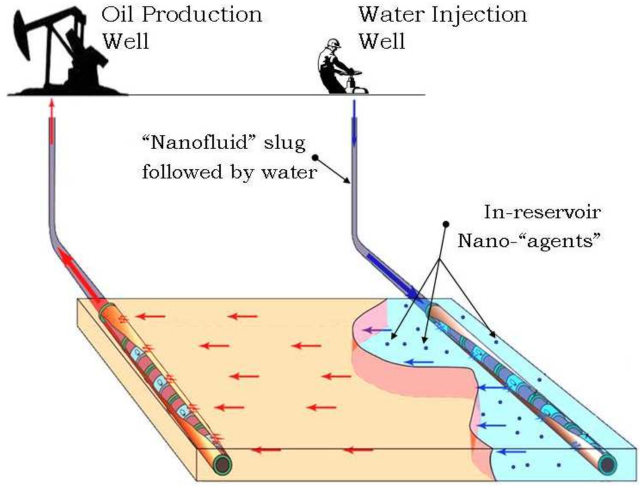

Figure 2: Power water injection is a common practice for pressure maintenance in Saudi Aramco fields. The process provides a plausible mean for displacing nano-agents into the reservoir. Ultimately, it is hoped that these will be interrogated remotely (in near real-time) for their location and the reservoir environment and properties. (The waterflood schematic is reworked from Reference [2].)

mapping the extent of the asset to moving ahead of the drill bit to pre-identify trouble zones. We envision that waterflooding will be used to inject and displace functionalized hydrophilic nano-agents that can be interrogated for their 3D-location and the in-situ reservoir environment and condition (pressure, temperature, saturation, etc.) Means of remote interrogation could include magnetic, RF/EM, or acoustic/seismic. Similarly, the process could postulate a nano-scale chemical delivery system to alter wettability, reduce interfacial tension, and enhance oil recovery deep into the reservoir. Means of activations in the latter case could include chemical, PH, electrical, or thermal.

This paper addresses a critical step on the road to acquiring in-situ reservoir molecular agents. It targets the limiting size of these devices and validate their transport mechanisms in the rock matrix. It details an experimental study on nanofluid coreflood [2] experiments in the carbonate ARAB-D [3].

2 PLAN

The initiative for having in-reservoir agents is part of a larger umbrella initiative for in-situ sensing and intervention (ISSI) at Saudi Aramco. ISSI is concerned with the support and the development of micro-nano-technologies (MNT) for upstream E&P use.

Logically, having in-reservoir nanodevices will require first and foremost determining the maximum usable size of these devices before attempting to develop interrogatable (passive) nanosensors or steerable (active) nanomachines. And this critical step has its own roadmap that involves: (1) making an assessment of the rock's pore throat size distribution with the hope to establish a reference and starting point on what nanoparticle size/size range to use, (2) acquire stable, uniform, and inert nanoparticle suspension with a narrow distribution of particle sizes, and (3) conduct coreflood experiments to validate the particles stability and their transport continuity. The next sections elaborate further on these elements of the roadmap that are ultimately geared towards attempting a field-scale trial of the material.

3 STARTUP PARTICLE SIZE

Earlier, we said that the first step in the roadmap is to make an assessment of the pore throat size distribution in the rock. For this purpose, we analyzed high-pressure mercury injection tests for 735 ARAB-D samples. The results are compiled in Figure 3. The histogram identifies the number of samples in the batch having a given critical pore throat entry size (e.g. close to 12 samples out of the 735 ones analyzed have a critical pore throat entry size in the order of 1,000nm or 1 micron). It is noted that the overall response of the distribution is bimodal with two peaks: one at about 40μm (a *macro*-sized pore network system) and another at about 800nm (a *micro*-sized pore network system). As a preliminary rule-of-thumb, we adopted a 500nm upper limit for these devices because it covers all samples in the *macro*-system as well as the majority (more than 90%) of the samples in the *micro*-system.

The 500nm size is a good starting upper limit of the nano-particles for direct plugging. Obviously, any particle larger than 500nm will have a very slim chance of staying mobile in the *micro* pore network systems of the rock. Smaller particles in large enough quantities or concentrations may also come together to form a bridge across the pore-throat entry and impact the rock permeability. ("Bridging" is a well known phenomena in sanding[4] and sand control.) This sets the usable size of the nanoparticles well below the 500nm limit. Another relevant rule-of-thumb was employed here. This one limits the size of the nanoparticles in solution to

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[2] A coreflood experiment emulates the waterflood process in the field using cylindrical core plugs from the reservoir rock formation. In this, fluid is injected at a constant rate at one end of the core and the change in injection pressure and effluent properties monitored.

[3] ARAB-D is the most profilic oil bearing formation of the Ghawar field in Saudi Arabia. Ghawar is the largest oil field discovered in the world. From its northern extremity the field extends southward some 150 miles as essentially one long continuous anticline, about 25 miles across at its widest point.

[4] Sanding is the transport of formation solids with the reservoir fluids.

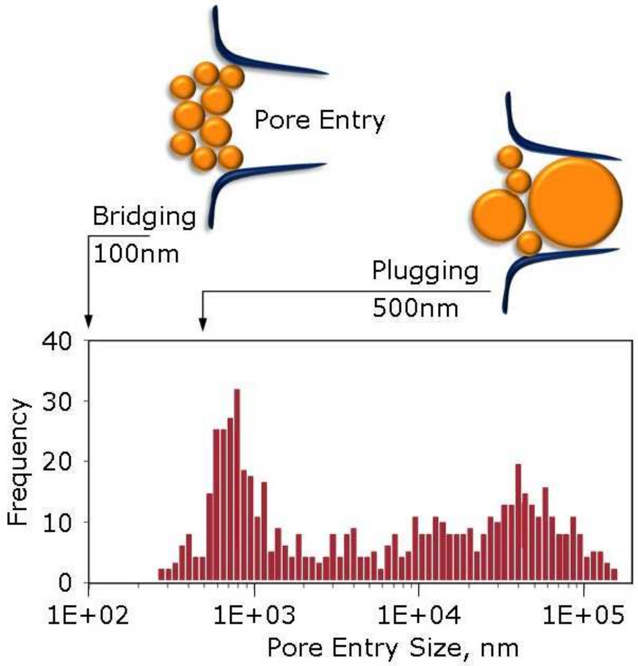

Figure 3: A bimodal response of the pore size distribution in the ARAB-D. This generated some preliminary rules-of-thumb. The nanoparticles size upper limit for direct plugging is set at about 500nm and for bridging at about 100nm.

1/7th-1/5th the critical pore throat size (i.e. 70-100nm range).

4 EXPERIMENTS

Now that we have established a rough basis on usable sizes, the next question is what type of nanoparticles to use? Acquired or functionalized nanoparticles, nanodevices, or nano-agents, should be safe to handle and dispose of. They should be environmentally friendly so that we can inject them with no concern into reservoir formations. The particles should be stable in suspension, should remain dispersed in solution, and should not interact with the carbonate rocks of the ARAB-D. A number of potential nanoparticle solutions were examined. The copolymer suspensions satisfied all of the set conditions. These are polystyrene beads cross-linked with di-vinyl benzene (DVB) solubilized in ultra pure water. The nanoparticle suspensions come in different concentrations and particle sizes and a narrow band of size variation in the solution. The mean size used in testing varied from 20nm to 200nm.

The coreflood system is depicted in Figure 4. Coreflooding starts with a WAN[5] test. If nanoparticles are not detectable in the effluent, a CIN[6] test is performed on the same sample. Now, if nanoparticles were detected in the effluent during the CIN phase, the injection nanofluid is replaced with ultra-pure water. This multi-phase process is needed to establish particles' size and concentration suitability and validate their interaction affinity to the carbonate matrix. The testing plan is presented in Figure 5.

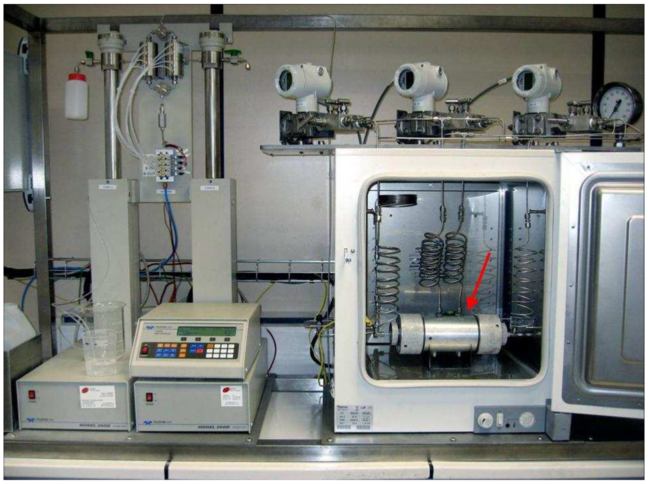

Figure 4: The coreflood testing and acquisition system. The arrow points to the coreflood apparatus holding the core plug. The system emulates the in-situ reservoir conditions in temperature and pressure.

To demonstrate the mobility of the nanoparticles through the rock, it is mandatory to be able to characterize the effluent as well as the influent fluid for particle size and size distribution. This is done using a DLS (Dynamic Light Scattering) device. In addition to the fluid, it is also essential that one characterizes the rock before, during, and following coreflood tests. A micro CT (X-Ray micro tomography) scanner is used to map and monitor the dynamics of the pore network system inside the rock at the micro-scale. Finally, it is essential to map the nanoparticles' morphology inside the sample following each test. This is aimed at assessing the distribution of the particles inside the sample and examining how nanoparticles position themselves or get together to plug pores, if any. For this, the core plug is sliced at different distances from the inlet and slices sent for ESEM (Environmental Scanning Electron Microscopy) analysis. Figure 6 demonstrates the particle morphology inside the sample following a coreflood test. The in-house ESEM has the capability to do EDS/EDX (Energy Dispersive Spectroscopy) for elemental composition of the material to allow differentiating between the polymer nanoparticles and the rock fines in the effluent.

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[5] WAN involves the continuous injection of particle-free water after injecting one pore volume of nanofluid.

[6] CIN stands for continuous injection of nanofluid.

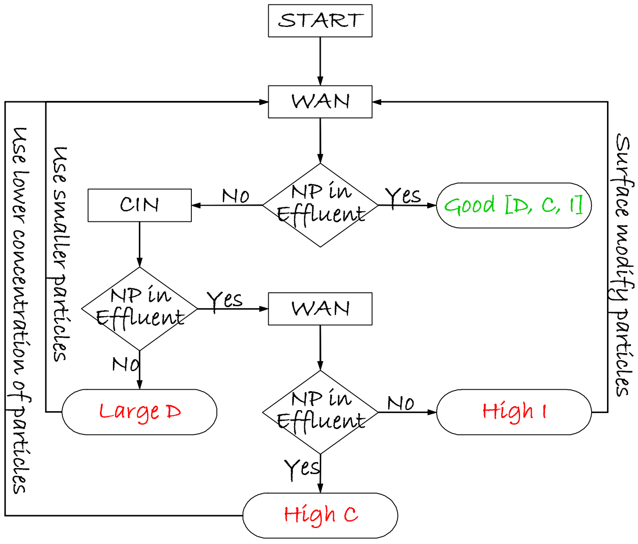

Figure 5: Nanofluid coreflood testing plan. D, C, and I stand for nanoparticle diameter, concentration, and interaction-affinity respectively.

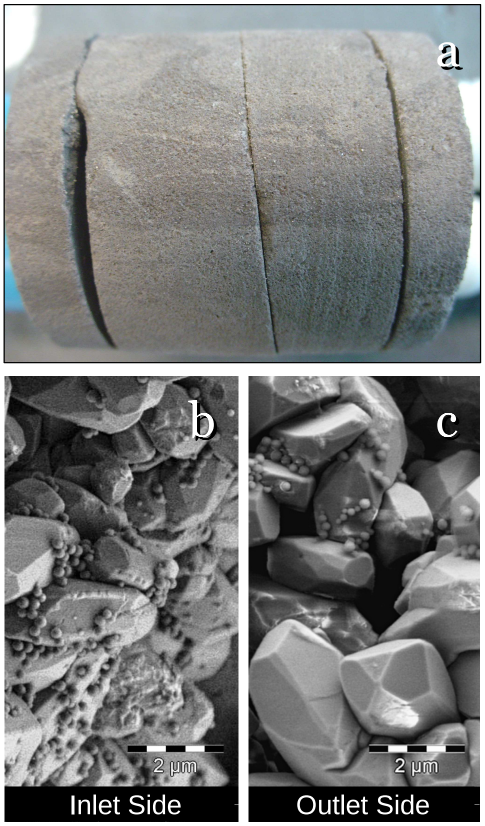

Figure 6: Following coreflood tests, samples are sliced and slices sent for ESEM analysis (a). Nanoparticles morphology is established from images at the inlet (b), the outlet (c), and intermediate locations within the sample. The scale bar in (b) and (c) meaures 2μm.

5 CONCLUSIONS

Reservoir nano-agents are the ultimate dream tools for the upstream E&P. They may help delineate the extent of the assets, map tortuosities in the rock, recognize super-k (super-permeability) pathways, map fractures and faults, identify bypassed oil locations in the field, optimize well placement and design, generate realistic geological models of the asset, and may be used for targeted delivery of chemicals deep into the reservoir to serve enhanced oil recovery (EOR) objectives.

To test the future reality of having nanodevices in the reservoir, we run nanofluid coreflood experiments on carbonate samples from the ARAB-D formation. The aim of these tests is to correlate transport potentials with size and concentration of the nanoparticles in suspension. The early conclusions from these experiments supported the possibility of having the right functionalization, size, and concentration of the particles to maintain the mobility of the nanoparticles in the reservoir. Accordingly, a critical step on the road to having in-situ reservoir nano-agents (sensors or devices) to illuminate the reservoir has been established. Overall, this could be seen as a small step for any one E&P entity but is undoubtedly a giant leap for the E&P industry.

The road to achieving full ISSI targets in the reservoir is long and (most probably) difficult. There need to be serious support/investment, dedication, and most importantly a will to collaborate among members of the E&P industry and between the E&P and the nanotechnology communities in this regard. There are many issues that remain to be addressed: How do we shield these devices in the reservoir medium? How do we communicate with these devices? How do we interrogate these devices? How do we handle the massive data from the extremely large number of these tiny devices? What are the long term HSE impacts? etc.

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