Oil Industry First Field Trial of Inter-Well Reservoir Nanoagent Tracers

Mazen Y. Kanj and Dmitry V. Kosynkin

Saudi Aramco, EXPEC Advanced Research Center, Dhahran, KSA.

ABSTRACT

This short manuscript highlights the industry's first proven reservoir nanoagents' design and demonstrates a successful multi-well field trial using these agents. Our fundamental nanoparticles tracer template, A-Dots or Arab-D Dots, is intentionally geared towards the harsh but prolific Arab-D carbonate reservoir environment of $100^{+\circ}$C temperature, $150,000^+$ppm salinity, and an abundant presence of divalent ions in the connate water. Preliminary analyses confirmed nanoparticles' breakthrough at a producer nearly 500m from the injector at the reservoir level; thus, proving the tracer nanoparticles' mobility and transport capability. This is considered industry-first and a breakthrough achievement complementing earlier accomplishments in regard to the nanoagents' reservoir stability with the first successful single well test and ease of scale up with the synthesis of one metric ton of this material. The importance of this accomplishment is not in how sophisticated is the sensing functionalities of this design but rather in its stability, mobility, scalability, and field application potentials. This renders the concept of having active, reactive, and even communicative, in-situ reservoir nanoagents for underground sensing and intervention a well anticipated near-future reality.

Keywords: Tracers, Nanoagents, Resbots, Waterflood, Reservoir Management

1. INTRODUCTION

Nanotechnology has delivered many ingenious solutions to the problems of hydrocarbon exploration and production that are already finding acceptance as commercial products. Deeper understanding of chemical and physical phenomena at the 1–100 nanometer scale resulted in the development of superhydrophobic and superhydrophilic coatings, soluble metal alloys used in hydraulic fracturing,[1,2] near-wellbore fines control agents[3] and shale-inhibiting water-based drilling fluids.[4] Another promising area of nanotechnology application in the hydrocarbon exploration and production lies in the use of engineered nanoparticles as reservoir traversing agents capable of monitoring or changing reservoir conditions. Several of these applications, such as superparamagnetic nanoparticles for electromagnetic imaging contrast enhancement, oil-sensing nanoparticles, surfactant nanoparticles and nanoparticle tracers are already in the fairly advanced stages of laboratory development.[5–7] Obviously, the feasibility of any nanoparticle-based reservoir agent is contingent upon its ability to survive the harsh conditions found in the hydrocarbon bearing formations until its mission is accomplished. Among the most difficult challenges are high salinity and hardness of connate water, high temperature and the presence of vast chemically active rock surface. Therefore, the design of any potential reservoir nanoagent must take these challenges into consideration even before trying to impart any useful functionality to it. Providing a particle, which is by itself incompatible with reservoir conditions, with a suitable coating has been tried extensively and resulted in markedly improved stability to flocculation and adsorption. However, the improved stability was still insufficient to facilitate particle migration through anything but trivial distances of reservoir rock represented by either a packed column of formation "sand" or core plugs.

The rational approach to reservoir nanoagent design was helped in our case by a fortuitous discovery of small carbogenic nanoparticles (A-Dots). The A-Dots can fit through even finest pores of carbonate rock of the Arab-D formation as their diameter is below 10nm and are brightly fluorescent to allow easy detection and quantification. Whereas their surface chemistry is yet to be fully understood, it makes them remarkably inert

---

Further author information: (Send correspondence to M.Y.K.)
M.Y.K.: E-mail: mazen.kanj@aramco.com, Telephone: +966 13 873-8069
D.V.K.: E-mail: dmitry.kosynkin@aramco.com, Telephone: +966 13 876-1763

in the conditions of Arab-D reservoir (up to 22% TDS, 100°C temperature, and 3,200psi pore pressure). In our previous report,[8] we demonstrated close to 86% recovery of the A-Dots from the reservoir in a huff-and-puff single well test. This paper provides details on a successful test of A-Dots' migration trough industrially meaningful distances of reservoir rock that confirmed their usefulness as a standalone fluorescent reservoir nanoagent.

2. SYNTHESIS AND SCALEUP

To achieve the maximum cost efficiency, the bench-top A-Dot preparation procedure was optimized using the simplex optimization method[9] with chemical reagents ratio, heating time and heating temperature as variables. The reagents were added to a screw-cap glass pressure tubes at room temperature and then the tubes were sealed, placed in a stainless steel protective container to minimize the potential blast damage and heated in an oven. When the heating was completed, the container was immediately removed from the oven and allowed to cool to room temperature before withdrawing the tubes behind a blast shield. The tubes were carefully opened to release the built-up gas, filled with deionized water and placed in a warm water bath to facilitate the dissolution of dark-brown resinous product. The product solutions were diluted with deionized water until their fluorescence became low enough for quantitative measurement with a fluorescent spectrophotometer (λ_{ex}=360nm, λ_{em}=450nm). The optimized synthetic conditions were supplied to a toll manufacturer and a one metric ton (1,000Kg) batch of the A-Dots was prepared and made available for the cross-well test. The nanoagent was prediluted with water to 80% strength by the manufacturer for easier transfer as it assumes a consistency of sugar candy at room temperature.

Prior to its use in the field, a 300Kg amount of the A-Dot concentrate was further diluted in batches with hot (60°C) tap water to about 30% in a recirculating device built from a 500 liters polyethylene water tank, a household electric water heater and a 0.45hp rotary water pump. The resulting dark-brown solution deposited a significant amount of bright-orange crystals* that were allowed to sediment for a week before being removed by decantation.

3. FIELD OPERATION

The field trial was undertaken on a configuration made of 4 pairs of injector-producer wells (Fig. 1). Wells in each pair are distanced nearly at 2,000ft apart at the surface. The wells are also drilled in a matured, well flooded, area to the base of the Arab-D reservoir to 7,500ft. These are all vertical wells that are cased and perforated. Wells I1-I4 are four power water injectors injecting at roughly 8,000BPD of seawater per well. Wells P1-P4 are producing at 8,000BPD per well. Injection and production operation in these wells has been ongoing for more than a year at the time of the A-Dots test. The water cut in these producers exceeds 95%. Previously, the team conducted inter-well chemical tracer tests as part of the monitoring and surveillance program for the same area. The objective of the tests were to determine the flow paths and connectivity between the injector-producer pairs and conformance mapping. At the time we decided to test the A-Dots, the connectivity between I3-P3 had been established using chemical tracers. Accordingly, we decided to inject in I3 and monitor breakthroughs at all 4 opposing producers, P1-P4.

The A-Dots injection field operation is summarized in Fig. 2. A total of 300Kg A-Dots tracer was added to 650 barrels of injection water. The A-Dots concentration in the mix is close to 3,000ppm. In addition to the A-Dots, we decided to add fluorescein sodium salt (NaFl) to the mix as a supporting tracer. Its extensive use has been reported in the literature in geothermal applications with highlighted stability in hyper saline brine conditions in these wells. We manually mixed 100Kg of this material in water before transferring it to the blenders for mixing with the A-Dots. The final concentration of the fluorescein in the injection mix is in the order of 1,000ppm. The tracer mix was filtered to 50μm to remove impurities and avoid damaging the well. The tracers injection was done offline from the seawater injection operation at I3. The injection rate of the tracer mix into I3 averaged at 6.5 barrels per minute (BPM). This is well below the wells capacity of 10BPM. Immediately after finishing injection, the test well was put back online and normal seawater injection resumed into the well.

---

*Solutions of this compound show intense fluorescence at 465 and 530nm. Its structure was established using X-ray crystallography and a detailed study of its chemistry is to be published elsewhere.
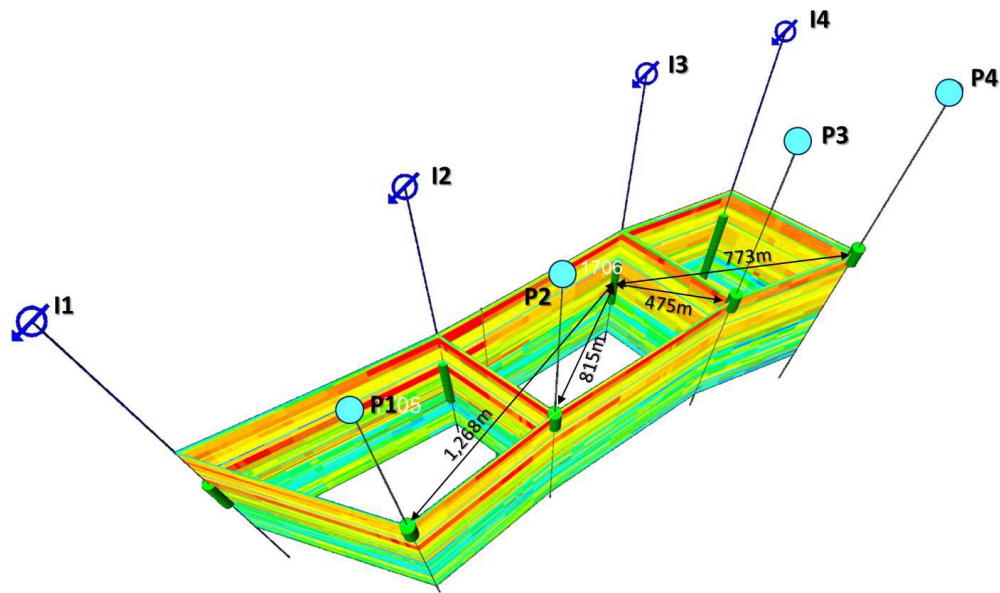
Figure 1. The layout of the wells in the test area. The green cylinder along each well's axis depicts the perforated zone in the casing. The reservoir formation layers are represented in colors in the 2-D vertical planes between wells. A-Dots were injected into the reservoir at I3 and are being monitored at all 4 producers, P1, P2, P3, and P4.
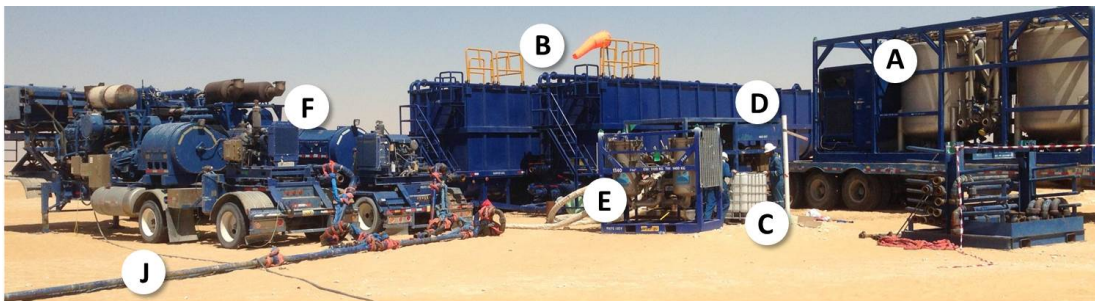

Figure 2. The operational setup of the test in the field. The setup included (A) blenders for high volume mixing, (B) frac tanks for holding injection-ready fluid, (C) a small mixing tank for manual mixing of the conventional chemical tracer, (D) a small pumping unit to transfer fluids between tanks, (E) a filtration unit, (F) high pressure injection pumps, and (J) an injection line connected to the wellhead at the test well, I3.
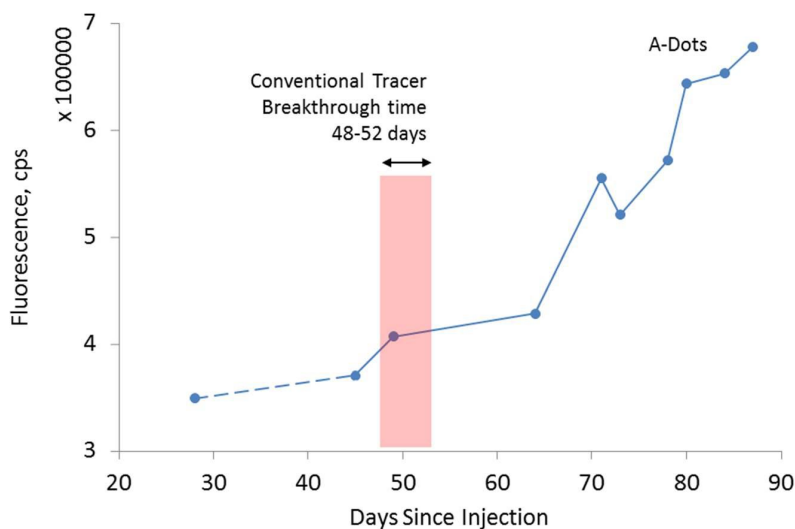
Figure 3. Preliminary analyses on samples collected from P3 up to 90 days into the test.

4. SAMPLING AND ANALYSIS

The four producer wells chosen for the test were monitored twice a week as the field conditions permitted. Samples of produced water (2 liters from each producer well) were collected from a sampling line near the wellhead. The line was flushed to waste ahead of collecting each sample to avoid contamination with fluorescent impurities. Collected samples contained a significant amount of crude oil (2-5%) that had to be removed before doing any spectrophotometric measurements. The water and oil were allowed to separate for 3 days and the water layer was sampled with a glass syringe equipped with a new stainless-steel needle. The aliquot of water (100ml) was then extracted with 10ml dichloromethane and the extraction repeated three times. The dichloromethane treatment removed the residual microdroplets of oil that were brightly fluorescent in the spectral region of interest along with a part of undetermined water-soluble fluorescent impurities. Overall, the dichloromethane treatment reduced the background fluorescence of the samples by a factor of about 3. A control experiment using a solution of A-dots (1ppm in synthetic brine with same ionic composition as produced brine) treated with dichloromethane in the same fashion demonstrated that the loss of A-Dots to this treatment was undetectable. To minimize the effects of inherent instability of the xenon arc discharge used as the light source in our spectrofluorometer and the photomultiplier tube used as the detector, we employed an internal standard of rhodamine B added to all samples at 0.1ppm. Therefore, all collected spectra were normalized to have the emission peak of rhodamine (λ_{em}=575nm) at the same intensity. Normalized spectra of rhodamine-labeled water obtained from each respective producer at the very beginning of the test were used as backgrounds for subtraction.

The A-Dots were detected at levels significantly exceeding the noise in the well, P3, nearly 50 days after the injection (Fig. 3). This preliminary result is inline with previous tests that used conventional chemical tracers. Thereafter, the concentration of the nanoagent increased steadily confirming the observed break-through. To quantify the A-Dots, calibration curves were built using a sample of injection solution obtained from the injection tank and kept at 100°C in a sealed screw-cap tube for the duration of the test to account for possible losses of fluorescence due to reactivity with water.

5. SUMMARY

Future implementation of nanoparticle based technology in the oil and gas industry is contingent upon survival of the nanoparticles in the presence of injection fluids, formation fluids and connate water, reservoir temperature and rock surfaces over periods of time (ranging from months to years) sufficient to reach the targeted areas of the reservoir. Therefore, we demonstrate successful recovery of fluorescent nanoparticles (A-Dots) after traveling through several hundreds of meters of carbonate reservoir rock deep in the underground. The particles were

injected into the Arab-D formation as a dispersion in filtered sea water in a watered-out part of Ghawar reservoir operated under linear drive conditions. Four nearby wells have been monitored weekly for particles' presence by fluorescent spectrophotometry of the produced water and the break-through in at least one of the wells was detected. This is consistent with previous tests in the same area that used conventional chemical tracers. The long-term survival of A-Dots in the actual reservoir conditions opens new horizons for the development of reservoir nanoagents with functionality beyond simple passive tracers through application of similar surface chemistry and structure to their design. The A-Dots themselves could also be developed into an industrial fluorescent tracer owing to their low cost and non-toxic nature.

ACKNOWLEDGMENTS

REFERENCES

[1] Zhang, Z., Xu, Z., and Salinas, B., "High strength nanostructure materials and their oil field applications," in [*Proceedings of SPE International Oilfield Nanotechnology Conference*], **SPE-157092** (2012).

[2] Aviles, I., Marya, M., Hernandez, T. R., Dunne, T., Mardis, M., and Baihly, J., "Application and benefits of degradable technology in open-hole fracturing," in [*Proceedings SPE Annual Technical Conference and Exhibition*], (2013).

[3] Kosynkin, D. V., Ceriotti, G., Wilson, K. C., Lomeda, J. R., Scoresone, J. T., Patel, A. D., Friedheim, J. E., and Tour, J. M., "Graphene oxide as a high-performance fluid-loss-control additive in water-based drilling fluids," *ACS Applied Materials & Interfaces* **4**, 222–227 (2011).

[4] Friedheim, J., Young, S., Stefano, G. D., Lee, J., and Guo, Q., "Nanotechnology for oilfield applications – hype or reality?," in [*Proceedings of SPE International Oilfield Nanotechnology Conference*], **SPE-157032** (2012).

[5] Morrow, L., Potter, D. K., and Barron, A. R., "Detection of magnetic nanoparticles against propane and shale reservoir rocks," *Journal of Experimental Nanoscience* (2014).

[6] Al-Shehri, A. A., Erika, E. S., Servin, J. M. F., Kosynkin, D. V., Kanj, M. Y., and Schmidt, K. K., "Illuminating the reservoir: Magnetic nanomappers," in [*Proceedings of SPE Middle East Oil and Gas Show and Exhibition*], **SPE-164461** (2013).

[7] Chang, Y. C. and Kanj, M. Y., "Controlled release of surfactant for enhanced oil recovery," *U.S. Patent* **8,946,132** (2015).

[8] Kanj, M. Y., Rashid, M. H., and Giannelis, E. P., "Industry first field trial of reservoir nanoagents," in [*Proceedings of SPE Middle East Oil and Gas Show and Conference*], **SPE-142592** (2011).

[9] Morgan, S. L. and Deming, S. N., "Simplex optimization of analytical chemical methods," *Analytical Chemistry* **46**, 1170–1181 (1974).