Chemical & Engineering News

Seeking to boost oil production, petroleum researchers turn to nanotech

Scientists and engineers are testing nanomaterials that can track oil stuck below ground and improve yields from wells

by Mitch Jacoby

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Getting the last drops of laundry detergent out of a bottle can be frustrating. Some people turn the container upside down and shake. Or they just let the contents drip out slowly. Others add water to dilute the liquid so it comes out faster. Consumers don't want to waste any of the product they've paid for.

The petroleum industry faces a similar challenge: how to squeeze the most oil and gas out of underground reservoirs. Scientists and engineers have come up with numerous innovations over the years to suck as much viscous oil as possible up through thousands of meters of packed rock and soil deep underground. But it's a tough task.

"Worldwide, the oil industry recovers—on average—only about one-third of the oil in the ground," says Martin E. Poitzsch, a reservoir engineering group leader with Aramco Services' research center in Boston. At some large Aramco reservoirs, the proportion of oil recovered exceeds 50%, Poitzsch says, but that's an exception to the rule.

Undaunted, oil companies continue searching for ways to boost that percentage. These days, some are tackling the job with the tiniest of tools—nanomaterials. The dimensions of these substances mean that they can slip into cracks and crevices below ground and carry out useful jobs. For example, researchers hope that once below ground, the particles will help locate and track underground reserves, coax more oil from them, and make the whole process more cost effective and environmentally benign.

To locate oil sources, geologists typically use seismic and magnetic methods to generate waves that propagate underground. The waves ping back like sonar, their reflections painting detailed subterranean pictures that distinguish rock formations from regions rich in oil and water.

After boring into oil-rich pockets, some of which hide more than 1,000 meters below ground, operators begin pumping from the wells. Underground heat and pressure help the oil flow up through these so-called production wells to the surface, but only about 10% of the overall cache comes up easily. Getting more requires a lot more effort.

“I had this naive idea that an oil field is an underground lake of oil just waiting to be poked with a straw so it could all come gushing out,” says Nancy A. Burnham, a physicist at Worcester Polytechnic Institute, of her knowledge of the petroleum industry before collaborating with researchers at Aramco.

In reality, thick, gooey oil is often trapped with water and brine in tiny fissures within spongelike rock, Burnham explains. So petroleum companies try to force more oil to the surface by drilling nearby injection wells. Down these wells they push pressurized water or gas, aiming to drive oil from the ground toward a production well, where it can be pumped up and out. That method can boost the yield to roughly 30%.

Extracting more of the oil remaining in that spot is often too difficult and impractical, so historically, oil producers abandoned it and moved elsewhere to drill more wells. But in recent years, dwindling oil reserves coupled with the high cost of searching for oil in new locations and digging new wells are driving companies to try to recover a greater fraction of the oil they know is already down there. That approach avoids the need to build the massive infrastructure required to produce and transport crude oil at a new location, a benefit to the environment.

To get more of the stuff out of the ground efficiently, oil companies are refining the production steps from start to finish. Many of those steps depend on fluids’ ability to navigate nooks and crannies in underground rock, explains Chun Huh, a specialist in nanomaterials and reservoir engineering at the University of Texas, Austin. That’s a task for which tiny particles can be readily customized and applied, he says.

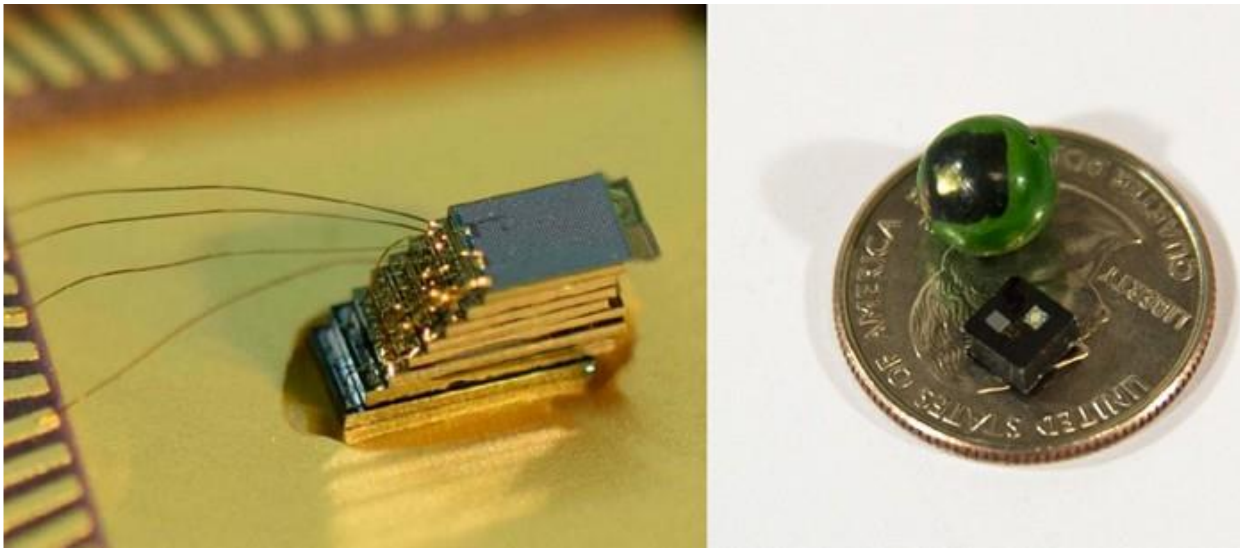
Applications of those materials come in many forms, a number of which spurred lively discussion during the American Chemical Society national meeting in Boston in August.

One role for nanoparticles that attendees examined during a meeting symposium organized by Huh, Poitzsch, and colleagues is as tiny scouts capable of reporting to scientists above ground what paths oil takes below ground from injection well to production well. A single reservoir may have many “injectors” and “producers” separated laterally by hundreds of meters. The intervening space consists of nonuniform rock, which can leave company engineers in the dark about the complex connectivity between the inputs and outputs.

“If you know that information, you can use it to optimize the injection scheme,” Poitzsch says, “and for almost no additional cost you may be able to recover a few percent more oil.”

Well operators can learn some details about what’s down there by lowering miniature instruments into a well via a tether. But the procedure is expensive, and the region they scope out extends horizontally only a few centimeters from the well. Another option involves injecting commercial chemical tracers, such as fluorobenzoic acids, and watching for them to appear at production wells.

But only a few distinct chemical tracers are available—too few to map the connectivity of large reservoirs, according to Aramco senior research scientist Wei Wang. He adds that some of those compounds cannot survive the high temperature, pressure, and salinity typical of many reservoirs. Furthermore, detecting chemical tracers requires extensive sample workup and advanced off-site analysis.



Measuring just 3 mm across (left), this device contains batteries, sensors, and other components needed to autonomously collect, store, and report temperature and pressure measurements. Encased in a polymer coating (right, black) and then in an outer coating to control buoyancy (right, green), this data logger is designed to travel safely through an underground oil reservoir.

In one of the first field studies aimed at determining whether nanomaterials could address some of those shortcomings, Aramco scientists injected hundreds of kilograms of inexpensive, fluorescent carbon nanodots down wells. The idea was that when the particles emerged later in oil pumped from production wells, researchers could detect them easily with portable fluorometers.

The multiyear study, begun in 2014, showed that the nanodots are indeed robust enough to survive a nearly 500-meter underground trip between wells. It also showed that the particles and the water in which they were injected take about 10 months to make the trip, information that can be used to improve the accuracy of simulations depicting fluid transport in the reservoir.

Since that proof-of-concept field test, Aramco scientists have been testing other types of nanoparticles with the aim of optimizing detection sensitivity. For instance, they recently reported simple procedures for preparing large families of nanoparticles that can serve as unique reservoir tracer bar codes. With a large number of distinguishable and easily detected bar codes on hand, engineers can map the connectivity between multiple injectors and producers.

In one case, they showed that polymer nanoparticles made from commercial styrenic and methacrylic monomers can be detected easily with a portable gas chromatography/mass spectrometry pyrolysis system. The heat from this instrument strips away contaminants from particles recovered from underground and unzips the polymers that make up the particles, generating large numbers of differing monomers that can be detected with high sensitivity (*ACS Appl. Mater. Interfaces* 2017, DOI: 10.1021/acsami.6b16050).

In another study, the team developed one-pot methods for embedding commercially available dye molecules in nanoparticles composed of a silver core and silica shell. The researchers showed they could detect the particles at the part-per-billion level and easily distinguish them by measuring their unique Raman and fluorescence signals.

Then to gauge how the particles might perform in future field tests, the researchers flowed tiny quantities of them through the narrow channels of microfluidic test chips. The tests indicated that the particles' intense optical signals made the nanomaterials easy to detect when confined in the microscopic channels, suggesting they may also be spotted in particulate matter recovered from wells even if they're hiding in tiny rock pores and fissures. The researchers also found that the particles stand up to seawater, which is commonly used for injection, and they generate strong Raman signals even after one year (*J. Phys. Chem. C* 2017, DOI: 10.1021/acs.jpcc.7b00688).

But what happens if the nanoparticle tracers, and consequently the oil they're tracking, get stuck in rock fissures and pores? Aramco's Shannon L. Eichmann teamed up with Worcester Polytechnic Institute's Burnham to measure the adsorption forces between particles and rock to explore ways to overcome those forces.

The team used the tip of an atomic force microscope as a stand-in for nanoparticles. The researchers capped the tip with hydroxyl and carboxyl groups, which are common nanoparticle ligands. Then they measured adhesion forces between the atomic force microscope tips and a calcite crystal, which is a surrogate for limestone, common in Middle East oil reservoirs. Running the experiments under saline solutions to represent salt water injected into underground wells, they found that elevated levels of Ca^{2+} ions reduce adhesion forces, which points to a simple, inexpensive way to increase nanoparticles' chances of completing an underground trek between wells (*Sci. Rep.* 2017, DOI: 10.1038/s41598-017-11816-7).

Particles recovered after crawling long distances through tiny rock formations provide valuable information. But they could provide even more info if, along the way, they collected pressure, temperature, and other data that could help identify oil-rich spots. Researchers working with the Advanced Energy Consortium (AEC) are testing prototypes designed to do just that type of underground sleuthing.

AEC was founded by the Bureau of Economic Geology at UT Austin to advance nanotechnology for oil and gas exploration and production. Its members include major energy companies, research institutions, and national laboratories.

According to Project Manager David T. Chapman, AEC has fabricated miniature electronic data recorders that have overall dimensions on the millimeter scale but feature nanoscale materials and circuitry. For example, one device, which measures just 3 mm along one side and can store thousands of readings, contains a solar cell, batteries, temperature and pressure sensors, a data processor, and other components. The pressure sensor has nanoscale diaphragms, and the battery features a nanostructured silicon anode, which enables it to hold charge at reservoir temperatures (130 °C) that cause most batteries to quickly fail.

To ensure survival of the tiny data loggers in harsh oil-field conditions, AEC team members have double encapsulated them in a hermetic sealing polymer and a jelly-bean-like outer casing that adjusts the devices' buoyancy to keep them moving below ground. The devices worked reliably when lowered via a tether and left at the bottom of a well for 14-hour stints, Chapman says. AEC members are now gearing up to conduct large-scale, tether-free tests.

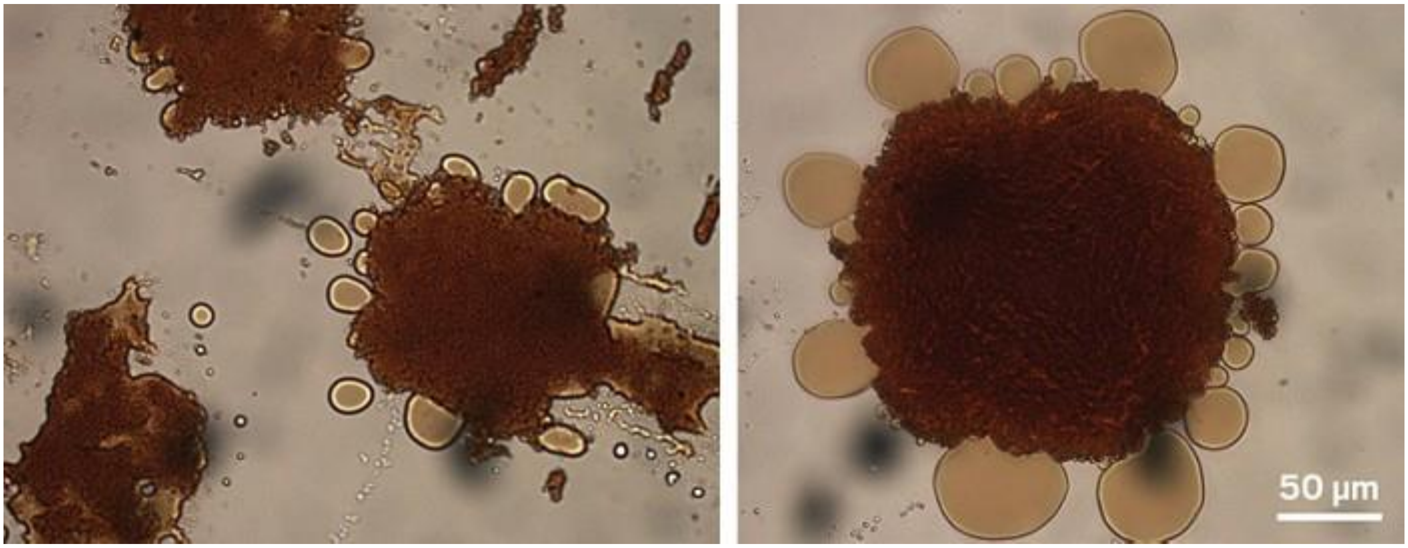
Industry scientists aren't looking to nanomaterials just to track oil reserves below ground. They also hope the materials will boost production efficiency.

One of the strategies that oil companies currently use to coax more thick oil out of the ground involves surfactants. The idea is that injecting these slippery materials into a well can help lower the interfacial tension between oil and water and improve the wettability of porous rocks. Those changes can increase petroleum's underground mobility, enabling injected water to better sweep the oil toward a production well. The process often works as intended, but things don't always go just the way engineers plan.

The key problem, according to Valery Khabashesku of Baker Hughes, an oil-field service company, is that sometimes surfactants adsorb and stick to the surfaces of porous rocks. That lowers the potential benefit and wastes the costly surfactant. Even worse, surfactants can plug rock pores and alter the wettability undesirably, reducing oil output instead of increasing it.

So Khabashesku and Baker Hughes scientists studied the ability of nanoparticles to mitigate the surfactant sticking problem in lab tests that simulate reservoir conditions. They used high pressure to form tightly compressed sand-pack columns with tiny pores and heated the columns to reservoir temperatures. Then they measured the flow of commercial surfactants through the columns using artificial seawater as the injection fluid. They found that pretreating the columns with negatively charged silica nanoparticles reduced surfactant adsorption by a factor of three. That simple step could let surfactants do their job of enhancing oil production.

Nanoparticles might also help improve the oil-recovery process above ground and do so in an environmentally beneficial way. As oil flows from production wells, a large volume of water comes with it, some of it the pressurized solution that was pumped into injection wells. The water typically contains micrometer-sized oil droplets that are tough to separate completely using gas flotation, membranes, and other conventional methods. So UT Austin's Huh and Saebom Ko, now a postdoc at Rice University, developed a simple and potentially low-cost procedure for separating the oil from water magnetically.



Credit: *J. Nanopart. Res.* 2017, DOI: 10.1007/s11051-017-3826-6
Driven by electrostatic forces, magnetic iron oxide nanoparticles (light brown) quickly collect and coalesce on the surfaces of oil droplets (dark brown) in an oil-water emulsion. Accumulation of the particles (after five minutes, left; 60 minutes, right) makes it simple to separate oil from water magnetically.

The team synthesized amine-functionalized magnetite (Fe_3O_4) nanoparticles and used them to treat oil-water emulsions. The researchers found that electrostatic attraction between negatively charged oil droplets and positively charged magnetic nanoparticles causes the particles to coalesce on droplet surfaces. The process can occur within minutes. And because of the aggregation of many magnetic nanoparticles on the droplet surfaces, the droplets are strongly attracted to a permanent magnet and easily separate from solution. Preliminary tests show the nanoparticles can later be separated from the oil by various methods—for example, by raising the pH—and reused.

“Magnetic nanoparticle applications could help reduce hazardous waste,” Ko says. She proposes that the technology, which could be implemented in a compact separation system, might be especially useful for offshore oil and gas production, where space is limited.

The petroleum industry has been supplying the world with staggering amounts of fuel for decades. Consumption sits at 100 million barrels per day currently and will likely remain high for years to come, even though renewable energy is becoming popular. That creates strong incentive for the industry to increase efficiency and become more cost effective.

Laboratory tests and some field trials indicate that nanomaterials can help meet those goals, but they have not yet been implemented on a large scale. Time will tell whether the tiny tools will make an impact on the giant industry.

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