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Nanotech Sensors To Reveal Reservoir

By Colter Cookson

Nanotechnology may be small, but its potential impact on ultimate oil recoveries and well economics is huge.

The vast sea of possible applications has only begun to be explored. The oil and gas industry has attracted a growing group of scientists and engineers who are looking for ways to turn nanoscale engineering into revolutionary products for exploration, drilling and production. In many cases, they are adapting ideas that have been proven already in the medical and military sectors to the harsh and everchanging conditions faced down hole.

Nowhere is the interest in applying nanotechnology to oil and gas more apparent than at the Advanced Energy Consortium. Although it is managed by the University of Texas at Austin's Bureau of Economic Geology, the group brings together academics from 30 universities across the globe, as well as engineers and geoscientists from eight of the world's largest oil and gas companies. These multidisciplinary researchers have numerous goals, but much of their work focuses on

	AEC's Research Thrusts
Thrust	Idea
Mobility	Get nanoparticles to move through the reservoir.
Contrast Agents	Use nanoparticles to "light" the front edge of waterfloods, as well as completions and the extent of hydraulic fracture networks.
Nanomaterial Sensors	Create tiny nanosensors that change in response to environmental conditions.
Microfabricated Sensors	Develop small electronic sensors that function down hole.

using nanotechnology to gather information so operators can make better decisions.

"Right now, the oil and gas industry can measure temperatures and pressures at the wellbore," says AEC Director Scott Tinker. "We are trying to extend the industry's reach and view by sending nanoscale eyes, ears and hands down hole. One day, we would like to be able to take direct measurements a kilometer from the wellbore."

To turn that dream into a reality, Tinker says AEC is pioneering three methods. The first involves sending ultrasmall electronic sensors down hole and recovering them to retrieve the data. The second augments the electronic sensors with chemical equivalents that are small enough to go even farther into the formation. The third relies on contrast agents that "light up" industry-standard logs and seismic images, allowing producers to track where fluids go during completions and waterfloods.

To ensure these sensors and contrast agents penetrate the reservoir, Tinker says AEC has dedicated considerable effort to understanding how nanoparticles behave

TABLE 2

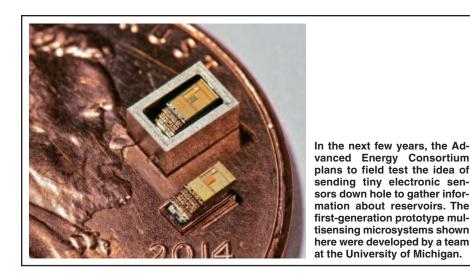
TABLE 1

AEC's Nanotechnology Applications and Goals		
Application	Goals	
Hydraulic Fracturing	Determine fracture location, direction, height and length. Investigate timing of frac flow, fracture closure and fluid cleanup.	
Waterflood and Interwell Reservoir Characterization	Image fluid flow in real time. Identify high-permeability zones, fractures and compartments. Determine rock properties such as permeability, porosity and wettability; as well as rock layers and depositional environment effects.	
Wellbore Measurements and Extended Well Logging	Develop micro- and nanosensors that can gather resistivity, sonic, and other well log data as far as 3-10 meters from the borehole.	
Enhanced Oil Recovery	Apply nanotechnology to enhance EOR chemicals such as surfactants, polymers, foaming agents, diverting gels and alkaline agents.	

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in complex rock and fluid systems, as noted in its research thrust summary (Table 1). Eventually, the sensors and agents could have numerous applications (Table 2).

Other nanotechnology pioneers include Oceanit, a research and development company with a cement that can detect and communicate well integrity issues, and the Tertiary Oil Recovery Project at the University of Kansas, which is using nanoparticles to remove scale-causing substances from produced water.

Electronic Sensors

According to David Chapman, who oversees AEC's semiconductor-based projects, the electronic sensors should be able to gather pressure, temperature and conductivity data, which can be used to infer oil saturations and water cuts.

"We had the idea of getting these data from the sensors while they were in the reservoir, but because it is unlikely we will be able to communicate that far, we instead are putting memory on the sensors, injecting them into the well, recovering them, and retrieving the data wirelessly," Chapman says.

Although AEC has made tremendous progress since its formation in 2008, it is years away from developing electronic sensors that can penetrate deep into the reservoir, Chapman acknowledges. "With the millimeter-scale devices we have now, we think we can get a sensor into a perforation or a fracture, but not through the pores in the rock," he says. "However, we are moving toward micron-scale devices, which would let us enter natural or induced fractures, and recover information during fracturing operations."

Making the sensors that small will require advanced batteries, Chapman notes. "At high temperatures, traditional batteries self-discharge rapidly," he explains. "We have spent several years working on hightemperature batteries that can hold a charge for a longer period and have the higher energy density needed to provide a useful amount of power at a very small size."

In conjunction with efforts to reduce sensor energy consumption, the battery research has paid off, Chapman assures. "We started with commercial batteries, which could power a sensor at high temperatures for only two to four hours. Today, we are miniaturizing an internally developed battery that is stable at 200 degrees Celsius and has a much greater power density. We do not know how long the battery will last, but we now can talk about weeks or months of device life."

AEC also has greatly extended the range of the wireless antennas used to transmit the sensors' data once the nanodevices are recovered. "At first, in highly concentrated brine, we could communicate only as far as the antenna's size, so if we had a millimeter-sized antenna, we could send the data only one millimeter," Chapman recalls. "We have seen improvements in that. Our goal is to be able to read the data as the sensors flow by in a reasonably-sized pipe. We are not there yet, but we think it is possible."

Powerless Sensors

For applications that will require the sensors to hold data beyond even the best battery's life, AEC is evaluating powerless sensors. "These would be comparable to radio frequency identification (RFID) tags used for inventory control." Chapman says. "Each tag has an antenna that receives RF signals and a capacitor. When you buy an item, the cashier exposes the tag to a high strength magnetic field, which destroys the capacitor, creating an irreversible but detectible change in how the tag responds when 'read' in an RF field.

"In a store, that change says the item has been purchased," Chapman continues. "In the oil and gas field, we think we can create devices that are changed permanently when exposed to oil. These devices would give only one measurement, not the time-stamped measurement table the electronic sensors provide, but we would not need to worry about battery life."

Nanoparticles that react to downhole conditions offer an alternative way to get measurements, notes Mohsen Ahmadian, the project director responsible for AEC's chemical sensor and contrast agent portfolios. "The idea is to design nanoparticles that can identify where oil is and how much remains in place, or look at regional temperature and pressure profiles," he says.

Similar to RFID tag-like devices, these nanoparticle reporters would change in response to environmental conditions. By putting them in capsules that gradually wear away, Ahmadian says it may be possible to gather information about specific areas in the reservoir.

"Like the ones pharmacologists use when they design drug delivery systems, the capsules would degrade as they travel through reservoir," he says. "So if we are interested in determining the extent of oil in place 10 meters from the wellbore, we would design a capsule that would have the possibility of exposing the reporter at that distance."

Chapman predicts that many applications will call for a combination of electronic sensors and chemical reporters. "Each part of the reservoir has different volume permissions," he explains. "In the wellbore or the perforations, I can easily send down a sensor that is a millimeter cubed. To get out into the fracture, I might need half a millimeter or onetenth of a millimeter, which is reasonable. But penetrating the rock itself would require micro- or nanometer devices, and building an integrated electronic device that small is still firmly in the realm of research."

That is where the nanoparticle reporters would come in. "The reporter might only be able to tell you it touched oil and maybe when it touched oil, but it can reach areas an electronic sensor cannot," Chapman says.

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Contrast Agents

To provide data in situations where recovering sensors and reporters would be impractical, or where real-time information is critical, AEC is developing contrast agents that would light up on well logs and seismic data. "This idea came from medical magnetic resonance imaging, which typically relies on nanoparticles that are injected into veins to differentiate between solid mass such as bones and soft mass such as tissue," Ahmadian relates.

In the oil field, the contrast agents could be mixed with the water used for enhanced oil recovery. "We might apply a slug of contrast agents at the front of the flood to make the front have a significantly higher electromagnetic signal than the rest of the flood. Then we would use geophysical tools to capture an electromagnetic image and see where the flood is going," Ahmadian details.

According to Ahmadian, this approach will offer greater fidelity than existing methods for tracking water. "We think we also can improve the depth of investigation," he adds.

A similar concept could be applied to hydraulic fracturing for 3-D images of fracture geometry. "Seismic and microseismic imaging are great at identifying where rock is cracking, but they do not necessarily delineate where the fluids or proppants are going," Ahmadian suggests. "By including electromagnetic contrast agents in the water, we are hoping to improve the resolution of the fracture extent in the x, y, and z dimensions."

Problems

For the contrast agents and reporters to work, Ahmadian says researchers must ensure that nanoparticles can survive in and move through varying reservoirs. "Most applications would require coatings to stabilize the nanoparticles and keep them from getting stuck," he says, noting that the coatings will vary based on the geology.

"We also may want the coating to direct the particles to the region we want to image. For example, if we are trying to determine where the oil is, we want the sensor to go toward oil," he relates. "That is one of the bigger challenges we are dealing with, so we have a large portfolio of research dedicated both to computational and experimental approaches to identifying appropriate coatings."

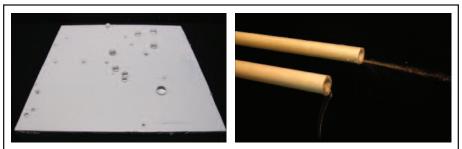
Because getting images deep in the reservoir will take large quantities of nanoparticles, the nanoparticles and coatings must be affordable, Ahmadian adds. He says researchers are looking at ways to manufacture the particles at a reasonable cost.

While field tests for the electronic sensors, nanoparticle reporters, and contrast agents are still two or three years away, AEC Associate Director Jay Kipper expresses pride in how far the research has come. "We started doing fundamental research, and now we are moving into the application phase to integrate our learnings into tools that are going to help our members' bottom lines and increase oil and gas recovery," he says.

To get to that point, Kipper estimates AEC has funded more than 400 researchers, including many who had never before worked on oil and gas problems. "We have opened a lot of eyes to the high-technology effort that the industry uses, as well as its commitment to being environmentally responsible. I am hoping these smart young people will stay in the industry and be able to come up with even better and cleaner ways to produce oil and gas."

Self-Sensing Cement

AEC is far from the only group that is developing nanotechnology for explo-



By applying nanoengineering to the surface, Oceanit can embed a coating in metal to repel water (left). In pipeline applications, this would reduce drag, increasing the pipeline's efficiency, as shown in the comparison of flow from a coated and uncoated pipe (right).

ration, drilling and production applications. The others include not only university organizations, but also companies such as Oceanit, a 29-year-old engineering and product development firm that is creating cement capable of warning operators about wellbore integrity issues.

"We have developed a nanomaterialbased admixture that is added to traditional cement before it is mixed," says Vinod Veedu, the company's director of strategic initiatives. "Once mixing starts, the admixture is distributed uniformly throughout the cement, allowing us to electrically, acoustically, or magnetically interrogate the cement to detect internal or external pressures and identify damage."

The self-sensing cement technology was developed through Oceanit's innovation fund for disruptive technology a few years ago. Since then, it has been tested thoroughly and now is moving toward the field in a range of applications. For example, it has been used to create concrete perimeters for the U.S. Department of Defense, Veedu reports.

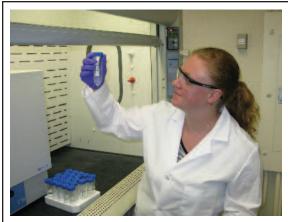
"When someone steps on these perimeters, the cement will send a clear signal that enables cameras and other systems to track that person's movement," he says. "The cement is sensitive enough to detect anyone who weighs more than 100 pounds, so we do not think the much higher pressures encountered in oil and gas will pose a challenge."

The admixture that enables the cement to sense pressure also strengthens it, Veedu adds. "Our goal was to keep the properties of typical cement, but when we tested the mixture's compressive strength, fracture strength, thermal conductivity, and other properties, we found a 30-40 percent improvement in performance," he says.

To adapt the admixture to the oil and gas industry, Oceanit has partnered with the U.S. Department of Energy and four major oil and gas companies. "That program is only nine months along, but we are making significant progress," Veedu reports. "We have demonstrated at the laboratory scale that the cement is qualified for the application and is capable of measuring the parameters of interest to oil and gas companies.

"Cement is price sensitive, so we want to make sure we can provide the material without increasing the cost by more than 10-15 percent," Veedu says.

He adds that the company is trying to develop cement that can be interrogated by tools already being deployed in the



industry.

Fluid-Repelling Coating

Oceanit also is adapting to oil and gas applications a coating developed to protect U.S. Navy hulls from corrosion, Veedu relates. By repelling water, he says the coating will enable producers to protect tubulars, offshore platforms and pipelines from corrosion, increase pump and pipeline efficiency, and prevent hydrates from forming.

To show how well the coating repels water, Veedu compares it to Teflon[®], an extremely water-repelling surface. "Teflon has a contact angle for wettability around 120 degrees. We have a much higher repelling capability with a contact angle around 175 degrees," he says.

"This technology is not a coating in the traditional sense," Veedu emphasizes. "A traditional coating is applied to the outside of the surface, like a bandage. Instead, we have a two-step process that embeds the coating within the outermost layer of the material."

This approach has many benefits, Veedu says. "We can apply the coating to flat surfaces or curves without any challenge, and it will be more uniform. It also is easy to scale, and it offers durability in high temperatures and pressures. In fact, in lab tests, the material has performed perfectly in temperatures between -40 and 300 degrees Celsius," he reports.

The coating also has demonstrated exceptional resistance to corrosion, Veedu says. "How long it resists corrosion will vary based on the environment, but we typically see at least a 20 percent improvement, compared with other materials," he details.

In many applications, Veedu predicts the coating will reduce drag 15-30 percent, which should increase pump efficiency. He points out that the company is developing variants that can repel water as well as oil, which should make this benefit available in a wider range of applications. "We also are looking at ways to prevent biofouling on ships and offshore platforms Karla Leslie is part of a team of researchers at the University of Kansas' Tertiary Oil Recovery Program that is developing nanoparticles designed to encapsulate scale-causing water contaminants. These particles could provide a more affordable way to prepare extremely salty produced water for reuse.

to simplify maintenance," he adds.

Enhanced Oil Recovery

Nanotechnology also could boost the effectiveness of enhanced oil recovery, says Karen Peltier, the director of labs with the Tertiary Oil Recovery Program at the University of Kansas. "We are looking to encapsulate oil field chemicals in a polymer system to protect them from the harsh environment found in the well. The goal is to make sure the chemicals make it into the formation before reacting," she details.

By tuning the capsules for specific applications, Peltier says operators will be able to control when the chemical activates. "There are some data that suggest we will be able to dial any delay we want," she comments.

Encapsulation techniques also could be used to treat water, Peltier suggests. "We are looking at using the complexes to trap contaminants such as barium and strontium that cause scale, as well as the radium that forms with the scale and makes it radioactive," she details. "These complexes would settle out of the water, allowing it to be reused."

Because this treatment process could work in a high-salt environment, Peltier predicts it will be less expensive than the traditional approaches to removing scalecausing cations, which usually require the operator to reduce the water's salt load. "There is some discussion that we will be able to recycle the nanoparticle complexes after they have settled out of the batch, which would reduce the cost," she says.

According to Peltier, the project is motivated in part by a desire to prepare for potential regulations. "Right now, radium is not a huge issue for many producers," she says. "However, because of public concerns, it is possible the U.S. Environmental Protection Agency or local agencies could pass regulations that will make radium a larger issue. We are trying to get a step ahead and find a solution in case that happens."

While TORP focuses on enhanced oil

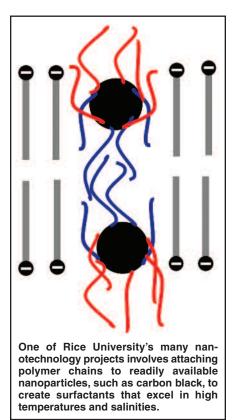
recovery, Peltier indicates the technology will be applicable to any situation where there is produced water, including completions. By making it easier for operators to recycle water, she says TORP hopes to reduce the industry's impact on local communities.

Nanoparticle Surfactants

Rafael Verduzco and many of his colleagues at Rice University, an AEC research collaborator, are trying to create nanoparticles that can act as a tougher alternative to surfactants. "Surfactants have a polar head that likes to mix with water and a nonpolar tail that will mix with oil," he notes. "We are attaching hydrophilic and hydrophobic molecules to nanoparticles' surfaces to create what are essentially nanoparticle surfactants.

"Why would we do that?" he poses. "There are nanoparticles that can be produced at a lower cost than surfactants, such as carbon black. Our goal is to modify these particles to easily disperse in water and mobilize the oil."

In addition to having a lower upfront cost, the nanoparticles might be recoverable and reusable in many applications, Verduzco reports. "Nanoparticles have the potential to survive in high-temperature environments, where many organic materials tend to degrade," he states. "Even if the nanoparticles are organic, they are much more robust because they have a core, which keeps them together, even if part of their polymer coating degrades."





Verduzco says the lab hopes to develop materials that can survive in temperatures as high as 90 degrees Celsius and salinities to 150,000 parts per million.

For these tough surfactants to become a reality, Verduzco says researchers must determine how to design nanoparticles with the most appropriate interfacial characteristics, interactions with other parts in solution, and reservoir mobility. "We have made a lot of progress addressing some of these fundamental questions," he reports.

Verduzco adds that Rice University also is developing viscosity enhancers. "Alkaline surfactant polymers are great at enhancing viscosity in low-temperature reservoirs, but at high temperatures, the polymer that is most widely used starts degrading, aggregating and precipitating out, which can clog the reservoir," he explains. "In addition to designing new polymers that will be more stable at high temperatures and high salinities, we are exploring using polymer-coated nanoparticles. That research in its early stages, but the idea has promise."