July 6, 2015

"Superparamagnetic Nanoparticle Utilization" Patents *from* UT-Austin

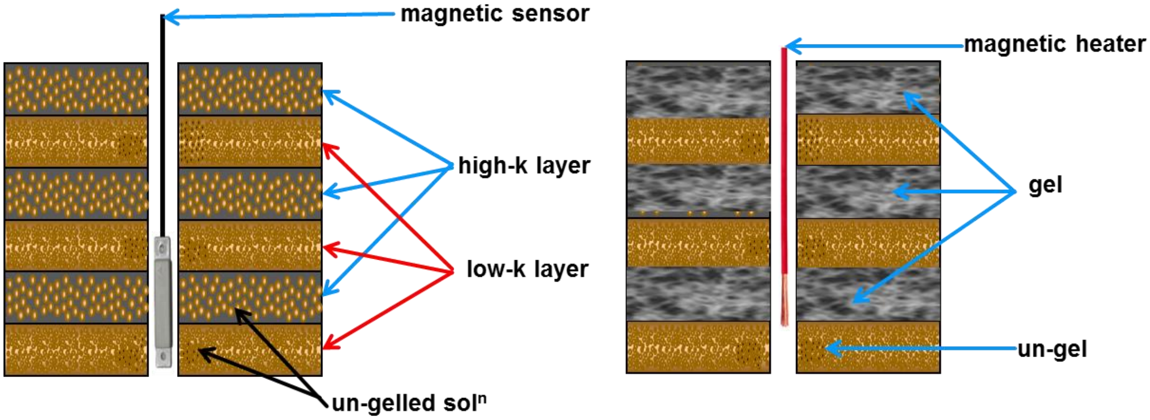
The superparamagnetic nanoparticles (SPMNPs) are widely employed in medical, pharmaceutical and other disciplines because they can be detected remotely with external magnetic excitation and sensing; can be moved in a desired direction and collected under a magnetic field gradient; and can generate intense, highly localized heat with application of magnetic oscillation at certain frequency range. In addition, by applying a specific surface coating to the particles, they can be delivered to target locations to carry out the above and additional functionalities. Such capabilities can be gainfully utilized for various oil and gas production and other applications. The "Nanoparticles for Subsurface Engineering" research team at University of Texas-Austin's Petroleum & Geosystems Engineering has been actively developing a variety of applications that employ SPMNPs, and recent patent applications from the team are briefly described below.

1. "Methods and Compositions for Conformance Control Using Temperature-Triggered Polymer Gel with Magnetic Particles"

Huh, C., Panthi, K. K., Mohanty, K. K., and Bryant, S. L.

When water or an improved oil recovery fluid is injected into a heterogeneous reservoir to displace oil, more of the injectant goes to the high-permeability layer and produces oil from the layer. With the oil removed, the effective permeability of the high-permeability layer becomes even higher, and virtually all of the subsequently injected fluid goes to the high-permeability layer, with the consequence that the oil still left in the lower-permeability layers is entirely bypassed. Various techniques, known as "conformance control" methods, are employed to divert the injected fluid to the low-permeability layers to produce the bypassed oil. The most prominent among them is the use of polymer gels to block the high-permeability layers. One critical weakness of the gel-based conformance control method is that, when a gel bank (or a polymer and a crosslinker chemical to generate a gel *in-situ*) is injected into a reservoir formation, it goes not only into the high-permeability layer (for which the gel is intended) but also into the low-permeability layer. For this reason, a successful conformance control is quite difficult.

Our novel technique first identifies the high-permeability layers for which the gel treatment is needed, and then forms the gel only in the target zones and not in the low-permeability layers. This "precision conformance control" is accomplished by using SPMNPs and the application of the magnetic oscillation of prescribed frequency and amplitude at the target zones at the wellbore. The polymer gel is created by adding SPMNPs to the temperature-responsive polymer and crosslinker and applying magnetic heating. If the polymer gel were created unintentionally at a certain layer, or there is a need to remove the gel blockage at the later stage of oil production, the gel there could also be broken and removed to restore the productivity from the layer.
(**PCT/US2014/563572; filed December 8, 2014**)

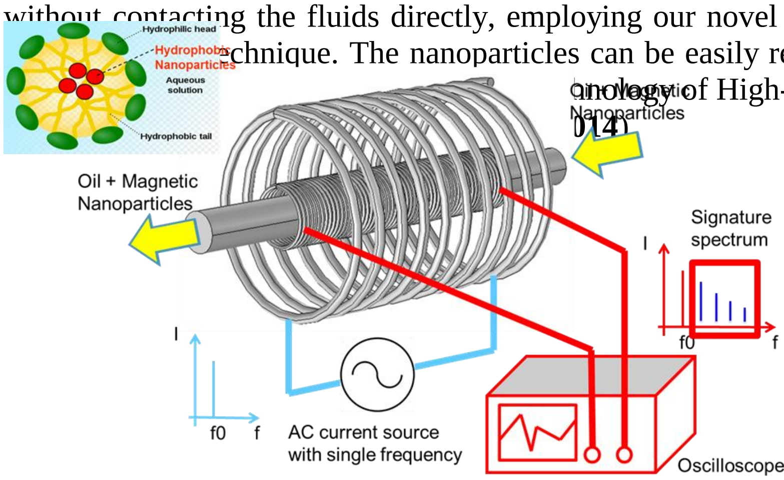


2. "Hydrophobic Paramagnetic Nanoparticles as Intelligent Crude Oil Tracers"

Huh, C., Milner, T. E., Nizamidin, N., Wang, B.*, and Pope, G. A.* (* *UT Biomedical Eng.*)

When an enhanced oil recovery (EOR) process is implemented at an oil reservoir, the ability to assess the process performance at an early stage of its operation can greatly help the optimal management of the process. Also, during the multiple-pattern implementation of EOR processes, it is difficult to distinguish the source of the oil produced at a production well, *i.e.*, what portion of the produced oil is mobilized by the IOR fluid injected at which injection well. A quantitative identification of the origin of the produced oil will greatly help the process optimization.

We developed a novel way of using hydrophobically surface-treated SPMNPs as "intelligent oil tracers", *i.e.*, which can carry out the above tasks. A variety of SPMNPs that show different magnetic susceptibility and unique magnetization responses to applied magnetic oscillation can be injected at different injectors. The hydrophobic nanoparticles are incorporated into the surfactant micelles that are injected for IOR. The concentrations of the nanoparticles in the produced crude oil and brine can be continuously and instantly measured individually, without contacting the fluids directly, employing our novel application of the magnetic particle ...chnique. The nanoparticles can be easily removed from the produced fluids, if ...nology of High-Gradient Magnetic Separation.

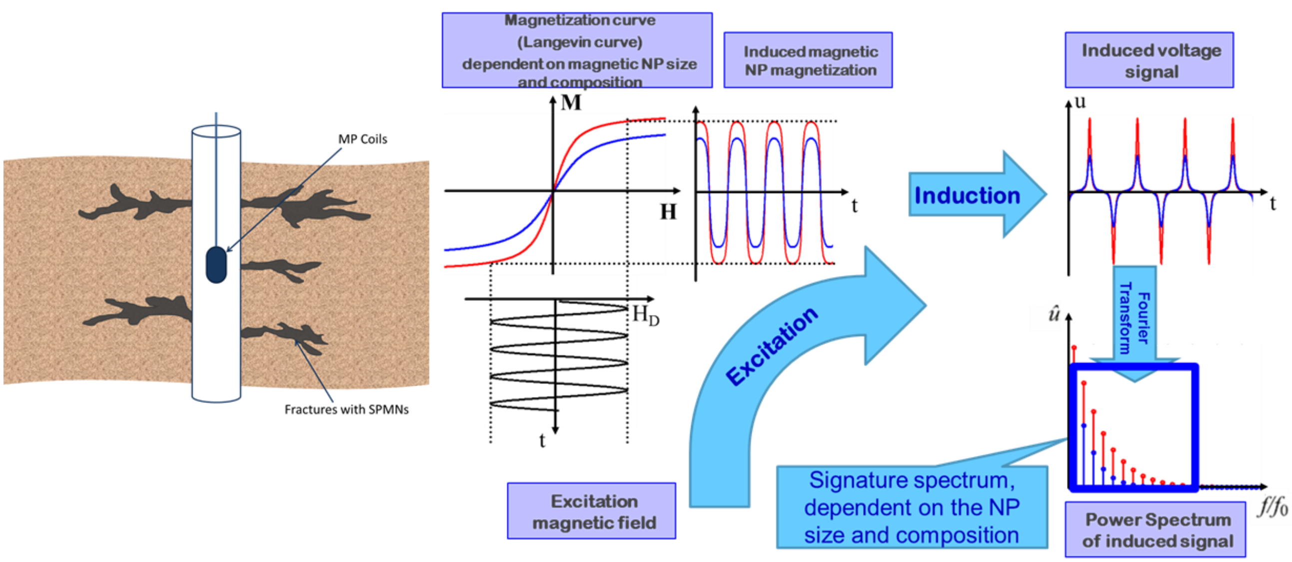


3. "Superparamagnetic Nanoparticles for Mapping of Rock and Fluids at Near-Wellbore Formations and for Drill Cuttings Analysis"

Huh, C., Milner, T. E., Wang, B.*, Ko, S., and Bryant, S. L.* (* *UT Biomedical Eng.*)

To map the internal geometry of porous rocks and to track the distribution and dynamics of fluids in them, various imaging tools such as x-ray CT and NMR/MRI are now widely employed in the upstream oil industry. We developed a novel way of mapping rock and fluids at near-wellbore formations and for drill cuttings analysis, utilizing the principle of the recently developed medical tomographic technique known as magnetic particle imaging (MPI). In the new method, SPMNPs that have the ability to attach to the target sites in the near-wellbore formation are injected at a well. When a magnetic field oscillation of prescribed frequency and amplitude is applied at the wellbore, a unique and known magnetization response from the nanoparticles can be measured, providing the spatial and temporal resolution of the particular rock and/or fluids attributes with improved depth of investigation than otherwise available. The finger-printing magnetization response signal from the nanoparticles can be uniquely extracted from the noise which will be generally present with the oilfield operations.

Our technique can also identify the presence and amount of the particular kinds of rock and/or fluids from the continuous stream of drill cuttings, by measuring the magnetization responses from the SPMNPs that were added to the drilling fluid. The detection measurement can be carried out non-invasively, automatically, and continuously.
(**PCT/US2015/037969; filed June 26, 2015**)



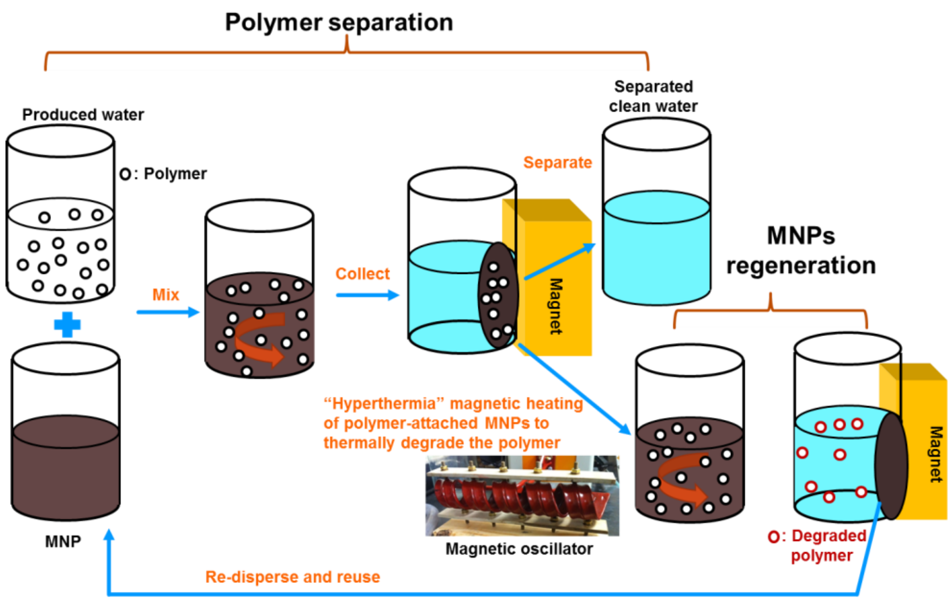
4. "Methods of Removing Contaminants from Aqueous Mixtures"

Huh, C., Ko, S., and Wang, Q.

During oil and gas production, a large volume of water, as much as 20 times of oil, is produced containing various contaminants, including left-over polymers and surfactants that were used for EOR processes. Treatment of the produced water for re-use or safe disposal is generally one of the largest oil-field operating expense. Several treatment technologies are available, but these current methods face the platform space constraints (for offshore operations), hazardous waste generations, and/or high energy consumption. We developed a novel way to overcome these difficulties, which consists of:

(a) Into the oilfield-produced water which contains the left-over polymers and surfactants from the EOR process application, specially surface-coated SPMNPs are added and mixed, so that the polymer (and surfactant) molecules attach to the surface of the nanoparticles.
(b) By applying a magnetic field gradient to the mixture, the EOR chemical-attached SPMNPs are collected, leaving behind a chemical-free, clean water. That water is withdrawn either for re-use or for environmentally safe disposal.
(c) The separated and concentrated SPMNPs are heated by applying a specific-frequency magnetic field oscillation, so that the polymers (surfactants) attached to their surface are thermally degraded to environmentally benign chemical forms. The heating, known as "hyperthermia", is highly localized, allowing efficient utilization of the magnetic energy to heat and degrade the chemicals that are attached right at the particle surface, very quickly.
(d) The SPMNPs that are now free of the EOR chemicals can be re-used for the magnetic removal process again.

(**US provisional 62,150,604; filed April 21, 2015**)



5. "Methods of Removing Deposits"

Huh, C., Mehta, P., Bryant, S. L., and Daigle, H.

This invention is an economic and operationally robust way to remove wax, asphaltene or hydrate deposits that occur in crude oil transport pipelines and oil production facilities, especially at the deep-water subsea environment. Our technique utilizes the concept of "hyperthermia", which is the practice of using SPMNPs and magnetic field application for a highly localized and focused delivery of heat, e.g., to destroy diseased human cells by burning, in medicine. The intense heat is generated by the nanoparticles themselves with a high energy efficiency, and the heating can be accomplished wirelessly with external magnetic field wave. By imbedding the SPMNPs in the inner lining of the oil pipelines and production facilities, and by applying magnetic field oscillation, a thin layer of the deposited wax at the boundary between the

hardware’s inner surface and the deposit, can be intensely heated, resulting in the detachment of the deposit from the hardware inner wall to the flowing oil. The “bits” of the detached wax will be carried by the flowing oil. No solvent or chemical is therefore employed for the removal, and the mechanical scraping using “pig” is not necessary, avoiding the potential abrasion of pipe’s inner wall. A small, battery-operated magnetic wave emitter “piglet” will be employed to deliver the magnetic energy to the nanopaint at the inner surfaces of the pipe. The freely floating, untethered emitter, whose cross-section is much smaller than the pipe cross-section, is neutrally buoyant and has a hydrodynamic design to keep it at the center of pipe and to help generate turbulent flow field near the pipe wall, so that the partially melted wax can be easily detached from the pipe’s inner wall. The emitter consists of the magnetic oscillation generating coil, a wave guide to focus the magnetic wave to the pipe wall, battery for power, and a RFID chip to transmit its location, all of which are encased in a sturdy plastic casing..
(**US provisional 62,150,599; filed April 21, 2015**)