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Nanotechnology in Upstream Oil and Gas

Peter Boul, Ph.D.

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Nanotechnology Research and Development in Upstream Oil and Gas

Peter J. Boul, Pulickel M. Ajayan

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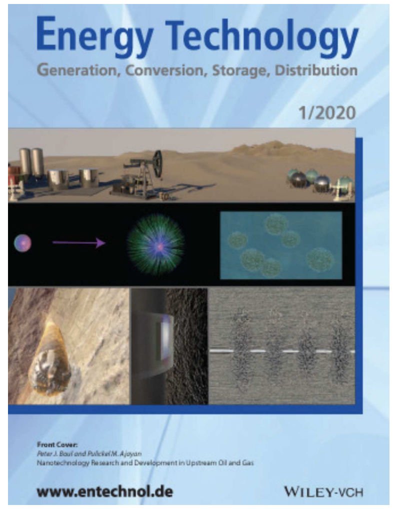

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What is Nanotechnology?

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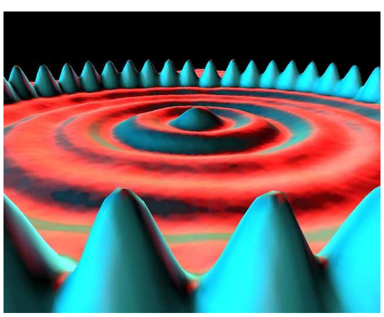

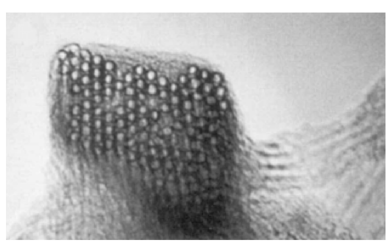

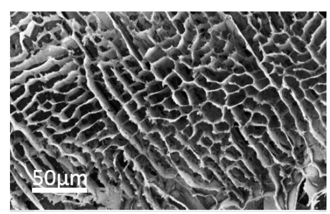

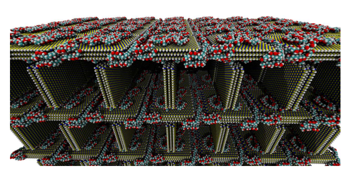

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M.F. Crommie, C.P. Lutz, D.M. Eigler. Confinement of electrons to quantum corrals on a metal surface. Science 262, 218-220 (1993).
Thess, A. et al., Crystalline Ropes of Metallic Carbon Nanotubes, Science 273, 483-487, (1996).
Owuor, P.S. et al. ACS Nano 11, 9, 8944-8952, (2017).

Characteristic Advantages of Nanomaterials

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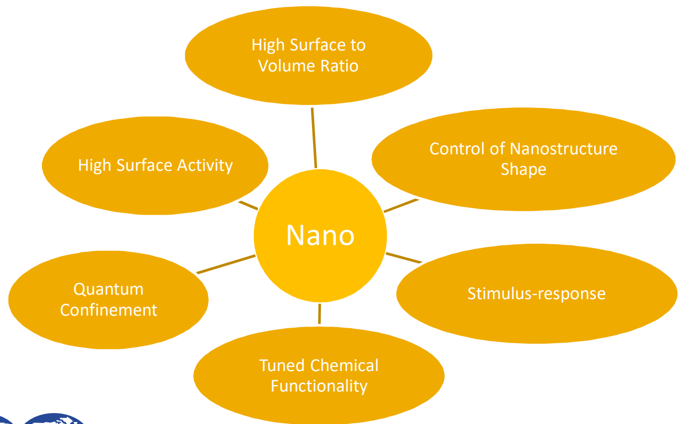

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Commercialized Nanotechnologies

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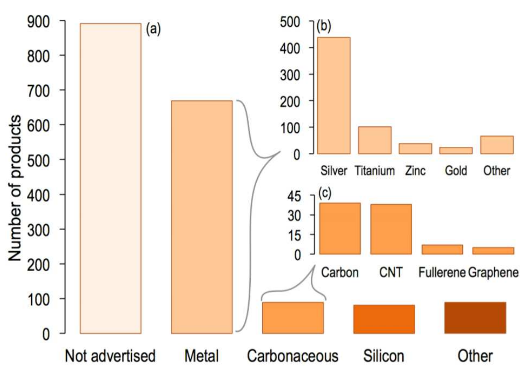
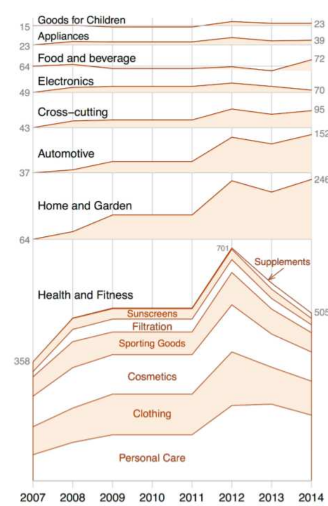


Claimed composition of nanomaterials listed in the CPI



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Woodrow Wilson International Center for Scholars and the Project on Emerging Nanotechnology created the Nanotechnology Consumer Product Inventory

Commercialized Nanotechnologies

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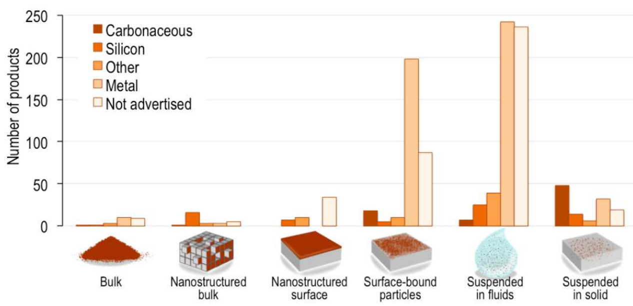

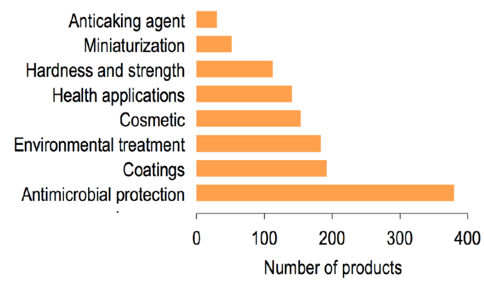

Woodrow Wilson International Center for Scholars and the Project on Emerging Nanotechnology created the Nanotechnology Consumer Product Inventory

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- Nanomaterial Synthesis
  - Bottom-up Approach
    - Wet Lab
      - Polymer synthesis
      - Self-Assembly / Supramolecular
    - Dry Lab
      - Chemical Vapor Deposition
      - Arc-discharge
      - Aerosol processes
  - Top-down Approach
    - Lithography
    - Mechanical milling
    - Chemical etching

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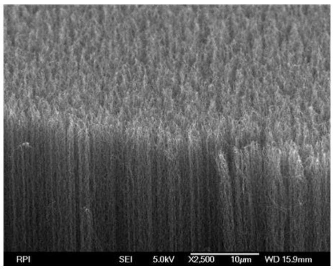
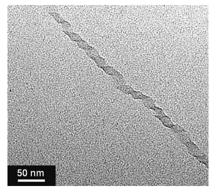
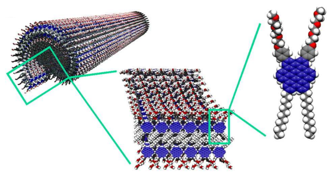
Dry Lab NanoFabrication



(a)

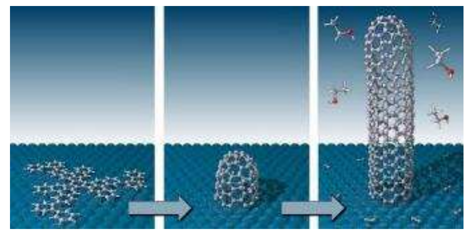
Wet Lab
Chemical Synthesis /
Self-Assembly





(b)

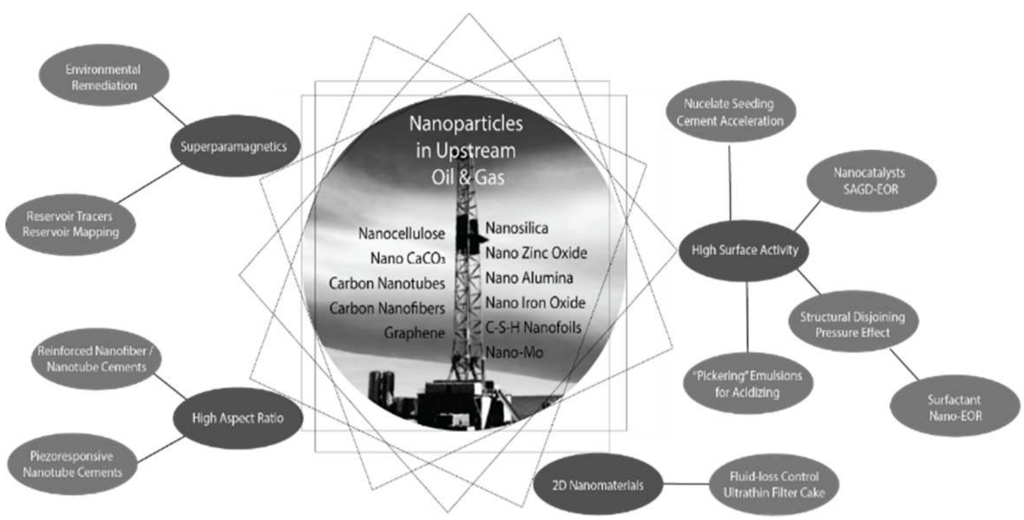
Wet Lab / Dry Lab
Chemical Synthesis /
Dry Lab NanoFabrication



(c)

(a) Yang, Z.-P., Ci, L., Bur, J.A., Lin, S.-Y., Ajayan, P.M. Experimental Observation of an Extremely Dark Material Made By a Low-Density Nanotube Array. *Nano Lett.* **2008**, 8, 2, 446-451
(b) Jin, W., FukushimaT., et al. Self-assembled graphitic nanotubes with one-handed helical arrays of a chiral amphiphilic molecular graphene. Proceedings of the National Academy of Sciences **2005**, 102 (31) 10801-10806.
(c) Sanchez-Valencia, J. R.; Dienel, T.; Groning, O.; Shorubalko, I.; Mueller, A.; Jansen, M.; Amsharov, K.; Ruffieux, P.; Fasel, R., Controlled synthesis of single-chirality carbon nanotubes. *Nature* **2014,** *512*, 61-64.

Nanomaterials in Upstream Oil & Gas



Nanotech Drilling Fluids

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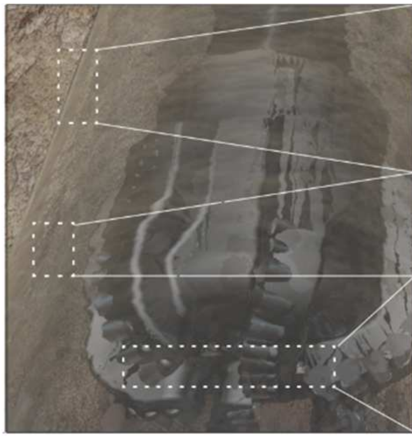

Wellbore Stability	WBMs containing functionalized **nanosilicas** display reduced erosion / water invasion of shale, in part through pore-plugging and high surface activity.
Filtration Control	**Graphene oxide** displays filtration control at low particle loading under HPHT conditions. Molecularly thin 2D material allows for ultrathin filter cake formation.
	Iron oxide nanoparticles complexed to bentonite platelets display superior HPHT filtration control. Clay modification with high surface area nanoparticles.
Fluid Rheology	**Carboxymethylated nanocellulose** enhances the temperature stability of formate brines up to 140 C. Bentonite WBMs exhibit superior thixotropy and filtration control with **nanocellulose**. The hig rface to volume ratio leads to this rheological effect.
Cooling the Bit	**Nano-ZnO** and **nano-CuO** increase thermal and electrical conductivity by 35%. **Nano-tin oxide** increases thermal and electrical conductivity by 30% and 15%, respectively. These physical property changes aree attributed to the higher surface areas available in colloidal nanoparticles for heat and electron transfer.
Pollution Control	Cadmium can be removed from drilling fluids with **nanomagnetite**.
Safety	**Nano-Zno** oxide is effective at rapidly savenging H_2S from toxic levels. Higher surface areas correspond with faster reaction rates and increased sensor sensitivity.

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Nanomaterials Synthesis – Synthesis of Nanosilicas

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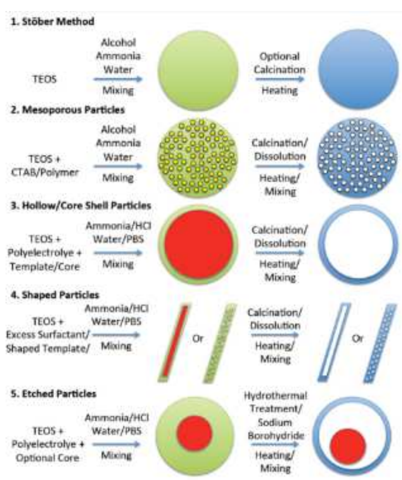

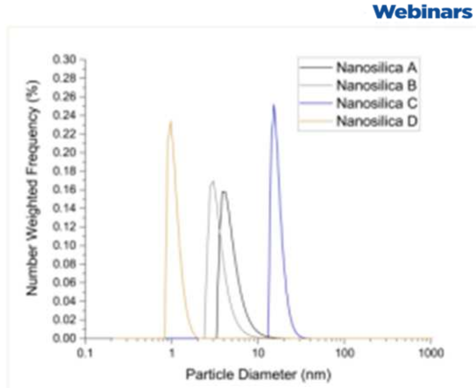

Nanosilica Functionalization

Nanosilica A – Sodium stablilized nanosilica

Nanosilica B – Functionalized nanosilica

Nanosilica C – Amino-functionalized nanosilica A

Nanosilica D – Amino-functionalized nanosilica

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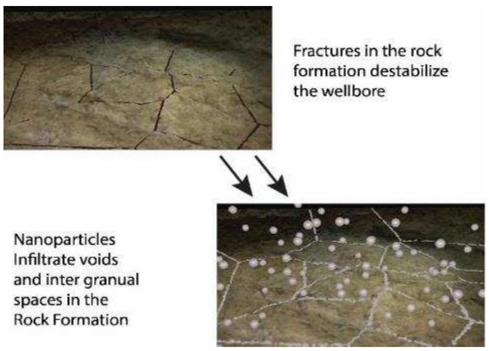
Liberman, A., et al. (2014) Surf. Sci. Rep. **69**: 132–158.

Wellbore Stability while Drilling with Nanosilica

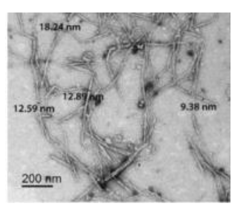
09-18-2019 Aramco Field Trial of Nano-shale Inhibitor
First Trial of a Nano Shale Inhibitor

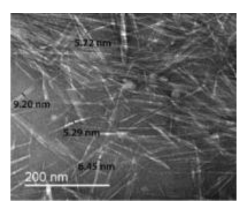


- Wellbore strengthening is a critical component sought in drilling through all formations.
- A strong wellbore is as important for oil or gas wells constructed through shales as it is for limestones and sandstones.
- To address some of the issues in drilling through water-sensitive shale formations, nano-sized particles can be designed to penetrate deeper into the formation and plug the shale pores to stop water invasion

Boul, P. J.; Reddy, B. R.; Zhang, J.; Thaemlitz, C., Functionalized Nanosilicas as Shale Inhibitors in Water-Based Drilling Fluids *SPE Drill. Completion* **2017,** *32* (2), 1-10.

Nanocellulose Preparation





Oxidation Methods (enzymes, mechanical degradation, etc.)

Strong Acid Treatment

Native Cellulose → Microfibrillated Cellulose → Cellulose Nanocrystals

Nanocellulose Performance in Formate Brines

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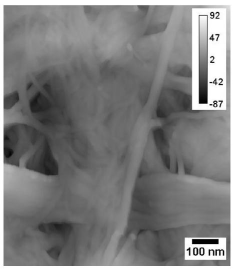
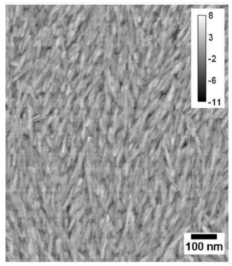
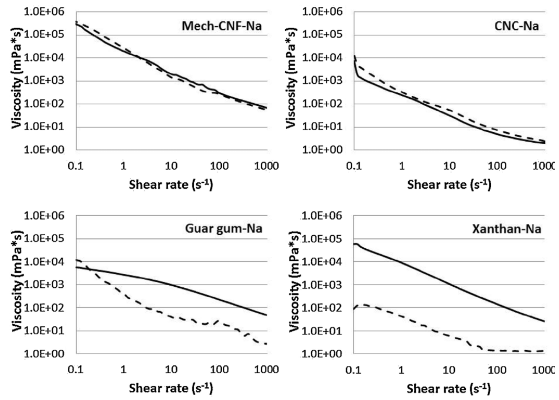




Mech-CNF-Na → CNC-Na



Viscosity as a function of shear rate for nanocellulose dispersions, xanthan and guar gum with sodium formate added, before (solid line) and after heat aging at 140◦C (dotted line) for three days. All samples had a solid content of 0.8%

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Heggset, E. B.; Chinga-Carrasco, G.; Syverud, K., Temperature stability of nanocellulose dispersions. *Carbohydr. Polym.* **2017,** *157*, 114-121.

Nanoparticles enhancing thermal conductivity of drilling fluids

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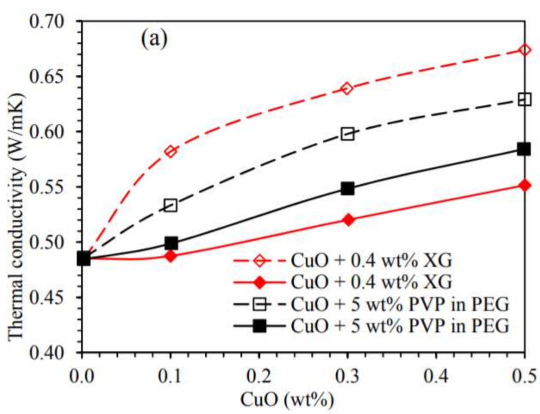

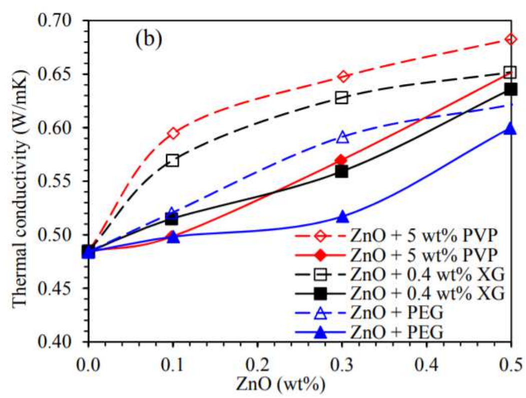

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Ponmani, S.; Nagarajan, R.; Sangwai, J. S., Effect of Nanofluids of CuO and ZnO in Polyethylene Glycol and Polyvinylpyrrolidone on the Thermal, Electrical, and Filtration-Loss Properties of Water-Based Drilling Fluids. *SPE J.* **2016,** *21* (2), SPE-178919-PA.

Waste Remediation

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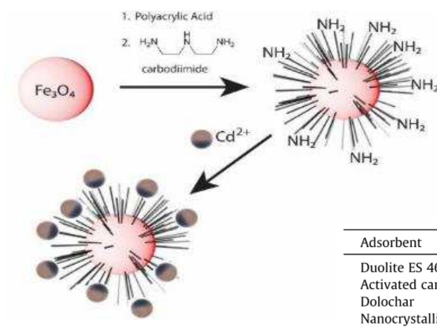

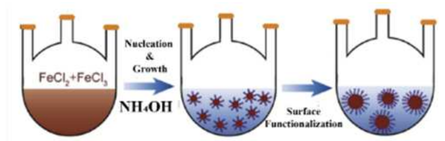

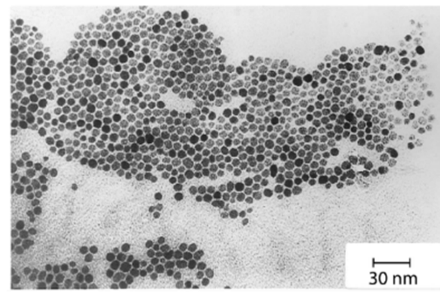

$$\frac{x}{m} = Kc^{1/n}$$

Adsorbent	K_f (mg/g)	n
Duolite ES 467 resin	2.73	3.11
Activated carbon	5.43	3.125
Dolochar	1.42	4.16
Nanocrystallite hydroxyapatite	122.854	41.667
Thiocarbamoyl chitosan	6.46	1.49
Magnetite nanorods	10.17	2.25
Composite nanofiber	58.81	3.378
CDpoly-MNPs	17.64	12.24
Magnetic nanoparticles	2.683	1.1136

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Alimohammadi, N.; Shadizadeh, S. R.; Kazeminezhad, I., Removal of cadmium from drilling fluid using nano-adsorbent. *Fuel* **2013,** *111*, 505-509.

Waste Remediation

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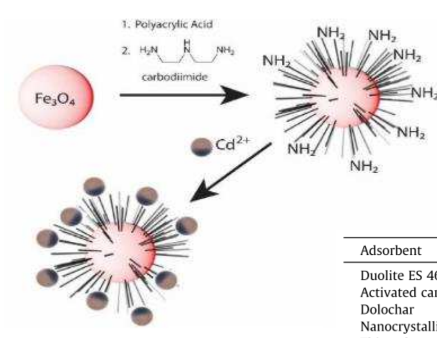

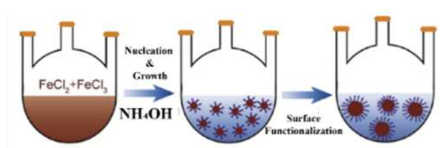

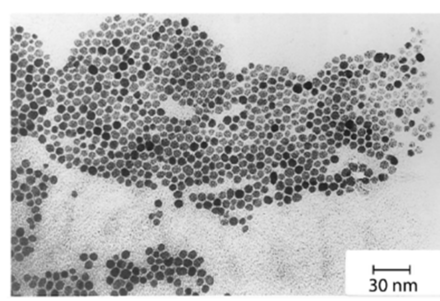

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Nanotech Oil and Gas Well Cements

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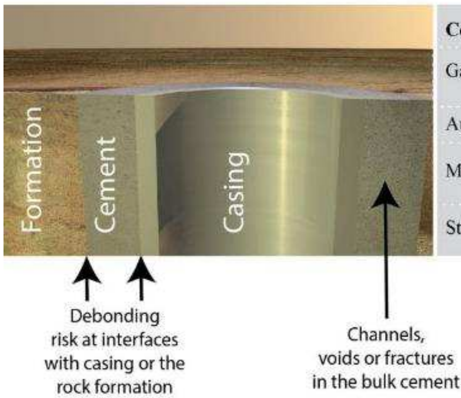

Cement Material Issue	Nanoparticle Solution
Gas migration	Nanosilica C-S-H nanofoils
Autogenous shrinkage	Nano-Magnesium oxide
Mechanical strength	Carbon nanotubes Nanosilica
Strength retrogression	Nanosilica

Well Conditions

High Temperature (up to 300ºC)
High Pressure (up to 200 MPa)
Dynamic thermal conditions during production cycling
Formation fluids (carbon dioxide, H_2S, water, brine)
Formation pore pressure
Formation composition (shale, sandstone, limestone salt)

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Cement Hydration Acceleration with Nanosilica

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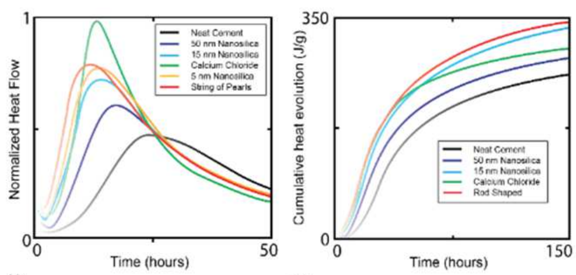

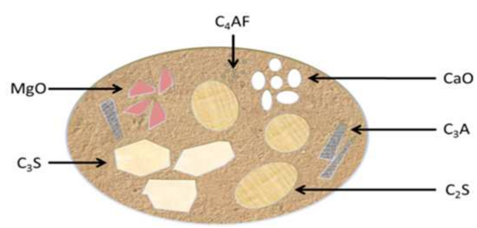

Real Phases in Clinker	Idealized chemical composition		Abbreviation
Alite	$3CaO.SiO_2$	(tricalcium silicate)	C_3S
Belite	$2CaO.SiO_2$	(dicalcium silicate)	C_2S
C_3A-alkali solid solution	$3CaO.Al_2O_3$	(tricalcium aluminate)	C_3A
Ferrite phase solid solution	$4CaO.Al_2O_3.Fe_2O_3$	(calcium alumino ferrite)	C_4AF

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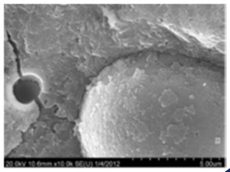
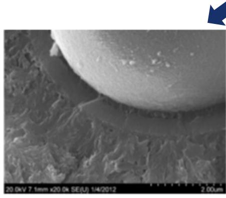
Pang, X.; Boul, P. J.; Cuello-Jimenez, W., *SPE Drill. Completion* **2014,** *29*, 98-105

Cement Hydration with Nanosilica and Fly Ash

(a)

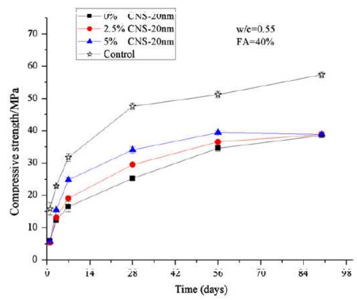


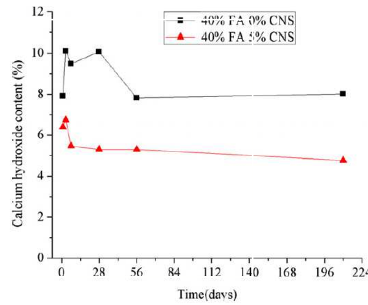
(b)



Interface of cement paste and fly ash particle (7 months old) with
(a) 0% CNS

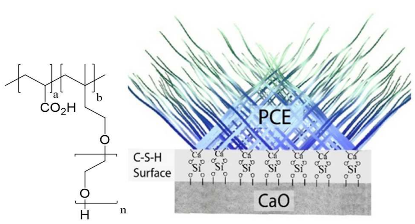
(b) 5%CNS-10 nm



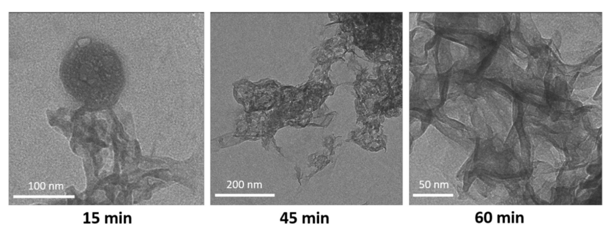


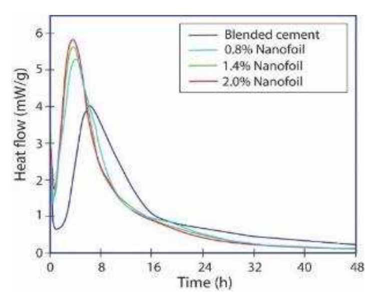
Kawashima, S.; Hou, P.; Corr, D. J.; Shah, S. P., Modification of cement-based materials with nanoparticles. *Cem. Concr. Compos.* **2013,** *36*, 8-15.

Cement Nanofoils



(a) (b)





(a) The molecular structure of polycarboxylate ether (PCE) superplasticizer.

(b) The surface pacification of C-S-H nanofoils with PCE.

Schönlein, M.; Plank, J., A TEM study on the very early crystallization of C-S-H in the presence of polycarboxylate superplasticizers: Transformation from initial C-S-H globules to nanofoils. *Cem. Concr. Res.* **2018,** *106*, 33-39.

Nanotube Synthesis – Chemical Vapor Deposition

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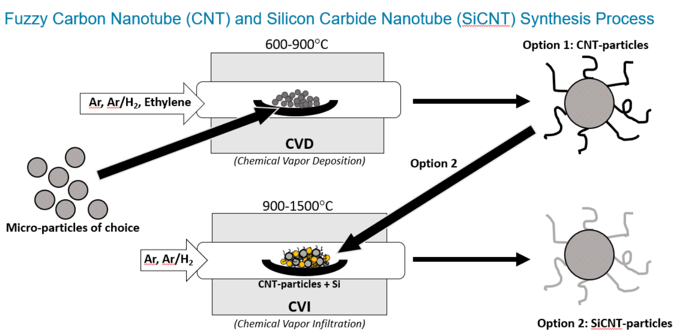
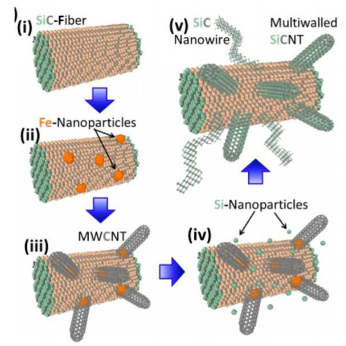
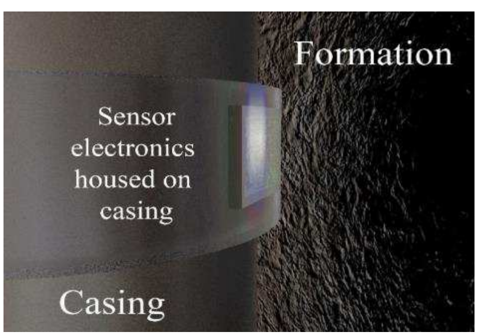
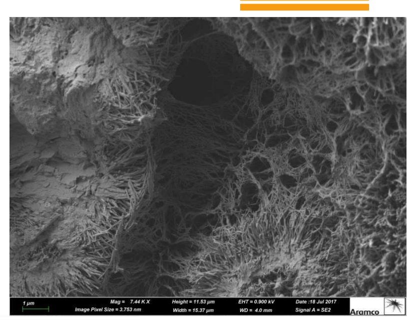


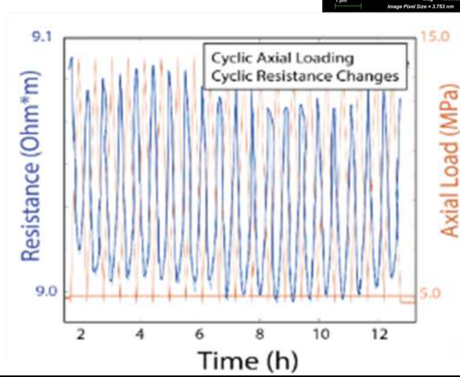


Hart, A. H. C.; Koizumi, R.; Hamel, J.; Owuor, P. S.; Ito, Y.; Ozden, S.; Bhowmick, S.; Amanulla, S. A. S.; Tsafack, T.; Keyshar, K.; Mital, R.; Hurst, J.; Vajtai, R.; Tiwary, C. S.; Ajayan, P. M., Velcro-Inspired SiC Fuzzy Fibers for Aerospace Applications. *ACS Appl. Mater. Interfaces* **2017**, *9*, 13742–13750.

Sensors in Cement

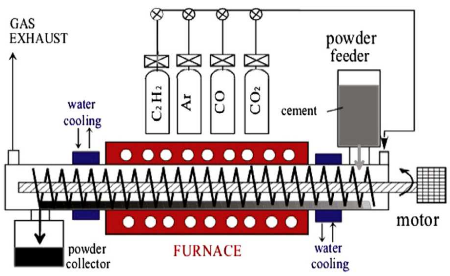


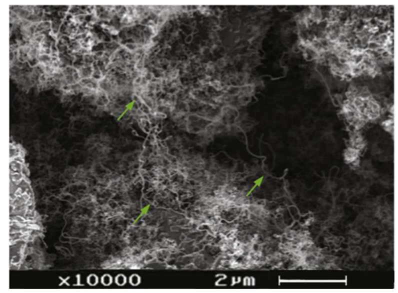




multiwall nanotubes in cement

- chemical vapor deposition (CVD) for high throughput processing of carbon materials on cement
- the cement is modified through catalytic functionalization

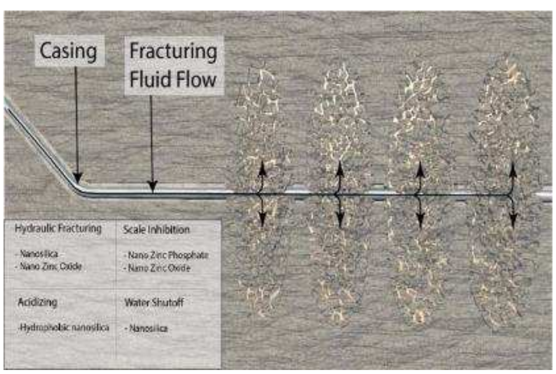


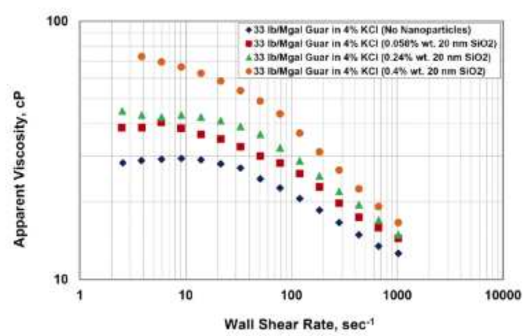


- CVD growth has the potential to eliminate the problems in dispersion of carbon nanotubes in water
- chemical functionalization of the CVD modified cement as a method to further enhance the interaction of the nanotubes oil well cement additives

de Paula, J. N.; Calixto, J. M.; Ladeira, L. O.; Ludvig, P.; Souza, T. C. C.; Rocha, J. M.; de Melo, A. A. V. *J. Pet. Sci. Eng.* **2014,** *122*, 274-279.

Production



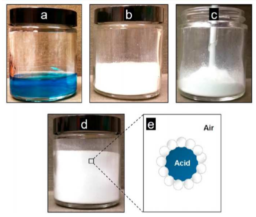


- NP-VES-fracturing fluid performance improvement
- NP-Cross-linked guar stable viscosity to 20,000 psi
- Water-less fracturing with nanopartice stabilized foams

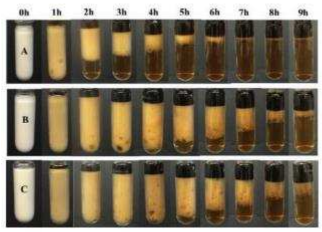
Nanosilica and Acidizing

Webinars

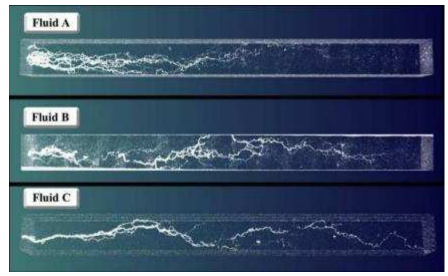
(a)5 wt % hydrochloric acid dyed with Nile Blue A (25 g);
(b)hydrophobic silica nanoparticles (2.5 g);
(c)dry acid powder flowing freely through glass funnel;
(d)dry acid powder (total product weight = 27.5 g);
(e)schematic of acid-in-air powder (white sphere represents the silica nanoparticles).



300°F



Acidizing Fluid	Abbreviation
Conventional Emulsified Acid (without additives)	Fluid A
Stabilized Emulsified Acid (Additive I)	Fluid B
Stabilized Emulsified Acid (Additive II)	Fluid C



15 hour shut-in at 3000 psi and 300 F

Cairns, A. J., et al. (2016). Presented at SPE International Conference & Exhibition on Formation Damage Control held in Lafayette, Louisiana, USA, 24-26 February 2016 - SPE-178967.
Singh, R., et al. (2017). "Microencapsulation of acids by nanoparticles for acid treatment of shales." Energy Fuels **31**: 11755-11764.

Production

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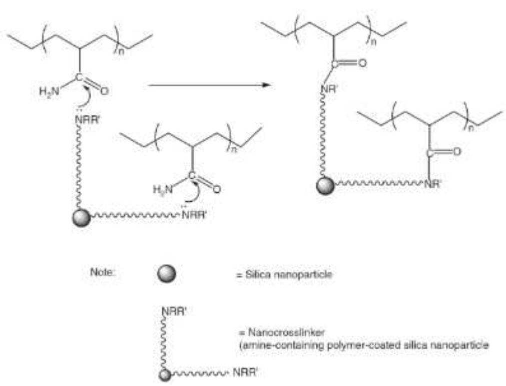
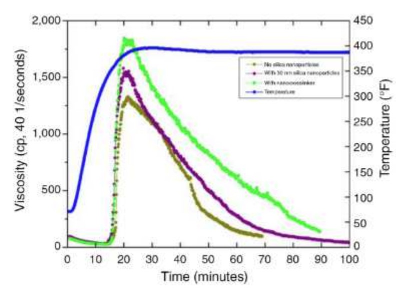
Nanogelants





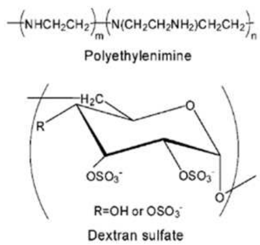
Functional nanosilicas cross-link acrylamides

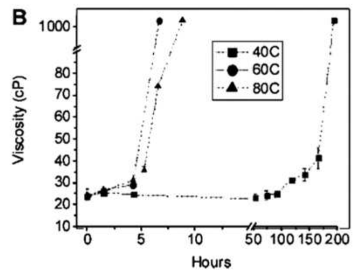
- Increased fluid stability up to 400 F
- Reduces the amount of acrylamide required for the same viscosity
- Breakable with bromate oxidizers

Liang, F.; Al-Muntasheri, G.; Ow, H.; J. Cox, Reduced polymer loading, high temperature fracturing fluids using nano-crosslinkers. . In *Presented at the Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi, 9-12 November. SPE-177469-MS.*, 2015.

Conformance gels and chemical delivery with nanocapsules

- Nanoparticle polyelectrolyte complexes entrap and control the release Cr(III) to effectively extend gelation time of HPAM gelants
- Self-assembly of polyethylenimine (PEI) and dextran sulfate (DS) resulted in the formation of ~100-200 nm particles that efficiently entrapped chromium while maintaining colloidal stability in water or gelant

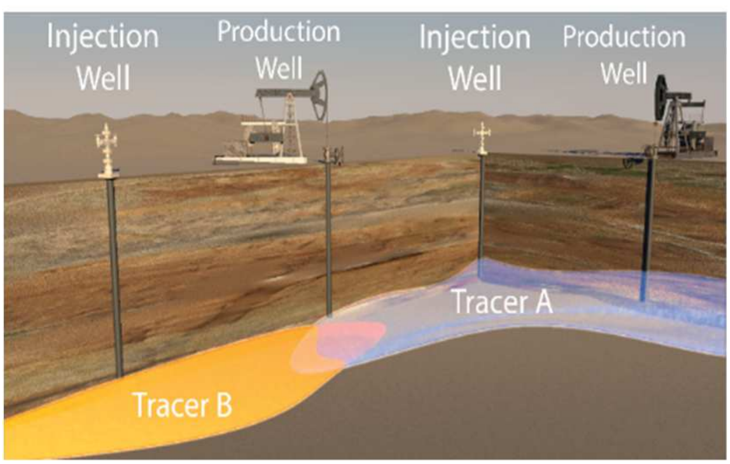




sample		diameter (nm)	polydispersity	zeta potential (mV)	pH	entrap eff (%)
I	before dialysis	170	0.15 ± 0.04	22.9 ± 2.2	9.70	
	after dialysis	153	0.15 ± 0.03	17.8 ± 2.3	8.96	94.3
II	before dialysis	173	0.16 ± 0.01	20.2 ± 1.5	9.63	
	after dialysis	151	0.10 ± 0.02	16.4 ± 2.4	8.99	93.6

Cordova, M., et al. (2008). "Delayed HPAM gelation via transient sequestration of chromium in polyelectrolyte complex nanoparticles." Macromolecules **41**: 4398-4404.

Reservoir Tracers

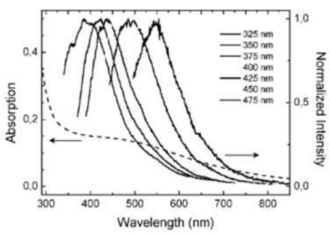


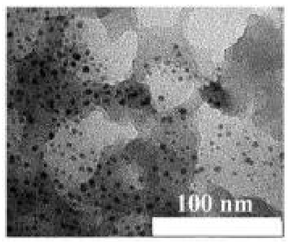
- Tracers are deployed for mapping reservoir architecture including reservoir flow paths, heterogeneities, and unswept areas of the reservoir.
- Surveys from these are a potentially powerful way of maximizing the yields from Improved Oil Recovery (IOR) and EOR techniques.
- The first oilfield scale demonstration of the use of nanoparticles as sensors for oilfield reservoirs was reported in 2011 by Saudi Aramco.

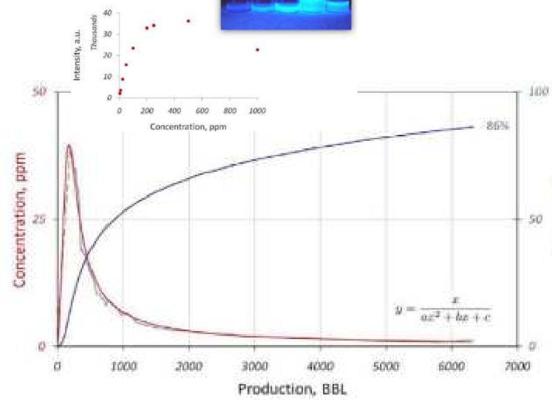
Reservoir Nanotracers Field Trial

Webinars

- The particles were luminescent carbon dots with a size range of 5 to 10 nm.
- To measure the particles concentration, their response to light was utilized as they are fluorescent. Their concentration was detected with an accuracy of 0.1 ppm using a fluorometer.
- Problems with these particles derives from strong autofluorescence from the highly fluorescent organic residues (e.g., polycyclic aromatic hydrocarbons) contained in crude oils under constant external excitation.







Bourlinos, A. B., et al. (2008). "Photoluminescent Carbogenic Dots." Chem. Mater. **20**: 4539-4541.

Kanj, M. Y., et al. (2011). Industry First Field Trial of Reservoir Nanoagents. . SPE Middle East Oil and Gas Show and Conference, 25-28 September, Manama, Bahrain. SPE-142592-MS.

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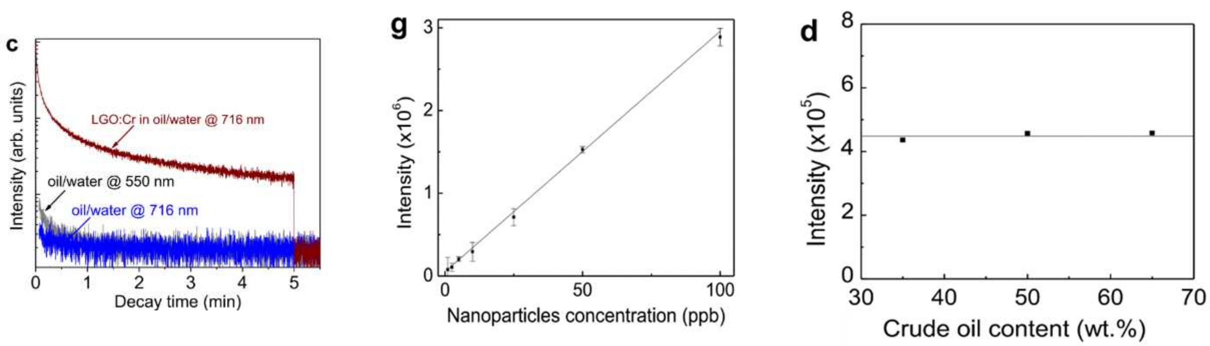
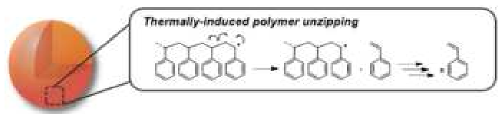
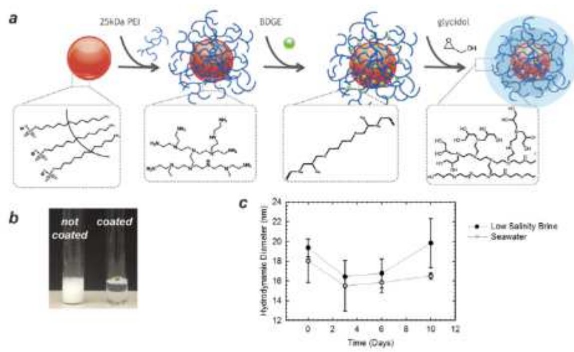
Near-IR Persistant Lumnescent Cr^{3+}-doped $LiGa_5O_8$ Nanoparticles (50 – 100 nm)

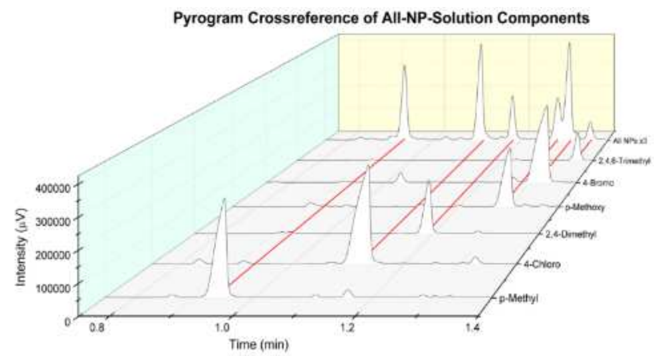


Chuang, Y.-J., et al. (2016). "Ultra-sensitive in-situ detection of near-infrared persistent luminescent tracer nanoagents in crude oil-water mixtures." Sci. Rep. **6**: 27993.

GC-MS Barcoded Nanotracers





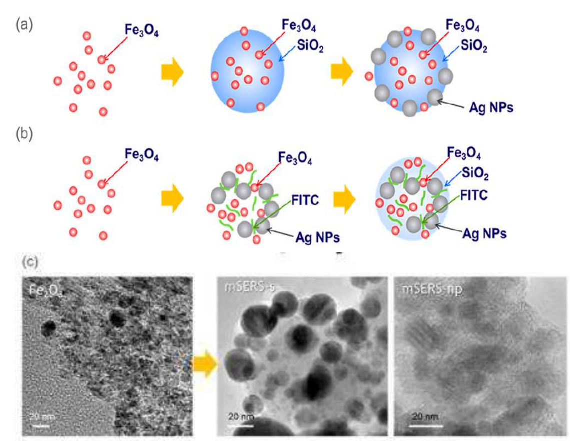


Cox, J. R., et al. (2017). "Pyrolyzable Nanoparticle Tracers for Environmental Interrogation and Monitoring." ACS Appl. Mater. Interfaces **9**: 13111-13120.

Nanoparticle SERS / SPIONS

- Lab-based detection is commonly performed using mass spectroscopy for molecules and provides a low limit of detection (LOD) but requires significant sample work-up.
- Surface-enhanced Raman scattering (SERS) phenomena, enhances the Raman signal on the order of 10^6–10^{15}.
- SERS particles are specifically designed such that magnetic cores (Fe_3O_4) are incorporated into a nonmagnetic shell (SiO_2) and then decorated with noble metallic particles (Ag) to create SERS hot spots.

Magnetic functionality in SERS-active nanomaterials has been demonstrated by synthesis of various core–shell nanostructures.

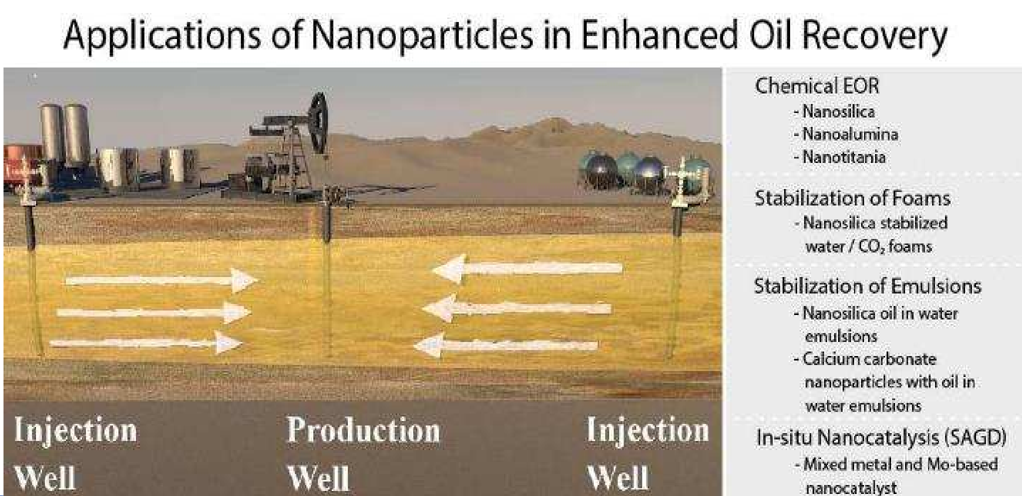


Chang, S., et al. (2019). "Magnetic SERS Composite Nanoparticles for Microfluidic Oil Reservoir Tracer Detection and Nanoprobe Applications." ACS Appl. Nano Mater. **2**: 997-1004.

Long-term Potential of Nanoparticle Tracers

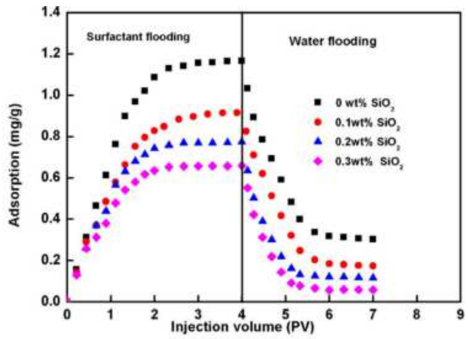
- Provide record of temperature, pressure, salinity or any other important reservoir rock/fluid property.
- Targeted delivery of specific chemicals to the reservoir such as: wettability alteration chemicals, scale inhibitors and water control agents.

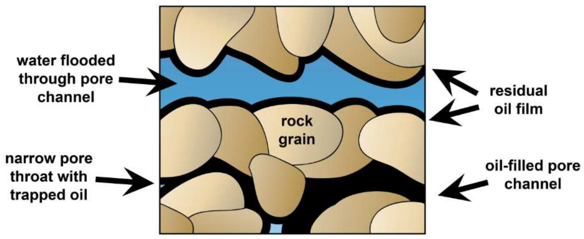
Production



Chemical EOR

- Polymer flooding methods
- Surfactant flooding methods
- Foam EOR methods

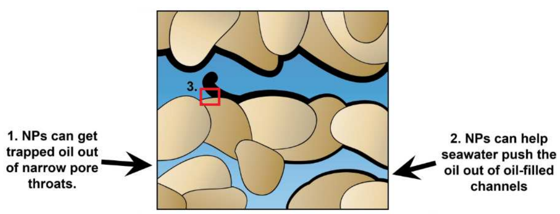


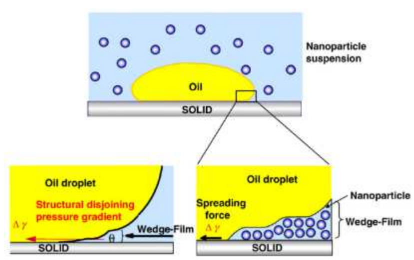


Colloidal nanoparticles have been shown to reduce the adsorption of surfactant molecules, and in this way increase oil recovery in comparison with cases where water without nanoparticles is used.

Wu, Y., et al. (2017). "Reducing surfactant adsorption on rock by silica nanoparticles for enhanced oil recovery." J. Pet. Sci. Eng. **153**: 283-287.

Nano-EOR Mechanism





- The detachment of an oil drop from the solid surface using a nanoparticle (without an added electrolyte) is that with the lapse of time, micelles diffuse into the wedge film and interact with the film surfaces.
- The micelle concentration in the film increases. The disjoining pressure increases significantly at a wedge thickness corresponding to one micelle layer.
- As a result of the pressure increase, the oil–solution interface moves forward, and the aqueous micellar solution spreads on the solid surface, detaching the oil drop.

Wasan, D. T. and A. D. Nikolov (2003). "Spreading of nanofluids on solids." Nature **423**: 156-159.

Lim, S., et al. (2016). J. Colloid Interface Sci. **470**: 22-30.

Why Nano-EOR?

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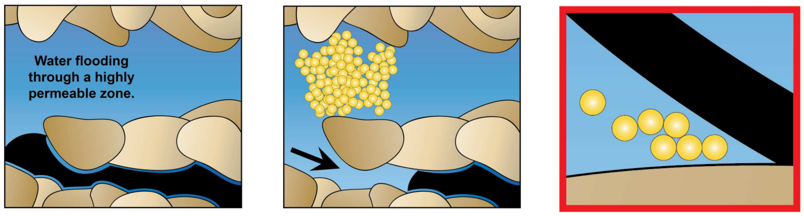

1. Nanoparticles can increase the viscosity of the seawater to help push it through oil zones.
2. Nanoparticles can lower the interfacial tension between the oil and seawater so oil that was lodged in tiny pore throats can be released into the water highways.
3. Nanoparticles can create a wedge-film that strips the oil droplets off the rock surface.
4. Nanoparticles and nano-gels can be used to selectively plug water paths, forcing the water to flow through oil–filled paths.

SPE International

https://www.ntnutechzone.no/en/2015/05/using-nanofluids-to-enhance-oil-recovery/

Nano EOR

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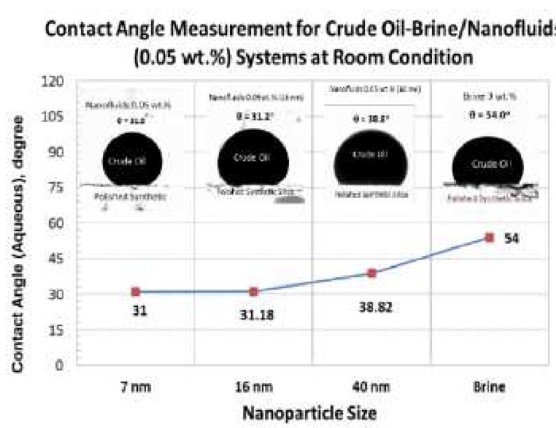
- Colloidal nanoparticles have been shown to change make sandstone cores more water wet.
- The change in contact angle increased with decreasing nanosilica diameter.
- Incremental oil recovery and displacement efficiency due to Nano-EOR increased as decreased nanoparticle size.

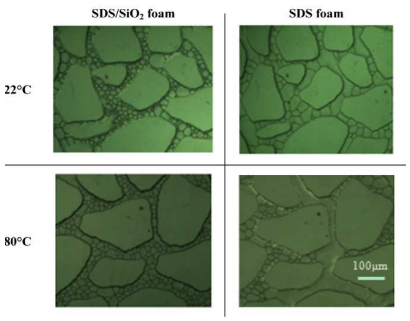


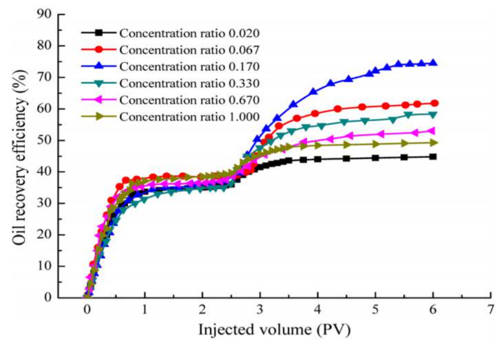
SPE International

Hendraningrat, L., et al. (2013). Effect of Some Parameters Influencing Enhanced Oil Recovery Process using Silica Nanoparticles: An Experimental Investigation. . SPE Reservoir Characterization and Simulation Conference and Exhibition, 16-18 September, Abu Dhabi, UAE. SPE-165955-MS.

Foam-EOR

Foam has been shown to be stabilized by nanosilica and increase oil recovery efficiency

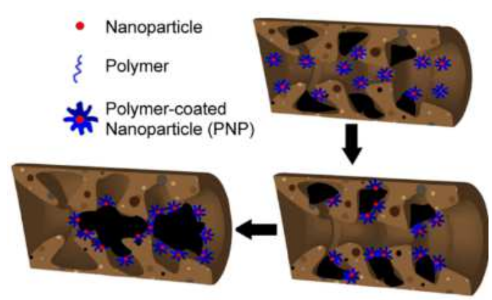




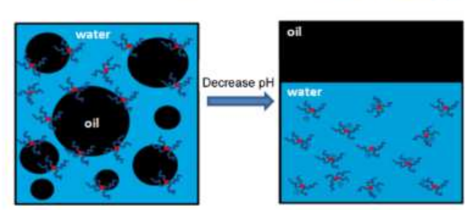
Li, S., et al. (2016). "Experimental study of the stabilization of CO2 foam by sodium dodecyl sulfate and hydrophobic nanoparticles." Ind. Eng. Chem. Res. **55**: 1243-1253.

Stimulus-responsive Nanoparticles - EOR

- The stimulus-responsive nature of these materials offers the possibility of control over the emulsification mitigating potential formation damage could be mitigated.
- DMAEMA nanoparticle results in water contact angle reduction from 76°to 62°at neutral pH.
- Reduction of the pH corresponds to an increase from 62°to 81°corresponding to an increase in IFT.



additive	total oil in column (mg)	oil recovery after 20 pore volumes (mg)	fraction of oil recovered (wt %)
none	806	2	<0.1
DMAEMA nanoparticle	822	81	9.9



Qi, L., et al. (2018). "Polymer-coated nanoparticles for reversible emulsification and recovery of heavy oil." Langmuir **34**: 6522-6528.

Advantages of Nanocatalysts

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Nano-Effects

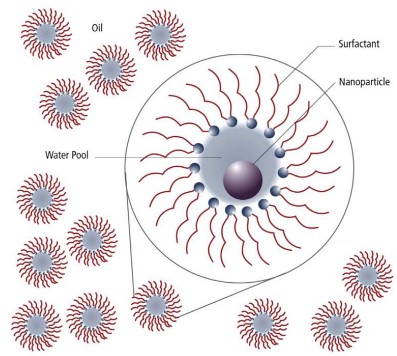
- Large surface-volume area ratio
- High surface activities

Improvement over fixed-bed catalysts

- No need for catalyst bed replacement
- Longer residence times possible for bitumens enabling more potential up-conversion

In-situ resource utilization

- Uses the heat from steam injection for activation of catalytic activity.
- Highly dispersed nanoparticles (ie Nano-Mo-Ni) adsorbed onto porous reservoir rocks.



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Hashemi, R.; Nassar, N. N.; Almao, P. P., Nanoparticle technology for heavy oil in-situ upgrading and recovery enhancement: Opportunities and challenges. *Appl. Energy* **2014,** *133*, 374-387.

Conclusions

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- Nanotechnology research and product development spans most of upstream oil and gas.
- Nanomaterial products are making their way into the field now.
- There remains huge potential in addressing technology challenges related to upstream oil and gas industry with nanomaterials and devices. This includes:
  - nanoparticles to provide incremental improvements to existing methods and procedures in extracting oil and gas
  - Transformative and disruptive nanotechnologies.

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Symposium :

Nanomaterials R&D in Upstream Oil and Gas

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Questions?

Thank you!

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