

Nanoparticle stabilized emulsion spontaneously forming during displacements in porous media

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One of the key concerns for CO₂ sequestration in the subsurface is that CO₂ is buoyant at the depths it is planned to be emplaced. Without a robust seal above the saline aquifer, sequestered CO₂ will potentially rise through the geologic strata and be emitted back into the atmosphere. Nature has shown the ability to provide robust geologic seals as large volumes of natural gas, oil and naturally occurring CO₂ (produced at depth by heating carbonate rocks) have been trapped in reservoirs for tens of millions of years. Risk assessment of large scale geologic sequestration will include estimates of the efficacy of the seals above potential CO₂ repositories (saline aquifers), and monitoring of storage sites will include regular measurements of pressures and compositions in overlying formations. Sequestration projects are likely to include remediation plans in case leakage occurs. Nevertheless the principle that prevention is cheaper than cure applies here, and it would be useful to engineer the sequestration in such a way that any potential leaks would be self sealing. An analogy would be “run flat” tires that are currently used on automobiles and bicycles. When these tires are punctured, the first pulse of escaping gas contains compounds which through the rapid expansion create a reaction that acts to seal the leak.

One potential method to induce self sealing for CO₂ is inspired by the observation (Espinosa *et al.*, 2010) that suitably chemically coated nanoparticles can stabilize a foam of supercritical CO₂ in brine. The nanoparticles adhere to the surface of CO₂ bubbles and prevent their coalescence. Such foams have been created in our lab by injecting the CO₂ phase and brine containing dispersed nanoparticles through a porous medium. To use this idea for secure sequestration, one could first inject nanoparticles into the upper portion of the prospective storage structure, or into locations where risk of leakage is expected to be greatest, or even into an overlying formation. Because the particles are much smaller than the pore throats in the rocks that will be used for storage, and because we can tailor the chemical coating on the particle surface to minimize interaction with the rock surface, nanoparticles can easily be transported through the aquifer. If the buoyant sequestered CO₂ were to rise through any of the nanoparticles treated rock, the nanoparticles would be attracted to the CO₂/brine interface. The nanoparticles effectively armor the interface, and if the CO₂ is in tiny droplets, these droplets will be stabilized (i.e. they will not coalesce) and form an emulsion.

The key is that the nanoparticle stabilized emulsions are much less mobile than the separate pure phases. Thus if the CO₂ spontaneously forms a foam as it moves along a leakage path, the foam will act to seal the leak. We expect that the emulsion will form where the CO₂ is moving the fastest, as the greater shear in this location will produce more CO₂ bubbles which then are stabilized by the nanoparticles.

To observe whether this hypothesized mechanism takes place we performed core floods where octane displaces a brine with and without nanoparticles (Figure 1). In these experiments, octane acts as low pressure analog to high pressure supercritical CO₂. In each of the experiments, a cylindrical core (length 30 cm diameter 7.5 cm) cut from a block of Boise sandstone was preloaded with brine (for the control experiment) or with brine with a 10% by weight suspension of silica nanoparticles. Octane was then injected to displace the brine phase at a flux of 0.02 cm/min. We observe the displacement in real time

within the pores of the sandstone using CT scanning. An important distinction from the experiments of Espinosa *et al.* (2010) is that here one phase displaces the other, rather than both phases being injected together.

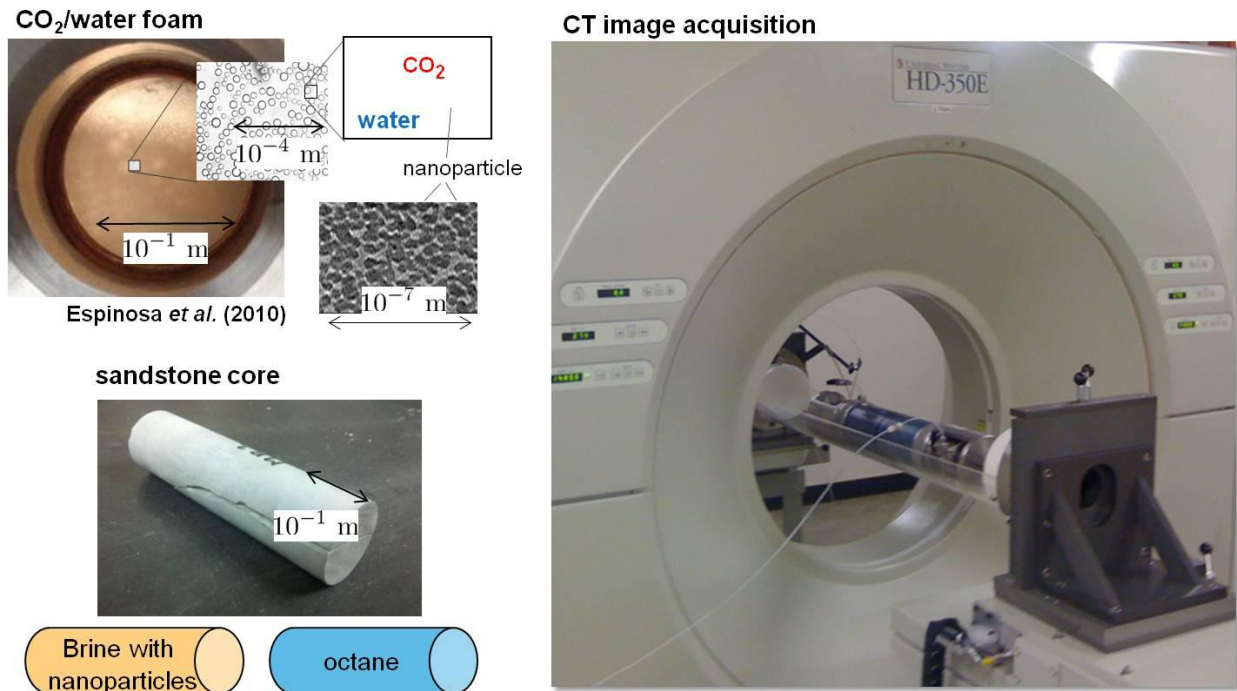


Figure 1. Left hand side: Preparation of the core for the experiments. Right hand side: CT scan device.

For the corefloods with brine as the initial fluid, the displacement behaved classically: the displacing octane front formed fingers, or preferential flow paths through the core. Viscous fingering is a well known phenomenon and occurs as octane has a lower viscosity than brine. This makes the front viscously unstable, i.e. any perturbation to the front will grow with time. These fingers can be seen in the CT images in Figure 2. Each slice is a different longitudinal position along the core, and within each slice one can see where the octane (cold colors), and the brine (warm colors) are located. The images show that the octane forms long fingers, and inside each finger is almost pure octane.

For the corefloods with a nanoparticle suspension as the initial fluid, the displacing octane moved in a much more uniform front through the core. This contradicts what would be expected from classical theory. The nanoparticle suspension is 20% more viscous than the brine, and if the phases remain distinct, the displacement would be more unstable than the control experiment, and longer preferential flow paths would be observed. Instead the CT images show that behind the uniform front, the octane and brine are well mixed. This can be seen in Figure 2. Here the octane phase (blue) has moved a much shorter distance even though the same volume has been injected. There is no evidence of fingers (the images are uniform), and behind the front there is a mixture of octane and brine (uniform green color rather than red or blue). As octane and brine spontaneously separate, this can only occur if an emulsion is forming in the core. In fact, when the octane is finally eluted from the core, it was observed to be a milky emulsion.

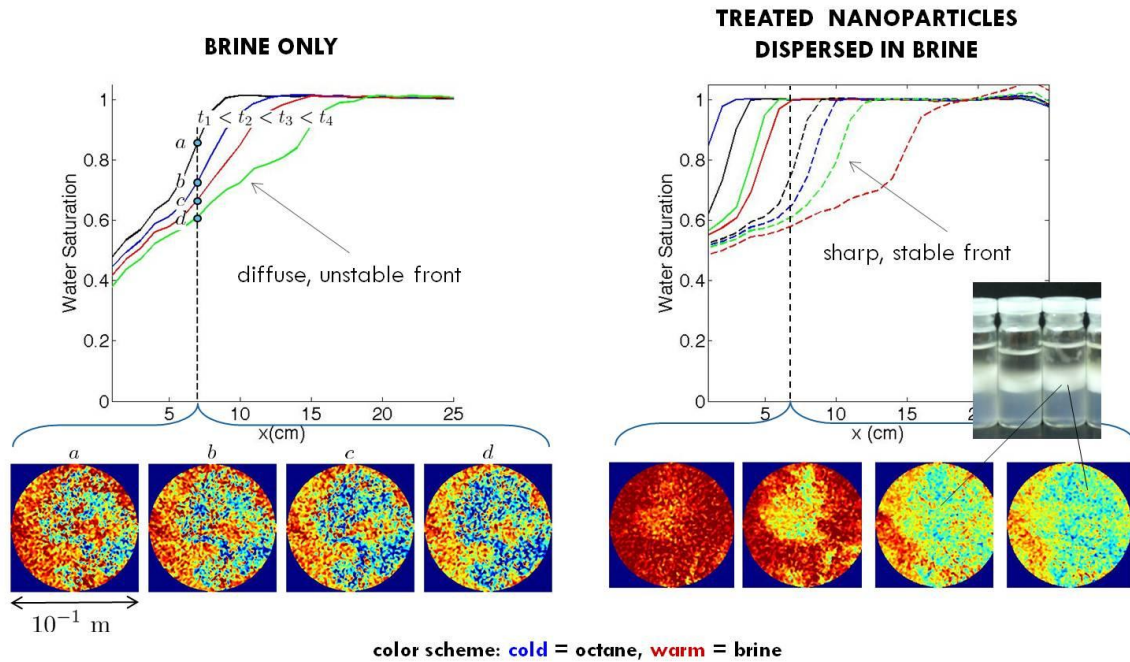


Figure 2. X-ray images reveal creation of stable, viscous emulsion *in situ*.

In the presence of nanoparticles, the displacement front becomes self-regulating at the small scale. That is, wherever the front starting moving faster due to its intrinsic viscous instability, the larger shear creates more emulsion, which very effectively slows down the front. The emulsion turns the positive feedback of a viscous instability into a negative feedback of stability. This is the sealing effect that we wish to impart to sequestered CO₂. For CO₂ sequestration if we pre-position nanoparticles along potential leakage paths, and the CO₂ encounters such a path (e.g. a fracture in the caprock), a CO₂/brine foam will form, reducing the effectively permeability of the leakage path.

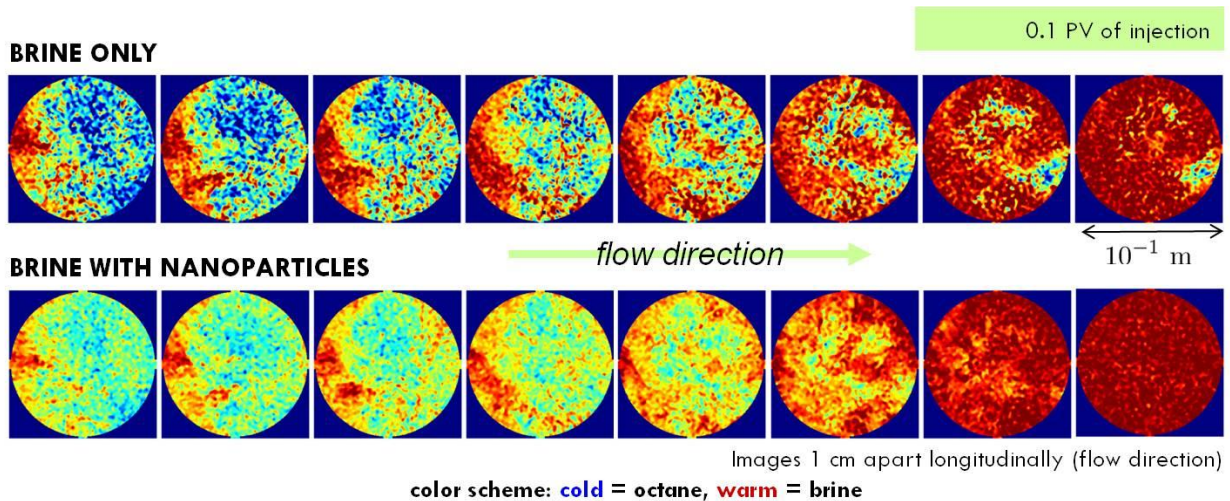


Figure 3. Upper part: Images of octane (cold colors) and brine (warm colors) after 0.1 pore volumes of octane are injected into a brine filled sandstone. Lower part: Images of octane (cold colors) and brine (warm colors) after 0.1 pore volumes of octane are injected into a naobrine filled sandstone.

We are currently setting up to perform the identical experiments using supercritical CO₂, performing experiments with a larger permeability contrast (i.e. with a fracture), and determining the dependence of the front dynamics on the concentration of nanoparticles. These experiments will determine the amount of nanoparticles needed to stabilize and seal the CO₂ displacement as a function of caprock geometry and CO₂ flow rate. The results can eventually be used in engineering CO₂ injection protocols.

Reference

Espinosa, D., Caldelas, F., Johnston, K., Bryant, S. L., Huh, C. (2010) Nanoparticle-Stabilized Supercritical CO₂ Foams for Potential Mobility Control Applications. Proceeding of the *2010 SPE Improved Oil Recovery Symposium* Tulsa, Oklahoma, USA, 24–28 April 2010.