UNSW
THE UNIVERSITY OF NEW SOUTH WALES
SYDNEY · CANBERRA · AUSTRALIA

Fundamentals of Wettability

Christoph H. Arns

Never Stand Still

School of Minerals and Energy Resources Engineering

ARTIST'S IMPRESSION COURTESY OF FRANCIS-JONES MOREHEN THORP

Some definitions

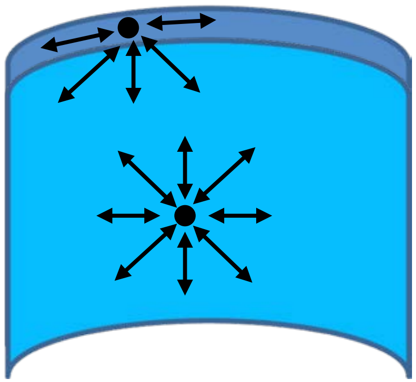
Wetting

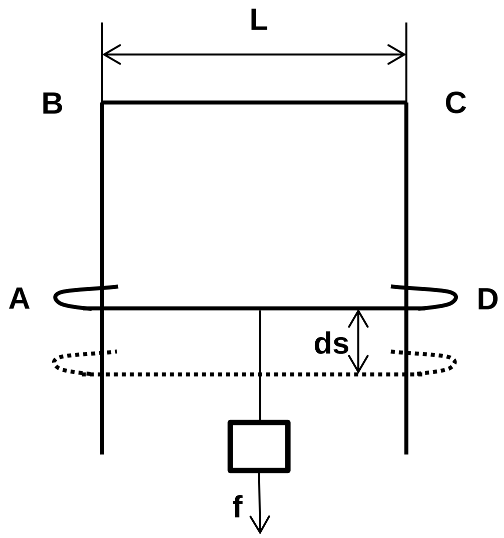
- ability of a liquid to remain in contact with a solid surface,
- resulting from intermolecular interactions when the two are brought together.

Wettability

- degree of wetting, determined by a force balance between adhesive and cohesive forces

Surface tension





Cohesive forces are stronger in the bulk and surface molecules are pulled inwards causing surface tension.

Soap film example (wireframe with one movable wire of length L); force *f* is necessary to balance surface tension:

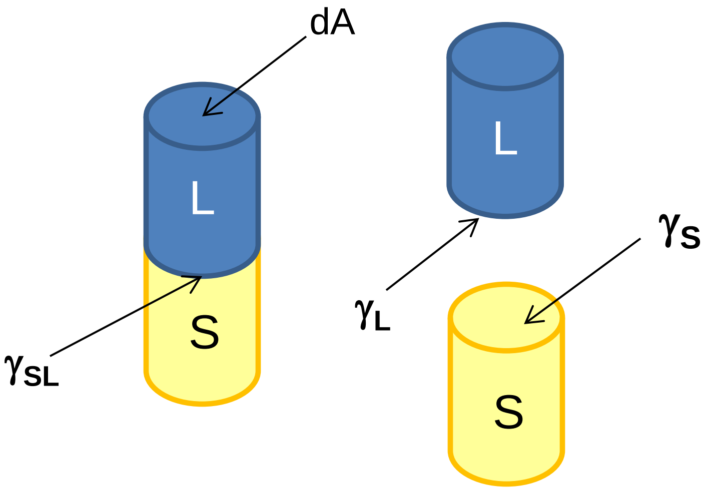
$$\gamma = f / 2L$$

Surface free energy (erg):

$$W = \gamma \Delta A$$

ΔA : area increase (cm)

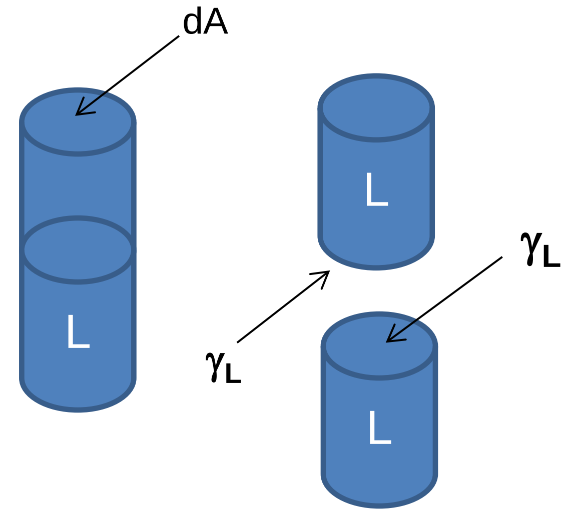
Work of adhesion and cohesion



Work of adhesion

$$W_a = \gamma_L + \gamma_S - \gamma_{LS}$$

(dA=1cm^2)



Work of cohesion

$$W_c = 2\gamma_L$$

Spreading coefficient

Comparing adhesive and cohesive work leads to the spreading coefficient:

$$S = W_a - W_c = (\gamma_L + \gamma_S - \gamma_{LS}) - 2\gamma_L$$

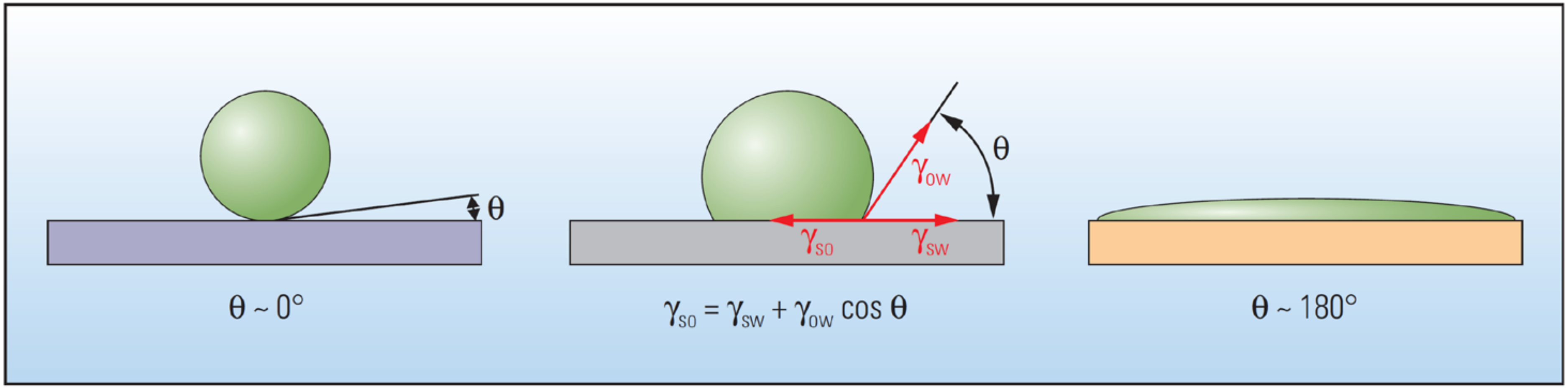
$$S = \gamma_S - (\gamma_L + \gamma_{LS})$$

$S > 0$: spreading (adhesion is stronger)

$S < 0$: form globules or a floating lens (cohesion prevails)

Contact angle

For S < 0 a contact angle can be defined:



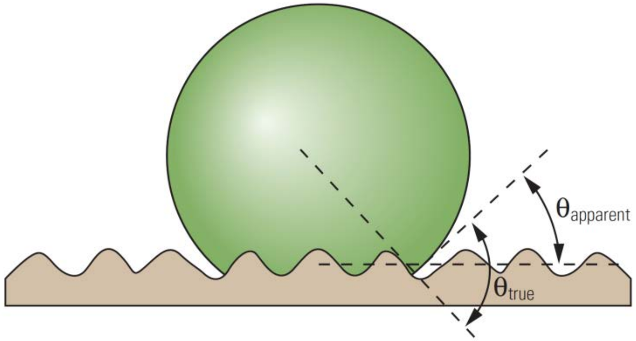
Contact angle. An oil drop (green) surrounded by water (blue) on a water-wet surface (*left*) forms a bead. The contact angle θ is approximately zero. On an oil-wet surface (*right*), the drop spreads, resulting in a contact angle of about 180°. An intermediate-wet surface (*center*) also forms a bead, but the contact angle comes from a force balance among the interfacial tension terms, which are γ_{so} and γ_{sw} for the surface-oil and surface-water terms, respectively, and γ_{ow} for the oil-water term.

[W. Abdallah et al., Oilfield Review 2007:44]

Contact angles on non-ideal surfaces

For non-ideal surfaces there is physical (e.g. roughness, micro-porosity) and/or chemical heterogeneity leading to

- apparent contact angles
- contact angle hysteresis: advancing and receding contact angles are different



[W. Abdallah et al., Oilfield Review 2007:44]

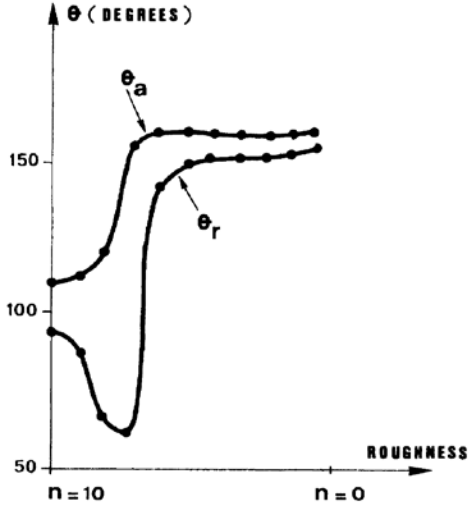
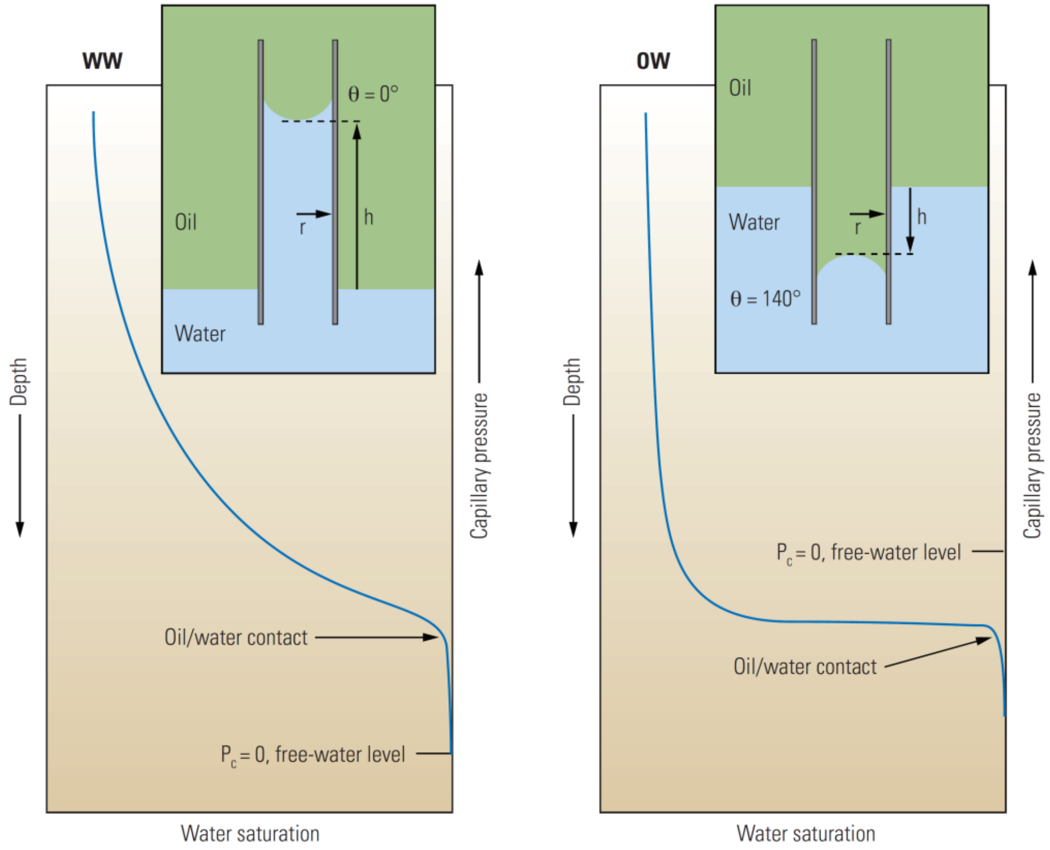


FIG. 8. Advancing and receding angles for water on fluorocarbon wax: a rough surface is obtained by spraying the wax. It is then made smoother by heating in an oven. The numbers *n* on the horizontal scale (0,1.0,10) refer to the number of successive heat treatments. Notice the abrupt jump of θ_r between $n=6$ and $n=7$ (after Dettre and Johnson, 1964).

[P de Gennes, Rev. Mod. Phys., 1985]

Capillary pressure and transition zones



$P_c = P_{nw} - P_w$

$P_c = \rho g h$

$P_c = 2 \gamma \cos\theta / r$,

where

P_c = capillary pressure

P_{nw} = pressure in nonwetting phase

P_w = pressure in wetting phase

ρ = density difference between phases

g = gravitational acceleration

h = height of capillary rise

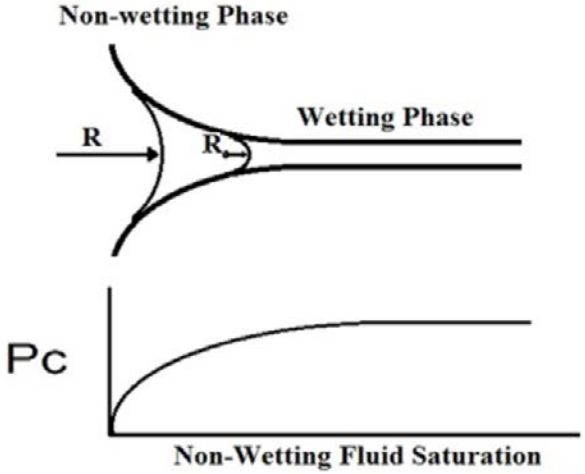
γ = interfacial tension

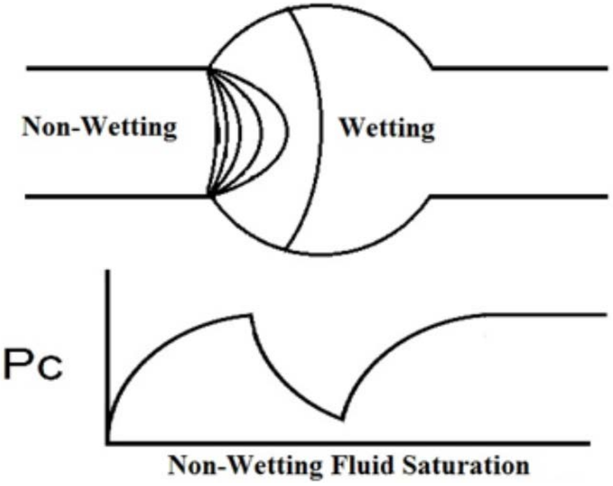
θ = contact angle

r = inner radius of capillary.

[W. Abdallah et al., Oilfield Review 2007:44]

Path integral for external work during drainage [*DE-FC26-03NT15408, Semi-Annual Report, 1/1/06–6/30/06, N. Morrow et al.*]





$$W_{100,S_a} = V_b\,\phi \int_{100}^{S_\alpha} P_c\,dS_\alpha$$

- Associated increase in surface energy:

$$\Delta F = \sigma_{\alpha\beta}\,(\Delta A_{\alpha\beta} + \Delta A_{\beta\gamma}\cos\theta)$$

- For zero contact angle:

$$\Delta F = \sigma_{\alpha\beta}\,(\Delta A_{\alpha\beta} + \Delta A_{\beta\gamma})$$

- Energy efficiency (=/ total work)

$$E_d = \frac{\sigma_{\alpha\beta}\,(\Delta A_{\alpha\beta} + \Delta A_{\beta\gamma})}{V_b\,\phi \int_{100}^{S_\alpha} P_c\,dS_\alpha}100$$

(Complete set of) 3D additive measures of morphology: the Minkowski functionals

$$V(Y) = V$$

$$S(Y) = \int ds$$

$$M(Y) = \int \frac{1}{2}\left[\frac{1}{r_1(s)} + \frac{1}{r_2(s)}\right] ds$$

$$K(Y) = \int \frac{1}{r_1(s) r_2(s)} ds$$

V: Volume

S: Surface Area

M: Mean curvature

K: Total curvature (Gaussian curvature)

ds: *surface element of* δY

r_1, r_2: *radii of curvature*

Y: *body in* IR^3

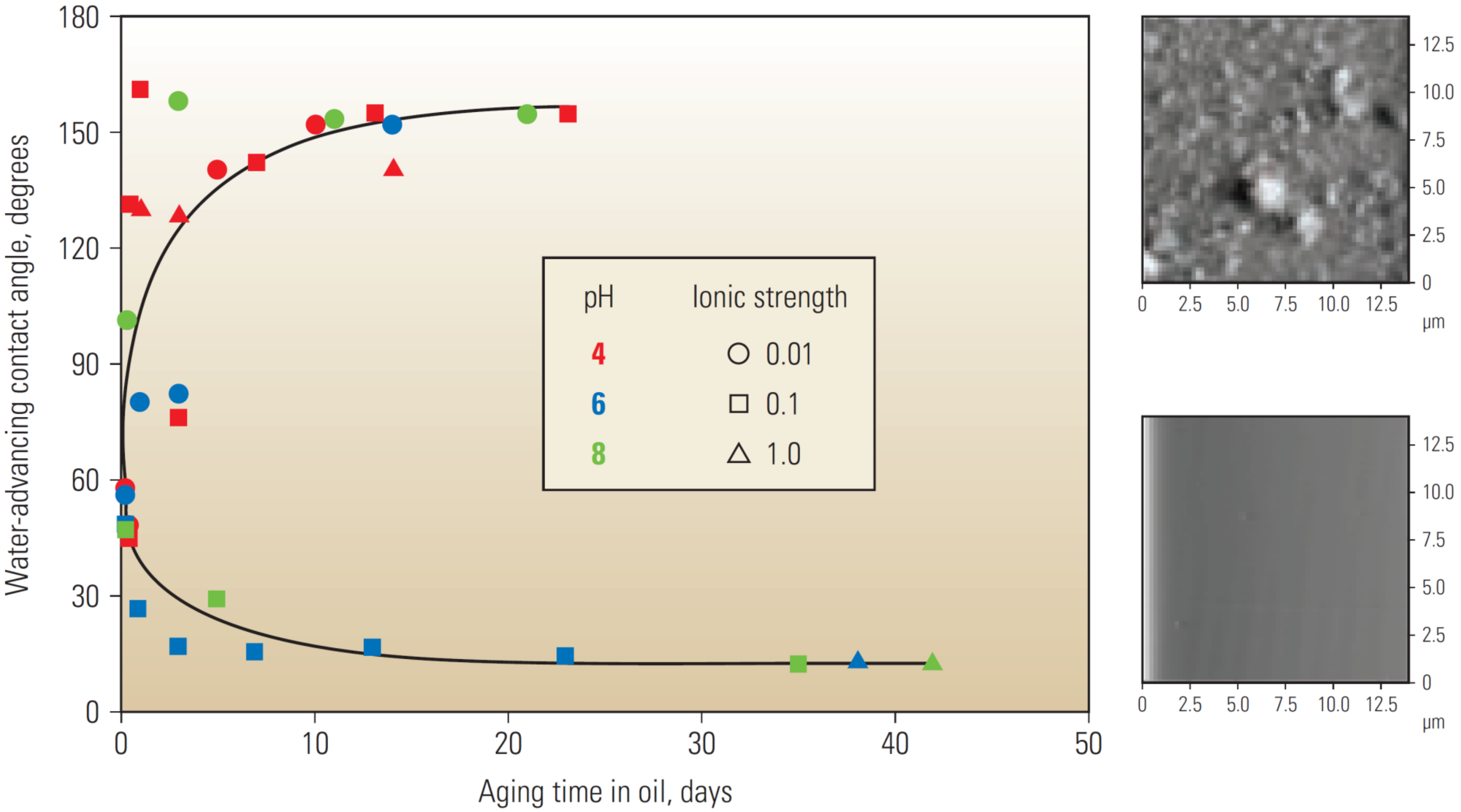
δY: *surface of Y*

Wettability reversal/alteration in SCAL (ageing)

- Core analysis applications
  - Typically require restoration of wettability state to strongly water-wet state
  - Subsequent alteration of core wettability to some degree of oil wetness (e.g. chemical)
  - Alternatively, ageing process may be used (ideally with native crude oils)
  - For benchmark outcrop rocks oil is arbitrary, making comparisons more complicated
  - Possible heterogeneous wettability as outcome of ageing (Kim et al. 1990; Graue et al. 2002)

- Wettability and asphaltene deposition studies involve at least two steps:
  - Setting initial condition of solid
  - Alteration of wettability by exposure of solid to long-chained hydrocarbons (at certain conditions)

Contact angle variations with aging…



[W. Abdallah et al., Oilfield Review 2007:44]

What do we see – wetting or wettability?

- Micro-CT, resolved fluids (3D/4D)
- Micro-CT, differential saturation; resolved fluids
- Micro-CT, differential saturation; fluids unresolved

- NMR

- Capillary pressure…

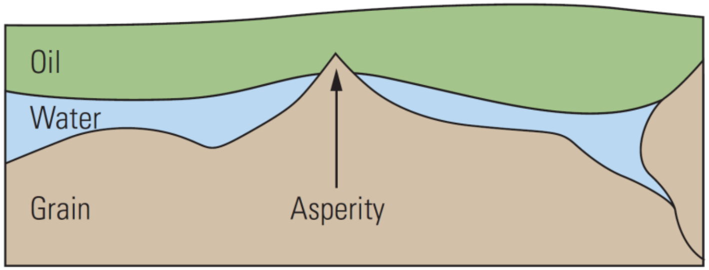
- Dielectric measurements…

Can we integrate this??

Plain morphological techniques mimicking wetting history

Capillary drainage transform

- Can model porous plate, gravity drainage, centrifuge, or MICP
- Assumes contact angle of 180 deg
- $4{,}000^3$ is fine (or even larger)
- Maybe useful as initial condition



Covering radius transformation

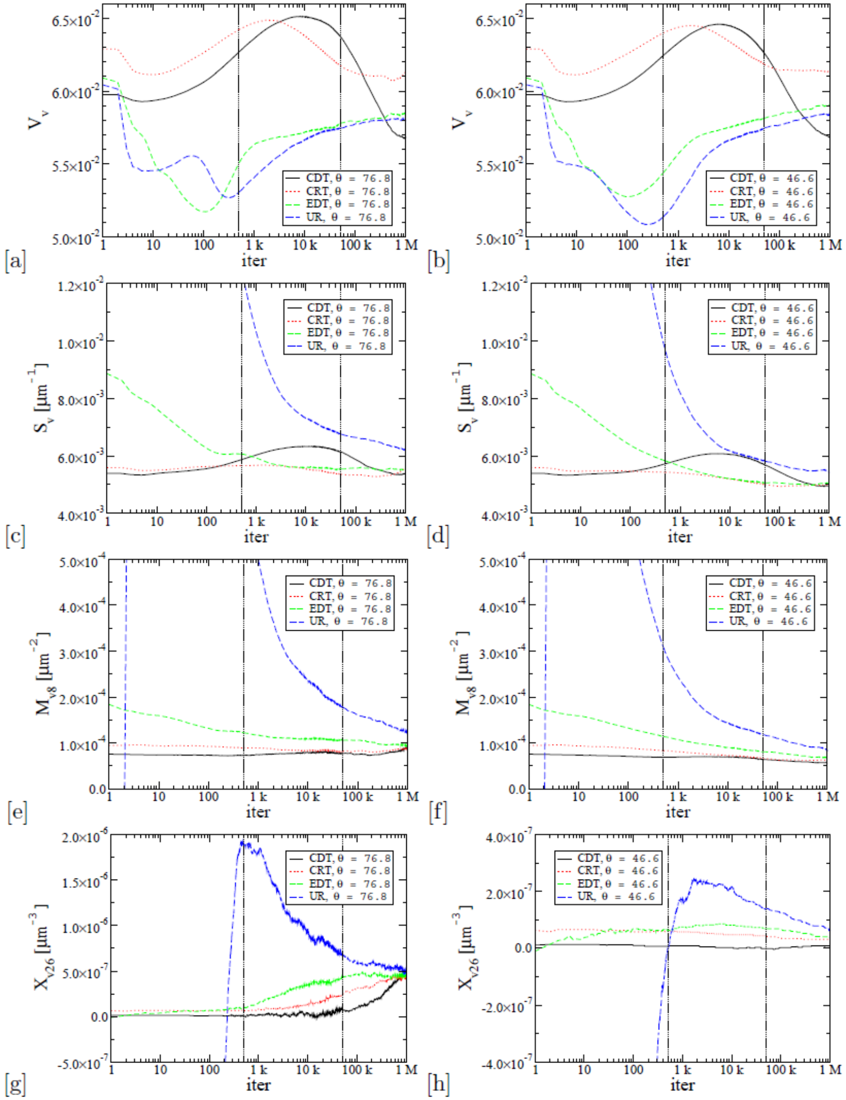
- Assumes contact angle of 180 deg
- $4{,}000^3$ is fine (or even larger)
- Maybe useful as initial condition

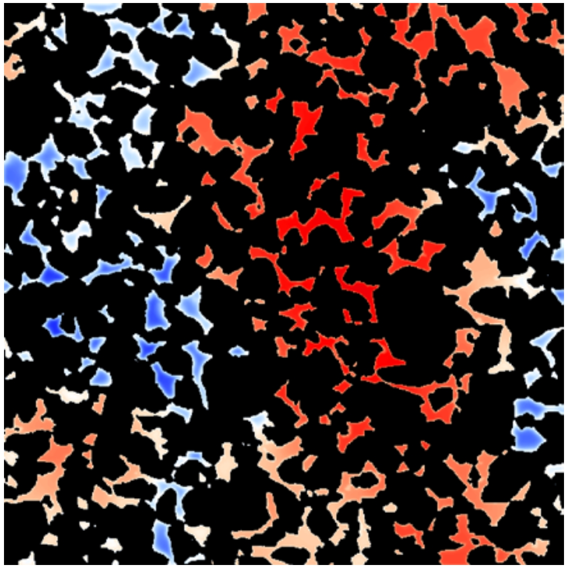
More complex morphological transforms

- e.g. M. Prodanovic; level-set techniques

Lattice Boltzmann techniques

- Accurate when it works
- Slow: practically limited to homogeneous rocks; ~1,000^3 feasible, but expensive
- Running many scenarios is prohibitively expensive
- Below: Berea (600x600x1200), at 300,000 iterations started from direct image





[LK Gbayan, submitted to WRR]

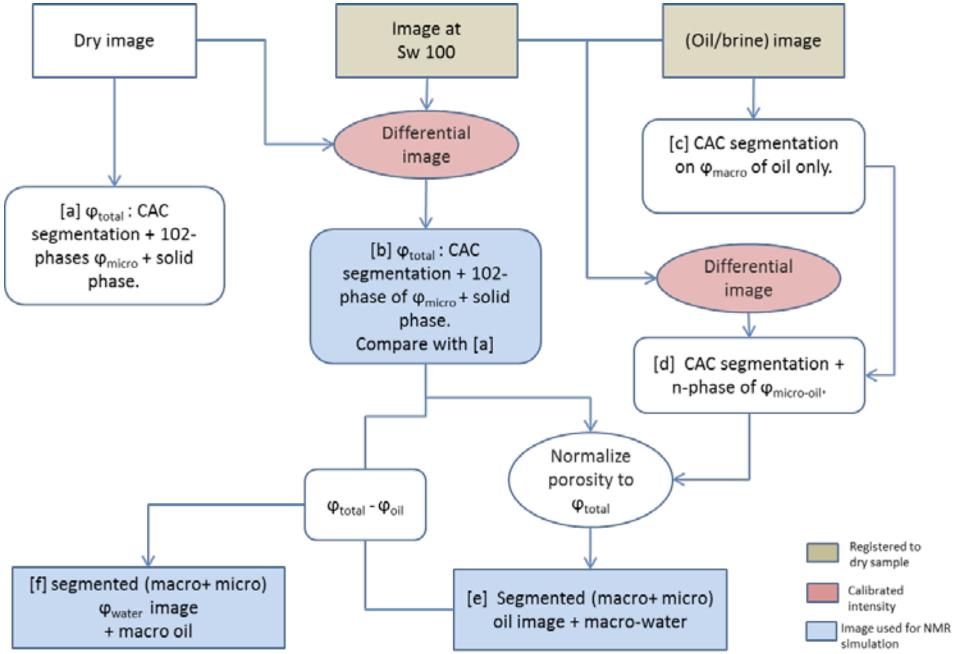
Network modeling

- Many parameters (needs calibration)
- Uses contact angles (or Pc curves)
- Fast (very very fast if comparing to LBM)
- Able to run large systems for heterogeneous rocks
- Less predictive

(=> Ask the experts in the room!!)

Direct imaging of (successive) saturation states

[Nawaf I. SayedAkram et al., SPWLA 2016, paper PP]



Dry image

Image at Sw 100

(Oil/brine) image

Differential image

[c] CAC segmentation on φ_{macro} of oil only.

[a] φ_{total} : CAC segmentation + 102-phases φ_{micro} + solid phase.

[b] φ_{total} : CAC segmentation + 102-phase of φ_{micro} + solid phase.
Compare with [a]

Differential image

[d] CAC segmentation + n-phase of $\varphi_{micro\text{-}oil}$.

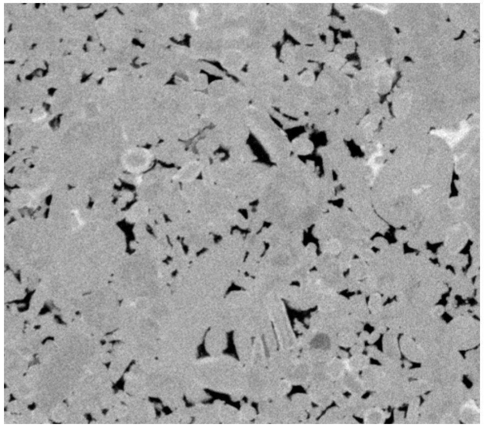
Normalize porosity to φ_{total}

φ_{total} - φ_{oil}

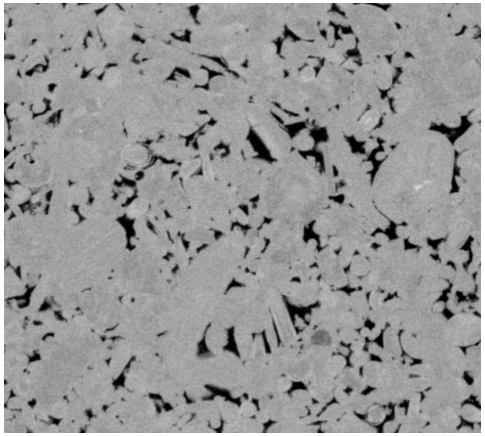
[f] segmented (macro+ micro) φ_{water} image + macro oil

[e] Segmented (macro+ micro) oil image + macro-water

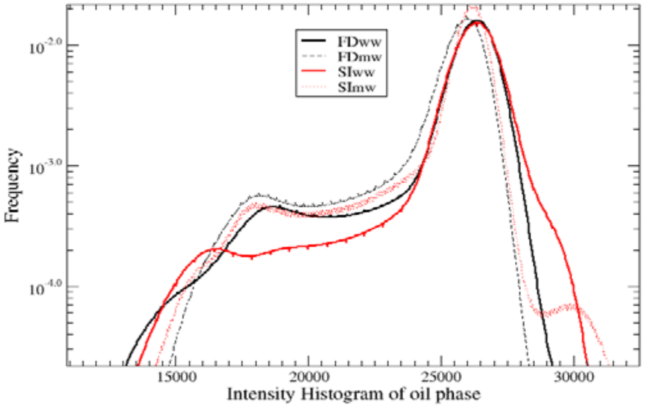
- ▨ Registered to dry sample
- 🟥 Calibrated intensity
- 🟦 Image used for NMR simulation



SI_WW

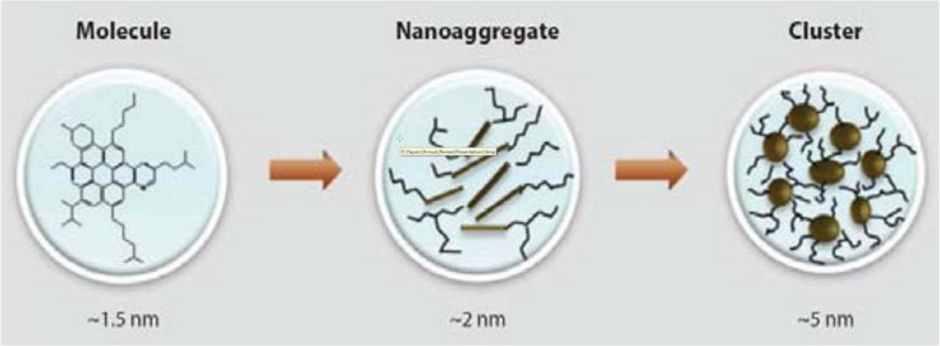


SI_MW



Asphaltenes

- Heaviest end polar fraction of crude oils, made of carbon, hydrogen, nitrogen, oxygen, sulfur and trace amounts of metal
  - insoluble fraction of oil in light alkanes
  - Soluble in basic aromatic solvents (Speight 1971, Appl. Spectrosc. Rev. 5, 211)
- Asphaltene dynamics in crude oils is major issue in petroleum engineering
  - asphaltene deposition
  - wettability change
  - permeability reduction
- Dynamics can be described by Yen-Mullins model (2010, Energy & Fuels 24, 2179) at molecular level
  - assumes asphaltene molecule as single moderately large polycyclic aromatic hydrocarbon with peripheral alkanes
  - Two-step aggregation mechanism: 1. formation of small nanoaggregates, 2. further clustering of aggregates



[Mullins et al.]

NMR wettability study 1/2

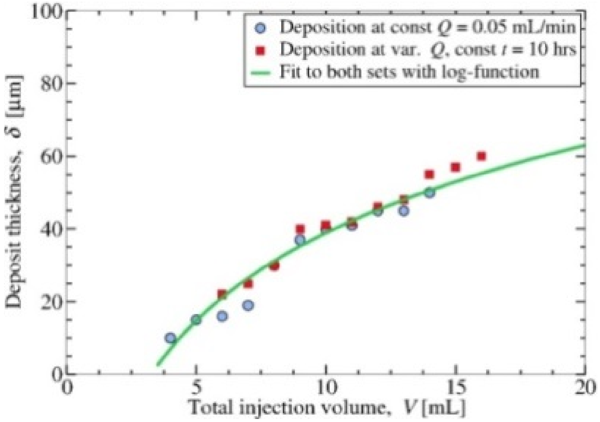
- Rate of asphaltene deposition in sandstone saturated with various synthetic oils after ageing and cleaning cycles; influence of oil composition on ageing efficiency
- Rate of wettability change and potential correlation to deposition rate
- Detection of asphaltene deposition and wettability change using NMR T_2 relaxation and T_2-store-T_2 relaxation exchange experiments
- Characterisation of mixed-wet systems
- Effect of surface-to-volume (surface topology) on deposition rate (and wettability change)

I. Shikhov et al., *Fuel*, 220:692-705 (2018).

NMR wettability study 2/2

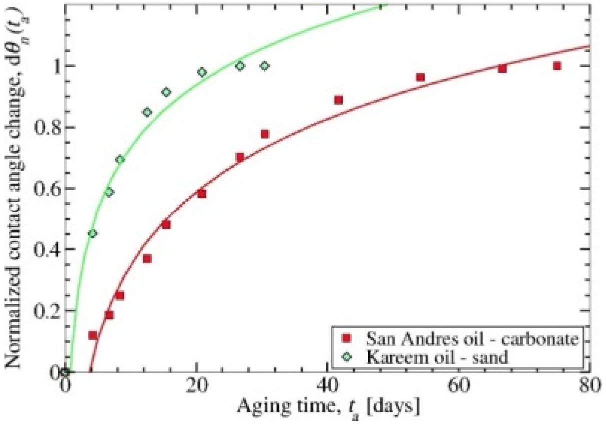
Asphaltene growth in capillary tube over 48h

[Zhuang et al., JPSE 2016, 145, 77]

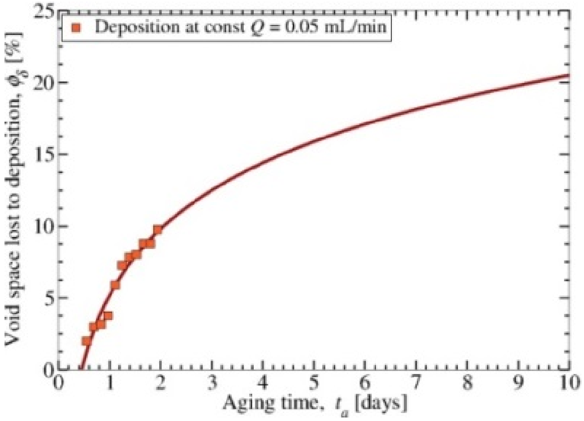


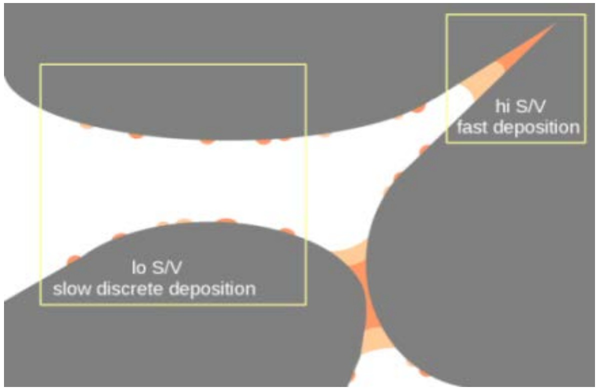
Excerpt from Treiber et al., SPEJ 1972, 12(6):531

(replotted as normalized contact angle change)



As above, but void space loss over ageing time

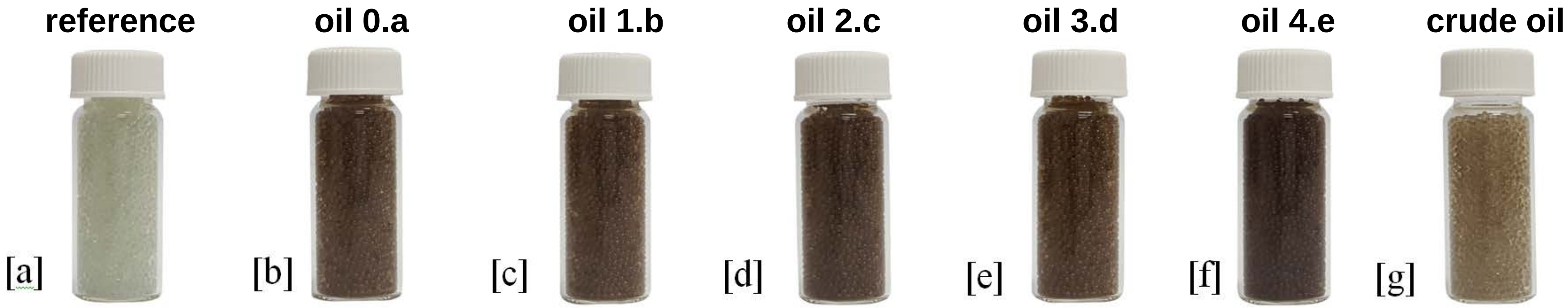




I. Shikhov et al., *Fuel*, 220:692-705 (2018).

Ageing procedure

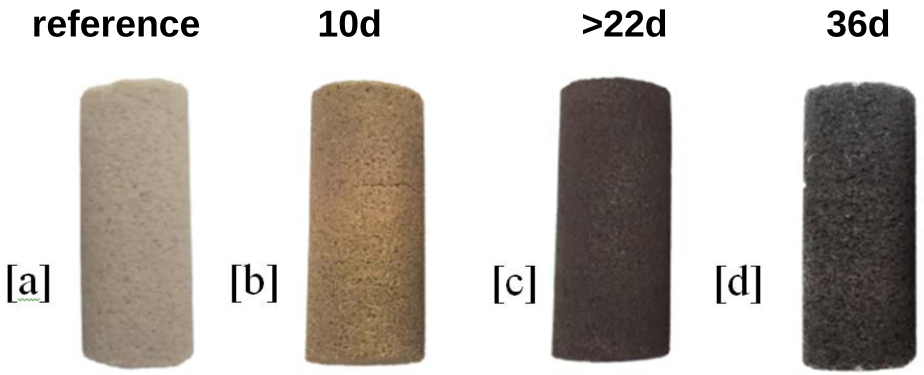
Bead packs after 14h ageing



Total sample #s

- 6+2 bead packs
- 36+2 Bentheimer plugs (3 oils, 12 time intervals)
- each sample aged once
- cleaning by soaking with n-hexane at room temperature for 6 days, replacing fluids every 12h

Bentheimer sandstone aged in synthetic oil 3.d



I. Shikhov et al., *Fuel*, 220:692-705 (2018).

Fluids

Table 1. Components of mixtures representing five synthetic oils.

Hydrocarbon	Bitumen, wt.%	Crude oil, wt.%	n-$C_{16}H_{34}$, wt.%	Toluene, wt.%
Synth. Oil "0.a"	41.7	0.0	0.0	58.3
Synth. Oil "1.b"	25.0	0.0	40.0	35.0
Synth. Oil "2.c"	15.0	30.0	15.0	40.0
Synth. Oil "3.d"	10.0	0.0	50.0	40.0
Synth. Oil "4.e"	5.0	30.0	30.0	35.0

Table 2. SARA analysis of base hydrocarbons and mixtures.

Hydrocarbon	Saturates, %	Aromatics, %	Resins, %	Asphaltenes, %	Volatiles + LOC
Crude oil	38.40	5.60	4.20	3.49	48.30
Bitumen C170	12.90	28.80	41.70	15.72	0.90
Synth. Oil "0.a"	5.38	70.31	17.39	6.56	0.38
Synth. Oil "1.b"	43.23	42.20	10.43	3.93	0.23
Synth. Oil "2.c"	28.46	46.00	7.52	3.41	14.63
Synth. Oil "3.d"	51.29	42.88	4.17	1.57	0.09
Synth. Oil "4.e"	42.17	38.12	3.35	1.83	14.54

I. Shikhov et al., *Fuel*, 220:692-705 (2018).

Recent results

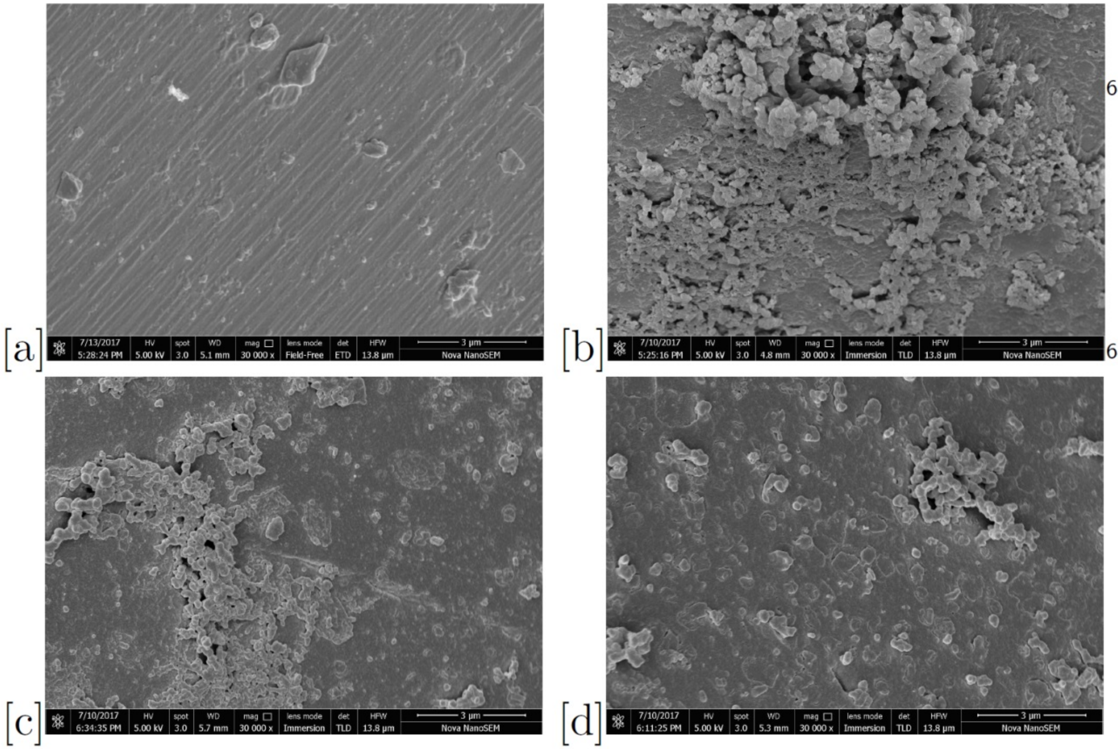


Figure 8: FESEM images acquired at 30,000-fold magnification shows [a] reference quartz grain surface; deposition and coverage of grain surface after 13 days of ageing in [b] oil 3.d, [c] oil 2.c and [d] oil 1.b, which also shows exposed quartz surface.

I. Shikhov et al., *<u>Fuel</u>*, 220:692-705 (2018).

Recent results

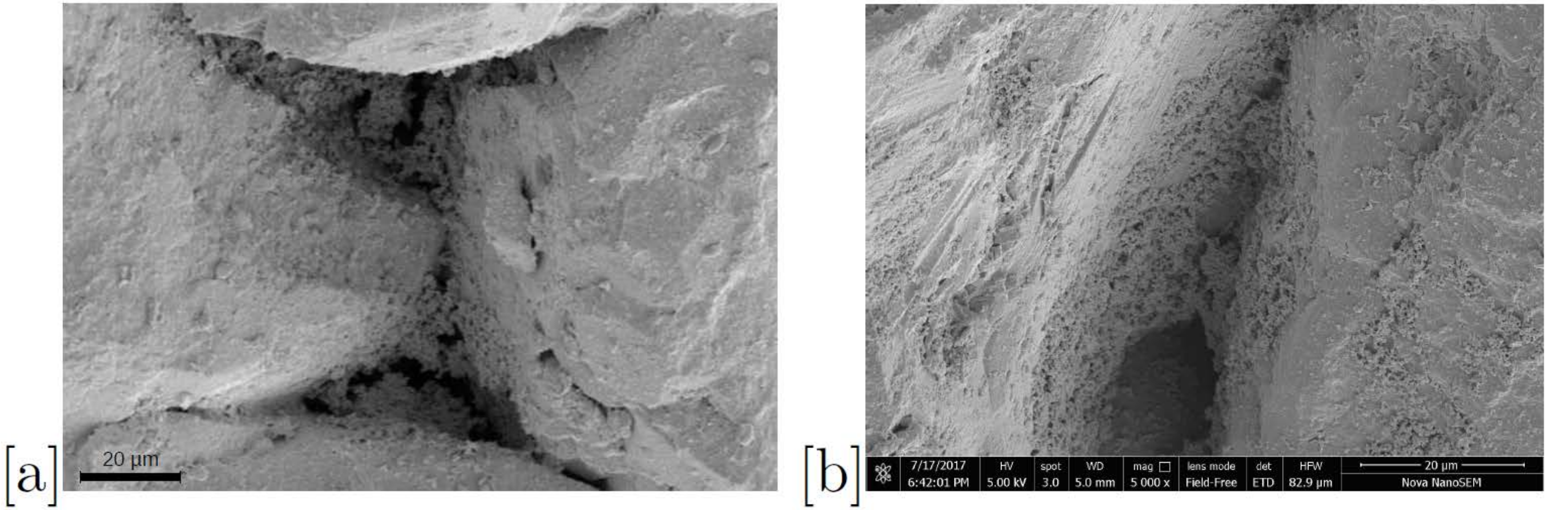


Figure 9: FESEM images showing developed accumulations in pore crevices: [a] in a core aged over 13 days in oil 2.c (such pores are rare), a segment of 1000x magnification image; [b] in a core aged over 52 days in oil 1.b (such pores are quite frequent), 5000x magnification.

I. Shikhov et al., *Fuel*, 220:692-705 (2018).

Recent results

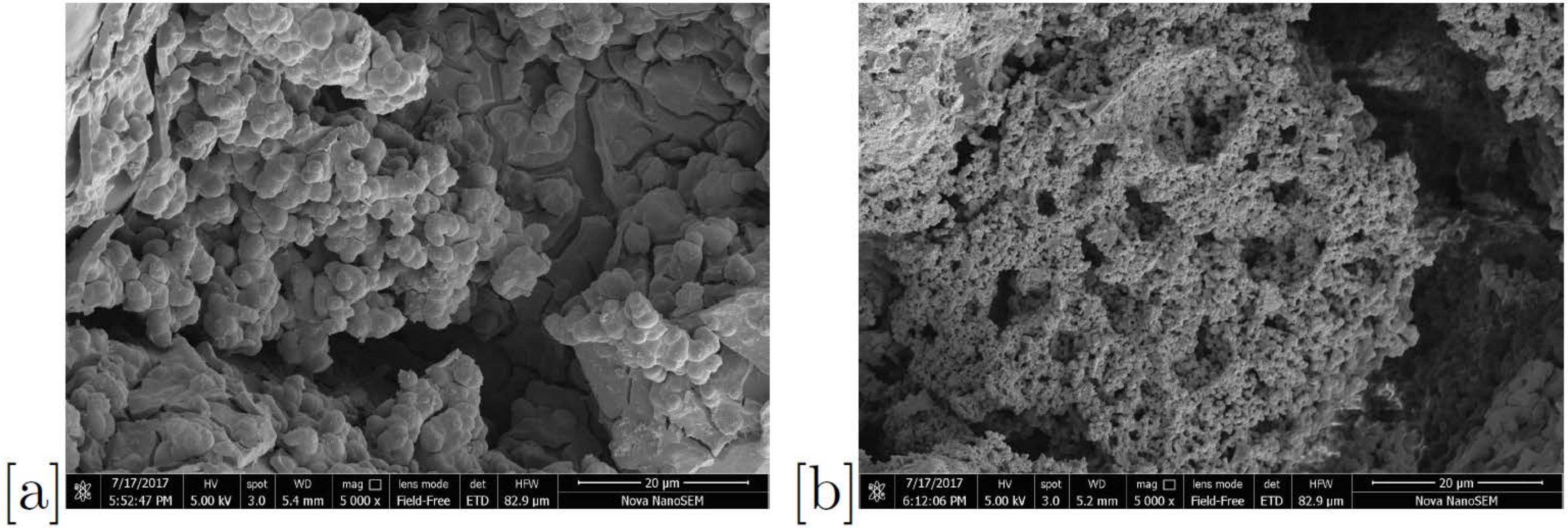


Figure 10: FESEM images obtained at 5000x magnification show aggregates in nearly completely clogged pores after 52 days of ageing in [a] oil 3.d; [b] oil 2.c.

I. Shikhov et al., *Fuel*, 220:692-705 (2018).

Recent results

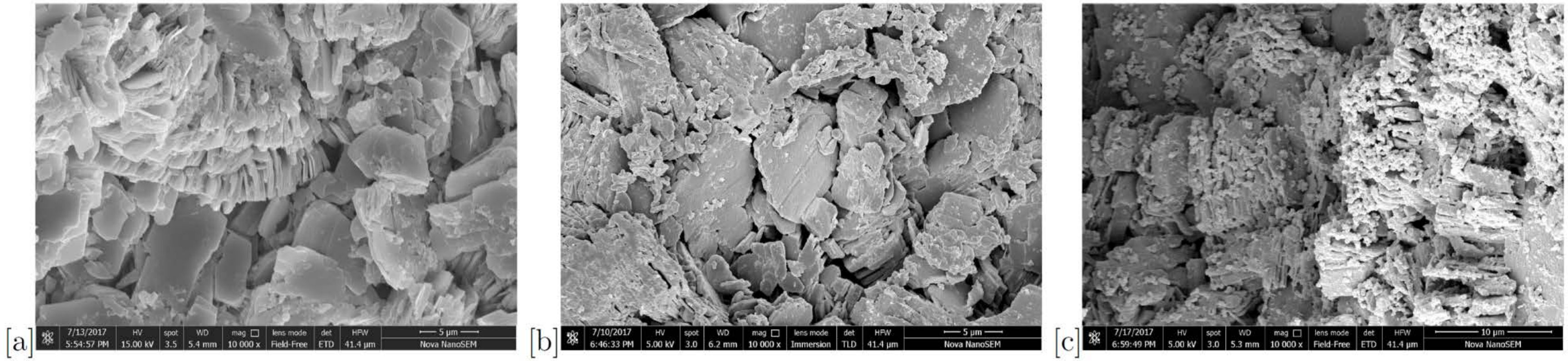


Figure 11: SEM images acquired at 10,000-fold magnification show kaolinite pockets in Bentheimer sandstone [a] clean reference; [b] after ageing in oil 2.c for 13 days; [c] after 52 days of ageing in oil 1.b.

I. Shikhov et al., *Fuel*, 220:692-705 (2018).

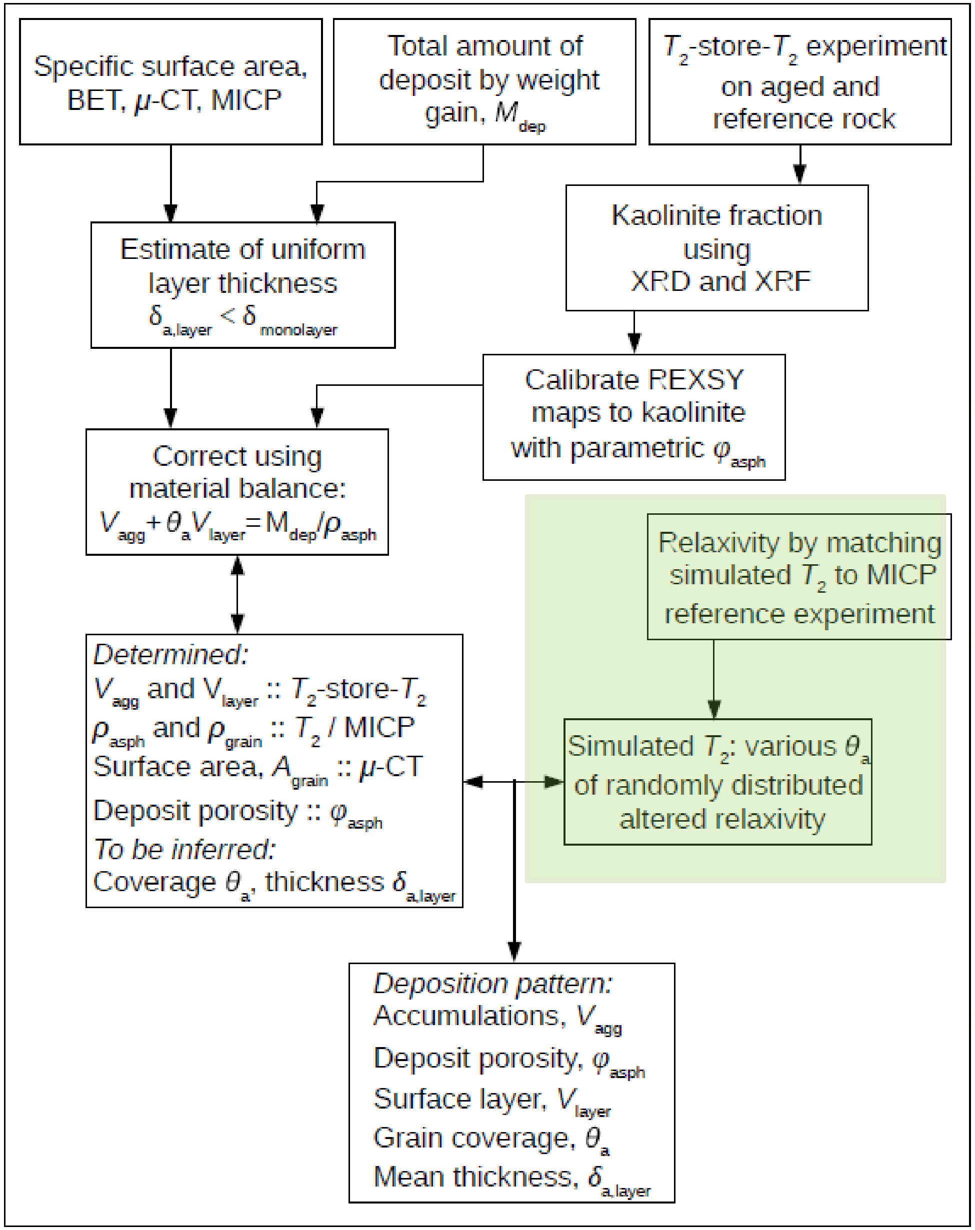
Workflow

- Combination of different techniques to quantify asphaltene deposity mode (single technique not sufficient)
- NMR alone has not enough sensitivity either
- Micro-CT based scenario modeling desired: need to fix as many parameters as possible

$$V_{a,total} = \frac{M_{dep}}{\rho_{asph}\ \phi_{asph}} = V_{agg} + V_{layer} =$$

$$= V_{agg} + \theta_a\ A_{grain}\ \delta_{a,layer},$$

$$\theta_a = \frac{V_{a,total} - V_{agg}}{\delta_{a,layer}\ A_{grain}} = \frac{\rho_{2,obs} - \rho_{2,grain}}{\rho_{2,asph} - \rho_{2,grain}},$$



Specific surface area, BET, μ-CT, MICP

Total amount of deposit by weight gain, M_{dep}

T_2-store-T_2 experiment on aged and reference rock

Estimate of uniform layer thickness $\delta_{a,layer} < \delta_{monolayer}$

Kaolinite fraction using XRD and XRF

Calibrate REXSY maps to kaolinite with parametric φ_{asph}

Correct using material balance: $V_{agg} + \theta_a V_{layer} = M_{dep}/\rho_{asph}$

Relaxivity by matching simulated T_2 to MICP reference experiment

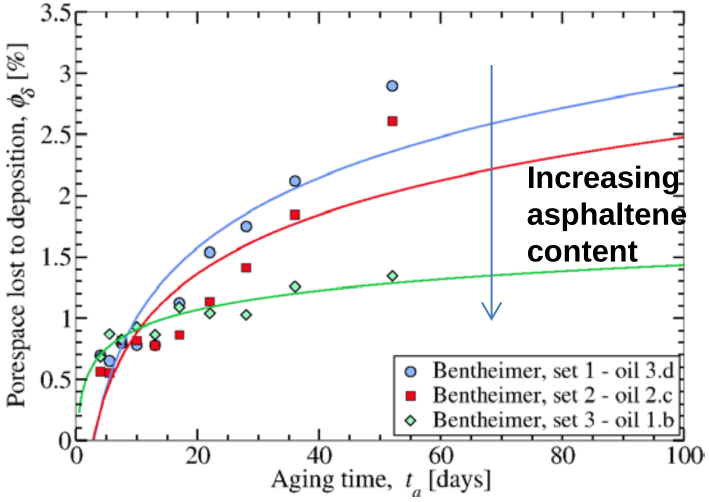
Determined:
V_{agg} and V_{layer} :: T_2-store-T_2
ρ_{asph} and ρ_{grain} :: T_2 / MICP
Surface area, A_{grain} :: μ-CT
Deposit porosity :: φ_{asph}
To be inferred:
Coverage θ_a, thickness $\delta_{a,layer}$

Simulated T_2: various θ_a of randomly distributed altered relaxivity

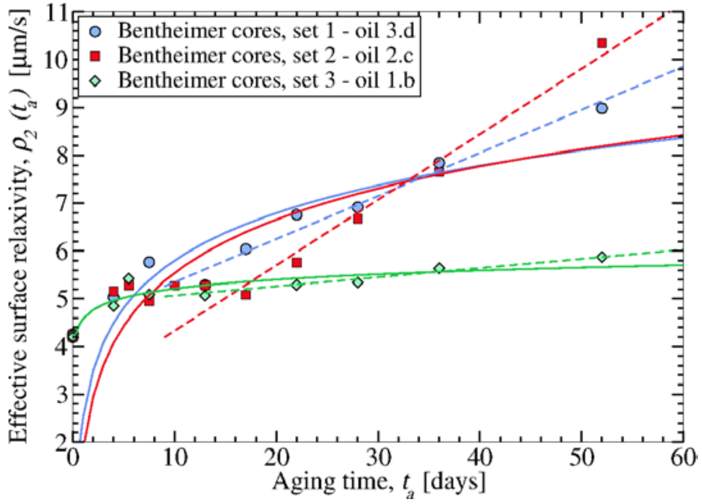
Deposition pattern:
Accumulations, V_{agg}
Deposit porosity, φ_{asph}
Surface layer, V_{layer}
Grain coverage, θ_a
Mean thickness, $\delta_{a,layer}$

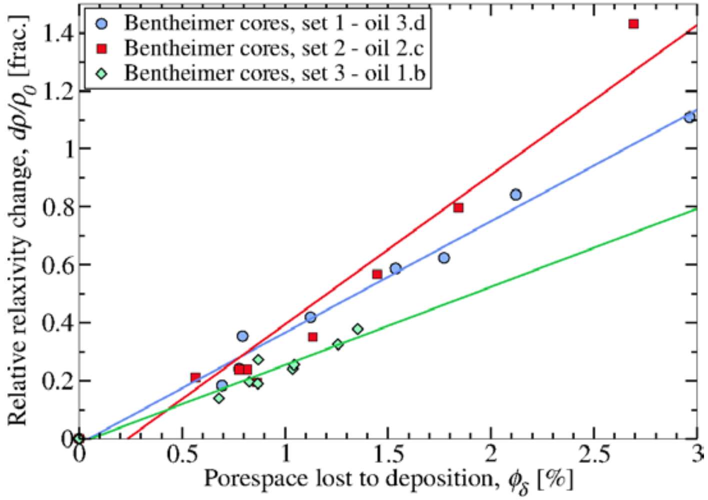
I. Shikhov et al., *Fuel*, 220:692-705 (2018).

Observed deposition dynamics



Increasing asphaltene content



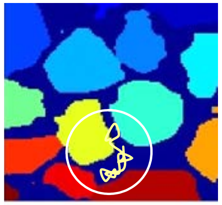


Classical NMR interpretation

$$M(t) = M_0(t)\sum_{p=1}^{N} a_p \exp\left[-\frac{t}{T_{2p}}\right]$$

Relaxation rates

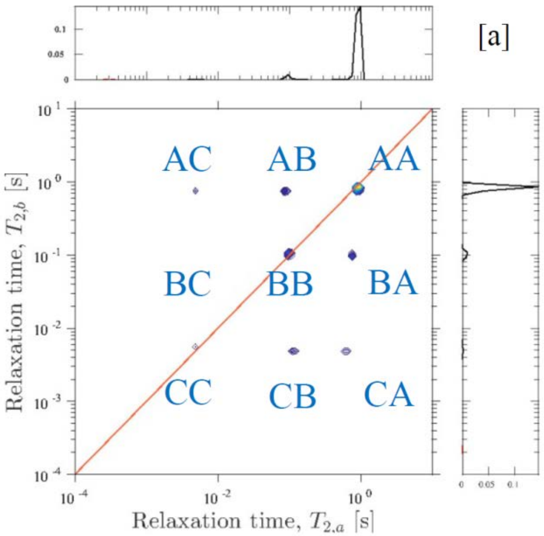
$$\frac{1}{T_{2p}} = \frac{1}{T_{2b}} + \frac{1}{NV_p}\sum_{i=1}^{N}\rho_{pi}S_{pi}$$



I. Shikhov et al., *Fuel*, 220:692-705 (2018).

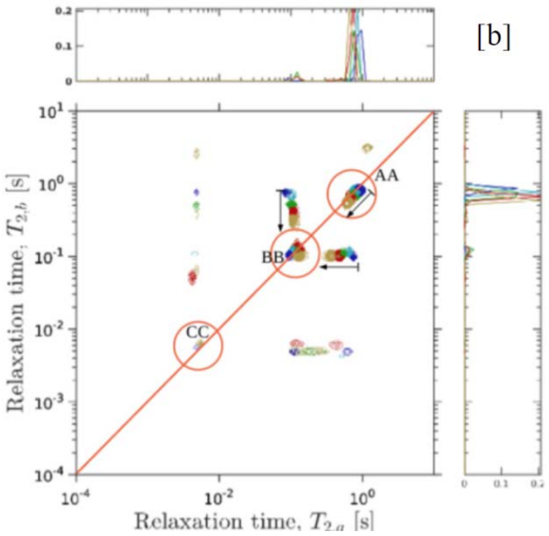
NMR T_2-store-T_2 relaxation exchange

reference



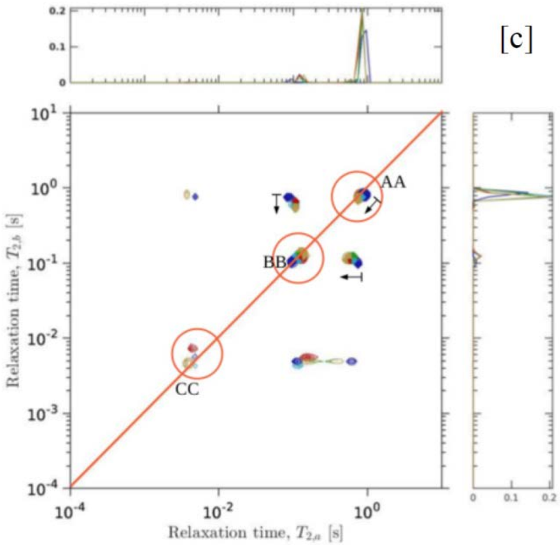
oil 3.d (0,4,22,36,52d)

(lower asphaltene content)



oil 1.b (0,4,22,36,52d)

(higher asphaltene content)



- T2a: 50,000 echoes linearly spaced (TE = 200μs)
- T2b: 80 echoes selected (log-spaced)
- Repeat after 60s (to insure stable temperature)
- SNR between 60 and 70 (8 scans)
- Mixing time τ_m = 100ms

I. Shikhov et al., *Fuel*, 220:692-705 (2018).

Some comments

- Wettability is a very large field…
- Only some points could be raised
- I approached mainly from the point of having a static distribution of fluids with a target for modeling the behavior of a core plug
- In the future we will consider disjoining pressure and its components (van der Waals, electrostatic, structural forces)

Thank you!