Effect of Asphaltenes on Water Wetting & Internal Corrosion in Oil-Water Pipe Flow

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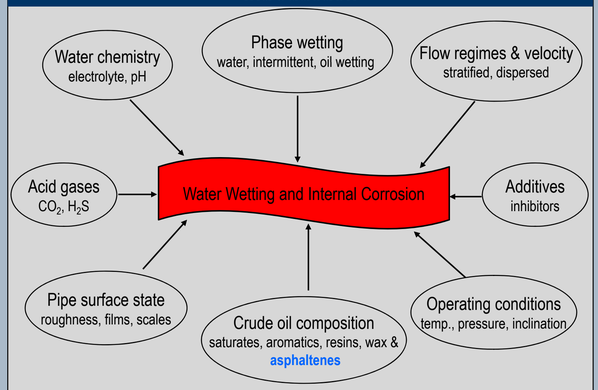
Introduction



Literature review - asphaltene

Asphaltenes are nonvolatile constituents which are found in crude oil, along with resins, aromatics and saturated hydrocarbons.

Characteristics of asphaltenes:

- Dark brown to black friable solids that have no definite melting point and usually foam and swell on heating to leave a carbonaceous residue. [1]
- Defined as the portion of crude oil insoluble in *n*-alkanes such as *n*-pentane or *n*-heptane yet soluble in aromatics such as benzene or toluene. [2]
- The highest molecular weight and most polar constituents in crude oil. The molecular weight is in the range of 400 to 1500 amu with a maximum around 750 amu. [1]
- Mainly composed of polyaromatic units with oxygen, nitrogen, and sulfur, (NSO-compounds) combined with minor amounts of heavy metals, particularly vanadium (V) and nickel (Ni) which occur in porphyrin structures. [3]
- Since asphaltenes are a portion of crude oil, their identity changes as the source of crude oil changes.
- So complex that there is no model compound available which resemble asphaltenes, to carry out tests asphaltenes needs to be extracted from crude.

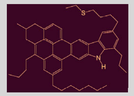


Figure 1: Asphaltene Structure (MW 708 amu). [4]

References:

[1] J.G. Speight, "Petroleum asphaltene part 1: asphaltene, resins and the structure of petroleum", Oil & Gas Science and Technology-Rev. IFP, Vol. 59, No. 5, pp 467-477, 2004.
[2] P.K. Kilpatrick et al., "Aggregation and solubility behavior of asphaltenes and their subfractions", Journal of Colloid and Interface Science, Vol. 267, pp 178-190, 2003.
[3] J.R. Becker, "Crude oil waxes, emulsions and asphaltenes", Tulsa: Penn Well Books,1997.
[4] Oliver C. Mullins, "Asphaltenes and polycyclic aromatic hydrocarbons", Schlumberger-doll research presented at SSRL 30th conference.

Research objectives

The following objectives are important to study effects of asphaltenes on water wetting and internal corrosion in oil-water pipe flow.

- Study the corrosion inhibitive benefits of asphaltenes in oil-water pipe flow.
- Study the effect of asphaltenes on the flow pattern of two phase oil-water flow.
- Study the impact of asphaltenes on pipe wall wetting.

Asphaltene precipitation procedure

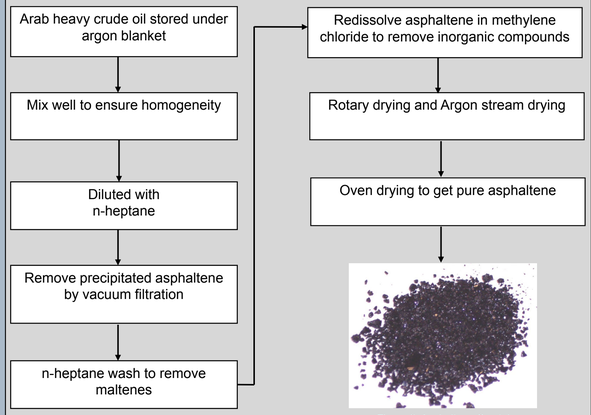


Figure 2: Asphaltene Crystals

Experimental set-up and test matrix

Glass cell (corrosion inhibition tests)

Table 1: Glass cell test matrix

Asphaltene source	Arab heavy crude oil
Oil phase	Toluene* (solvent)
Asphaltene concentration	0, 0.1, 1 and 5 wt% in toluene
Material	Carbon steel (C-1018)
Water phase	1.0 wt% NaCl
Partial pressure of CO_2	1 bar
System pressure	1 bar
pH	5.0
Temperature	25°C
Rotation speed	1000 rpm

*Toluene is neutral solvent and representative of crude oil.

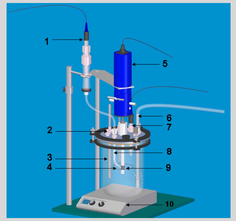


Figure 3: Schematic of glass cell

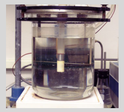
1. Reference electrode
2. Gas outlet
3. Temperature probe
4. Pt counter electrode
5. Rotator
6. Gas inlet
7. pH-electrode
8. Luggin capillary
9. Working electrode
10. Hot Plate

Experimental procedure

1. Glass cell (corrosion inhibition tests)

Step 1: Partitioning

This is the initial condition. Coupon is in water phase.



Solvent + Asphaltene added at the top. Keeping coupon in water phase, corrosion rate measurement done every 20 minutes.

Figure 4: Partitioning step

Step 2: Corrosion inhibition

Initial condition coupon wetted by water

Coupon wetted by asphaltene for 15 min.

Coupon put back in water phase measure corrosion rate

Figure 5: Corrosion inhibition step

Step 3: Persistency

After repeating corrosion inhibition step several time, coupon (working electrode) is permanently placed back in the water phase and corrosion rate measurements are done.

2. Contact angle & Interfacial tension tests (surface active properties)

Table 2: Surface active properties test matrix

Oil Phase	Toluene + Asphaltene
Asphaltene concentration	0, 0.1, 1, 5% wt in toluene
Water Phase	1.0 wt% NaCl, pH 5.0, CO_2 saturated, 25°C
Material (wettability test)	C-1018

Effect on Wettability : Steel-oil contact angle tests
Effect on flow pattern : Oil-water interfacial tension tests

Wettability test design

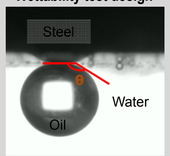
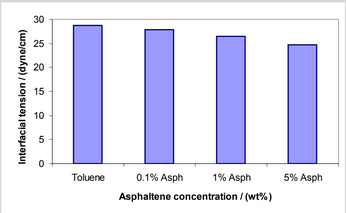


Figure 6: Oil droplet in water phase

Test results

Oil-water interfacial tension tests



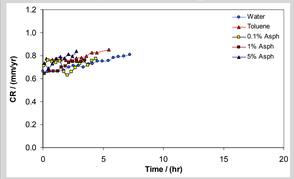
Oil-water interfacial tension is an important parameter to understand the effect of addition of asphaltene on oil water flow pattern.

After addition of asphaltene, oil water interfacial tension does not decrease by significant amount. Hence addition of asphaltene does not affect oil-water flow pattern.

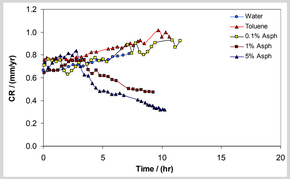
Test results

Glass cell (corrosion inhibition tests)

Step 1: Partitioning



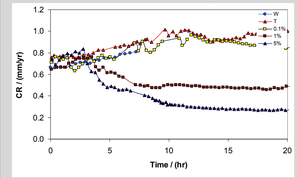
Step 2: Corrosion inhibition

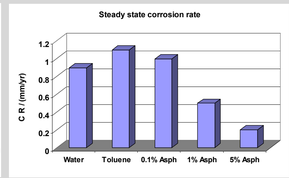


Corrosion rates for asphaltene test matrix is nearly same as pure water inhibition case. Hence it can be concluded that asphaltene does not partition into water phase.

Pure toluene and toluene + 0.1% asphaltene solution has no effect on corrosion rate. Higher concentrations of asphaltene(1% & 5%) causes significant reduction in corrosion rate.

Step 3: Persistency

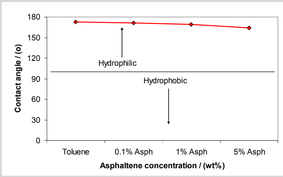


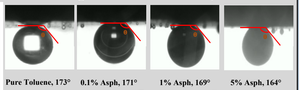


1% and 5% asphaltene has reduction in corrosion rate which means a protective layer of asphaltene formed on coupon. From persistency test it was observed that corrosion rate stabilizes hence the formed protective layer is non reversible and permanent.

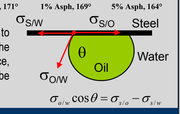
For 1% asphaltene the steady state corrosion rate falls by 50% and by 75% for 5% asphaltene, as compared to pure water corrosion rate.

Wettability tests (Steel-oil contact angle measurement)





Addition of asphaltene to oil do not affect the wettability of steel surface, and it continues to be hydrophilic



$$\sigma_{s/w}\cos\theta = \sigma_{s/o} - \sigma_{s/w}$$

Conclusions

- Asphaltene causes significant reduction in corrosion rate.
- As concentration of asphaltene increases corrosion rate decreases.
- Asphaltene forms strong protective layer on steel surface which acts as a barrier for corrosive agent and hence reduces the corrosion rate.
- Asphaltene (dissolved) does not affect oil water flow pattern in pipe flow.
- Asphaltene does not affect the wettability of the steel surface, it continued to be hydrophilic.

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Sponsors: