

Chemical mitigation of calcium naphthenate deposits and sodium carboxylate emulsions by interface crowding inhibitors

Mohammed M. Ahmed^{a,*}, K. S. Sorbie^a, J.P. Vijn^b

^a Institute of Petroleum Engineering, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS, Scotland, UK

^b Champion Technologies Europe BV, Langestraat 169, 7491AE Delden, The Netherlands
(* corresponding author: mohammed.murtala@pet.hw.ac.uk or maahmed2@yahoo.com)

Formation of either hard type “calcium naphthenate precipitates” or soft type “sodium carboxylate/emulsions” during crude oil production can lead to severe flow assurance problems. These may occur due to certain physical and chemical changes which happen when acidic or heavy crudes are produced [1]. A number of different mitigation approaches have been published in the open literature to assist in achieving trouble free oil production by preventing naphthenate formation. No one particular approach is considered to be the most efficient in all cases but rather it is field specific depending on the particular field situation. Originally, this problem was solved by deploying large volumes of (usually organic) acid but more recently the use of lower levels of chemical inhibition has been used very effectively.

In this paper, 4 naphthenate inhibitors (NI 1, NI 2, NI 3 and NI 4) were tested in the laboratory using static bottle test experiments on extracts from field calcium naphthenate, sodium carboxylate and emulsion forming crude oil samples. To form the naphthenate deposit the oil was mixed with synthetic brine with pH adjusted to 9 (Na⁺: 25000ppm & Ca⁺⁺: 20000ppm). Naphthenic acids used in this study were extracted from field calcium naphthenate and sodium carboxylate deposits or emulsions using a method based on the extraction procedure described in [2]. Experiments have been performed for a range of naphthenic acid concentrations in the extracts i.e. [HA] = 7500ppm, 3000ppm and 1000ppm. (TAN for HA = Mwt 200 ranges from 2.1 to 0.84 and 0.28 mg/g) and TAN for Mwt 1230 ranges from 0.34, 0.15 and 0.05 mg KOH/g oil)

The results showed good inhibition efficiency using NI 1 & NI 4 naphthenate inhibitors in both extracts of calcium naphthenate, sodium carboxylate and emulsion forming crude, whilst NI 2 & NI 3 inhibitors were observed to have some compatibility problem at higher brine pH. However, NI 2 & NI 3 naphthenate inhibitors are usually deployed at a moderate brine pH and/or in conjunction with minimum concentration of acetic acid. In particular, the effect of the inhibitors on the brine pH is considerable. In the control experiment the brine pH increases after contacting the naphthenic acid solution, due to the partitioning of naphthenic acid to the oil-water interface and subsequent dissociation and formation of naphthenate. The addition of an inhibitor reduced the pH decrease of the brine, compared to the control hence indicating that the inhibitors prevent the naphthenic acid partitioning and dissociation on the oil/water interface and subsequently hindering the formation of naphthenates. Deploying the inhibitors at a higher temperature proves to be much more effective in the naphthenate mitigation and the effect of higher temperature (i.e. 60°C) on the efficiency of the naphthenate inhibitors was also studied and the results are presented in this paper.

References

- [1] Sorbie, K. S. et al. (2006) Proceeding of the Royal Society of Chemistry, Chemistry in the Oil industry IX.
- [2] Mohammed, M. A., Sorbie, K. S. (2009) Colloids and Surface A: Pysiochem. Eng. Aspect 349, 1-18.