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Calcium Naphthenate Solid Deposit Identification and Control in Offshore Nigerian Fields

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Abstract

Two operated fields in offshore West Africa began experiencing aggressive solid deposition challenges soon after the onset of water breakthrough for Field A and Field B. This led to significant process control and flow assurance issues in the crude processing plants. Problems experienced included: plugging of separator bridles, hydrocyclone liners and level control valves, solid loading in overboard water, poor oil-water interface and loss of retention time in separators and plugging of reject lines of the produced water treating vessels.

An extensive solid deposit identification campaign was undertaken in order to establish the composition of the samples. Calcium naphthenate (CaN) scale was identified as the major component in the solids, the first major occurrence experienced in the Gulf of Guinea for the operators of fields A and B. A competitive screening of CaN inhibitors resulted in the pre-selection of a low dose non-acidic formulation. The CaN inhibitor formulation selected in the laboratory was then trialed in the two offshore fields, according to a well-defined set of key performance indicators (KPIs).

Results from the field trials indicated significant reduction in the solid deposition rate. The flushing of separator sight glasses reduced from three times per shift to once in four days. Hydrocyclone liners and induced gas floatation units opened for inspection following five weeks of treatment showed no significant CaN scale present. Online oil and water filtration exercise showed downward trend in solid deposition across the FPSOs in the systems of both Field A and Field B. Produced water quality was not compromised. The CaN issue is now under control and subject to a surveillance campaign.

This paper showcases an operational excellence approach to solving the CaN problem in the face of increasing solid deposition challenges in offshore operations as seen in the Gulf of Guinea and currently in other parts of the world.

Background.

Calcium naphthenate (CaN) scale represents one of the many production chemistry challenges which result from the presence of naphthenic acids in crude oil production systems^{1,2}. For the deposition of CaN to occur, so-called ARN acids (tetra-acids with molecular weight above 1200 Dalton) need to be present in the crude oil. Identification and structural studies of ARN acids have been discussed in other publications^{3,4}. Both the ARN acids as well as the other naphthenic acids present in a produced crude oil, may react with the cations present in the water under a specific set of conditions. It is a known fact that naphthenic acid phase behavior is a function of produced water composition and pH⁵. If the pH of the produced water increases above pH 6 (due to depressurization) and if there is sufficient calcium, there will be a competition of the different naphthenic acids to precipitate as scale. Selectivity towards the divalent ions has been explained via cation size and hydrated water number⁶. The kinetics of the reaction between ARN and produced water cations is very fast⁷. ARN acids have up to four acid groups and are surface-active, and, thus they can react to form a network with the calcium ions in the produced water⁷. This network is very sticky, insoluble in oil or water, and settles out in the water leg of the separator and from there it is carried through the water treatment plant. Therefore within the operating asset, the precipitation and deposition of CaN has been reported as a serious threat to safeguarding stable production activities. Nevertheless, the management of the CaN problem has progressed significantly over the last 20 years since the first published field cases^{8,9}. Practical control philosophies have been outlined and various chemical treatments available discussed^{1,10}. In addition, better analytical and modeling tools are made available to study the production chemistry drivers for CaN deposition^{11,12,13}. Where chemical treatment for CaN needs to be implemented in a producing asset, this comes with additional challenges including material

compatibility, permits and export/disposal fluid specification. That is why it is important in field development projects to be able to identify the risks of CaN formation at an early stage. A few published references have addressed this topic^{14,15}.

This paper describes the occurrence of CaN in two different production systems. In addition, the work detailed here will cover the steps taken to identify a fit-for-purpose CaN inhibitor formulation from laboratory to field trial. The most important findings from the field trials are discussed together with some lessons learned. Once the CaN chemical treatment solution has been identified it requires to be incorporated into the portfolio of chemical applications for the facility. There is also a need for continuous monitoring/surveillance to optimize the treatment and ensure that production is maintained.

Field occurrence.

CaN precipitation and deposition was observed in two offshore facilities. The facility from Field A comprises a 220K bopd FPSO, comprising 13 wells and associated subsea installations located in a water depth of 1000 meters in the Gulf of Guinea. The facility from Field B consists of two main satellite platforms each with 16 well slots plus one 6 slot platform making up the production field area producing into a FPSO. It is located in the shallow depths of Estuary Area of the Gulf of Guinea, approximately 32 meters water depth. The process fluids are transferred from the platforms to the FPSO which has a capacity of 150K bopd. Table 1 presents a comparison of Field A and B process fluids. Note that the produced water samples are taken at surface conditions. Even though the total amount of calcium ions is low for both fields (indication of water mixing, condensed and formation), the pH values are very high indicating ideal conditions for the CaN solids to form.

Table 1. Produced water and crude oil fluid property for Field A and Field B.

Properties	Field A	Field B
Crude API	29	34
Crude TAN (mg KOH/kg crude)	0.5-0.8	0.2
Produced water calcium ion (mg/l) at surface	250	50
Produced water pH at surface	8.2	8.15

With the onset of water production, precipitation of CaN first manifested itself in difficulty in the treatment of both water-in-oil and oil-in-water emulsions. This was not immediately identified as CaN however because of co-production with sand and other solid particles. Subsequently, the CaN issue become more severe. The relatively short residence times in both facilities resulted in separation problems. This was co-current with large quantities of solids dropping out in main vessels (e.g. separators, hydrocyclones) thereby reducing their efficiency and affecting flow assurance. In addition, key process control equipments (such as level control bridles) were clogged making steady operation of the plant difficult. The nature and quantity of CaN were very unlike any inorganic or organic solids that were typically found in the Nigerian fields and facilities (sticky at first, but hardening on exposure to air). Figures 1 and 2 present examples of blocked equipment witnessed in the facilities affected by CaN. Note that the vessels where CaN was seen to form contain phase separation, depressurization or are used to treat bulk fluids after separation. Appendix i and ii present a simplified process diagram layout of both facilities and the locations where solids were sampled.



Figure 1. Field A facility. Images showing hydrocyclone package liners and separator coated with CaN solid deposits.



Figure 2. Field B facility. Images showing CaN solid removed from the Coalescer vessel.

Prior to the identification of CaN and appropriate mitigating chemistry, high OPEX cost and man-hours were expended to manually remove solids from both facilities. Compounding the challenges experienced is the fact that the solids hardened on exposure to air, hence requiring special high pressure tools deployed at additional cost, for removal. From a logistics perspective solids had to be transported from the facilities. The overall amounts of CaN solid formed were low in the range of a few mg/l. However, over a six-week vessel cleaning operation, approximately 30 tons of solids was sent onshore for incineration. Vessel cleaning during the facility shut-down alone was estimated to cost USD 6 million.

Solid Identification and Chemical Selection.

Solid identification. To illustrate the process taken to correctly identify the solids as CaN from our facilities, data from samples captured at the facility from Field B is now discussed. Samples analyzed included solids from the coalescer manway, recovery unit and 2nd stage separator. Clear identification of CaN for both Field A and B was achieved using a combination of two techniques: X-ray fluorescence (XRF) and Mass Spectrometry (MS), following internal analytical protocols. Presence of wax was ruled out by using High Temperature Simulated Distillation (HTSD).

Table 2 presents the XRF results as wt % for the samples studied. The data indicates presence of calcium, oxygen and iron as major components. Calcium suggests presence of organic calcium salts. Iron suggests corrosion by-products. Trace silica and metal components are also present, which are indication of other solids in the system. The field in question also has wells producing sand, which stick to the CaN deposits.

Table 2 XRF results showing wt% of components detected in the facility from Field B samples. Please note cations are expressed as oxides.

Component name	Recovery unit	Coalescer manway	2 nd Stage Separator	2 nd stage separator
N	0.44	0.33	0.48	0.22
H	10.14	10.41	8.58	11.60
C	74.72	74.72	64.63	82.74
Na ₂ O	0.32	0.13	0.29	0.12
MgO	0.04	0.09	0.17	0.04
Al ₂ O ₃	0.25	0.45	0.71	0.05
SiO ₂	0.68	1.34	3.85	0.14
P ₂ O ₅	0.33	0.29	0.46	0.09
SO ₃	1.16	1.18	2.13	0.64
Cl	0.30	0.27	0.29	0.34
K ₂ O	0.03	0.05	0.11	0.01
CaO	4.07	5.73	7.94	2.47
TiO ₂	0.02	0.07	0.15	0.02
MnO	0.08	0.06	0.10	0.01
Fe ₂ O ₃	6.06	2.73	6.74	0.72
ZnO	0.40	0.11	1.08	0.05
Br	0.00	0.00	0.00	0.00
SrO	0.11	0.16	0.25	0.21
ZrO ₂	0.03	0.03	0.02	0.00
BaO	0.84	1.84	2.03	0.54
PbO	0.00	0.02	0.02	0.00

Figure 3 presents the MS results from a selected sample from Field B. The ARN acid peaks are clearly identified which has been reported in all soap scale samples in the open literature. This was also observed in all other samples from facilities from Field A and B. The results from the analytical tests were conclusive evidence that the deposits were mostly CaN. As a further confirmation, a dissolution test was performed. The field samples were shown not to be soluble in hydrochloric acid or toluene, but had a good solubility in acetic acid.

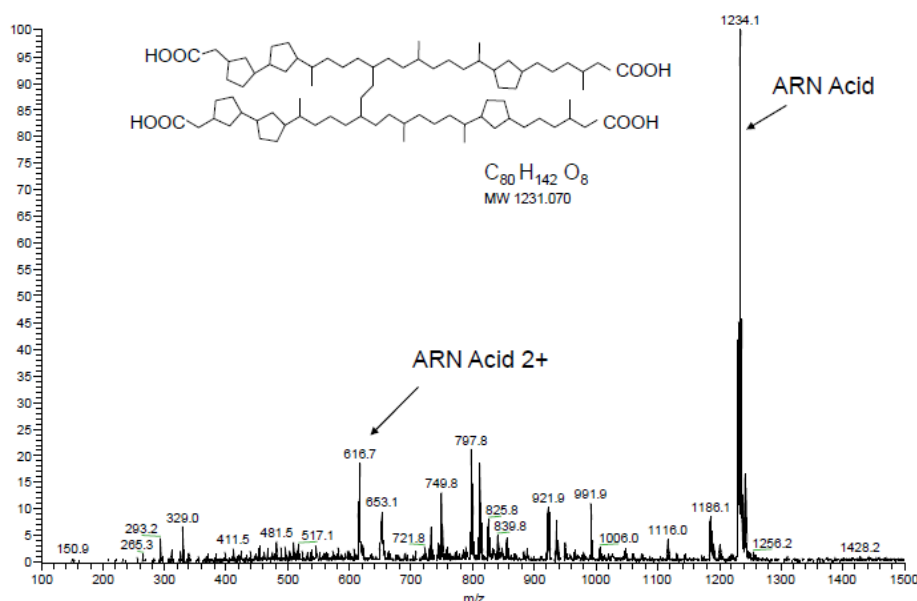


Figure 3. MS results for a selected field sample from the facility from Field B. ARN acid ionization showed at 616 and 1234 m/z.

Chemical Selection. Once the CaN was identified for both fields, tests were conducted to initially short-list CaN formulations which could be then field trialed for inhibition. The key objective in selection a CaN formulation was to focus on non-acidic chemistries, due to the perceived risks of corrosion with more traditional acids (e.g. acetic acid¹⁶). Various methods of CaN inhibitor testing have been discussed in the literature together with possible mechanisms involved^{17,18,19}. It is difficult to simulate the exact flow regime found under field conditions in the laboratory. However, it has been observed that most CaN inhibitors sequester the ARN acids and have both an interface and bulk effect on the treated fluids⁷. It is essential that CaN inhibitors are tested in the laboratory prior to field trial/implementation to avoid produced fluid upsets^{20,21}.

A simple gravimetric test was used to firstly compare the formulations tested in the laboratory. Initially the test comprised of using large concentrations of ARN spiked in crude in the bottle tests together with formulation concentrations of 1000 ppm and synthetic brine. The ARN was separated from the field deposits using an internal procedure. Synthetic brines were prepared with compositions similar to what was found in the field. The pH of the system was adjusted to above 8.0 with NaHCO₃. pH adjustment was made to simulate fluid property changes as per field conditions. All tests were conducted at 50°C and shear was induced using an Ultra Turrax mixer at 24000rpm for 1 minute followed by the use of a shaking table for 10 min. The mixture was then left standing for 24 hrs during which the deposit at the interface was monitored. Filtration under vacuum of the crude/brine/solid mixture was then carried out over a pre-weighted 5 micron Millipore filter. Solids captured were rinsed with water followed by xylene to remove excess crude. The residue on the filters was then determined after overnight drying at 80°C. Inhibitor performance was determined by comparing the amounts of CaN formed during this procedure. Under such severe conditions, it was expected that a large amount of CaN solids would be precipitated. The choice of high dose rate was to mimic acidic formulations, which are known to be used at concentrations between 100 to 1000ppm^{1,21}.

Figure 4 shows the results for 3 chemicals evaluated in terms of mass of CaN reduction during the test procedure with the spike ARN fluids. Clearly Chemicals A showed a noticeable effect compared to the blank and the other formulations tested. This can also be observed in Figure 5 showing the images of filter residue after overnight drying. Although the overall amount of solids generated in these tests were small (mg/l), they were consistent with field observations.

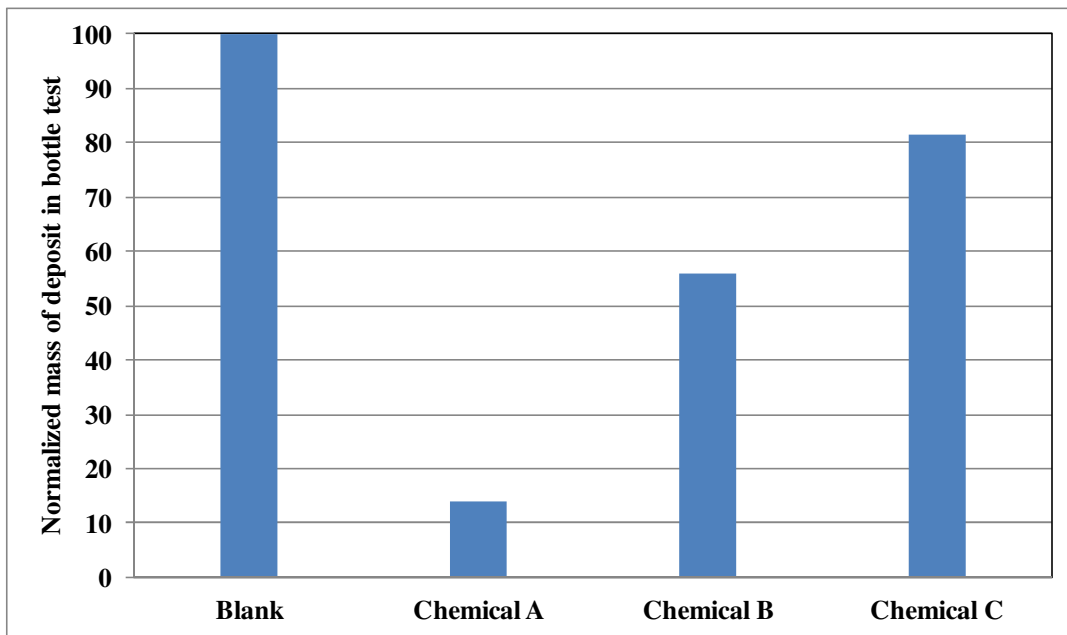


Figure 4. Normalized mass (mg/l) of deposit in bottle test to test inhibitor formulations.

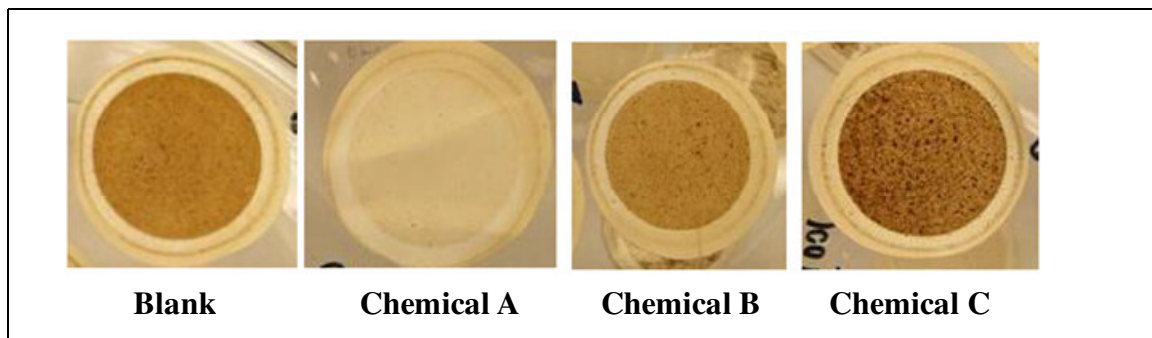


Figure 5. Images of residue after drying on filter paper showing the effects of different CaN inhibitor formulations.

An additional test was conducted using Chemical A together with crude oil and synthetic produced water. The same procedure described for the bottle tests was used here. In this case the concentration of ARN is the indigenous level as found in the produced fluids. For these less severe tests, a formulation concentration of 50ppm was used. It is known that under field conditions, other parameters would be important to judge inhibitor performance. For instance, presence of other naphthenic acids in the system changes the mechanism by which the inhibitors work⁷. Hence the test with crude oil with no spiked ARN is more realistic. For these tests, the reduction in CaN mass was lower, 30% (with 50ppm formulation) as opposed to over 80% (with 1000ppm formulation) in the test with spiked ARN. This lower reduction was not of concern since under field conditions, the CaN formulation is also applied with a demulsifier. It was decided to optimize this during the field trial.

Field Trial Execution

Pre-Trial Data and KPI. Overall it should be said that the addition of a new chemical product to the portfolio of an existing asset for a trial, should follow certain pre-defined set of key performance indicators (KPIs) and elaborate management of change (MOC) process. The KPIs were: excellent crude dehydration (BS&W within specification of <0.5wt%), overboard water within regulatory discharge limits (< 29ppm oil in water), significant reduction in solid deposition (with evidence in reduced vessel bridle flushing frequency), increased hydrocyclone efficiency, excellent instrument control performance, clear oil/water interface in vessels.

For the field trials, a number of HSSE checks were also performed on the CaN formulation to ensure fit-for-purpose application. The preliminary compatibility of the formulation with other production chemicals used in each facility was carried out. Furthermore material compatibility was conducted together with the chemical supplier. To ensure that adequate information was captured during the field trial it was decided to implement a sampling program covering critical process fluids. In-line solid deposit filtration and oil-in-water were selected as major process indicators since these are tied to the

production permit and license-to-operate. The in-line filtration (1.5 micron) was conducted using sidestreams comprising a regulator and filter holder. A total volume of 10 liters (maximum) was typically filtered for these tests.

Figure 6 presents an overview of some in-line filtration results and some solids captured after multiple pre-flush on the facility of Field B before the CaN inhibitor trial. Stream pressures and volumes treated are indicated where applicable. It can be seen that solids were found in the: LP separator, the 2nd stage separator and the 2nd stage separator bridle and sight glass level indicator.

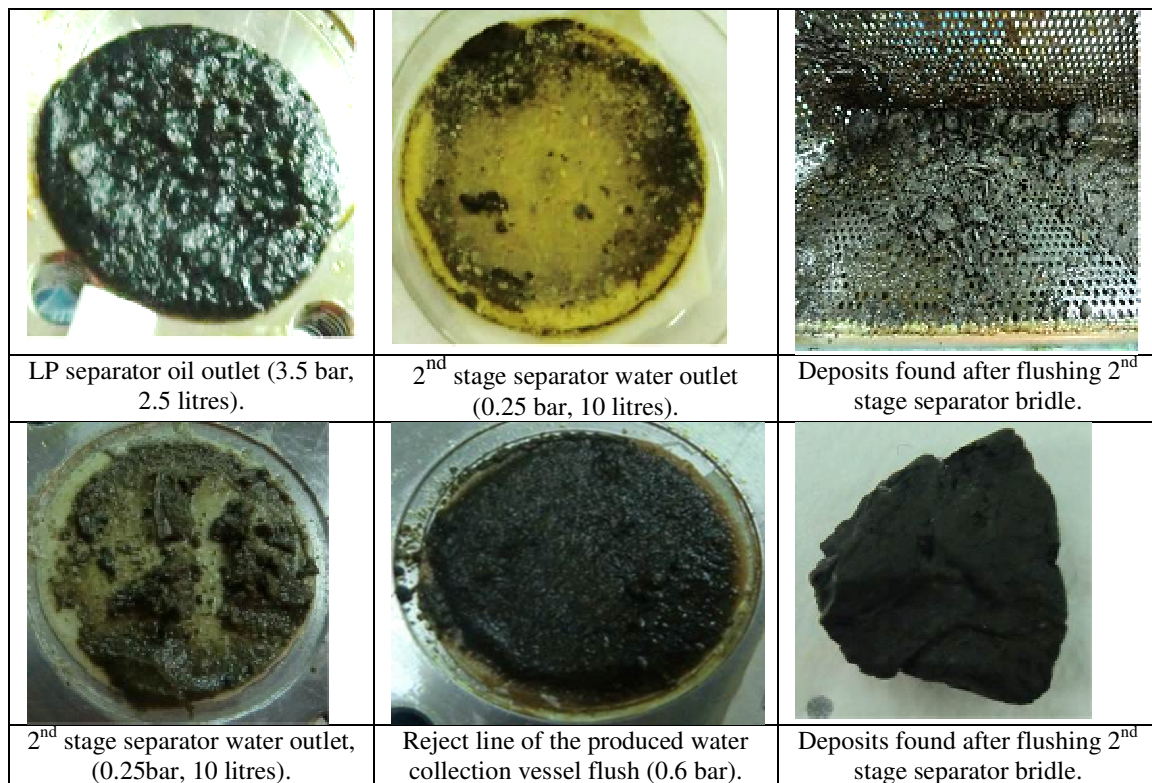


Figure 6. Images of in-line and flushing solids taken at the facilities of Field B, before the CaN field trial.

Field Trial. The treatment philosophy during both trials in the facilities of Field A and B was to inject CaN formulation in the either the HP separator or at the manifold. The 2nd stage separator water outlet and the reject line of the produced water collection vessel were chosen for monitoring. Flushing of the separator bridle was also monitored. CaN formulation injected varied between 5 to 10ppm. During the field trial, the system was allowed to stabilise over a period of 2 to 3 days, during which the monitoring of the KPIs took place. It was agreed that if adjustment of chemical rates was required that this would also take place over a few days up to 50ppm, which was the dose rate used with the laboratory tests for Chemical A.

Upon injecting initially 5ppm followed by 10ppm of CaN into the HP separator, a remarkable reduction of the amount of CaN solid was observed. The accumulation in the bridle line reduced significantly as witnessed during routine flushing. A sharp interface was obtained on the 2nd stage interface level indicator, and flushing frequency reduced from daily to once in three days. After a few days of inhibitor injection, a thread shaped deposit was retrieved. This is the last remainder of the CaN accumulated in the vessel. After retrieving this material the flush water contained trace amount of solid particles. Figure 8 presents images taken from these observations.

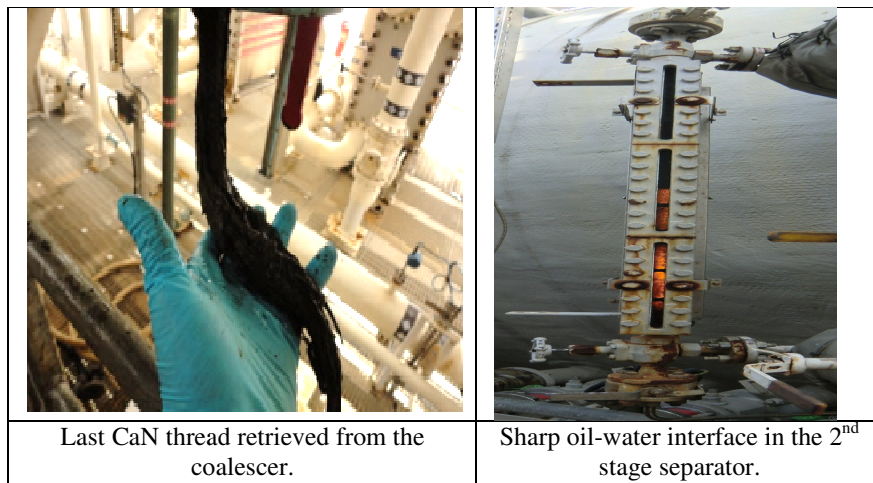


Figure 8. Images of flushing solids taken at the facilities of Field B, during the CaN field trial.

Compared with the in-line filtration results before the field trial, during injection of the CaN formulation there was a sharp reduction in the number of particles observed in the water treatment process. Figure 9 shows images of samples taken from the 2nd stage separator. Similar good results over time were observed from other streams such as the flotation unit shown in Figure 10. Nevertheless during the field trial BS&W was not negatively affected. Figure 11 shows the changes in BS&W with CaN injection rate during the field trial. It should be noticed that after the field trial, the injection rate was reduced to 5ppm because of some haziness found in the produced water.

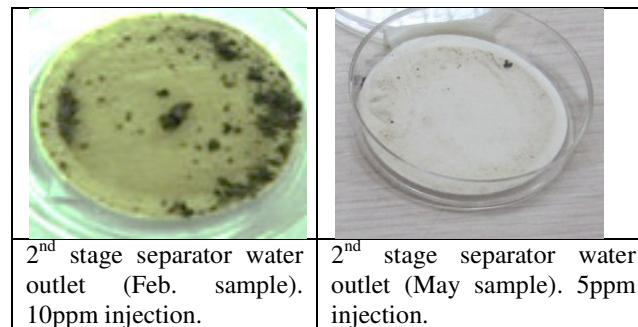


Figure 9. In-line filtration samples from 2nd stage separator water outlet taken during the CaN formulation field trial.

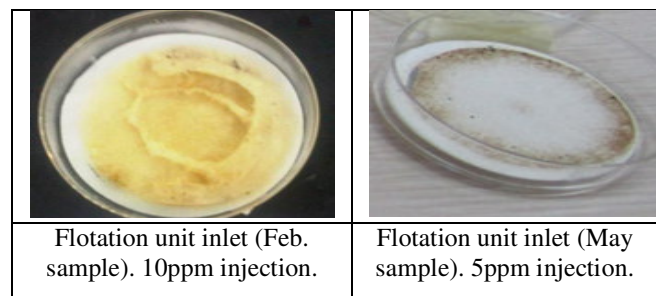


Figure 10. In-line filtration samples from the flotation unit.

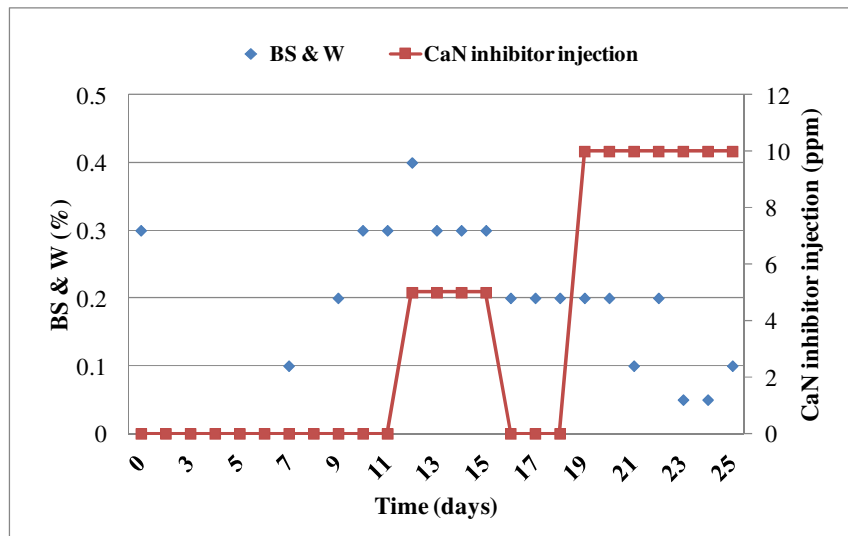


Figure 11. BS&W and CaN injection during the trial at the facility for Field B.

Long term application and surveillance.

After the field trial was finalized, it was decided to continue further with the injection of the CaN to investigate long-term effects. A second objective was to implement surveillance measurements. The evolution of the solid deposition rate in terms of kg/m^3 , obtained with the in-line filtration measurements for various vessels is shown in Figure 12. It can be observed that the effect of the CaN inhibitor formulation is seen throughout the process facilities, reducing the overall solid load. The major reduction in solid has been in the 2nd stage separator and coalescer outlets. There is some fluctuation in deposition rate amounts for the other vessels. However the reduction in solids content means that the facility can be better managed. The water quality is not significantly affected, and seems to improve because there is less carry over due to oil-coated CaN particles. No negative long-term effects of the inhibitor on the BS&W was observed. The application of the inhibitor seems to help resolve the water-in-oil emulsion better, resulting in dryer export crude. As can be seen in Figure 12, the inhibitor however does not completely inhibit solids formation. The bridge in the 2nd stage separator in Facility B requires flushing to remove solids every couple of days. This operation is manageable and the frequency can be controlled by the operations crew.

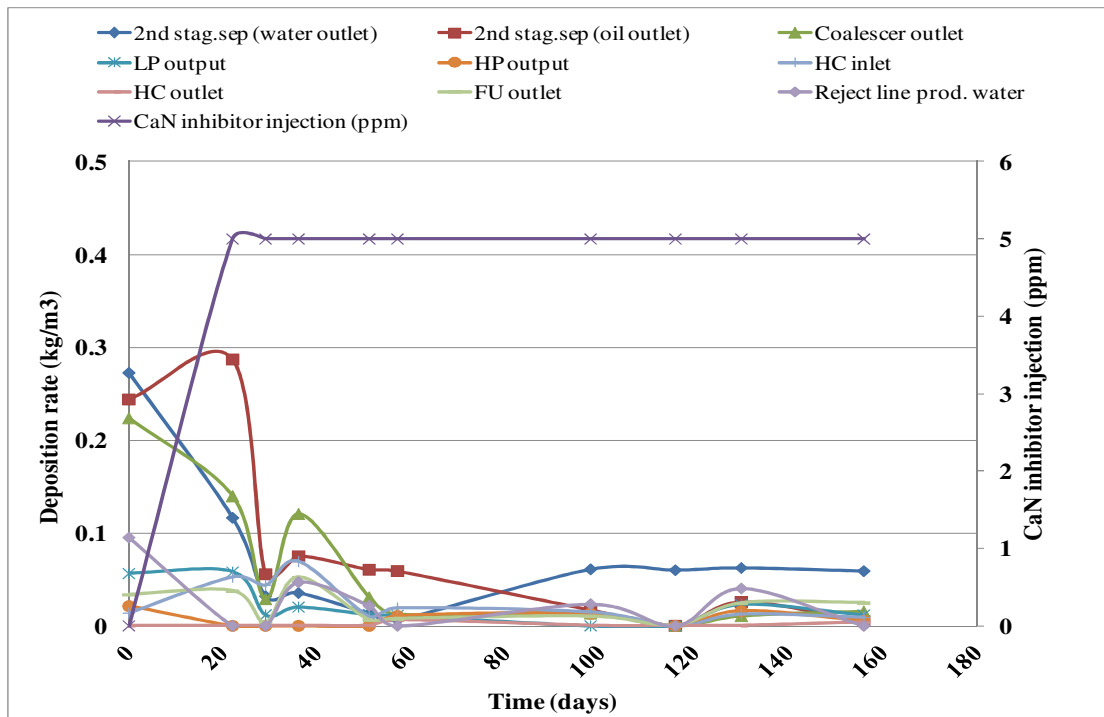


Figure 12. Deposition rate (kg/m³) for various vessels and CaN injection during long term surveillance for the facility for Field B. HC = hydrocyclone, FU = flotation unit.

After months of application, the inspection of the hydrocyclone interior showed clean surfaces and no visual signs of plugging (shown in Figure 13). The chemical treatment costs are easily paid back by the prevention/reduction of production upsets and prevention of defferment. In addition to the routine sampling program for the facilities, a long-term surveillance program for CaN is now in place. Side stream filtration on produced water (1.5 micron) is carried out on site weekly across different points in the process. Optimization of chemical rates is performed on a daily routine of checks, because of the narrow range of injection (e.g. < 10ppm).



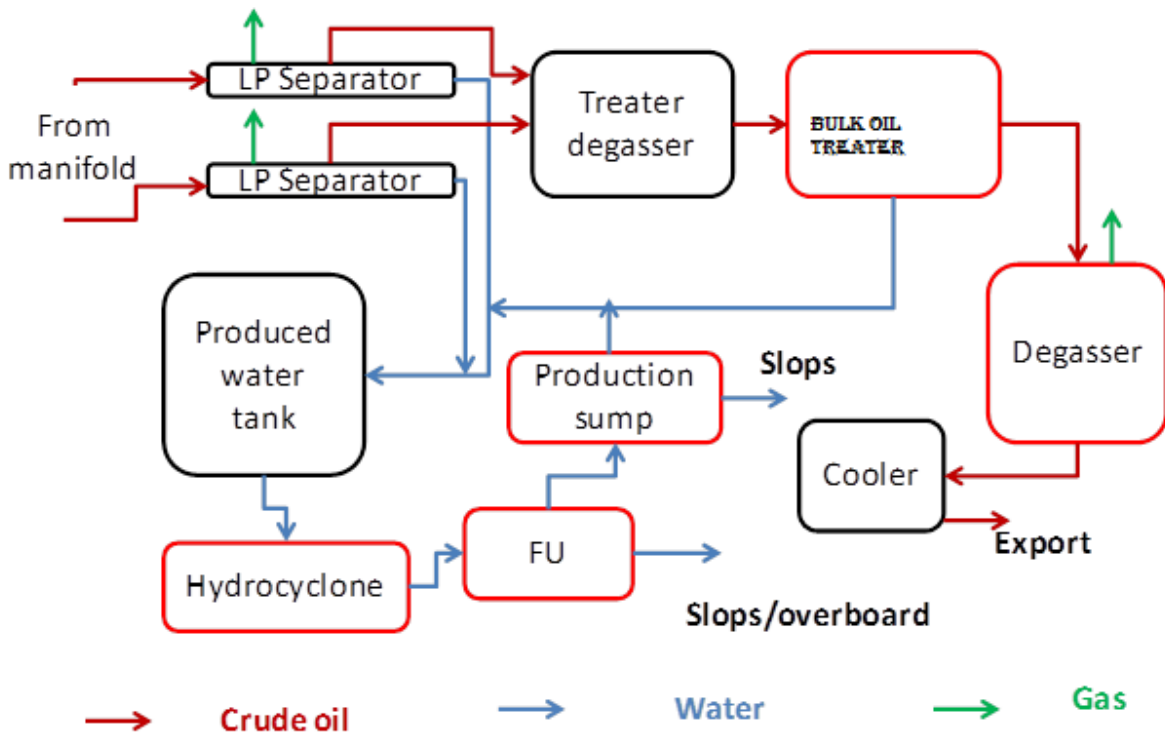
Figure 13. Hydrocyclone interior after long-term application with CaN inhibitor formulation at the facility from Field B.

Conclusions and final considerations.

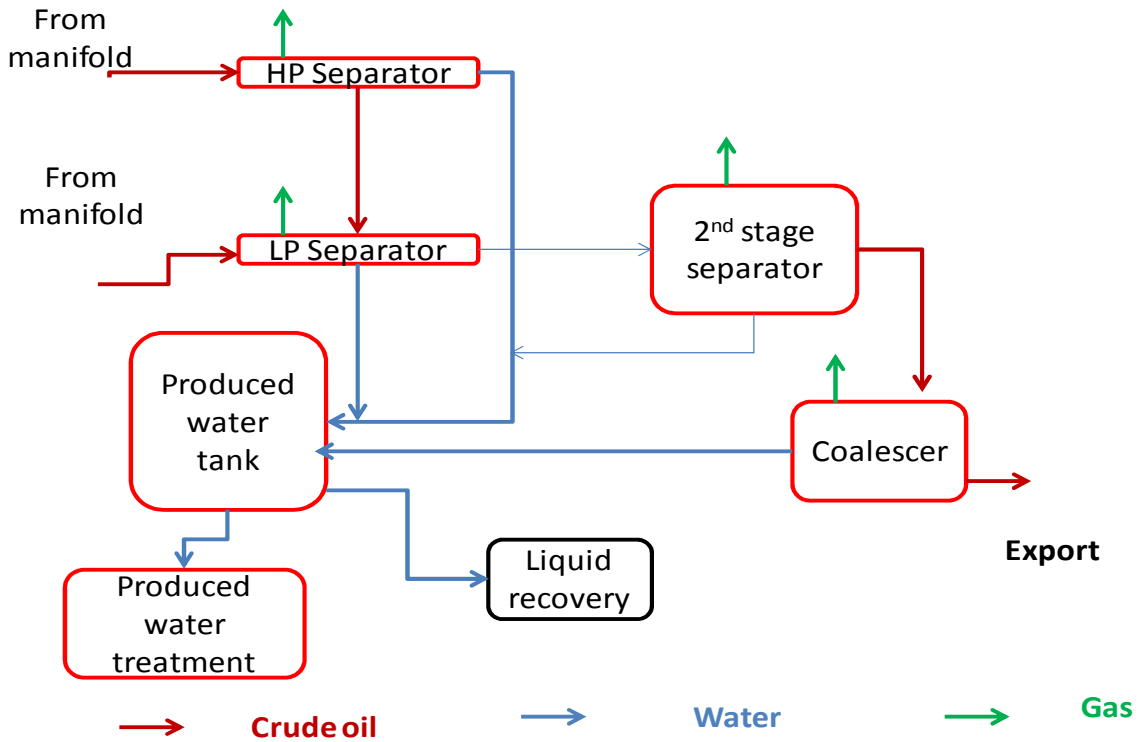
From the work discussed in this paper the following conclusions and considerations can be put forward.

- Severe solid deposition was shown to be a detrimental consequence of production water breakthrough in offshore facilities.
- Analytical characterization provided sufficient evidence to identify predominantly CaN in these deposits.
- Fit-for-purpose inhibitor selection was conducted where a non-acidic formulation was identified.
- Prior to successful field trials, key performance indicators (KPIs) were established. Critical to this was the implementation of in-line filtration and flushing in key vessels.
- Successful field trials were conducted showing the beneficial effects of the CaN inhibitor formulation on solids loading in the facilities, without affecting the BS&W export indications. This was achieved with low dose rates (5-10ppm).
- The facilities from Field A and Field B now operate with continuous inhibitor injection. Though this does not eliminate completely the solids formation, it allows crude oil production to proceed, safeguarding system integrity.
- A surveillance plan is in place to monitor produced fluid streams.

Appendix i. Simplified process diagram of facility at Field A. Red circles indicate where CaN was found.



Appendix ii. Simplified process diagram of facility at Field B. Red circles indicate where CaN was found.



Acknowledgements.

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