Diagnosis and Treatment of Naphthenate Deposits Embedded With other Organics and Inorganics

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Abstract: Napthenate solid deposits in oil wells tend to contribute towards vital flow assurance issues and production decline due to formation damage, increase in the weight of the crude by almost 12% and restriction in the production tubing and around the wellbore. This paper showcases an operational excellence approach in diagnosis of oil producing wells, which might have the potential to form naphthenate deposits along with other inorganic scale, corrosion product and organics. In this work, deposits, crude and formation water samples from an oil field located offshore Peninsular Malaysia was used as a case study to quantify the presence of naphthenates. Various analytical tests such as modified SARA analysis, cationic and anionic analysis of formation water, Total Acid Number (TAN) analysis, pH of the crude sample and also X-Ray diffraction (XRD) on the samples were conducted in the laboratory to understand and affirm the occurrence of the naphthenates. Based on the analytical results, it was concluded that naphthenate deposit was the main issue in the well. Also, there were possibilities of wax and other inorganic deposition to take as identified by the test results. Hence a single step micro emulsion formulation was designed that can enhance the productivity of the well by injecting the formulation into the designated zones to dissolve naphthenate embedded with inorganic material, simultaneously dissolve/disperse organic deposit, break the naphthenate induced tough emulsions and change the wettability characteristics of the formation rock towards water wetting to ease the flow of oil into the wellbore. The formulation of the speciality micro-emulsion is vastly based on the characteristics of the formation fluid, nature of the sample, reservoir and operating conditions. The application of this study is a preliminary attempt to establish guidelines for early detection of problems related to naphthenate and possible chemical remedial, thereby, stimulating preventive measures and attenuation plan which can be formulated and replicated in wells with naphthenate problems in various parts of the world.

Keywords: Naphthenates, SARA analysis, cationic and anionic analysis, Total Acid Number (TAN) analysis

I. INTRODUCTION

Production chemistry remains a remarkable challenge to oil and gas production in both, mature fields and the new fields [1]. Deposition of various types of deposits including inorganic scales and organic deposits, corrosion and separation remain key challenges requiring technical solutions to ensure continued production, most importantly from ageing fields which are often producing beyond their original design life [2]. There have also been new fields with such issues which are naturally present due to the reservoir conditions and crude characteristics [3].

Of the production problems, one of the major issues faced by many operators is the deposition problem of naphthenates along with other organic and inorganic scales [4]. This is a vital flow assurance problem for oil producers in various aspects as such deposits can hinder the production of oil through, formation of troublesome deposit in production systems and around the well bore, formation of very tough emulsion due to the resulted sludgy foam and increase in the weight of the crude by almost 10-12% [5].

Presence and deposition of naphthenates along with other organic and inorganic scales or formation of tough micro-emulsion are one of the most serious oilfield issues which has resulted shutdown in most of the offshore facilities [6]. However even in onshore facilities, although naphthenate deposit might not be a major issue, formation of organic and inorganic deposit has resulted in major flow assurance problems in mature fields. Napthenate solid deposit in oil wells result in production decline due to formation damage and restriction in the production tubing [7]. Moreover, it reduces the efficiency of the pipelines and surface facilites such as separaters and de-salters as well.

Naphthenate solid deposits form when naturally occurring naphthenic acids in the crude oil with high TAN (above 0.5) reacts with metal ions (eg: Ca^{2+}, Na^{2+}) in the produced water under the right conditions of temperature and specific pH values [8]. Naphthenic acids are found in many crude oils, but can be troublesome in higher concentrations [9]. A TAN of greater than 0.5 will decrease the price that refineries pay for a crude oil because of the corrosion that such acids cause in refinery systems [10]. The deposition of other type of organic and inorganic scales can occur mainly due to various factors such as changes in temperature, pressure and composition/morphology of the crude oil over time. [11]

A well from an oil field offshore of Peninsular Malaysia (i.e Well A) was used as a case study to depict the process of problem identification and remedial of the same. The chosen field is one of the first deep water developments in Malaysia which has been in production since 2007 which located Deep water offshore Peninsular Malaysia. The pro forma net production was reported near 63,000 bbl oil/day in 2014.

Revised Manuscript Received on February 05, 2019.

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II. CASE STUDY

Well A was reported unable to kick-off after shut-in which was mainly due to high skin or loading issue. As observed on the well production data, fluctuation of GOR and declining oil production was related to deposit restriction down hole which is closely lead to the difficulty to kick-off. Also high emulsion production as shown in Figure 1, increased the density of the crude which made it even difficult to flow out the crude from the reservoir. Based on the production data provided by the Operator of the well, it was observed that the wells experienced rapid increase of water cut as the GOR fluctuates over period of time. Tubing Clearance Check (TCC) was done and results as follow:

- RIH 2.735'' gauge cutter and encountered HUD at 1848'
- RIH 3.0'' wire scratcher and encountered HUD at 2159'

For each run, the tools were covered with a hard and sticky wax like deposit. The hard, black, wax like deposit was then retrieved from the tool string. The samples of the crude, water and deposit samples were received for further analysis. To get a better understanding of the nature of the sample and to design an effective treatment method, the samples were assessed for, compositional analysis and characterized by dissolution tests. The deposit sample from the tool string was black in color and looked like a tar ball, was moist and particulate in texture as shown in Figure 2.

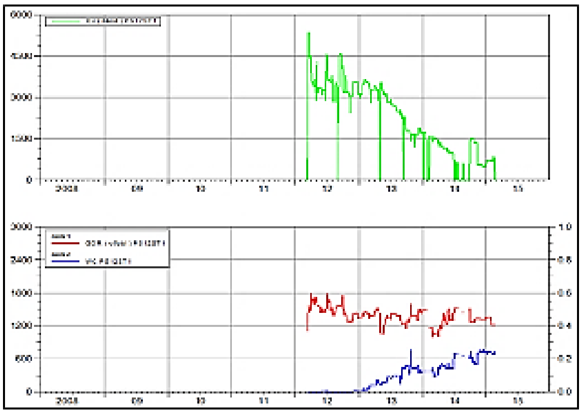

Fig. 1 Production trend of well A

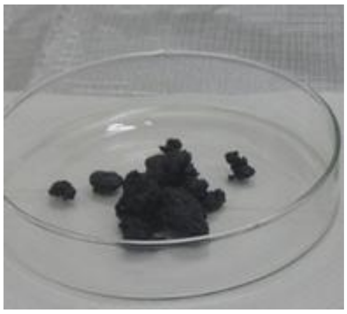

Fig. 2 Recovered sample from well A

Preliminary Tests were conducted with the samples using different type of solvents. These simple dissolution tests were conducted in order to identify/confirm presence of organic and inorganic composition of sample. Upon completion of the dissolution test as shown in Table 1, it was possible to conclude that the deposit sample was predominantly composed of organics with minute amount of inorganics

Table. 1 Dissolution test

Test	Observation	Verdict
Organic Solvent at ambient/ elevated temperature	- Development of dark brown color. -Some portion dissolved/ dispersed and remaining settled down. -When heated up, the sample dissolves slightly more.	-Indicates existence of sufficient organics
With 15% HCl	-Development of pale yellow color on standing. -Sample showed very little dissolution.	-Indicates the presence of very small amount of corrosion products. -Indication of minute quantity of scales.
Acid soluble sample + colorless ATC solution	-Solution turns to very light red color	- Confirms the presence of small amount of corrosion products

Upon completion of the dissolution test, it was possible to conclude that the deposit sample was predominantly composed of organics with minute amount of inorganics. However to understand more on the compositional analysis of the deposit, XRD tests were carried out on the deposit sample. Further testing were conducted on the sample. The inorganic portion mostly consisted of chlorites, Calcium and sodium ions according to XRD & SEM testing. Further compositional analysis known as SARA was conducted on the deposit sample. The obtained results validated the

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previous findings by LOI since the results are in the same range. As shown in Table 2, compositional analysis known as SARA was conducted for the deposit sample. Table 3 shows the Composition analysis on deposit sample from well A.

The analysis of deposit showed that the deposit from well A was rich in micro-crystalline wax and naphthenates. Although the naphthenate content does not seem to be high however it is sufficient enough to contribute to the high melting point of the deposit sample. Sufficient amount of high molecular wax (micro-crystalline wax) in the sample along with high content of naphthenates contribute to the high melting point of 98˚C. The melting point was not sharp due to high content of naphthenates. It is concluded that the alkali metal naphthenates remove the corrosion products from the surface of the tool and agglomerate with them in the presence of higher organics like micro-crystalline wax, resins and asphaltenes to form a tar like deposit.

Test on the crude revealed that physical characteristic exhibited very light oil with tough emulsion . There was no existance of free water. The emulsion showed 38.0% and the oil showed 62.0%. In addition, small lumps appeared when transferring the sample. Figure 3 shows the sample physical appearance and properties. SARA Analysis was conducted on the crude sample in order to determine the detailed composition of the sample and the results is shown in Table 4.

Table. 2 SARA Analysis results on crude sample of Well A

SARA Analysis			
		Sample basis (%)	Dry basis (%)
Volatiles		33.40	-
Saturates	Macro crystalline wax (low mol . wt.)	1.63	2.45
	Micro-crystalline wax (very high mol. Wt.)	1.79	2.68
Total Saturates		3.42	5.14
Asphaltenes		42.03	63.12
Resin		2.19	3.30
Aromatics		1.28	1.92
Naphthenates		3.04	4.56
Residue		14.55	21.85
*Total		99.92	99.87

- *The manual laboratory practice takes into account the volatile nature of the crude/ volatiles present in deposit where a portion of this composition gets dissipated through the testing apparatus and processes. The standard deviation of up to 7% is widely accepted range in laboratory practice of establishing SARA composition.*

Table. 3 Composition analysis on deposit sample from well A

LOI RESULTS		**XRD FOR MINERAL CONTENT**		**SEM/ Atomic %**		**LAB ANALYSIS OBSERVATIONS**		**INFERENCE**
Moisture	24.34	BaSO4	52.0	Oxygen	46.62	Dissolution Test	Sample contains high amount of organics with other inorganic insoluble.	
Organics	49.27	K2CO3	23.8	Carbon	16.88			All Lab Analysis results corroborated with LOI, XRD and SEM results.
Inorganics	26.39	Chlorite	9.7	Chlorine	7.31			
		CaCl2	4.7	Sodium	6.33			
				Silicon	5.33			As a conclusion, sample is high with organics along with Barium sulphate and other inorganics
				Sulphur	4.89			
				Calcium	4.84	Chloride Test	Sample contains chloride.	
				Barium	2.96			
				Aurum	1.83			
				Ferum	0.87			
				Aluminiu m	0.81			
				Potassium	0.49			

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The compositional analysis identified that the crude was paraffinic in nature with predominant macro -crystalline wax. In term of asphaltene stability, the potential of its precipitation to form nucleation for wax deposit was not high. Aromatic content was enough for easy flow and low pour point. However there is enough naphthenates present in the sample to form stable emulsion along with asphaltene. The lumps of stabilised emulsion are observed physically.

The naphthenates induced emulsions were normally tough and can't break on standing or even at elevated temperature of 80-90⁰ C. As the water content was high, the metallic ions present in it form metal naphthenates on their combination with naphthenic acid content of crude.

Fig. 3 Sample physical appearance.

Table. 4 SARA Analysis results on crude sample of Well A

SARA Analysis			
Pour point: 15˚C			
		Sample basis (%)	Dry basis (%)
Volatiles (moisture+ organic)		45.93	-
Saturates	Macro crystalline wax (low mol. wt.)	19.54	36.13
	Micro-crystalline wax (very high mol. Wt.)	0.02	0.04
Total Saturates		19.56	36.16
Asphaltenes		0.66	1.22
Resins		4.45	8.23
Aromatics		28.00	51.77
Naphthenates		0.47	0.86
Total		99.07	98.23
CII		0.64	

*The manual laboratory practice takes into account the volatile nature of the crude where a portion of this composition gets dissipated through the testing apparatus and processes. The standard deviation of up to 7% is widely accepted range in laboratory practice of establishing SARA composition. **Colloidal instability index: **Colloidal instability index is a ratio in between unfavorable organics species over the favorable species in a crude system. Favorable species will behave as a solvent to disperse and avoid precipitation of unfavorable ones. In presence of high content of unfavorable species over the favorable, the tendency for their colloidal precipitation increases. Colloidal Instability Index (CII), is the ratio of saturates+ asphaltenes + naphthenates over aromatics + resins fractions. It is reported that if CII is more than 0.9, instability is indicated. If it is less than 0.7, the crudes are generally stable.

III. PROPOSED TREATMENT

Conventional treatment methodologies are insufficient in order to treat the problems caused due to the deposition of naphthenates, since the naphthenate deposits co-precipitate along with other inorganic scales, micro crystalline wax and other products. Through conventional methods in the current market such as acidization or solvent treatment, the formulation tend to only dissolve/disperse a single species which result in inefficient tubing or wellbore cleaning. Hence a multiple batch treatment method might be require which might consume more time and still result in an inefficient cleaning of the deposits. Also the rapid reactions might not allow the chemicals for deeper penetration and hit the desired target. The proposed treatment method involves pumping downhole of a single-step stimulation formulation that iscapable of dissolving naphthenate embedded with inorganic materials and simultaneously dissolve / disperse organic deposits present. Based on the sample analysis, the formulation was modified, and then tested with the deposit and crude sample to analyse the compatibility and the capability of the formulation in the treatment process.

Dissolution Test of the Samples using the Customized Formulation

1 gram of the sample was taken in a test tube and 5 ml of designed formulation was added to it and allowed to soak overnight. Next, the tube was gently shaken to observe dissolution or dispersion as shown in Figure 4. It was observed to dissolve or disperse. 5 ml of water is then added, mixed with the contents and kept undisturbed for 3-4 hours to observe any settling at the bottom. The tube was tilted and no settling at bottom was observed.Based from the chemical analysis such as the dissolution test, SARA analysis, LOI, XRD and SEM results, deposit sample of well A was found to be predominantly organic in nature with Asphaltenes deposition along with other soluble or insoluble inorganics and naphthenate deposits. It was detected to dissolve/disperse in the designed formulation. Therefore, well A is recommended for treatment with this formulation for dissolution or dispersion of the deposit in tubing and around well bore for improved productivity.

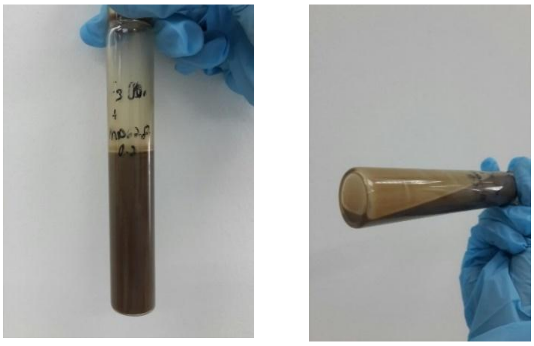

Fig. 4 Dissolution Test on the Deposit Sample from Well A

Compatibility test on the crude and water sample

The crude sample that possess a high amount of emulsion was tested. 20ml of the emulsion was taken into 3 different centrifuge tubes. One of the tubes was marked as blank and kept at 60˚C without addition of any chemical. The second tube was kept at ambient temperature, 2ml of the formulation was added and it was kept for standing without shaking. The third one was heated to 60˚C in water bath for 5 min, 2ml of the formulation was added and again kept in water bath for 10 min. The results are illustrated as Figure 5.The emulsion was very tough almost solid like with no significant or visible separation of water and oil even by heating to 60˚C. Addition of formulation at ambient temperature seems to cause slow separation of oil and water, nevertheless due to dense texture of the emulsion the penetration rate was slow. On the other hand, addition of formulation into the emulsion while heating at 60˚C managed break the emulsion with complete separation of water and oil. There was no rag formation at interface of oil & water. The designed formulation is also compatible with the crude

Possible Treatment Approach

A specialty micro-emulsion formulation that is almost 40% organic acid and 60 % solvent, was designed as per the compositional analysis of the deposit sample and the crude sample from well A, and was tested in the laboratory for the dissolution /dispersion of the deposits. Compatibility test of the formulation with the respective crude was also performed. Laboratory dissolution tests were conducted with no mechanical agitation and at ambient temperature to test the effectiveness of the formulation. Under field conditions agitation can be provided with mechanical force (via pumping) and heat afforded from (down-hole temperatures), leading to better dissolution rates and efficiencies than laboratory conditions [4].

The designed micro emulsion formulation can be used to improve the productivity of the well by injecting it into the tubing and around wellbore to dissolve/disperse these naphthenate deposits embedded with inorganics and organics. A sequence of fluid consist of pre-flush, formulated chemical and post-flush are to be pumped into the well for better results. The pumping operation can be either be done by bull heading method or when the well is not producing. The treatment requires soaking the tubing and the near wellbore with the chemical formulation in order to increase the cleaning efficiency, ensure complete dissolution and dispersion of the deposits and a deeper penetration into the wellbore matrix. The volume required for the treatment of the tubing and near the wellbore can be calculated based on the well schematic of the candidate well. Pumping rate can be controlled accordingly with the value of maximum allowable surface tubing pressure (MASTP) in order to avoid any tubing fracture or formation fracture.

Prior to the treatment as shown in Figure 6, bull heading of chemical can be done on the string to be treated. Deposit can then be allowed to be soaked with the chemical in the well for about 8 hours in order to give ample of time for the reaction of chemical with the deposits in the tubing and also near wellbore. Upon completing the soaking period, the well can be flown back in order displace the dissolved deposits and unspent chemical. Since the formulation is completely compatible with the reservoir fluid, no post operation problems will be encountered. Fluid sample from flow back can be taken every one hour to monitor and to make sure the entire unspent chemical, if any, is fully unloaded.

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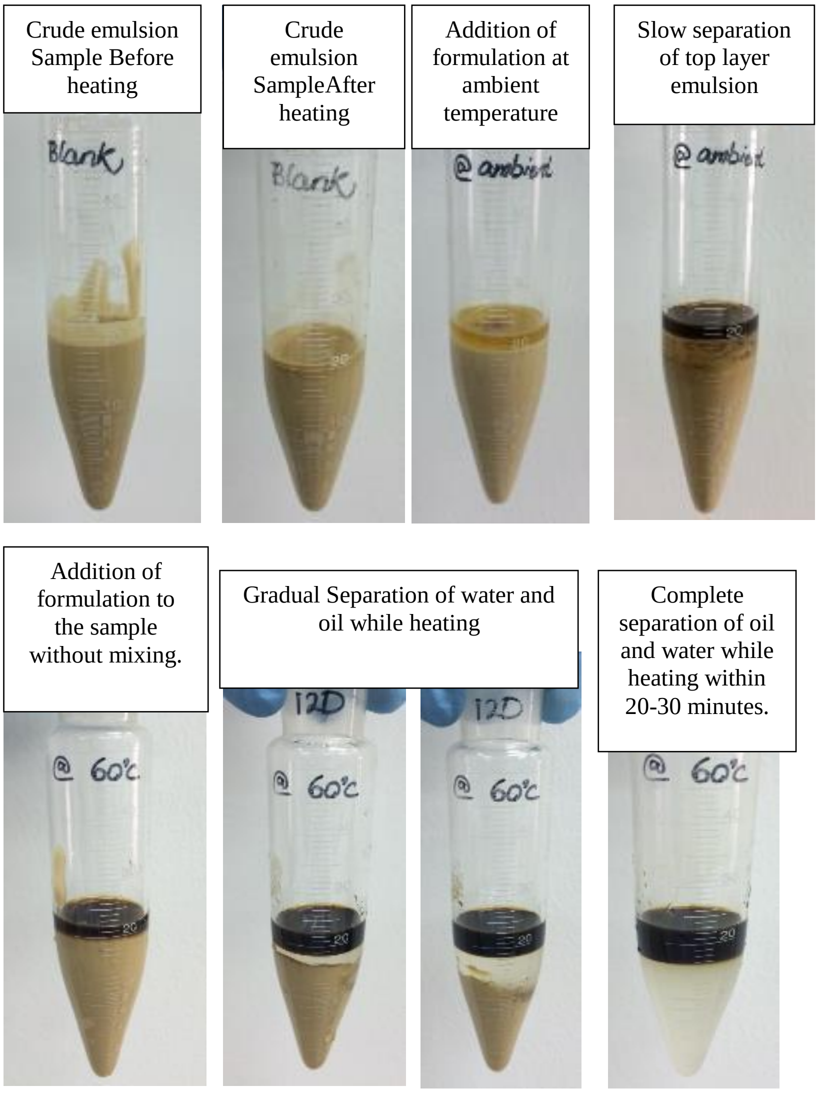

Fig. 5 Compatibility of the formulation with the crude emulsion

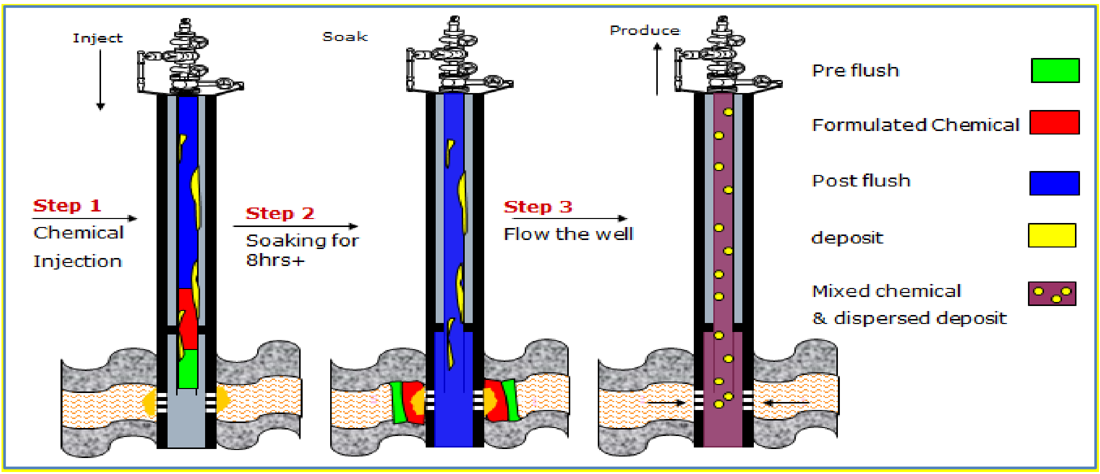

Fig. 6 Treatment method

IV. CONCLUSION

With increasing number of oil wells that produce crude with high acid nature, these crudes have a very high potential to yield naphthenate as deposits along with other inorganic and organics that may result in a decline in the production due to the flow assurance problems caused. These deposits leads to the blockage in the tubing and the near wellbore region.

Based on the various analytical and physical tests on the crude and deposit sample from well A, a micro-emulsion formulation was designed to dissolve/disperse the naphthenate induced deposition and emulsion caused in the candidate well A.

In the laboratory scale experiments, the designed micro emulsion formulation was able to fully dissolve and disperse the naphthenate deposits alongside other organic and inorganic scales. The same micro emulsion formulation also managed to break the emulsion with complete separation of water and oil at a higher temperature with no rag formation at the oil-water interface.

The designed chemical formulation is considered highly economical since it allows the chemical treatment to be in a single micro-emulsion pack. Hence, the lead time for the treatment can shorter as it does not need to be mixed on site and also has a storage life of more than six months.

The designed formulation can also perform an efficient cleaning of the running and the near wellbore region as it require a single batch to dissolve and disperse naphthenates embedded with other inorganic scales and micro crystalline organics. With a higher penetration rate into rock matrix with control reaction kinetics, the designed formulation ensures effective cleanup around the wellbore region.

This methodology in this paper was designed to assist in designing a suitable chemical formulation to restore well performance and its productivity by various testing and analytical processes that is practiced for the identification of naphthenates along with other organic and inorganic components. The composition or the formulation of the speciality micro-emulsion formulation primarily depends on the characteristics of the crude and the deposition.

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