

# Corrosion Management Methods of High TAN Crude

## Case study: (Fula Crude Oil-Sudan)

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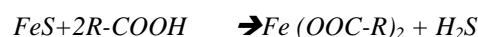
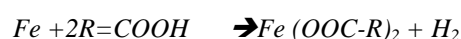
### Abstract

Sudan heavy crude share represents 18% of the global production. Fula heavy crude with high TAN and salt content affects the price and the environmental specifications, due to serious corrosion problems at the processing units of Khartoum refinery. In this study corrosion management methods for Fula processing equipment had been investigated. Diluents effect on properties improvement; metallurgical equipment selection had been explored. Smart Guard method suggested as an overall corrosion monitoring and control method for corrosion management in Khartoum refinery.

**Keywords:** High TAN crude, Fula crude, corrosion treatment method.

### 1. Introduction

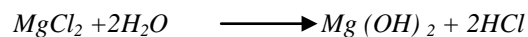
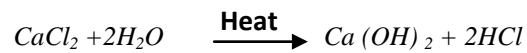
Crude corrosively problems have been studied since 1950's because of their technical and economic impact on production and refining operations. Crude quality is determined by measurement of some crude properties such as the specific gravity and acid content, which is also a factor in determining the corrosive properties of the crude entering the refinery. For heavy crude, the API gravity is 18 degrees or less [1]. The total acid number, TAN exceeding 1.5 to 1.8 mg KOH/g the crude considered corrosive; however, corrosion problems can occur in crudes with TAN numbers as low as 0.3, for several reasons, including velocity and the nature of the acidic species present [2]. Heavy crude have the highest naphthenic acids content among all the crude types [3]. Processing of high acid crudes results in significant high temperature corrosion (230-400 °C) of refinery carbon steel processing equipment, following the equations bellow



The existent of unsalted water is one of crude corrosion reasons, so heavy crude desalting unit can reduce the corrosion rate. But due to their high viscosity, heavy crude oils cannot be transported with conventional pipelines and acquire additional treatment. An efficient flow assurance method is to dilute the heavy oil with a less viscous hydrocarbon phase such as condensate, naphtha, kerosene or light crudes. Dilution with a light hydrocarbon is also necessary in heavy oil industry before froth treatment of heavy crude (removing water and solids) due to the similar density of water and heavy crude [5]. Chlorides and solids in water may lead to serious corrosion problems in downstream upgrading units and must be removed [6].

## 2. Main Corrosion Type of High Acid Crude (HAC):

1.  $H_2S-HCl-H_2O$  corrosion.
2. Heavy metal corrosion.
3. Catalyst poisoning, salt corrosion, ash deposition, coking and scaling on catalyst bed.



Construction materials such as carbon steel, 5Cr-II2 Mo and 9Cr-1Mochrome steel, 410SS, are resistant to sulphur corrosion, and need to be up graded to better quality construction materials like 316SS, 5Cr-1 or 2Mo, 9Cr-1Mo chrome steels, 317SS, aluminized steel . Cathleen Shargay et al. indicated that places like side stream piping require up-gradation to 317 SS or 316L SS with 2.5% Mo [7].

4.  $H_2S-HCN-NH_3-H_2O$  corrosion.
5.  $NH_4Cl-NH_4HS$  corrosion: Nitrogen components causes serious plugging and under scale corrosion.

Multi solutions are existing for corrosion management .Naphthenic acid removal, corrosion inhibitors, crude dehydration and desalting, and crude properties improvement (density and viscosity) [8]. Controlled process, with optimum parameters is important for corrosion reduction.

## 3. Fula processing problems

Fula crude from Western Sudan wells has such properties of high density and viscosity ,Low API ,low sulfur, high acid value, high water content, high calcium content. It can classify as heavy crude with acid value, TAN of 5 mg KOH/g Table 1. Due to Fula compositions corrosion in distillation columns overhead lead to high cost for maintenance or renewable.

The study represents some possible corrosion management methods of Fula heavy crude in Khartoum refinery-Sudan. The research viewed the diluents effect on properties improvement, metallurgical protection and Smart Guard method.

#### 4. Materials and Methods

Fula crude, from Block six- Sudan with the following properties, Table 1, was refined in Khartoum Refinery Company (KRC).

Table 1: Fula Crud Properties:

Property	Value
Density (15°C), Kg/m <sup>3</sup>	936.2
API°	19.6
Kinematic viscosity (100°C), mm <sup>2</sup> /s	69.42
Water content, m%	0.10
Acid number, mg KOH/g	2.60
Sulfur content, %	0.04
Calcium content, ppm	1287

#### 4.1 Fula Corrosion Management Methods

The following methods have been suggested for corrosion reduction at Fula processing units.

##### 4.1.1 Vis Breaking process

(CNPC) and Sudan government agreed to build a visbreaking unit to reduce the viscosity from 5000 mpa.s at 29°C to 1600 MPa.s at 29°C or less to meet the transporting condition of the pipeline. Upstream partially processing of Fula Crude in Visbreakers can improve the crude pump ability, reduced Ca and iron content of the crude associated with partial desalting and TAN reduction [9].

##### 4.1.2 Fula Naphtha Blends

Comparison between many of naphtha and kerosene ratios (15-35 wt %) with Fula had been investigated at elevated temperatures for properties improvements. The fact that rheological properties reduction will enhance crude desalting process and sequentially crude equipment corrosion. Naphtha was selected for Fula dilution depending on viscosity and density reduction [10]. See Figures (1) and (2).

##### 4.1.3 Corrosion inhibitors

The corrosion inhibitor reacts with metal surface to form protective films that inhabit the metal corrosion. Sulfur- based corrosion inhibitor was applied to the refinery crude units to eliminate the fouling seen with caustic and phosphate ester and still maintain adequate high temperature naphthenic acid corrosion control.

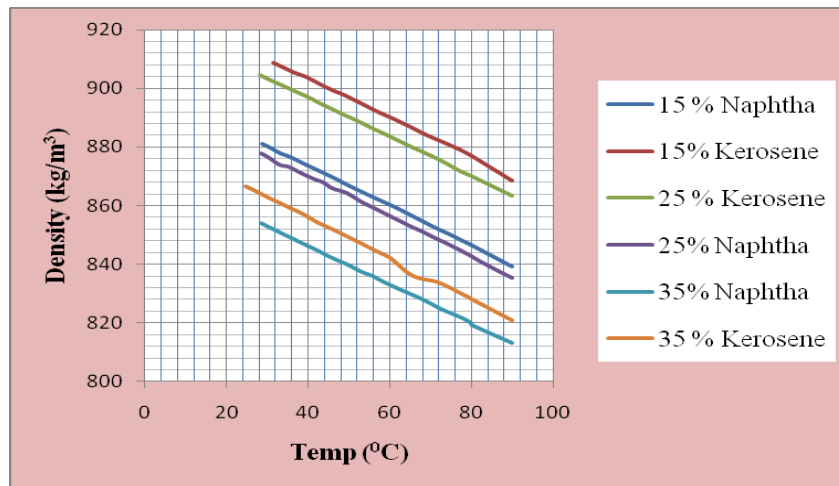


Fig 1: Density of Fula blend with Naphtha and Kerosene

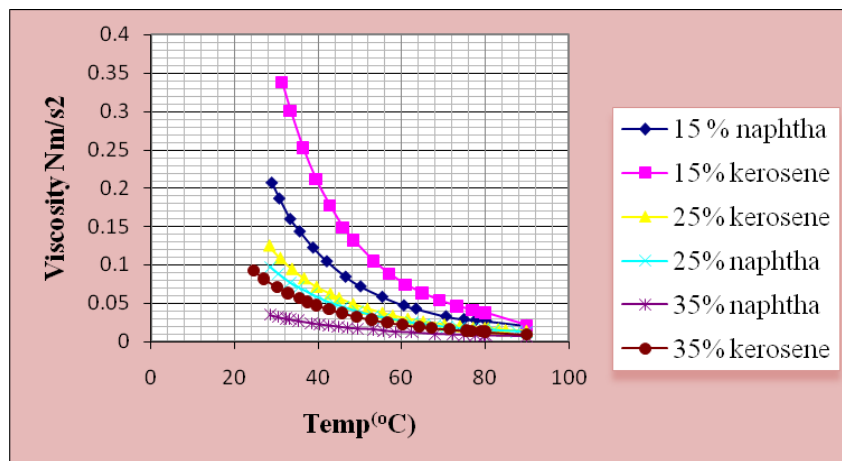


Fig 2: Viscosity of Fula blend with Naphtha and Kerosene

#### 4.1.4 Naphthenic acid removal

Predominate commercial methods available for extraction of naphthenic acid from oil used an aqueous solution of caustic soda to pull the acid into the water phase. Over dosing of caustic has however resulted in caustic embitterment (stress corrosion cracking) of down steam heat exchangers and equipment.

#### 4.1.5 Metallurgical Protection

Two types of alloys were used in Khartoum refinery units, the following corrosion rate (mm/year) were reported for carbon steel and 316 SS  $\geq 2.5\%$  Mo and 317 SS, Tables 2,3.

For metallurgical protection against naphthenic acid attack, the carbon steel showed higher corrosion rate with compare to 316 SS .Incorporation of higher molybdenum (2.0-4.0%) into the carbon steel alloy( AISI 316SS) , corrosion rates will be reduced .

Table 2: Estimated corrosion rates for carbon steel (mm/y) [11]:

Sulfur	TAN	Temperature (°C)							
(Wt. %)	(Mg/g)	<232	233-260	261-288	288-316	316-343	344-371	372-399	399+
0.2	> 4.0	1.02	2.04	2.55	4.09	4.60	5.11	7.15	7.66
0.21-0.6	> 4.0	0.51	0.77	1.28	1.79	2.30	3.06	3.58	4.09
0.61-1.0	> 4.0	0.64	1.02	1.53	2.55	3.06	3.83	4.60	5.11

Table 3: Estimated corrosion rates for 316 SS with  $\geq 2.5\%$  Mo and 317SS (mm/y),[11]:

Sulfur	TAN	Temperature (°C)							
(Wt. %)	(Mg/g)	<232	233-260	261-288	288-316	316-343	344-371	372-399	399+
0.61-1.0	$\leq 4.0$	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
	4.1-6.0	0.03	0.03	0.03	0.03	0.05	0.10	0.10	0.13
	> 6.0	0.03	0.03	0.05	0.08	0.10	0.13	0.18	0.26

#### 4.1.6 Metal Removal

Exclibur technology for metals removal include First, promote crude dehydration and salt removal in crude storage tanks, then applied a Baker Petrolite pretreatment chemical to crude transporting line. Crude oil was allowed to settle for at least 48 hours before being blended with other crude. Application of this crude pretreatment program provided overall desalting system performance .Second, a specialized emulsion breaker was selected and applied that effectively controls the emulsion stabilizing tendencies of the high TAN, high calcium naphthenate content . The calcium removal efficiency reached (85-95%),and iron removal to 70% [12].

#### 4.1.7 Corrosion control

Smart Guard method for naphthenic acid corrosion can be used at KRC to minimize the corrosion rate. This assessment included a review of unit metallurgies, operating conditions, and equipment configuration. Baker Petrolite calculated process stream TANs, sulfur levels and velocities in high temperature areas, and completed a probability of failure analysis using the Smart Guard predictive software tool. Based on this analysis, a corrosion mitigation plan developed for crude blend (TAN 0.3-1.3 mg/g). In addition the method included development of a high temperature corrosion inhibition strategy using Smart Guard corrosion inhibitor [13] .

### 5. Decision and Conclusions

Controlling high TAN and high acid crude is a long life controlling process. Multi monitoring and controlling method can be studied for lower corrosion rates, for instance:

1. Use of high temperature corrosion inhibitors was successfully evaluated as a mean to mitigate naphthenic acid corrosion.
2. The technology for mitigate the corrosion potential of high acid crude like: caustic and phosphate ester corrosion inhibitors were effective in controlling the naphthenic acid corrosion but result in fouling in the crude, vacuum and hydrotreaters.
3. Sulfur- based corrosion inhibitor was applied to the refinery crude units to eliminate the fouling seen with caustic and phosphate ester and still maintain adequate high temperature naphthenic acid corrosion control.
4. Corrosion resistant alloys can be predicted for areas with severe corrosion rates.
5. There is an approach to install high alloy equipment and piping systems that are resistant to corrosion by naphthenic Acids. This approach is only economically attractive if a secure long-term supply of corrosive crude is available at attractive prices.
6. Some crudes have also caused overhead system corrosion because of their poor desalt ability.
7. It is possible to develop a series of operating envelopes in terms of TAN and sulfur .For each operating envelope, a specific corrosion control action is required. The economically best option is to run to the limit of a chosen corrosion control level. This approach maximizes the amount of corrosive crude that can be processed for a given level of corrosion control.
8. Preferred corrosion control actions include the following:
  - Use of naphthenic acid corrosion inhibitor.
  - Focused inspection and corrosion monitoring.
  - Limited alloy upgrading.

## **6. Recommendation for further work**

Over the next five years it is forecast that HAC supply will continue to increase significantly, with production rising across the world, all of these crude oils has significant acid numbers, and therefore corrosion management is vital to insure that corrosion risk is minimized. In addition to high temperature corrosion management, many of these high acid crudes can be harder to desalt and lead to increase overhead corrosion, fouling and product stability issues.

The recommendations for further work, among others, include the following:

1. Application of cheap diluents which are environmentally – friendly and having a high volatility, such as methanol. For better desalting efficiency.
2. Coupling many treatment methods for corrosion treatment, such as removal of naphthenic acids, and metal ,salt abolition
3. Search for good decalcicizing agent (esters, amine components) because Fula high calcium content was one of the side effects of naphthenic acids existence and corrosion.
4. Conduct a more comprehensive corrosion risks economical studies based on the crude assay and prices.

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## References

- [1] <http://www.wikipedia.org/crudeoil>, Kaolin J-comp bell, Nov, 2007.
- [2] <http://www.connection.com/> Nov, 2007.
- [3] Brient, j. A, Doyle, M.N and Wessner, P.J, 1995, "Naphthenic acids ", Encyclopedia of Chemical Technology, ,(P.1017-1029), ,John Willy sons, ,New York.
- [4] Gregory Roach Technical considerations for HAC processing (e-mail:groach@kbsat.com).
- [5] X. A. Wu, J. Czarnecki, Energy and Fuels 19 (2005) ,1353.
- [6] X. Wu, Energy and Fuels 17 (2003) 179.
- [7] Ernesto Blanco, F., Hopkinson Brian, "Experience with naphthenic acid corrosion in refinery distillation process units", *Corrosion* 83, NACE, Anaheim, California (1983) Paper No. 99.
- [8] <http://www.ogj.com/Nov,2007>.
- [9] Chinese National Petroleum Company (CNPC)- Sudan, 2008,personal contact.
- [10] Afaf G. A, PhD Thesis, University of Khartoum, Chemical Eng. Dept , ,Aug,2007.
- [11] HibaA.Badia, ElafE.Hassan , Afaf G Abadi ” Corrosion Treatment of High TAN Crude”, design project, June 2008
- [12] Dang yuming,Zhangjianjun and Xiao , KRC basic design studying material, Production preparation group of KRC Expansion Project Department,2008
- [13] M. Kulich, KRC, DCU- CDU overhead corrosion, Jan 2008.