

## IRON SULPHIDE AND COKE FOULING FROM SOUR OILS: REVIEW AND INITIAL EXPERIMENTS

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### ABSTRACT

In sour oils at elevated temperature, iron sulphide and coke deposition are among the most important causes of fouling. Deposits are generally found to contain both carbonaceous material (coke), and inorganic material. A review of relevant literature is presented, to attempt to identify underlying fouling mechanisms. The fouling process is considered to involve two reactions: coke formation and FeS formation. Sources of iron and sulphur are discussed, along with temperature effects on the reactions. The interactions between corrosion and fouling are considered. One view of the fouling process is that deposits are initiated via formation of FeS particles in suspension by reaction of H<sub>2</sub>S or organic sulphides with iron oxides from upstream corrosion processes, leading to particulate fouling. An alternate view is that a film of iron sulphide forms first on the surface, the carbonaceous mesophase then wets the iron sulphide surface, leading to a strongly adherent carbonaceous layer.

The interactive processes of chemical reactions leading to formation of precursors and the physico-chemical process of deposition and further reaction in the deposit layer have not been fully understood. The links between corrosion and fouling have not been clearly demonstrated. In this paper, the evidence for, and the implications of these various process-side fouling mechanisms are discussed. An experimental program has been devised to distinguish among the proposed mechanisms, and initial results are presented.

### INTRODUCTION

In oil refinery crude oil pre-heat trains down-stream of the de-salter, and on the tube-side of furnaces which treat heavy fractions, two types of fouling predominate. These are: inorganic fouling, in which deposits mainly consist of FeS and salts, and organic fouling due to asphaltenes which ultimately result in coke deposits. These two types of fouling may occur together, or separately, depending on circumstances.

Figure 1 shows results of a survey on probabilities of fouling of each type for crude unit pre-heat trains and furnaces (Lemke, 1999). In the former, at low temperatures fouling is likely to be due to inorganics, and as the temperature rises along the train exiting the crude furnace at about 350°C, fouling appears more likely to be caused by organics. Similar trends in results are shown for hydro-desulphurizer units (Lemke, 1999).

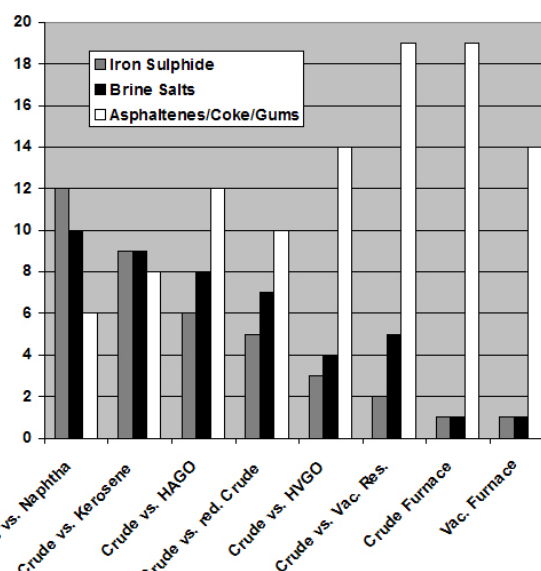


Figure 1. Probability of different types of fouling in crude units [0= Unlikely, 20 = Very Likely] from Lemke (1999).

Considerable evidence of mixed organic and inorganic deposits exists in the literature, some examples of which are found in Table 1. For the crude oils CO-1 to CO-4, results were obtained in re-circulation flow or stirred batch laboratory units, and temperatures are taken to reflect those in crude oil pre-heaters. For heavy fractions HF-1 and HF-2, results are from the tube-side of an industrial bitumen

Table 1 Crude oil and heavy fraction fluid and deposit compositions \*

Fluid	CO-1	CO-2	CO-3	CO-4	HF-1	HF-2
% As	8	7	2	9	19	19
% S	1.8	3.7	1.3	3.7	5.0	5.0
Fe (ppm)	10	4	1-21	2-65	340	340
T <sub>b</sub> (°C)	320	260	270	270	350	500
T <sub>s</sub> (°C)	370	390	375	382		
Deposit						
% C	51	29	23	46	7	58
% Fe	21	27	49	37	48	20
% S	17	22	15	12	26	14
S/Fe (at.)	1.4	1.4	0.5	0.6	0.9	1.2
% Ash	32	56	71	44		
Ref.	B	Y	S	S	P	P

\* As = asphaltene content, CO = crude oil, HF = heavy fraction from bitumen; References: B= Bennett et al.,2009, Y = Young et al., 2009, S= Srinivasan and Watkinson,2005, P =Parker and McFarlane,2000

LC Finer and coker furnace units, where fluid temperatures reach 350 and 500°C, respectively. Deposits range from 7% to over 50 % wt. carbon content. Oils in Table 1 contain 1.3 to 5 % S. In the deposits, sulphur content is from 12-26 %, which includes both organic sulphur and sulphur associated with FeS and other minor metals. In these cases, S has concentrated in the deposits. This is not always the case (Lemke and Stephenson, 1998). In general, in the absence of significant amounts of FeS, some sulphur species aid deposition, and others reduce it (Watkinson and Wilson, 1997). This effect is most significant under autoxidation conditions; under inert conditions, species effects are muted but still present. Iron is present in the heavy fractions at 340 ppm, and in the crude oils at below 65 ppm, but is highly concentrated in the deposits at concentrations of 20 to 49%. Atomic S/Fe ratios in deposits range from 0.5 to 1.4. Apparently sulphur-rich FeS (S/Fe>1) may occur because some of the sulphur is associated with the organic part of the deposit, or because of the presence of pyrrhotite, Fe<sub>1-x</sub>S (as reported by Bennett et al, 2009). Other deposits appear to be iron-rich for FeS (S/Fe<1) because of the presence of iron oxides, or perhaps due to high iron from ex-situ corrosion, as was subsequently found in the work of Srinivasan and Watkinson (2005). The mineral contents of the deposits of Table 1 are well above 10 % wt., above which Panchal (2006) recommends that the focus of fouling should be first on the source of the inorganic species.

### Sources of Sulphur and Iron in Feedstocks

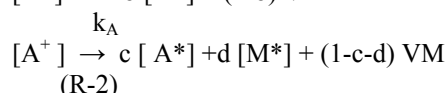
Sulphur is inherent in crude oils, and is more concentrated in heavy fractions. It can be present in a number of forms, such as mercaptans, sulphides, di-sulphides and the like (Payzant et al., 1986; Mitra-Kirtley et al., 1998; Shi et al., 2010). Crude oils, bitumen and their heavy fractions may have sulphur contents from less than 1 % to over 6 %.

Iron usually has two sources. For crude oils, inherent iron content is in the range 0.04 to 120 ppm (Mushrush and Speight, 1995). For heavy crudes or bitumens, iron contents are usually in the range 120-500 ppm (Gray, 1994). Corrosion of upstream piping or process equipment can also contribute significantly to dissolved iron content, for example as naphthenates, or result in particulate iron oxides being generated. Other metals such as Ni and V are found in significant amounts as well.

### Reactions Leading to Deposits

It is obvious from Table 1 that mixed organic and inorganic deposits form during the heating process. From a simplified viewpoint, one can consider that two fouling processes occur, the formation of coke and the formation of FeS. These may occur in parallel or in series, independently or with interactions, as will be shown below. They also may occur in the bulk, the thermal boundary layer or on the wall. Indeed in tube-side furnace fouling, coking and sulphidation reactions also occur within the deposit layer itself (Gentzis et al., 2000).

**Formation of coke:** A number of models are available for formation of coke from asphaltenes in the absence of hydrogen. Asphaltenes are usually present in heavier crudes, and can also be produced from maltenes [M<sup>+</sup>], by thermal reactions such as (R-1). In the thermal conversion model summarized in Wiehe (2008), the formation of asphaltene cores [A\*] from unreacted asphaltenes [A<sup>+</sup>] occurs by a first order reaction (R-2).



When the solubility of A\* in the surrounding fluid is reached, an instantaneous phase separation occurs, precipitating coke. The generation of asphaltene cores is given by

$$r_{A^*} = k_A C_{A^+} \quad (1)$$

Thus the rate of coke formation should be roughly proportional to the asphaltene concentration of the fluid. An example of this well-established relation is given in Table 2, where for fixed coking conditions of 1-hour at 400°C, the coke yield is roughly proportional to asphaltene (or the MCR) content of the fluid. Rahmani et al., 2003 have shown that k<sub>A</sub> increases linearly with the sulphide content of the feed-stock, as the sulphide bonds are more easily broken. The coke formation reaction is known (Wiehe, 2008) to have an activation energy of about 150 kJ/mol, and hence it is not surprising that rates of coke deposition increase strongly with surface or film temperature. Therefore at the high temperature end of the crude pre-heat train (T<sub>b</sub>~300°C), or in furnaces where H<sub>2</sub> is not present to stabilize the reaction, high coking rates are to be expected.

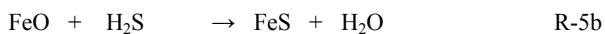
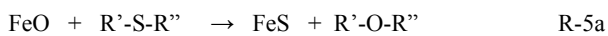
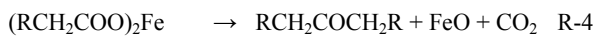
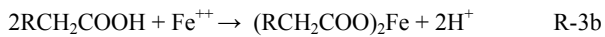
Table 2 Coke yield at 400°C in one-hour, as a function of asphaltene content of feedstock (Yue *et al.*, 2004)\*

Feedstock	% As	% MCR	% Coke Yield
VHGO	0	0.2	0.06
KHGO	0	2.8	0.2
Cold Lake Bitumen	15.4	11	10.0
50% VHGO-50% PI	16.9	13.7	8.4
25 % VHGO-75% PI	24.6	20.4	27.3
25% KHGO-75%PI	24.6	21.0	33.0
100% PI	32.0	27.1	41.6
As from PI	100.0	32.0	46.2

\*As = asphaltene concentration, MCR=Micro-Carbon Residue, VHGO=Virgin heavy gas oil, KHGO=coker heavy gas oil, PI = + 524°C fraction; % by Volume

**Formation of FeS:** The formation of iron sulphide in a hot flowing oil is believed to involve two processes: the corrosion of iron by sulphur compounds, and the

decomposition of iron salts, for example of naphthenic acids (Panchal et al., 1999). Two different mechanisms were proposed for the reactions depending on the presence or absence of oxygen; here we consider only the latter case. The three steps are shown in simplest terms below: corrosion of iron by organic acids (which occurs on the walls of upstream piping or equipment), thermal decomposition of acid salts, and reaction of iron oxide with organic sulphur or  $H_2S$ .



These reactions can occur on the heat transfer surface, resulting in build-up of FeS films. Alternately, reactions R-3b, R-4 and R-5 can occur in the bulk fluid, giving rise to particulate FeS which may subsequently deposit. If reaction R-3a occurs on corroding upstream equipment, particulate FeS can be formed on the heat transfer surface.

With dissolved iron in the feed, steps R-3b, R-4 and R-5 can occur in non-corroding systems as well. Parker and McFarlane (2000) expected that soluble organic iron species such as iron carboxylates and iron naphthenates, are likely to decompose at the high temperatures experienced in furnaces. Their decomposition temperatures of roughly  $300^\circ C$  and  $>400^\circ C$  respectively, would be exceeded at the furnace conditions of  $T_b \sim 500^\circ C$  and  $T_s \sim 600^\circ C$  reported by Gentzis et al., 2000. Thus FeS could form and deposit in the furnace tubes. At the lower temperature range common for heat exchangers, Panchal (2006) reported that iron acetate decomposes to iron carbonate at  $282^\circ C$ , and to iron oxide at  $370^\circ C$ . Evidence for the thermal decomposition of iron salts in deposit formation is shown in Figure 2. Here, oil-soluble iron acetate was added to a gas oil, and resulted in higher fouling at 100 ppm Fe.

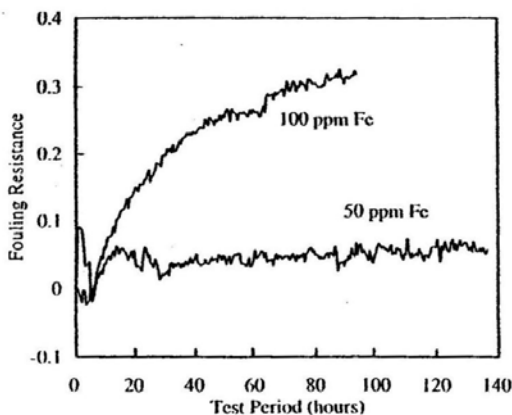


Figure 2. Effect of addition of soluble iron acetate on fouling of a gas oil (Panchal et al., 1999)

Iron oxides may be involved in deposition processes at lower temperatures where they might remain un-sulphided

or where water is present. Cosultchi et al. (2001) proposed a deposition mechanism which included adsorption of sulphur or hydroxyl-bearing compounds on tubing surfaces, and dissociation of sulphur compounds. In the absence of water this leads to the formation of iron sulphide. They note that pyrrhotites are mostly generated at temperatures below  $473K$  and in sulphur-poor atmospheres.

For the formation of insoluble FeS in oils, kinetics are not well established. For reaction of dissolved iron species with active sulphur species in the oil, one could assume a reaction of the form:

$$r_{FeS} = a_1 k_{FeS} C_{Fe^{++}}^m C_S^n \quad (2)$$

where  $k$  is a reaction rate constant with an exponential dependence on temperature. Lemke and Stephenson (1998) analyzed over 30 visbreaking furnace feeds, and deposits from 20 plants. Rough correlations were found between sulphur content of feed and of deposits, and between iron content in the feed and the deposit, as shown in Figures 3 and 4. These trends support the idea of deposits forming from reactions of sulphur and iron species. The authors suggest that the primary source for iron in the deposits is the iron-containing inorganic debris such as iron oxide dispersed in the feedstock. Likewise, Bennett et al., 2009, attribute the iron in their deposit (Table 1 above) to the sediment in the oil.

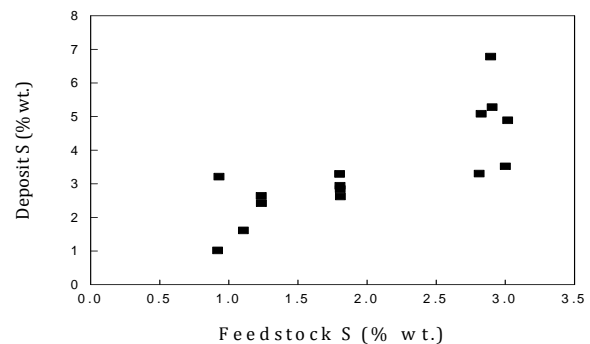


Figure 3. Visbreaker furnace deposit sulphur content versus sulphur content of feed (Lemke and Stephenson, 1998).

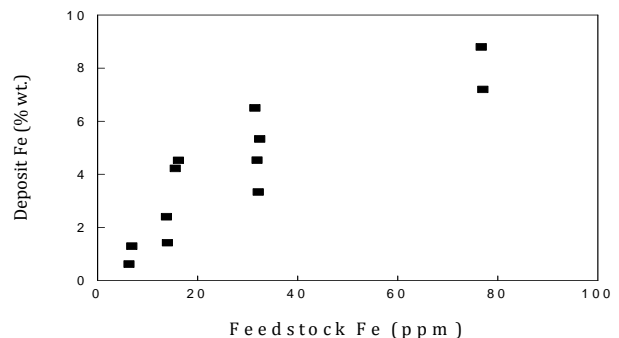


Figure 4 Visbreaker furnace deposit iron content versus iron content of feed (Lemke and Stephenson, 1998)

For reaction of soluble sulphur species with a carbon steel surface (e.g R-3a), the adjusted “McConomy curves” used for sulphidic corrosion (Gaverick, 1994), can be examined. These curves show corrosion rate (mm/year) on carbon steel and different alloys versus temperature for an oil containing 0.6 % S. A second plot shows a multiplier for the corrosion rate versus sulphur content of the oil. From these curves, a power law kinetic equation was fitted for carbon steel:

$$r''_{\text{FeS}} = a_2 k''_{\text{FeS}} C_S^n \quad (3)$$

Here the concentration of iron in the metal wall is considered a fixed constant, and is absorbed into the value of  $k''$ . From the carbon steel dissolution rates in mm/year, at 260°C to 316°C, and from the multiplier curve for oil sulphur contents from 0.28 to 2 %, an activation energy of 50.9 kJ/mol, and an “n” value of 0.36 was extracted, whence

$$r''_{\text{Fe}} = \rho_w(-dx/dt) \quad [\text{kg/m}^2\text{-y}]$$

$$= 148.7 \rho_w \exp(-50936.5/R_g T) C_S^{0.36} \quad (4)$$

where  $C_S$  is wt. % sulphur in the oil, and T is in K.

#### Temperature effects in combined coke and FeS fouling:

Given the above activation energies for coke formation and for FeS formation, the effect of temperature can be examined. Figure 5 shows both rates at a given temperature divided by their corresponding values at 350°C, plotted versus temperature. It is evident that as temperature rises, the coke formation reaction increases much more rapidly than the FeS formation reaction, in support of Fig. 1. At low temperatures the rate of FeS formation would exceed that of coke formation.

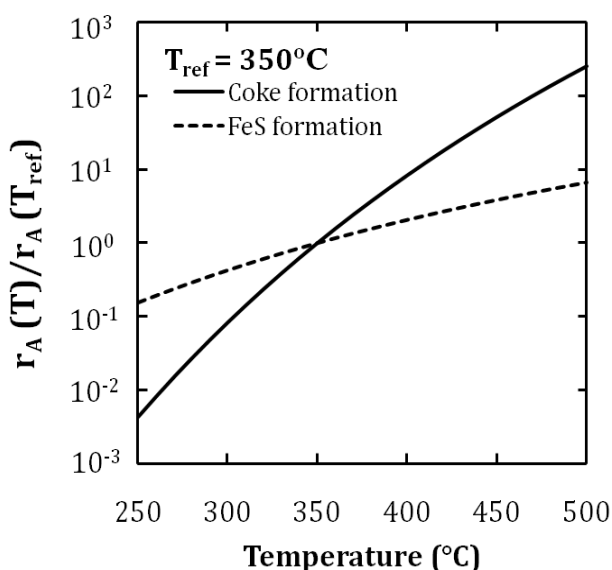


Figure 5. Rates of coking and FeS reactions relative to their values at a reference temperature of 350°C.

Figure 6 shows some data from Srinivasan (2008) for two oils of Table 1, which also supports this trend. As the film temperature increases, the ash content in the deposit decreases (as the organic fraction increases). For a given film temperature, the deposit ash fraction is lower and the organic fraction is higher, for oil CO-4, the oil with higher asphaltene content.

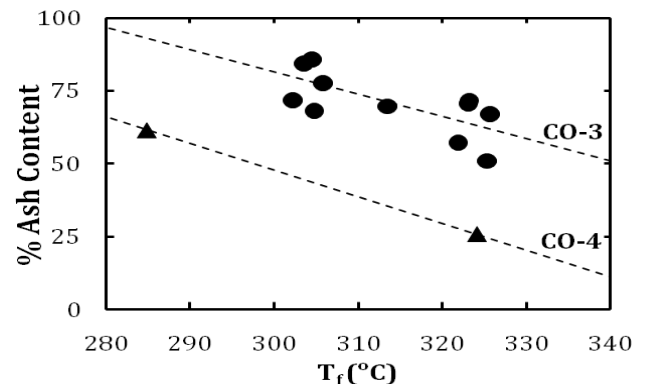


Figure 6 Effect of film temperature on deposit composition for two oils of Table 1 (Srinivasan, 2008).

#### Corrosion and its interactions with and fouling

The corrosion of refinery equipment has become increasingly significant in recent years as the acid content in crude oils being processed has progressively increased. Corrosion is an important inducement to fouling (Bott, 1995; Somerscales, 1997; Panchal *et al.*, 1999). Physical and chemical interactions of corrosion processes which affect fouling in the sour oil systems are summarized in Table 3. Corrosion layers can act to enhance chemical reactions of fouling and to intensify mass transfer due to viscous sublayer thinning, reducing stopping distance for particles to wall and by providing particle interception (Crittenden and Alderman, 1988; Pareek *et al.*, 1994; Santos *et al.*, 2004) or because of their roughness simply serve to increase physical entrapment of particulates. Compared to a rough surface, a smooth non-corroded surface may inhibit the attachment of gum or coke-like particles, thereby reducing fouling. FeS layers may or may not adhere to the surface. In the latter case even as the wall becomes thinner overall thermal resistance will remain essentially constant, because wall resistance is a small part of the overall thermal resistance. With pure FeS deposition, thermal effects may also be small because of the relatively high thermal conductivity of FeS ( $\lambda_d \sim 5 \text{ W/m-K}$ ). Roughness effects are likely to be significant in both situations. Compared to FeS, coke deposits tend to have very much lower thermal conductivity, and hence create greater thermal resistance per unit thickness.

Therefore, understanding of corrosion behavior and mechanisms in oil processing is of importance to understanding fouling. Chernov *et al.* (2002) discussed the causes and mechanism of corrosion on oil-field pipelines. Kane and Cayard (1998) summarized typical methods of assessing crude oil corrosivity. Many parameters influence

the crude corrosion process. The total acid number (TAN), flow velocity regime, temperature, sulphur content, and materials of construction are known controlling variables. However, TAN alone is also believed to be insufficient to estimate oil corrosion (Slavecha *et al.*, 1999, Zeinalov *et al.*, 2009) as the main species that account for petroleum corrosion are naphthenic acids and sulphur compounds (Laredo *et al.*, 2004).

Table 3 Key physical and chemical interactions of corrosion and fouling in sour oil systems

Factor	Effect
Corrosion of upstream equipment (ex-situ corrosion)	Generates dissolved and particulate metal species which cause downstream fouling
Corrosion of heat transfer surface (in-situ corrosion)	Forms rough surface which may mask thermal fouling, enhance adhesion and trapping of particles, create dead zones, etc.
Sulphur content and species in oil Naphthenic acids	Sulphidation is necessary for coke formation and adhesion High sulphide content may increase coke formation rates and mitigate naphthenic acid corrosion FeS formation may inhibit or accelerate coke formation
Coke formation	Coking at high temperature may protect metal from FeS formation

It is difficult to separate corrosion caused by naphthenic acid from that of sulphur compounds due to the coexistence of the two species in oil and similar temperature range of corrosion for both (Zetlmeisl, 1996). In fact, corrosion by naphthenic acid and sulphur compounds usually occurs simultaneously, and they will have influence of various degrees on each other during the corrosion process (Yepez, 2005). As mentioned above, the content of sulphur in crude oils and heavy oils is usually between 0.2-6 wt.%. Many researchers have studied the different sulphur compounds in crude oil and bitumens, for example, Payzant *et al.*, 1986, and Shi *et al.*, 2010. It has been observed that higher sulphur content will mitigate naphthenic acid corrosion. For instance, Slavcheva *et al.*, (1998, 1999), found that addition of 0.1 % H<sub>2</sub>S to oils tended to decrease the corrosion rate, most likely due to formation of stable iron sulphides in competition with the soluble iron naphthenates.

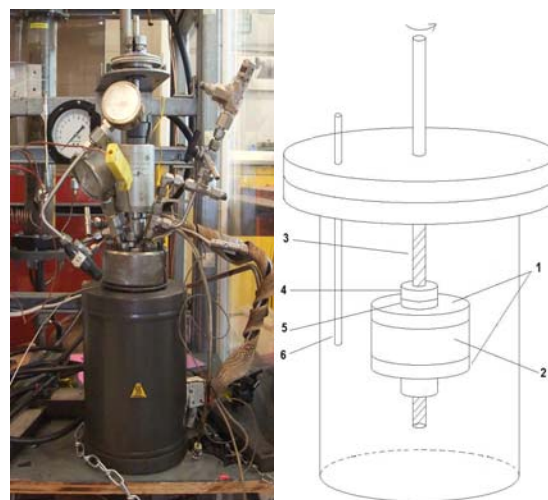
### Suggested Fouling Mechanisms

Considerations from the above literature suggest three possible fouling mechanisms, designated as mechanisms A, B and C. Different mechanisms may apply at low temperature than at high temperature, and on corroding vs non-corroding surfaces. Mechanism A, iron sulphide particulate fouling, is suggested by Lemke and Stephenson (1998), and is supported by results of Bennett *et al.*, 2009. Particulate FeS has also been found by Laursen and Frandsen (1998) to be involved in combustion unit deposits. It is assumed that the deposit forms following the formation of FeS particles in suspension, according to reactions such as R-1 to R-3. Fouling steps would include: i) FeS particles

are formed in the bulk or thermal boundary layer and deposited on the metal surface. ii) Coke is then deposited, possibly at accelerated rates due to the presence of FeS (Wiehe, 2008 pp 271). Mechanism B, iron sulphide film fouling, was proposed by Cosultchi *et al.* (2001) from low-temperature studies, and is supported by the description of the FeS layer which is wet by carbonaceous mesophase liquid film (Wiehe, 2008). The organic deposit thus forms after the formation of an FeS layer. Gentzis & Rahimi (2003), have observed massive, non-particulate sulphide layers within deposits. Further FeS formation is inhibited by the coke layer. Mechanism C, simultaneous FeS and coke formation, as suggested by Gentzis *et al.* (2000), invokes decomposition of iron salts as described by Panchal *et al.* (1999) which originate in the feed, not from upstream corrosion. The presence of coke does not inhibit FeS formation, which then appears throughout the deposit. This mechanism was suggested based on deposits from a coker furnace, which consisted primarily of carbonaceous material with high concentrations of iron sulphide.

### INITIAL EXPERIMENTATION

An experimental program has been designed to discriminate among proposed mechanisms, and includes tests with metals of different susceptibilities to sulphidation. Initial experiments were performed using a 600 ml stirred batch reactor manufactured by Parr Company. A rotary cylinder consisting of a ring of carbon steel or stainless steel 1.1-cm. long and 3.81-cm. outside dia. was fixed to two flanges of the same diameter made from MACOR, a type of machinable ceramic. The cylinder was driven by a magnetic drive with a motor controller. The rotation speeds were determined by tachometer. Thermocouples were used to measure the bulk temperature, and for temperature control. The reactor and inner structure are shown in Fig. 7.



1-MACOR flanges 2-coupon 3-threaded shaft 4-locknuts 5-spring lock  
6-thermocouple

Fig. 7. Structure of Stirred Batch Reactor

The main constituents of the test oil are given in Table 4. It contains about 5.1 % wt. sulphur, and 750 ppm of iron, along with other metals. The high Si and Al contents reflect its oil sands origin and its recovery via mining.

Table 4 Composition of MEBR test oil

Element	C	H	N	S			
(% wt.)	81.9	10.1	0.58	5.1			
Metal	Fe	Al	Ca	Ti	Si	V	Ni
(ppmw)	750	940	140	310	1380	280	110

The cylindrical coupons were prepared before testing mainly according to ASTM G1. Firstly, they were processed by 320, 600, 1000 and 1500 grit 3M sand paper to remove surface flaws, rinsed with water, then with toluene-heptane solution (1:1 in volume), and dried in hot air for 30 min. The average roughness of the coupon surface was determined to be 0.68  $\mu\text{m}$  using a Mitutoyo SJ-210 surface roughness tester. The coupons were then mounted in the rotating cylinder.

Tests were carried out at three temperatures. For each run, 350 mL of MEBR was placed in the quartz-lined reactor, and the sample heated to temperatures of 350°C, 370°C and 390°C, separately. The rotation speed was fixed at 700 rpm, and duration for each run was 25 h. The rings were then washed with 1:1 vol. toluene-heptane solution (heptol) to remove oil and dried in hot air for 30 min. Weakly adherent material was brushed off the metal and added to the spent oil. After each run, 2.5 ml of the spent oil and the feed, were diluted with 50 ml heptol and then filtered with 22  $\mu\text{m}$  filter paper to determine their heptol-insoluble contents.

The heptol insolubles were analyzed using a Shimadzu TGA-50 thermo-gravimetric analyzer under nitrogen atmosphere. First, the temperature was elevated to 110°C at a heating rate of 10°C/min and held for 60 min. to dry the samples. Then the temperature was elevated to 900°C at a heating rate of 20°C/min and held for 30 min., to remove the volatiles. Then the atmosphere was switched from nitrogen to air and held for 30 min., to burn the non-volatiles and leave the ash. Figure 8 gives the absolute concentration of the different fractions of the insolubles. Table 5 lists the operating conditions, the total concentration of insolubles and their compositions determined by TGA.

The concentration of heptol insolubles in the feed is 16 g/L. For the 25-hour carbon steel experiments, as the temperature is raised from 350 to 390°C, the concentration of heptol insolubles increases from 20 g/L to 107 g/L. At 350°C, the insolubles show the highest ash content, and the lowest organic content (VM + NV). As temperatures rise further to 370°C, the insolubles show increased volatile matter, probably because of the increasing content of heavier components due to reactions of asphaltenes, and the percentage of non-volatile carbonaceous material (fixed carbon, or coke) almost doubles. At 390°C, the accumulation of coke on the surface may prevent further corrosion, and the weight of ash formed decreased. The ash

content reaches a minimum, and the organic fraction (Volatile + Non-volatile) reaches its maximum of 88 %. Thus the absolute amount and the percentage of organic material increases steadily with reactor temperature. This seems to reflect expected behavior from Figures 1, 5 and 6. Compared to carbon steel, reaction in the presence of 316-stainless steel at 390°C shows about 40 % less total insolubles formation, but almost similar percent composition. Small weight decreases were observed for the carbon steel, and a small weight gain for the 316 stainless steel sample. These expected trends should be confirmed in further experiments, which will also include examination of the surface layers using EDX.

Table 5 Test Conditions and TGA Results\*

	Feed	Run 1	Run 2	Run 3	Run 4
Coupon material		CS	CS	CS	316 SS
$T_b$ (°C)		350	370	390	390
Re		5020	6243	5020	5020
$\tau_w$ (Pa)		10.4	9.6	8.9	8.9
$C_b$ (g/L)	16	20	58	107	62
% wt.					
VM	37	28	28	32	29
NV	29	21	40	56	60
Ash	34	51	32	12	11
Coupon weight change, %		-2.2	-2.8	-0.08	+0.84

\* Rotation speed = 700 rpm, duration = 25 hours.  
CS = carbon steel 316 SS = 316 stainless steel  
 $C_b$  = Heptol insolubles concentration ( g /L)

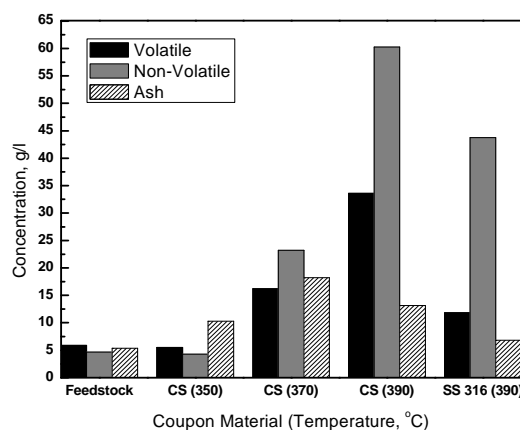


Fig. 8 Heptol insolubles concentration and composition of feed and products after 25-h heating.

## CONCLUSIONS

A survey of previous literature has shown that mixed iron sulphide and coke deposits are common in higher temperature equipment which processes sour oils. Reaction pathways which lead to mixed deposits have been examined

for temperature effects. Corrosion and fouling interactions have been examined. Mechanisms of fouling have been suggested. An experimental program has been initiated to distinguish between particulate and film formation of FeS, and deposition on corroding versus non-corroding surfaces.

## NOMENCLATURE

$a_1, a_2,$	Constants in rate equations
As	Asphaltene
A+	Asphaltene concentration ( $\text{kg}/\text{m}^3$ )
A*	Asphaltene core concentration ( $\text{kg}/\text{m}^3$ )
b,c,d	stoichiometric constants
C	concentration ( $\text{mol}/\text{m}^3$ )
D	diameter of cylinder (m)
E	activation energy ( $\text{kJ}/\text{mol}$ )
k	rate constant
$k''$	rate constant incorporating iron concentration
KHGO	coker heavy gas oil
m	reaction order
M+	maltene concentration ( $\text{kg}/\text{m}^3$ )
M*	maltene core concentration ( $\text{kg}/\text{m}^3$ )
MCR	Micro- carbon residue
n	reaction order
N	rotation speed (revs/min)
NV	non-volatile matter, or fixed carbon
PI	pitch fraction (boiling points $> 524^\circ\text{C}$ )
r	rate of reaction ( $\text{kg}/\text{m}^3\text{s}$ )
$r''$	rate of surface reaction ( $\text{kg}/\text{m}^2\text{s}$ )
R	hydrocarbon end group
$R_g$	gas constant ( $\text{kJ}/\text{kmol K}$ )
t	time (s)
T	temperature (K)
TAN	total acid number
VHGO	vacuum heavy gas oil
VM	volatile matter
x	thickness (m)
$\tau_w$	shear stress at surface (Pa)
$\rho$	density ( $\text{kg}/\text{m}^3$ )
$\nu$	kinematic viscosity ( $\text{m}^2/\text{s}$ )
$\mu$	dynamic viscosity ( $\text{kg}/\text{m}\cdot\text{s}$ )
$\lambda_d$	deposit thermal conductivity ( $\text{W}/\text{mK}$ )
Re	rotational Reynolds no. ( $\pi D^2 N / 60 \nu$ )

## Subscripts

A	A* asphaltene and asphaltene core disappearance
b	bulk
f	film = (wall + bulk)/2
FeS	iron sulphide
$\text{Fe}^{++}$	dissolved iron
M	maltene reaction
S	sulphur
w	wall

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