CORROSION CONTROL IN REFINNING PROCESSES

CORROSION :

- Corrosion is the deterioration of substance or its properties because of its reaction environments.
- Corrosion is one of many environmental influences that can reduce the life of refinery units.

TYPES OF CORROSION

1. Chemical corrosion
2. Electrochemical corrosion

CHEMICAL CORROSION

- This phenomenon is due either to Van der Walls adsorption forces or to a direct chemical reaction.
- Chemical corrosion results from the direct action of an aggressive agent on the units metallic surface.
- Aggressive agents are – naphthenic acid, phenols, aliphatic acid, dry gases like – hydrochloric acid, hydrogen sulphide, sulphur dioxide etc.

Electrochemical corrosion

- Electrochemical corrosion can take place when water is present in the liquid state.
- Water contains some aggressive ionic substances such as NaCl, MgCl_2, HCl etc.
- The metallic surface is susceptible to electrochemical attacks.

FORMS OF CORROSION

- Uniform corrosion : It is characterized by uniform corrosion over an entire exposed area.
- Galvanic corrosion : it is associated with a reaction resulting from the electrical coupling of dissimilar metals.
- Crevice corrosion : it is form of localized corrosion occurring at locations where easy access to the bulk environment is prevented, such as at mating surface of metal s or assemblies of metals and nonmetals.

Pitting corrosion :

- It is highly localized phenomenon that result s in deep penetration into the metal at only few spots,
- It is prevalent in passive alloys such as stainless steel and aluminium alloys.

Selective leaching corrosion :

- This corrosion is frequently encountered when minal is used in amine systems ; copper is selective leached from copper alloy in the presence of oxygen.

Fretting corrosion :

- It is the deterioration at the interface of two contacting surfaces under load , accelerated by relative motion between them that is of sufficient magnitude to produce slip.

Intergranular corrosion :

- It is occurs at or along the grain boundary of a metal or alloy.

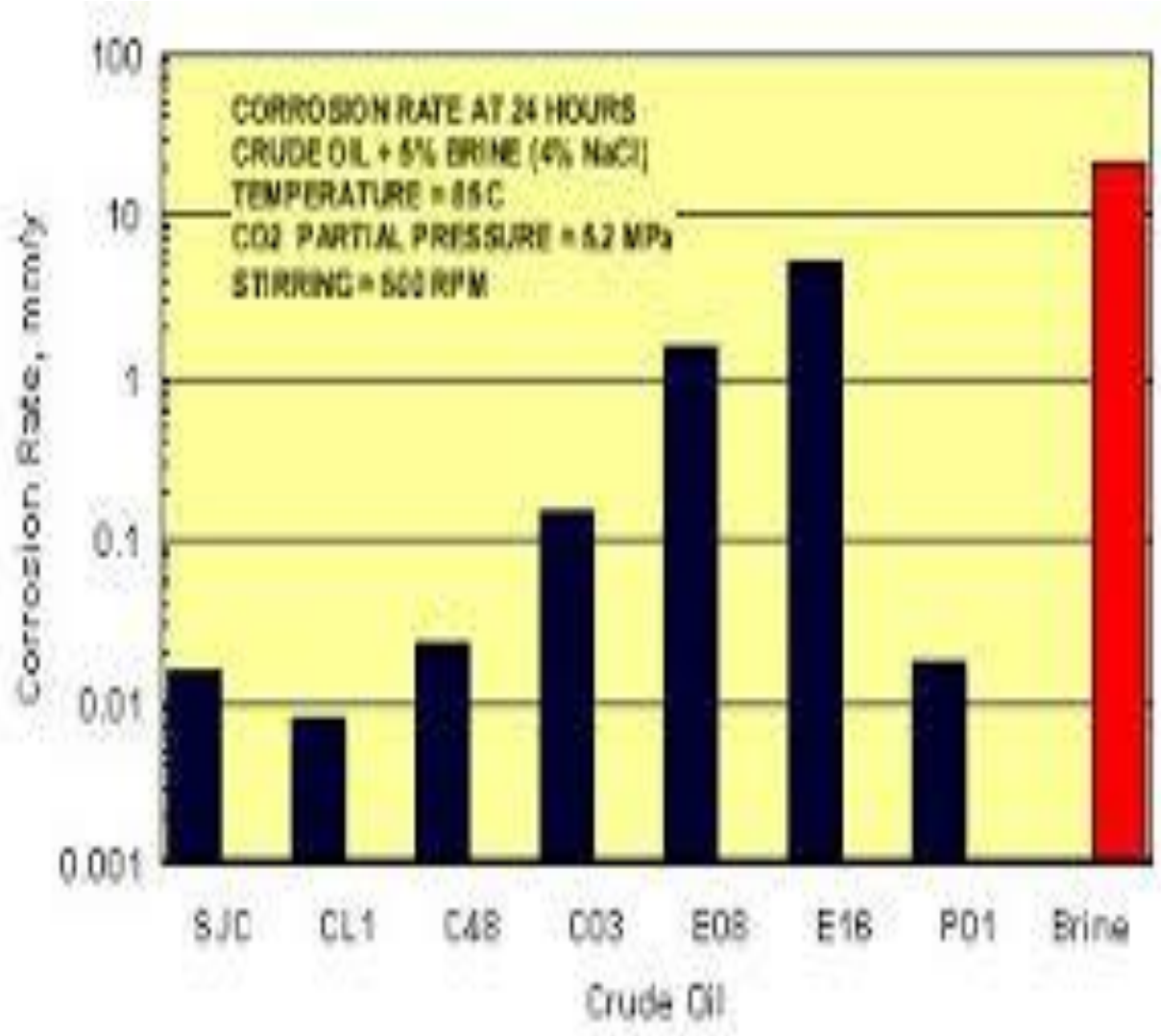
Corrosion control in crude oil distillation

Atmospheric Distillation :

- Crude oil contains many corrosive agent such as chlorides , organic acids , water and sulphur compounds.
- Corrosive action of naphthenic acids is a function of acidity , concentration and temperature. At room temperature the naphthenic acids are not corrosive.
- Naphthenic acids corrosion begins at 225˚C-250˚C, increase with increase temperature.

Vacuum Distillation :

- Vacuum distillation units operate at high temperature.
- The main corrosive agents are naphthenic acids and sulphur compounds.
- Naphthenic acid corrosion appears in the tubes and the return- bends of the furnace and at the flash section of the vacuum tower.
- Corrosion due to sulphur compounds occurs in the radiant section of the furnace, transfer line , flash section of the vacuum tower etc.


CORROSION RATE AT 24 HOURS
CRUDE OIL + 5% BRINE (4% NaCl)
TEMPERATURE = 65 C
CO2 PARTIAL PRESSURE = 5.2 MPa
STIRRING = 500 RPM
100
10
1
0.1
0.01
0.001
Corrosion Rate, mm/y
SJC
CL1
C48
C03
E08
E16
P01
Brine
Crude Oil

Concentration of inhibitor (ppm)	Alloy	Corrosion Rate (mm/year)	Efficiency (%)
25	Fe	0.145	85.0
	C1010	0.201	79.2
	A516Gr70	0.194	80.4
50	Fe	0.225	75.8
	C1010	0.136	76.8
	A516Gr70	0.388	60.8
100	Fe	0.332	65.7
	C1010	0.328	66.1
	A516Gr70	0.352	64.4

Corrosion control in thermal cracking

- The major cause of corrosion in a thermal cracking plant is from sulphur compounds in the cracking feedstock.
- The organic sulphur compounds are thermally decomposed according to the following schemes:

1. Sulphides decompose to form marcaptans and olefins.
2. At high temperature, sulphides decomposes to hydrogen sulphide, hydrogen, carbon and olefins.

3. Disulphides decomposes at high temperature to form the sulphides, free sulphur, mercaptans, olefins, thiophenes, hydrogen sulphides and hydrogen.

Corrosivity of amine system

I. Three major parameters affect carbon steel corrosion in amine system are-

- pH
- Temperature
- Velocity

2. Additional aspects that should be considered in predicting corrosivity are the effects of

- Amine degradation.
- Impurities in Amine system.
- Oxygen contamination of sore amine system.
- High Chloride concentration.

Corrosion control in steam and condensate line

- Corrosion ,if left uncontrolled ,in steam condensate system can lead to blockages in steam traps , iron returning to the boiler via the feed tank which may lead to hot spots , corrosions deposits returning to the feed tank promoting corrosions here and potentially leading to feed line blockages , a reduction in steam purity and finally plant shutdown.

Causes of corrosion

- Two major causes of corrosion:
- Oxygen result in pitting corrosion.
- A low pH gives rise to generalized thinning of piping
- Reactions-
- $2HCO_3$ ---------> $CO_3^{2-} + CO_2 + H_2O$
- $CO_3^{2-} + H_2O$ ------> $2OH^- + CO_2$
- $CO_2 + H_2O$ -----> H_2CO_3.

When bicarbonates and carbonates break down in the boiler,one of the product is carbon dioxide.

Carbon dioxide flashes with steam and combine with the condensed steam to form carbonic acid.

Reactions–

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CO_3^{2-} + H_2O ------> $2OH^-$ + CO_2

CO_2 + H_2O -----> H_2CO_3.

In the steam and condensate system, the combination of O_2 and CO_2 can be devastating CO_2,which makes the process self-perpetuating.

$Fe + 2H^+ + HCO_3^{2-}$ -------> $Fe(HCO_3)_2 + H_2$.

$4Fe(HCO_3)_2 + O_2$ -----> $2Fe_2O_3 + 4\ H_2O + CO_2$.

Corrosion control through use of chemicals

Various treatment include-

- Oxygen scavenger
- Neutralizing inhibitors
- Filming inhibitor

Neutralizing amines

- Neutralizing amine act as a volatile alkalis being carried with the steam.
- The most frequently used neutralizing amine are cyclohexylamine , morpholine, isobutanolamine and diethylamino ethanol.
- Sufficient neutralizing amines should be dosed to raise the condensate pH to between 7.8 and 8.5 for all iron system, if copper is present, However, pH value above 8.3 can proved deterimental.
- The actual dosage depend upon three factor-the type of amine used, the CO_2 concentration and the rate of evaporation.
- The amount of CO_2 evolved in the steam is dependent on the alkalinity of feed water and any entrained CO_2 gas.
- $NaHCO_3$ -------->$Na_2CO_3+H_2O+ CO_2$
- $Na_2CO_3 +H_2O$ ---------> $2NaOH+ CO_2$

Filming amines

- These amine protect condensate system from both carbon dioxide and oxygen corrosion by forming a mono molecular, non wettable, protective film on metal pipe.
- The most effective filming inhibitors are saturated, straight chain, primary aliphatic amines in which the carbon chain contain 10 to 18 carbon atom.
- The advantage of using filming amines are that they effectively protect both high and low pressure condensate return system from CO_2 to O_2 attack.
- Dosing rate is not affected by CO_2 content,hence more economical.

Corrosion from combustion products

There are two types of corrosion from combustion products-

- Low Temperature corrosion from Sulphur tri oxide.
- High temperature corrosion from fuel ash.

Low Temperature corrosion from Sulphur tri oxide.

- When fuel is burnt with excess air, (about 3% sulphur) fuel is converted into sulphur trioxide.
- Corrosion will occur where metal surface are below the acid dew point.(Dew point varies from 116-138°C).

High temperature corrosion from fuel ash.

- High temperature corrosion of fuel oil is due to its ash content.
- The ash content of fuel represent the metallic impurities suggest sodium, potassium, vanadium, nickel.
- The parameters which effect high temperature corrosion includes-
  - Temperature
  - N_a/V Ratio in the fuel oil
  - Excess air.

Thanks