"ECONOMIC ANALYSIS OF CORROSION CONTROL

IN PETROLEUM REFINERIES"

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ABSTRACT

Economic analysis of corrosion problems and their prevention or control was found to gain very little importance in the last 10 years according to the published work surveyed.
This article surveys the most important work in this area and shows the magnitude of corrosion problems as cost analysis measures indicate. It also refers to the need for continuous research in this field of vital importance in the coming era.

Data from several sources have been tabulated to highlight the magnitude of the corrosion problems, rates, and costs.

1. INTRODUCTION

Corrosion problems in refineries are reported (11, 12) to be significant in size and severity. Stress corrosion cracking, for example was found to cost a large chemical company $4.1 million in 1971 (11). Ludwig (12) indicated that refineries pend up to one cent per barrel of crude charge to inject antifoulants into their crude units in the hopes of retarding fouling in their preheat train and/or reducing coking in their heaters. This translates to a cost of $350,000 per year on a 100,000 bpd crude unit.

These figures show the magnitude of corrosion problems in the refining industry, yet there was very little research in the economic evaluation of the corrosion problems and their control. On-line search on the last ten years showed that more than 43,000

articles have been published investigating corrosion problems in refineries. Less than 0.1% of these articles contained some economic analysis of such problems. In this article we try to summarize and highlight the work done in this area in an era where only money is of vital importance.

2. EXPANSION OF REFINING TECHNOLOGY

Refinery technology expansion is a composite of many factors of which monitoring of equipment, corrosion control, catalyst life and major advances in controlling exchanger fouling and furnace coking are the key factors. Table 1 predicts catalytic reforming as an example of refining technology forecasts up to the year 2000 (2). Catalyst life is taken as a measure of the future requirements which might also reflect the need for longer equipment life through corrosion control.

The table shows the operating ranges from 1950 up to the year 2000. The ultimate objectives are to increase the reformate yield in reforming units from 65% to 95% with octane number reaching 100.

This may be achieved by reducing the operating pressures to about 25% of its values. The catalyst life would increase by about 10-15 times its value in 1950.

Table 1: Refining Technology Forecasts to the Year 2000 (2).

Year	Operating Pressure Psig	Reformate Yield %	Octane Range	Catalyst Life Year
1950	500-700	65	75-85	2
1975	200	75	100	10
2000	120	81-95	100	20-30

3. CRUDE OIL DISTILLATION UNITS

In refineries the most susceptible units to severe corrosion are the primary crude oil distillation units, either atmospheric or atmospheric/vacuum pipestills, in which the

condensers and cokers are attacked very severely. Another serious problem is the corrosion and deposition of scale on cooler tubes on the recirculating water side.

An investigation which lasted about 27 years on a refinery processing corrosive sour crudes summarized in Table 2 shows the idling time percentage lost due to repair and breakdown in the refinery units. Table 3 shows the increase in expenditure on repairs and maintenance after 2-3 years from start up of a refinery with sour crude (13).

Table 2: A USSR Study for a Refinery Processing Corrosive Sour Crudes During 1938-1965 (13).

Year	Salt contents in crudes reaching units mg/lit		Idling time due to repair and breakdown % of total calendar time of operation	
	APS & VPS	CU	APS & VPS	CU
1938-1942	1650	800	15-20	35-40
1943-1945	350	380	8-10	28-34
1946-1960	150-250	150-250	8-10	20-25
1961-1963	150-170	150-170	7-8	18-20
1963-1965	25	25	—	—

APS = Atmospheric Pipestill Unit
CU = Combination Units
VPS = Vacuum Pipestill Unit

Table 3: 2-3 Years After Running the Refinery with Sour Crude — Increase Expenditure (13).

— Repair jobs in the refinery as a whole	= 10-12%
— APS + VPS + Ther. Crack + one CU	= 35-40%
— 1 ton crude processed, rose by	= 35-40%
and that for combination units by	= 60-80%
Pipe Stills	= 25-30%
Columns & tanks	= 40-50%
Heat exchangers	= 20-25%
Pumps	= 4-5%
Others	= 8-10%

The units of particular interest in atmospheric distillation are:

i)   Preheat train-preheating cold crude by heat exchange with hot streams from downstream processes. Such trains may contain 20 or more shell-and-tube exchangers for a refinery processing 100,000 barrels per day.

ii) Furnace — supplying the remaining heat requirement for the crude feed by direct firing. Heat duties in these multiple furnaces can approach 10 million Btu/hr (2,9000 MW/hr).

iii) Pipestill tower — fractionating crude charge into cuts. Live steam is usually injected for stripping.

iv) Overhead system for condensing naphtha stream. A typical overhead system has upward of 8 shell-and-tube or air-fin exchangers.

The main impurities in the crude processed which contribute to corrosion in the atmospheric unit are; acid forming inorganic salts, organic acids and sulfur compounds (9, 10, 11, 12). Organic nitrogen and oxygen compounds and organometallic compounds may accelerate or retard corrosion depending on conditions. For example, organic nitrogen compounds in catalytic cracking units operating on vacuum gas oil feed stock give ammonia which raises the pH of the medium and reduces the corrosion of carbon steel, but increases the danger of corrosion cracking of brass parts in condenser/cooler systems (3). The joint presence of several corrosive components leads to an acceleration of corrosion. For example, H_2S on an iron surface forms a protective film of FeS_2, which breaks down under the influence of HC1 to form H_2S which will again react with iron and in effect, serve as a catalyst for dissolution of iron. When moisture is present, a large part of the corrosive gases dissolve in the water forming highly corrosive condensates in the low-temperature zones.

4. REFINERY VACUUM DISTILLATION UNITS

The corrosion process in a vacuum unit results from direct action of the chemically

aggressive agents on the metallic surface of the equipment. Organic compounds (naphthenic acids and phenols, and dry gas-H_2S, R-SH and oxygen), attack vacuum unit equipment especially at high temperatures, even above the dew point of water (8).

5. COOLING SYSTEM IN THE REFINERY

Condensers, coolers and heat exchangers make up about 40% of the entire refinery equipment. Major maintenance and reconditioning of these units account for about 25-30% of the total cost for maintenance of the refinery (3).

Corrosivity of recirculating water is determined by the pH, dissolved oxygen, carbon dioxide, chlorides, sulfate and sulfide ions. Sometimes corrosion may be attributed to oily materials, solid contaminants, and biological growth deposited on the metal. According to the type of recirculating water, refineries may be classified into three groups as shown in Table 4.

Table 4: Types of Recirculating Water Used in Refineries.

Groups	% of total Plants	Specifications of Recirculating Water Used					
		Salt PPm	Cl mg/l	SO$_4$ mg/l	pH	Oily Material mg/l	S.S.* mg/l
I	90%	2000	10-350	10-480	6.5 - 9.5	0.750	0-180
II	8%	2000-1000	50-2300	300-3400	6.5 - 8.7	0.750	0-180
III	2%	Sea Water					

The table shows that 90% of the refineries use water containing about 2000 ppm salt while only 2% of the refineries use sea water for cooling. Maintenance and service life for cooling systems depends upon the material of construction of the tube bundles, as shown in Table 5. The table shows that the shortest service life is that of carbon and Si-Mn steels and longest is the Cr-Ni steels and arsenic-alloyed brasses. However, direct losses are generally ten times the cost for protection against corrosion (3). The rate of corrosion and rate of deposit formation was measured in a Russian refinery

*Suspended solids

(4). The data are shown in Table 6.

Table 5: Service Life of Cooling Systems .

Material of Tube Bundles	Length of Operation Between Maintenance, Year	Service Life Year
Carbon steel	0.5 - 2	1 - 5
Si-Mn steel	0.5 - 2	1 - 5
Cr steel	1	4 - 5
Cr-Ni steel	1 - 4	3 - 8 or more
Brass	1 - 2	5 - 10
A1 alloys	1 - 2	1 - 8

Table 6: Corrosion and Scaling in Cooling Systems (4) .

Problem	Rate		Units	Remarks
	Min	Max.		
Corrosion in carbon steel system	0.21-1	2-3	mile/year	Corrosion is non-uniform
Deposits on heat exchange surface	2-7	10-18	kg/m/year	

The corrosion problems in these units can be controlled by:

1. Corrosion inhibitors.

2. Passivators (inorganic additives) as chromate-phosphate-zinc mixtures — but these mixtures are toxic.

3. Organic additives — which are water dispersible — 100 mg/1 reduces corrosion from 60-95%, deposits by 70-80% and the corrosion rate is less than 0.1

mile/year. However, such additives increase the amounts of oily materials and solid contaminants in the water. Part of the recirculating water should be cleaned by filteration or flotation (3).

Corrosion inhibitors are the most widely used measures for reducing corrosion and deposits problems in water recirculating systems. Table 7 summarizes the most important inhibitors in use (3, 6).

Table 7: Comparison Between Corrosion Inhibitors Used for Cooling Systems

No.	Type	Action	Performance
1.	Chromates	Anodic inhibitor — forms a passive gamma iron oxide film on the steel surface.	— One of the most successful. — But with 220 ppm chromate pitting corrosion of mild steel occurs and also increase of fouling under reduced conditions. — Chromates fail if water contains SO_2 or organics.
2.	Dianodic treatment	Anodic inhibitor — which uses chromate/phosphate combinations.	— Suitable in case of presence of SO_2 or organics in water. — Zinc dianodic treatment is not favoured by EPA due to the toxicity of chromium sludge.
3.	Organic phosphonates & combinations of inorganic phosphates	Cathodic inhibitors — forms barrier type films as $CaCO_3$, $Ca_3 (PO_4)$, $Zn (OH)_2$ etc.	— Inferior to chromates. — Require strict conditions for application as pH, feed.
4.	Dianodic II	Acts as anodic or cathodic inhibitor.	— Excellent, more economical

treatment — mixture of poly and orthophosphate

It causes deposition of control agents as $Ca\ Co_3 + Ca_3\ (PO_4)_2$ and $Ca\ SO_4$; and a Cu corrosion inhibitor.

and no environmental problems.

— Fouling and mild steel turberculation

Data for mild steel corrosion rates obtained (6) with the phosphate/zinc treatment are shown in Table 8. Cathodic protection is used in some refineries to control corrosion of specific pieces of equipment but the results obtained have not yet been evaluated. Salt deposition in condensers and coolers has been prevented by use of HC1. Injection of the recirculating water by this acid gave 100% protection from corrosion.

Table 8: Corrosion Rates (mpy)* from Coupons Exposed to a Recirculating Cooling Water

Material	Zn Phosphate 47 days	Dianodic II 45 days
Mild steel	5.6	1
Preheated mild steel	5.1	0.3
Admiralty	0.9	0.0

Previous year average corrosion — Mild steel 1.2 Admiralty 0.8

*mpy = mile per year

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