GENERAL INTRODUCTION

1. CORROSION IN PETROLEUM PROCESSING

Corrosion destroys about 30% of the steel produced in the world every year. Petroleum enters partly in this by 1-1.5% . Sherwood[1] stated that in the U.S.A. the annual damage to refinery equipments through corrosion is 14-18 cents per barrel, or about $ 400 million. Freedman and Dravniecks[2] estimated the total cost to be somewhat, approaching $ 300 million annually. They also stated that the cost would be considerably higher if inhibitors were not used to control corrosion rates in critical refinery equipments.

Crude oil (still containing some water) is usually put through a series of heat exchangers to bring it to the temperature needed for the first fractionation step. Corrosion takes place in these iron exchangers as well as in the lines leading to and from them. The temperature changes involved are from room temperature gradually as high as 275°C. The fluid then enters the fractionator. Corrosion takes place with the tower itself, with the overhead condensing and accumulating system, and in the reboiler. While the material in the tower and reboiler is mostly crude or fractions, the liquid and gases in the overhead system consist of water, acidic gases and light ends . An extremely corrosive system, therefore, arises.

Corrosion is a major problem in petroleum refineries. Its economic importance has increased enormously with the development of complicated refineries with increased through put and higher cost of replacement items[3]. Corrosion leads to a decrease in the life of distillation towers, drop in production due to shut down and repair, high costs and reduction in quality.

The corrosivity of crude oils depends upon their sources, operational conditions and method of processing. The heavier crude oil showed an average corrosion rate (1.43 mm./year) more than three times that showed by the lighter crude[4]. This was explained by the higher salt and sulphur contents of the heavier than the lighter crudes.

Most crude oils contain varying amounts of salt (3-10 %). These salts are mainly chlorides of Na, Ca, and Mg[5], the latter having the most effect. These salts are hydrolyzed when the crude is heated in furnaces prior to entering the tower or in the distilling column and passed to the overhead equipments. Zakharochkin et al[6] showed that the calcium salt hydrolyzes to the extent of 3.5-10% and the magnesium salt to 50%, while the sodium salt is practically not hydrolyzed under the distillation conditions of atmospheric pressure and temperature. The sulphur compounds present in crude oils decompose under the action of temperature to produce hydrogen sulphide which, along with HCl, comes out into the overhead system.

Thus hydrochloric acid and hydrogen sulphide are responsible for the corrosion attack experienced in the overhead systems[7-9]. While the corrosive properties of H_2S by itself are not severe in low temperature units as at higher temperature, the attack can become quite serious when the effect of H_2S is reinforced by HCl.

Field investigations in the crude unit overhead system showed that, corrosion was mainly attributed to chlorides and to a lesser extent to sulphides. The overhead chloride level was directly correlated to corrosion, and reduction of chloride level to less than 40 ppm. resulted in significant drop in corrosion. At chloride level above 90 ppm., corrosion was severe[10].

1.1 Factors Affecting Corrosion:[11]

The major variables involved in refinery corrosion problems can be summarized as follow:

- Type of metal.
- Liquid composition.
- Temperature.
- Fluid velocity.

1.1.1 Type of metal:

The metals involved are most frequently iron and Admiralty.

A fairly good portion of the metal in use, for the lower and less severe conditions, is carbon steel. Stainless steels of varying compositions are used at the higher temperatures e.g. in trimming steel valves or in high temperature furnace tubes. Admiralty metal is used mainly in overhead condenser systems .

1.1.2 Liquid composition :

The fluid composition varies considerably depending upon the particular location in the refinery. It varies from the sour, acidic, and crude oil-water mixture, that enters the refinery to the final finished products (e.g. gasoline). Overhead systems are unique in that they consist of light hydrocarbons and water. Much of the light hydrocarbons are returned to the tower as reflux. This operation is probably the single largest application for corrosion inhibitors on the process side of refineries. In the case of crude heat exchangers, distillation units, and desalting units, considerable brine can also be present of composition similar to that in oil production. Dissolved gases are the prime cause of the solution acidity, which leads to very severe corrosion. The most common corrosive agents[9], in this category, are hydrochloric acid, acetic acid, other short-chain aliphatic acids, carbon dioxide, oxygen, naphthenic acids and hydrogen sulphide.