CHAPTER-I
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INTRODUCTION

SECTION-I : HISTORY OF AMMONIA PRODUCTION

Anhydrous ammonia is the richest source of nitrogen (82 Wt % N) of all the fertilizer material available. Ammonia is also the basic component of different fertilizers because of its increased solubility that the presence of ammonia imparts to other important chemicals, such as ammonium nitrate, ammonium sulfate, urea and diammonium phosphate. It is also the most water soluble of the common gases (1).

Today, ammonia has achieved the status of an international bulk commodity as common as oil or iron ore, to be shipped by vessels or pumped through cross country pipelines.

A) PRODUCTION OF AMMONIA

The World's production capacity for ammonia was 93 million tons in 1977 and was 137 million tons by 1985. Today, it may be more than 200 million tons.

Production of ammonia by developing and developed countries (2) is given for 1989-90 in Table 1.

This growth in plant capacity over the years is mostly attributed to the development of large single line centrifugal compression systems for air, synthesis gas and refrigeration, alongwith large capacity reforming furnaces and the developments in the preparation and purification of synthesis gas which is of comparable importance to the synthesis reaction itself.

Ammonia is the leading product of the entire fertilizer/petrochemical industry. At present, in our country, 90% of ammonia production is used as or for fertilizers. In U.S.A., it is 70% compared to India. World average use of ammonia as/or for fertilizers is a staggering 80% (3).

B) A BRIEF DESCRIPTION OF THE DEVELOPMENT IN THE MANUFACTURE OF AMMONIA (3), (4) AND (5)

Preparation of ammonium salts, as early as 4th century BC by Egyptians from ammonium chloride, called by them as sal ammoniac or ammon, is given in many references. It is said to have been produced from the soot of camel's dung. At the same time, Arabs used ammonium carbonate called hartshorn by them, by the destructive distillation of the antlers of the hart. Until the turn of the century, nitrogen supply was entirely dependent on natural resources of nitrogen, namely mineral deposits and amimal and vegetable wastes from industries other than agricultural like animal manures, seed meals, fish scraps, packing house wastes, sewage sludges, leather scraps, dried blood, chilean nitrate and ammonium sulfate from the coking of coal.Research on the production of ammonia was started by Priestly in 1754. He heated sal ammoniac (ammonium chloride) with lime to produce ammonia.

Haber and Bosch, however, were the first to develop a commercial process, whereby ammonia could be produced by direct reaction of hydrogen and nitrogen over a catalytic surface, in Germany in the begining of the 20th century.

In 1913, the first commercial Haber-Bosch process went onstream at Badische Anilin and Sodal Fabrik (BASF) in Ludwigshafen-Oppan with a design capacity of 30 metric tons per day, with osmium as catalyst, which was rare and hard to handle.

In the U.S. the ammonia synthesis grew rapidly during the first world war, primarily because of the urgent war time need for nitrates. Casale, Fauser, Claude and Morit Ceris processes were developed at about this time, mostly differing with Haber-Bosch process with respect to the synthesis loop pressure.

A rapidly expanding ammonia industry in the late 40's and 50's is attributed to the second world war and the Korean War.

In the 1960's ICI Ltd. introduced and developed steam reforming of naphtha in Europe.

The commercial development of ammonia synthesis is rightly considered as one of the most significant technological advances benefitting all mankind. The nobel committee in stockholm bestowed the Nobel Prize on Fritz Haber in 1918 and on Carl Bosch in 1931.

Reforming of natural gas or naphtha, whereby the hydrocarbons are converted to carbon monoxide, carbon dioxide and hydrogen by reacting with steam (water gas shift reaction) is an important part of the ammonia production. Pressurised reforming of natural gas was first used commercially in the 60's reducing power consumption and leading to the dominance of steam natural gas reforming over partial oxidation process.

The synthesis gas coming out of the reformer contains carbon dioxide in large quantities and for various reasons like it is poisonous to the

[illegible]
synthesis catalyst, it has to be removed from the synthesis gas.

Water was used as absorbent of carbon dioxide in the 1900's, but it was replaced by hot potassium carbonate and ethanol amine processes, thereby reducing the equipment and power requirements considerably.

In the 1960's, the expensive and cumbersome copper liquor scrubbing process for final carbon dioxide removal was replaced by methanation, which permitted two stage shift conversion.

The discovery in the late 60's of a low temperature shift catalyst further improved the efficiency of carbon dioxide removal systems.

SECTION-II : IMPORTANCE OF CARBON DIOXIDE REMOVAL IN AMMONIA PRODUCTION (6)

In the reforming of naturally occuring gases or naphtha in the manufacture of ammonia, carbon dioxide invariably makes its presence felt in the synthesis gas.

Before the synthesis reaction is carried out to obtain ammonia, it is absolutely necessary to carry out removal and recover carbon dioxide from synthesis gas (6). Therefore, the following paragraphs are devoted to the availability and applicability of carbon dioxide. In short, the advantages of carbon dioxide removal from synthesis gas and the points which calls for its removal before synthesis reaction, its usages and applications, are discussed.

Generally carbon dioxide is present as a component of synthesis gas, which is then separated, recovered and prepared for commercial use [illegible] as a solid (dry ice), liquid or gas. Although it is present in the atmosphere and produced by metabolic processes of animals and plants, carbon dioxide cannot be recovered from these sources because of its low concentration. It is also a byproduct of many commercial processes other than ammonia production like Hydrogen production, substitute natural gas production, fermentation, limestone calcination, certain chemical synthesis involving carbon monoxide, reaction of sulfuric acid with dolomite etc.(6).

A) USES AND APPLICATIONS OF CARBON DIOXIDE (6 & 7)

Carbon dioxide is used in beverage carbonation, chemical manufacture, fire fighting, foundry-mold preparation, greenhouses, mining operations, oil well secondary recovery, rubber tumbling, therapeutical work and in welding.

Reaction of carbon dioxide with ammonia in the first stage of urea synthesis to form ammonium carbonate and subsequent dehydration to yield urea, is probably the most important reaction of carbon dioxide which is used world wide in the production of urea.

The reaction of urea molecules to form Melamine, which is an important chemical used in the Melamine-formaldehyde resins, is also an indirect important application of carbon dioxide.

Carbon dioxide is also used extensively in the manufacture of methanol, by the reverse of the water gas shift reaction.

Carbon dioxide is added to aging or nearly depleted oil wells for secondary oil recovery, thereby increasing oil production. This is the fastest growing use of carbon dioxide.

The uses of carbon dioxide can be distributed in the following manner:

- 40% as a raw material in the production of urea/methanol/ Melamine
- 35% in secondary oil recovery units in oil wells
- 10% as a refrigerant
- 5% in beverage carbonation
- 10% in miscellaneous applications

Pertaining to ammonia production, for each ton of ammonia produced, more than a ton of carbon dioxide is generated, stressing the importance of cabon dioxide recovery from synthesis gas.

B) CARBON DIOXIDE AS AN IMPURITY IN SYNTHESIS GAS (7, 8)

The poisonous effect of carbon dioxide on the ammonia synthesis catalyst should also be considered because it is directly related to the production and economics of ammonia industry.

For a given operating pressure and desired production, ammonia synthesis catalyst is the key factor for vessel and exchanger design in the synthesis loop and therefore, it indirectly influences the make up gas purity requirement. In short, the economics of the total process is determined by the performance of the ammonia synthesis catalyst.

Magnetite (Fe_3O_4), is the principal component of the catalyst with various promoters like aluminium oxide, potassium oxide, calcium oxide, magnesium oxide, silica, vanadium pentoxide and cobalt oxide. Promoter additions depends upon operating temperature, synthesis gas purity and pressure.

Arsenic, antimony, bismuth, boron, lead, phosphorus, cadmium, carbon, zinc and their oxides, all have got negative effect on the activity of these catalysts.

Gaseous oxygen compounds like carbon monoxide and carbon dioxide are not significant poisons. These compounds have greater affinity for the catalyst than nitrogen and therefore are preferentially adsorbed on the catalytic surface.

Carbon dioxide has a reversible effect on iron catalyst. Activity of a damaged catalyst can be restored by reduction with clean synthesis gas. The damage to the catalyst depends upon the quantity of the poison in the synthesis gas. Therefore, degree of poisoning rises with growing partial pressure ratio. However, the continuing exposure of carbon dioxide causes the growth of iron primary crystallite on the catalyst. The damage here is irreversible in nature and is very serious at high pressure.

Continuing exposure of carbon dioxide leads to more water vapour, which comes in contact with already reduced catalyst and induces recrystallization.

It is established that at about 250 ppm of carbon dioxide content in the convertor, the production of ammonia can decline by 15% per month, and at a carbon monoxide content of 5 ppm, the decline is 4.5% per month.

C) OTHER FACTORS WHICH CALLS FOR CARBON DIOXIDE REMOVAL (9)

1. As the synthesis gas is compressed before it enters into the

convertor, 'Liquefaction' of the gas can occur which is a major process complication.

2. Where nitrogen wash systems are used, 'solid carbon dioxide plugging' can occur.

3. And lastly, the presence of carbon dioxide in the synthesis gas dilutes the nitrogen-hydrogen mixture, thereby affecting overall plant performance.

SECTION - III : DIFFERENT CARBON DIOXIDE REMOVAL SYSTEMS

The synthesis gas produced by steam reforming or partial oxidation by water gas shift reaction, contains a considerable amount of carbon dioxide, depending on the carbon content in the fuel.

Carbon dioxide produced in generating synthesis gas from different feed stocks (10) is given in Table (2).

Carbon dioxide, the so called acid gas, has a tendency to form weak acid in water solution to form carbonic acid.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

This carbonic acid undergoes reversible reactions with amines or with alkaline salts,

$$2R\text{-}NH_2 + H_2CO_3 \longrightarrow (R\text{-}NH_3)_2\,CO_3 \text{ or } 2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$K_2CO_3 + H_2CO_3 \longrightarrow 2KHCO_3$$

to form carbonates and bicarbonates which can be decomposed on heating to recover carbon dioxide and the amine or salt.

Various carbon dioxide removal processes can be classified broadly into three categories, namely :

1 Chemical absorption process
2. Physical absorption process
3. Chemical and Physical absorption process

1) CHEMICAL ABSORPTION PROCESS :

The process employs water and chemical solvents in which carbon dioxide enters into a reversible chemical reaction. It has the advantage of being able to reduce the concentration of carbon dioxide to low levels even at low total pressure of the gas streams.

a) Water scrubbing (10) : This is the oldest method of carbon dioxide removal. Easy availability and low cost are the two main advantages. Simple plant designs,no heat load, non reactivity with impurities like carbon disulfide, oxygen and no heat exchangers or boilers required, are some other advantages. But disadvantages outnumber these. Excessive loss of hydrogen since hydrogen also dissolves in water at high pressure, high pumping cost due to recirculation, impurities in the product carbon dioxide limits its use in urea and other production. Above all, corrosion of equipment becomes a serious problem since water becomes acidic and free oxygen in water greatly increase the corrosion rate. So this system is practically abandoned.

b) Monoethanol amine (MEA) process (11-13) : This is a relatively simple process based on counter current extraction in the absorber and subsequent regeneration in the regenerator of MEA. Absorption is carried out at high pressure and temperature slightly about r.t., while regeneration is carried out at low pressure and high temperature.

Advantages are 1. moderate price, 2. High reactivity , 3. excellent stability, 4. easy regeneration, 5. very low concentration of carbon dioxide in the exit synthesis gas.

Disadvantages are 1. MEA reacts with carbon dioxide and carbon disulfide non-regeneratively, but this is overcome by addition of caustic to the solution, 2. High steam requirement for the regeneration, 3. Corrosive nature of the solution, particularly the degradation products of MEA, like N-(2-hydroxyethyl) ethylenediamine. To overcome this problem, low concentration of MEA (15 to 20%) solution is always recommended.

c) Diethanolamine (DEA) process (14) : Its action is similar to MEA. It is a weaker base than MEA, has low reactivity and higher cost, but the advantage is that it does not degrade to any appreciable degree with synthesis gas containing carbon sulfide or carbon disulfide etc. 20-30% DEA can be used for scrubbing synthesis gas for removal of carbon dioxide.

d) Triethanol amine (TEA), Methyl diethanol amine (MDEA) (15-17) Di-isopropanolamine (DIPA) and Diglycolamine (DGA) process : All works in a similar way like MEA or DEA. When TEA or MDEA is used, the desorption of the solution is acheived simply by pressure reduction, but the absorption of carbon dioxide by these solvents is very slow.

DIPA is reported to be less corrosive than MEA or DEA. It has also got a greater selectivity of hydrogen sulfide over carbon dioxide than MEA or DEA, and therefore, is extensively used in refinery gas streams. DIPA solutions also require less heat for regeneration.

e) Giammarco-Vetrocoke process (18): It is based on absorption of carbon dioxide in potassium carbonate solution. To increase the absorption effeciency of the potash solutions, many chemicals like arsenic trioxide, glycine, amino acids, boric acid, selenium and telurium salts are added, which are termed activators. Corrosion inhibitors like vanadium pentoxide, potassium dichromate etc., are also added to the solution.

The absorption effeciency of the potash solution increases by a factor of 10 to 20 by the addition of arsenic trioxide activator. Dut to this high activating capacity, shorter absorbers and regenerators of carbon dioxide are required. Regeneration is also achieved readily and at low steam consumption.

Split Stream method is a further improvement by which low carbon dioxide concentrations can be achieved in the exit synthesis gas. This process has been widely accepted worldwide.

f) Benfield process (19-23) : MEA process is much economical when carbon dioxide content is low in synthesis gas. Hence in industries the bulk carbon dioxide is removed by hot potash process and is followed by MEA process.

Benfield process, developed by H.E. Benson and J.H. Field was originally hot potassium carbonate process, but later promoted Benfield process was developed ; with which it is possible to reduce the level of carbon dioxide to 500 ppm or less in only one step rather than two as in the combined hot carbonate-MEA process. It essentially uses 20% potassium carbonate, 3% DEA and vanadium pentoxide as corrosion inhibitor.

Other commonly known chemical absorption processes for carbon dioxide removal are (24-28):

g) Catacarb process : Developed by Eickmeyer and associates, in which an aqueous solution of potassium carbonate and amine borates as catalyst and potassium metavanadate as corrosion inhibitor is used.

h) Alkazid process : Developed by BASF, Germany, uses an aqueous solution of potassium salt of methyl amino propionic acid.

i) Alkacid process : Developed by J G Farbenin industry, West Germany, uses a combination of three different absorption solutions, namely sodium alanine, potassium salt of diethyl or dimethyl glycine and sodium phenolate.

2) PHYSICAL ABSORPTION PROCESS :

Employs non-aqueous organic polar compounds in which carbon dioxide is dissolved physically. It is particularly attractive for bulk removal of carbon dioxide from high pressure gas streams. Exessively large circulation rates are needed to reduced carbon dioxide to the desired level.

a)Resticol process (29) : Developed by Lurgi, West Germany, operates at low temperatures of - 30 Deg. C. to 50 Deg. C. and uses cold methanol as solvent. The process is mainly used for complete and simultaneous removal of carbon dioxide, hydrogen sulfide, organic sulfur compounds, ammonia, higher hydrocarbons and other impurities from coal gasification crude gas and reformed gas.

b) Purisol process (29, 30) : Developed by Lurgi, West germany uses N- Methyl 2-Pyrollidine (N-MP) for carbon dioxide and hydrogen sulfide absorption from high pressure gas streams. The process is chiefly used for removal of carbon dioxide from high pressure gases with high carbon dioxide content to a low residual content especially from synthesis gases produced by partial oxidation of heavy hydrocarbons or reforming of natural gas or naphtha.

c)Fluor solvent process (31) : Developed by Fluor Corporation Ltd. California, uses anhydrous propylene carbonate (4 methyl dioxolone-2).

d)Selexol process (31-34) : Developed by Allied Chemical Corporation, U.S.A. uses dimethyl ether polyethylene glycol for removal of carbon dioxide from high pressure gas streams. It is best suitable for high pressure absorption services.

3) CHEMICAL AND PHYSICAL ABSORPTION PROCESS :

Employes both chemical and physical solvents for carbon dioxide removal and is used especially in high pressure gas streams.

a) Sulfinol process (34-35) : The process uses a mixture of sulfolane (tetrahydrothiophene 1, 1-dioxide), an alkylamine (di-isopropanol amine) and water in various proportion depending upon the application. A typical formulation contains 40% by wt sulfolane, 45% by wt diisopropanolamine and 15% water. It can be used in synthesis gas and natural gas services.

4) CARBON DIOXIDE REMOVAL SYSTEMS USED IN GUJARAT STATE FERTILIZERS CO. LTD., BARODA

a)Giammarco Vetrocoke process with glycine (GV-glycine) (37) This process essentially consists of two stage removal of carbon dioxide from synthesis gas. First stage incorporates use of GV-glycine solution and the traces of carbon dioxide is removed by absorption in 20% monoethanol amine (MEA) solution. The product synthesis gas contains around 25 ppm carbon dioxide.

Reactions of glycine (a.1) and MEA (a.2)

(a.1) $R\text{-}NH_2 + CO_2 + H_2O \longleftrightarrow (R\text{-}NH_3)_2CO_3$

$(R\text{-}NH_3)_2CO_3 + CO_2 + H_2O \longleftrightarrow 2(R\text{-}NH_3)HCO_3$

(where $R = CH_2COOH$)

(a.2) $2C_2H_4OHNH_2 + CO_2 + H_2O \longleftrightarrow (C_2H_4OHNH_3)_2\ CO_3$

which reacts again with $(CO_2 + H_2O)$

$\longleftrightarrow (C_2H_4OHNH_3)\ HCO_3$ OR

$2\ C_2H_4OHNH_2 + CO_2 \longleftrightarrow C_2H_4OHNHCOONH_3C_2H_4OH$

These reactions are exothermic and the vapour pressure of these compounds increases rapidly. The absorbed gases are stripped from the solution by further application of heat.

Typical composition of GV-Glycine solution is given in Table (3).

Typical composition of the synthesis gas before and after removal of carbon dioxide, using GV-Glycine is given in Table (4).

Material of construction of the absorber and regenerator is carbon steel matching with following standards.

Shell thickness	-	24 mm
Absorber	-	JIS SM 418
Regenerator	-	JIS G 3106 SM 418
Corrosion allowance	-	1.6 mm

b) Giammarco-Vetrocoke system (GV-Arsenic trioxide) (39)

Potassium carbonate activated with arsenic trioxide is employed to remove carbon dioxide from the synthesis gas using the split stream method. Residual carbon dioxide in the synthesis gas is maintained at less than 0.1% from around 22%.

The removal of carbon dioxide is accomplished by two steps

1 An absorption step at elevated pressure where carbon dioxide component is removed from gas stream and

2 Regeneration step where spent solution is regenerated by stripping with steam at atmospheric pressure and reused in the absorption step.

3. Continuous/ intermittent aeration is carried out at the bottom of the absorber.

Arsenic trioxide added to the solution forms arsenite with potassium salts. It activates the potash solution to absorb more carbon dioxide thereby achieving maximum effeciency. Potassium arsenite (K_3AsO_3), formed here also acts as a corrosion inhibitor for carbon steel material of the absorber/regenerator, thereby preventing any damage. Continuous oxygen supply at a steady rate/ intermittent supply at required rate maintains the concentration of K_3AsO_3 in the solution.

Reactions occuring in the absorption and regeneration steps (38)

Activation by arsenic oxide (absorption)

$$3K_2CO_3 + As_2O_3 \longrightarrow 2K_3AsO_3 + 3CO_2$$

$$2K_3AsO_3 + 6CO_2 + 3H_2O \longrightarrow 6KHCO_3 + As_2O_3$$

For regeneration :

$$2KHCO_3 \longrightarrow K_2CO_3 + CO_2 + H_2O$$

Anticorrosive action of As_2O_3 may be due to many reaction products of it with potassium carbonate/ bicarbonate.

A typical composition of GV solution is given in Table (5).

A typical composition of the synthesis gas before and after removal of carbon dioxide, using GV, is given in Table (6).

The schematic flow diagram of the process is shown in Figure (1). Material of construction of the absorber and regenerator is carbon steel matching with the following standards :

Shell thickness - 40 mm
Absorber - SM 50B
Regenerator - SA 515 Gr 60
Corrosion allowance - 4 mm

c) Benfield System (Potassium Carbonate - Diethanol amine) (40)

Potassium Carbonate is activated by diethanol amine in this process. Vanadium pentoxide is added as corrosion inhibitor. Synthesis gas containing 18% carbon dioxide at the entry of the absorber with less than 0.1% carbon dioxide. Absorption is carried out at high pressure and low temperature and regeneration of the benfield solution is carried out at low pressure and high temperature. The reactions in the absorption and regeneration process are as under (38)

(Where R = $(C_2H_4OH)_2$)

$2RNH_2 + CO_2 + H_2O \longleftrightarrow (R\text{-}NH_3)_2CO_3$

$(R\text{-}NH_3)_2 CO_3 + CO_2 + H_2O \longleftrightarrow 2RNH_3HCO_3$

also $2RNH_2 + CO_2 \longleftrightarrow RNHCOONH_3R$.

A typical composition of Benfield solution is given in Table (7).

A typical composition of the synthesis gas before and after removal of carbon dioxide, using Benfield, is given in Table (8).

Material of construction of the absorber and regenerator is carbon steel matching with the following standards :

Shell thickness - 18 mm
Absorber - SM 50 B
Regenerator - 515 Gr 60
Corrosion allowance - 3 mm

SECTION - IV : CORROSION CHARACTERISTICS OF CARBON STEEL IN AQUEOUS SOLUTIONS

The section is divided into three main parts, Viz :

a) Corrosion

b) Inhibitors passivators

c) Evaluation of inhibitors/passivators

A) CORROSION :

Shoesmith (41) described corrosion of metals in aqueous environments, as an electrochemical reaction. For metal corrosion to occur, an oxidation reaction (generally a metal dissolution or oxide formation) and a cathodic reaction (such as proton or oxygen reduction) must proceed simultaneously.

Oxidation (anodic) $Fe \longrightarrow Fe^{+2} + 2e^-$

Reduction (cathodic) $2H^+ + 2e^- \longrightarrow H_2$ (in acidic media)

Overall reaction $Fe + 2H^+ \longrightarrow Fe^{+2} + H_2$

For corrosion of iron in a solution containing dissolved oxygen, the equations would be :

Anodic $Fe \longrightarrow Fe^{+2} + 2e^-$

Cathodic $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

Overall $2\ Fe + O_2 + 4H^+ \longrightarrow 2\ Fe^{+2} + 2H_2O$

The corrosion process thus has been treated as two separate reactions occuring at two distinct sites on the same surface. These two sites are known as the anode, or metal dissolution site, and the cathode, or the site of the accompanying reduction reaction. Since electrons are liberated by the anodic reaction and consumed by cathodic reaction, corrosion is expressed by electrochemical current and can be studied by various electrochemical techniques.

Electrochemically defining, the total current flowing into the cathodic reaction must be equal, and opposite in sign to the current flowing out of the anodic reaction. This current is known as corrosion current (i corr) and can be used as a gauge of the rate of corrosion process since it is related to mass of corroded metal by Faraday's law :

$$i\ Corr \cdot t = \frac{nFW}{M}$$

where i corr is in amperes

t is time for which the current has flowed

nF is the number of coulombs required to convert 1 mol of metal to corrosion product, where n is the number of electrons involved and

F is the Faraday constant

M is the molecular weight of metal

W is the mass of corroded metal

It is to be noted here, that several cathodic reactions may simultaneously support the corrosion and the area of the cathodic and anodic sites may be very different. These type of inequalities can have serious implications since it leads to localised attack like pitting or cracking.

Aqueous corrosion of carbon steel is a complicated process that can occur in various forms and is affected by various chemical, electrochemical and metallurgical variables including :

a) Composition and metallurgical properties of metal

b) The chemical (composition) and physical (temperature, conductivity, pH etc.) properties of the environment

c) The presence or absence of surface films

d) The properties of the surface films, such as resistivity, thickness, nature of defects and coherence

e) Velocity of the solution

f) Galvanic coupling with higher or lower alloys

The control of aqueous corrosion can be achieved by controlling any one of the rate determining steps in the corrosion process, and this step is the one with the smallest exchange current density.

B) INHIBITORS/PASSIVATORS :

An inhibitor is a chemical substance which when added in small concentration effectively decreases the corrosion rate (42). Putilova et al (43) classified inhibitors into 1st order, those which retard the onset of corrosion but do not decrease its rate ; 2nd order, immunizers ; and 3rd order, passivators. The 1st and third order inhibitors are further subdivided into chemical and electrochemical inhibitors. These electrochemical inhibitors are further classified into cathodic, anodic and mixed.

Metal or alloy is passive when it substantially resists corrosion in an environment where thermodynamically there is a large free energy decrease associated with its passage from the metallic state to appropriate corrosion products.

Fundamental difference in the mode of action of passivators and inhibitors lies in the mode of actions of these compounds on the metal surface. From electrochemical polarization point of view, a passivator tends to shift the 'corrosion potential' (Ecorr) of the system significantly towards noble direction during anodic polarization and a typical 'S' shaped curve is obtained. Cathodic potential remains almost unchanged in this case. However, in the case of inhibitors Ecorr is not very much shifted because the cathodic and anodic polarization are affected to a similar degree. This is the reason for which passivators are sometimes referred as 'anodic inihibitors'. Therefore, the anodic polarization effect of passivators is reflected in the reduction of corrosion current (Icorr) and shifting of Ecorr to a noble direction substantially, but with inhibitors, the Icorr is reduced, but the shift in Ecorr is not substantial.

Keir (44), Wenzel (45) and Gmelia (46) in their studies had observed corroion resistance of iron in concentrated nitric acid and related it to a passive state.

Schinbein (47) and Hisinger et al (48) studied the passivity phenomena by anodic polarization study of iron in concentrated nitric acid.

Electrochemical nature of the phenomena of passivity and occurence of several degress of passivity is also cited by Wetzlar etal (49).

Faraday (50) showed that low corrosion rate is not a measure of passivity, but the magnitude of current produced in such cell is a better criterion and accordingly a passive metal is one that is appreciably polarized by a small anodic current. Anodic polarization passivates iron, whereas cathodic polarization destroys it.

THEORIES OF PASSIVITY :

1. Oxide film theory : The basis of the oxide film theory is that the passive film is always a diffusion barrier layer of reaction products like metal oxide or other compound, which separates metal from the environment.

Evans (51) states that passivity is due to a formation of a protective film on surface and the film may not always be an oxide film. This view is also supported by Hedges (52) and Mears (53).

Hoar and Evans (54) shows that chromate ion reacts with ferrous ions and precipitates an adherent film on the metal surface.

Glasstone (55) studied iron in concentrated nitric acid and concluded that the acid reduces the thin adherent film of ferric oxide. Measurement of chromate, reduced on iron surface have been extensively reviewed by surface studies (56-60) and it was proved that trivalent chromium and hydrated chromium oxide (Cr_2O_3) remains on the metal surface along with ferric oxide.

2.Adsorption theory : Adsorption theory is also known as electron configuration theory. Langmuir (61) pointed out that the passivity of tungsten was due to the adsorption of 'oxygen atom' (O). Tamman (62) revealed that the passivity of iron, nickel, cobalt and chromium was due to adsorbed 'O' rather than oxide.

Kabanov (63) and Frankenthal (64) argued that the peculiar higher activation energies for adsorption of 'O' on such transition metals reveals the chemical bond formation and hence such films are called chemisorbed in contrast to lower energy films which are called physically adsorbed films. On these transition metals, the life of chemisorbed film is much larger since such films slows down the anodic dissolution rate and decreases the exchange current density. Higher activation energy in these metals due to the presence of electron vacancies or unpaired electrons, which forms strong covalent bonds with corrosive environment components, allows even less than a monolayer of film on the surface to exhibit passivating effect.

Uhlig (24) correlated noble values of flade potential (Ef) for iron with the potential calculated for chemisorbed film of 'O' on the surface of iron and suggested that on the metal surface initial layer of atomic 'O' is formed, over which a molecular 'O' is chemisorbed to give a thick film.

It is practically difficult to arrive at a firm conclusion on the mechanism and theory of passivity for a particular given system. The advancement of various modern analytical techniques has proved that the film formed on iron contains ferric oxide ($Fe_2 O_3$) as well as the reaction products of passivators in the layer.

Specificity of the action of corrosion inhibitors on corrosion cracking studied by electrochemical techniques by Podobaer (66) had shown that the specificity was associated with their unlike effect on the cathode and anode processes. He pointed that substances that inhibit general corrosion also inhibit corrosion cracking, which is the general rule for all media and metals.

C) EVALUATION OF INHIBITORS/PASSIVATORS :

Corrosion rate measurements of materials in various system and under different experimental conditions gives an indication of the characteristics of the systems. Literature available on the corrosion rate measurements are numerous (42, 51, 67-75). Measurement of weight loss of the material in the solution with and without inhibitor is a direct measure of the inhibitor effeciency. According to Mercer (76) replicate testing and visual observations are to be carried out in this type of evaluation since an inhibitor which prevents general or uniform corrosion may permit localised corrosion which will not be adequately reflected by the weight loss.

Mercer (76, 77) in a detailed study pointed out that solution analysis and determination of the concentration of the inhibitor during test priod is also sometimes used for evaluating inhibitor performance.

Electrochemical methods of testing are now widely used in inhibitor testing. Several methods are available which include measurement of electrode potential, polarization of electrode reactions, galvanic currents, electrical resistance, capacitance and electrochemical impedance.

The measurement of the electrode potential of a metal as a method of inhibitor testing can provide supportive evidence, but is seldom of use in isolation. In aqueous solutions, the variation of potential with time in a positive direction is an indication of passivation behaviour.

Skold etal (78), Straumann's et al (79), and simmons (80) argued that the electrochemical corrosion is the result of the current flow between anodic and cathodic areas of a metal surface. the effect of inhibitor therefore will be to reduce this current. This reduction in current can be measured by anodic or cathodic polarization. It can be obtained by displacing the open circuit potential (unpolarized OCP) of the metal by applying gradually increasing voltages from an external current source to produce a linear plot of potential against log current density, i.e. the Tafel region (Figure-3). Extrapolation of the OCP value will provide the corrosion current density. A disadvantage of the method is that it can be used to provide reliable results only once in a particular test, since the displacement of potential over hundreds of millivolts necessary to define the linear portion of the curve will result in significant changes in specimen and solution.

This drawback is overcome by the linear polarization method, which involves only a slight change of < 20 millivolts in the potential from the rest value. The linear relationship between the applied current densities and the potential in the low current region was also established.

Stern and Geary (81) showed in 1957 that there is a linear relationship between overvoltage (cathodic and anodic) and current densities at potentials slightly removed from OCP.

Based on the kinetics of the electrochemical reactions and on the concept of mixed potential theory as treated by Wagner and Traud (82), an equation was derived by them which related quantitatively the slope of the polarization curve in the vicinity of OCP (Ecorr) to corrosion current (Icorr).

Stern - Geary equation is given as :

$$Rp = \pm \frac{ba \times bc}{2.3 \times Icorr\ (ba + bc)} \qquad \text{——— (1)}$$

Where Rp = polarization resistance

ba = anodic Tafel

bc = cathodic Tafel

Icorr = corrosion current

In many cases, the slope of a straight line obtained due to cathodic and anodic curves is used as Rp and bc and ba are constant, so the factor on the right hand side of equation (1) becomes :

$$\frac{ba \times bc}{2.3\ (ba + bc)} = B \text{ (Constant)}$$

$$\text{Therefore} \quad Rp = \pm B / Icorr \text{ ——— } (2)$$

When cathodic process is under diffusion control, the slope of Tafel region (bc) is infinity and equation (1) can be written as:

$$Rp = -\ ba/\ 2.3\ Icorr \text{ ——— } (3)$$

$$\text{Similarly } Rp = bc/\ 2.3\ Icorr \text{ ——— } (4)$$

Equations (3) and (4) finds useful applications in the study of passivity and evaluation of passivators.

Linear polarization method relies on the constancy of the term B. If B is really a constant, then the corrosion rate studied is a true and correct indication of actual corrosion behaviour. Even if B is slightly fluctuating, the LPR method can be used to evolve critical concentrations of inhibitors needed to achieve maximum effeciency and also to compare relative effeciency, since higher the value of Rp, higher the effeciency of inhibitor.

Many electrochemical parameters which can be evaluated from a polarization curve and can be compared for inhibitor evaluation is given in Figure-4.

Sutcliffe et al (83), Fessler et al (84) and Brown et al (85) established the correlation between electrochemical parameters and stress corrosion cracking (SCC). Suceptibility to SCC, intergranular in nature has been shown to occur in certain ranges of electrode potentials, anodic to that corresponding to maximum (anodic) current density measured potentiodynamically. The determination and quantification of relationship existing between electrochemical parameters and the susceptibility to SCC of carbon steels in inhibited and uninhibited solutions by means of electrochemical measurements was done extensively by Armstrong and Coates (86) and is depicted in (Figure-2) showing corrosion, SCC and passive zone.

The technique of galvanic current measurement is based on the fact that measurable galvanic current flows between different metals in aqueous systems. Effective inhibition thus will substantially reduce these currents. In this study, area ratios of the metals is to be considered very precisely. Zero resistance ammeters, which nullifies all other currents in the systems and measures galvanic current only is used (76, 87).

Electrical resistance measurement method is used in-situ for measuring inhibitor effeciency. It relies on the principle that dc ohmic resistance of a precisely made wire will increase in inverse proportion to its cross-section and therefore the progress of corrosion and its inhibition can be monitored from changes in the electrical resistance of a test probe (88).

In polarization studies, when passivation occurs, anodic and cathodic Tafel are never constant due to high polarization of carbon steel material.AC impedance technique, which uses very small excitation amplitudes (5 to 10 mv) overcomes this, providing a wealth of kinetic and mechanistic information. The application of a sinusoidal wave form of varying frequency to the corroding and inhibiting system, can distinguish between the various components making up the total impedance of the system (89). Rp can then be calculated and from it inhibitor performance can be evaluated. AC impedance studies pertaining to corrosion evaluation has been extensively carried out and main features of it are very low extent of polarization of the working electrode, separation of solution resistance and charge transfer resistance, determination of double layer capacitance, Rp measurements etc. (90-104).

TABLE - 1

Production of ammonia by developing and developed countries (2) for 1989-90

	Ammonia production in 1000 Metric tonnes N.
All developed countries	30,022
All developing countries	797
World total	30,819

TABLE - 2

Carbon dioxide produced in generating synthesis gas from different feed stocks (10)

Feed Stock	Process	Tons Carbon dioxide per ton of ammonia
Natural gas	Steam reforming	1.22
Natural gas	Partial oxidation	1.63
Naphtha	Steam reforming	1.42
Naphtha	Partial oxidation	2.09
Heavy fuel oil	Partial oxidation	2.49

TABLE - 3

Typical Composition of GV-Glycine Solution

Glycine (Monoamino acetic acid)	50 gms/ litre
Potassium carbonate	200 gms/ litre
Potassium bicarbonate	100 gms/ litre
Vanadium pentoxide	0.2 gms/ litre (Corrosion inihibitor)

TABLE - 4

Typical composition of the Synthesis gas before and after removal of carbon dioxide (%)

Constituents of Syn.gas	Before	After
Argon	0.30	0.30
Nitrogen	21.66	24.24
Hydrogen	58.71	74.62
Methane	0.25	0.50
Carbon monoxide	0.08	0.13
Carbon dioxide	20.00	<0.20

TABLE - 5

A typical composition of the GV solution

Potassium carbonate	150 gms/ litre
Potassium bicarbonate	90 gms/ litre
Arsenic trioxide	120 gms/ litre

TABLE - 6

Typical composition of the synthesis gas before and after removal carbon dioxide (%)

Constituents of Syn.gas	Before	After
Argon	0.30	0.30
Nitrogen	18.12	23.89
Hydrogen	58.59	75.04
Methane	0.45	0.60
Carbon monoxide	0.14	0.17
Carbon dioxide	22.40	< 0.20

TABLE - 7

Typical composition of Benfield solution

Potassium carbonate	30 to 32%
Diethanolamine	3 to 3.4%
Vanadium pentoxide	0.6 to 0.7%

TABLE - 8

Typical composition of the synthesis gas before and after removal of carbon dioxide (%)

Constituents of Syn.gas	Before	After
Argon	0.30	0.30
Nitrogen	20.10	25.04
Hydrogen	60.17	73.92
Methane	0.31	0.38
Carbon monoxide	0.12	0.16
Carbon dioxide	19.00	< 0.20

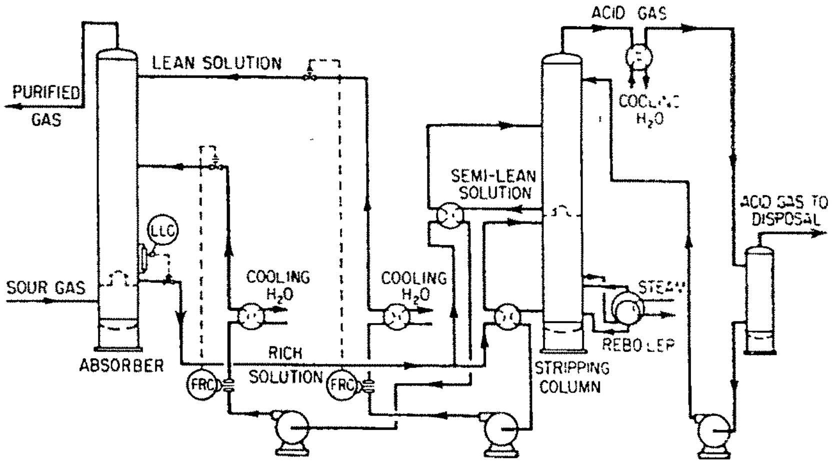

FIG.1 : PROCESS FLOW DIAGRAM FOR CARBON DIOXIDE REMOVAL SYSTEM - SPLIT STREAM METHOD

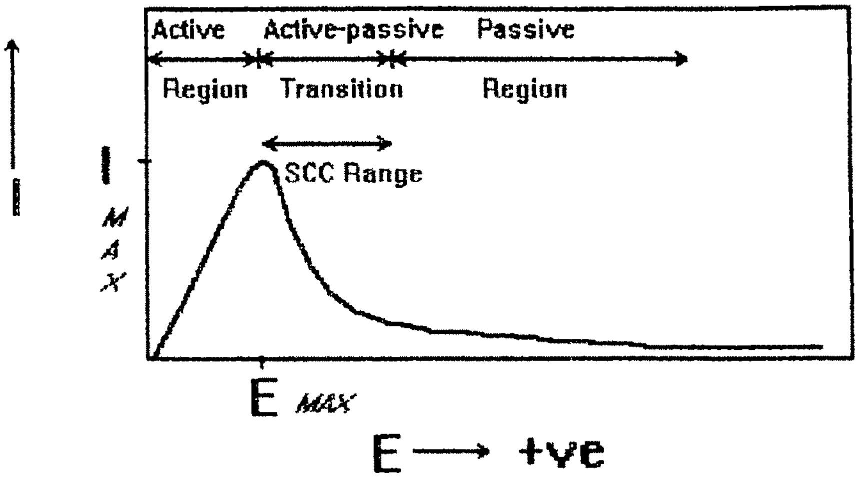

FIG.2 : SCHEMATIC i - E CURVE SHOWING RANGE OF MAX. SUSCEPTIBILITY TO SCC FOR STEEL IN CARBONATE, BI-CARBONATE SOLUTION

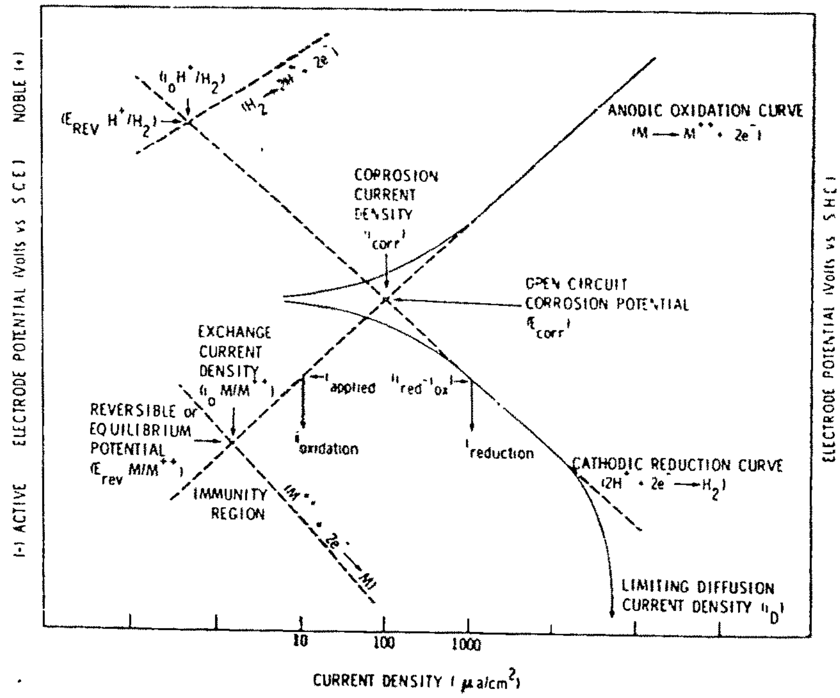

FIG.3 : HYPOTHETICAL CATHODIC AND ANODIC POLARIZATION DIAGRAM SHOWING TAFEL REGIONS.

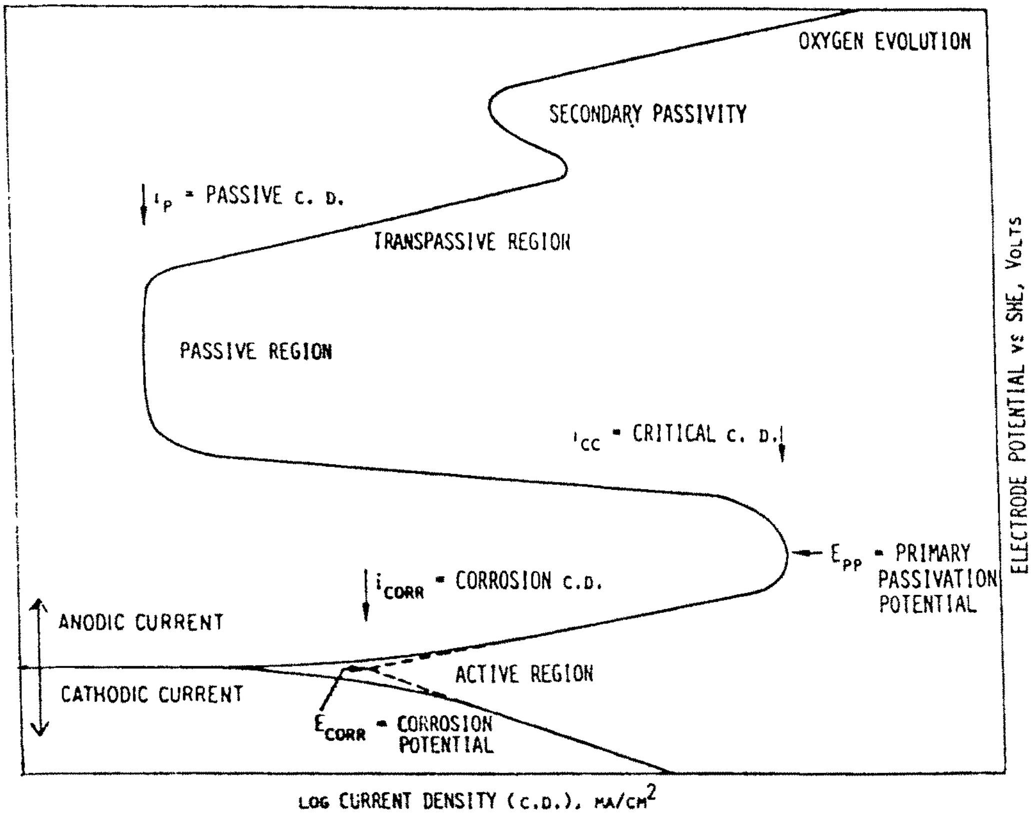

FIG.4 : HYPOTHETICAL CATHODIC AND ANODIC POLARIZATION PLOTS FOR A PASSIVE METAL

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