EROSION-CORROSION STUDIES OF STEEL

A Thesis

Submitted To The Department Of Chemical Engineering, Bangladesh University Of Engineering And Technology, Dhaka, In Partial Fulfilment Of The Requirement For The Degree Of MASTER OF SCIENCE IN ENGINEERING (Chemical).

BY

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ABSTRACT

The corrosion and erosion-corrosion behaviour of low carbon steel plates and malleable cast iron tees and elbows were investigated in corrosive media prepared by dissolving commercial sodium sulphite and sodium bi-carbonate (ratio 6:1) in distilled water by weight loss method.

Concentration of environment was varied from 0.4 to 1.4 lb/gallon and its effects on steel plates were studied both in stagnant and flowing condition. In stagnant condition corrosion rate varies asymptotically and in flowing condition it varies parabolically. By varying velocity of the media upto 14 FPS, it has been established that corrosion rate attains a maximum value at 5.7 FPS. Critical velocity for the system is 6.6 FPS above which corrosion rate increases with further increase of velocity.

pH of media was varied from 5 to 10 and it was observed that the nature of the curve is similar to that found in literature (32). Due to presence of chloride in corrosive media, corrosion rate increases with increase of chloride content. But the severity of attack of chloride was reduced due to presence of other ingredients as compared to salt solution of the same chloride concentration.
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CHAPTER ONE

1.0. INTRODUCTION AND OBJECTIVES
1.1 INTRODUCTION

Corrosion is the destructive attack on a metal or an alloy by chemical change, electrochemical change or physical dissolution in any environment. This excludes mechanical processes which destroy metallic articles by grinding it as metallic dust. Such purely mechanical process, in absence of any chemical changes, is called erosion. But often corrosion and erosion operate simultaneously and alternately and the damage is frequently far greater than the damage caused when either occurs alone. This disastrous combination of destructive agents at a very high velocity of the environment or metal is called erosion-corrosion. In this process, metal is removed from the surface as dissolved ion or corrosion product, which are mechanically swept away from the metal surface. Erosion-corrosion depends on the nature of the protective film formed by the corrosion product, velocity of the system, turbulence, suspended solids content, pH of solution, galvanic interaction and nature of metal and alloys.

Erosion-corrosion is characterized in appearance by grooves, gullies, waves, rounded holes, and valleys and usually exhibits a directional pattern. Figure 1.1 shows a longitudinal cross-section of a 4-inch dia flow line failure due to erosion-corrosion in a high production oil well at BU-ATTIFEL field, LIBYA (1), which shows a directional pattern of erosion-corrosion.
Fig. 1.1: Directional Pattern of Erosion-Corrosion around a single pit.

Longitudinal cross section through a single pit. (8X)

Schematic of pit formation on the inner surface of the steel pipe.
Types of corrosive media causing erosion-corrosion include aqueous solution, organic systems and liquid metal. All types of equipments exposed to moving fluids are subjected to erosion-corrosion which includes piping system, particularly bends, elbows and tees; valves; pumps; blowers; centrifugals; propeller; impeller; agitator; agitated vessels; heat exchanger tubing such as heaters and condensers; measuring devices such as orifice; turbine blades; nozzles; ducts and vapour lines; ball-mill; baffles; and equipments subjected to spray.

For a long time it has been established that the corrosion behaviour of metals or alloys may vary in flowing condition from that observed under static conditions. Most of the corrosion data in the literature are based on static test (if velocity is not mentioned), so these data are insufficient for practical use. So it is essential to study corrosion behaviour of metals or alloys in flowing condition combining all other dependent variables of the process industry.

To study the effects of high velocity, various methods have been used. One of the widely used procedure is to use test specimens in the form of discs which can be rotated at the desired speed, either partly or wholly immersed in the test solution. The other way is achieved by moving the liquid past a stationary specimen. Because of complex effect associated with the difference in velocity from point to point on a rotating specimen, the latter method of test was selected for the present work.

Khulna Newsprint Mill, Khulna, experienced a serious corrosion problem of piping system including valves, bends,
tees, elbows, etc. adjoining newly installed autoclaves under BMR scheme and it was reported to be a case of erosion-corrosion. So for the present research work, the same corrosive media was selected to test its behaviour on low carbon steel specimens by varying velocity of media, concentration of environment, pH and chloride content in the media.

1.2 OBJECTIVE OF THE PRESENT RESEARCH WORK

Low carbon steel plate and malleable cast iron tee and elbow were used to study the corrosion behaviour in corrosive media prepared by dissolving commercial grade sodium sulphite and sodium bi-carbonate in the ratio 6:1 in distilled water. The variables were concentration of corrosive media, velocity and pH of liquor and chloride content in the liquor. Corrosion tests were conducted with the following objectives:

a) To study the effect of velocity on corrosion rate of an impingement plate when the liquid is allowed to hit the specimen surface at different velocity.

b) To study the effect of concentration change of sodium sulphite and sodium bi-carbonate mixture on erosion-corrosion of impingement plate, tee and elbow.

c) To study the effect of pH on erosion-corrosion of plate, tee and elbows.
d) To study the effect of chloride concentration in a mixture of sodium sulphite and sodium bi-carbonate (ratio 6:1 concentration: 0.8 lb/gallon) on plate, tee and elbow.

e) To compare corrosion rates of impingement plate under flow condition and static condition.

f) Comparative study of corrosion rate of elbow and tee to find the effect of system geometry on erosion-corrosion.
CHAPTER - TWO

2.0. LITERATURE REVIEW
2.0 LITERATURE REVIEW

2.1 INTRODUCTION

It is established that whenever a corrosion process takes place in a medium both oxidation and reduction reactions take place simultaneously. According to mixed potential theory, "During the corrosion of an electrically isolated metal sample, the total rate of oxidation must equal total rate of reduction" (4). A corrosion reaction consists of an oxidation (anodic) reaction which is primarily dissolution of metal ion:

\[ M \rightarrow M^{n+} + ne \quad (2.1) \]

and a reduction (cathodic) reaction. The primary reduction reaction or reactions may be any one or combination of the reactions given below, depending on the condition of the environments:

a) In acid solutions where hydrogen gas is evolved; reduction of hydrogen ion takes place:

\[ 2H^+ + 2e \rightarrow H_2 \quad (2.2) \]

also with availability of oxygen, oxygen reduction may take place:

\[ O_2 + 4H^+ + 4e \rightarrow 2H_2O \quad (2.3) \]
b) In approximately neutral or in basic solutions
Oxygen reduction may take place as per equation:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 4\text{OH}^- \]  
(2.4)

c) In oxygen deficient environment in presence of adequate dissolved sulphate, the sulphate reducing bacteria reduces sulphate to sulphide according to following reaction (2,3):

\[ \text{SO}_4^{2-} + 4\text{H}_2 \rightarrow 4\text{H}_2\text{O} + \text{S}^{2-} \]  
(2.5)

d) The metal ion may be reduced and deposited

\[ \text{M}^{n+} + ne \rightarrow \text{M} \]  
(2.6)

e) If the metal has two or more valancies, the metal ion concentration may lead to reduction of the higher valent ion as an alternative cathodic reaction in acid solution

\[ \text{M}^{3+} + e \rightarrow \text{M}^{2+} \]  
(2.7)

From the above mentioned simple corrosion reaction processes, it is evident that the availability of different reactants to the corroding site and the subsequent removal of corrosion products can play an important role in the overall process. The transport of the reactants and the products
to and from the corroding site is dependent on the relative motion of the metal with respect to its environment. Therefore, in many cases, the corrosion rate is dependent on the velocity of the environment. Apart from the consideration of transport processes, high velocity and turbulent conditions may result in erosion-corrosion which involves combined effect of corrosion and mechanical abrasion. Since corrosion is involved in erosion-corrosion process, all the factors that affect corrosion should be considered. The factors that are directly pertinent to erosion-corrosion are velocity of environment, surface film, turbulence, impingement attack, pH, temperature, suspended solid, galvanic coupling, and nature of metals or alloys.

2.2 EFFECT OF VELOCITY ON CORROSION AND EROSION-CORROSION

The primary condition for a corrosion process is that the material must be brought into contact with the metal surface and the metal atoms must move away. There is no simple answer to the question of what an increase in velocity will do. It is necessary to know the details of the exposure conditions and what materials are involved.

Motion generally increases total weight loss by supplying the corrosives at a faster rate. The boundary layer at the metal surface becomes thinner due to flow, so that it is easier for the corrodant to reach the surface and there is less restriction of corrosion by diffusion processes. On the other hand at high relative motion, the character of cor-
rosion products may change and become more protective. If the corrosion process is controlled by activation polarization, velocity have no effect on corrosion rate. Some metals resist corrosion in certain environments due to formation of bulky and readily visible protective film on their surface. These metals when exposed to high velocity, mechanical damage or removal of films can occur resulting in accelerated attack.

When the velocity becomes extremely high, mechanical effect is added to the corrosion process. Erosion can completely remove protective film or layers of corrosion products and keep corrosion going on at a high rate. Turbulence, vibration and other conditions may lower the pressure locally to cause cavitation in the liquid, which may then lead to mechanical damage by the hammering action resulting from the subsequent collapse of the vapour bubbles. Damage caused by erosion-corrosion and by cavitation-erosion can be severe and rapid.

From these facts, it can be appreciated that velocity by itself has little direct effect on corrosion. It exercises its influence indirectly by its effect on factors that are of major importance in determining the pattern and rates of corrosion.

In neutral water solutions the oxygen concentration is of major importance in determining corrosion rate of most metals. Local variation in oxygen content may set-up oxygen concentration cells which cause pitting and local attack. Motion generally would be expected to eliminate these differential aeration cells but would tend to increase the total
corrosion by supplying more oxygen.

Another type of concentration cell affected by motion is a metal ion cell (5). Metal ion concentration cells are most apt to form near crevices or recessed areas where metal ions have a chance to build up. Conversely, a fresh stream of solution impinging upon a particular area may wash away the metal ions locally and causes such areas to become relatively anodic and to corrode.

Films of corrosion product or other deposits are of major importance in determining corrosion rates. Generally, such film tends to exclude oxygen and therefore tends to be protective. The protectiveness of film will vary with its uniformity and the conditions under which it is formed. Since velocity affects these things, it may affect the protective character of the film. Thus at high velocity owing to the greater availability of oxygen, ferric hydroxide might be precipitated in close contact with the metal surface and be protective, whereas at lower velocity ferrous product might be precipitated away from the metal and be nonprotective.

Corrosion rates usually decrease with time. This is due in part to gradual thickening of the protective films. If the films are thick enough, changes in velocity might be unnoticed at the metal surface. At high velocities, however, erosion action can remove the protective films. Turbulence may cause this to occur locally and lead to rapid pitting and impingement attack.
The initial effect of increasing velocity in neutral water is to increase corrosion rate and was investigated by a number of investigators (6,7,8,9,10). The reproduced data with rotated specimens of mild steel in air saturated Cambridge tap water is shown in figure: 2.1. Friends et. al. (11) studied the effect of velocity in acid solution and found that the rate of corrosion increases with increase of velocity. Speller and Kendall (9) found that in neutral water the corrosion rate was low in laminar flow, increased rapidly in the transition range and continued to increase, but at a lower rate, in turbulent flow in pipes. Whitman (12) postulated that effect of higher velocities should be to increase the corrosion as a result of increased diffusion rate of oxygen and the subsequent breaking down of protective films on the metal surface. Wilson (13) thought that velocity was important in determining the thickness of the film through which oxygen must diffuse in the corrosion process.

A number of investigators (14,15,16,17) have found that at higher velocities the corrosion rate may decrease again. Roetheli and Brown (16) worked with rotating steel specimens in oxygenated water and found that with an increase of rotational speed, corrosion increased to a maximum, then decreased to a low value, and finally increased to a high value at very high speed. They attributed the decrease to the formation of a protective film of ferric-hydroxide, because of greater supply of oxygen.
Fig. 2.1 shows that corrosion increased with oxygen concentration up to 18 ml per liter (6). At still higher oxygen concentrations, however, the corrosion may drop to low values with the iron tending to become passive (18). Groesbeck and Waldron (19) found that in distilled water moving at 0.25 ft/sec, the corrosion rate of mild steel was 330 mdd with 16 ml of oxygen per liter but that at 24 ml per liter the corrosion had dropped to 30 mdd in 48 hr test at 30°C. Thus the effect of velocity and oxygen concentration are interrelated.

The condition of metal surface is another factor affecting the inflection point. This was studied by Russell, Chappell, and White (17). They pointed out that the results showing passivity at high velocity were obtained by starting with clean specimens. When the test specimens were rusted at the start corrosion at high velocity was at a rapid rate. This was confirmed by Forest, Roetheli, and Brown (20), who also showed that the passivity induced on clean specimens at high speed would not persist after the motion was stopped.

Increase in velocity greatly results in increased attack. But the effect may be nil or slow increase until a critical velocity is reached, and then the attack may increase at a rapid rate. This critical velocity is reported to be about 3 ft/sec (16). The same effect was observed in other
Figure 2.1: Effect of Velocity and Oxygen Concentration on Corrosion of Steel

Five- to seven-day tests in water in 23°C.
experiments (15,17) and has been attributed to erosion, at
the velocity, beginning to strip away protective films.

Erosion corrosion of aluminium in white fuming nitric
acid (21) was studied and it was found that erosion-corrosion
increases with increase of velocity. Aluminium can form film of
aluminium nitrates and aluminium oxide in fuming nitric acid.
Little or no attack was found at very low velocity. At an
intermediate velocity 1 to 4 ft/sec, the action of the solution
was sufficient to remove the nitrate film but it was not
sufficient to destroy more adherent oxide film. Velocities
above 4 ft/sec apparently remove much of the oxide and erosion-
corrosion occurs at a faster rate. Results of erosion-corrosion
studies of some stainless steel in fuming HNO₃ is given in (21).
Stainless steel is attacked autocatalytically by more dilute
solution of nitric acid (22,23). As the velocity of the acid
is increased, the corrosion reaction products of nitric acid
are carried away more rapidly and the corrosion rate of stain-
less steel is reduced.

Velocity can decrease attack and increase the effec-
tiveness of inhibitors by supplying the chemicals to the metal
surface at a higher rate. Higher velocity of corrosive media
prevents deposition of scale on metal surface. Such deposition
of scale may cause crevice corrosion. So, it can be said that
under certain circumstances higher velocities also decrease
attack by preventing the deposition which may cause crevice
corrosion. On the other hand, solids in suspension moving
at high velocity may have scouring effect and thus destroy
surface protection.
2.3 EFFECT OF SURFACE FILM ON EROSION-CORROSION

The nature and properties of the protective surface films that form on some metals or alloys are very important from the standpoint of resistance to erosion-corrosion. The ability of these films to protect the metal depends on the speed or ease with which they form when originally exposed to the environment, their resistance to mechanical damage or wear, and their rate of reforming when destroyed or damaged. A hard, dense, adherent, and continuous film would provide better protection than one that is easily removed by mechanical means. A brittle film that cracks or spalls under stress may not be protective. Sometimes the nature of the protective film that forms on a given metal depends upon the specific environments to which it is exposed and this determines its resistance to erosion-corrosion to the fluid.

The erosion-corrosion of carbon steel discs in aqueous \( \text{H}_2\text{S} \) solution increases with fluid velocity at 120°C (24). This can result in significant metal losses at high fluid velocities. Dissolution or the dispersal of the iron sulphide film formed on carbon steel is accelerated by an increasing fluid velocity, but this is balanced by the formation of a fresh iron sulphide film on the disc surface with increased corrosion. The rate of formation of iron sulphide film on carbon steel surface is almost instantaneous which is also consistent with (25). Therefore, if the dispersal of the
freshly formed film continues without any protection of the surface, loss of iron from the surface will proceed at increasing rate at higher fluid velocities, due to erosion corrosion. But with a preconditioned carbon steel disc having a pyrite-pyrrhotic surface, no detectable loss of iron occurs even at higher velocities (24).

Lead depending on the formation of lead-sulphate or lead-oxide protective surface in sulphuric acid environment shows its corrosion resistant property. Lead gains weight when exposed to dilute sulphuric acid because of surface coating or corrosion product formed. In strong sulphuric acid the lead sulphate is soluble and is not protective. Under static conditions lead shows no deterioration in dilute sulphuric acid due to formation of lead oxide film. But under high velocity conditions, the attack increases with temperature.

The resistance to corrosion of stainless steel depends on its passivity. Type 316 stainless steel in sulphuric acid-ferrous sulphate slurry shows no weight loss and was completely passive under stagnant conditions. But at high velocity due to break down of passive film, it shows high rate of deterioration which is about 4500 mpy at 55°C keeping the velocity 39 ft/sec (4) and erosion-corrosion in this case increases with temperature of the environment.

Copper and brass in sodium chloride solution with and without oxygen show that copper was attacked more than brass in oxygen saturated solution. Copper was covered with a black and yellow-brown film of CuCl₂ and brass was covered with a dark gray film of CuO. The better resistance of brass was due to the greater stability or protectiveness of the dark gray film.
Titanium resists erosion-corrosion in many environments because of stability of TiO$_2$ film, although titanium is a reactive metal. It shows very excellent corrosion resistance to seawater, chloride solution and fuming nitric acid. The protectiveness of corrosion products in many environment was also discussed earlier.

It would seem likely that metals would be more rapidly attacked at higher temperature as water ionizes highly at higher temperature. But Decker, Wagner and Marsh (26) report that at 320°F corrosion rate was lower than 250°F. In this case cast carbon steel forms a more tenacious oxide film on the surface of the metal at high temperature than at lower ones. During tests it was observed that at 320°F and 385°F a black magnetic iron-oxide and at 250°F a red film of ferric oxide was formed. The black films were more tenaciously bonded to the specimens and were more difficult to remove than the red films, which caused reduction of corrosion at higher temperatures.

2.4 EFFECT OF TURBULENCE ON EROSION-CORROSION

Turbulence or turbulent flow condition is primary factor for many erosion-corrosion failures. Turbulence results in greater agitation of liquid at the metal surface resulting in more intimate contact between the environment and the metal. This type of failure occurs in the inlet ends of the tubings in the condensers and smaller shell and tube heat exchangers frequently which is designated as "Inlet tube corrosion". The attack is usually confined to the first few inches of the tubing at the inlet. Turbulence exists in this area due to contraction because the fluid is flowing from a
large pipe into a smaller diameter pipe.

Types of flow obtained depends on the rate of fluid flow and also on geometry or design of the equipment. Analysis of flow condition shows that Reynolds number lies above $2.1 \times 10^3$ confirming the turbulent condition of the system. In addition to high velocities, crevices, deposits, sharp changes in cross section and other obstructions that disturb the laminar flow pattern may result in erosion-corrosion. Impellers and propellers are typical components operating under turbulent condition.

Flow condition at the wellhead of Bu-Attifel field (1) was turbulent and corresponding Reynolds number was 75000. As a result severe erosion-corrosion was experienced on the flow line down stream of the choke valve. The sudden reduction of pressure was from 1400 psi to 800 psi between the oil head and the flow line causing extremely vigorous turbulent flow. Vortical oil flow at the oil head produces centrifugal forces that increase the volume fraction of the heavy constituents in the fluid flowing very close to the inner pipewall surface. This increases friction and high velocity accelerates the wearing process.

2.5 EFFECT OF IMPINGEMENT ATTACK

Many failures due to erosion-corrosion are directly attributed to impingement attack. Impingement attack is a form of erosion-corrosion in which the liquid strikes the metal surface at a high velocity—a situation that can occur at bends, tees, elbows and sudden changes in cross section.
In majority of cases of impingement attack, geometrical features of the system result in turbulence at one or more parts of the metal surface. Attack can occur in this way with a solution that is free from gas or air bubbles or suspended solids but it is markedly accounted when they are present (27).

Bengough and May (28) report that "Almost static boundary layer of water adjacent to the metal surface prevents the impingement of rapidly moving water. However, if the water contains air bubbles that have diameters that are greater than a certain critical value (the thickness of boundary layer) the bubbles on striking the boundary layer are subjected to differential forces that disrupt them and the boundary layer thus enabling the water to impinge on the metal surface at the point of bubble disruption with consequent removal of protective films". Chambelland Carter (29) consider that the attack is due to highly turbulent flow at the attack area, which can be caused by air free water at comparatively high speeds and a lower speed if air bubbles of a certain size are present in water. The turbulent fluid breaks through the boundary layer and causes continuous breakdown of protective films and removal of metal ion. Generally the pit developed due to impingement attack are free from corrosion product and are undercut at the forward end (30).

This type of attack is found in the piping systems specially at bends, tees, elbows, valves where the fluid is to change direction; steam turbine blades, particularly in the exhaust or wet steam ends; entrainment separators; external component of aircraft; parts in front of inlet pipes in tanks; cyclones; any other applications where impingement conditions exist.
A low-iron 70-30 cupro-nickel was exposed to a jet of sea water containing entrained air bubbles (31). The peak velocity of fluid was 12 ft/sec. Corrosion was severe where the jet impinged and the protective film was eroded away.

Laboratory tests with fuming nitric acid and B214 cast alloy (21), showed very severe attack at a 90° degree elbow at the centre of the outside arc. The greater turbulence at elbows and changes of direction of flow promotes erosion-corrosion at these areas.

2.6 EFFECT OF P^H ON EROSION-CORROSION

Fontana and Luce (32) studied the erosion-corrosion of steel at 50°C and velocity of 39 ft/sec in distilled water. They found that variation of corrosion of steel with different P^H was due to the nature and composition of the surface scale formed. It has been found that erosion-corrosion was severe at lower P^H and decreases to a minimum at P^H 6, increased again to P^H 8 and then becomes nil at P^H 10 or above. The scale on the specimens exhibiting high rates of deterioration was granular in nature and consisted of magnetic Fe_3O_4. Below P^H 5, the scale cracked, probably because of internal stresses and fresh metal was exposed to the environment. So corrosion rate was very high. In the region of low attack the corrosion products were Fe(OH)_2 and Fe(OH)_3 which are more protective in nature because they hinder transfer of oxygen and ions.

Severe erosion-corrosion was also reported by Wagner, Decker and Marsh (33) in tests simulating conditions in centrifugal boiler feed pump handling condensed steam at 250°F. The water had been deaerated but
contained 0.01 to 0.02 ml of oxygen per liter and velocity in these tests were maintained 65 to 450 feet/sec. They found that carbon steel suffers severe corrosion than chromium steel or stainless steel. The results of the tests of cast carbon-steel specimens indicates that at 250°C the rate of erosion-corrosion attack increases with $p^H$ between 7.6 and 8.4 and the rate at 8.4 being about double that at 7.6. Another test conducted at Ohio State University on similar material using distilled water at 122°F, the rate at $p^H$ 8 was about 10 times that at $p^H$ 6 (26). It was noted that at the end of the test at 250°F and $p^H$ 8.4 (26), the specimens were exceptionally clean. This seemed to indicate that the higher $p^H$ retarded the formation of protective oxide films on the specimens, thereby promoting metal wastage.

2.7 EFFECT OF TEMPERATURE ON EROSION-CORROSION

Temperature increases the rate of almost all chemical reactions. When one reactant is a metal, the complexity of the system is increased because of added complication of electro-chemical effects. Many corrosion systems show a rapid or exponential rise in corrosion rate with increasing temperature.

The effect of several commercial ferritic and austenitic steel was tested from room temperature to 900°C (34). All the steel showed constant or decreasing erosion rate as the temperature was increased until a temperature reached where a marked increase in erosion rate began to occur with temperature. Austenitic steels were found to have lower erosion rate than ferritic steels and hardness had no influence on erosion rate.
Increasing temperature from 37°C to 55°C, erosion-corrosion of type 316 steel in sulphuric acid-ferrous sulphate slurry at velocity of 39 ft/sec. increases from almost zero to 4500 mpy. Also, erosion-corrosion of hard lead in 10% sulphuric acid at 39 ft/sec. velocity increases about 4.5 times with increase in temperature from 35°C to 90°C (4). Increasing temperature from 90°C to 205°F increases the attack to about ten times as reported by Fairchild (35).

2.8 EFFECT OF SUSPENDED SOLIDS ON EROSION-CORROSION

Effect of suspended solids in a corrosive environment is related with turbulence and impingement. Suspended solids help to break the protective film formed and increases corrosion. Corrosion becomes severe when velocity of the environment increases and specially when fluid is impinging on a surface.

Koltz (36) studied effect of suspended solids at a velocity of 15 m/sec and 700-1000 degree centigrade temperature in oxidizing environment. The diameter of the particles was 5 to 100 μm. He observed that large corroding particles resulted in an increased scale thickness on the eroded-corroded surface compared to the scale thickness on the only corroded side with the same conditions.

Erosion-corrosion due to suspended solids is an acute problem in catalytic cracking, fluidized bed combustion reactor, high pressure oil head and coal liquefaction and gasification plants.
2.9 EFFECT OF GALVANIC COUPLING

When dissimilar metals are in contact in a flowing system, galvanic or two metal corrosion can influence erosion-corrosion. Galvanic effect may be nil under static conditions but may be greatly increased when the environment is moving at faster rate. Type 316 stainless steel at a velocity of 39 ft/sec shows its excellent erosion-corrosion resistant property. But when the alloy is coupled with lead, the passive film formed was destroyed by the combined effect of galvanic corrosion and erosion-corrosion. Corrosion rate increases several-fold after galvanic coupling and corrosion rate is enhanced by increase of temperature (4).

Work of Fontana and Luce (32) shows that at lower pH range there are cracks in the Fe$_3$O$_4$ scales. The increased attack of steel is the doubtless contribution of the scale. Because the scale is cathodic to the substrate steel by an amount of about 500 mV. (4).

Changes in motion can produce surprising galvanic effects. In sea water, at low velocity it makes little difference whether steel is coupled to stainless steel, Titanium, copper or nickel. At high velocities, the cathodic polarization of stainless steel and titanium is much easier than other materials (37), so that at high velocity the galvanic corrosion produced by coupling steel to stainless steel or titanium is much less than that produced by coupling steel to copper or nickel. The effect of velocity on galvanic corrosion of steel with other metals in sea water is tabulated by LaQue (37).
2.10 EFFECT OF NATURE OF METAL OR ALLOY

The performance of different material under erosion-corrosion conditions depends on chemical composition, corrosion resistant property, hardness, and metallurgical history of metals and alloys. The composition of metal largely determines its corrosion resistance. If the metal is active or an alloy composed of active metals, its corrosion resistance is due to its ability to form and maintain protective films. If the metal is noble, it possesses a good inherent corrosion resistance. Under same condition, a metal with good inherent resistance will be expected to show better performance to erosion-corrosion. For example 80% Ni and 20% Cr alloy is superior to an 80% iron-20% Cr alloy because of better inherent resistance of nickel than iron.

Wagner, Decker and Marsh (33) reported that wrought carbon steel are much inferior to cast carbon steel in their ability to withstand erosion-corrosion attack. A cold rolled low carbon free-machining steel shows severe attack due to lack of homogeneity in structure. Hot-rolled carbon steels are considerably better than plain carbon steel. Austenitic stainless steels were determined to have lower erosion rate than ferritic steels (34). Chromium bearing steels are much more corrosion resistant than the carbon steel and 18-8 steels have the highest resistance. At 250°F the erosion-corrosion resistance of chromium bearing steels are roughly proportional to their chromium content. But at higher temperatures, the relative advantage of high chromium is greatly reduced (26).

The addition of a third element to an alloy often increases its resistance to erosion-corrosion. Addition of 0.5% iron instead of 0.05% Fe
to 70-30 cupronickel reduces erosion-corrosion rate from 199 to 39 mdd at a velocity of 27 ft/sec. (4). Addition of molybdenum to 18-8 makes type 316 more resistant to corrosion and erosion-corrosion. Addition of 0.025% Cu to type 316 reduces its erosion-corrosion to almost zero by sulphuric acid-ferrous sulphate slurry at 39 ft/sec. In all these cases, the addition of a third element produces more stable protective films that resist erosion-corrosion. LaQue and Mason (31) showed that impingement attack of 70-30 cupro-nickel alloy in sea water containing air bubbles at a velocity of 12 FPS was much reduced by addition of 0.5% Fe. The addition of iron in 90-10 cupro-nickel related in sea water at 14 and 30 FPS was investigated by Stewart and LaQue (38) and they obtained similar results.

Erosion-corrosion resistance of stainless steel varies depending upon their compositions. Durimet 20 (30% Ni, 20% Cr, 3.5% Cu, 2% Mo) exhibits better performance than 18-8 steel in fuming nitric acid, sea water, and many other environments not only because of better inherent resistance but also because of more protective films formed.

Soft metals are more susceptible to erosion-corrosion because they are subjected to more mechanical wear. Hardness is a fairly good criterion for resistance to mechanical erosion or abrasion, but it is not necessarily a good criterion for predicting resistance to erosion-corrosion. Hardening by heat treatment results in changes in microstructure and heterogeneity which generally decreases resistance to corrosion. For example, precipitation hardened stainless steel would not be expected to give good performance as type 304 stainless steel under erosion-corrosion conditions.
Cast iron sometimes shows better performance than steel under erosion-corrosion conditions, particularly in hot strong sulphuric acid. The iron in the cast iron is corroded, but the remaining graphitized layer consisting of the original graphite net work and corrosion products provides protection.

2.11 EROSION-CORROSION MEASUREMENT TECHNIQUES

Different methods are used to find out erosion-corrosion and to test erosion-resistance of metal or alloy. Some of them are presented below:

1) Erosion-corrosion tester: The method for testing erosion-corrosion in boiler feed water pump and regulating valve is outlined by Boetchen (26). In this method the feed water flowed at a high velocity and with great turbulence between the plain and slotted specimen of the material to be tested. The resulting attack produced a combined erosion-corrosion effect similar to that encountered in boiler feed pumps and regulating valves.

The tester provides a receptacle within which the test specimens are held firmly in position. A costellated brass retaining ring is employed for positioning the specimen and the retaining ring is in turn positioned by a small pin in the side of the test specimen. Fig. 2.2 presents a cutaway view of the tester with specimens in position.

The lower and upper chambers of the tester are sealed by a tongue and groove joint using a copper-jacketed asbestos gasket so as to compel water to flow through the specimen test slot when the desired pressure differential is applied across the tester.
Fig. 2.2: Sectional View of a Erosion-corrosion Tester.
2) Rotating Disk Apparatus (39):

The U.S. Naval Applied Science Laboratory (NASL) rotating disc apparatus provides a high velocity flow field at a relatively low cost. The apparatus consists of a cylindrical test chamber in which a disc, mounted on a shaft, is rotated axially to the chamber at any desired shaft speed. Water fills and flows through the chamber at an observed flow velocity under controlled pressure and temperature. A cross-sectional view of the apparatus is shown in figure 2.3.

Basically this apparatus was designed for testing erosion-corrosion resistance of coatings by NASL. But this apparatus can be used for testing impingement corrosion and cavitation-erosion by simple modification.

3) High Speed nozzle apparatus (39):

The NASL high speed nozzle apparatus is designed and constructed to supplement the rotating disc apparatus in investigating the performance of coatings or materials in high velocity liquid flow environment. It provides an advantage that the velocity of the liquid relative to the specimen may be identified more precisely than in the rotating disc apparatus. The nozzle apparatus consists essentially of a nozzle in which a specimen is mounted axially and through which water is flown at a controlled flow rate and upstream pressure. Similar apparatus has been used by International Nickel Co. in studying the high velocity corrosion and erosion of metals (4).
Fig. 2.3: Cross-section of a rotating disk apparatus. The unit provides a high velocity flow field.

Fig. 2.4: High speed nozzle apparatus for evaluating the performance of protective coatings subjected to high velocity liquid flow.
4) Closed all-metal set-up

Willging, Hirth, Beck, and Fontana (21) developed a closed all metal setup for testing erosion-corrosion. Primarily it was developed for testing aluminium in fuming nitric acid but it is suitable for most other environments.

Test specimens are hung in the tank and also placed in a bracket so that the returning liquid from the pump impinges on the specimens in the bracket. Other test specimens are the pump itself, lines, valves, elbows, tees and orifice plates which are installed in the piping system. Galvanic or two metal corrosion can also be tested by this setup by joining pipes or flanges of different metals.

**EROSION-CORROSION STUDY IN CAKE AND SLURRY**

One frequently encountered industrial problem is erosion-corrosion by slurry or wet cakes. No standard method exists for evaluation of wear under erosive corrosive conditions encountered in screw conveyors, chutes, knife blades, pipings, etc. One simple erosion-corrosion testing device was described by Lee (40) and a diagram of the tester is shown in Figure-2.6.

The test specimen is positioned on a bed of rotating drum filter in such a manner that the specimen rubs against the filter cake under a constant load. The same principle has been used in filter cake chutes, troughs, settling tank rakes, etc. After a specific period of rotation, the weight loss of the specimens were found out using this method. Lee (40) summarizes the results of 160 hr. runs of a number of alloys tested
Fig. 2.5: Erosion-Corrosion Test in a Rotating Filter.

Fig. 2.6: Erosion-corrosion Testing Device for Slurry.
with titanium dioxide filter cake (45% solid) and in the slurry feed to filter.

APPLICATION OF THIN LAYER SURFACE ACTIVATION TO STUDY EROSION-CORROSION (41)

Accurate measurement of surface metal loss in erosion-corrosion processes is a fundamental requirement in characterizing the phenomenon, and a variety of techniques are available which can be applied in specific cases. Many of these, however, cannot be applied in situ. Other methods which can be used in situ, such as electrochemical techniques, may be limited by other considerations, for example the low conductivity of aqueous environment in case of erosion-corrosion under boiler feed water conditions. Recently, a new technique has become available which overcomes many of the limitations associated with conventional methods of measuring surface losses in situ, namely "thin layer activation".

In this method, a thin layer of the specimen surface is activated by charged particle bombardment, and the surface loss of specimen activity using appropriate radioactive counting equipment. Since only a thin surface layer of the specimen is activated, the activity levels involved in this technique are much lower than would be the case with bulk activation by neutron irradiation. Typically, activity levels of only a few micro-curies are required, so that only elementary radioactive handling procedures are normally necessary. As a result of limited depth of activation, changes in activity due to surface loss are relatively large compared with total...
activity levels, and consequently the inherent sensitivity of the technique is high.

**EROSION-CORROSION MEASUREMENT BY ELECTROCHEMICAL METHOD**

By specially designed flow cell, impingement corrosion can be measured by electrochemical technique. The flow cell can be constructed by glass fittings. The systematic diagram of a cell used for impingement corrosion measurement (42) is shown in figure 2.7.

Corrosive media passes from the valve at the supply line into the U-bend fitted with a small-bore outlet leading to waste. This serves as an air release for occluded air bubbles which may occasionally be present in the environment. From the U-bend, the environment passes into a T-piece, the arm of which is filled with a small bore tube. This serves as an injection point for additive, if necessary. The lower end of the T-piece is connected to a gas feed pipe which fits into a Y-piece main pipe section. The gas feed pipe terminates in a 38 mm length and 1.6 mm internal diameter tubing which is located directly over the specimens. The corrosive media passing from the gas feed pipe impinges directly on the specimen, passing through the Y-piece to a rotameter. 5.64 mm dia, 10 mm long specimen together with an electrical connection encapsulated in a perspex mount using an epoxy resin (Araldite) and allowed to cure at room temperature for 24 hours.
Fig. 2.7: Schematic diagram of a flow cell for Erosion-corrosion testing by electrochemical method.
CHAPTER-THREE

3.0. PRESENT WORK

EXPERIMENTAL SET-UP, EQUIPMENT AND METHODOLOGY
3.0 PRESENT WORK -Experimental Set-up, Equipment and Methodology.

3.1 INTRODUCTION

Present work consists of preparation of samples, testing the samples in a closed cycle non-metallic rig using different corrosive media. After 100 hour exposure, the samples were removed and cleaned. The specimens were weighed on analytical balance and weight loss due to corrosion was found.

3.2 PREPARATION OF SAMPLE

105 x 76.5 mm rectangular samples were cut by shearing from a big 1/8 inch thick plate. These samples were used as impingement plates during the test. For static test samples of size 52 x 26 mm were also cut from same sheet in the same way. The samples were cut from sheet to minimize exposed end grain (52,53) and to have a large surface to mass ratio and also small ratio of end area to the total area. Analysis of the steel plate shows that it was hot rolled low carbon steel with carbon content of 0.17%. Microphotograph of the steel is shown in appendix -4, Figure-7.1.

To study the effect of system-geometry on corrosion rate a 90° elbow and an one side blocked tee were used. 'Crane' elbow and 'Crane' tee were used for this purpose. Analysis of materials of tee and elbow is shown in Appendix 4.
ALL DIMENSIONS ARE IN mm

Fig. 3.1: Specifications of Test Specimens
a) Impingement Plate
b) Static Test Sample
Before cleaning, the sharp sides of the rectangular plates were smoothened by a hand file. The plates were then drilled as per specification shown in figure 3.1. The plates were then ground with silicon carbide emery paper in the following sequences: grit no: 80, 120, 180, 240, 320, 400. Finally the samples were finished on silicon carbide paper of grit 600, degreased with ethanol or acetone and weighed on an analytical balance.

The inside areas of the other samples, tees and elbows, were ground with emery paper to remove all rust and finally degreased with ethanol and acetone. These samples were also weighed on an analytical balance.

During the tests, only one face (102 x 76.5 mm) would be subjected to impingement attack of the plates, so all other surfaces of the plates including the inside surface of the drill, were coated with polystyrene so that the edges were not exposed to the environment. For coating, Polystyrene foam was dissolved in xylene and several coats were applied on the surfaces one after another. On exposing the samples to normal temperature, xylene evaporates and coating becomes harder. Coating of about 1.5 mm to 2.0 mm thick was applied on each sample. After complete drying, the uncoated side of the sample was cleaned with xylene to remove any trace of polystyrene and degreased with ethanol and acetone. Before applying coating, the dimensions of the samples were measured with the help of a slide calliper.

3.3 : EXPERIMENTAL SET-UP

A closed loop all nonmetallic set-up was used for conducting the erosion-corrosion tests and PVC, plastic and glass were used as components. All
TEST SPECIMEN TEE.

TEST SPECIMEN ELBOW.

ROTAMETER.

GLASS VALVE FOR FLOW CONTROL.

IMPINGEMENT PLATE.

PVC TANK.

POLYPROPYLENE PUMP.

FIG. 3-2: EXPERIMENTAL SET-UP.
Figure 3.3: Photograph of Experimental Set-up
metallic components (except rotameter float) which were exposed to electrolyte were coated with polystyrene. This reduced accumulation of corrosion products in the system (21) and reduced unwanted participation of corrosion products during the tests.

A plastic drum of 15 inch dia and 30 inch height was used as a storage tank for the corrosive media. The tank was connected with suction side of the polypropylene pump with the help of a rubber hose. Two glass valves were used for controlling flow rate. A rotameter was used for measuring flow rate. One 90 degree elbow and one tee were used for changing direction of flow which were also used as test samples in this case. The corrosive liquid from the tank was pumped and allowed to hit the impingement plate which was clamped with the support attached with the wall of the tank. The flow diagram of the experimental set-up is shown in figure 3.2.

3.4 PREPARATION OF CORROSIVE MEDIA

Salt solution, sodium sulphite solution, sodium bicarbonate solution and a mixture of sodium sulphite and sodium bicarbonate (ratio 6:1) solution at different concentration were used as corrosive media. The chemicals were dissolved in double distilled water prepared by 'SIMAX' laboratory distilled water unit.

3.5 VOLUME OF TEST SOLUTION

As stipulated in NACE standard TM-01-69, the preferred minimum volume to area ratio is 250 ml of solution per square inch of specimen (52). 20 gallon solution was used for each experiment which ensured the desired
requirements. Large ratio of volume of solution to area of specimen was used to avoid any appreciable changes in corrosiveness of solution either through exhaustion of corrosive constituents or accumulation of corrosion products which might affect further corrosion.

3.6: METHOD OF SUPPORTING SPECIMENS

Both tee and elbow were attached in the piping system with the help of flanges. The detailed design of the flange is shown in figure 3.5.

To support impingement plate in the tank, two stainless steel bolts were attached with the wall of the tank so that a sample could be clamped by passing the bolts through the hole on the samples. To avoid any undesirable effect of galvanic coupling, insulation of impingement specimen was accomplished by placing two Teflon pieces on both sides of the specimen. Two stainless steel nuts were used to hold the specimens tightly. The arrangement is shown in figure 3.4.

3.7: METHODOLOGY

Test specimens like tees and elbows were placed in glass piping system for closed loop recirculation of corrosive media from plastic tank by a polypropylene pump. Different media were circulated at different velocity and allowed to hit the impingement plates placed in the tank. About two-thirds of the tank was filled with liquid and the level in the tank was kept constant above the specimen position.
1. PVC TANK WALL
2. STAINLESS STEEL BOLT 76 mm LONG
3. LOCK NUT (S.S)
4. TEFLOM TUBE (INSULATOR)
5. IMPINGEMENT PLATE

FIG. 3.4: SCHEMATIC DIAGRAM SHOWING ATTACHMENT OF IMPINGEMENT PLATE WITH TANK
After a test exposure of 100 hours the test specimens were isolated from the system and cleaned. The weight loss for each specimen was found. The same experiment was carried out at different velocities.

At a particular velocity, the weight loss for different test specimens were found out by varying pH of solution, sodium sulphite and sodium bicarbonate concentration and chloride content in sodium sulphite and sodium bicarbonate solution.

3.8: CLEANING SPECIMENS AFTER EXPOSURE

Change in weight of the specimen is used for calculation of the corrosion rate, so cleaning of specimen is one of the most important steps in corrosion testing. Mechanical cleaning procedure was applied for cleaning specimens in this case.

At first the loosely bonded corrosion products were washed by holding the specimen under a stream of tap water. Then the surface was vigorously brushed with the help of a medium hard nylon brush. After removal of corrosion products by brushing, the samples were washed with distilled water. It was then dried and degreased with acetone before weighing.

3.9: ANALYSIS

After cleaning and drying, the specimens were weighed on an analytical balance with an accuracy corresponding to that of original weight. The weight loss was then converted to corrosion rate expressed as mm/py.

When pitting type corrosion occurred, photograph and microphotograph of the specimens were taken and compared.
3.9: **ACCESSORIES**

The accessories used at different stages of this work are mentioned here:

(a) **Analytical balance:**

Two polish origin Zakta dy Mechaniki Precezyinei analytical balances of the type WP-11 and WA-21 were used to take weight of different specimens and chemicals. The accuracy of the balances were:

\[
\begin{align*}
\text{WP-11} & \quad - \quad 0.1 \text{ mg.} \\
\text{WA-21} & \quad - \quad 0.2 \text{ mg.}
\end{align*}
\]

(b) **pH meter**

Corning M 120 digital pH meter was used to measure pH of different solutions.

(c) **Rotameter**

A precision bore flow meter FP 2 -27-G-10/80 of F & P Ltd., England, was used to measure flow rate of corrosive media. The calibration curve of the rotameter is shown in figure 3.8.

(d) **Distilled water**

An all glass laboratory distillation unit made by SIMAX, czechoslovakia, was used to prepare double distilled water from available tap water.

(e) **Slide calliper**

A "MITUTOYO" slide calliper was used for measurement with the following specifications:
3.10: **FABRICATION WORK**

The following fabrication works were done for completing the experimental set-up.

1. Fabrication of one perspex collar for connecting glass bend with discharge line of the pump. Detailed drawing of the collar is shown in figure 3.6.

2. Fabrication of two perspex collars to connect glass pipes with rotameters. Detailed drawings of the collars are shown in figure 3.7.

3. Fabrication of four steel flanges for connecting tee and elbow with glass pipes. Detailed design of the flanges are shown in figure 3.5.
Fig. 3.5: Detailed design of flange (4 nos.) to connect tee & elbow with glass piping system (Material: steel)
FIG. 3.6: DETAIL DESIGN OF PERSPEX COLLAR TO CONNECT DELIVERY LINE OF PUMP WITH GLASS PIPING SYSTEM
Fig. 3.7: Detailed design of Perspex collar to connect Rotameter with Glass Piping System.
No of collar required = 2

All dimensions are in mm
No of thread per inch = 12.
FIG. NO. 3.8: ROTAMETER CALIBRATION CURVE.
CHAPTER FOUR

4.0. RESULTS AND DISCUSSION
CHAPTER 4

4.0 : RESULTS AND DISCUSSION

4.1 : Effect of Environment Concentration on Corrosion of Steel in Stagnant Condition

Hot rolled low carbon-steel plates were used as specimens of static test to find the effects of environment concentration on corrosion rate of steel in stagnant condition. Concentration of liquors were varied from 0.4 lb/gallon to 1.4 lb/gallon and durations of exposure were taken as 100 hours. After 100 hours exposure, it was found that the specimens were covered with a black layer. They were then cleaned by brushing with a nylon brush, degreased with acetone, dried and weighed on an analytical balance. The weight loss due to corrosion was found.

To explain the formation of the black coating on the specimen surface, it was necessary to study the corrosiveness of the neutral sulphite cooking liquor in detail.

Basically neutral sulphite cooking liquor is prepared in three ways:
a) dissolution of commercial chemicals in water at a desired concentration or absorbing sulfur burning gas in sodium carbonate solution to attain the desired concentration (b) same as (a) with the addition of Kraft recovery furnace smelt to the liquor as buffer chemical when a neutral sulphite mill and a Kraft mill are operated in conjunction so as to practice "cross-recovery". and (c) by operation of independent neutral sulphite recovery process. Cooking liquor prepared by any one of the above process contains mainly sodium sulphite, sodium carbonate and sodium bicarbonate. Thiosulphate would always be present over a wide range of concentration (43). Many investigators (43,45,46,47 and 48) found that thiosulphate was mainly responsible for formation of black coating on iron surfaces.

Horowitz (45) concludes that corrosive effect of thiosulphate ion is due to the formation of thiosulphate iron complex, so that the participation of sulphite species could be neglected. Vasquez and others (46) showed that the thiosulphate was able to produce pitting of mild steel at a potential more positive than the potential of the active passive transition and the
main corrosion related to pitting was FeS. The presence of FeS was confirmed
by detecting the presence of \( \text{H}_2\text{S}^\cdot \), when the black material was dissolved in
dilute \( \text{H}_2\text{SO}_4 \) (46). Also localized corrosion of mild steel showed isolated
spots of black corrosion product (46).

It was already known that the thiosulphate ions were meta-stable and
undergo different reactions yielding sulphur species. For example, thiosul-
phate tends to decompose in alkaline solution into sulphide and sulphate ion (47)
according to the following reaction:

\[
\text{S}_2\text{O}_3^{2-} + \text{OH}^- \rightarrow \text{SH}^- + \text{SO}_4^{2-}
\]  

(4.1)

This reaction was enhanced by the presence of cations which forms insoluble
sulphide.

\[
\text{Fe}^+ + \text{SH}^- \rightarrow \text{FeS} + \frac{1}{2}\text{H}_2
\]  

(4.2)

The \( \text{OH}^- \) required for the reaction (4.1) was supplied by reduction of
oxygen in alkaline solution.

\[
\text{O}_2 + 2\ \text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\ \text{OH}^-
\]  

(4.3)

So amount of \( \text{O}_2 \) dissolved in the system also controls the rate of reaction
i.e. corrosion rate.

Also, in acid solution thiosulphate disproportionates as follows:

\[
\text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{S} + \text{H}_2\text{SO}_3
\]  

(4.4)

Formation of sulphurous acid and its effect on steel is very aggressive.
Kesler (43) reported thiosulphate as a cathodic depolarizer in neutral sulphite cooking liquor. The depolarizing action of thiosulphate was governed by $p^H$ of the liquor, where decreasing $p^H$ allows increasing depolarization. The mechanism by which thiosulphate is a direct cause of steel corrosion in cooking liquor was proposed by the following reaction (43).

$$S_2O_3^{2-} + H^+ + HSO_3^- + S$$

In solutions, even slightly acidic, thiosulphate decomposes at a rate governed by the $p^H$ of the solution to form elementary sulphur and bisulphite (43). Elementary sulphur in its different forms reacts with iron to form iron sulphide.

$$Fe + S \rightarrow FeS$$

Electroreduction of thiosulphate ion to elementary sulphur was reported by Newman and others (48), according to the following reaction:

$$S_2O_3^{2-} + 6H^+ + 4e \rightarrow 2S + 3H_2O$$

This elementary sulphur reacts with iron to form iron sulphide.

$$Fe + S \rightarrow FeS$$

The presence of sulphur and ferrous sulphide inside the pit of iron and stainless steel in presence of sulphide and thiosulphate were also reported by others (49, 50).
FIG. 4·1: CORROSION RATE CONCENTRATION CURVE IN STAGNANT CONDITION OF MEDIA.

NATURALLY AERATED SYSTEM

EXPOSURE TIME: 100 hour.

CONCENTRATION OF CORROSIVE MEDIA EXPRESSED AS Na₂CO₃, lb/gallon.
The presence of thiosulphate in the test liquor prepared for the stagnant condition were detected by the method described in appendix-3.

After 100 hour exposure in stagnant solution, it was found that the specimen surfaces were covered with black film of FeS. The presence of FeS was confirmed by dissolving the black film in HCl and detecting the familiar smell of H₂S.

The corrosion rate vs concentration of corrosive media curve is shown in Figure 4.1. With increase of concentration of corrosive media, the concentration of thiosulphate in the system increases. Since corrosion of steel in stagnant condition muchly depends on the concentration of thiosulphate, corrosion rate of steel increases with increase of concentration of corrosive media i.e. concentration of thiosulphate. At higher concentration (1.4 lb/gallon) both uniform type and pitting type corrosion was found and corrosion rate was high.

4.2 EFFECT OF VELOCITY ON CORROSION OF STEEL

To study the effect of velocity on corrosion of steel in corrosive environment concentration (0.8 lb/gallon, expressed as Na₂CO₃), the liquid was allowed to hit the specimen at different velocities. The corrosion loss data are shown in appendix 5 and the corrosion rate vs velocity curve is shown in Figure 4.2.

At zero velocity i.e. in stagnant condition of the environment, corrosion loss was due to the formation of black film of FeS on the specimen surface which has been discussed earlier. As velocity of the environment increases, corrosion rate also increases. At lower velocity, the sample surface was covered with a thin brown film of corrosion product. The black
NATURALLY AERATED SYSTEM
DURATION OF EXPOSURE = 100 hour.
CONCENTRATION OF CORROSIVE MEDIA:
0.8 lb/gallon.

FIG. 4-2: EFFECT OF VELOCITY ON CORROSION OF STEEL.
coating of FeS was not visible and it was washed away in flowing condition of the environment. The system was alkaline in nature and the corrosion product was probably Fe (OH)₂.

The probable formation of Fe (OH)₂ passes through a complex reaction path formally written as: (51).

\[ \text{Fe} + \text{H}_2\text{O} = \text{Fe(OH)} + \text{H}^+ + e \] (4.8a)

\[ \text{Fe(OH)} = \text{Fe(OH)}^+ + e \] (4.8b)

\[ \text{Fe(OH)}^+ + \text{OH}^- = \text{Fe(OH)}_2 \] (4.8c)

The initial step (4.8a) was the decomposition of water yielding OH adsorbed species; step (4.8b) implies the formation of intermediate Fe(OH)⁺ which later neutralizes in the base solution finally yielding the hydrous ferrous hydro-oxide layer. The OH⁻ for the step 4.8c was generated by the reaction (4.3). The thickness of the layer of Fe(OH)₂ depends on the availability of absorbed O₂ in the environment which was consumed by the reaction,

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e = 4\text{OH}^- \] (4.3)

The formation of Fe (OH)₅ species was detected by different investigators (51,52, 53) by different techniques. With the increase of velocity of the corrosive media, the thickness of corrosion product deposited on the specimen surface increases. This was due to higher supply of oxygen to the specimen surface. At velocity of 5.4 ft. per sec, a thick corrosion product accumulated on the specimen surface. High velocity causes this thick film to break down and disappear from the surface in an irregular fashion. This
exposes fresh metal surface of the specimen to the environment. Photograph of such an irregular non uniform corrosion product scales/film on the specimen surface is shown in Figure - 7.4. The variation of thickness of film formed on the specimen surface could be the cause of formation of differential aeration cell, concentration cell and crevices between the scale/films and the metal. The combined interaction of all these phenomenon causes more corrosion. This type of corrosion was found at a velocity of 5.4 ft/sec. A localized type of non-uniform attack was found at this stage and photograph of the specimen surface after cleaning is shown in Figure-7.5, (Appendix-6).

At higher velocity of the environment, the thickness of film formed on the specimen surface becomes thinner and corrosion rate decreases. At fluid velocity of 5.9 ft/sec, the specimen surface was covered with a thinner uniform continuous film. Upto fluid velocity of 5.9 ft/sec, crevice corrosion was found around the hole at the contact area of specimen and the teflon tube. Formation of local action cells thus was another reason of high corrosion at this velocity range.

With further increase of velocity, it was found that the surface was covered with a thinner continuous film. This film was more adherent and it was not possible to remove it by usual way of brushing. Weight loss in this case was very low. This lower corrosion at higher velocity can be explained by passivation of steel specimen by the formation of stronger protective film of $\text{Fe(OH)}_3$ on the surface of the specimen.

$$2\text{Fe(OH)}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow 2 \text{Fe(OH)}_3$$ (4.9)
Since the system was open and was not air tight, higher velocity of environment allowed more oxygen to diffuse to the surface of specimen and converted less protective unstable film of Fe(OH)$_2$ to stronger protective film of Fe(OH)$_3$. This phenomenon was found at fluid velocity of 6.6 ft/sec.

Above this velocity, corrosion rate again increases with increase of velocity. At this stage, high velocity of the environment was sufficient to remove the protective film of Fe(OH)$_3$. The higher corrosion rate was due to break down of passive film due to high velocity and a fresh metal surface was continuously exposed to the environment. Above a fluid velocity of 6.6 ft/sec, the weight loss of metal was due to combined interaction of corrosion process and mechanical process i.e. erosion due to high velocity. Corrosion in this zone can be designated as erosion-corrosion.

The velocity at which corrosion rate was minimum was the critical velocity for the present system which was around 6.6 ft/sec. Above critical velocity, corrosion rate increases with increase in velocity but no crevice corrosion was found around the hole of the samples. High velocity of the environment made it possible to circulate the corrosive environment more uniformly which washes away the concentration build up areas or dead pockets and eliminate crevice corrosion.
4.3 EFFECT OF ENVIRONMENT CONCENTRATION ON EROSION-CORROSION OF STEEL IN FLOWING CONDITION

From the corrosion rate-velocity curve it was found that the erosion-corrosion of steel starts above a velocity of 6.6 ft/sec. A fluid velocity of 8.7 ft/sec was selected for testing erosion-corrosion of different specimens like tee, elbow and impingement plate. Concentration of environment was taken from 0.4375 lb/gallon to 1.40925 lb/gallon.

As concentration of liquor increased, corrosion rate of impingement plate increases. Graph showing the relationship between corrosion rate and concentration is given in Figure 4.3. Since the area of tee and elbow exposed to the environment was very difficult to measure, so weight loss in mg was taken as a measure of corrosion. The weight loss for tee and elbow were plotted against concentration and they are shown in Figure 4.4 & 4.5. The nature of curves for tee and elbow and impingement plate were very close and corrosion rate increases with increase of concentration of corrosive media.

The increase of corrosion rate with the increase of concentration can be explained in the following way:

Many investigators found that the corrosion of steel in environment containing sulphite, carbonate, bicarbonate and thiosulphate, was only due to presence of thiosulphate which were discussed earlier. Kelser(43) studied the effect of thiosulphate concentration on polarization of mild steel in neutral sulphite cooking liquor at pH of 9.5 and 8.7. In each case the cathodic current density increases markedly with the increase of concentration of thiosulphate. In this case, as concentration of
FIG. 4: EFFECT OF CONCENTRATION OF CORROSIVE MEDIA ON CORROSION OF IMPINGEMENT PLATE IN FLOWING CONDITION.

VELOCITY OF MEDIA = 8.7 FPM.
DURATION OF EXPOSURE = 100 hour.

DURATION OF EXPOSURE = 100 HOUR
NATURALLY AERATED SYSTEM

CONCENTRATION OF CORROSIVE MEDIA, lb/gallon
EXPRESSED AS SODIUM CARBONATE
DURATION OF EXPOSURE – 100 HOUR
NATURALLY AERATED SYSTEM

FIG. 4.4: EFFECT OF CONCENTRATION OF CORROSIVE MEDIA ON CORROSION OF ELBOW IN FLOWING CONDITION
DURATION OF EXPOSURE - 100 HOUR
NATURALLY AERATED SYSTEM

FIG. 4.5: EFFECT OF CONCENTRATION OF CORROSIVE MEDIA ON CORROSION OF TEE IN FLOWING CONDITION.
environment increase, the amount of thiosulphate in corrosive media also increased. Higher concentration of thiosulphate increases the corrosion rate of steel at a higher rate.

During study of the effect of velocity, it was found that fluid velocity of 8.7 ft/sec. was sufficient to break the passivity of steel. The present study was also done at fluid velocity of 8.7 ft/sec, and no corrosion product was found on the specimen surface. Here corrosion product was washed away by the velocity of the environment. So, fresh metal surfaces were continuously exposed to the environment causing metal loss at a higher rate.

To study the effect of system geometry during change in direction of fluid, tee and elbow were used as test specimens. Due to sudden change of direction, the weight loss of specimens were due to impingement attack and turbulence. As the direction change becomes sharper, the corrosion rate or weight loss increases. So, it was found that total weight loss in mg of tee material was greater than that of an elbow.

It was mentioned earlier that the corrosion process in this case is diffusion controlled. In flowing condition of environment, corrosion rate of steel at a particular corrosive environment concentration was higher than that at stagnant condition. In stagnant condition, the diffusion was due to natural convection but in flowing condition, the diffusion was due to forced convection. So, in flowing condition higher amounts of corrosive agent can diffuse to the metal surface for which corrosion rate was high.
4.4  **EFFECT OF $p^H$ ON EROSION-CORROSION OF STEEL**

The effect of $p^H$ on erosion-corrosion of steel was studied for impingement plate, tee and elbow. The $p^H$ of the solutions were adjusted by varying concentration of $\text{Na}_2\text{SO}_3$ and $\text{NaHCO}_3$ at a ratio of 6:1 in the range 8.3 to 10.0. $p^H$ 8.0 was maintained by dissolving $\text{Na}_2\text{SO}_3$, $\text{NaHCO}_3$ and $\text{Na}_2\text{CO}_3$. $p^H$ below 7.0 were adjusted by adding HCl in a solution of 0.8 lb/gallon $\text{Na}_2\text{SO}_3$ and $\text{NaHCO}_3$ (ratio 6:1) mixture. The $p^H$ of solution during the experiment, was tested at one hour interval by $p^H$ meter and was adjusted as per requirement. After any adjustment three successive tests were made at 5 minute intervals to check the accuracy of adjustment. The desired value of $p^H$ were maintained within ± 0.2.

Minimum corrosion rate was found at $p^H$ 10.0. For impingement plates, when $p^H$ of solution is decreased, the corrosion rate increases slowly upto $p^H$ of 8.5. Then corrosion rate increases sharply and attains a maximum value at $p^H$ 8.0. As $p^H$ of the solution decreases corrosion rate falls further and it attains another minimum value at $p^H$ 6.0. The corrosion rate increases at a high rate, when $p^H$ of solution is maintained at 5.0. The corrosion rate-$p^H$ curve for impingement plate is shown in Figure 4.6.

Weight loss values for tee and elbow are plotted against $p^H$ of solution. The nature of curves for tee and elbow is the same as that for impingement plate. But rate of weight loss with change of $p^H$ in the range 8.5 to 10.0 was higher for tee and elbow than that for impingement plate. This is mainly due to wakes and eddies generated during sudden change in flow direction. The weight loss-$p^H$ curves for tee and elbow are shown in Figure 4.7.
NATURALLY AERATED SYSTEM
DURATION OF EXPOSURE = 100 hour
VELOCITY OF CORROSIVE MEDIA
= 8.7 FPM.

FIG. 4.6: EFFECT OF pH ON CORROSION RATE OF IMPINGEMENT PLATE.
FIG. 4.7: EFFECT OF pH ON CORROSION RATE OF TEE AND ELBOW.

DURATION OF EXPOSURE = 100 hour.
VELOCITY OF MEDIA = 8.7 FPM.
NATURALLY AERATED SYSTEM.
KESLER (43) studied the effects of $p^H$ on corrosion of steel in the same type of solution containing $Na_2SO_3$, $NaHCO_3$, $Na_2CO_3$ and different amounts of thiosulphate. At $p^H$ 11.0, he found that the corrosion loss was minimum and amount of thiosulphate had no effect on corrosion rate. At $p^H$ 9.5, thiosulphate had a marked effect on polarization curve. At a liquor $p^H$ of 8.7, the effect of thiosulphate was very pronounced. In this case, the height of maximum anodic current seems to be roughly proportional to the concentration of thiosulphate in the liquor, and cathodic depolarization increases greatly at the same time. The depolarization action of thiosulphate was governed by the $p^H$ of liquor, where decreasing $p^H$ allowed increased depolarization (43). The mechanism by which thiosulphate acts as a direct cause of steel corrosion has been discussed earlier. The main reaction involved is:

$$S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S \quad \ldots(4.5)$$

"The decomposition reaction of thiosulphate ion to produce elementary sulphur and bisulphate ion is probably best represented by the concept of a stable equilibrium between free sulphur and bisulphate ion. This equilibrium is controlled by $p^H$ of solution, decreasing $p^H$ shifts the direction of equilibrium (Equation 4.5) so as to produce more elementary sulphur and bisulphite ion. This free sulphur is in very finely divided and reactive state and can easily carry out its function as a cathodic depolarizer". (43).

Also at $p^H$ 8.0, the formation of $Fe_3O_4$ film was reported by Fontona and Luce (39), which was granular in nature. The formation of $Fe_3O_4$ passes through a series of steps. Iron first electroxidizes to $Fe(OH)_2$ (54),
which further electroxidizes to \( \text{FeO} \)OH in the second level (55). The iron oxyhydroxide layer is transferred to more stable films approaching \( \text{Fe}_3\text{O}_4 / \)hydrated \( \text{Fe}_2\text{O}_3 \) structure (56). The granular nature of \( \text{Fe}_3\text{O}_4 \) makes it less protective in erosive-corrosive condition and corrosion rate was high. The velocity of fluid in this case was maintained in erosive-corrosive condition. After exposure, the impingement plates were found clean. The corrosion products formed on the surface were washed away due to high velocity. So fresh metal surface was continuously exposed to the corrosive environment and corrosion rate was high.

At \( p^\text{H} 6.5 \) and 6.0 the specimen surface was covered with this film of corrosion product which was not washed away by the velocity of the environment. This corrosion product forms a protective film on the surface of the metal for which corrosion rate was low.

When \( p^\text{H} \) of solution decreases to the acidic side i.e. at \( p^\text{H} 5.0 \), the corrosion rate of steel specimen increases sharply. A pitting type corrosion was found and the pits were covered with corrosion products. On brushing, fresh surfaces were exposed. This high rate of corrosion can be explained by the following way:

Thiosulphate in the solution acts as a depolarizer. In alkaline solution thiosulphate ion tends to decompose into sulphide and sulfur. In acid solution thiosulphate decomposes yielding \( \text{H}_2\text{SO}_3 \) and elemental sulphur (44).

\[
\begin{align*}
\text{S}_2\text{O}_3^{2-} + 2\text{H}^+ & \rightarrow \text{S} + \text{SO}_2 + \text{H}_2\text{O} \\
\text{SO}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_3 \\
\text{S}_2\text{O}_3^{2-} + 2\text{H}^+ & \rightarrow \text{S} + \text{H}_2\text{SO}_3 \\
\end{align*}
\]

(4.4)
Formation of elementary sulphur and $\text{H}_2\text{SO}_3$ makes the system very aggressive and corrosion rate increases. Since velocity of the system was within erosive corrosive condition, the corrosion product formed on the specimen surfaces were washed away and weight loss was considerably high. Moreover Berge and others reported that sulphite ions were pit producer on iron surface in acid medium (57). Sulphite in acidic condition forms sulphuric acid (58).

$$\text{SO}_3^{2-} + 2\text{H}^+ \rightarrow \text{SO}_2 + \text{H}_2\text{SO}_3$$

Formation of $\text{H}_2\text{SO}_3$ in acidic condition is also another reason for high corrosion at $p^H$ of 5 and at lower values.

4.5 EFFECT OF CHLORIDE CONTENT IN CORROSIVE MEDIA ON EROSION-CORROSION OF STEEL

Chloride concentration in the test concentration media (a mixture of $\text{Na}_2\text{SO}_3$ and $\text{NaHCO}_3$ in the ratio 6:1 having concentration 0.8 lb/gallon) was varied from 100 ppm to 10,000 ppm for this study. The velocity of the environment was maintained at 8.7 ft/sec.

Due to presence of $\text{NaCl}$ in media, corrosion loss of steel increases with increase in chloride content. The rate of increase of corrosion was initially high and it continues upto 5000 ppm of chloride content in the solution for the impingement plates. After 5000 ppm corrosion rate increases at a comparatively lower rate with increase of chloride content. The variation of corrosion rate with chloride content in test liquor is shown in Figure 4.8 for impingement plate.
NATURALLY AERATED SYSTEM
CORROSIVE MEDIA CONCENTRATION = 0.8 lb/gallon.
DURATION OF EXPOSURE = 100 hour.
VELOCITY OF MEDIA = 8.7 FPS.

FIG. 4.8: EFFECT OF CHLORIDE CONCENTRATION IN CORROSIVE MEDIA ON CORROSION RATE OF IMPELLER PLATE.
NATURALLY-AERATED SYSTEM

CORROSIVE MEDIA CONCENTRATION = 0.8 lb/gallon.
DURATION OF EXPOSURE = 100 hour.
VELOCITY OF MEDIA = 8.7 FPS.

Fig. 4.9: Effect of chloride concentration in corrosive media on weight loss of tee and elbow.
Curves with similar nature were obtained when weight loss due to corrosion was plotted against chloride contents in the corrosive media which are shown in Figure 4.9. The increase in corrosion rate due to addition of chloride ion in the system was due to the protective film break down capability of chloride ion. Ashworth and others (59) showed that in alkaline environment, chloride has the capability of breaking down passivity of mild steel with formation of pits. Initially corrosion rate due to presence of chloride ion in corrosive media increases sharply upto 3000 ppm after which corrosion rate increases at a lower rate. With the increase of chloride content in the systems the solubility of dissolved oxygen decreases. So at higher chloride content corrosion rate increases at a lower rate.

The erosion-corrosion behaviour of steel in 7000 ppm sodium chloride solution was studied separately and the results are shown in appendix-10. The corrosion rate was 0.6019 mmpy. But presence of same amount of chloride in test corrosive media had reduced the corrosion rate to 0.2254 mmpy (appendix-9). In case of pitting corrosion of iron by halogen ion, the pitting tendency depends on the kind of inert ions present in the electrolyte (60). So in this case, the interaction of sulphide and bi-carbonate ion of the corrosive media with chloride ion reduces corrosion rate of steel.
CHAPTER - FIVE

5.0. CONCLUSIONS AND SUGGESTIONS
5.0 CONCLUSIONS AND SUGGESTIONS

5.1 CONCLUSIONS

The following conclusions may be made from the results obtained:

(All tests were conducted in naturally aerated system)

a) Thiosulphate impurity plays an appreciable role in corrosion of steel in the system under study.

b) High concentrations of corrosive media (mixture of Na$_2$SO$_3$ and NaHCO$_3$) in stagnant condition should be avoided. Since pitting type corrosion occurs in this case.

c) Operation at lower velocity is more damaging than at relatively higher velocity.

d) At lower velocity, corrosion losses were due to combined interaction of velocity, uniform type corrosion by corrosive agent, crevice corrosion and pitting type corrosion at the freshly exposed surfaces due to breakdown of corrosion product films.

e) At critical velocity, a passive film forms on the surface of the specimens and corrosion rate falls instantaneously.
f) Critical safe velocity of corrosive environment for the present system depends on the amount of dissolved oxygen since corrosion rate depends mostly on the amount of dissolved oxygen.

g) Above critical velocity, corrosion rate increases with increase in velocity. The rate of increase of corrosion above critical velocity is lower than that below critical velocity.

h) At higher velocity, corrosion loss is due to break down of passive film and it is erosion-corrosion type.

i) $p^H$ above 10.0 is necessary to maintain a minimum corrosion rate for the present system.

j) Acidic condition of corrosive media is very harmful and it should be avoided.

k) $p^H$ of corrosive media should not be kept at 8.0 because of much higher corrosion rate compared to that at $p^H$ 6.0 or 10.0 and above.

l) Chloride ion in corrosive media increases corrosion rate several fold and therefore should be avoided.

m) Sharp bends in the piping system in process flow should be avoided.
5.2 SUGGESTIONS FOR FUTURE WORK AND IMPROVEMENT OF SET-UP

During investigation of effect of velocity on corrosion of steel, it was found that upto a fluid velocity of 4.4 fps corrosion rate increases with increase of velocity. With further increase in velocity corrosion rate decreases and at fluid velocity of 6.6 fps corrosion rate was minimum (Figure 4.2). The present system was equipped with an open storage tank and the system was not deoxygenated or deaerated. So, absorbed oxygen in the corrosive media plays an important role in passivation of steel at higher velocity.

To establish the role of absorbed oxygen in the corrosive media, further study in this area is essential. This can be done by the following ways.

Different sets of corrosion rate data are to be taken by bubbling air, oxygen and pure nitrogen separately in the corrosive media by varying velocity of the media. Before this, the experimental set-up should be made perfectly air tight.

If oxygen is the main reason for passivation of steel, bubbling of oxygen or air will passivate steel earlier i.e. at lower velocity of the corrosive media. Deoxygenation will change the behaviour of steel with velocity.

It is well known that, in most of the cases temperature variation causes a direct effect on corrosion rate and corrosion rate increases with
increase of temperature. Due to some difficulty, this study was not made with the present system. The present system was equipped with an open storage tank. The difficulty lies with open tank for conducting experiments at higher temperature is the evaporation loss of water. This evaporation loss will create problem in maintaining concentration of media at a particular level. This problem can be solved by closing the open area of the tank perfectly and venting the system through a condenser and returning the condensate to the tank again. This will reduce evaporation loss at higher temperature of the system.

To study the effect of temperature, it will be necessary to heat the solution to the desired temperature. Heating can be done with the help of an electric heater. To control the temperature of the system, a bimetallic thermostat can be used. The thermostat should be connected in series with the heaters and the metallic rod of the thermostat should be dipped in the corrosive media. As there is a circulation of liquid in the tank, the variation of temperature, within the tank would be low and a temperature with an accuracy of $\pm 1^\circ C$ can be maintained.

The effect of suspended solids in the media was not studied in this work. For this, the amount of suspended solid in the media and size of the solid both can be varied for studying their effect on erosion-corrosion. Existing experimental set-up can be used for this purpose. But it should be equipped with one agitator to prevent the settling of the solids in the tank. The size of the solids should be selected keeping in mind that the piping material of the experimental set-up is mostly glass.
The weight loss method for corrosion testing is very time consuming but electrochemical method for corrosion measurement is accurate and less time consuming. By proper cell design as in Figure 2.7, electrochemical methods can be used to evaluate erosion-corrosion (42) which would be less time consuming.
CHAPTER-SIX

REFERENCES
REFERENCES


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CHAPTER-SEVEN

APPENDIX
## APPENDIX 1

### CALIBRATION OF ROTAMETER

<table>
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<th>ROTAMETER READING</th>
<th>Time of collection of water (Sec)</th>
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Water Temperature = 30 degree C
APPENDIX-2

Corrosion rate calculation.

Corrosion rate in mm per year = 87.6 $\frac{W}{D\times A\times T}$

where $W$ = Weight loss in mg
$D$ = Density of specimen in gm/cc
$A$ = Surface area exposed in cm$^2$
$T$ = Duration of exposure in hour

Since Density of the impingement plate was 7.68 gm/cc, and duration of exposure was 100 hr

Corrosion rate = $\frac{87.6 \times W}{100 \times 7.68 \times A}$

= 0.1140625 $\frac{W}{A}$

mmpy = 0.1140625 $\frac{W}{A}$
APPENDIX-3

DETECTION OF PRESENCE OF THIOSULPHATE IN SODIUM SULPHITE (58)

The presence of thiosulphate in sodium sulphite can be detected by the following procedure:

5 ml. of Na$_2$SO$_3$ solution was taken in a test tube and few drops of silver nitrate was added to it. Silver nitrate forms with thiosulphates a white precipitate of silver Thiosulphate, Ag$_2$S$_2$O$_3$, that rapidly changes colour first it turns yellow, then brown, and finally black as the white precipitate of silver thiosulphate was converted to the black silver sulphide:

\[ \text{Ag}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{A}_2\text{S} + \text{H}_2\text{SO}_4 \]
SPECIFICATION OF TEST SPECIMEN

(a) Impingement plate and static test samples

Material: Steel
Carbon content: 0.17%
Type: Hot rolled
Density: 7.68 gm/cc

(b) Elbow

Material: Malleable Cast Iron
Carbon Content = 2.93%

(c) Tee

Material: Malleable Cast Iron
Carbon Content = 2.79%
Fig. 7.1: Microphotograph of Impingement Plate (X 200)
Figure 7.2: Microphotograph of 'Crane' Elbow (X100)

Figure 7.3: Microphotograph of 'Crane' Tee (X100)
APPENDIX 5

Effect of concentration of corrosion media (mixture of Na$_2$SO$_3$ and NaHCO$_3$ in ratio 6:1 expressed as Na$_2$CO$_3$) on corrosion of steel in stagnant condition.

Naturally aerated system
Temperature of system: 29°C

<table>
<thead>
<tr>
<th>Concentration of corrosive media (lb/gallon)</th>
<th>Weight loss (mg)</th>
<th>Surface area of the sample (cm$^2$)</th>
<th>Corrosion rate (mmpy x 10$^3$)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0.65</td>
<td>29.2392</td>
<td>2.5336</td>
<td>Black film was formed</td>
</tr>
<tr>
<td>0.6</td>
<td>0.80</td>
<td>29.0776</td>
<td>3.14</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.8</td>
<td>2.1</td>
<td>29.4000</td>
<td>8.15</td>
<td>&quot;</td>
</tr>
<tr>
<td>1.0</td>
<td>3.7</td>
<td>29.72</td>
<td>14.20</td>
<td>&quot;</td>
</tr>
<tr>
<td>1.2</td>
<td>4.4</td>
<td>29.5148</td>
<td>17.00</td>
<td>&quot;</td>
</tr>
<tr>
<td>1.4</td>
<td>8.3</td>
<td>29.399</td>
<td>32.20</td>
<td>Pitting type corrosion was found with black coating.</td>
</tr>
</tbody>
</table>
Effect of velocity on corrosion of steel.

Concentration of corrosion media = 0.8 lb/gallon (express as Na₂CO₃)

Naturally aerated system
Temperature of system = 30°C ± 1°C

<table>
<thead>
<tr>
<th>Velocity of fluid ft/sec</th>
<th>Area exposed cm²</th>
<th>Weight loss mg</th>
<th>Corrosion rate mmpy x 10⁻³</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>29.408</td>
<td>2.1</td>
<td>8.15</td>
<td>Test was conducted in stagnant condition</td>
</tr>
<tr>
<td>2.612</td>
<td>77.78</td>
<td>105.628</td>
<td>154.9</td>
<td>Formation of film on metal surfaces/crevice corrosion</td>
</tr>
<tr>
<td>4.315</td>
<td>77.643</td>
<td>149.45</td>
<td>219.55</td>
<td>Crevice corrosion and pitting type corrosion</td>
</tr>
<tr>
<td>5.394</td>
<td>77.509</td>
<td>202.82</td>
<td>298.47</td>
<td>&quot;</td>
</tr>
<tr>
<td>5.933</td>
<td>77.5491</td>
<td>158.1</td>
<td>232.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>6.635</td>
<td>77.002</td>
<td>0.7</td>
<td>1.037</td>
<td>Uniform attack</td>
</tr>
<tr>
<td>7.88</td>
<td>78.2821</td>
<td>12.7</td>
<td>18.5</td>
<td>&quot;</td>
</tr>
<tr>
<td>9.34</td>
<td>77.67</td>
<td>22.0</td>
<td>32.3</td>
<td>&quot;</td>
</tr>
<tr>
<td>10.87</td>
<td>77.89</td>
<td>52.86</td>
<td>77.41</td>
<td>&quot;</td>
</tr>
<tr>
<td>13.92</td>
<td>77.78</td>
<td>76.78</td>
<td>112.3</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
Fig. 7.4: Photograph Showing Deposition of Thick Corrosion Product Scale/Film on Impingement Plate at Velocity of 5.83 fps; Duration = 100 hr.

Fig. 7.5: Non-Uniform Type Corrosion of Impingement Plate at Velocity of 5.83 fps; Duration = 100 hr.
Effect of concentration of corrosive media (mixture of Na$_2$SO$_3$ and NaHCO$_3$ in the ratio 6:1 express as Na$_2$CO$_3$) on erosion-corrosion of steel in flowing condition:

Naturally aerated system
Velocity of corrosive media = 8.7 ft/sec.
Temperature of system = 27 $^\circ$C
Duration of exposure = 100 hour

<table>
<thead>
<tr>
<th>Concentration of corrosive media lb/gallon</th>
<th>Total weight loss</th>
<th>Surface area of impingement plate cm$^2$</th>
<th>Corrosion rate of impingement plate mmpy x 10$^3$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Impinge-Elbow</td>
<td>Tee</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>mg</td>
<td>mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4375</td>
<td>2.2</td>
<td>4.625</td>
<td>6.305</td>
<td>75.87</td>
</tr>
<tr>
<td>0.4958</td>
<td>2.6</td>
<td>12.40</td>
<td>24.2</td>
<td>76.00</td>
</tr>
<tr>
<td>0.5698</td>
<td>6.8</td>
<td>63.25</td>
<td>89.75</td>
<td>76.683</td>
</tr>
<tr>
<td>0.800</td>
<td>10.05</td>
<td>221.1</td>
<td>271.2</td>
<td>77.285</td>
</tr>
<tr>
<td></td>
<td>204.0</td>
<td>335.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9765</td>
<td>11.1</td>
<td>154.9</td>
<td>209.8</td>
<td>75.919</td>
</tr>
<tr>
<td>1.20925</td>
<td>15.88</td>
<td>345.0</td>
<td>260.85</td>
<td>76.711</td>
</tr>
<tr>
<td>1.40925</td>
<td>13.87</td>
<td>388.5</td>
<td>333.5</td>
<td>77.80</td>
</tr>
</tbody>
</table>
APPENDIX-8

Effect of pH of solution on erosion-corrosion

Velocity of solution : 8.7 ft/sec.
Duration of exposure : 100 hour
Temperature of system : 24 ± 1°C
Naturally aerated system

<table>
<thead>
<tr>
<th>pH of solution</th>
<th>Total weight loss</th>
<th>Surface area of impingement plate</th>
<th>Corrosion rate of impingement plate mmpy x 10³</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Impingement plate</td>
<td>Elbow</td>
<td>Tee</td>
<td>sq. cm.</td>
</tr>
<tr>
<td>5.0</td>
<td>334.1</td>
<td>583.39</td>
<td>678.25</td>
<td>76.6</td>
</tr>
<tr>
<td>6.0</td>
<td>17.8</td>
<td>128.25</td>
<td>213.9</td>
<td>78.08</td>
</tr>
<tr>
<td>6.5</td>
<td>44.2</td>
<td>168.2</td>
<td>287.3</td>
<td>76.61</td>
</tr>
<tr>
<td>8.58</td>
<td>22.0</td>
<td>204.0</td>
<td>335.0</td>
<td>77.67</td>
</tr>
<tr>
<td>8.77</td>
<td>13.87</td>
<td>221.0</td>
<td>271.2</td>
<td>77.178</td>
</tr>
<tr>
<td>8.0</td>
<td>177.94</td>
<td>443.53</td>
<td>480.15</td>
<td>78.34</td>
</tr>
<tr>
<td>9.06</td>
<td>11.1</td>
<td>154.9</td>
<td>209.8</td>
<td>75.92</td>
</tr>
<tr>
<td>9.27</td>
<td>15.88</td>
<td>245.0</td>
<td>260.85</td>
<td>76.71</td>
</tr>
<tr>
<td>9.32</td>
<td>6.80</td>
<td>63.25</td>
<td>89.75</td>
<td>76.68</td>
</tr>
<tr>
<td>9.68</td>
<td>2.2</td>
<td>46.25</td>
<td>63.05</td>
<td>75.87</td>
</tr>
<tr>
<td>10.0</td>
<td>3.062</td>
<td>13.65</td>
<td>49.05</td>
<td>77.038</td>
</tr>
</tbody>
</table>
Fig. 7.6: Pitting Type Corrosion (X 20) at pH 5.0

Velocity = 8.7 fps
Duration = 100 hr.

Fig. 7.7: Pitting Type Corrosion (X 20) at pH 8.0
APPENDIX-9

Effect of chloride concentration in corrosive media (mixture of Na₂SO₃ and NaHCO₃ in the ratio 6:1 expressed as Na₂CO₃) on erosion-corrosion of steel.

Naturally aerated system

Velocity of corrosive media = 8.7 ft/sec.

Duration of exposure = 100 hour

Temperature of system = 28 ± 1°C

Corrosive media concentration = 0.8 lb/gallon

<table>
<thead>
<tr>
<th>Chloride concentration in corrosive media ppm</th>
<th>Total weight loss</th>
<th>Surface area of impingement plate cm²</th>
<th>Corrosion rate of impingement plate mmpy x 10³</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Impingement plate mg</td>
<td>Elbow mg</td>
<td>Tee mg</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>10.46</td>
<td>141.25</td>
<td>193.25</td>
<td>75.53</td>
</tr>
<tr>
<td>300</td>
<td>20.2</td>
<td>-</td>
<td>-</td>
<td>75.67</td>
</tr>
<tr>
<td>500</td>
<td>32.70</td>
<td>205.4</td>
<td>229.9</td>
<td>75.412</td>
</tr>
<tr>
<td>700</td>
<td>16.8</td>
<td>-</td>
<td>-</td>
<td>75.44</td>
</tr>
<tr>
<td>1000</td>
<td>84.3 65.3</td>
<td>259.4</td>
<td>271.8</td>
<td>76.604</td>
</tr>
<tr>
<td>3000</td>
<td>100.35</td>
<td>325.45</td>
<td>380.27</td>
<td>75.92</td>
</tr>
<tr>
<td>5000</td>
<td>124.90</td>
<td>414.95</td>
<td>487.8</td>
<td>76.06</td>
</tr>
<tr>
<td>7000</td>
<td>150.25</td>
<td>368.83</td>
<td>444.6</td>
<td>76.03</td>
</tr>
<tr>
<td>10000</td>
<td>161.85</td>
<td>443.2</td>
<td>515.3</td>
<td>76.23</td>
</tr>
</tbody>
</table>
Corrosion rate of impingement plate in distilled water and 0.7% NaCl solution.

Temperature of system = 26 ± 1°C
Velocity of environment = 8.7 ft/sec.
Duration of exposure = 100 hour

Naturally aerated system

<table>
<thead>
<tr>
<th>Environment</th>
<th>Area of weight loss (sq. cm)</th>
<th>Corrosion rate (mg. mmpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>76.4978</td>
<td>204.9</td>
</tr>
<tr>
<td>0.7% NaCl Solution</td>
<td>75.5977</td>
<td>398.9</td>
</tr>
</tbody>
</table>
Fig. 7.8: Erosion-corrosion of Impingement Plate in 0.7% NaCl Solution Velocity = 8.7 fps
Duration = 100 hr.

Fig. 7.9: Pitting Type Corrosion of Steel Specimen in Distilled Water
Velocity = 8.7 fps
Duration = 100 hr.