Effect of Chloride Ion on 316L Stainless Steel & Its Simulation in Cyclic Cooling Water

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Abstract— **Sustainability of Chloride ion concentration in the cooling water or cyclic cooling water circuit are in increasing trend continuously because chloride ion concentration of makeup water gradually increasing trend or sometimes for increasing of cycle of concentration in cyclic cooling water chloride ion also increasing mostly stress and pitting corrosion also increasing equipment failure due to chloride ion. The effect on chloride ion on Stainless steel 316L in simulated cooling water system to be defined with the saturation of all the water parameter with effect of the ions with chloride ion**

Keywords— *Cooling water treatment, Sewage treatment plant, Water treatment plant.*

A.   INTRODUCTION:

Waste/sewage water generated by the people living in metropolitan cities as well as in small cities has been a major problem and gradually chloride level in the waste/sewage water observing increasing trend, when the same treated water taking and make up in cyclic cooling water which are impacting at metal specially SS:316L as stress and pitting corrosion etc. So it is very necessary to handle this treated water very delicately to make our cyclic water system smooth, the same may be handled with the help of ion simulation in the system and may reduce the of chloride ion effect in cyclic cooling water.

With the help of ion simulation, may reduce the operation cost and metallurgy life.

Going forward to use the waste water treated water. Basically sewage are generating from people and the sewage getting high chloride due to the salt consumption by people and this is the necessary to consume by people so we are not able to reduce chloride level in sewage inlet and the same chloride it has to as it is available in the treated water, so our aim to provide study intended report to evaluate and understand the chloride behavior, influence with SS:316L and its simulation in cyclic cooling water also a theoretical proof.

It is well known that stainless steel has a great corrosion resistance property in the oxidizing corrosive environment because of the passive film which forms on the steel surface to protect the material from destroyed from atmosphere. However in the many acidic corrosive mediums such as sulphuric acid, acidic solution and other solution including Cl^-, the passivity cannot stay for long time, it generally believed that the passive film on the stainless steel is double layer which is considered of passive film forms, the Fe oxides and hydroxides which are mainly full up in the outer layer. We may considered that Fe_2O_3 and CrO_3 are two major

component then the passive film forms, thus the film will be broken with the dissolution with of the Cr_2O_3. Beside many corrosive ions can be found in the cyclic cooling water and Cl^- is the main ion which are responsible for the corrosion. [1]

So that in this report and practical information have to study bout the Cl^- ion and its simulation with the cation's present in the cyclic cooling water also the adverse effect of the Cl- ion with variation of general cation and specific inhibiter like silicate, molybdate, zinc etc

Avoid combining SI and CGS units, such as current in amperes and magnetic field in oersteds. This often leads to confusion because equations do not balance dimensionally. If you must use mixed units, clearly state the units for each quantity that you use in an equation.

B. IMPURITIES IN THE CYCLIC COOLING WATER

➢   TOTAL SUSPENDED SOLID:

Total suspended solids (TSS) are particles that are larger than 2 microns size found in the cyclic cooling water. Anything smaller than 2 microns (average filter size) is considered a dissolved solid content.

➢   TURBIDITY

The turbidity of water is the measure of ability of light passing through sample. Its ability to measure against a turbidity index. The water having turbidity index five allows no passage of light, while index one shows little or no turbidity (NTU) [2].

➢   TOTAL HARDNESS

Total hardness is the sum of the calcium and magnesium ion concentrations, both expressed as calcium carbonate or as cation in milligrams per liter (mg/L)

➢   CALCIUM HARDNESS (Ca^+):

Calcium hardness is measures as total calcium present in the water, generally measured as carbonate mg/ltr.

➢   MAGNESIUM HARDNESS (Mg^+):

Magnesium hardness is measures as total magnesium present in the water, generally measured as carbonate mg/ltr.

➢ CHLORIDE (C$_L^-$):

Chloride ion is developing from the salt combination of calcium; magnesium sodium etc. and generally some common chlorides include sodium chloride (NaCl) and magnesium chloride. [3]

➢ SULPHATE (SO4-):

Sulfate ion content refers to the quantitative concentration of the polyatomic anion of sulfur and oxygen chargers present in a cyclic cooling water solution.

➢ TEMPERATURE (^0C)

The temperature of water is very important for saturation index of the cooling and make up water because temperature of water affects the solubility of total dissolve solid in the water. The temperature of cooling and make up water is also very significant for circulation purposes because, at high temperature hardness may start precipitation.

➢ TOTAL DISSOLVED SOLIDS

Dissolve solids can be present in the form of minerals, salts and metals, organic, inorganic matter in makeup and cooling water. The dissolve solids occur in water by the contact with substances in soil, on surfaces and in the atmosphere. The dissolve solids can be separated from water by, evaporation, electro dialysis, reverse osmosis and ionexchange. [4]

➢ ALKALINITY:

Alkalinity is the measure of water's ability to how much it can neutralize the acids. In other words we can say also that it is the buffering capacity of water. Bicarbonate, carbonate and hydroxyl ions are responsible for the variation of alkalinity of the water. Carbon dioxide from the different sources is also responsible for variation alkalinity of the water. Alkanity of the water also participate in the saturation index of the cooling water [2].

➢ HARDNESS

Minerals of calcium and magnesium present in the water are responsible for hardness, so hardness indicates the concentration of these minerals in water's. Deposits are the major problem in hot water due to these minerals in pipeline. Hard water also has many advantages, especially to generate positive site of saturation index.

➢ METAL

Metals in water may harm in the cooling water system even in little quantity. It can be divided into two categories : toxic and non-toxic metal. These metals are present in natural water due to dissolution from natural deposits and discharges of industrial wastes.

➢ ORGANICS :

Color, taste and odor are affected by the organic matter present in water. Halogenated compound to be formed in the water undergoing chlorine disinfection due to the presence of organic matter. Organic matter present in water affects the solubility of oxygen that interferes the water treatment process/program. Presence of organic matter is the most important for cause of the BOD increase.

➢ CHLORIDES (Cl$^-$)

Chlorides are there in groundwater naturally. Higher concentration of chloride creates much harm at cooling water system such as making hydro-choric acid after reaction with hydrogen and resulting pitting corrosion also due to high chloride ion stress corrosion occurs.

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➢ pH

pH is the measure of hydrogen ion concentration in cooling water. In other words it can be said that it is the measuring of acidity or alkalinity of water. The biological and chemical reaction is affected by the pH. Water with lower pH level has more chlorine contact time for disinfection.

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➢ CORROSION (MPY)

Corrosion is a natural phenomenon that converts a refined metal into a more chemically stable oxide.

$$4Fe\ (OH)_2 + O_2 \longrightarrow 2Fe_2O_3 + 4H_2O$$
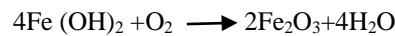
C. EXPERIMENTAL:

a. **Instrument working principle:**

The same experiment was carried out with a standard SS316 electrode/probe.
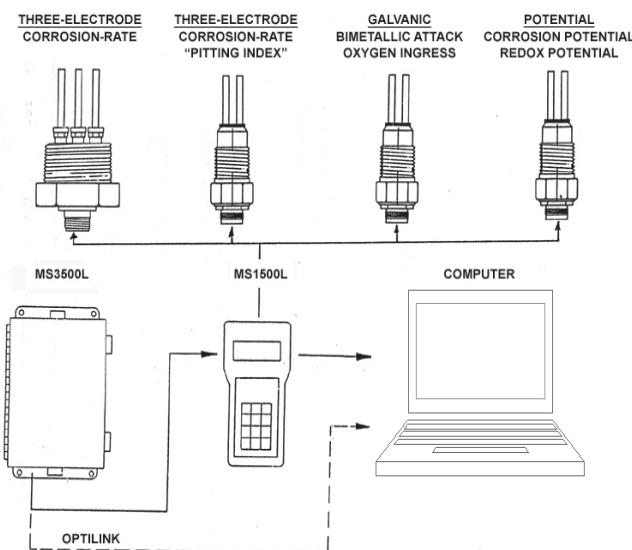

Fig: 1 Instrument connection [2]

b. Theory of Operation Overview of Linear Polarization:

When a metal/alloy electrode is immersed in an electrolytically conducting liquid of sufficient oxidizing power, it will corrode by an electrochemical mechanism. This process involves two, simultaneous, complementary reactions. At anodic sites, metal will pass from the solid surface into the adjacent concentrated solution and, in so doing, leave a surplus of electrons at the metal surface. The excess electrons will flow to nearby sites, designated cathodic sites, at which they will be consumed by oxidizing species available in the corros... ...

A sim... ...c solution, it is illustra... ...

$$\frac{1}{R_P} = \frac{\Delta I}{\Delta E} = 2.3 \frac{(b_a + |b_c|)}{b_a \cdot b_c} \times I_{CORR}$$

c. Chemical phenomena on electrode: [2]
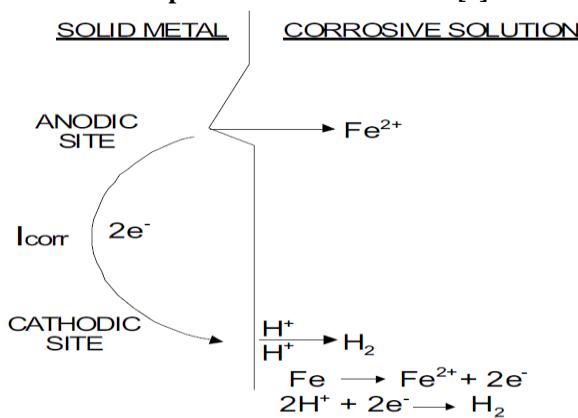
This electron flow, or movement of electric charge, constitutes of an electric current I_{COR}. Since the flow of electric current in such a situation can be equated to loss of metal mass, or volume, by Faradays Laws of equation, I_{COR} is a measure of corrosion rate. The relationship of I_{COR} to corrosion rate is shown in the *Equation 1* [2]:

$$C = \frac{Icor}{A} X \frac{t}{F} X \frac{E}{d} X D \qquad \text{-------(1)}$$

C   = corrosion rate (MPY)
Icor   = corrosion current (mA)
A   = surface area of metal/alloy (cm2)
t   = no. of second in 1 year   (31,536,000)
F   = Faraday's constant (96,494 coulombs. (gm.equ)-1)
E   = Equivalent weight of metal (gm.(g.equ.)-1)
d   = density of metal (gm.cm-3)
D   = conversion factor, centimeters to mils.

Equation 1 reduces to:

$$C = \frac{Icor}{A} X \frac{E}{D} X 128.67 \qquad \text{---(2)}$$

Since E and d are known for all metals, and A can be fixed, a measurement of Icor would allow corrosion rate to be determined. Unfortunately, direct measurement of Icor is not possible, since anodic and cathodic sites on a metal surface are continually shifting within a continuously conducting surfaces.

Indirect measurement of Icor is possible. This can be achieved by applying a small potential shift (ΔE) to a corroding metal surface, and measuring the current (ΔI) required to maintain this potential displacement.

ΔE/ΔI, commonly called the polarization resistance, is inversely proportional to ICOR. This relationship is contiguous in the Stern-Geary equation [2]:

$$\text{----------------- (3)}$$

Rp = Polarization resistance (ohms)
b_a = anodic rate constant (mV. decade -1)
b_c = cathodic rate constant
(mV. decade -1)
Rearrangement of equation 3 gives:

$$I_{COR} = \frac{\Delta I. \ (b_a \ b_c)}{2.3 \ (b_a + b_c) \ \Delta E} \qquad \text{----------(4)}$$

Substituting from equation. 4 in to 2.

$$C = \frac{\Delta I. \ (b_a \cdot |b_c|)}{2.3.A. \ E.(B_a + |b_c|)} \times \frac{E}{d} \times 128.67 \qquad \text{------------(5)}$$

The ratio (ba• | bc |) / (ba + | bc |) is assumed to be constant.

Practical measurement instruments fix the polarizing voltage at, some small value, for which equation on 3 holds true. This is usually 10mV or 20mV.

Measurements made with corresponding weight loss data. [3]

d. Tested Electrode specimen:

The experiment was carried out in the standard non passivated single- electrod cell; the working electrode was as stainless steel 316L with the surface area 2.5cm2, the chemical composition (wt pct) as a fallowed: [1]
Table: 1: Chemical composition of the electrode.

Chemical composition of electrode	Value Wt (%)
Carbon	0.014
Silica	0.6
Manganese	0.8
Chromium	17.14
Nickel	12.54
Sulphur	0.0073
Iron	68.8587

All assessment ware carried out at temperature of $(32\pm1)\ ^0C$ and at pH 7.0 respectively.

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d. CHEMICAL COMPOSITION OF THE SIMULATED COOLING WATER: [1]

Water parameter	Concentration
pH	7
Temperature (^{0C})	32
Total hardness (mg/ltr) as $CaCO_3$	100
Ca^{2+} (mg/ltr) as $CaCO_3$	60
Mg^{2+} (mg/ltr) as $CaCO_3$	40
$SO4^{2-}$ (mg/ltr)	100
$HCO3^-$ mg/ltr	200
Na^+ mg/ltr	90
Cl^- as $CaCO3$ (mg/l)	100-2000

D. RESULTS AND DISCUSSION:

Corrosion versus Chloride ion curve in cooling water:
The corrosion curve obtained are shown in the fig.1 at temperature $32^{0C} \pm 1$
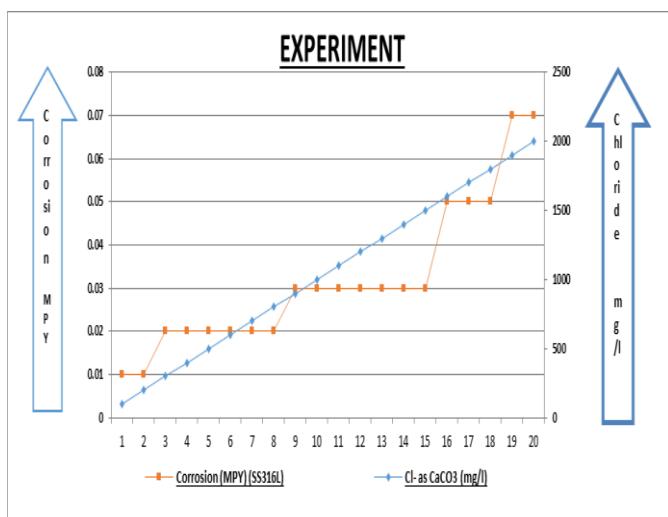
Fig:2: Graphical trend between corrosion and chloride ion level in cooling water

E. **Graphical trend between corrosion and chloride ion level in cooling water:**
a) The graph obtained are shown on Fig: 2, the temperature was content at 32 ± 1^{0C} of cooling water.
a) Variation of the chloride level in the cooling water resulting the affection on corrosion potential of the cooling water.
b) Remaining water parameter was constant so that residual chloride participating to polarize the metal surface so that corrosion increases gradually.
c) High chloride level in the cooling water pertaining the high corrosion level high polarization by the cooling water to metals surface.
d) Practical data are:

Cl- as CaCO3 (mg/l)	100	200	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
Corrosion rate (MPY) (SS316L)	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.05	0.05	0.07	0.07

F. CONCLUSIONS:

a) We can say that with reference to the increasing of

b) Chloride ion level, also increasing the corrosion and polarization capacity of the cooling water and remaining water parameter at constant.
c) With the addition of chloride ion in the experiment sodium concentration also increases gradually with the mole ration of chloride.
d) So we can also say they chloride ion concentration and the corrosion potential of the cooling water directly proportional to each other.

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