DISSOLUTION PATTERN OF MILD STEEL COMPONENTS AND THEIR CORROSION PRODUCTS IN 3% SODIUM CHLORIDE SOLUTION AND THEIR EFFECTS ON FURTHER AGGRAVATION OF CORROSION

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Abstract : Mild steel due to its versatile properties like strength, ductility is mostly used in various fields like construction, transport and industrial components. Mild steel is prone to atmospheric corrosion; especially in marine atmosphere, corrosion is more pronounced. The focus of the present work is to know the behavior of the metal and corrosion product upon exposure to 3% Sodium chloride solution. Dissolution pattern of these components along with the fresh steel was analyzed. Macroscopic observation of the dissolution pattern reveals most interesting features like bubble formation and collapse of bubble and crystallization of sodium chloride in the nests. Various types of changes occurring during this dissolution process were recorded. XRD analysis of corrosion product so obtained in short time exposure to aggressive environments was done. SEM images taken after the drying stage resembled the same patterns as macro corrosion.

IndexTerms - Bubble formation, anodic dissolution, nesting, pitting, Corrosion.

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I. INTRODUCTION

Because of their good mechanical properties Iron and steel alloys are the most preferred materials throughout the world [1]. As Iron is one of the most widely used materials in our daily life due to its unlimited applications, many investigators concentrating on the corrosion protection of iron in corrosive environments[2-5]. Several researchers have been investigated the corrosion type and its inhibition in harsh environments [6–13]. As most of the world's population is surrounded by the marine atmosphere, the harsh corrosive nature of marine pollutants especially the sodium chloride is one of the most unavoidable and having innocuous nature of damaging internal structure of the huge constructions , a trial was made to know the behavior of these aggressive species during corrosion and its effects were analyzed by conducting dissolution pattern of mild steel components and their corrosion products in 3% NaCl solution.

Ongoing debates regarding the reaction mechanism of incorporation of chloride ions into the structure during the hydrolysis and the type of earlier species formed, their removal by hydrolysis from the growth of colloidal species with mono- and dinuclear complexes binding of chloride ions to mononuclear complexes and their simultaneous release for the formation of poly nuclear clusters [16, 17].

Archaeological wrought iron objects inner core is normally covered by a dense corrosion product layer, comprises mostly magnetite and maghemite strips in a goethite matrix [18]. From these layers of corrosion, information on the actual shape of the object, how the anodic sites at the interior core metal interact with the surrounding chloride ions as counter ions to the metal ions at anodes. Due to these processes production of ferrous chloride solution at the location of metal surface at the anodic sites within pits. Corrosion Prevention will be done by the process of galvanization of parent metals by which metal was protected to some extent by the consumption of sacrificial anodes. Pieces of zinc or magnesium alloy are attached to pump bodies and pipes. The metal to be protected becomes the cathode and does not corrode. Whereas anode corrodes, thereby providing the desired sacrificial protection. Salinity is a measure of the amount of salts in the water. Because dissolved ions increase salinity as well as conductivity, the two measures are related. The salts in sea water are primarily sodium chloride (NaCl). Whatever layer formed by the process of corrosion of mild steel samples is deposited above the zone of corrosion attack [19, 20].

The corrosion product layer thus formed is not good enough to protect the parent metal due to its porous, fragile and non adherent nature. Various studies were done on the type and nature of the corrosion products. In our present study more thrust was given for the morphological changes occurring during the dissolution process of corrosion product layers as well as newly formed corrosion product layer behavior. By knowing what actually happening during the process of corrosion of steel in aggressive salts will definitely will be useful for combating the corrosion to some extent. Crevice corrosion is a process of localized corrosion attack in acid-chloride conditions occurring at the specific locations like under deposits, beneath the gaskets, in imperfect welding regions, interfacial regions between washers, and within pits and cracks. Crevice corrosion damages a protective thin oxide layers on the metal surface. A small passive current can pass through the protective film if the conductive nature of the corrosion product so formed is good. As the film does not have a high electrical conductivity, metal dissolution occurs at a very slow rate in the presence of the protective film. Whereas, in concentrated acid-chloride solutions, the protective film will be destroyed during

the periods of a change in solution pH and chloride concentration lead to a critical state that is called the critical crevice solution. Crevice corrosion progresses due to the differences in inside and outside solution like differential aeration, pH, metal ion concentration as well as chloride ion concentration [21, 22].

II. EXPERIMENTAL METHODOLOGY

One of the experiments one new and one long time corroded nut were tested for the nature and type of corrosion and their products formation during the dissolution pattern in 3%NaCl solution. The synthesized corrosion product is characterized by standard techniques such as XRD, SEM. The XRD patterns are recorded at room temperature in the 2θ range of 10° to 90° using Cu-Kα radiation (λ=1.5405Å). The mild steel specimens were immersed in 3% NaCl solution for a period of 360 h. After 360 h, the specimens were taken out and dried. The nature of the surface film formed on the surface of the mild steel specimen was analyzed by using JEOL (JSM 6610L) Scanning electronic microscopy. Effect of 3%NaCl solution on long time corroded steel nut.

III. RESULTS AND DISCUSSION

One of the experiments one new and one long time corroded mild steel nut were tested for knowing the nature and type of corrosion and their products formation and their distribution during the dissolution pattern in 3%NaCl solution.

On the new nut at a specific location 3% NaCl solution applied in drops (Fig1a), after six days bubble formation (Fig 1b) observed at that specific location. Sample shown in Fig 1b and longtime corroded old nut are immersed in 3% NaCl solution in separate containers as shown in Fig. 2
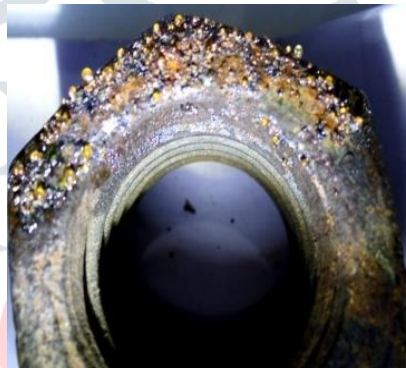

Fig 1a: April 17-2016

Fig 1b: April 22-2016

Fig 1: New nut treated with 3%NaCl solution.
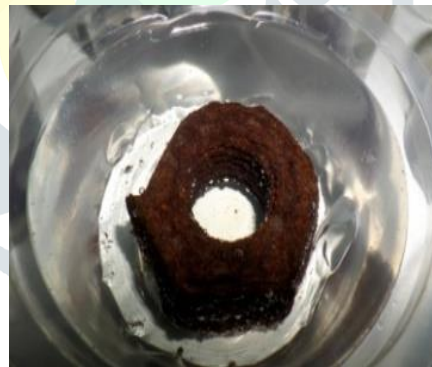

Fig 2a: April 23-2016

Fig 2b: April 23-2016

Fig. 2 Dissolution pattern of slightly corroded, longtime corroded nuts in 3% NaCl solution

Instantly dissolution observed in the container having nut with freshly formed bubbles (Fig 2a).The color change is due the instant dissolution of freshly formed liquid from the bubbles. Whereas in container 2 there is no instant color change indicating longtime corrosion product dissolution is not occurring in 3% NaCl solution. In new nut comparatively corrosion attack is more at the zone of bubble formation (Fig 3a). Complete drying and again bubble formation observed within 29 days (Fig 3b).

Whereas in old nut with the same amount of electrolyte, the previously formed corrosion product layers are separated from the parent metal within 6 days .Undulations at both the metal and corrosion product layer observed. Most of the electrolyte is absorbed, adsorbed to the corrosion product layers (Fig 3d).
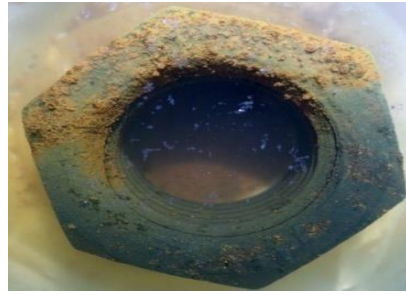
Fig 3a: April 24-2016

Fig 3b: May 22-2016

Fig 3c: Apr 29-2016   Fig 3d: May 08-2016

Fig. 3 : Dissolution pattern of slightly corroded and longtime corroded nuts in 3% NaCl solution

Comparatively in old nut dissolution is more, as it is having more reactive area due to the removal of already formed long time corrosion product layer (Fig 3c). During the process of corrosion initial stage corrosion product is not that much compact when compared to as long time corrosion product layers. Are these long time corrosion product layers so formed are really protective are not ? Anyhow whatever corrosion product layer formed is protective to some extent from the atmospheric pollutants. To know how the dried Nacl distribution is happening in the process of above corrosion experiment ,SEM , XRD analysis of the experimented longtime corroded product was done .

XRD analysis of corrosion product of long time corroded nut kept in 3% NaCl solution
XRD study of the long time corrosion product kept in 3% NaCl showing most intense lines of FCC spinal structure of magnetite (Fe$_3$O$_4$) with major peaks at 35.6 ° corresponding to (311) plane. Other peaks for magnetite at 30.31° (220), 43.43° (400), 57.24° (511) and 62.5° (440) are close to JCPDS:89-3319 [23]. It is usually known that the interior part of the rust, close to the base metal has low oxygen concentration and magnetite formation also occur on the underlying steel which has lost the previously formed rust layer due to the exfoliation morphology of this corrosion product compound [24]. The composition of the rust layer also depends on the characteristics of the formed surface electrolyte layer during exposure of the steel to the atmospheric corrosion process, which varies according to the type of surrounding atmosphere [25]. It is reported that even after 25 years of meta stability of βFeOOH (Akaganite) having the potential to release tunnel-bound chloride for further, cyclic, corrosion of iron in contact with it [26]. In this XRD pattern no Akaganite peaks were detected as the specimen taken for this study is longtime corrosion product.
By the deposition of salt particles on a metallic surface acceleration of corrosion will occur, it is more in case of chlorides which can give rise to soluble corrosion products in water. Cl$^-$ ions are abundant in marine atmospheres, where the fundamental source is by their passage over oceans and salt lakes .
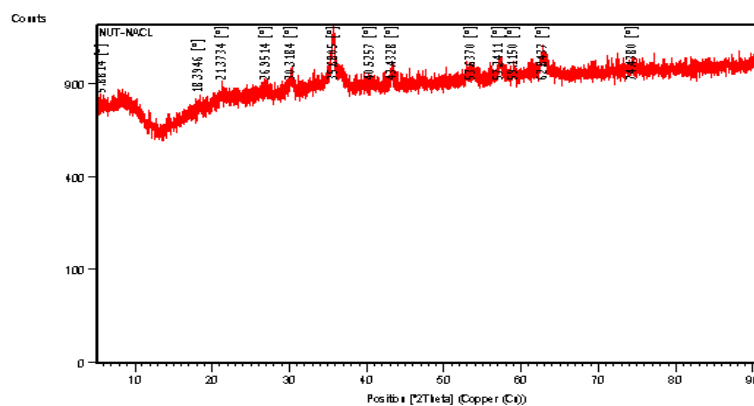

Fig 4 (AUG 23-2016): XRD of corrosion product of long time corrosion product of mild steel.

Table 1: Comparative XRD data of magnetite and nut

hkl	MAGNETITE d A /2Θ / I/I	NUT (LONG TIME CORRODED) d A /2Θ / I/I
220	2.96/30.32/29	2.94/30.31/41.22
311	2.52/35.3/100	2.51/35.68/100
400	2.09/43.32/20	2.08/43.43/21.76
422	1.71/53.89/8	1.70/53.64/11.48
511	1.61/57.34/24	1.61/57.24/24.70
440	1.48/62.96/34	1.48/62.85/37.59

The corrosion product so obtained (Fig 3d), was analyzed to know the morphological changes occurring during this dissolution process. SEM (model JEOL (JSM 6610L) was used for this study. From this study Micro level bubble formation observed at the contact surface of the long time corrosion product layers and fine micro cracking of the corrosion product near these bubbles observed (Fig 4a). According to Ambler and Bain, only salt particles and droplets of more than 10 μm cause corrosion when their deposition on a metallic surface.

Enlarged view of these bubbles was showing clear cut cavity. The size of the micro bubble is measured, having dimensions of 208.226 and 269.237 micro meters (Fig 4b). Inside these bubbles thin layers of corrosion product (Fig 4c) were also observed. The most important and innovative features observed is the residence of the NaCl in the form of micro crystals of size 81.942 and 82.767 micro meters respectively inside the so formed bubbles and nests (formed due to the collation of these micro bubbles (Fig 4d) [27-31].
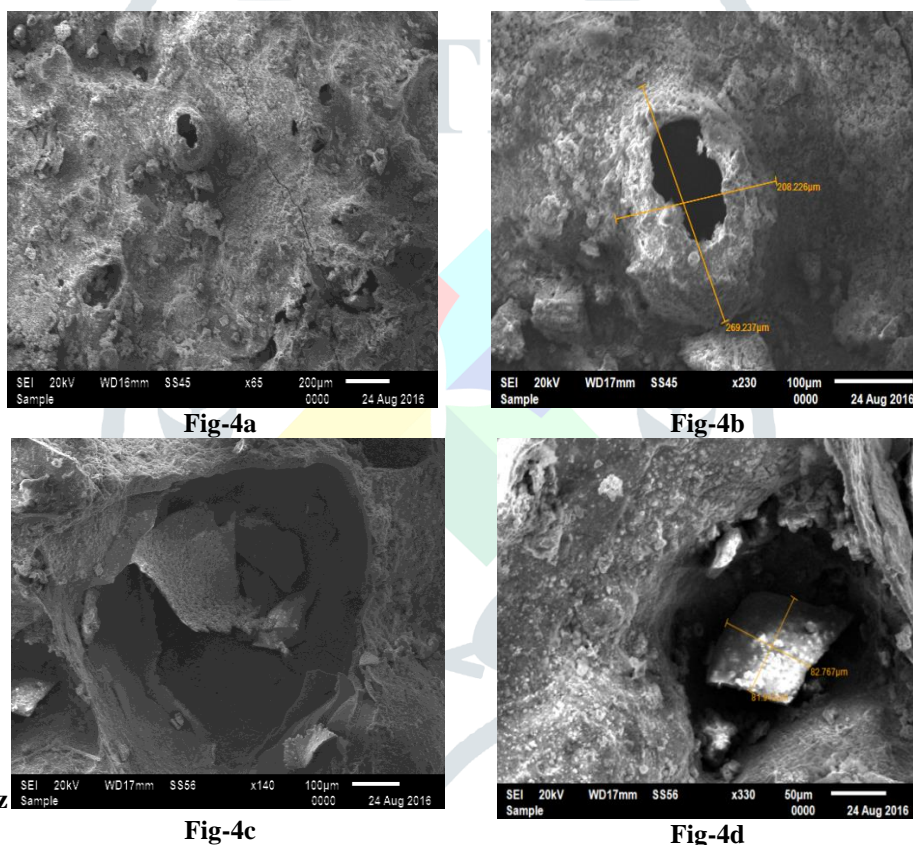

Fig-4a

Fig-4b

Fig-4c

Fig-4d

Fig.4 : SEM analysis of long time corrosion product layers kept in 3% NaCl solution

IV. CONCLUSION

During wet dry cycles of corrosion process the entrapped aggressive species may further dissolve internally and aggravate the process of anodic dissolution and pit formation, growth and filling of these pits with internally formed electrolyte will occur. Due to this processes aggravation of the internal corrosion damage with the conductive electrolyte and the available conductive magnetite layer. Corrosion of metals occurs through the phenomenon of an electrical conductance,. Dissolved salts in water promotes electrical conductance. As 3%NaCl solution is having high electrical conductance. Corrosion is rapid when a solution in the crevices is having high electrical conductance may lead to the internal pitting corrosion process and ultimately damaging the metal internally. Care should be taken during maintenance practices of corroded pipelines etc., for the removal of the corrosion product having dried up internal salts, as these are aggressive and having hygroscopic nature, even slight entry of moisture, humidity the major internal damage to the components will occur. Further detailed study is needed for assessing individual effects which are responsible for the major damages occurring due to the exposure to marine environments.

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