

# THE INFLUENCE OF ATMOSPHERIC COMPONENTS AND CONTAMINANTS ON THE CORROSION OF METALS

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## ABSTRACT

This paper generally describes the developments involved in the study of corrosion of metals under the atmospheric conditions. Types of corrosion damages were described and iron was mainly used as an example. The possible electrochemical reactions governing the corrosion processes were divided into the anodic oxidation process and the cathodic reduction process. The cathodic reduction processes discussed are the proton reduction, oxygen reduction including those involving the production of peroxide intermediates and the cationic reduction. The role of components/pollutants of the atmosphere such as sulphur dioxide, oxides of nitrogen, chloride iron, hydrogen sulphide, hydrogen chloride, chlorine and solid matter are also discussed.

## INTRODUCTION

Rozenfeld<sup>1</sup> defined atmospheric corrosion as "...the process whereby metal and metal alloys deteriorate in the atmosphere as a result of electrochemical and chemical reactions that take place on their surface". It is thus a widespread problem that is of much concern to the society since most building structures, metal installations and equipment are indeed exposed to the atmospheric environment. As such it is understandable why this subject has created much interest among the corrosion scientist.

In studying atmospheric corrosion of metals, it is important to consider the physical and chemical nature of the atmosphere. More important, the effects of contaminants in it, which is known to have great influence.

Generally, the corrosion index climatic condition, of a geographical condition can be divided into three types. They are the rural atmospheric condition, industrial atmospheric conditions and finally the marine atmospheric conditions.

The rural atmospheric condition is considered as comparatively clean from pollutants. Therefore factors that influence corrosion processes of metal in this kind of atmosphere are limited to humidity, diurnal fluctuation of temperature, rainfall and dew formation. On the other hand, in the industrial atmospheric conditions, pollutants such as dust particles, gaseous contaminants such as  $\text{SO}_2$  and  $\text{NO}_x$  produced from industrial activities and combustion of fuels, are known to have deleterious effects on exposed metals. While in the marine environment, corrosion of metal is largely influenced by chloride ions.

Atmospheric corrosion of exposed metal is thus a major problem. Several billion dollars are spent each year on solving problems posed by corrosion. These include the cost of protection, replacement of corroded metal parts and event cost incurred due to the failure of mechanical parts as a result of corrosion.

## **PROCESS OF CORROSION**

The actual process of corrosion is very complex in nature. Nevertheless it has been generally agreed that corrosion of metal is an electrochemical process. It involves one site of the metal undergoing an oxidation reaction (i. e. the anodic site) and some other part of the metal undergoes a reduction reaction (the cathodic site). Since it is an electrochemical reaction in nature, the presence of electrolyte is essential for the ionic transfer reaction, while the electron transfer is done via the corroding metal.

The understanding of this process can be better enhanced by looking at the processes that take place in a differential aeration cell. This cell has its two electrodes of the same types, immersed (or covered) in a common electrolyte that has a different exposure to aeration (oxygen supply).

Due to the difference in concentration of oxygen, the electrodes developed a difference in potential, causing electrons to flow from the negative electrode to the positive electrode.

If we were to look at a piece of iron that has a layer of electrolyte on its surface, the same phenomena may occur. At the peripheral of the electrolyte is an area where the metal aerated (therefore more oxygen can reach the metal through diffusion), while at the center is the area where less oxygen is available. With the formation of rust or other reaction products, the amount of oxygen reaching the center area will be even less. This will create an ever bigger potential difference between the peripheral and the center region of the metal. Therefore the center area will act as an anode, where metal dissolution will occur and the peripheral will act as the cathode. This phenomenon accounts for the pitting damage of iron under rust.

## **TYPES OF CORROSION DAMAGES**

Corrosion may be classified according to the damages done on the outward appearance or alterations done to the physical properties of a metal. Considering these damages, corrosion can be classified into five main types.

### **i) Uniform attack**

This includes the commonly called rust in iron, or tarnishing of silver. Another example of uniform attack is the "fogging" of nickel and high temperature oxidation of metals.

### **ii) Pitting**

This is a localised type of attack. The corrosion rate being greater at some areas than at others. Pitting may be described as two types, the deep pits or the shallow pits, depending size of the anodic area. Iron buried in soils may corrode with the formation of shallow pits, while steels immersed in sea water will corrode with the formation of deep pits. Other types of pitting corrosion are the impingement attack also know as corrosion-erosion, fretting corrosion and cavitation corrosion.

### **iii) Dezincification and Parting**

This type of corrosion is normally refered to corrosion of zinc alloys only. It normally leaves a porous residue of copper and corrosion products. The alloy when corroded often retains its original shape, and may appear undamaged except for tarnishing of the surface, but its tensile, strength and especially ductility is seriously reduced. Parting is similar to dezincification in the sense that one

or more reactive component of the alloy corrodes preferentially, except it normally occurs in noble metal alloys such as gold-copper or gold-silver.

iv) Intergranular corrosion

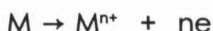
This is localised type of attack occurring at the grain boundaries of the metal causing the loss of strength and ductility.

v) Cracking

This phenomenon normally occurs to metals that are subjected to repeated or alternate tensile stresses in a corrosive environment.

## CORROSION OF METALS

Corrosion of metals is an electrochemical process. Thus the general principles of metallic corrosion involve the process of oxidation and reduction. At the anode, the dissolution process of metals into ion occurs as follows:



In order to complete this reaction, there are three possible reduction processes that may take place.

i) Proton reduction (in acid solution)



or



ii) Oxygen reduction (in acid solution)

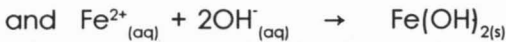
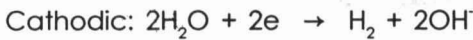
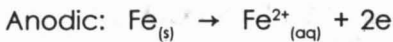


iii) Oxygen reduction (in neutral solution)



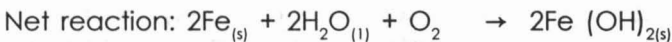
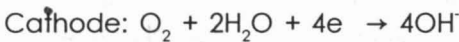
Which of these cathodic reactions will take place, depend on the acidity of the electrolyte and also the amount of oxygen available. When little or no oxygen is present (as in the case of iron embedded in moist clay), the most probable cathodic reaction will be the reduction of hydrogen ion and water.

In this reaction, hydrogen gas and hydroxide molecules are the products. The overall reaction will thus be:



$\text{Fe(OH)}_2$  is rather insoluble in water and will precipitate at the anodic site. When this happens, it will inhibit further formation of  $\text{Fe}^{2+}$ . The formation of  $\text{Fe(OH)}_2$  coating combines with the relatively slow reduction process of  $\text{H}_2\text{O}$  has retarding effect on the corrosion process of the metal. Thus corrosion under the absence of oxygen is a slow process.

While, if both oxygen and water are readily available, the chemistry of the corrosion is somewhat different, and the rate may be about 100 times faster compared to the process in the absence of oxygen. In this case, the overall reaction will be as follows:



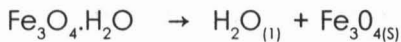
If only limited oxygen is available, further oxidation of  $\text{Fe(OH)}_2$  will be limited to the formation of black magnetite, i.e.,



green hydrated

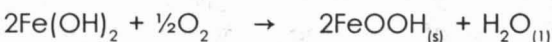
magnetite

AND



black magnetite

On the other hand, if oxygen and water are readily available, further oxidation of  $\text{Fe(OH)}_2$  will form red brown hydrated ferric oxide, i.e.,



red brown rust

From the above discussion, it is therefore noted that the presence of water and oxygen is vital in the formation of rust. Oxygen is important due to its high reactivity and abundance, while water acts as the electrolyte.

# ELECTROCHEMICAL REACTIONS GOVERNING THE CORROSION PROCESSES

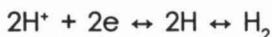
## The Anodic Oxidation Process

The attempt to understand the actual anodic processes are always complicated by its passivation phenomena. Problems often arise in clarifying the stages that actually determine the overall speed of the anodic reaction. Different investigators have different views on the anodic potential phenomenon. Some workers<sup>2, 3</sup> assume that the reason for anodic polarization is due to the retardation of the metal ionisation process, while others<sup>4</sup> suggested that the polarization is due to the sluggishness of the formation of hydrated ions which occur during the process of anodic dissolution of metal. Another significant contribution, are the concentration polarization phenomena, which arise from the diffusion rate of ions. Isgaryshev<sup>5</sup> on the other hand, assume that anodic polarization is determined by the process of ionic discharge rather than metal ionisation. While there is sufficient basis that the theory of retarded discharge of ions is applicable to the anodic processes, we can safely assume that the overall rate of the anodic reaction is actually determined by the metal ionisation reactions.

## The Cathodic Reduction Process

### i) The Proton Reduction

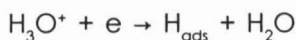
Many of the corrosion processes that involve the reduction of hydrogen ions are those of metals in acidic solutions as well as magnesium in neutral electrolytes.



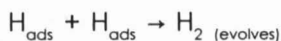
However this reaction was found to occur with significant overpotential. This significant overpotential is caused by the electrode polarization (activation polarization) rather than concentration factor, which may arise from any of the stages of the electrochemical reduction of hydrogen ions as outlined below:

1. Diffusion and migration of hydrogen ions to the cathode.
2. Dehydration of hydrogen ions,  $\text{H}_3\text{O}^+ \rightarrow \text{H}^+ + \text{H}_2\text{O}$
3. Entrance of hydrogen ion into the composition of the double layer that developed at the electrode.

4. Discharge of hydrogen ions:



5. Recombination of hydrogen atoms to form molecules



or



6. Diffusion of hydrogen atoms or molecules from the cathode.

However it has been established by Frumkin and his associates<sup>6</sup> that the overall hydrogen reduction reaction (the rate determining reaction) for a large number of metals, is determined by the hydrogen ion discharged reaction (i. e. reaction four), as this reaction requires a certain amount of activation energy.

On the other hand, some workers<sup>7</sup> has agreed that the rate determining factor for the cathodic reduction process for some metals is the recombination of hydrogen atoms into molecules stage (i. e. reaction five, the consequent reaction). This is especially true for metals with large heat of adsorption for hydrogen value.

## ii) The Electrochemical Reduction of Oxygen

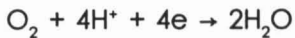
The cathodic oxygen reduction in a corrosion process is regarded as the type that occurs most often. This is especially true in cases where the electrolyte is neutral.

Unlike the hydrogen reduction process, the oxygen reduction reaction is controlled by concentration polarization. This is due to the fact that oxygen is less soluble in electrolytes. Thus most corrosion rates that involve only the oxygen reduction reaction occurring at the cathode, will be governed by the cathodic reduction reaction.

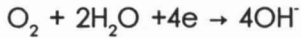
However several workers have proved that in the case when rust layer is formed, cathodic reduction of oxygen is no longer the significant contributor towards corrosion rate. The overall rate of reaction may now be influenced by the reduction of rust.

Looking further into the oxygen reduction reaction, it may be described as follows;

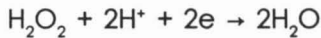
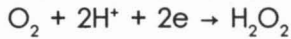
In acidic electrolyte:



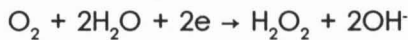
In neutral electrolyte and basic electrolyte



Owing to the transfer of four electrons in all of the reaction above, Rozenfeld<sup>10</sup> felt that the overall reactions of the oxygen reduction is not a single step reaction. He proposed the formation of  $\text{H}_2\text{O}_2$  as an intermediate, and suggested the following reaction process.



or

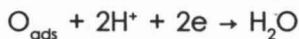
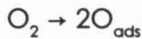


and  $\text{H}_2\text{O}_2$  is further reduced,



In fact Roich<sup>8</sup> showed that  $\text{H}_2\text{O}_2$  was indeed produced in the atmospheric corrosion of zinc and nickel.

Another mechanism proposed, is the direct reduction of oxygen molecules to water without the formation of  $\text{H}_2\text{O}_2$  as the intermediate.



This reaction involves two electrons<sup>9</sup> and is said to proceed catalytically<sup>10</sup>.

- iii) The Electrochemical Reduction of Cations existing in several stages of oxidation.

The other possible cathodic reaction is the reduction of cations existing in several stages of oxidation. Thermodynamically it has been proven that this reaction is possible for cations or even inorganic anions which are present in several oxidation stages.

## ATMOSPHERIC CORROSION

In the following discussion of atmospheric corrosion on metals, iron will be used as a representative. Although I am aware that the atmospheric corrosion behaviour of iron may differ from that of other metals in terms of chemical reaction



mechanisms and corrosion products, it can be used to illustrate the general understanding of corrosion subject.

## Composition of the Atmosphere

The composition of the atmosphere is very important in studying atmospheric corrosion. The atmosphere in its "undisturbed" form (or unpolluted) contains about 78.95% nitrogen, 20.95% oxygen and a number of other gases including the inert gases. The concentration of these gases are very low (best presented in ppm by volume). Argon is 9300 ppm, Neon is 18 ppm, Helium is 5.2 ppm, krypton is 1.1 ppm and xenon is 0.1 ppm. The level of carbon dioxide varies around 330 ppm depending on the area where it is measured. Other major components of the atmosphere include water and moisture.

Nitrogen, the inert gases, carbon dioxide and carbon monoxide appears unimportant in the corrosion of metal. Nevertheless, both the carbon dioxide and carbon monoxide are known to participate in the formation of secondary product, especially on non-ferrous metal.

Oxygen and moisture on the other hand, has great influence on the corrosion of metal. Oxygen is important due to its high reactivity and abundance, while moisture will always act as the electrolyte medium. The amount of water present in the atmosphere is referred to as the relative humidity (RH). The critical RH value is the value of RH required to cause enough moisture to develop on the surface of a metal to initiate corrosion.

Vernon<sup>11</sup> established a relationship between the ambient humidity and degree of corrosion. He found that iron does not corrode easily in air which is less than 70% relative humidity. A slight attack in the non-polluted areas may take place when RH value exceeds 70%. However in an atmosphere contaminated with dust, salt particles and industrial pollutants, corrosion may take place at even lower percentage of relative humidity.

In his other paper<sup>12</sup>, he also pointed out that not all kinds of dust produce the effect of rusting. Silica particles was found to cause no rusting while ammonium sulphate is very effective.

## **ATMOSPHERIC CORROSION BY AIR POLLUTANTS**

Although there are enormous kinds and forms of atmospheric pollutants, the ones that are generally considered important in causing corrosion are  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{Cl}^-$  ions and particulate.

### **a) Corrosion by Sulphur Dioxide**

In the atmosphere, the presence of oxides of sulphur in the gaseous form is normally due to the combustion of the sulphur containing fuels. Thus corrosion by the oxides of sulphur normally occurs in the industrial areas where these activities are abundance.  $\text{SO}_2$  gas is known to be one of the most potent causes of atmospheric corrosion. Hudson & Starumanis<sup>13</sup>, have shown that most atmospheric corrosion of metals are rapid in areas with high concentration of  $\text{SO}_2$ . His work was supported by Schikorr<sup>14</sup>, who discovered that rusting is more rapid for an area in seasons of the year when  $\text{SO}_2$  concentration of the atmosphere is high.

The mechanism of atmospheric corrosion caused by  $\text{SO}_2$  contaminants is still a subject under investigation. However earlier work by Schikorr has shown that some cyclical change must be involved in the atmospheric corrosion of metals involving  $\text{SO}_2$  contaminants. This is evident when he found that a small amount of  $\text{SO}_2$  is able to produce a relatively large amount of rust.

Two possible cycles have been proposed. First, the Acid Regeneration Cycle<sup>15</sup>, has been considered thoroughly by Schikorr, and many other workers and second is the electrochemical cycle.

#### **The acid regeneration cycle**

The presentation of this cycle may have changed, but essentially it involves the oxidation of ferrous sulphate to ferric sulphate. Ferric sulphate is then hydrolysed to give hydrated ferric oxide (rust) and sulphuric acid. The acid will then attack the iron to produce new ferrous sulphate which will then be oxidised and hydrolysed to produce more acid, and the cycle will repeat again. According to Schikorr, for the process of hydrolysis of ferric sulphate to hydrated ferric oxide to occur, it will have to depend a lot on the relative humidity. He found out that with a relative humidity of below 75%, the reaction is very slow.

## The Electrochemical Cycle

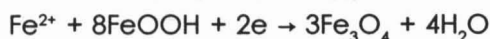
In this mechanism, Evans and Taylor<sup>17</sup>, suggested that ferrous sulphate was formed when iron is exposed to moist air containing SO<sub>2</sub> in the first stage. Soon after this happens hydrated ferric hydroxide will form and condition will be favourable for the formation of an electrochemical cell:



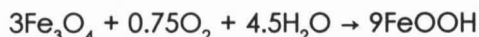
In this case the anodic reaction will be



The electrons produced will be used up in the cathodic reduction of rust to form magnetite:



The magnetite will then be oxidised by oxygen to form rust.



The cycle indicated that there will be a net gain of one additional FeOOH molecule for every one Fe<sup>2+</sup> ion. This reaction will then continue on. This suggestion was supported experimentally in their early work which uses the cell:



## The Specific Adsorption Model

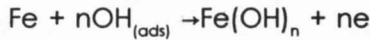
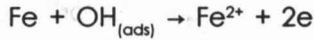
Another mechanism of SO<sub>2</sub> corrosion of metal was put forward by Duncan and Spedding<sup>18, 19, 20</sup>. In his studies, SO<sub>2</sub> was assumed to react only on specific and limited sites of the metal surface. Experimental results revealed that both the surface electrolyte solution reaction model (SESR) and the specific adsorption model (SAS) play a very important role in the corrosion of metal by SO<sub>2</sub>.

## Acceleration of the Anodic Reaction

In other experiment, Mikhailovski<sup>21</sup>, suggested that the reaction of SO<sub>2</sub> on metal involved the dissolution and oxidation of SO<sub>2</sub> to sulphate which will be followed by a subsequent reduction of the pH value. The unoxidized SO<sub>2</sub> will then be reduced to adsorbed sulphide or sulphur.



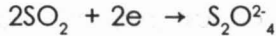
Then the OH<sup>-</sup> and adsorbed sulphide will react with the metal through the following reaction:



Therefore the anodic reaction is accelerated, with Fe<sup>2+</sup> and H<sub>2</sub>S being the product.

## Acceleration of The Cathodic Reaction

This theory was first proposed by Rozenfeld<sup>22</sup>, who described that the acceleration of corrosion by SO<sub>2</sub> gas is due to its depolarising effect on the cathodic site. In solution, SO<sub>2</sub> gases dissolve to form SO<sub>3</sub><sup>2-</sup> ions. The electrochemical reduction of SO<sub>3</sub><sup>2-</sup> will compete with the oxidation of itself to SO<sub>4</sub><sup>2-</sup> by the dissolved oxygen. However, without a catalyst, this oxidation process is slow<sup>27</sup>. Under this condition, the SO<sub>2</sub> gases may stay long enough in the solution to act as a cathodic depolariser according to the following cathodic reduction reaction as suggested by Rozenfeld:



This is especially so since SO<sub>2</sub> gas is more soluble in water when compared to oxygen, and therefore it might be reduced more readily than oxygen at the cathodic site. This will allow the anodic dissolution rate to increase.

Although this argument may be true, other workers<sup>23</sup> has demonstrated that it will only happen in conditions when the metal is exposed to an exceptionally high concentration of SO<sub>2</sub> and in an environment where the oxygen is depleted, which is not the case in the actual atmospheric environment condition.

In fact, the study done by A. Cox and S. B. Lyon<sup>28</sup>, on the effect on sulphur dioxide on the corrosion of mild steel in a more realistic concentration of SO<sub>2</sub> in the atmosphere has shown that the reduction of SO<sub>2</sub> to other species is not evident, in an aerated thin film electrolyte. Hence although cathodic reduction is accelerated in the presence of SO<sub>2</sub>, this phenomena does not contribute significantly to the actual corrosion of metal in the atmospheric environment.

## **b) Corrosion by Oxides of Nitrogen**

The oxides of nitrogen present in the atmosphere are in forms of  $N_2O$ ,  $NO$  and  $NO_2$ . The concentration of  $N_2O$  in the atmosphere is between 0.25 – 0.5 ppm. This concentration, combined with its a low reactivity characteristic, causes  $N_2O$  to be unimportant in atmospheric corrosion. Neither  $NO$  nor  $NO_2$  causes direct degradation to metals. However,  $NO_2$  may react with water from the atmosphere to form nitric acid, which has deleterious effect on metal surfaces. Studies on the effect of  $NO_x$  has been quite limited. Haynie<sup>24</sup>, in his work on the direct and synergistic effects of relative humidity, sulphur dioxide, nitrogen dioxide and ozone on corrosion rate of steel, found that  $NO_2$  produce neither accelerating nor inhibiting effect. Johansson<sup>25</sup> found that  $NO_2$  causes little corrosion on polished mild steel, copper, zinc and aluminium at the temperature of 22°C and humidities of 50% and 90%. However, when combined with  $SO_2$ , the corrosion of mild steel at 50% and copper at 90% is significant.

Nitrogen oxides has been reported<sup>25,26</sup> to cause stress corrosion cracking in copper based alloys. This was thought to be due the reaction of nitrogen oxide and the metal surface to form ammonium salt. The mechanisms of corrosion by nitrogen oxides have not been thoroughly understood. Although some attempts were made, the explanation offered were non satisfactory.

## **c) Corrosion by Chloride ions**

Corrosion of metals by chloride ions normally occur in the coastal areas. Though chloride ions are known to stimulate corrosion of metals, the actual mechanisms involve are still not very clear. However, it is known that chloride ions promotes pitting or stress corrosion cracking, and is very common in the corrosion of easily passivating metals.

As mentioned earlier, the actual corrosion mechanism of metals caused by chloride ions is yet to be studied and clarified. However adsorption theory states that when chloride ions are adsorbed on to metal surface, it will compete with dissolved  $O_2$  or  $OH^-$ <sup>29</sup>. Once in contact with the surface,  $Cl^-$  favours the hydration of metal ions and therefore promote the accumulation of electrolyte. This formation of electrolyte will then facilitate the dissolution

of the metal into its ions. The adsorbed chloride will further help to increase the exchange current (decrease overpotential) for anodic dissolution.

If the metal surface has an oxide layer, Cl<sup>-</sup> ions will penetrate the oxide films through pores or defects found on this layer. Other effect of Cl<sup>-</sup> ion on oxide film, is the colloidal dispersion of the layer, causing an increase in its permeability. This phenomena accounts for the difficulty of iron and stainless steel to passivate in a solution containing an appreciable concentration of Cl<sup>-</sup> ions. Instead, these metals will continue to dissolve at high rate, both in the active and passive potential ranges. This effect is so pronounce that iron and stainless steel are not readily passivated anodically, in a solution of chloride (with appreciable concentration).

The breakdown of passivity of metal surface caused by Cl<sup>-</sup> ions occurs locally rather than generally. The preferred sites being determined perhaps by small variations in the structures of the passive film and its thickness. This promote the formation of minute anodes of active metal surrounded by large cathodic areas of passive metal. The potential difference between these areas are large enough to create high current densities at the anode causing high rate of metal dissolution. This is accompanied by the cathodic protection of the metal area immediately surrounding the anode. This fixes the anode position and results in pitting corrosion. The fixed position of the anode and the protected surrounding cathodic area will result deep pitting which is far apart from each other. Infact observation of the corroded metal surface will reveal that the number of deep pits per unit area is always less than the density of the smaller shallow pits.

The lesser extent of pitting corrosion to metals known to be quite resistant to chloride ions like titanium, tantalum, molybdenum, tungsten and zirconium as compared to non resistive metals like iron, chromium, nickel, cobalt and stainless steels, is probably because the former metals have higher affinity for oxygen than the latter, making it more difficult for chloride ion to displace oxygen from the passive layer.

Another factor that must be mentioned here is about further activity of the Cl<sup>-</sup> ion after formation of the corrosion products. It is found that the activity of chloride ion is greatly influenced by the reaction products form. If the products can form stable basic chloride, such as those found in zinc, copper and cadmium, then further chloride

ion activity will be reduced. In the case of iron, no stable basic chloride is formed, thus it is affected by action of chloride far more strongly than the former metals.

#### **d) Corrosion by Hydrogen Sulphide, Hydrogen Chloride and Chlorine**

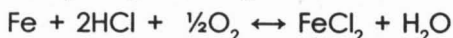
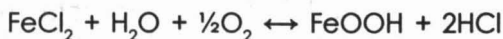
The corrosion of metals caused by these species is treated collectively in this paper due to the fact that, though their effects are very profound, they are related customarily to locally-occurring industrial emissions.

Hydrogen Sulphide is an extremely reactive pollutant. It is capable of reaction with most metals used in construction of buildings, including the relatively more stable ones like copper or silver. They are known to react even with very small amount of hydrogen sulphide to form tarnish sulphide layers are known to deteriorate the electrical properties of the metals.

Corrosion of metals by hydrogen sulphide can occur very rapidly with the primary formation of sulphides as the product. Thus copper corrode in hydrogen sulphide to form CuS. Other metals with high affinity for sulphide ions also corrode rapidly in hydrogen sulphide to form primary sulphide products which will then be converted to other compounds through secondary reactions. Rusted form of iron samples, exposed to high concentration of hydrogen sulphide were found to contain S(II), S(0) and S(IV) species.

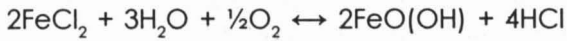
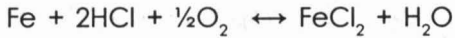
The early studies on corrosion of metals by hydrogen chloride was done by Feitnecht<sup>30</sup>, Barton and Bartonova<sup>31</sup>. The experiments concluded that, for a metal surface exposed to atmospheric hydrogen chloride (in concentration of 10<sup>-4</sup> to 10<sup>-2</sup> percent by volume) the gas is first adsorbed on the surface. Reactions with the surface will only occur if a critical humidity is exceeded, to produce the corresponding metal chloride.

Barton and Bartonova, in the same paper, further proposed the following reaction mechanism for corrosion of iron in HCl gas after the initial formation of FeCl<sub>2</sub>:



These reactions were found to be independent of the rate of diffusion of the reacting species to the corrosion product-metal interface but are controlled by the rate of chemical reaction itself.

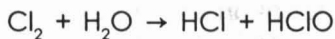
In another experiment, Askey et al.<sup>32</sup>, exposed mild steel to HCl whose concentration presentation rate to the atmosphere was close to that found in urban areas. He found that the corrosion rate was 18 times faster than in an unpolluted area. However, increasing the HCl presentation rate further, did not result in any significant increase in corrosion rate. From these observations, the workers suggested the following reaction mechanisms:



The suggested mechanism revealed a reaction cycle. HCl reacts with iron to produce ferrous chloride which will then be oxidized to FeO(OH) with HCl being again produced. The reproduced HCl will again react with iron to produce fresh ferrous chloride and the cycle continues. Therefore, it can be seen here that once the reaction has started, further reactions are independent of external source of HCl.

Metallic corrosion caused by chlorine may be severe but is rarely responsible for the profound corrosion promotion in the atmosphere. Normally chlorine concentration in the atmosphere is higher in industrial areas that has chemical plants. The effect of chlorine on corrosion of metals is due to its high solubility in water.

Chlorine reacts with water according to the following reaction:



The ClO<sup>-</sup> ion produced is able to promote the cathodic reduction reaction:



While the produced chloride ion will now influence the anodic reaction as mentioned in the earlier discussions. Other factors that must also be considered, is the production of hydrochloric acid from the first reaction that causes the acidification of the surface electrolyte.

It should also be noted that the hygroscopic nature of the chloride ion produced will lower the critical humidity for the corrosion processes to occur. This will lengthen the time of wetness and thus promote corrosion.

The effects of both gaseous hydrogen chloride and chlorine on metal corrosion are more intense than that of



chloride ions from salts. This is due to the acidic character of the two former species that cannot be compensated by the corrosion product and thus quicken the dissolution process of metals.

### **e) Effects of Solid Matter'**

Dust seems notably influential in the initial stages of atmospheric corrosion when there are still no other corrosion products formed. However, when the products are already formed, most likely it will assume complete control of the corrosion processes. The effects of dust on metallic corrosion depend greatly on its constituent and its solubility. Solid matter that contains sulphate, chloride and similar anions are known to accelerate the anodic processes. The other factor that must also be considered, is whether it is hygroscopic in nature or not. A "hygroscopic solid matter" may promote condensation of moisture and therefore increase the time of wetness. On the other hand, solid particles with very high water uptake ability, such as silica gel or soot, bind water very strongly to itself that it is not available for electrolyte formation.

Thus, solid matter deposited from the atmosphere may or may not exert an accelerating influence on atmospheric corrosion, depending on its solubility, chemical components and characteristics.

## **CONCLUSION**

In many respects the above discussion on atmospheric corrosion is not a complete one. A great deal of studies on other aspects of atmospheric corrosion has been done and is still progressing, that is not mentioned in this paper. However it is hoped this paper will serve to provide a general understanding on the processes involved in atmospheric corrosion.

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