Investigation of the Effects of Physicochemical Behaviour, Design, and Contaminants on Corrosion Mechanisms for Coatings

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Abstract

Advanced coating systems have been developed to address the challenges of coating life and corrosion mechanisms in various industries. These coating systems are designed to provide enhanced protection, prolong the lifespan of coated surfaces, and reduce the effects of corrosion. A corrosion study with respect to contaminants (water soluble salts like sulphates, chlorides and nitrates etc.), design of the components (macro and micro defects developed due to improper design and physic-chemical behaviour of coatings (adhesion, permeation of air and moisture) etc. was done by several scientist and found that these elements prove to be the deciding factors in rate of corrosion. In addition to metal surface preparation, coating thickness, permeability to water and oxygen, and coating chemistry, the existence of soluble salts (chloride, nitrate, and sulphate) and their effect on the coating-metal interface were investigated. Corrosion is also a result of macroscopic flaws brought on by poor handling, design, and construction. Surface irregularities have their own role in determining the life of the coating. The corrosion process can be slowed down or stopped by certain coating solutions.

Keywords: Corrosion, contaminants, resins, coatings, corrosion mechanism.

INTRODUCTION

The slow degradation of a material brought on by an electrochemical or chemical reaction with its surroundings is known as corrosion. Metals have a higher electric conductivity than non-metals, such as ceramics, plastics, rubber, concrete, etc., and their corrosion is typically electrochemical in nature. Corrosion is the breakdown of non-metallic, electrically non-conductive materials due to chemical processes [1].

On the atomic scale, a metal surface that appears smooth and uniform from a macroscopically perspective actually has a mosaic or lineage structure, while the crystal substructure is made up of blocks that have been somewhat deformed due to uneven crystal development. The disarray of metal lattice can be caused by vacancies, dislocations that are often linked to surface steps and long terraced growth spirals, as well as by grain boundaries and sub boundaries [2]. Additionally, some macroscopic defects may arise from inadequate design, processing, welding, handling, or operation. Mechanical actions such as rolling, rubbing, and sliding cause strain on a material's surface. Differentiating electrochemically from its surroundings, a worn surface can lead to several kinds of corrosion [3].

The majority of significant macroscopic defects are caused by the presence of stress, especially tensile stresses. Numerous aspects of materials,

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including chemical reactions, mechanical strength, and electrical qualities, are also influenced by all of these surface flaws. As a result, corrosion is basically a surface phenomenon, and resistance to corrosion frequently arises from a coating that forms on the metal surface. Both the surface activity and mechanical properties of metals and non-metals can be altered by the surface active substances that are present on them. Tribological characteristics of solid surfaces, such as adhesion, deformation wear, friction, etc., are highly dependent on the active molecules or ions that have been absorbed from the surface (i.e. environmental elements) [4].

The way organic coatings work is by shielding substrates from chemical and physical damage. On the other hand, under certain situations—such as when the substrate is contaminated—the coating may actually facilitate this attack rather than impede it. Two main phenomena can occur at the coating-metal interface: blistering (local osmotic cells) of the coating and under film corrosion. These can be caused by soluble foreign ions, such as sulphate, or chloride or leached ions (from the coating in presence of trace amounts of water and oxygen). Blister formation and growth can also be caused by other mechanisms, such as phase separation, swelling during film production, temperature cycling, adhesion loss, etc. [5, 6].

EFFECT OF CONTAMINANTS

The existence of pollutants, such as water, oxides, salts, moisture and organic compounds, among others. The performance of coatings is negatively impacted on steel surfaces before coating materials are applied. It is difficult to completely remove these chemicals. In industrial and marine environments, respectively, sulphate and chloride ions are the most prevalent pollutants. The combustion of coal and other fuels, as well as seawater spray which, depending on the wind, can travel many kilometres inland are the sources of these pollutants. Contamination with chloride can also come from de-icing salts used on public highways. Saline deposits with a gross characterization were seen on the organic coatings used on bridges. Anions included carbonate, sulphate, nitrate, and chloride; cations were mostly found in sodium, calcium, and ammonium, as well as cations that leached out of pigments. Sulphur dioxide, which is also widely dispersed, is a major air pollutant in places with dense populations and substantial concentrations of industry [7, 8].

BLISTERING AND ADHESION

Blister formation in organic coatings on metal surfaces, especially steel, is thought to be primarily caused by osmosis among other causes. Here, osmotic pressure may range from 2500 to 3500 kPa , but the coatings' mechanical resistance to deformational forces is much lower, at 6 to 40 kPa. Blisters form when there is a loss of adhesion in that particular place; the covering remains intact in the remaining areas. Even before the blistering became apparent, the sticky tape test showed a reduction of adhesion. It is evident that while the interfacial forces maintain the film on the substrate in the vicinity of the blister, they are insufficient to withstand the force exerted by the tape [9]. Anodes and cathodes can link electrolytically directly due to the weaker coating/metal contacts. Oxygen depolarizes cathodic regions in electrochemical corrosion by generating hydroxyl anions. The intense alkaline reaction of the aqueous solution in these blisters is caused by cations migrating to cathodic regions and forming NaOH in the presence of salts, such as NaCl, which act as electrolytes. Cations may migrate through the coating or along the coating-metal interface and end up in cathodic regions. Even though the films are somewhat permeable, the diffusion rates of Na cations are extremely sluggish [10]. The initial concentration of osmotically active substances in the film-substrate interface is frequently lower than that of the external aqueous solution of NaCl in salt-spray or immersion studies. This disparity increases the cation diffusion through the coating to the cathodic regions of the metal surface. Thus, blister formation in cathodic sites is caused by the migration of sodium ions from paint film [4].

The most common mechanism that coatings use to control corrosion is creating a physical barrier between the metal surface and the surrounding environment. This barrier prevents moisture, oxygen, and other corrosive substances from reaching the metal surface, thereby inhibiting the corrosion

process. Coatings achieve this barrier effect through various means, such as forming a protective film, layer, or barrier on the metal surface. These coatings can be applied in the form of paints, primers, sealants, or specialized coatings designed specifically for corrosion protection. Thus, the primary goal of coatings in corrosion control is to create a protective barrier that prevents the underlying metal from being exposed to corrosive elements, thereby extending the lifespan of metal structures and Equipments.

ORGANIC COATINGS

Paints that guard against rust can now be produced at a very high quality. An organic coating should last 15 to 20 years with proper surface preparation and adequate film thickness. Pores, crater, mechanical damage, and regions with low film thickness, such as edges, are typically the only places where corrosion occurs more quickly (Figure 1).

These flaws are typically impossible to completely prevent. Because of this, it is crucial that the paint be able to stop rust from spreading around any defects in the surface. Regarding the coating's lifespan, the metal substrate profile is also crucial. Poor flow is experienced by the very viscous coating on a surface profile with an even peak-to-valley pattern. A fast-curing, extremely viscous coating will not wet out a profile with bent-over peaks, broken surfaces, etc. of course, water will quickly fill any gaps in the coating-metal contact at the point of penetration, fostering the chemical reactions required to generate blisters [1, 11].

We also know that the coatings degrade one molecule at a time, rather than failing by the square inch. The results of blast cleaning were noted. Excellent flow out on a protective coating was supplied by the physical arrangement of metal surfaces that had been prepared by silica sandblasting or aluminum oxide blasting. It was discovered that steel shot's crater-like profile offered the best flow-out properties, whilst steel grits had the least favourable surface.

When applying protective coatings using the airless spray method, there are typically more cavities or trapped bubbles in the film than when using a standard sprayer applicator. This implies that the application method affects coating life as well.

There has been a new plasma coating technology that greatly increases car steel's resistance to corrosion. The majority of research has been conducted on certain water-soluble pollutants, such as iron sulphate and sodium chloride. For the investigation, a variety of organic binders and water-soluble pollutants, such as sulphates, chlorides, and nitrates, are collected [12].

Corrosion prevention involves implementing measures to inhibit or mitigate the degradation of metal surfaces caused by chemical reactions with the surrounding environment. Two of the most important factors to consider in corrosion prevention are:
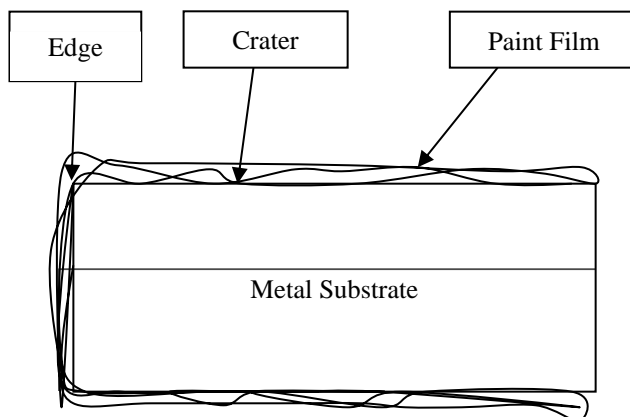

Figure 1. Weak Point of a Coatings.

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Protective Coatings or Paints: Applying protective coatings or paints to metal surfaces creates a barrier between the metal and corrosive elements such as moisture, oxygen, and chemicals. These coatings act as a protective shield, preventing direct contact between the metal surface and the corrosive environment. Examples of protective coatings include epoxy coatings, polyurethane paints, and corrosion-resistant primers.

Galvanic Protection: Galvanic protection methods are used to prevent corrosion by controlling the electrochemical reactions that occur between different metals in contact with each other. This is important because when two dissimilar metals come into contact in the presence of an electrolyte (such as moisture), an electrochemical reaction known as galvanic corrosion can occur. Other important considerations for corrosion prevention include proper material selection, regular inspection and maintenance, controlling environmental factors (such as temperature and humidity), and implementing corrosion management strategies tailored to specific applications and environments.

EXPERIMENTAL

The varnishes, which were designated in the same sequence as the resins in the accompanying table, were made by dissolving the selected resins composition (Table 1) in appropriate solvents with an acceptable consistency for brush application.

Glass panels and cold-rolled mild steel were ready for various tests. Using Ford Cup No. 4, the viscosity of the prepared binder solution was determined. According to conventional test procedures, the films were examined for hardness, adhesion, corrosion scratch resistance, acid and alkali resistance, and adhesion. To prepare artificial sea water (a representative sample) for the corrosion scratch test, the following chemical amounts were dissolved in one litre of water as shown in Table 2.

TEST FOR CORROSION SCRATCH

The mild steel panels measuring dimensions 50 mm X 100 mm X 1 mm thick were cleaned, sanded, and coated.

The coated panels were allowed to cure completely for seven days at room temperature in the laboratory. Wax was used to edge them, and a sharp blade was used to scuff one side of each panel against the substrate. After 500 hours of exposure to artificial (synthetic) sea water, the panels were cleaned with distilled water and dried before being checked for rust. Periodically, the samples were examined to assess blistering and rusting. The adhesion and groove were identified using standard procedures [13].

HUMIDITY TEST

Panels made of mild steel that had not rusted were cold rolled. The specimen was contaminated on one side. As controls, clean steel panels were utilized. Reagent grades and distilled water were used to create solutions of sodium chloride, sodium sulphate, and sodium nitrate. After applying the clear coatings, the coated specimens were allowed to cure completely for a week at room temperature in the laboratory. A strippable coating was then applied to safeguard the specimens' uncontaminated reverse side. Wax was used to seal the edges. Two coating thicknesses of 20 μm and 60 μm were applied. 100 hours and 400 hours were the exposure times. Throughout the test, the specimens were closely examined for blistering and rusting in accordance with ASTM D714 and D610, respectively. By weighing the samples both prior to the application of the pollutants and following the test and removal of the coating and corrosion products, the gravimetric method was used to calculate the under film corrosion rate [14].

RESULTS AND DISCUSSION

Each and every varnish underwent the following laboratory tests: adhesion, hardness, corrosion scratch test, acid resistance, and alkali resistance [13, 14]. The acquired results are summarized in Table 3.

Table 1. Resins/Binders with Their Composition.

S.N.	Resins	Compositions
1.	Phenolic	Oil soluble alkyl modified phenol formaldehyde
2.	Polyurethane	Polyester resin and aliphatic isocyanate (42:38)
3.	Cardanol	Cardanol-epoxy (3:1)
4.	Alkyd	64% oil length Long linseed oil

Table 2. Composition of Artificial Sea water.

S.N.	Salt	Weight. g
1	NaCl-Sodium chloride	23.5
2	$MgCl_2$-Magnesium Chloride	5.1
3	Na_2SO_4-Sodium Sulphate	3.9
4	$CaCl_2$-Calcium Chloride	1.1
5	KCl-Potassium Chloride	0.66
6	$NaHCO_3$-Sodium bicarbonate	0.2
7	KBr-Potassium Bromide	0.1
8	H_3BO_3-Boric Acid	0.25
9	$SrCl_2$-Strontium Chloride	0.24
10	NaF-Sodium Fluoride	0.003
11	Water to make	964.947
	Total	*1000*

Table 3. Test Results

Varnish Sample No.	Acid Resistance	Alkali Resistance	Corrosion	Adhesion and Hardness
1.	Passed	Passed	A*	Good
2.	Passed	Passed	A*	Good
3.	Passed	Passed	A*	Good
4.	Passed	Passed	A*	Good
5.	Passed	Passed	B**	Good

* Only rust in the groove; no spreading beneath the film; strong adhesion along the sides of the groove; no film flaws
** A little area of further rust beneath the covering, together with the rust in the groove, but no loss of adhesion

The findings of the humidity test after 100 hours and 400 hours of exposure are shown in Table 4. Rusting was rated visually and the findings were compared with the ASTM D-610 specification.

The blister performance at 100 hours and 400 hours is displayed in Table 5. By using a visual inspection, blistering was graded and compared to the ASTM D714 specification. After 100 hours and 400 hours, the gravimetric method was used to calculate the under film corrosion rate, which is displayed in Table 6.

All of the varnishes' laboratory test results are displayed in Table 3, where it can be seen that they all have good film properties and that, with the exception of one varnish based on alkyd, which has a slight rust spot under the coating, all of them have good corrosion protection in the corrosion scratch test [8]. The majority of corrosion activities occur at the coating-substrate interface, where the permeability of the coating determines the availability of oxygen. The chemical structure and coating thickness are the common factors that determine permeability. A non-polar binder has the opposite effect from a highly polar binder, which has good gas barrier qualities but is very vulnerable to water permeability. However, water permeability is usually more than what is required for the process of corrosion [15]. Even if an organic covering has a high oxygen permeability, corrosion cannot occur as easily as it can on a bare surface. Both oxygen and water are necessary for the cathodic response of the metallic substrate

corrosion, and their impacts on the corrosion process are discussed here. Table 4 shows that panels coated with vinyl polyurethane, phenolic, and cardanol have the lowest corrosion rates, whereas panels coated with alkyd usually exhibit the highest. Table 7 demonstrates that vinyl and alkyd have greater oxygen permeability than the other materials.

Table 4. Results of Humidity Test

Resin/binder (coating thickness in µm and concentration in mg/m²)	Rusting grade***					
	NaCl *Time (hours)*		*Na₂SO₄* *Time(hours)*		*NaNO₃* *Time (hours)*	
	100	*400*	*100*	*400*	*100*	*400*
Phenolic						
(20)*200**	10	10	9	9	9	10
(20)*700**	10	9	9	8	8	8
(60)*200**	10	10	9	9	10	10
(60)*700**	10	10	9	8	9	8
Polyurethane						
(20)*200**	10	10	9	8	10	9
(20)*700**	10	8	8	7	8	7
(60)*200**	10	10	9	9	10	9
(60)*700**	10	10	8	7	7	9
Cardanol						
(20)*200**	10	10	9	8	9	9
(20)*700**	9	9	8	7	9	8
(60)*200**	10	10	10	9	10	9
(60)*700**	10	9	9	8	9	8
Vinyl						
(20)*200**	9	8	9	9	10	9
(20)*700**	8	8	9	8	9	7
(60)*200**	10	10	10	9	10	10
(60)*700**	9	8	7	7	10	9
Alkyd						
(20)*200**	10	9	10	8	9	8
(20)*700**	9	8	8	7	8	8
(60)*200**	10	10	9	9	10	9
(60)*700**	9	9	8	7	7	8

- **film thickness in µm*
- ***concentration of contaminants (mg/m²)*
- ****ASTM D610 specification*
- *numerical rusting scale of rusted surface, exposed as area in % :10 for <0.03%, 8 for <0.1%, 7 for <0.3%, 6 for <1%, 5 for <3%, 4 for <10%, 3 for <16%, 2 for <33% and 1 for <50%*

Table 5. Blistering Outcomes.

Resin/binder (coating thickness in µm and concentration in mg/m²)	Rusting grade***					
	NaCl *Time (hours)*		*Na₂SO₄* *Time (hours)*		*NaNO₃* *Time (hours)*	
	100	*400*	*100*	*400*	*100*	*400*
Phenolic						
(20)*200**	10	*8MD*	*8MD*	*6MD*	*8MD*	*6M*
(20)*700**	*8MD*	*6MD*	*6D*	*4F*	*6F*	*4F*
(60)*200**	*8MD*	*6M*	*6M*	*4M*	*8F*	*6MD*
(60)*700**	*6MD*	*2MD*	*4MD*	*4F*	*4M*	*4F*

Polyurethane						
(20)*200**	10	8MD	8M	6MD	8D	6M
(20)*700**	10	6MD	6M	2F	4F	4F
(60)*200**	8MD	6D	6M	4M	8F	6D
(60)*700**	6D	2MD	4M	4F	4M	4M
Cardanol						
(20)*200**	8M	6MD	8M	6M	8M	6M
(20)*700**	8MD	6MD	6MD	4M	4F	2F
(60)*200**	10	8MD	6M	4M	8F	6F
(60)*700**	6MD	4D	4M	4F	4M	4F
Vinyl						
(20)*200**	6MD	6M	6M	6MD	8MD	8D
(20)*700**	4MD	4D	4M	2MD	2MD	2M
(60)*200**	8MD	6F	6F	6M	8M	8F
(60)*700**	8D	4F	4M	4F	6M	6D
Alkyd						
(20)*200**	6MD	6M	8M	6M	6F	6M
(20)*700**	6M	4F	6M	4F	4F	4MD
(60)*200**	8M	6MD	6MD	6M	8F	6MD
(60)*700**	6M	4F	4M	4MD	6M	4F

- *film thickness in μm
- **concentration of contaminants (mg/m^2)
- ***ASTM D714 specification
- numerical rusting scale :10-no blister, 8-smallest size blister can be seen with necked eyes and 6,4,2 in increasing order of blister size, D=dense, MD=medium dense, M=medium, F=few

Table 6. Under Film Corrosion.

Resin/binder (thickness in μm and concentration in mg/m^2)	Under film corrosion rate10^{-4}g/cm^2/day					
	NaCl Time (hours)		*Na$_2$SO$_4$* Time (hours)		*NaNO$_3$* Time (hours)	
	100	400	100	400	100	400
Phenolic						
(20)*200**	NO	NO	NO	NO	NO	NO
(20)*700**	8	NO	NO	NO	NO	NO
(60)*200**	NO	NO	NO	NO	NO	10
(60)*700**	NO	10	NO	15	28	20
Polyurethane						
(20)*200**	NO	NO	NO	NO	NO	NO
(20)*700**	NO	32	NO	NO	NO	NO
(60)*200**	NO	NO	NO	NO	NO	NO
(60)*700**	NO	NO	NO	NO	NO	NO
Cardanol						
(20)*200**	20	10	NO	NO	33	63
(20)*700**	180	96	20	8	87	72
(60)*200**	NO	NO	NO	NO	NO	NO
(60)*700**	NO	14	NO	NO	NO	21
Vinyl						
(20)*200**	NO	15	30	NO	NO	NO
(20)*700**	70	52	45	10	20	NO
(60)*200**	NO	NO	NO	NO	NO	NO

(60)*700**	NO	NO	NO	6	8	NO
Alkyd						
(20)*200**	40	33	21	8	14	21
(20)*700**	244	170	55	43	112	97
(60)*200**	20	9	NO	NO	12	6
(60)*700**	48	29	44	NO	27	19

- **film thickness in µm*
- ***salt concentration (mg/m²)*
- *NO= not observable*

Table 7. Water and Oxygen Permeability of Resins.

Types of Resins	Permeability	
	Water	*Oxygen*
	Mg/cm²/day	
Phenolic	17.41	8×10^{-3}
Polyurethane	16.12	13×10^{-3}
Cardanol	15.2	21.6×10^{-3}
Vinyl	3.34	113×10^{-3}
Alkyd	8.20	82×10^{-3}

Table 8. Occurrence of Atmospheric Sulphur Compounds According to ISO N43E.

Deposition rate SO_2, mg/m²/day	Concentration in air µg/m³	Atmosphere Type
0-25	0–28	Clean, rural area
25-65	28–70	Urban area
65-120	70–125	Industrial area
120-260	125–280	Heavily polluted area

Numerous specialists have also asserted that oxygen permeability, particularly in cases with low film thickness, is the primary component that governs the corrosion process. Consistent with previous research, the findings in Table 5 indicate that water at the coating-metal interface is the primary cause of adhesion failure. As water seeps through the film and reduces the concentration of contaminants, the coating functions as a semi-permeable membrane, allowing the contaminants to form blisters. Blister causes the covering to degrade (Table 7). Tables 5 and 6 demonstrate how the polar character of resins exhibits more blistering, as seen in phenolic and, polyurethane and the non-polarity exhibits stronger rusting, as seen in alkyd and vinyl. Water diffusion hence regulates the coating's loss of adherence. It is possible to conclude, based on Tables 4, 5, and 6, that 100 hours is long enough for water to soak through the coating and dissolve impurities that are present at the coating-metal interface, but not long enough to cause the coating to perforate due to rust growth or water accumulation. The kind of contaminants does not significantly affect the concentration of contaminants at the interface, which is susceptible to under-film corrosion. Low film thickness coatings are more susceptible to under-film corrosion. While corrosion is less affected by increasing coating thickness (above 35–40 µm to 60 and 80 µm), corrosion below 20 µm is highly reliant on film thickness. The oxygen permeability initially declines with increasing layer thickness and then nearly constant beyond a particular thickness [16, 17]. In addition to being hazardous from a biological standpoint, sulphur dioxide also exhibits a potent corrosive effect shown in Table 8.

A wet layer of rust absorbs over 100% of sulphur dioxide was quickly converted to sulphate, a hazardous substance involved in the corrosion process. extremely contaminated The sulphate ion that is generated when iron sulphate is oxidized to iron oxide (Fe_2O_3) reacts with more iron. The relationship between the rate of sulphur dioxide deposition and integral corrosion is depicted in Figure 2.
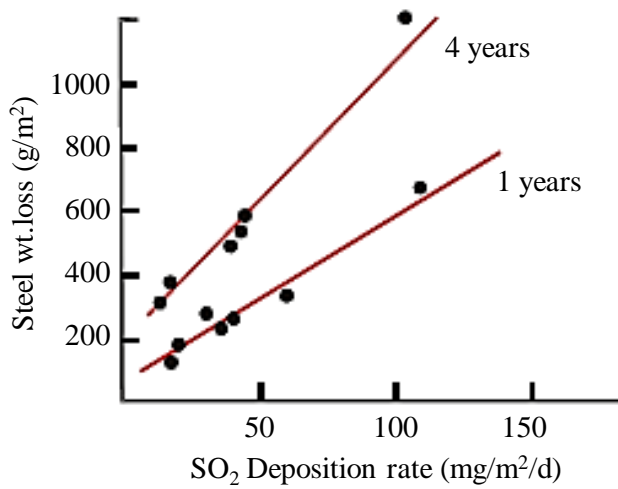
Figure 2. Integral Corrosion vs. Sulphur Dioxide Deposition Rate.

Table 9. Airborne Salinity Occurrence According to ISO N53E

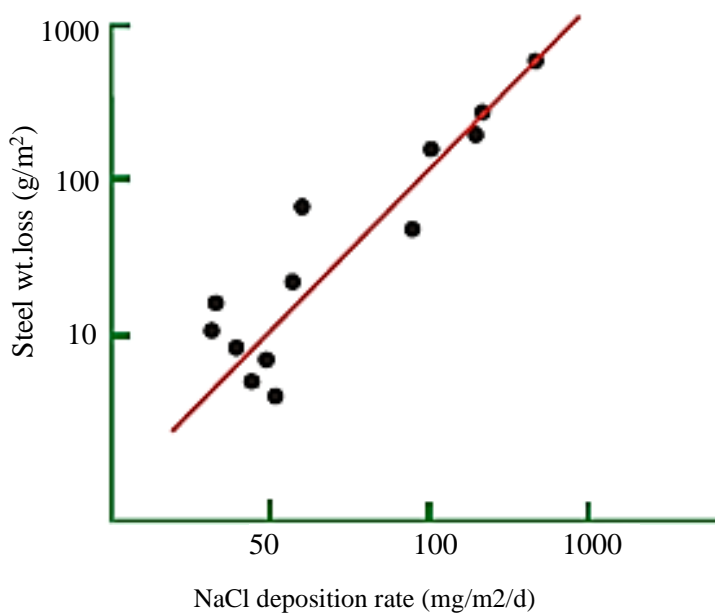| NaCl deposition rate mg/m²/day	Atmosphere type
Up to 40	Clean, rural area > 200–300 meter from sea level
40 to 80	Marine, <200 meter from sea level
80 to 450	Marine, outside splash zone area
450 to 1400	Splash zone area

NaCl deposition rate (mg/m2/d)

Figure 3. Integral corrosion vs. Sodium chloride Dposition Rate.

In the natural world, sodium chloride is primarily found around coasts and is not widely distributed in road salt. Table 9 provides rates of outdoor deposition [16]

Due to the soluble and hygroscopic nature of iron chlorides, their increased surface conductivity, and their active prohibition of passivation, sodium chloride has a stimulating effect on corrosion [8]. When

exposed outdoors without air pollution, there is a direct correlation between the rate of sodium chloride deposition and integral corrosion (Figure 3).

Table 10. Solubility of Reaction Product

Reaction salts product	g dissolved salts/100 g H_2O
$FeCl_2$	68.1 at 20°C
$FeSO_4$	low soluble
$Fe(NO_3)2.6H_2O$	82.9 at 20°C

As can be seen from Table 10, the solubility of pollutants at the interface is low for sulphates and high for nitrates due to their high osmotic pressure, high solubility, and low dilution, which results in a low corrosion rate [8, 18].

CONCLUSIONS

It is concluded that there is no universally applicable mechanism of cathodic dissolution, rather, interfacial separation rather than cohesive failure due to coating deterioration is more prevalent in coatings that are more resilient to alkaline hydrolysis. When the oxide is thick, it can sometimes be an indication of impending disbondment because hydroxyl ions are easier to get at the metal oxide contact than at the oxide-polymer junction. Stopping the oxygen influx will reduce the rusting to some degree. Additionally, it is evident that even with low film thickness, sodium sulphate does not exhibit notable corrosion and that chloride contaminations are more corrosive than nitrate contaminations. Moreover, corrosion might be more heavily supported by

1. Regulating osmotic pressure, which is also influenced by the kinds of impurities present at the coating-metal contact.
2. The saline solution's conductivity at the interface is another crucial element that influences how quickly corrosion occurs when conductivity rises.
3. Other crucial factors in corrosion are coating thickness and structure. First, corrosion reduces with thickness; after a given thickness, corrosion nearly always remains constant. Additionally, it has been noted that double layer coating, which provides a parallel film thickness, is superior to single thick coating in terms of corrosion management.
4. The corrosion process known as under film corrosion is determined by the concentration of the corrosion stimulant and the presence of oxygen.
5. The aqueous electrolyte solution's osmotic pressure, ionic conductivity, oxygen solubility, and water solubility of the corrosion products all influence the steel corrosion's kinetics.
6. If the metal surface is not adequately prepared for coating, even the greatest protective coating may fail prematurely due to disbonding.

According to the study, metal protection and coating performance can both be greatly enhanced by properly planned coating systems put on the substrate with a basic understanding of coatings. For the convenience of research academics, researchers, industrialists, etc., a concise summary of the investigations conducted by different scientists is provided here.

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