Role of air microbes on atmospheric corrosion

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Microorganisms enhance deterioration of materials of construction. In the present study, the influence of air microbes on existing concrete pile and on mild steel coupons is reported. *Pseudomonas* sp., *Bacillus* sp., *Micrococcus* sp., *Moraxella* sp., *Anthrobacter* sp., *Streptococcus* sp., *Staphylococcus* sp. and *Acinetobacter* sp. were identified on the concrete pile. The growth and distribution of bacteria was due to the presence of humidity and SO_2 in the atmosphere of the industrial area, leading to the proliferation of microbes on the materials under study. Corrosion rate of mild steel in polluted site was found to be 0.116 mmpy, whereas in an unpolluted site it was only 0.021 mmpy. The higher rate was due to the simultaneous action of pollutants and air microbes on corrosion of materials. The study shows that the atmospheric corrosion of materials in polluted environment was due to significant contribution of the combined action of heterotrophic bacteria, iron bacteria, manganese oxidizing bacteria and thiobacilli.

Keywords: Atmospheric corrosion, bacteria, mild steel, polluted environment.

SEVERAL factors, namely humidity, SO_2, Cl^- level, etc. affect atmospheric corrosion of steel. The corrosion rate of steel in industrial areas tends to be high because of high concentration of SO_2 in the atmosphere. Besides, Cl^- concentration in the atmosphere is usually high at the sea coast, although the concentration varies greatly from coast to coast and season to season, depending on the direction and the strength of prevailing winds, which also influence atmospheric corrosion. Industrial atmospheres that contain appreciable amounts of SO_2 and $FeSO_4$, formed by the corrosion reaction, accumulate in small, shallow and discrete corrosion pits, 0.5–1 mm in diameter, on the steel surface under mounds of the corrosion product films and named as 'ferrous sulphate nests' by Schwarz[1], who discovered their existence. Sulphate (SO_4^{2-}) anions migrate to the anodic sites (pits) and a greater number of these nests are formed in atmospheres with higher concentration of SO_2. Microorganisms can live in many environments such as water, soil and air where aerobic bacteria, fungi and algae can develop. Growth of bacteria is enhanced by the presence of mineral ions[2] from N, P, S, Fe, Mn and Ca. S-oxidizing bacteria are aerobic bacteria that oxidize elemental S or S-bearing compounds, producing H_2SO_4, which is highly corrosive to many metals. *Thiobacillus ferroxidans* and *T. thiooxidans* are capable of growing under acid pH values (1.0 or less). Ferrobacteria obtain their energy from the transformation of Fe^{2+} to Fe^{3+} salts. This occurs in anodic zones, accelerating the formation of rust. Fe-oxidizing bacteria, such as *Gallionella*, *Sphaerotilus*, *Leptothrix* and *Crenothrix*, oxidize iron from Fe^{2+} ion (a soluble form) to Fe^{3+} ion, which is insoluble[2]. Fe and Mn bacteria may be aerobic and oxidize Fe^{2+} to Fe^{3+}, which can attract the Cl^- and produce $FeCl_3$. In the literature, the bacteria-induced corrosion in atmospheric corrosion studies has not been reported. In the present study, the presence of air microbes in an industrial (polluted) environment and their action on deterioration of mild steel and existing structures, viz. steel rods and concrete structures has been investigated.

Mild steel (C, 1–2%; Mn, 0.1–0.2%; P, 0.40–0.50%; S, 0.02–0.03%) coupons of 6×4 in size were used to study atmospheric corrosion. The coupons were machine-polished to mirror finish and degreased with trichloroethylene and rinsed with deionized water.

The prepared coupons were exposed[3] in the atmosphere of a petrochemical industry located nearer to Karaikudi, Tamil Nadu, where sulphur is used as the main raw material for production. The chemical factory is 5 km away from Karaikudi. Some coupons were also exposed in the sheltered and unpolluted environment at the Central Electrochemical Research Institute (CECRI), Karaikudi. After 24 days of exposure, the coupons were removed to study corrosion rate and microbiological analysis. Besides, the samples for microbiological analysis were also collected from an existing telephone concrete pile located just opposite to the chemical industry. Concrete pieces and corroded reinforced rods were collected in sterilized containers and transported to the CECRI Microbiology Lab for microbiological enumeration and identification.

After 24 days of exposure, the specimens were removed from the location cited above and the biofilms were scraped-off from all the specimens using a sterilized knife. The biofilms were diluted separately, adding 9 ml of sterilized distilled water to each. Distilled water was also used to study the blanks. The total viable bacterial counts was enumerated by pour-plate technique using *Thiobacillus* agar medium, Mn agar medium, Fe bacterial agar medium and nutrient agar medium (Hi Media, Mumbai). Next, 1 ml aliquot of appropriate dilution was pipetted out into the sterilized petri plates and 20 ml each of nutrient agar medium, *Thiobacillus* agar medium, Mn agar medium, Fe bacterial agar medium was added separately into each petri plate. Each of the samples was mixed thoroughly by rotating the plate, clockwise and anticlockwise, and allowed to solidify. The inoculated plates were incubated at 37 ± 0.1°C. Duplicate plates of each of the above petri plates were also maintained. The bacterial counts were made after 24–48 h of incubation. Petri

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plates with 30–300 colonies were selected and the total viable bacterial counts were made. The bacterial population was expressed as the number of colony forming units (CFU) per ml of water sample containing the biofilms.

Morphologically dissimilar and well-isolated colonies were randomly selected and streaked onto each of the nutrient agar medium, *Thiobacillus* agar medium, Mn agar medium and Fe bacterial agar medium plates to obtain pure cultures. After noting colony morphology along with colour, the selected pure colonies were subcultured in each of the nutrient agar slant, *Thiobacillus* agar slant, Mn agar slant and Fe bacterial agar slant. The slant cultures were then stored at 4°C in a refrigerator for further biochemical analysis. Subcultures of the bacterial strains were made once in 30 days to keep the bacterial strain viable. The bacterial strains isolated from mild steel coupons were identified up to generic level by employing the standard characteristics described in *Bergey's Manual of Systemic Bacteriology*.

The initial weight of each of the specimens was measured to ±0.1 mg. After 24 days, the final weight of each of the steel specimens collected from the telephone poles just opposite the industry and the control specimens exposed at sheltered and unpolluted environment were measured, and the corrosion rates were calculated using the formula:

$$\text{Corrosion rate} = \frac{534\,W}{DAT}\ \text{mpy},$$

where W is the weight loss in mg, D the density of the metal used, A the area in sq. inch, T the exposure time in h, and mpy, mils per year.

After 24 days, the exposed specimens were removed from the industrial area and the biofilms were scraped-off using a sterilized knife. Both the control and the experimental specimens were dried at 60°C on a hot plate. These dried biofilms were transferred to eppendorf tubes and subjected to XRD analysis. The XRD patterns were recorded using computer-controlled XRD-system, Panalytical, Model: MPD (Multi purpose diffract meter θ–2θ) with CuK_α radiation (wavelength λ = 1.5418 Å, Ni filtered) at a range of 40 kV, 20 Amp. The builtin Software for the Peak Search and Search Match programs was used to identify the peaks.

The dried biofilms were transferred to eppendorf tubes and the spectra were recorded between 4000 and 400 cm^{-1} wavenumbers on a Nexus 670 FTIR Spectrometer (Thermo Nicolet) equipped with the DTGS Detector and averaging of 128 scans. The spectrum resolution was 4 cm^{-1}. Datapoint resolution was approximately one point per wavelength. The digitalized spectrum was processed using OMNIC$^{(R)}$ software. To minimize problems arising from unavoidable base-line shifts and to enhance the resolution of superimposed bands, data of the first and second derivatives of the original spectra were smoothened.

SO_2 content was measured by SO_2^- meter, Model Toximate T, 11-OLDHAM, France and Cl^- content was estimated by wet-candle method[3].

The count of bacteria on exposed panels placed nearer to the chemical industry and exposed to sheltered area is presented in Table 1. The count of heterotrophic bacteria (HB), Mn-oxidizing bacteria, Fe and thiobacilli was 1.2×10^4, 3.4×10^4, 2.7×10^5 and 2.9×10^4 CFU/ml respectively in mild steel exposed to industrial polluted atmosphere (Table 2). In control panels (exposed at the CECRI area), no significant count was observed. In the existing concrete structure, count of HB, Mn oxidizers, Fe oxidizers and H_2SO_4 producers was 3.7×10^8, 1.9×10^8, 2.95×10^8 and 0.56×10^8 CFU/ml respectively. For the steel rod sample, the count of HB, Mn oxidizers and Fe oxidizers was 0.38×10^8, 0.32×10^8 and 0.4×10^8 CFU/ml respectively. The following isolates were identified in the existing structures of steel rod and concrete. *Bacillus*, *Micrococcus*, *Acinetobacter* and *Pseudomonas* as HB; *Streptococcus*, *Staphyloccus* and *Acinetobactor* as Mn oxidizers, and *Moroxella*, *Anthrobacter* as Fe bacteria. Microorganisms play an important role in promoting deterioration of porous construction materials. A study in Germany[4] indicated that microorganisms participate in at least half the cases of deterioration. It is well known[4–6] that bacteria of the genus *Thiobacillus* are responsible for the destruction of sewage pipelines by excretion of H_2SO_4. Two types of bacteria were implicated in biodegradation, viz. aerobic S-oxidizing bacteria (SOB) and anaerobic SO_4^{2-} reducing bacteria (SRB)[4,6,7]. In addition, Moosavi *et al.*[8] showed the effect of SRB on the corrosion of reinforced concrete in seawater. Rozhanskaya *et al.*[9] suggested that while studying the process of concrete corrosion, the activity of HB should not be ignored. Maruthamuthu *et al.*[10] investigated the influence of HB on concrete exposed to low Cl^- water system. Microbial corrosion of metals exposed to air in tropical marine environments was studied by Parra *et al.*[11]. In the present study, on existing structures of concrete and reinforced

Table 1. Enumeration of bacteria on existing structures of concrete and steel rod at industrial site

System	HB (CFU/ml)	Mn (CFU/ml)	Iron (CFU/ml)	*Thiobacillus* (CFU/ml)
Concrete	3.7×10^8	1.9×10^8	2.95×10^8	0.56×10^8
Steel rod	0.38×10^8	0.32×10^8	0.4×10^8	No colonies

Table 2. Enumeration of bacteria on mild steel exposed to industrial polluted atmosphere

HB (CFU/ml)	Mn (CFU/ml)	Iron (CFU/ml)	*Thiobacillus* (CFU/ml)
1.2×10^4	3.4×10^4	2.7×10^5	2.9×10^4

steel rod, significant number of Mn oxidizers, Fe oxidizers, H_2SO_4 producers and HB was noticed.

Cl^- and SO_2 levels during December 2005 were 38 and 12 mg/sq. m/d respectively, and relative humidity was above 85%. Temperature varied during the month[12] from 20°C to 30°C. Humidity and SO_2 in the industry area encouraged the proliferation of microbes on concrete and mild steel. In the present study, thiobacilli and H_2S-positive strains were also noticed, indicating that the adsorption of sulphide encouraged the growth of bacteria, and the physiological activity of bacteria may have reduced the pH of concrete and deteriorated the quality concrete and steel rod. Fe oxidizers converted Fe^{++} to Fe^{+++} and formed ferric oxides. Mn oxidizers reduced the strength of the steel rods by conversion of Mn^{++} to MnO_2.

XRD patterns for existing structure of steel rod and concrete are presented in Figure 1 *a* and *b*. XRD observations for steel rod revealed the presence of FeOOH, Fe_2O_3, FeOOH and Fe_3O_4. On concrete structure, $CaSO_4$, CaO, $CaSiO_3$ and calcium aluminium silicate were noticed.

XRD observations of steel exposed to the industrial area and sheltered area are presented in Figure 2 *a* and *b*. For the mild steel coupon exposed to the industrial area, FeS peaks were distinctly observed. A sharp peak was noticed at standard *d*-value of 1.931 Å of FeS. The control coupons exposed to CECRI revealed FeOOH, Fe_3O_4, FeOOH and FeO phases and revealed the absence of FeS.

Figure 3 *a* shows the FTIR spectrum of the steel rod with peaks at 3139 cm^{-1}, indicating the presence of NH for NH_2 group, and at 1708 cm^{-1}, indicating the presence of C=O group for the –COOH group. Another peak at 1632 cm^{-1} indicates the presence of SH stretch and CH, and that at 1442 cm^{-1} was noticed for CH_3 group. A peak at 1023 cm^{-1} revealed the presence of C=O structure for C–O–C alicyclic anhydride. Besides, for the substituted benzene, peaks at 879 and 796 cm^{-1} and for C–Cl, a peak at 465 cm^{-1} were seen on the existing structure of the steel rod.

Figure 3 *b* shows the FTIR spectrum for the concrete sample collected from the industrial area. NH stretch for $–NH_2$ group was seen at 3418 cm^{-1}. C=O stretch for CONH group was seen at 1875 and 1796 cm^{-1}. CH def CH_3 group was also seen at 1436 cm^{-1}. Another peak at 1038 cm^{-1} indicated the presence of carbonyl group (C=O stretch) of C–O–C alicyclic anhydride group. Besides, substituted benzene peaks were also seen at 876, 786 and 688 cm^{-1}.

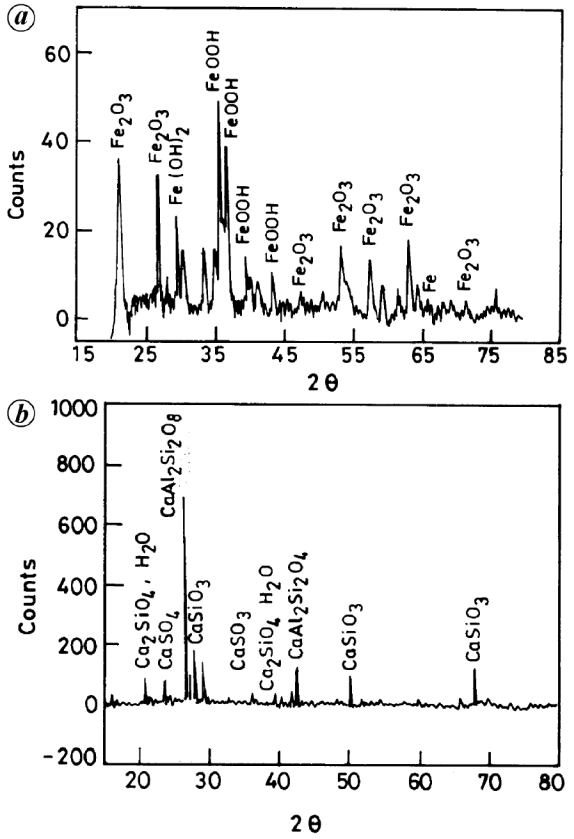

Figure 1. XRD pattern of (***a***) steel rod and (***b***) concrete exposed to polluted atmosphere of chemical industry.

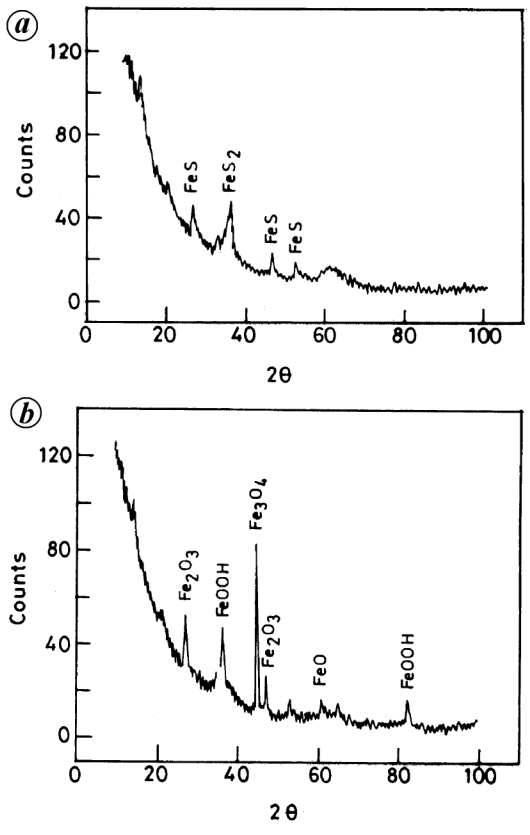

Figure 2. XRD pattern of mild steel exposed to (***a***) industrial area and (***b***) sheltered area.

Figure 4 *a* shows the FTIR spectrum of steel exposed at the industrial area. Peak at 3380 cm^{-1} revealed the presence of NH stretch for NH_2 group. Another peak at 1620 cm^{-1} indicated the presence of SH peak. Peaks at 1440 and 1353 cm^{-1} indicated the presence of CH def for CH_3 group. Another peak at 1019 cm^{-1} indicated the presence of C=O stretch. Besides, the presence C–Cl was seen at 458 cm^{-1}. In the control system (Figure 4 *b*), NH stretch, CH aliphatic stretch and CO stretch for C–O–C alicyclic group were identified at peaks of 3415, 2923 and 1020 cm^{-1} respectively. A peak at 1714 cm^{-1} indicated the presence of C=O stretch for the –COOH group. Besides, C=C of aromatic nuclei and CH_3 group were noticed for the control coupons. Presence of organic functional group indicates the adsorption of biofilms under atmospheric condition. It can be assumed that the corrosivity of steel in polluted areas depends upon the bacterial physiology by adsorption of sulphate.

The corrosion rate of mild steel exposed just opposite the chemical industry and the sheltered area of CECRI is presented in Table 3. The corrosion rate of mild steel exposed to the industrial area was 0.116 mmpy and that of sheltered area was 0.021 mmpy.

The stability of concrete exposed to the environment is governed largely by its ability to substantially maintain alkaline conditions. The concrete in contact with the environment may undergo gradual deterioration with decrease in pH. Durability of concrete is adversely affected by SRB and SOB, as was reported earlier[7,13]. However, the effect of corrosion by atmospheric bacteria on degradation of concrete and corrosion of reinforcement steel rod is less documented[11]. The effect of HB on concrete was investigated by Maruthamuthu *et al.*[10], who reported that the production of sugar by HB affects the durability of concrete. The present study concludes that atmospheric HB degraded concrete by dissolving in acid the Ca^{-} complex present in cement. The FTIR study on the concrete structure revealed the presence of the $–NH_2$ group, CONH, C=O stretch and C–Cl. It can be shown that these groups were due to the adsorption of biofilms on the concrete and mild steel coupons. The S-peak revealed the impact of air pollutants (SO_2) on the exposed mild steel. It can be claimed that the thiobacilli encourage the corrosion of steel. The study of XRD peaks indicated the presence of $CaSO_4$ on the concrete, and the large number of peaks due to ferric oxide formed on the steel rod. A sharp peak due to the presence of FeS on the exposed mild steel was also observed.

It has been reported that HB consume C and P from the environment, and if consumed in excess, the HB release them in the form of glucose-6-phosphate (G6P)[14]. Such bacterially produced G6P adversely affects the concrete. Because the specimens were exposed to sulphide-polluted environment, bacterial chelated compound of Ca^{++} might

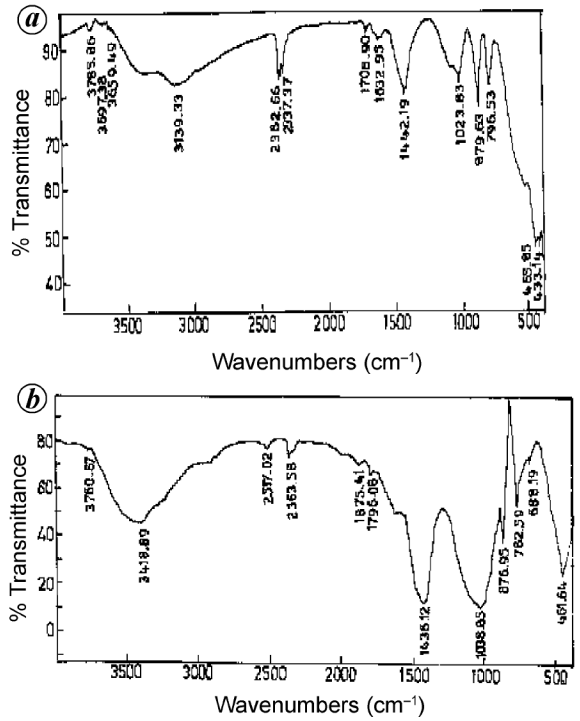

Figure 3. FTIR spectrum of the existing structure of (***a***) steel rod and (***b***) concrete collected from polluted industrial area.

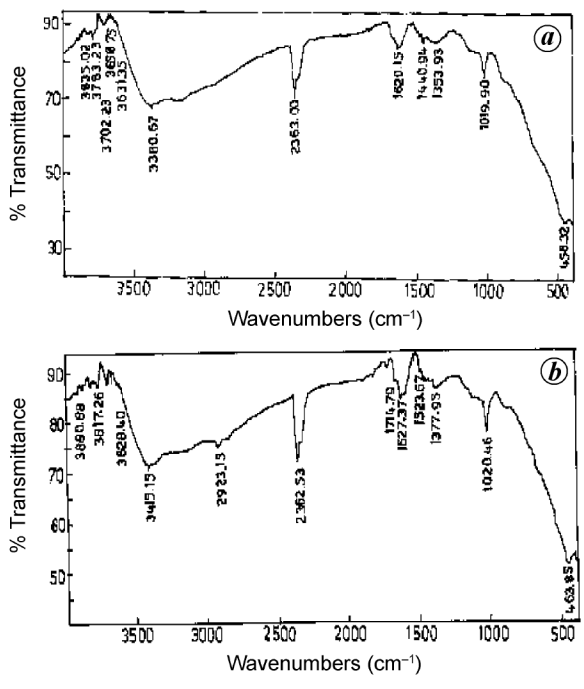

Figure 4. FTIR spectrum of (***a***) mild steel exposed to industrial site and (***b***) mild steel exposed to sheltered area (control system).

Table 3. Corrosion rate of mild steel in industrial and sheltered area

Exposure area	Weight loss (g)	Corrosion rate (mmpy)	Duration (days)
Industrial	0.9327	0.116	24
Sheltered	0.1682	0.021	21

have been converted into $CaSO_4$, the presence of which was noticed in XRD. The SO_4^{2-} might have been formed from SO_2 (air pollutant) in the presence of oxygen. The latter is well supported by the observations of May and Lewis[15] on the decay of buildings due to the action of bacteria. The corrosion rate of mild steel exposed to polluted site was 0.116 mmpy, whereas that exposed to (sheltered area) unpolluted environment was only 0.021 mmpy. The increase in corrosion rate was five times that of control. It is claimed that the higher corrosion rate was due to the role of pollutant with air microbes on the corrosion of specimens and that the atmospheric corrosion of specimens exposed to polluted environment was due to significant contributions of combined action of HB, IB, MOB and thiobacilli.

Microorganisms enhance deterioration of materials of construction and steel structures. In the present study, *Pseudomonas*, *Bacillus*, *Micrococcus*, *Moraxella*, *Anthrobacter*, *Streptococcus*, *Staphylococcus* and *Acinetobacter* were identified as the air microbes on a concrete pile. It is concluded that the deterioration is due to the presence of bacteria. The study by FTIR indicated the presence of NH_2 group, C=O stretch and C–Cl, which was due to the adsorption of biofilms on the specimens exposed to the industrial atmosphere. $CaSO_4$ and FeS peaks were noticed on mild steel and concrete exposed to the industrial area. Increase in corrosion rate of mild steel was five times more compared to that of control. It is claimed that the higher corrosion rate of steel was due to the simultaneous action of pollutants with the air microbes on the specimens. The atmospheric corrosion of concrete and steel exposed to polluted atmosphere of the chemical industry might be due to Mn oxidizers, Fe oxidizers, HB and acid producers.

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A generalized method for seismic evaluation of existing buildings

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Current Indian codes do not address the evaluation of seismic resistance of existing building stock, which may not have been designed for earthquake forces. An appropriate level of safety needs to be ensured for occupants of these buildings through strengthening measures, if found deficient. Existing buildings not designed in accordance with the philosophies of current seismic codes need to be assessed for their expected seismic performance in future earthquakes. The proposed method provides for a consistent yet flexible framework to assess the ability of existing buildings to reach an adequate level of seismic performance related to life safety of occupants. The elements of

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