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Microbiologically influenced tuberculation of carbon steel

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Abstract

The influence of dissolved oxygen content, microbial density and flow rates on the tuberculation of carbon steel was studied in tap water in the laboratory as well as in an open reservoir water. In the laboratory study, tuberculation was observed only in raw water under flowing conditions associated with high density of iron-oxidizing bacteria and ample supply of oxygen. Both nucleation and growth of tubercles were facilitated by increase in the flow rate of the water up to a maximum flow rate of 120 l/h. The coupons exposed to the open reservoir water under sunlit condition did not show well-developed tubercles, possibly owing to calcium carbonate precipitation on the coupons, mediated by algal photosynthesis. However, coupons exposed to the reservoir water under dark condition showed higher density of iron-oxidizing bacteria and well-developed tubercles. X-ray diffraction studies of corrosion products formed on carbon steel showed that ferrihydrite formed in the presence of iron-oxidizing bacteria is poorly crystalline. The present study supports the view that although IOB has a major role in the initiation, growth of the tubercles is controlled by an oxygen-concentration cell mechanism.

Keywords: Tuberculation, carbon steel, iron-oxidizing bacteria, ferrihydrite, oxygen-concentration cell.

1. Introduction

Raw-water cooling systems which employ carbon steel as the major material of construction experience tuberculation of the pipe surfaces. It is a form of concentrated cell corrosion and is observed on steel and cast iron surfaces exposed to oxygenated waters. Tubercles are mounds of corrosion products and deposits that cap localized regions of metal loss. It can choke pipes, leading to diminished flow and increased pumping costs.

Several case histories of tubercle formation have been reported in the literature.[1] For example, in a mill-water-supply system, leaks developed beneath large tubercles after 20 years of service. In another case involving a nuclear utility, turbine-cooling water system piping made of carbon steel was moderately tuberculated after two years of no treatment, resulting in 30% reduction in cross-sectional area. In the service water system of one of our own nuclear reactors, due to improper water treatment during the initial years of commissioning, the system led to heavy tuberculation and thinning of walls of the carbon steel (CS) pipes, finally resulting in replacement of small diameter pipes.[2] The association of iron-oxidizing bacteria (IOB) in the formation of tubercles has been noted by several workers.[3, 4] However, the role of microorganisms and different water-quality parameters, and how they bring about tuberculation is still unknown. The aim of the present study is to find out the importance of dissolved oxygen, microbial density and flow rate on CS tuberculation. Attempts were also made to distinguish microbiologically influenced corrosion (MIC) of CS from normal chemical corrosion by analysis of the corrosion products.

Table I
Composition of CS material

Element	C	Mn	S	Si	Fe
Wt%	0.3	0.59	0.034	0.1	Bal

2. Experimental procedure

ASTM A 106 Grade B carbon steel coupons (25 × 20 × 5 mm), obtained from pipe material (Table I), were polished up to a final 600-grit finish, cleaned and degreased with acetone. Immersion studies were done as per ASTM G 31.

The studies were carried out by exposure of coupons in water, sterile and raw, in conical flasks under closed, open, and open and aerated conditions, both in the laboratory as well as in an open reservoir. The coupons were also exposed to flowing water (under sterile and raw conditions) in Perspex tanks of 50-l capacity at two flow rates, namely, 3-7 and 120 l/h. The water was sterilized by passing through a commercially available water purifier. Since the microbial density in the sterile water increased to 10^4–10^5 cfu/ml after a few days, the experiment was discontinued after 10 days. In the open reservoir, one set of coupons was suspended in water from a stainless steel frame and exposed to normal day-and-night conditions (sunlit condition) and another inside a box with an open bottom, blackened to prevent exposure to sunlight (dark condition).

The CS coupons were withdrawn after various intervals of time ranging from 1 to 120 days. These are then subjected to detailed metallurgical, microbiological and microscopic studies. Water samples also were collected at frequent intervals and analysed for their chemical and microbiological contents. Corroded CS coupons were cleaned by chemical treatments with Clarke's solution and corrosion rate was assessed by weight loss method as per ASTM G1-90. X-ray diffraction (XRD) and particle analysis of the corrosion products were also done. The organic content of the deposit was estimated by calculating weight loss on heating at 650°C for 3 hours. IOB were cultured and identified as per the procedures given in Bergey's manual.[5]

3. Results and discussion

Corrosion rates of carbon steel coupons exposed to static raw water and sterile water under closed conditions and to both open and aerated raw water are shown in Fig. 1. There are many reports in the literature showing higher corrosion rates in nonsterile waters than in sterile waters.[3, 4] However, in the present study, very low corrosion rates were observed in both sterile as well as raw water under static conditions (Fig. 1). This might be due to decrease in dissolved oxygen (DO) with time, as both the sets were kept tightly closed to prevent contamination of the sterile system (Table II). The DO in water was identified as one of the major factors responsible for CS corrosion under various water-chemistry conditions.[6] In the present study, when CS coupons were exposed to static freshwater under aerated condition, providing ample supply of oxygen, an increase in corrosion rate (6.7 mpy) was observed. The density of IOB in the deposits at the bottom of flasks containing raw water under static and closed conditions was found to be 1×10^2 cfu/ml. Scanning electron microscopic (SEM) photographs of the 15-

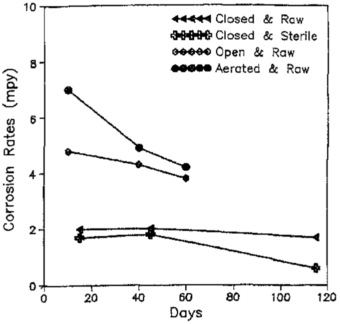

FIG. 1 Corrosion rates of carbon steel under various static water conditions.

day-old coupons showed was not seen on the coupons exposed for 45 and 110 days. In the static sterile sets, neither IOB nor tubercle initiation was observed. No visible tuberculation could be observed on coupons in static water under open and aerated conditions though the oxygen concentration was higher compared to static and closed conditions.

Coupons exposed to flowing raw water, which has sufficient amount of oxygen and microorganisms showed higher corrosion rates (Fig. 3) and initiation of tubercles in one month (Table III) which grew into well-developed tubercles within a period of 2–5 months. This is in contrast to the tests in static raw water, which showed no tubercles. The coupons exposed in the dynamic sterile system for 10 days showed black deposits on the surface compared to

Table II

Changes in water quality and bacterial density on the coupons exposed to tap water under static conditions in the laboratory

Experimental condition		Exposure time (days)	DO (ppm)	TVC in water (cfu/ml)	TVC on coupon (cfu/cm^2)	IOB on coupon (cfu/cm^2)
Tightly closed	Raw	0	7.8	3.0×10^6	—	—
		45	2.8	1.0×10^5	3.0×10^6	—
		110	2.3	5.0×10^4	3.0×10^5	—
	Sterile	0	7.8	—	—	—
		45	4.6	3.0×10^4	2.0×10^4	—
		110	0.3	1.0×10^4	2.0×10^3	—
Open (no aeration)	Raw	0	5.8	3.0×10^6	—	—
		40	5.9	2.8×10^6	3.0×10^6	—
		60	6.1	3.0×10^6	2.8×10^6	1.5×10^2
Open and aerated	Raw	0	8.1	2.0×10^6	—	—
		40	7.9	2.8×10^6	2.7×10^6	—
		60	8.2	3.0×10^6	3.2×10^6	1.2×10^2

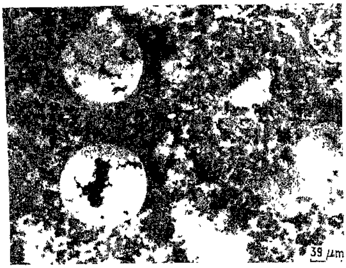

FIG. 2a SEM photograph of CS coupon exposed to static raw water for 15 days showing initiation of tuber-

FIG. 2b. SEM photograph of CS coupon exposed to static raw water for 45 days showing mounds of corrosion products that have not properly grown into a tuber-

brick-red deposits in the raw water samples (Fig. 4). Coupons exposed to flowing raw water started visibly accumulating small mounds of corrosion products within 15 days in the tank with faster flow rate (120 l/h). The tubercles on CS coupons showed brick-red-coloured deposits compared to dark blackish-brown deposits in the areas where uniform corrosion was observed (Fig. 5). Complete removal of the tubercle revealed bright metal surface (Fig. 6) and regions of accelerated attack with saucer morphology. The SEM photographs of this area showed an intergranular type of corrosion (Fig. 7). In some coupons, the edges where tubercles developed were totally distorted and this is shown in the coupon cleaned of all corrosion products (Fig. 8). The changes in the dissolved oxygen content and the density of different types of bacteria on the coupons are given in Table III. The density of IOB was higher (3.2×10^4 cfu/cm^2) on these coupons compared to that on the coupons exposed to static raw water (1.5×10^2 cfu/cm^2).

IOB play an important role in the corrosion of water pipes.[7] Kuhr and Vlugt[8] also showed that aerobic bacteria caused the formation of tubercles in water pipes, while anaerobic bacteria further enhanced the rate of attack within tubercles. Many workers have observed IOB associ-

Table III
Changes in water quality and bacterial density on the coupons exposed to tap water under flowing conditions in the laboratory

Experimental condition		Exposure period (days)	DO in water (ppm)	TVC in water (cfu/ml)	TVC on coupon (cfu/cm^2)	IOB on coupon (cfu/cm^2)
Slow flow rate (3-7 l/h)	Sterile	0	7.2	2.0×10^1	—	—
		10	6.9	1.0×10^2	2.0×10^2	—
	Raw	0	7.8	3.1×10^6	—	—
		10	7.1	3.2×10^6	3.8×10^6	4.2×10^3
		60	6.9	2.5×10^6	4.2×10^6	5.6×10^3
		120	7.0	2.0×10^6	4.0×10^6	2.8×10^4
Fast flow rate (120 l/h)	Raw	0	7.8	3.0×10^6	—	—
		10	8.1	3.8×10^6	4.0×10^6	6.0×10^3
		60	7.9	3.0×10^6	5.5×10^6	3.2×10^4

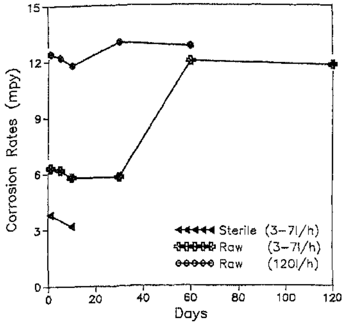

FIG 3 Corrosion rates of carbon steel under various flowing water conditions

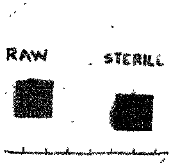

Fig 4 Carbon steel coupons exposed in static water and sterile water for 10 days showing brick-red corrosion products in raw water and black corrosion products in sterile water

ated with tubercles over pits on steel surfaces and IOB play an important role in the corrosion of CS pipes in freshwater.[9, 10] Metallic iron is unstable in water, corrodes, and releases Fe^{2+} ions into the medium. IOB is attracted to the source of Fe^{2+} ions and utilize them as their energy source by oxidizing them to ferric ions.[11] Little and Wagner[12] observe that iron is a component of respiratory enzymes such as haeme-containing and iron-storage compounds such as ferritin and ferrichrome. Electron transport through cytochromes to oxygen yields adenosine triphosphate (ATP), the chief energy source for a living cell. Since the reaction $Fe^{2+} \rightarrow Fe^{3+} + e^-$ yields very little energy (11.3 K cal/g-atom), large quantities of ferrous ion must be proc-

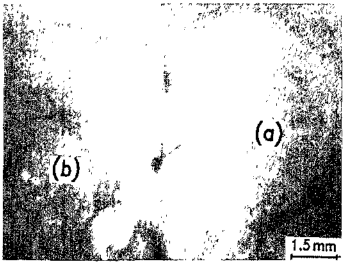

FIG 5 Stereomicroscopic photograph of carbon steel coupon with (a) growing tubercles (yellowish brown) and (b) tubercles that had stopped growing (brownish

FIG 6. Stereomicroscopic photographs of carbon steel coupons where corrosion products are removed completely to show the bright surface of metal attack beneath tubercles.

FIG 7. SEM photograph of the cleaned CS coupon showing intergranular type of attack beneath the tubercle.

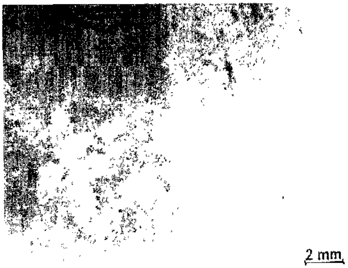

Fig. 8. Cleaned carbon steel coupon showing unevenly corroded edge of the coupon beneath tubercles formed on exposure to running tap water.

essed to meet the cell energy requirements. Due to their capacity to oxidize iron and their requirement for large quantities of ferrous ion, IOB are a potential hazard in the freshwater-cooling systems where CS is used. IOB exist in a metastable condition as they compete with oxygen, as well as utilize it for iron precipitation.[7] The tubercle and associated IOB, which are themselves efficient scavengers of oxygen, consume the oxygen which attempts to enter the under-tubercle region.[12] This may lead to the development of oxygen-concentration cell in which the region under the tubercle is free of oxygen, while the outside region is relatively oxygen-rich. Therefore, in CS tuberculation, microbes (IOB) help in the establishment of oxygen-concentration cell under the tubercles. So, in the absence of oxygen, neither chemical nor biological corrosion could take place explaining the observed low corrosion rate and insignificant difference in the corrosion rates between sterile and raw water under static and closed conditions. However, the absence of tuberculation in static raw water under open and aerated (oxygen-rich) conditions and presence of well-developed tubercles in the dynamic raw-water conditions showed the importance of flowing water in the tuberculation. In the literature, a case study[13] on CS corrosion in a plant river-water system showed that stagnant conditions favoured neither IOB growth nor tuberculation due to scarcity of DO, whereas velocities of 2–7 ft/s with moderate DO content encouraged tuberculation in the same systems. The present study confirmed that tuberculation of CS does not occur in stagnant conditions with very low DO content. Medium flow conditions with ample supply of DO (6–8 ppm) led to an increase in the density of IOB (2.8×10^4 cfu/cm^2) associated with severe tuberculation. Increased flow rates (120 l/h) in this experiment led to faster tuberculation and increased corrosion rate, along with higher density of IOB (3.2×10^4 cfu/cm^2). However, literature data showed that very high flow conditions[14] are not favourable for tuberculation. Therefore, the relationship between flow and tubercles is dichotomous. Tuberculation occurs only under flowing conditions and fails to grow under no flow or very high flow conditions. Case studies further confirm this observation, as equipment experiencing severe turbulence-like pump impellers never showed tubercular growth. Water-flow rates could influence the growth of tubercles by replenishing dissolved oxygen, aggressive anions, suspended particulate and

Table IV
Changes in water quality and the bacterial density on the coupons exposed to reservoir water under sunlit and dark conditions

Experimental condition	Exposure period (day)	DO in water (ppm)	TVC in water (cfu/ml)	TVC on coupon (cfu/cm^2)	IOB on coupon (cfu/cm^2)
Sunlit	0	7.7	8.0×10^6	—	—
	10	7.6	8.1×10^6	7.0×10^6	—
	60	8.0	3.0×10^7	1.8×10^7	1.8×10^2
	120	8.3	2.8×10^7	4.9×10^6	3.0×10^3
Dark	0	7.7	8.0×10^6	—	—
	10	7.6	8.1×10^6	1.0×10^5	—
	60	8.0	3.0×10^7	4.2×10^6	3.7×10^2
	120	8.3	2.8×10^7	5.2×10^6	2.0×10^4

microbial cells. In the present study, organic content of the deposits forming the tubercles was 10.9%.

The exposure study of CS coupons in the open reservoir (field conditions) under sunlit and dark conditions also supports the oxygen-concentration cell mechanism. Total density of different types of viable bacteria on the CS coupons exposed under both dark and sunlit conditions is given in Table IV and the corrosion rates are plotted in Fig. 9. Tubercles were initiated on all the coupons, both in dark and sunlit conditions. However, the areas in between the tubercles formed on the coupons exposed under sunlit conditions were covered with algal mats in a short time (Fig. 10). After 5 months, well-developed tubercles were observed only on coupons exposed to dark conditions where there was no algal settlement.

Detailed analysis of CS corrosion products revealed several interesting features XRD analysis of corrosion products on CS exposed for 10 days both in raw and sterile water yielded

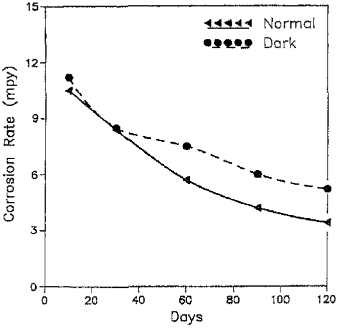

FIG 9. Corrosion rates of carbon steel in reservoir water in 'normal and 'dark' conditions

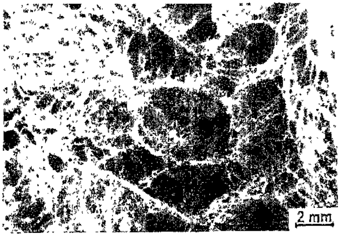

FIG 10. Stereomicroscopic photograph of algal fibres on CS coupon exposed in open reservoir under normal day-and-night conditions

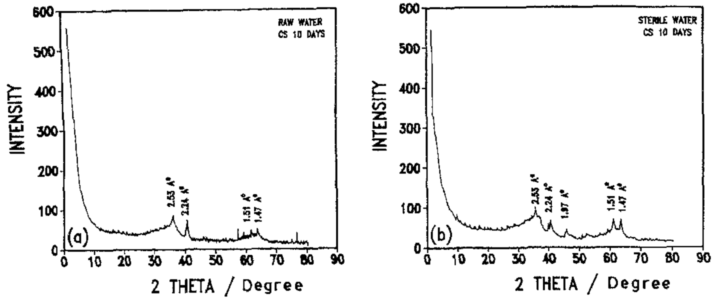

FIG 11. X-ray diffraction pattern of corrosion products formed on CS coupons exposed for 10 days in (a) raw water and (b) sterile water.

ferrihydrite (Fe (III) oxide, $5Fe_2O_3.9H_2O$) (Fig. 11). However, the degree of crystallinity of ferrihydrite was different in sterile and raw-water systems. According to Tuhela *et al.*,[15] the number of XRD peaks as well as the position of the most intense peak can be used as an indicator of the ferrihydrite crystallinity. In the XRD pattern of well-crystalline ferrihydrite[16], six distinct peaks corresponding to d-values of 1.47, 1.51, 1.72, 1.97, 2.21 and 2.53 Å are present with the d-value of the main peak being 2.53 Å. XRD of the corrosion products obtained from raw-water experiments showed smaller peaks at 1.47, 1.51 and 2.21 Å and absence of peaks at 1.97 and 1.72 Å. This indicates poor crystallinity of the ferrihydrite formed in raw water compared to that formed in sterile water. Carlson and Schwertmann[17] had also suggested that poorly ordered ferrihydrite forms aggregate more readily than better-ordered ferrihydrite explaining the clumping of the corrosion products and thereby nodule initiation leading to tuberculation. According to Schwertmann and Taylor[18], although ferrihydrite is thermodynamically unstable and usually less well ordered compared to lepidocrocite (γ FeOOH) and goethite (αFeOOH), it seems to be kinetically favoured under conditions where Fe(III) is supplied at very high rate, like in the case of rapid oxidation of dissolved Fe(II). Such rapid oxidation may take place in the presence of IOB. The rapid accumulation of the ferrihydrite mediated by IOB can initiate nodules. Therefore, the principal role of microbes (IOB) in CS tuberculation is to initiate the establishment of corrosion cell by the formation of nodules.

XRD analysis of the corrosion products which formed well-developed tubercles on CS showed maghemite (γFe_2O_3) and goethite (α FeOOH) peaks (Fig. 12) compared to peaks of ferrihydrite in the small nodules (initial corrosion products). XRD analysis of the deposits on the CS coupons exposed to sunlit conditions in the reservoir water showed dominant peaks of $CaCO_3$ (calcite) along with maghemite (γ Fe_2O_3) (Fig. 13). Earlier studies[19] had shown that utilization of CO_2 for algal photosynthesis shifts the pH to higher values, leading to $CaCO_3$ precipitation. Since the $CaCO_3$ scale insulates the metal surface from the environment, the oxygen-concentration cell will not be effective, preventing the growth of tubercles. Studies by other workers[20,21] also suggested that calcium carbonate coatings prevented corrosion and in

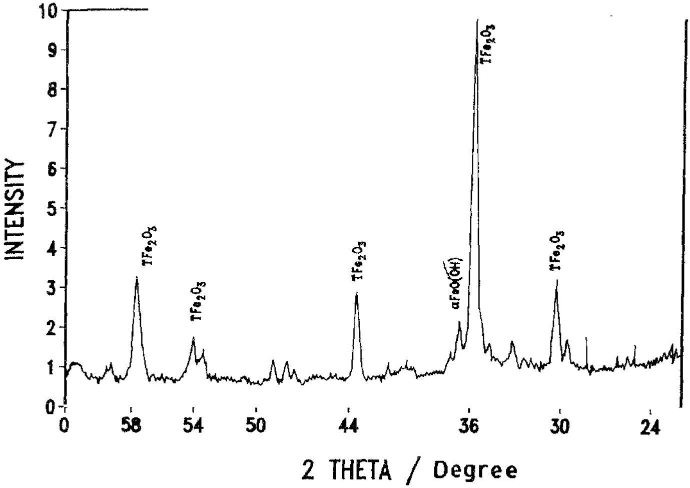

FIG 12. X-ray diffraction pattern of corrosion products formed on CS coupon (tubercle) exposed for eight months in running tap water.

many cases, lime treatment was used to eliminate 'red-water' complaints. Carbon steel coupons exposed to dark conditions, where prominent tubercles developed in five months, did not show any algal attachment or CaCO$_3$ peaks in the deposit analysis. Thus, it appears that the

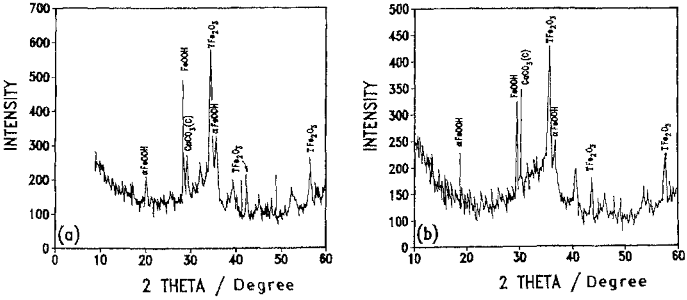

FIG. 13. X-ray diffraction pattern of corrosion products formed on CS coupons exposed for five months in (a) dark reservoir water and (b) normal reservoir water.

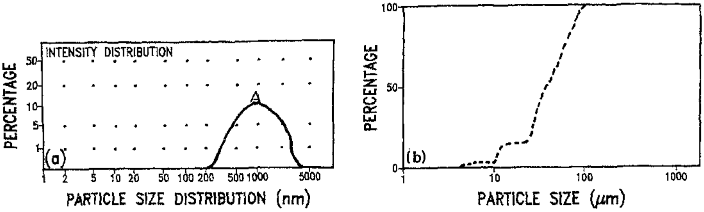

FIG 14. Particle-size distribution of corrosion products formed on CS coupons exposed in (a) raw water (10 days) and (b) sterile water (10 days).

maintenance of oxygen-concentration cell is more important in the growth of tubercles, though IOB play an important role in the initiation of tubercles. Earlier workers[12] had shown that tubercles of ferric hydroxide on CS created under-deposit corrosion, which was independent of the biochemical activity of the bacterial cells. Some case studies[22, 23] had also shown that coatings of cement, coal tar or deaeration with oxygen scavengers prevented CS corrosion drastically.

The present study on CS tuberculation has important relevance with respect to the problems of corrosion and tuberculation in cooling-water systems. Figure 15 shows thick iron bacterial filaments on CS specimens exposed to the cooling-water system of one of the reactors in Kalpakkam. Filaments of IOB, found in our CS specimens used for laboratory studies are shown in Fig. 16. The present study has shown that although the tuberculation of CS is initiated by IOB, the growth of tubercles is maintained under constant supply of oxygen irrespective of the bacterial density. Hence, treatment with biocides and chlorine must be undertaken in a clean system to prevent tubercle initiation. In an infested system under-deposit attack may progress unless steps are taken to disrupt the oxygen-concentration cell which appears to be the principal mechanism of carbon steel tuberculation.

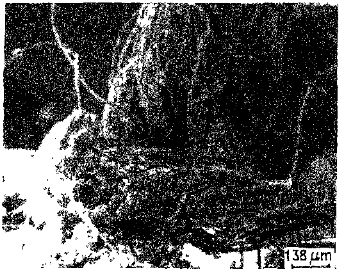

FIG. 15 SEM photograph of thick iron bacterial filaments on coupons exposed to cooling-water system.

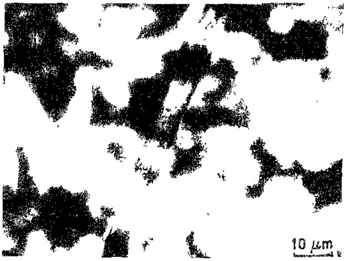

FIG 16. Optical microscopic photograph of iron bacterial filaments on corroded coupons exposed to laboratory studies

Many workers have referred to a noncrystalline amorphous phase associated with MIC of steel and cast-iron pipes.[24] Analysis of the particle size of the CS corrosion products in the raw-water systems showed significantly smaller particle size compared to the corrosion products in sterile system. Some earlier Mossbauer studies have also indicated the association of a colloidal phase with microbial corrosion of steel and cast-iron pipes.[25,26] In the present study, very small particle size (~1 μm) and noncrystallinity, which assist in the clumping of the corrosion products, were found to be associated with IOB-mediated tuberculation (Fig. 14).

5. Summary and conclusions

Microbiologically influenced tuberculation of carbon steel was studied by exposure of coupons in flowing water in the laboratory as well as in an open reservoir under sunlit and dark conditions. The salient results and conclusions are the following:

1. Tuberculation of carbon steel was found to initiate on the coupons exposed in laboratory water when iron-oxidizing bacteria are present and these grew only when there is a minimum flow of water that ensures sufficient supply of oxygen (6–8 ppm) and nutrients. This suggests that corrosion of carbon steel under tubercles takes place by the formation and continued maintenance of oxygen-concentration cells.
2. No tubercles were formed on the CS steel coupon exposed under sunlit conditions in open reservoir whereas well-defined tubercles were observed on coupons exposed under dark conditions. This seems to be because of the formation of $CaCO_3$ scales resulting from photosynthetic activity of algae in the presence of sunlight.
3. XRD and particle analysis of corrosion products on CS showed poorly crystalline and smaller particles in the presence of bacteria. Since the poorly crystalline ferrihydrite formed in the presence of IOB has a tendency to form aggregates, it plays a major role in the initiation of nodules, which later grow into tubercles.

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