

Industrial corrosion failure – Case studies

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ABSTRACT

The significance of corrosive processes on industrial failures is possibly less appreciated in our country than other industrialized nations. Whereas, there has been a proliferation of corrosion consultants in developed countries, it is only of late that we see the Indian industries realising the need for specialized treatment of their corrosion problems. Indeed, corrosion failures are insidious, and universal in occurrence. The forms and manifestations of the corrosive processes are too numerous. Moreover since corrosion is a function of alloy composition, environment, component design, metallurgy, temperature and a host of other factors, generalization of corrosive processes and subsequent modelling proves to be futile. Thus corrosive failure analysis often turns out to be an exercise where component and industry specific diagnostic tools have to be employed, so that the failure analysis is often unique for the particular component tested. The solution of corrosive failures thus requires an understanding of the process environment, and sometimes an examination of the related processes, in addition to whatever information that can be gleaned from the affected component itself. The latter often requires thorough microscopic examination of the damaged part. Quite significant information about the corrosive process can often be found in the footprints left by the process, that is, the corrosion product or debris left near the site of corrosive attack. The analysis of the fluid environment that was in contact with the affected component is also often necessary. The microstructural examinations reveal irregularities in the component metallurgy as well as throw light on the physical manifestations of the corrosive process. Environmental analysis yields clues on the corrosive species responsible for the process. Corrosion product analysis helps in determining the chemistry as well as mechanism of the process. So, these exercises carried out simultaneously often reveal enough information about the damage mechanism. The present paper illustrates how the diagnostic methods can be employed to failure analysis through two case studies.

CASE I : IDENTIFICATION OF CORROSION MECHANISM IN A BOILER DRUM BY CORROSION PRODUCT ANALYSIS

The corrosion of boiler drums is intimately linked to the deterioration of the protective oxide film separating the steel substrate from the boiler fluid, which often contains constituents conducive to corrosion. Various forms of corrosion occur in the boiler drums and such occurrences can be due to (i) improper water treatment practices, (ii) improper maintenance and cleaning, (iii) faulty operation and improper service condition and (iv) improper material selection. Since the material requirements for conventional boilers are not very stringent, the latter is rarely to blame for corrosion damage of boiler drums.

In all cases of corrosion, a compromise of the protective oxide film next to the steel substrate has to occur prior to material degradation. Ideally a ferric oxyhydroxide (FeOOH) film would be the best in terms of passivity, however such a film quickly degenerates to the less protective but still adequate magnetite (Fe_3O_4) layer. It is evident that to identify the type of corrosion in a boiler drum, knowledge of the oxide film structure is essential, in addition to information on the water chemistry, the boiler material metallurgy and the service conditions. In this article we present how the particular type of corrosive attack in a boiler drum interior could be identified by analysing the corrosion product, layer by layer. The degradation mechanism was implicit in the analysis of the material near sites of corrosion, each stratum of the corrosion layer corresponding to different degrees of deterioration of the oxide film.

Salient Features

During annual inspection, the interior of a boiler drum that had seen active service for more than thirty years, was found to have areas of intense local corrosion. The boiler drum material had the following composition: (in weight %)

C	S	P	Mn	Si	Ni	Cr	Fe
0.23	0.108	0.041	0.65	0.15	0.10	0.15	Balance

The operational pressure and temperature of the boiler were 6.8 MN/M^2 (200 lb/in^2) and 300°C respectively. The areas of attack were characterized by mounds of corrosion product 20–30 mm in height. On removing the loose corrosion product, craters were revealed showing metal gouging. The larger craters were upto 25 mm in diameter and had depths of upto 10 mm which was a significant fraction of the wall thickness (25 mm) of the drum. All areas of attack were located near the six-o-clock position of the horizontal drum and near joints of welded brackets that supported a distributor pipe and near expansion joints connecting

the downcomer pipes with the drum interior.

Investigative Procedure

A detailed investigation of the corrosion damage was carried out that included feed water analysis, boiler water analysis, corrosion product analysis and in-situ replication of the damaged areas followed by microscopic observation. In this article, the results of the corrosion product analysis shall be presented with some reference to the replica studies.

After opening the boiler drum for inspection and prior to any other operation, the tubercles/mounds of corrosion product were sectioned with a fine chisel into five approximately horizontal layers and each layer stored separately. The material thus obtained were in loose powdery form with some thin flakes. These were analyzed by Energy Dispersive Spectroscopy (EDS) using a Scanning Electron Microscope (SEM), which yielded the elemental composition of the different strata of the corrosion product. The powders were also analyzed by X-ray Diffraction (XRD) using Co-K α radiation. The various phases in the corrosion product were identified by referring to various powder diffraction files of the JCPDS (Joint Committee on Powder Diffraction Studies).

After the corrosion products had been removed, the underlying craters were prepared for in-situ replication. The surfaces were ground with a portable grinder and then polished by different grades of emery paper and finished by cloth polishing with alumina paste (0.05 mm). The polished area were etched with 2% Nital solution, followed by cleaning with methanol and acetone. The process of replication involved moistening of cellulose acetate tape with acetone and then sticking it to the polished surface. The acetate tape was peeled off after it had dried. Replicas were also obtained from undamaged regions of the drum interior for comparison. The replicas were observed under SEM.

Observations

Microstructural observation of the replicas revealed that irrespective of the location, ferrite and pearlite were observed with some evidence of banding (Fig. I.1). Fig. I.2 shows a higher magnification microstructure of the substrate beneath the craters. It is evident that there is no discernible deterioration of the cementite in terms of spheroidization of the lamellae of cementite in the pearlite colonies. There is no evidence of cracking, intergranular or transgranular, which rules out the possibility of any form of stress corrosion cracking. The latter was a possibility since craters can act as crack initiators and in the presence of residual stresses or operational cyclic or static stresses, hydrogen embrittlement, caustic embrittlement and corrosion fatigue are often observed.

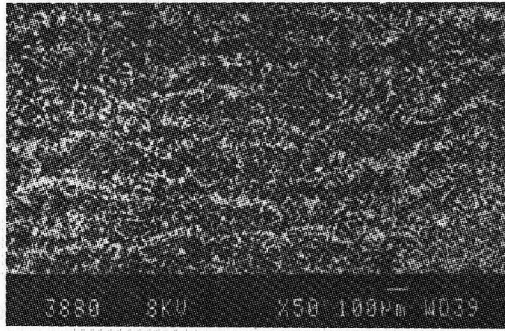


Fig. I.1 : Low magnification microstructure of the boiler drum material

The results of the analysis of the corrosion products are tabulated in Table 1. It must be appreciated that the choice of five layers was a practical consideration and there was no presupposition as to the nature of the layered structure. Some intermixing of compounds in the different layers was inevitable and the distribution of the phases in the different layers was naturally continuous and not discrete as may be wrongly concluded from the layer wise analysis. The elemental analysis revealed significant presence of Ca, P and Si in the outer layers and their absence or insignificant presence in the inner layers close to the substrate. These are the elements constituting the scale forming compounds (Calcium carbonates, phosphates and silicates) whose presence in the outer layers was detected by XRD analysis. The presence of such scale formers in the outer layers was indicative of inefficient water treatment. Whereas these compounds are detrimental to heat flow, from a corrosion point of view they are benign. The most important revelation of the elemental analysis was the presence of C1 and S in all the layers and their significant presence in the inner layers.

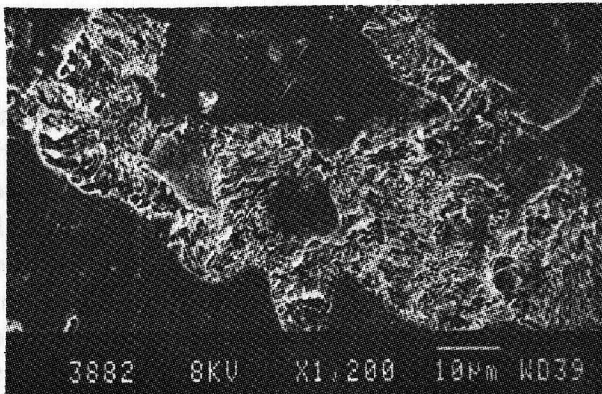


Fig. I.2 : High magnification microstructure of the substrate beneath the damaged sites

Table 1 : Analysis of the corrosion product layers

Layer #	XRD Analysis			EDS Analysis*
	Most prominent phase/s	Significant presence	Minor presence	Major elements** Present
1.	CaSO ₄ CaCO ₃ Ca ₅ (PO ₄) ₃ (OH) Fe ₂ O ₃	CaO.SiO ₂ .H ₂ O	Ca-silicates Ferrous chloride Ferric chloride Fe ₃ O ₄ SiO ₂	Ca, P, Si, Fe, Cl S, Na, Mg
2.	Fe ₂ O ₃ Fe ₃ O ₄		Ca-phosphate SiO ₂	Fe, Ca, P, Si, Cl S
3.	Fe ₃ O ₄	Fe ₂ O ₃	SiO ₂	Fe, Ca, Si, Cl S, P
4.	Fe ₃ O ₄	α -FeOOH Fe ₂ O ₃	FeSO ₄ .H ₂ O Ferrous chloride	Fe, Cl, Si, S Ca
5.	α -FeOOH β -FeOOH Fe ₃ O ₄	Fe ₂ O ₃	FeSO ₄ .H ₂ O	Fe, Cl, S Ca

* Element with atomic number less than 12 cannot be detected by EDS, thus the presence of Oxygen and Carbon cannot be determined by this method.

** Elements are arranged in decreasing order of presence with the bold-faced elements showing significant presence

Deductions

The phase analysis by XRD revealed a sequential deterioration of the protective oxide film. The innermost layer contained protective ferric oxyhydroxid and magnetite. The relative amounts of these protective compounds diminish in the outer layers along with an increase in the amounts of the non-protective ferric oxide (Fe₂O₃), which was the only iron containing compound in the outermost layer. The presence of β -FeOOH in the innermost layer has special significance since the common ferric oxyhydroxides found in rust layers are α -FeOOH and/or γ -FeOOH [4-6]. β -FeOOH is found predominantly in steels exposed to chloride media, hence its presence corroborates the EDS finding of significant chlorine in the corrosion product next to the substrate. In view of the presence of

relatively small amounts of ferrous and ferric chlorides, it may be intriguing what compound accounts for the chlorine. This can be explained by the latter's solubility of upto a few weight per cent in β -FeOOH. It is possible that some chlorine containing transition compounds remained undetected during XRD analysis due to peak overlap. However, it is evident that chlorine and possibly sulphur has an important role in the overall corrosion process. This is obvious on examining the heights of the intensity peaks corresponding to chlorine and sulphur, in the different layers. The huge accumulation of chlorine and significant sulphur content near the substrate, as compared to the outer layers, indicate that these elements and especially chlorine, are causative agents for metal gouging.

With the help of replica studies, we could eliminate various forms of stress assisted cracking and intergranular attack as the causes of material degradation. The corrosion product analysis helped to rule out chelating corrosion and caustic corrosion, both being mechanisms known to produce craterlike material gouging. The former produces chelated iron complexes and the latter produces ferrites and hypoferrites, none of which was observed in the corrosion product. The location and appearance of attack and the data obtained by analysing the corrosion product indicated crevice corrosion as the mode of attack and the rest of this discussion will elaborate on this type of corrosion.

The regions susceptible to crevice corrosion are those where the corroding media can stagnate locally thus allowing selective accumulation of the harmful ions. As mentioned earlier, the various joints near the six-o-clock position of the drum were affected which were ideal sites for water stagnation. Chloride and sulphate anions accelerate the crevice attack once initiated. It would suffice to say that these anions lead to local acidification and consequent metal dissolution. The mechanism of attack in this particular instance was as follows. It is hard to say whether the successive deterioration of the iron oxide and oxyhydroxide is a consequence of chloride attack, or it occurred independently and simultaneously with the crevice attack. It is certain that such a deterioration of the oxide layer aided the propagation of the crevice attack. The nature and constitution of the overlying compounds was most conducive to crevice corrosion. The porous hematite, which was found even in the innermost layer, provided easy access for the Chloride (and Sulphate) anions to reach the substrate, where, by hydrolysis, local acidification occurred lowering the pH of the solution sufficiently to allow metal dissolution and metal gouging from the substrate. Chloride at least has some role in altering the overlying product. Some of the chloride is incorporated in the β -FeOOH formed on the exposed substrate, which naturally is much less resistant than other passive oxyhydroxide. In this fashion the various compounds formed overlying the craters are non-protective allowing the crevice corrosion mechanism to proceed unchecked.

CASE II : CORROSIVE DAMAGE OF FERTILIZER PLANT HEAT EXCHANGER TUBES

Leak was observed during service in heat exchanger tubes used in the synthesis section of the ammonia unit in a fertilizer plant. As many as ten tubes were found to have developed very fine pin holes. The manufacturers of these tubes were supplied with the failed tube, who were of the opinion that the leak was not due to manufacturing defects but might have been due to operational problems. They ascertained that the chemical composition and the mechanical properties of the failed tube were well within the acceptable range.

NML was requested to investigate the probable cause of such leakage. For this purpose tubes subjected to three different service conditions were provided namely, (i) tube containing pinhole due to service exposure, (ii) service exposed tube without pinhole, (iii) virgin tube.

Salient Features

The following operational and metallurgical features were given special consideration in our investigation and subsequent analysis.

- * The tubes were of SA179; they experienced synthetic gas on the shell side and cooling water on the tube side.
- * The water velocity through the tubes was about 1.17 m/sec
- * The water was given low chromate treatment. Chlorination was also practised.
- * Dissolved oxygen was not analyzed by plant personnel.
- * No abnormality in the water flow was observed
- * Ten pinholes were observed in various tubes.

Investigative Procedure

Our investigation was mainly microscopic along with semi-quantitative Energy Dispersive Spectroscopic (EDS) analysis of the corrosion products, scales and substrates. The investigative strategy involved thorough scanning electron microscopic (SEM) observation of the tube interior and exterior surfaces and the cut section (through thickness). EDS studies of various unusual microstructural features, corrosion products and scales were done with the objective of establishing the corrosion mechanism. In the tube which was supposed to contain pinholes, the location of pinhole could not be detected by liquid die penetration and soap bubble tests. Hence, we were forced to resort to sectioning the tubes and performing the tedious task of sequential polishing of such sections, observing them under a microscope and repolishing after removing some material (0.5 mm depth at a time). The choice of the first section was decided based on

the boroscopic observation of the inside surface of excessive corrosion layer. It was possible to locate a few partial pinholes. These were subjected to optical as well as scanning electron microscopic observations. Comparative observations of the virgin tube section as well as the service exposed undamaged tube were also performed.

Observations

Service exposed, undamaged tube

When a section was taken across the thickness, a layer of what appears to be corrosion product was observed close to the inner surface (Fig. II.1). Thin finger like intrusions into the matrix were also observed, a occurrence which may be significant considering the pinhole type of failure observed in other tubes. This corrosion product layer is about 50–150 μm thick. It may be deduced from the same micrograph that decarburization has occurred even near the inner wall of the tube. This decarburization would have some bearing on the mechanical properties, especially surface toughness and wear resistance. Although it would be presumptuous on our part to say that surface erosion would be accelerated due to the decarburization of the region adjacent to the inner tube wall, the possibility of such occurrence cannot be ruled out. It is also beyond our understanding as to how under the near ambient temperatures and the environment present inside the tube, decarburization could have occurred near the inner wall.

It is possible that the finger like projections shown in Fig. II.1 are the precursors to the pinhole actually observed in some other tubes. We believe that these porous layers are the results of a corrosion mechanism which left behind the porous intrusions, denuding the steel substrate of coherency and strength as well as providing the channel for water leakage. The corrosive mechanism will become clearer from the subsequent discussions. The next set of micrographs are of the interior surface of the tube and provide a good idea of the corrosive mechanism. The interior surface is seen to have corroded in a peculiar fashion (Fig. II.2). It is characterized by spherical and hemispherical particles (Fig. II.3) of varying sizes which are loosely bound to the surface, and areas having a relatively more adherent scale (Fig. II.4). The loose porous particles were analyzed and found to show Fe, Cl (Fig. II.5). It seems to us that these are chlorine rich oxides or hydroxides of iron (note : O and H cannot be detected by EDS). Such products are non-protective and allow easy access of the corrodent to the substrate. Evidently the chromate treatment was only partially successful in forming a protective surface scale, the chromate rich nature of such scales is noted from the EDS analysis of this scale (Fig. II.6).

Damaged tube

The severity of decarburization was evident in the damaged tube (containing pinhole) as shown in Fig II.7. The decarburization would have an indirect effect in accelerating pinhole attack. This would result in a softening of the inner and outer surfaces, and subsequent cratering of the inner tube surface, like the one shown, would be easy. These craters and pits act as initiation sites for pinhole attack.

The pinholes initiated at the inner surface, either from the bottom of craters or incipient pits. The growth of such pits were very insidious so that the extent of material removal was often not appreciated by a casual observation of the surface. This is very well illustrated in Fig. II.8, which shows a partial pinhole which had initiated at the inner tube surface. Subsequent propagation had occurred along with branching. SEM observations of such pinholes reveal that the pinholes have corrosion products in them (Fig. II.9) which were analyzed by energy dispersive spectroscopy (EDS) and revealed iron (Fe) as the only detectable element. Light polishing was able to remove these corrosion products and a shallow trough corresponding to the pinhole could be observed. Whereas many pinholes were observed in the damaged tube, such pinholes, even partial ones were absent from the service exposed but undamaged tube obtained from the third stage intercooler. The fact that the latter experienced higher pressure service than the damaged second-stage intercooler tube, would mean that the supplied tube was possibly not responsible for failure due to metallurgical defect inherent in them. However, in making this statement we have assumed that the chemical composition of the three tubes supplied were identical and that the environment and mechanical and thermal stresses experienced by tubes in all the three stages are similar (if not identical). It is our belief that some service irregularity affected the second stage intercooler to cause pinholes and as such the supplied tubes are not exceptionally prone to pinhole attack.

Discussion

The phenomenon observed here has been reported in literature and occur under the following conditions:

1. Local water stagnation, due to debris or biomass present, or geometrical pockets,
2. creation of an oxygen concentration cell resulting in oxygen pitting.

Such a mechanism is most common when the dissolved oxygen is present in significant amounts in the cooling water. Alternately presence of putrefying biomass may also cause such concentration cells. However the chlorination treat



Fig. II.1 : Corrosion product layer on the inner tube surface, protruding into the metal substrate, shown on a section taken across the tube width

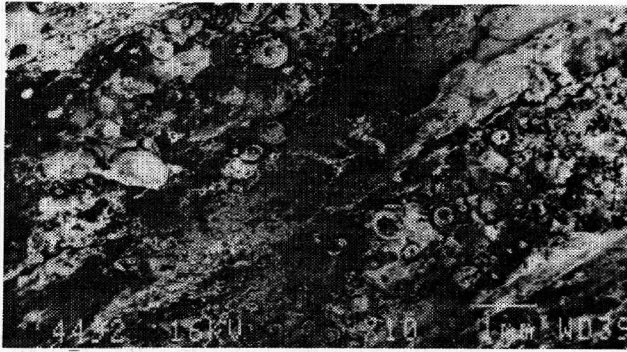


Fig. II.2 : Corrosion debris on the inner tube surface of the service exposed tube

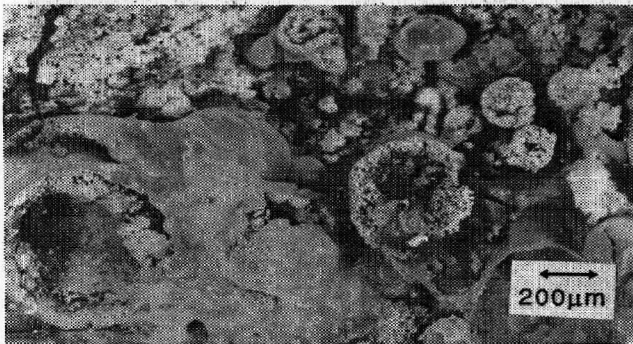


Fig. II.3 : Spheroidal and hemi-spheroidal corrosion products observed on the inner tube surface

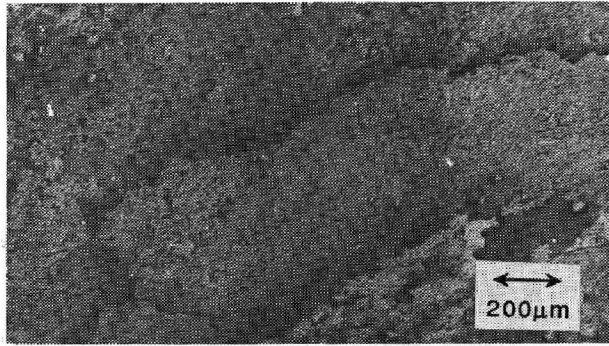


Fig. II.4 : Chromium rich scales observed on the inner tube surface

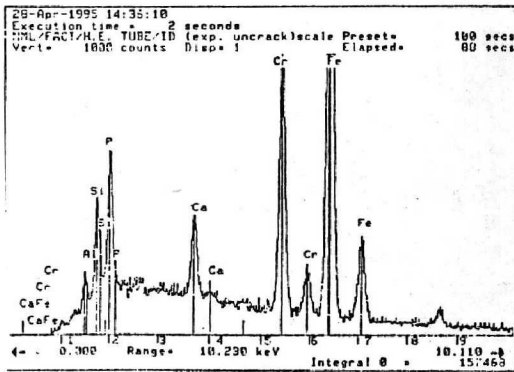


Fig. II.5 : Elemental distribution in the hemispherical corrosion product

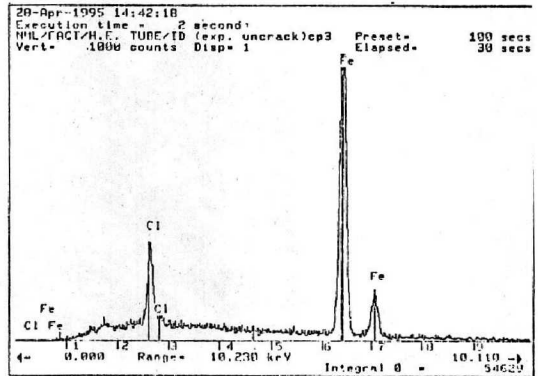


Fig. II.6 : Elemental distribution in the scale type corrosion product

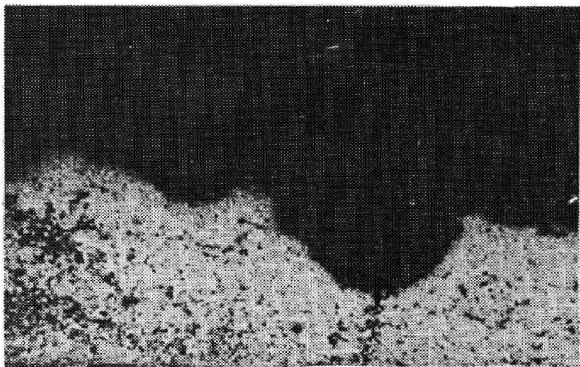


Fig. II.7 : Cratering in the damaged tube. Decarburization near the inner tube surface is evident

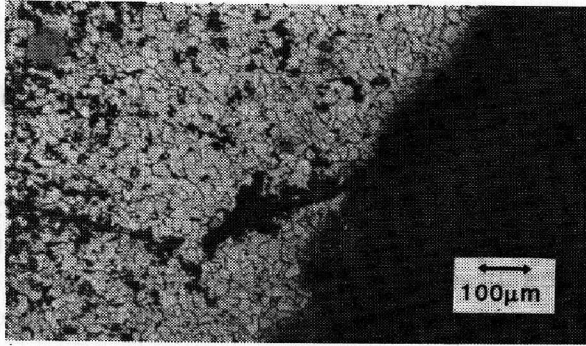


Fig. II.8 : Optical microscopic observation of a partial pinhole.

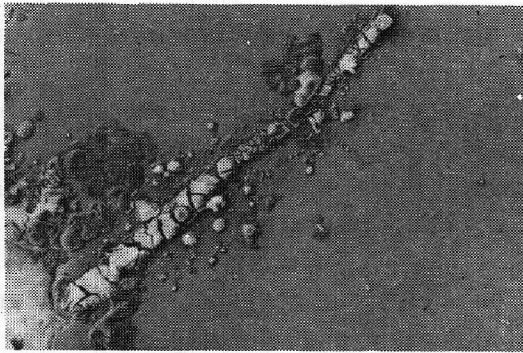


Fig. II.8 : SEM observation of a partial pinhole

ment should have been effective in eliminating micro-organism. A word of caution is needed here since chlorine is a well known agent for pitting. Chlorides may create local acidic environment where metal dissolution is facilitated. Our EDS observations tend to substantiate such a fear; the significant chlorine present in the corrosion product clearly indicate an active role of chlorine in pitting. It should be noted that not only free chlorine but chloride anion, like other halides, has an accelerating effect on corrosion. Thus maintaining a low amount of free chlorine is not sufficient, but a low value of dissolved chlorides is also desired.

In the absence of any data on dissolved oxygen content in the cooling water (the plant did not maintain any record of this parameter) it is difficult to say with certainty that the pitting type attack observed is oxygen pitting; however a comparative study with other failures reported in literature suggest that the morphological similarities with oxygen pitting are abundant. Let us reiterate that a similar phenomenon may occur due to microbial action - but the operators can easily verify whether the chlorine dosing was effective. It is also evident that dissolved chlorides participate in the corrosive process. We feel that the chromate treatment for surface passivation was not very successful. This may be due to the

adverse effect of chlorides which would interfere with the protective film formation.

In a nutshell, the corrosive mechanism was probably as follows. The protective film formed on the tube interior had many local flaws and porosities due to the detrimental action of chlorides. Oxygen or chloride pitting at such locations led to local metal dissolution, creating small pits surrounded by cup like hemispherical deposits. These pits were possibly precursors to pinholes observed elsewhere in the failed tubes. The pits intruded into the metal substrate, leaving behind porous corrosion products in their wake, which provided sufficient path for water leakage.

Conclusions

1. Decarburization of the damaged tube was indirectly responsible for the pinhole attack.
2. Such decarburization is not inherent to the supplied tube, it was possibly a result of service irregularity.
3. The attack mechanism is oxygen pitting with contribution of chlorides to the attack, as suggested by the detection of chloride occasionally in the corrosion products.
4. The pinhole initiation is either at crevices or pits in the inner tube surface.
5. The first stage intercooler tube and third stage intercooler tube do not demonstrate excessive proneness to pinholes or pitting. Assuming the material chemistry and the environmental and operational conditions of these tubes to be similar to the damaged second stage tube, such damage may be due to service problems rather than faulty tube metallurgy.

Suggestions

1. The cooling water treatment had to be looked into, since the chromate treatment did not seem very efficient.
2. A proper monitoring and control of the amount of dissolved chlorides was essential.
3. The amount of biomass/microorganism in the cooling water (no data to that effect was provided), had to be rendered insignificant.
4. The dissolved oxygen content had to be monitored, if found too high, proper oxygen scavengers may be required to be added to the cooling water.
5. The supplied tube material did not seem to be at fault, service irregularities were to be blamed - it was beyond the scope of this investigation to pinpoint such irregularities.