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Failure analysis of copper pipes used in the heat exchangers in fan coil units

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ABSTRACT: Heat exchangers (HE) consist of copper and steel pipes and are used for heating and cooling the ambient air. One of the main problems seen in HE is the leakage on copper pipes. In this study, failed and properly working copper pipe samples used for different durations were examined in detail. The microstructural analyses were performed using optical microscopy (OM) and scanning electron microscopy (SEM) to detect corrosion occurrences on copper pipe surfaces. In addition, corrosion products of the samples were defined by X-Ray Diffraction (XRD), Energy Dispersive Spectroscopy (EDS) and Fourier-Transform Infrared Spectroscopy (FTIR) analyses. The formation of interconnected tunnels in cross section of the failed copper pipe sample that were in microscopic dimensions and corrosion products were observed. Consequently, all the analyses result that were obtained from the samples pointed out a corrosion mechanism known as ant-nest corrosion. It was concluded that the main reason of corrosion was related to ethylene glycol type additives which were used in HE along with mains water.

KEYWORDS: Ant-nest corrosion; Copper pipe; Failure analysis; Heat-exchanger; Microstructural analysis

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RESUMEN: *Análisis de fallos de los tubos de cobre utilizados en los intercambiadores de calor de los ventiloconvectores*. Los intercambiadores de calor (IC) están formados por tubos de cobre y acero y se utilizan para calentar y enfriar el aire del ambiente. Uno de los principales problemas que se observan en los IC son las fugas en las tuberías de cobre. En este estudio, se examinaron en detalle muestras de tuberías de cobre fallidas y en buen estado de funcionamiento utilizadas durante diferentes periodos de tiempo. Los análisis microestructurales se realizaron mediante microscopía óptica (MO) y microscopía electrónica de barrido (MEB) para detectar los casos de corrosión en las superficies de las tuberías de cobre. Además, se definieron los productos de corrosión de las muestras mediante difracción de rayos X (DRX), espectroscopia de energía dispersiva (EDS) y análisis de espectroscopia infrarroja con transformada de fourier (FTIR). Se observó la formación de túneles interconectados en la sección transversal de la muestra de tubería de cobre fallida que tenían dimensiones microscópicas y productos de corrosión. En consecuencia, todos los resultados de los análisis que se obtuvieron de las muestras apuntaban a un mecanismo de corrosión conocido como corrosión por nido de hormiga. Se concluyó que la razón principal de la corrosión estaba relacionada con los aditivos de tipo etilenglicol que se utilizaban en los IC junto con el agua de red.

PALABRAS CLAVE: Análisis microestructural; Análisis de fallos; Corrosión por nido de hormigas; Intercambiador de calor; Tubo de cobre

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1. INTRODUCTION

Corrosion can generally be defined as a degradation process that metallic materials are exposed to under certain environmental conditions, involving chemical reactions that can significantly alter the properties of metallic materials (Gialanella and Malandruccolo, 2020). Metallic materials are electrochemically oxidized to ions, oxides or some other compounds due to corrosion phenomenon (Tait, 2018). Corrosion can occur in various solutions (both acid and alkaline aqueous solutions) and various ambient conditions. Some corrosive ions, such as halide ions and various sulfur-containing ions, can also reduce material corrosion resistance (Li *et al.*, 2016). Basically, corrosion reduces the material's performance and shorten its service life (Zhao and Mirzaeifar, 2021). Replacement and repair of various equipment and facilities in industrial areas are important losses caused by corrosion. As a result, corrosion is recognized as a serious problem that directly or indirectly causes huge financial losses (Rezaei *et al.*, 2021).

Fan coil units generally include parts such as fans and heat exchanger coils. Heat exchanger systems are basically used to heat or cool process fluids. The operation of a processing unit depends on the proper functioning of this component. In the design of many heat exchangers, the interconnection of different metals, sedimentation, thermal gradients in the fluid and the metal surface, high fluid velocity in certain regions or the presence of stagnant fluid in some regions are possible situations (Nguyen *et al.*, 2020). That may lead to increasing of corrosion in the heat exchanger, acceleration of damage, and failure of equipment (Rezaei *et al.*, 2021).

Copper is in group IB of the periodic table and its electronic configuration is [Ar] $3d^{10}$ $4s^1$. When copper loses its outermost s-electron, the copper ion Cu^+ is formed. A second electron loss from the d-shell is required to form another copper ion, Cu^{2+}. The presence of the d-electrons for coordination enables copper to easily form compounds with chemicals (NH_3 and CN^- etc.). As the copper is not a reactive element, its corrosion resistance is generally high (Vazdirvanidis *et al.*, 2019). Copper (pure) and its alloys are widely used in industrial fields as they have high electrical and thermal conductivity, corrosion resistance and attractive visual appearance (Wallinder *et al.*, 2014; Hamidah *et al.*, 2021). Therefore, copper is widely preferred in heat transfer units such as refrigerators, air conditioners and evaporators (Bastidas *et al.*, 2006; Zhou *et al.*, 2018).

Although copper has a good corrosion resistance, various corrosion formations such as pitting corrosion, erosion corrosion, microbiological influenced corrosion are observed in different applications in copper pipes (Vazdirvanidis *et al.,* 2019). Constitutively, corrosion of copper is the result of the loss of copper metal to solution. This situation results when electrons are lost by copper metal, the solid phase is turned into soluble, and occurring of dissolved cupper (Cu^+) and/or copper (Cu^{2+}) ions (Lytle and Nadagouda, 2010). The presence of chlorine, natural organic matters, microbial extracellular polymeric matters and elevated temperature are some of the conditions that affect the corrosion resistance of copper in waters (Boulay and Edwards, 2001). Also, in some cases, it is observed that copper is able to get corroded even from chlorinated domestic water (Fontana, 1986; Vazdirvanidis *et al.*, 2018).

In the last century, many incidents have been reported regarding the failure of copper pipes used in heat transfer units. The notion of ant-nest (formicary) corrosion was first expressed in the 1970s. This type of corrosion is one of the most common types of corrosion observed in copper and causes serious failures in copper pipes (Bastidas *et al.*, 2008; Zhou *et al.*, 2018). It has been stated that ant-nest corrosion causes nearly 10% of copper heat exchanger failures worldwide (Cozzarini *et al.*, 2020). Ant-nest corrosion is a type of local corrosion similar to pitting corrosion. The morphology of ant-nest corrosion is characterized by the growing of lengthwise pits that form by interconnecting incidental micro cavern channels (not noticeable by naked eye observation) (Notoya, 1997). Microscopic tunnels generally begin to form on the surface of the copper pipes and progress to the pipe wall. The direction of these tunnels not need fully being limited to the gravitation aspect (Bastidas *et al.*, 2008). Ant-nest corrosion generally occurs when moisture, oxygen and a specific corrodent (organic acid) are present on the copper surface at the same time. The most prevalent reason of this type of corrosion is the existence of chlorinated organic compounds or hydrolysis products generated by the decomposition of aldehydes or esters to carboxylic acids, such as formic or acetic (Elliott and Corbett, 2001). Since the corrosion rate of ant-nest corrosion is fairly rapid the corrosive tunnel formations migrate fully through the tube wall and may induce leaking (Elliott and Corbett, 2001; Bastidas *et al.*, 2006; Cozzarini *et al.*, 2020).

In this study, the failure analyses were carried out on corroded copper pipe samples that were used in heat exchanger in a fan coil unit. In this content, failed and properly working copper pipes were evaluated for comparison. Corrosion zones of samples were characterized in detail by microstructural (OM and SEM) and chemical (XRD, EDS and FTIR) analyses. When all the analyses were taken into consideration, it was understood that the type of corrosion seen in the failed sample was ant-nest corrosion. The examples of ant-nest corrosion and studies in the literature were examined in detail and the results on the causes of this corrosion were revealed.

2. MATERIALS AND METHODS

The copper pipes used in this study had a diameter of 10 mm and a thickness of 0.5 mm with a chemical purity of 99.95% Cu along with trace elements such as Mg, Pb, Zr and Bi. They were taken from heat exchanger systems which operate from room temperature up to 80 °C and were located inside the fan coil units used for heating and cooling the ambient air. The copper pipes are used in closed environments and mains water passes through them. Ethylene glycol is sometimes added to water to prevent freezing. Also, the heat exchangers are connected to the waterworks and there are steel pipes in the waterworks. Samples tagged as C1 (2-months used, no leakage problem), C2 (2-years used, no leakage problem) and C3 (2-years used, leakage problem). Although C3 sample showed leaking problem, there were no visible leakage points or holes on the inner or outer surface when examined by eye. Only considerable difference between failed and proper working pipes was present of black corrosion product inner surface of C3 sample. Figure 1 shows the images of copper pipe samples just before they were cut for the analyses and cold molding for microstructural examination. Subsequently, the grinding and polishing processes were done respectively, and the samples were made ready for metallographic examination. The morphology of copper pipe samples was examined with optical microscope (OM) (Nikon LV 100) and SEM (Zeiss Gemini SEM 500) devices. The phases (in corrosion products and in the copper pipe samples) were identified by XRD analyses which were carried out with a sample rotation range of 0 to 80 2θ degrees using CuKα radiation (λ=1.5405 Å). The spot and areal type EDS analyses were performed to investigate the elements in the samples using Zeiss Gemini SEM 500 device with an EDS detector. In addition, FTIR spectroscopy was performed to evaluate the functional groups (C-Cl) on the corrosion products of C3 sample. Corrosion products on the inner surface of the C3 sample were carefully scraped from the copper tube for performing this analysis. The existence of different structures other than oxide structures was investigated by examining the corrosion products in powder form.

3. RESULTS AND DISCUSSION

3.1. Optical microscope analysis

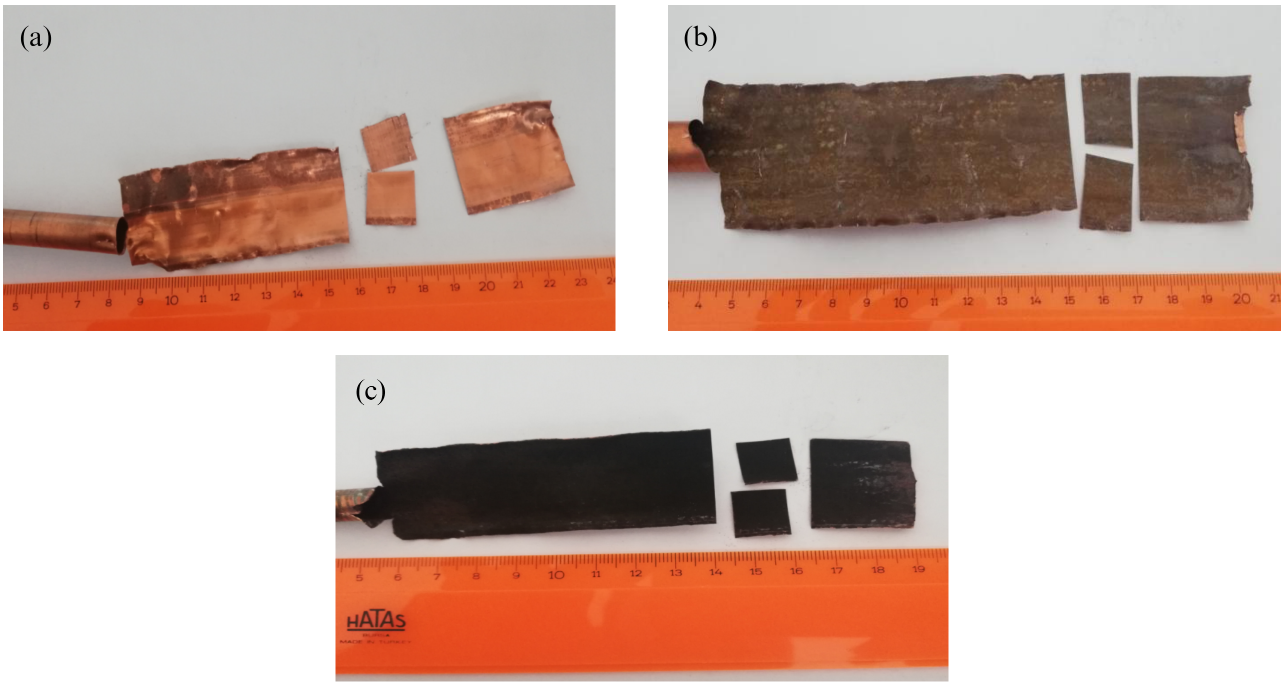

Figure 1. a) 2 months used sample (C1) **b)** 2 years used sample (C2) **c)** 2 years used sample with black corrosion product covered surface and leakage problem (C3)

When all the samples were examined by naked eye, there was no clear failure on the sample surfaces. Thus, all samples' cross sections were examined by optical microscope in order to observe and find evidence for the possible corrosion and failure modes. Figure 2 shows the images of both failed and defect free copper pipe cross sections. It can be seen that there are no cracks or micro tunnel formations in the C1 and C2 samples. On the other hand, tunnel-like formations and defects were discovered in the C3 sample. When the working conditions and the failure type of the C3 sample considered, tunnel formations could be evaluated as the main reason of leakage. Since there was no visible corrosion damage on the sample inner surface and the material was operating in a fluid-liquid environment at 70-80 °C, it was determined that the corrosion in the C3 sample was similar to ant-nest corrosion (formicary corrosion). Ant-nest type corrosion occurs on the surface of the copper pipe in the form of very fine pinhole-like leaks that are not visible to the human eye. When examined under a microscope, ant-nest type corrosion pits show a tunnel structure connected to each other along the copper pipe (Moss, 1969; Peltola and Lindgren, 2015). In addition studies in the literature showed copper pipes that were exposed to formic acid and similar corrosive environments resulted with tunnel structure and failed because of ant nest corrosion (Situmorang and Kawai, 2018; Zhou *et al.*, 2018; Cozzarini *et al.*, 2020).

3.2. SEM and EDS analyses

Figure 3 and Fig. 5 shows SEM images of C1, C2 and C3 samples, respectively. When the images of the C1 sample were examined, micro cracks and contamination-like structures were observed in various regions of the sample surface (indicated by

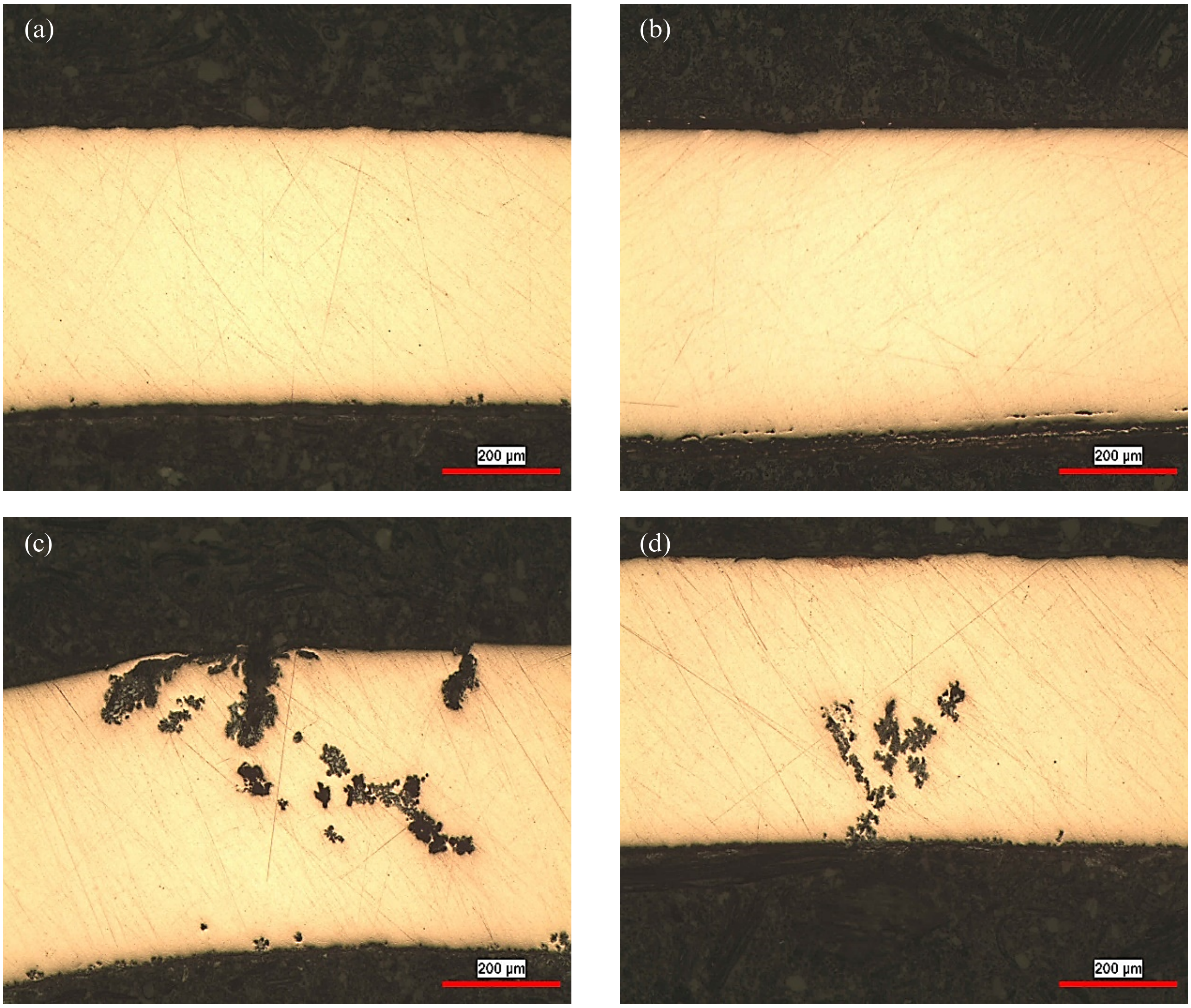

Figure 2. Optical microscopy images of copper pipe cross sections **a)** C1, **b)** C2, **c)** and **d)** C3 samples.

arrows). The presence of two structures was considered as a result of SEM analysis in Fig. 3a. When the C2 sample was examined by naked eye, a dark brown structure was seen easily on the surface of the sample. In Fig. 4, it was seen that dust-like structures deposited on the sample surface with different ratios in the different regions on the sample surface. In addition, microcrack formation which thought to be related to bending stresses applied during sample preparation process was observed at various regions in both C1 and C2 sample. SEM images of the C3 sample in Fig. 5 showed that the inner surface of the sample was apparently covered with a black corrosion product. It was observed that the amount of corrosion product accumulated on the surface was much higher than C2 sample. Also, the amount of corrosion product deposition on the surface showed regional differences and there were various microcracks and large cavities on the surface of these. In addition, it was thought that different structures exist due to contrast differences in Fig. 5a. According to SEM results, it was determined that the corrosion products on the surface increased over time and at the same time, these corrosion products were too high amount in the samples exposed to corrosion. In order to observe leakage locations more clearly, corrosion products on the surface were removed by gentle cleaning and it was demonstrated in Fig. 6. It was seen that there were various cracks and pits on the surface that could cause leakage, indicated by the arrow in Fig. 6.

When the literature was examined, similar pits and cracked structures were found in the corrosion studies of copper pipes used in heat exchangers and air conditioners. In a study by Peltola and Lindgren (2015), similar fractured structures were found in a corrosion study of the copper pipe used in the heat exchanger. Authors determined that ant-nest corrosion occurred and caused damage in copper pipes. It was stated that ant-nest corrosion products were dark colored on the copper pipe surface. Zhou *et al.* (2018) examined a copper pipe damaged in an air

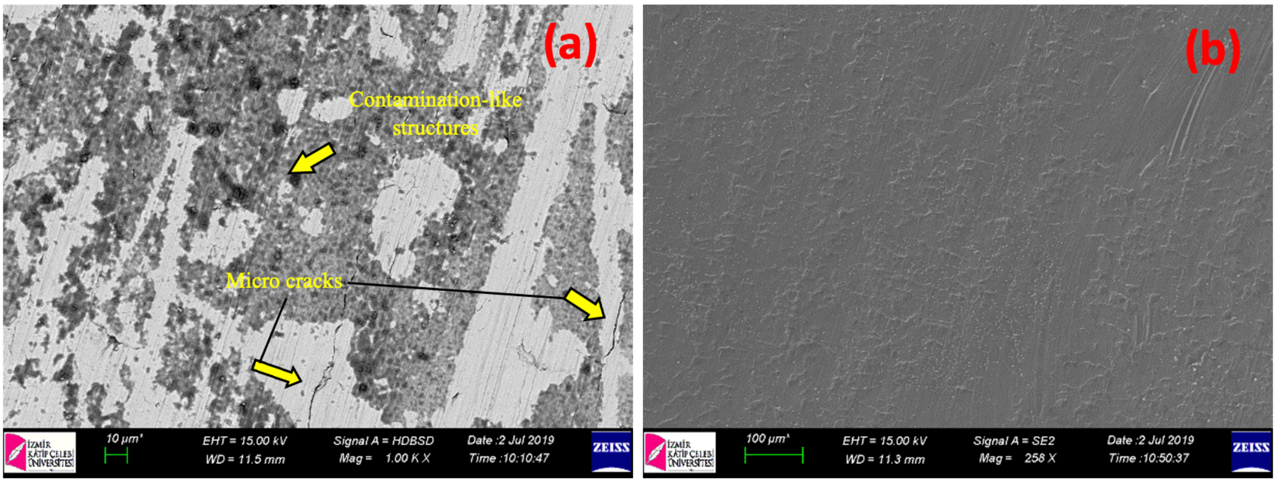

Figure 3. a) SEM-BSD and **b)** SEM-SE images of C1 sample inner surface.

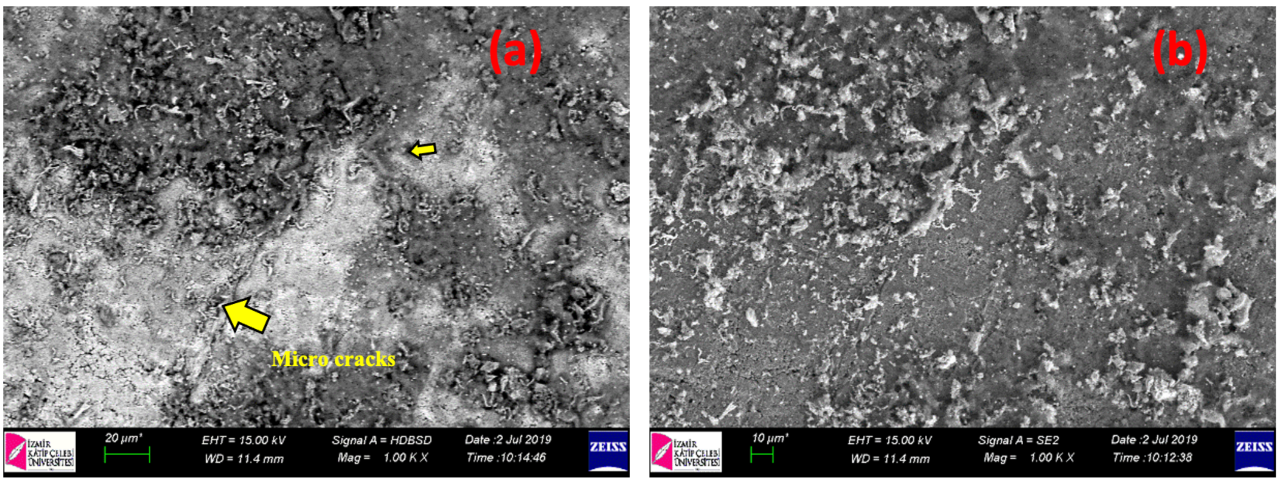

Figure 4. a) SEM-BSD and **b)** SEM-SE images of C2 sample inner surface.

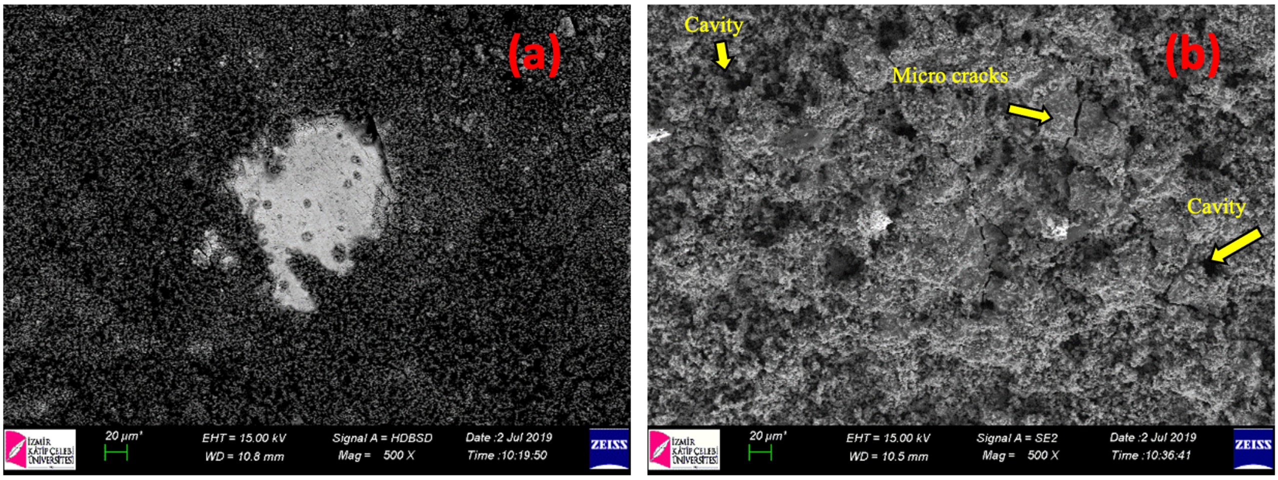

Figure 5. a) SEM-BSD and **b)** SEM-SE images of C3 sample inner surface covered corrosion products.

conditioning system. The authors determined that samples were subjected to ant-nest corrosion with the occurrence of various pits. In a study conducted by Bastidas *et al.* (2006), copper pipes damaged by ant-nest corrosion that were used in air conditioners for 2-3 months were examined. In that study, they determined that various cracks and pits were formed interior of the copper pipe. Similarly, Cozzarini *et al.* (2020) observed corrosion formations in heat exchangers and detected black corrosion product accumulation and ant-nest corrosion which was similar to our study. In our study, when the SEM images of the corroded C3 sample found in Fig. 6 were compared with the literature, pits and cracks

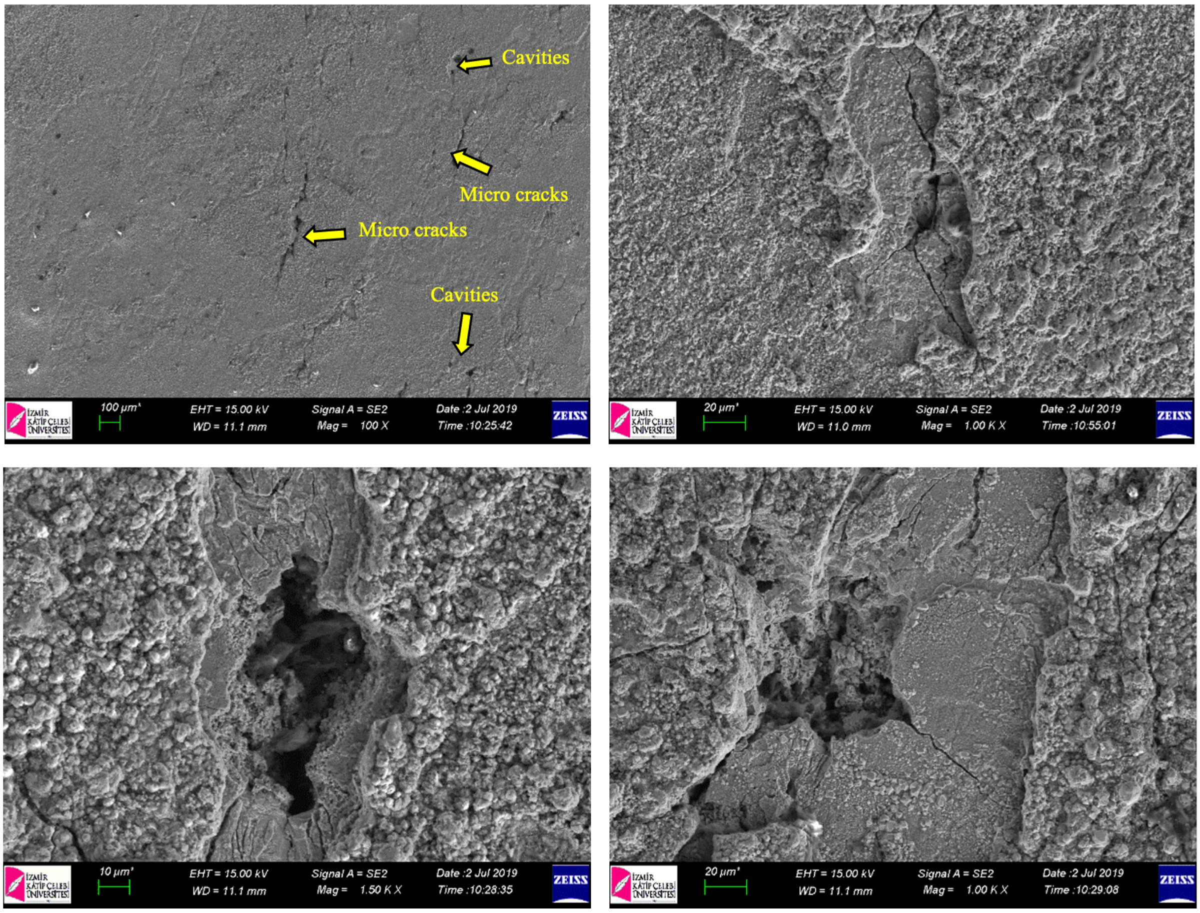

Figure 6. SEM images of C3 sample inner surface (leakage areas).

similar to ant-nest corrosion were observed. As can be seen in Fig. 5, an accumulated layer was formed on top of these pits. The fact that this accumulated layer was different in color (black) from the copper pipe in the SEM-BSD analysis was shown in Fig. 5a. This color difference indicates the presence of a different structure. In addition, crystal structures were seen around the corrosion hole in SEM images. Similar structures have been specified as copper oxide structures, which are specified as corrosion products in various studies (Peltola and Lindgren, 2015; Vazdirvanidis *et al.*, 2019). It has been stated that these structures were related to the ant-nest corrosion starting point (Peltola and Lindgren, 2015).

Figure **7** demonstrated elemental analysis of C1 sample inner surfaces by EDS analysis. The observed contamination-like structures were revealed that these regions contain elements such as Cu, O, Fe, P and C. It was determined that the light-colored areas were metallic copper and contained only Cu, while the gray and black areas contained Cu, O and Fe elements. Figure 8 showed elemental analysis of C2 sample inner surface. As a result of the EDS analysis, Cu, O and Fe elements were determined on the sample surface along with small amounts of Si, Ca and S. While the light-colored regions contained only Cu, O and Fe, elements such as Si, Ca and S were also seen in the regions where dark deposition was higher. It was seen that Fe element concentration increased in the dark areas where the contamination and amount of deposition increases. The heat exchangers from which the copper tube samples were taken are connected to installations consisting of steel tubes. Thus, steel pipes which were connected to the heat exchangers, were determined as one of the main reasons for the existence of Fe element on the inner surface of samples. Furthermore, another reason for the existence of elements such as Fe, Si, Ca and S was thought to be mains water, since it circulates through these installation pipes and copper pipes.

The elemental analysis of the inner surface of failed sample C3 was given Fig. 9. It was seen that the light-colored region contains Cu and O, and the dark colored corrosion product covered region contains Cu and O as well as Fe and Si elements. It was determined that the corrosion product formed on the surface contains high amounts of Fe and O elements. Kuźnicka (2009) examined the corroded copper heat exchanger that has been used for 5 years and detected pits and surface microcracks formations. Their EDS analysis showed that the corrosion products formed on the inner surface consisted of elements such as Fe, Si, C, and Ca. Similarly, Lachowicz (2020), performed EDS analysis on the corrosion products on the inner surface of a damaged copper pipe and their results showed that while the light-colored copper pipe region consisted of Cu and O elements, dark colored corrosion products contained Fe, C, O and Cu. They determined the damage was due to ant-nest corrosion and water-insoluble residual particles accumulated and surface cracks on the surface played an important role on the initiation of corrosion. According to literature, when small amount of elements such as Fe, Mn and Ni are in the copper structure, the color of corrosion products can shift to orange, brown or even black (Jones, 2001). In the context of literature knowledge, it was understood that the color of the inner surface of our samples was changed because of contaminating elements such as Fe, Si, P and Ca. It was thought that elements such as Fe and Si deposited on the surface of C3 sample could be carried to the surface by the water flow through the pipe like others.

For better understanding of corrosion formation, elemental analysis of the gently cleaned leakage area of the C3 sample were given in Fig. 10. While the analysis made from the pit's edge and corrosion product area showed the occurrence of Cu and O along with Fe, analysis carried out inside the pit revealed the existence of a high percentage of C element. When the studies in the literature were examined, it was seen that the amount of C was higher in the EDS analysis performed from the leakage area compared to the other regions. It was stated that the reason for this is the formic acid-like structures that play an active role in the formation of ant-nest corrosion (Zhou *et al.*, 2018). Bastidas *et al.* (2006) pointed that the formic acid which is essential in ant-nest corrosion can be generated by the pyrolysis of ethylene glycol or hydrolysis of various organic solvents that contains chlorine. Therefore, it was concluded that the EDS results obtained in our study were compatible with the literature and that C element in the leakage area was caused by acidic formations.

3.3. XRD and FTIR analysis

X-ray diffraction analysis was performed on the samples which were taken from each pipe. The analysis was applied to the inner parts of the copper pipes. Figure 11 shows the XRD pattern of C1, C2 and C3 samples.

Although O and Fe elements were detected on the surface of C1 sample by EDS, in the XRD analysis of the C1 sample only metallic Cu peaks were seen. Since there were no other phases beside copper, it was understood that corrosion and oxidation occurrences did not occur in sample C1. XRD analysis results of C2 copper pipe, which was used for 2 years, showed that there were two different phases in the structure. One of them was metallic Cu and the other one was Cu_2O (copper (I) oxide). It was understood that contamination product was formed in the copper pipe during the 2-year usage period. Since

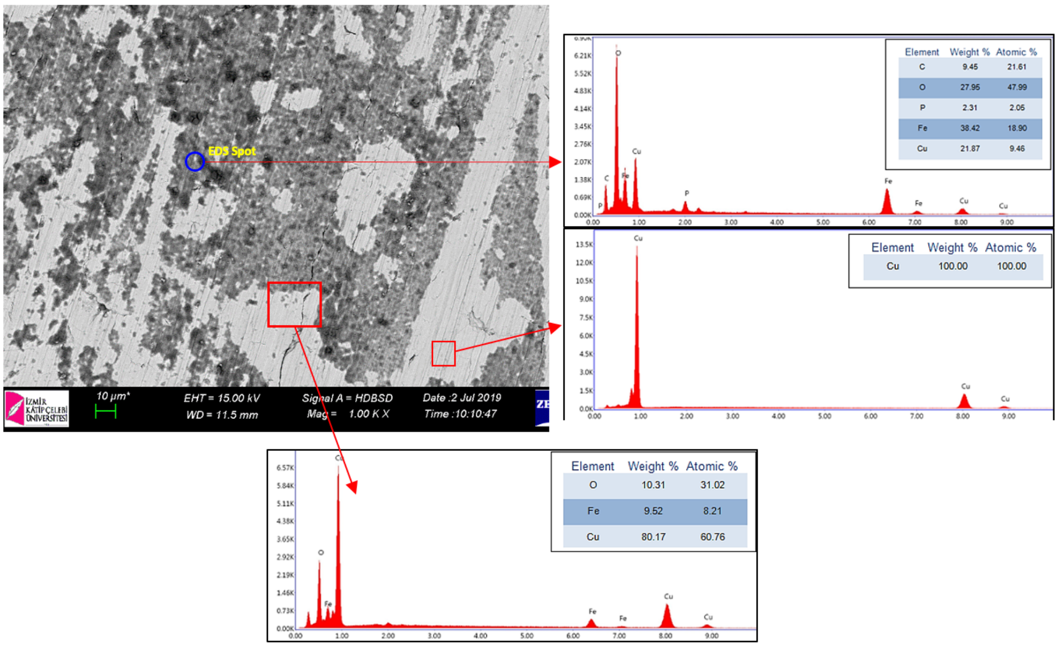

FIGURE 7. Elemental analysis of the C1 sample.

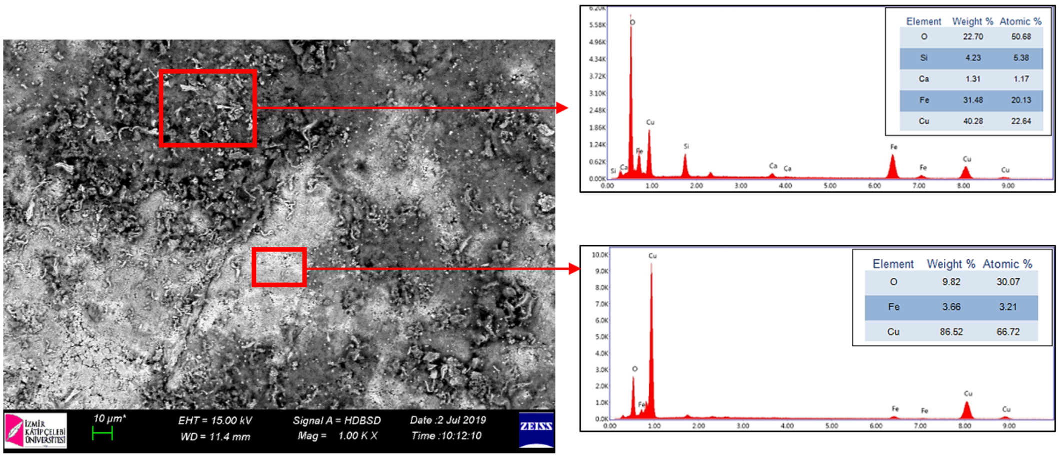

FIGURE 8. Elemental analysis of the C2 sample.

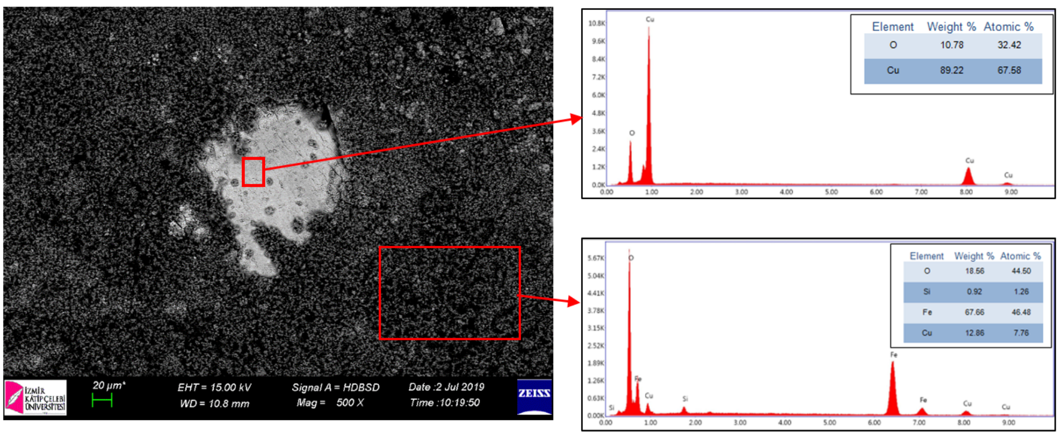

FIGURE 9. Elemental analysis of the C3 sample.

we detected Fe and O elements by EDS on both C1 and C2 samples, we can conclude that these samples were exposed to contaminating environment from two months to two years usage. However, this formation did not cause serious damage to the pipe. Zhou *et al*. (2018) obtained similar metallic Cu phase by XRD for copper pipes that were not exposed to formic acid environment. They also revealed that the exposure of copper pipes to the formic acid resulted with the formation of Cu_2O phase. In accordance, our findings showed that even without corrosion formation, a considerable amount of Cu_2O can deposit on the inner surface of samples. As a result of the XRD analysis of C3 sample, 4 different phases (compounds and elements) such as Cu, Cu_2O, CuO and Fe_3O_4 were detected on the inner surface of the copper pipe. It was found that this sample contained a secondary copper oxide phase along with iron oxide phases that were different from the C2 sample. Cozzarini *et al.* (2020) found Cu, CuO and Cu_2O phases in a copper pipe which was failed due to ant-nest corrosion. They also stated that there was a black corrosion product on the surface of the failed pipes which was similar to our study. In a different study, Bastidas *et al.* (2006) examined the ant-nest corrosion formation under presence of organic acids such as formic, acetic, propionic and butyric acid. The results showed that various copper oxide formations can be found on the surface of corroded samples along with as copper formate and copper acetate formations. The literature studies showed that oxide formations can be detected inside the pitting holes or around the leakage areas as corrosion products. Thus, formation of different oxides could be attributed to corrosion formation or the amount of corrosion. Lee *et al.* (2016) stated that the Gibbs free energy change to form Cu_2O is smaller than CuO and CuO can be formed either by oxidation of Cu or secondary oxidation of Cu_2O. In this context, CuO formation in the C3 sample could be caused by excessive amount of Cu_2O formation which can be correlated with corrosion. On the other hand, the black corrosion product structure formed on the surface also contained Fe_3O_4 phase apart from other studies. It was not clear whether the Fe_3O_4 formed due to pollution of mains water, steel pipes connected to the heat exchanger or corrosion. However, when the studies in the literature were examined, it was stated that contamination-induced Fe atom causes damage to progress faster. It was thought that Fe compounds may damage passive copper oxide layer (Kuźnicka, 2009). In addition, Lachowicz (2020) stated that impurities such as oxide or phosphides may act as potential corrosion initiation sites for ant-nest corrosion. Thus, it can be concluded that the amount of Fe ions on the surface and the formation of Fe_3O_4 phase may increase the possibility of corrosion formation directly or indirectly, but existence of C in pit holes plays a

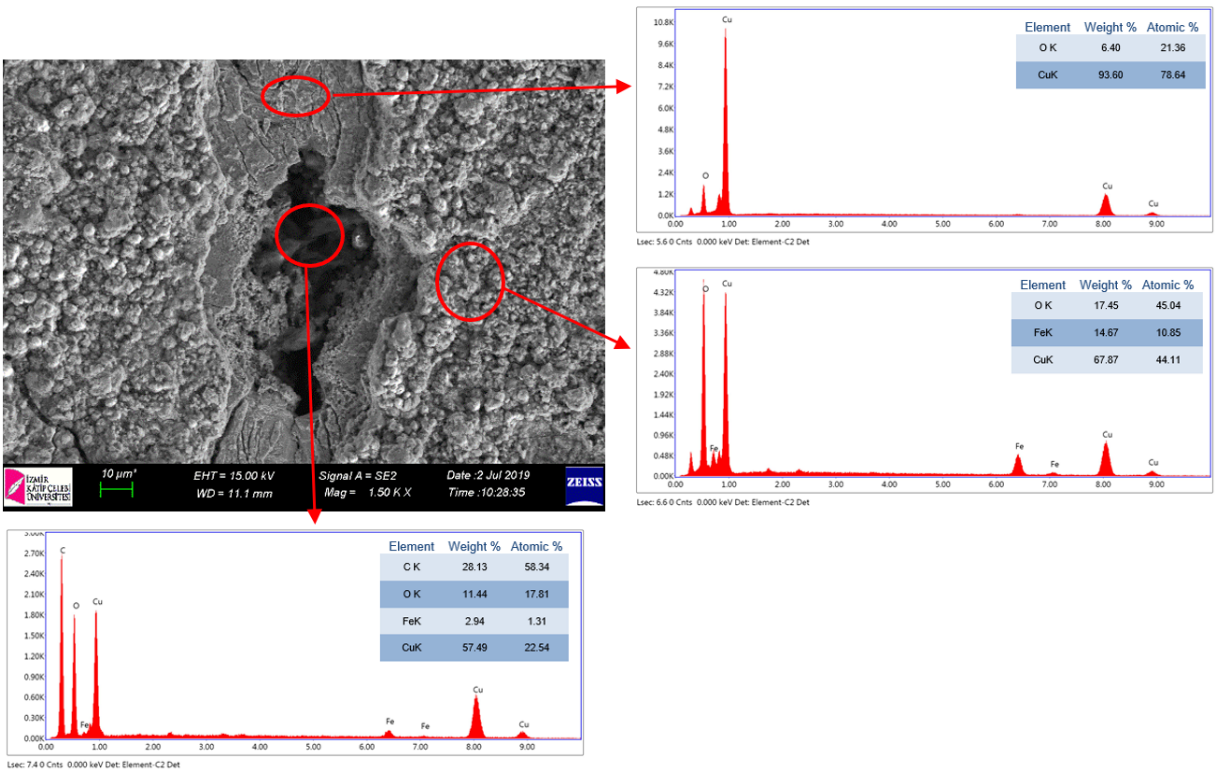

Figure 10. Elemental analysis of C3 sample inner surface (leakage area).

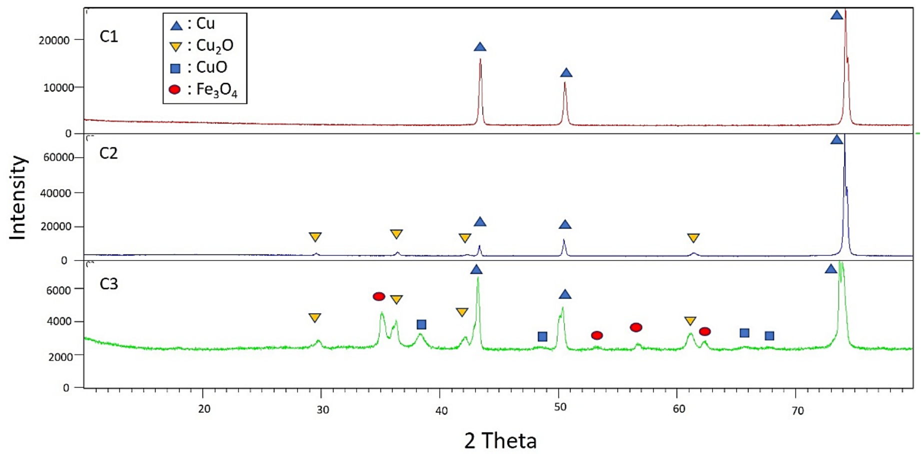

Figure 11. XRD patterns of C1, C2 and C3 samples.

key role in corrosion. On the other hand, May *et al.* (1991) states that protective films of copper(I) oxide and copper(I) chloride are more likely to form in the ethylene glycol-water solution than in aqueous, especially at low chloride concentrations, and this could be inhibit corrosion of the copper components of the cooling system. However, it was stated that the conditions in a vehicle cooling system are favorable for the oxidation of ethylene glycol and breakdown products such as glycolic and formic acids were often found in coolants; and this cause the pH of the fluid to decrease. Under these conditions, it was reported that the formation of copper(I) oxide and copper(I) chloride protective films are less likely even in the presence of chloride ions and thus corrosion of copper components is expected. FTIR spectroscopy was carried out for evaluating the functional groups (especially C-Cl stretching) in the corrosion products of C3 sample. Figure 12 shows the FTIR spectra of corrosion products of C3 sample. Bands around between the 850 cm^{-1} and 550 cm^{-1} (Khan *et al.*, 2016) corresponds to C-Cl stretching caused by presence of Cl in mains water circulating in copper pipe. Thus, the presence of Cl ions in the water in the system is proven.

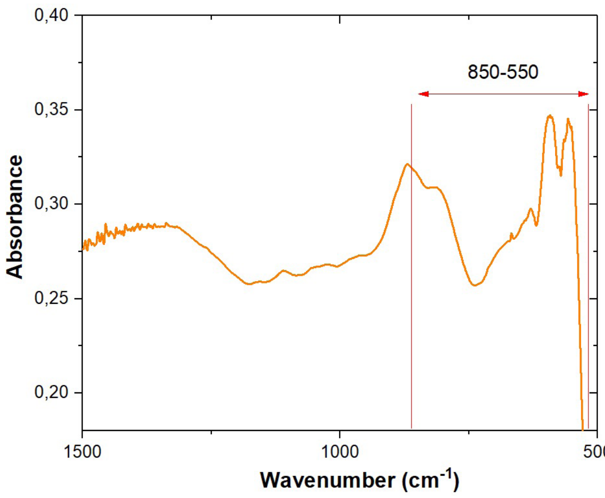

Figure 12. FTIR spectra of corrosion products of C3 sample

All in all, we can conclude that main reason of corrosion was depended on the amount of ethylene glycol type additives, chloride ion concentration and pH value of water which resulted with the formation of formic acid in coolant water.

4. CONCLUSIONS

A case study was carried out for copper heat exchanger pipes that had worked under similar conditions. In this context, a comparison was made between copper pipes showing leakage failure and copper pipes working properly.

Optical microscopy analysis revealed ant-nest and pitting formations on the cross section of failed tubes. SEM analysis showed the pitting and cracking formations on the inner surface of failed tubes. Also, EDS analysis in the leakage area showed high amount of C content besides Cu, O and Fe elements which indicates the ant-nest corrosion formations. In addition, XRD analysis unveiled that failed tubes contained CuO and Fe_3O_4 phases unlike defect-free tubes.

Considering all the results, it was concluded that C3 sample failed because of ant-nest corrosion. The presence of Cl in the working environment was detected by FTIR analysis. As a conclusion, it was concluded that the factors that cause the formation of ant-nest corrosion are ethylene glycol type additives, organic solvents containing chlorine and the pH value of the water. For this reason, it is thought that checking the pH value and contents of water periodically may provide a benefit to prevent corrosion.

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