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Identification of corrosion and damage mechanisms by using scanning electron microscopy and energy-dispersive X-ray microanalysis: contribution to failure analysis case histories

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Abstract. Emphasis is placed on the evaluation of corrosion failures of copper and machineable brass alloys during service. Typical corrosion failures of the presented case histories mainly focussed on stress corrosion cracking and dezincification that acted as the major degradation mechanisms in components used in piping and water supply systems. SEM assessment, coupled with EDS spectroscopy, revealed the main cracking modes together with the root-source(s) that are responsible for the damage initiation and evolution. In addition, fracture surface observations contributed to the identification of the incurred fracture mechanisms and potential environmental issues that stimulated crack initiation and propagation. Very frequently, the detection of chlorides among the corrosion products served as a suggestive evidence of the influence of working environment on passive layer destabilisation and metal dissolution.

1. Introduction

Failure analysis processes aim in determination of the overall damage mechanism (e.g., mechanical overload, corrosion, fatigue, wear) and its specific form and root-cause (e.g., corrosion or damage form and source/initiation) leading ultimately to the failure and to the suggestion of improvement in order to mitigate similar failures in the future. In the present work, the contribution of scanning electron microscopy (field emission SEM) assisted with elemental microanalysis (energy-dispersive X-ray spectrometry) in analysing, determining and identifying mechanisms of corrosion failures in certain metallic components is highlighted. Microfractographic examination using SEM employing secondary and backscattered electron detectors can also characterize the mechanical behaviour and fracture mode of the material under certain environmental conditions which in combination with elemental microanalysis enables outlining the service history towards better understanding of the failure sequence and assisting in the implementation of preventive strategy. Electron trajectories and interaction volume sizes are deduced using statistical modelling (Monte Carlo simulations), see [1]. Quantitative chemical analysis of macroscopic sample volume is usually conducted through specific analytical techniques, such as optical emission and atomic absorption spectroscopy. The utilisation of SEM/EDS microanalysis in fractography and failure analysis provides a unique capability in detection, interpretation and documentation of failure analysis projects; the merits of SEM in fractographic evaluation are highlighted in [2].



2. Experimental

Microstructural and morphological evaluation was conducted on mounted cross-sections, after water grinding with up to #1200 grit SiC abrasive papers, followed by fine polishing using diamond and silica suspensions. Immersion etching was performed in appropriate FeCl_3 solution followed by rinsing in ethanol and hot air-stream drying. In the present study, immersion etching affects the surface chemistry by deposition of reaction products; therefore it was used only for microstructural evaluation after the performance of microanalysis which was conducted on as polished sections prior to etching. Higher magnification observations on damaged surface and localized chemical analyses were conducted, employing a FEI XL40-SFEG scanning electron microscope using both secondary (SE) and backscattered imaging modes (BSE) coupled with an EDAX energy-dispersive X-ray spectrometer (EDS). Au-sputtered mounts were used for SEM microstructural evaluation under a 20 kV accelerating potential.

3. Case histories

3.1. Stress corrosion cracking of a machineable brass alloy distributor

Water distributor is a component that is used in various plumbing installations, dividing and adjusting the main water supply flow to various stream lines for further use. Fracture surface examination of a brass distributor revealed a characteristic intergranular fracture mode, while the surface was covered by corrosion products (figure 1). SEM observations of a transverse section indicated intergranular cracking with multiple branching, which strongly suggests the occurrence of stress corrosion cracking (SCC) (figure 2). The SCC process is induced by the synergistic action of corrosive environment and stress fields (e.g., residual or applied tensile stresses from component fabrication and/or over torque during installation). The material sensitivity against SCC is enhanced to be result of surface work hardening (due to cold working from machining operations) and local stress concentration imposed by abrupt section/design changes. SCC is initiated on the metal surface and is favoured by three main contributing factors: sensitive material, residual or applied tensile stresses and corrosive environment. SCC is considered as a delayed failure process, where cracks are initiating and propagating at slow rates until stresses applied in the remaining section exceed the fracture strength of the material. SCC is also termed in copper and copper alloys systems as “season cracking” and is mainly promoted by the presence of NH_3 and humidity and it is a more common failure mode for cold worked brasses with more than 15 % Zn. Two main models of SCC general corrosion mechanism are proposed [3]:

- (i) Anodic dissolution or chemical model. According to this mechanism, after the passive surface film is fractured, metal anodic dissolution is initiated at the tip of the crack and grows through an active path, which is the least free energy route.
- (ii) Mechanical/stress model. According to this specific mechanism the absorbed species alter the stress state at atomic level provoking crack nucleation and facilitating crack propagation.

The entire SCC process comprises several physicochemical processes that involve mostly heterogeneous reaction steps, where the limiting step defines the process control rate. A pit, dent, scratch or other discontinuity acting as stress raiser is a potential SCC contributor, since it may induce a crack to nucleate, especially as the critical notch radius decreases due to stress concentration effects. Intergranular cracking occurs also as a result of hot-shortness which results in fusion of low-melting constituents segregated at grain boundaries causing grain boundary de-cohesion. This type of failure can be found in case of high speed and/or high temperature extrusion [4, 5].

3.2. Dezincification corrosion of a machineable leaded brass component

Dezincification is the result of: Zn selective leaching or both Zn and Cu leaching followed by copper deposition. Characteristic studies of dezincification of brass alloys are presented in Refs. [6-7]. Zinc selective attack leads to the formation of a porous Zn-depleted layer showing poor mechanical strength, toughness and wear resistance.

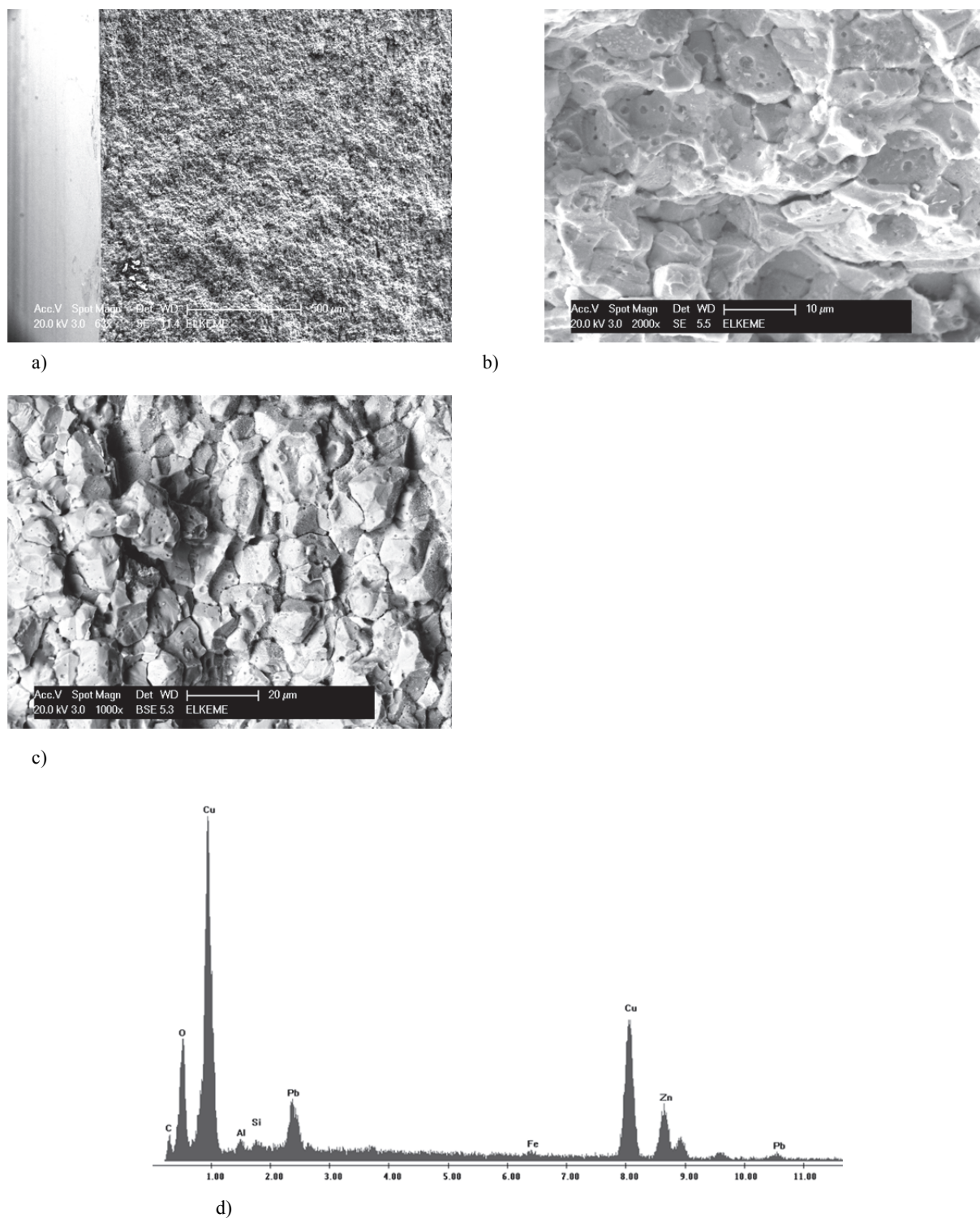


Figure 1. a-c) SEM micrographs (BSE and SE imaging) showing the fracture surface of the ruptured brass component; note the intergranular fracture mode; d) EDS spectrum indicating the elemental chemical composition of fracture surface – the presence of Cu, Zn oxides is evident (ZAF corrected - standardless).

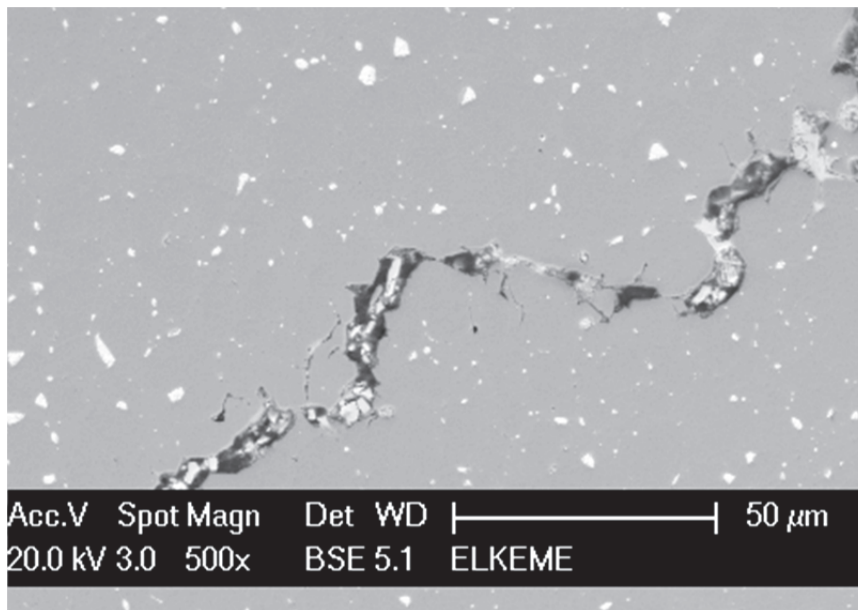


Figure 2. SEM micrograph of as-polished section, transverse to the main crack direction, depicting intergranular cracking and secondary branching remaining also as characteristic indications of SCC in machineable brass. The areas of white contrast in the matrix correspond to lead particles that segregated preferably at grain boundaries.

A threaded brass component demonstrated progressed dezincification, reaching a depth up to $\sim 100\ \mu\text{m}$ (figure 3). Dezincification kinetics follows a parabolic rate law controlled by diffusion, see also [7]. In two phase $\alpha+\beta$ brass alloys the difference in electrochemical potential of the adjacent phases establishes a galvanic coupling, stimulating selective dissolution of Zn ions originating mainly from the β -phase, followed by an equilibrium concentration among neighbouring grains. The degradation of the α -phase occurs at an advanced stage of the dezincification process. In parallel migration through the porous network aggravate the corrosion conditions, accelerating dissolution leading to chemical attack on copper, through the formation of CuCl_2^- -complex anions. Sensitivity of brass dezincification is significantly reduced in case of single α -phase brass and especially for Zn contents lower than 15 %, see [8].

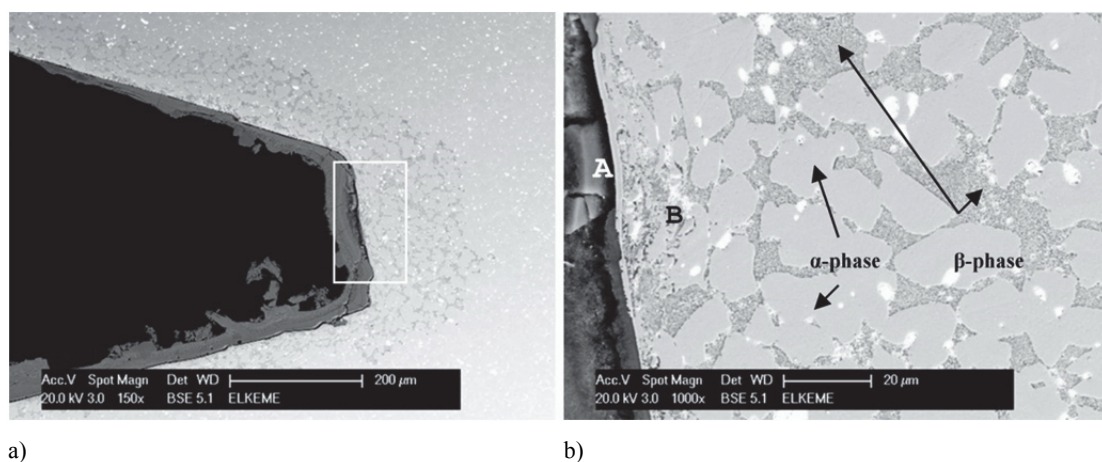


Figure 3. a) BSE-image of as-polished section showing a dezincification area in the threaded brass component. b) Detail of the boxed area presented in a). The morphology of corrosion layer suggests that it is the result of layer (uniform) dezincification.

The addition of minor alloying elements, such as Sb and As operating as inhibiting constituents, improves significantly the dezincification corrosion resistance of brasses in aqueous service environments. Depending on service environment conditions (e.g., temperature, corrosive media), two main forms of dezincification are encountered: uniform and plug-type (localized) dezincification, where penetration is steep and leads very frequently to perforation and leakage [9]. SEM micrographs and EDS spectra showing the form of degradation and Zn concentration gradients and selective attack of β -phase, due to differential Zn dissolution are shown in figures 3 and 4.

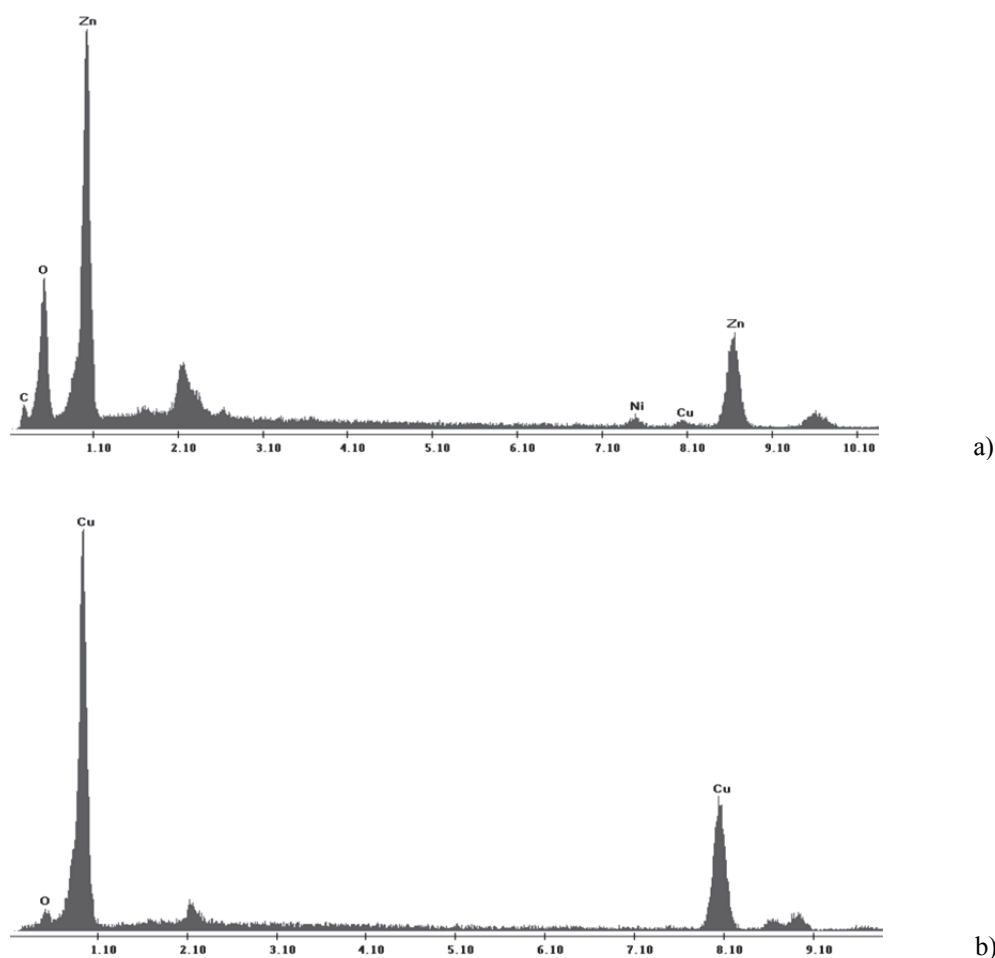


Figure 4. EDS spectra (ZAF corrected - standardless). a) The scale consisting mainly of ZnO (approximate location – A in figure 3b; b) the Zn depleted area showing predominantly the presence of Cu (approximate location – B in figure 3b).

3.3. Pitting corrosion of a deoxidized high phosphorus Cu (CuDHP) water tube

A sample from copper water-tube, which experienced leakage during service after a short-time period, was evaluated using SEM-EDS of 1 mm wall thickness. Deoxidized high phosphorus Cu (P: 0.015 - 0.040 wt%; Cu: 99.90 wt% min) is the main construction material for the fabrication of water and refrigeration pipes. The investigation of failure strongly suggests that the leakage resulted from inside-out driven pitting corrosion. Layers of scale products were massively accumulated on the water side surface. No microstructural abnormality of the CuDHP, that could be connected to the

failure was found. The nature and stacking sequence of scale deposits, addressing the operated corrosion phenomena, was evaluated by SEM-EDS analysis. The examination of outer surface scale (green copper patina) indicated the presence of characteristic spherical nodules composed of acicular crystals, corresponding to complex copper carbonates (malachite), see figure 5. Transverse sections adjacent to the leakage area were made to highlight the form of corrosion. The inner tube surface suffered from severe pitting corrosion, while corrosion product inner surface deposits located on that area fell in to two main categories: mixed hydroxides-chlorides on the floor of the pit, copper oxide crystals (Cu_2O) and outer-thick copper hard scale (e.g., carbonates), see figure 6.

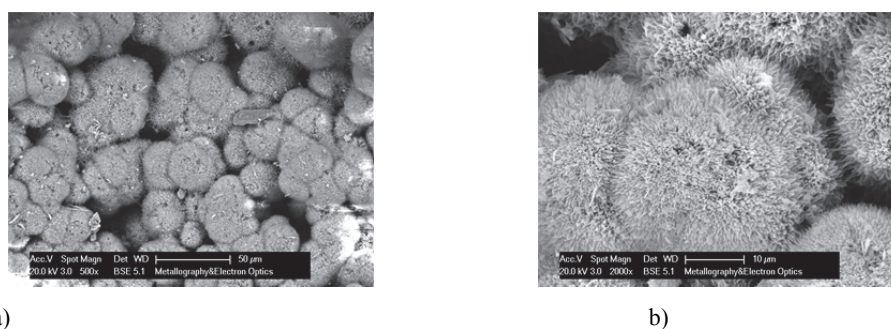


Figure 5. SEM micrograph (BSE images). a) Pit cap surface showing the presence of characteristic nodular aggregates composed of malachite crystals; b) detail of a) revealing the acicular nature of malachite crystals.

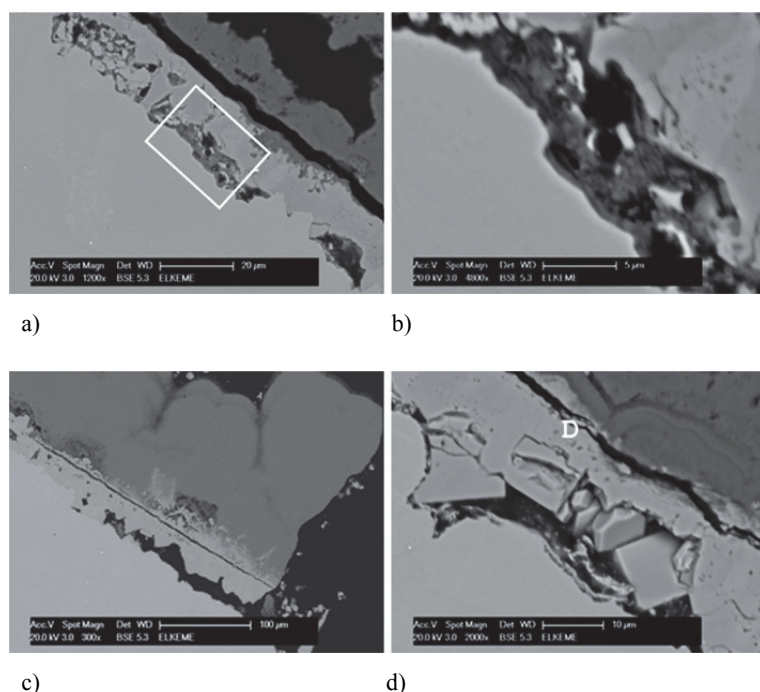


Figure 6. SEM micrograph (BSE images) of a polished transverse section of the corroded inner surface of a CuDHP water tube. a) Layered structure of corrosion products: mixed copper chlorides alternating with copper oxide (Cu_2O) and on top copper carbonates; b) the rectangular area outlined in a) at higher magnification; c) nodular malachite crystals on the pit cap at another location on the transverse section; d) cubic oxide crystals close to the metal/oxide interface.

Perfectly formed cubic copper oxide crystals (Cu_2O) are found underneath the carbonate deposits (see figure 6d) while discontinuous layers of mixed copper chlorides were detected on the floor of the pit. Though the presence of complex hydroxyl-chlorides compounds such as $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$

initially decreases the corrosion rate, their porous nature and poor adhesion to the base metal frequently leads to detachment and loss of the film sustaining the corrosion process [10]. Selective area elemental analysis conducted by EDS, verified the presence of mixed hydroxy-chlorides and carbonates (figure 7). The presence of carbonates and chloride salts causes cold water type pitting corrosion, referred to as Type I-pitting (see also Refs. [11-12]). Type I pitting is a very severe form of corrosion, leading to accelerated corrosion rates, and it is influenced by the concentration of chlorides and bicarbonates. Corrosion pits can provoke failures through stress corrosion cracking (SCC) as they constitute stress concentration sites. Failure analysis of copper tube affected by the synergy of pitting corrosion and SCC is presented in [13]. Several case histories of copper tube damage in service, including SCC, microbiologically influenced corrosion (MIC), pitting corrosion and fatigue are reviewed in [14, 15]. In the majority of the investigated cases, water supply conditions and quality were the major failure contributors. Water chemistry (physicochemical and microbiological parameters including pH, conductivity, total organic carbon, etc.) should be investigated to pin-point precisely the root cause of the leakage failure. Regular water quality monitoring during installation together with sufficient maintenance and appropriate water treatment (adjusting salinity and hardness as well as dosing corrosion inhibitors and controlling the microbial content) as well as avoidance of stagnation periods are suggested as further actions to prevent corrosion failures.

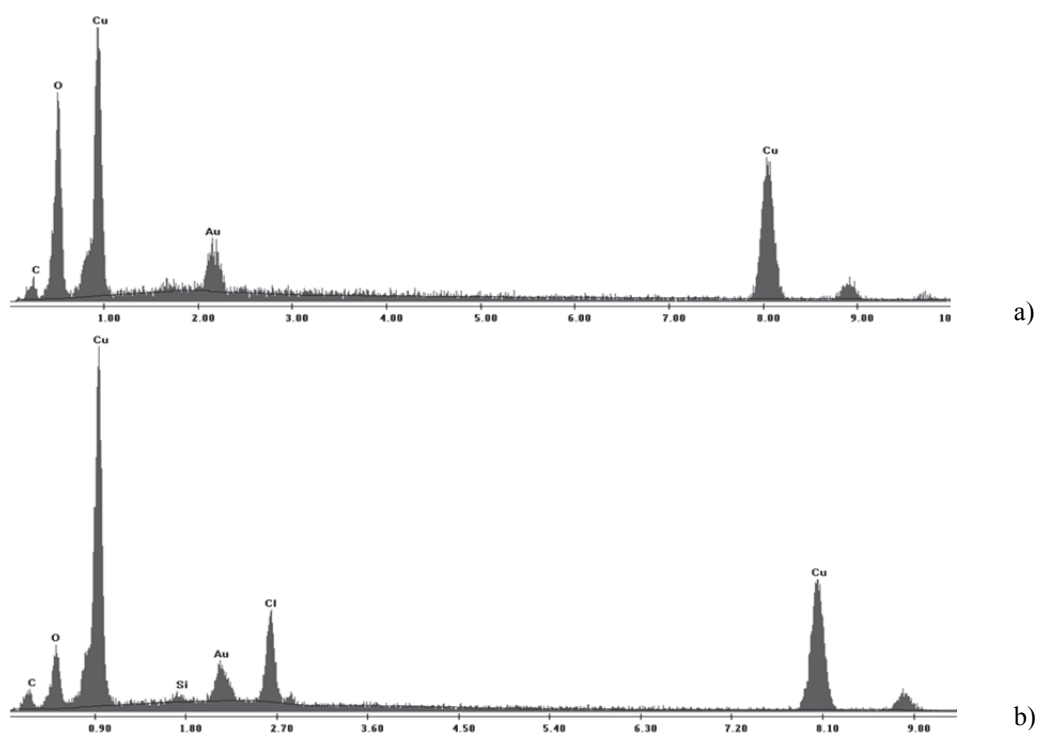


Figure 7. EDS spectra (ZAF corrected – standardless analysis). a) At the surface of the pit confirming the presence of copper carbonate crystals (malachite) – approximate location D in figure 6c; b) Scale attached to the metal substrate consisting of mainly copper (hydro)oxide-chlorides (approximate location – C in figure 6b). Note the presence of significant Cl, considered to be a contributing factor to passive layer destabilisation and pitting initiation. Also note that the energy scale is different on spectra a) and b).

4. Conclusion

Scanning electron microscopy coupled with energy-dispersive X-ray spectrometry constitutes an exceptional analytical technique, offering high spatial resolution and microanalytical capability. The utilisation of SEM/EDS microanalysis provides deep insight and understanding of corrosion and damage mechanisms, outlining the fracture history along with the identification of environmental contributing factors, effectively assisting in failure prevention.

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