Characterization of localized corrosion processes on copper pipes using the technique of X-ray microtomography.

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Abstract. *The technique of optical microscopy analysis is used to characterize its various processes that occur in localized corrosion of copper pipes. To apply this technique, the metal is embedded and polished so that the image obtained represents a flat section of localized corrosion. However, corrosion processes whose morphology occurs as branched corrosion, as in the case of the ant nest corrosion or formicary corrosion, this form of analysis presents some difficulty in demonstrating more accurately the ramifications. The objective is to demonstrate the feasibility of X-ray microtomography techniques for the perfect characterization and documentation of the morphology of the corrosion event. For this study, we used two samples of copper tube that failed by leaking after being kept in contact with polyurethane for a period of one year. For the characterization of failure, we used a Skycan microtomography model 1172. The images were acquired with a resolution of 7um, 100kV voltage and current of 100uA and processed through by gray level binarization. Using this technique it was possible to obtain an accurate determination of the origin point of the corrosion process and its way of expansion, enabling full characterization of the phenomena of localized processes which branched morphology presented itself, as the case of formicary corrosion.*

Keywords: *copper corrosion, ant nest corrosion, X-Ray microtomography*

1. INTRODUCTION

Ant-nest corrosion, sometimes referred to as formicary corrosion, describes a particular form of localized corrosion found in copper tubes used for refrigeration and air conditioning applications. The nature of the attack is of a submicroscopic nature; pits created by this type of corrosion are so fine that they are not visible to the unaided eye (Elliott and Corbett, 1999).

Some laboratory studies have been successful in replicating ant-nest corrosion found in the field using carboxylic acids, hydrochloric- solvents, and petroleum- and water-based drawing and finning lubricants. Case studies reported in the past two years suggest that this form of attack continues to be a problem in the heating, ventilation and air conditioning (HVAC) industry. It is reiterated that approximately 10% of all preliminary failures of copper tubes used in the HVAC industry are the direct result of ant-nest corrosion on a worldwide scale (Elliott and Corbett, 2000). Bastidas et al (2006) also reports that many copper tubes used in air conditioning fail after a2 or 3 months of use due to the contact with carboxylic acids.

The technique of optical microscopy analysis is used to characterize its various processes that occur in localized corrosion of copper pipes. To apply this technique, the metal is embedded and polished so that the image obtained represents a flat section of localized corrosion. However, corrosion processes whose morphology occurs as branched corrosion, as in the case of the ant nest corrosion or formicary corrosion, this form of analysis presents some difficulty in demonstrating more accurately the ramifications. On the other hand, the X-Ray microtomography is a technique which has been used to several applications, such as investigate pore-space in carbonate rocks (Arns et al., 2005) and sandstone rocks (Diógenes, 2009). The X-Ray microtomography technique is limited to the equipment spatial resolution, which represents the smaller object the equipment can detect and the contrast resolution.

The objective is to demonstrate the feasibility of X-ray microtomography techniques for the perfect characterization and documentation of the morphology of the corrosion event. For this study, we used two samples of copper tube that failed by leaking after being kept in contact with polyurethane for a period of one year. For the characterization of failure, it was used a Skycan microtomography model 1172. The images were acquired with a resolution of 7um, 100kV voltage and current of 100uA and processed through by gray level binarization. Using this technique it was possible to obtain an accurate determination of the origin point of the corrosion process and its way of expansion, enabling full characterization of the phenomena of localized processes which branched morphology presented itself, as the case of formicary corrosion.

2. METHODOLOGY

2.1. Mechanism Review

Elliott and Corbett (2000) provide a full review of how the ant-nest corrosion process occurs. This paper reproduces a part of his approach.

Residual organic compounds that remain on copper tubes during production and fabrication into chiller units, are able to advance to ant-nest corrosion only with the simultaneous presence of moisture, air and the decomposition of the organics to acids. It is concluded that the mechanism of the ant-nest corrosion is a modified pitting process involving a very small pit (termed a "micro-anode") where the copper base-metal oxidizes and dissolves according to:

$$Cu^{o} \rightarrow Cu^{+} + e^{-} \quad (1)$$

In the presence of carboxylic acid (e.g., formic acid) the copper ions react to form an unstable copper (I) complex:

$$Cu^{+} + HCOO^{-} \rightarrow Cu(CHOO) \quad (2)$$

This species is further oxidized to form a copper (II) carboxylate (e.g., copper (II) format) and copper (I) oxide (cuprite):

$$4\ Cu(CHOO) + \tfrac{1}{2}\ O_2 \rightarrow 2\ Cu(CHOO)_2 + Cu_2O \quad (3)$$

Copper (II) format has a monoclinic crystalline form and is blue in color. Micro-cracks develop and radiate outward within the pit due to the wedging effect of the deposited copper (I) and copper (II) complexes. The micro-cracks expose more surfaces of copper and the process proceeds within the micro-crack to give the copper (I) complex according to:

$$Cu(CHOO)_2 + Cu^{o} \rightarrow 2\ Cu(CHOO) \quad (4)$$

Thereon, reactions 3 and 4 repeat over and over until tunnels are formed leading to ultimate through wall penetration. If, however, there is any disruption in the presence of the basic three components (i.e., moisture, air and organic acid), then the micro-cell mechanism shuts down and ant-nest corrosion ceases to propagate. Therefore, a tube may be infected with ant-nest corrosion but failure has not resulted in a leak.

2.2. Experiment

The samples were hollow cylinders composed of pure copper. Each one had 1cm of diameter, with a 0.4cm wall thickness. Both of the samples were part of a refrigeration system in which there had a leaking failure. After the acknowledgement of the leaking, the samples were cut to the length of 3cm, as exposed in the Fig. 1.

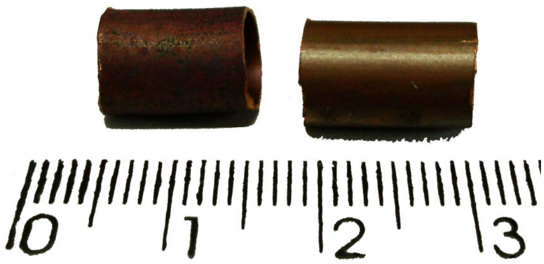


Figure 1. Test copper tubes used in this experiment

The regular procedure to analyze an ant-nest corrosion would include a sample preparation. The technique of optical microscopy analysis is used to characterize its various processes that occur in localized corrosion of copper pipes. To apply this technique, the metal is embedded and polished so that the image obtained represents a flat section of the localized corrosion. A sample image extracted from Elliott and Corbett (2000) is observed at Fig. 2.

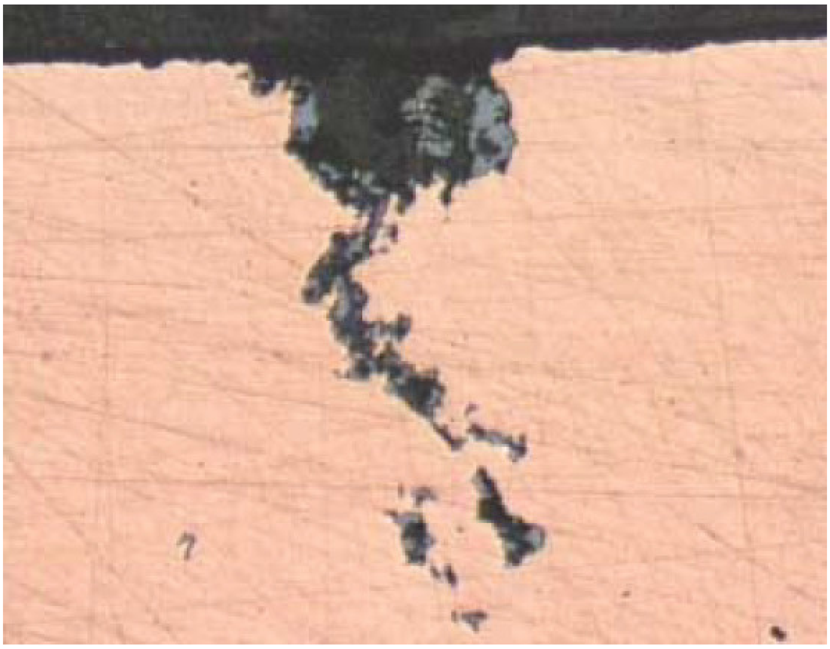


Figure 2. Image of a copper tube which leaked by ant-nest corrosion extracted from Elliott and Corbett (2000)

Since the chosen technique was the X-ray microtomography, the samples were not grinded, polished or embedded, as the regular preparation procedure and, besides the cutting, they required no further preparation. To characterize the ant nest corrosion, and its branches, it was used a Skycan microtomography model 1172, as exposed at Fig.3.

Figure 3. Skycan microtomography model 1172

The images were acquired with a resolution of 7µm, 100kV voltage and current of 100µA. The rotation was of 360º and the step of 0.4 º. The equipment could achieve a 1 µm resolution, but the authors considered the 7 µm resolution sufficient to represent the ant-nest corrosion phenomena, considering the 100x amplification Eliott and Corbett (2000) adopted in their work. There may be corrosions process smaller than this scale, however this will not be investigated in this research. The X-ray technique results in images which show sections of the original sample. For each sample it was acquired 1.226 images, comprising 8.52mm of the physical sample. One section extracted from the position 0.459mm can be observed in the Fig. 4.The grey “circle” is the copper tube named sample A.

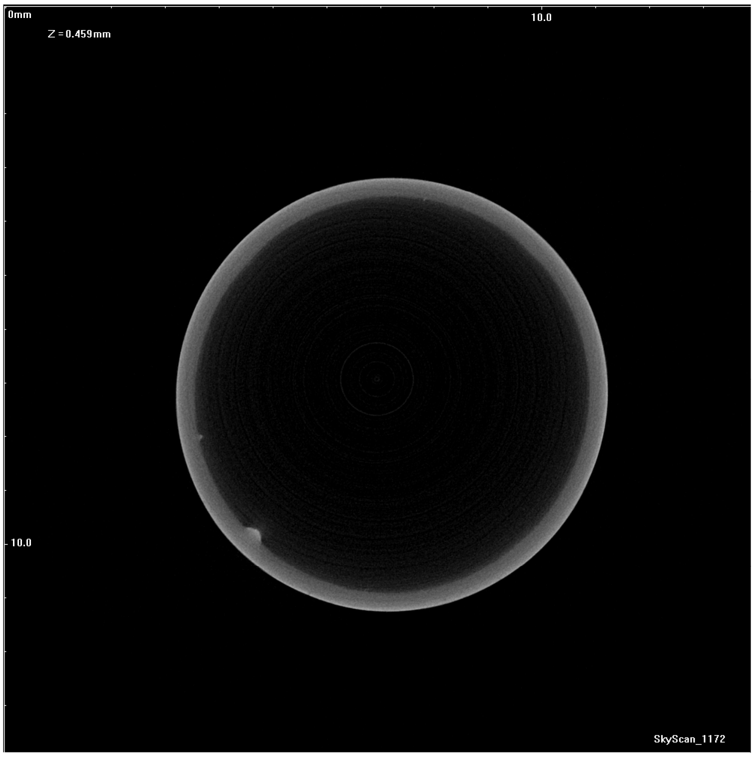
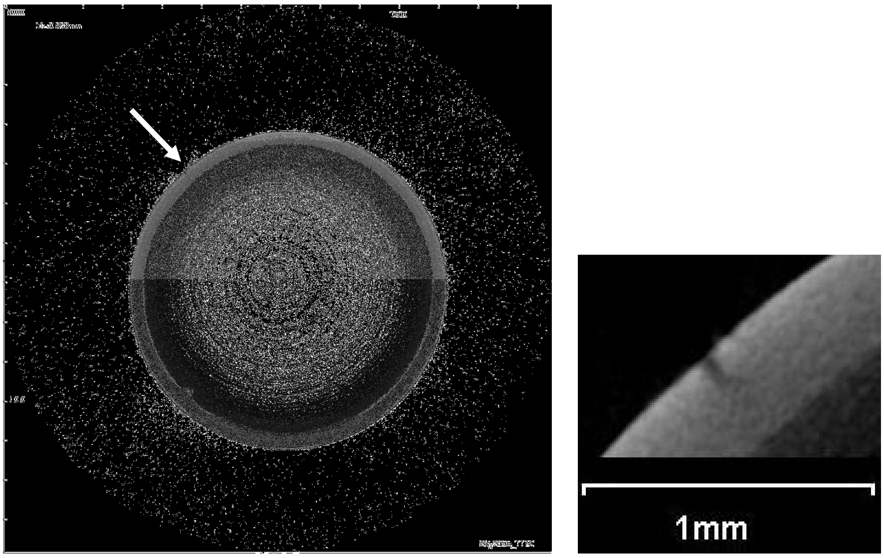


Figure 4. Copper microtomographic image acquired from sample A

Following the images sequence, at the position 0.696mm, it can be seen a localized corrosion, which is indicated by an arrow at Fig. 5 (a). This corrosion extended itself until the image located at position 0.904mm, comprising a 31 images sequence. The corrosion detail can be observed in Fig. 5 (b).



(a) (b)

Figure 5. Copper microtomographic image acquired from sample A at position 0.696mm

After locating the corrosion process, the images were stacked, a region of interest (ROI) was selected and the latter was binarized. This procedure was executed with the MicroImage software. The ROI was chosen so it would be greater than the corrosion. It was adopted a grey-level threshold binarization. The images were exported to the Paraview software and the entire corrosion can be observed at Fig. 6. The upper part of the image is the inner side of the sample, while the lower part of the image is the outer part of the sample, where the corrosion began. Notice that the corrosion process was very curved, and would have been difficult to observe it just using regular techniques. The isolated points are noisy data and must not be considerate.

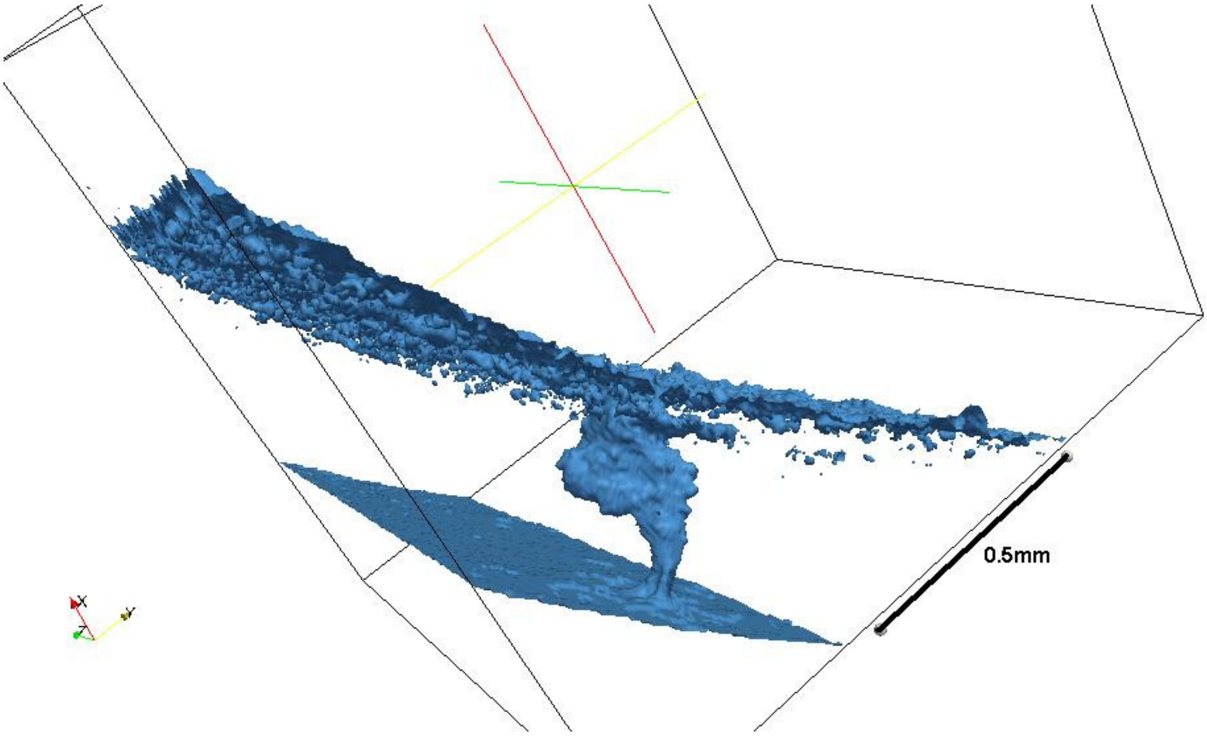
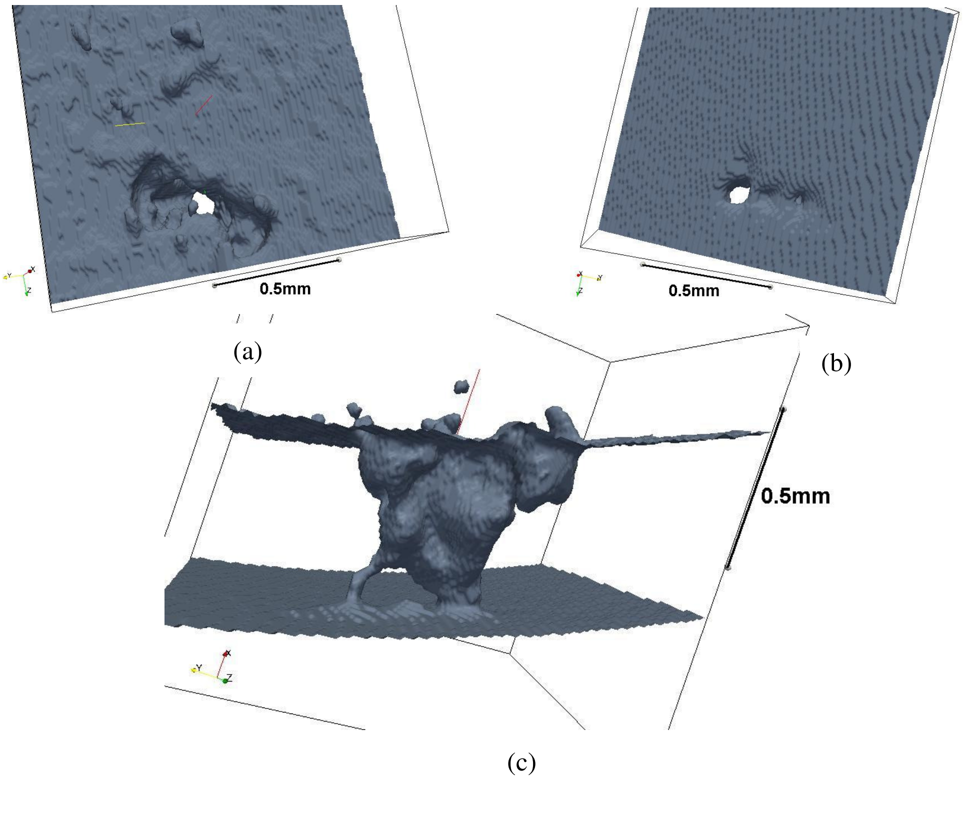


Figure 6. 3D image of a sample A comprising approximately 0.3mm

At the sample B, at the height 1.51mm it was detected another corrosion event. This one was bigger than the previous, and extended itself for 80 images, comprising 0.5mm. This corrosion can be observed in detail in the Figs 7 (a), (b) and (c). The figures expose different angles of the same phenomenon. The Fig 7 (a) exposes the internal wall of the sample, the 7 (b) shows the outer wall and the 7 (c) presents the side view angle of the corrosion, with the upper part of the image representing the inner side of the sample. This corrosion started at two different points which merged into one. This one formed a larger process which percolated.



(a) (b)

(c)

Figure 7 corrosion at position 1,51mm (a) internal wall of the sample, (b) outer wall, (c) side view angle

3. CONCLUSION

This study showed the feasibility of the X-ray microtomography technique to characterize ant nest corrosion processes in copper tubes. The corrosion spots were detected and well defined at the analyzed resolution. This research intends to propose characterization techniques which will increase the understanding of this phenomenon in the future. The 7 µm spatial resolution adopted in this research seemed to be sufficient to characterize the ant-nest phenomena in the realized experiment; however this spatial resolution should be more investigated in a future research.

4. REFERENCES

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