Corrosiveness of Brazilian Candiota Coal

Anderson Cagliari[1], Nayana Simon de Vargas[2],
Luciana Machado Rodrigues[3]

[1,2,3] Universidade Federal do Pampa - UNIPAMPA, Engenharia Química, Campus Bagé, Av. Maria Anunciação Gomes de Godoy, 1650, 96413-170, Bagé - RS, Brazil.
e-mail: andersoncagliari@unipampa.edu.br; nayana.eq@gmail.com; luciana.rodrigues@unipampa.edu.br

ABSTRACT

Candiota city, in the south of Brazil, is located near the largest reserves of mineral coal of the country. This coal is used for thermoelectric power generation. The extraction of coal from open-cut mines involves operations may generate at least some particulate matter into the atmosphere. These particles retained on the surface of metallic structures exposed to the atmosphere, may adsorb gases such as CO, CO_2, SO_2 and NO, which, in combination with humid air form corrosive substances, such as HNO_3 and H_2SO_4. This paper aims to evaluate the influence of Candiota coal on the corrosion of buried steel structures and exposed to atmosphere containing particulate matter from coal combustion. The coal sample was characterized by SEM (scanning electron microscopy), thermogravimetric analysis (TGA), surface area analysis (BET method), electrical conductivity (EC) analysis, FTIR and Raman spectroscopy. Corrosion was simulated by exposure of steel samples to coal particles and thermoelectric industrial atmosphere. Electrochemical tests of solutions leached from the coal were conducted by voltammetry to evaluate the soluble compounds corrosiveness. The corrosion rate was determining following the technical standard ASTM G1-90. Localized attacks and corrosion products formations were detected in API 5L Grade B steel exposure to coal. The average corrosion rate for the samples in direct contact to the pulverized coal was 0.15 mm/year, while in samples exposed to the atmosphere from industrial power plant was 0.30 mm/year. It is concluded that API 5L Grade B steel metal structures, exposed to atmospheres rich in Candiota coal and its derivatives, must be properly protected and monitored to avoid future damage caused by corrosion.

Keywords: coal, corrosion, pipeline, carbon steel.

1. INTRODUCTION

Coal is a non-renewable fossil fuel, formed from the decomposition of organic matter under certain conditions of temperature and pressure [1]. It is recovered from the ground by mining processes, which may be underground or open-cut operations depending in part on the depth and overburden material under which the coal occurs [1]. In Brazil, the main coal reserves are located in the states of Paraná (PR), Santa Catarina (SC) and Rio Grande do Sul (RS); the city of Candiota (RS) is located close to the largest open-cut reserves of coal in the country [1]. The chemical composition of coal varies depending on its geological history, but the material consists essentially of carbon, oxygen, nitrogen, and sulfur, associated with minerals, including quartz, kaolinite, illite, feldspar, calcite, dolomite and pyrite [2]. The main current uses of coal include the generation of electricity through thermal power plants, generation of heat for different production processes, and generation of steam used in some manufacturing industries [1].

The extraction of coal from open-cut mines involves operations such as blasting, crushing, grinding, screening, separation and transportation [3]. These processes may generate at least some particulate matter into the atmosphere. Although many of these particles are inert to metallic materials, they may have the capacity to adsorb other, more aggressive substances [4].

The particles retained on the surface of metallic structures exposed to the atmosphere, may adsorb gases such as CO, CO_2, SO_2 and NO, which, in combination with humid air form corrosive substances, such as HNO_3 and H_2SO_4. In addition to the formation of substances harmful to metals during extraction of the coal, when coal is burned for power generation or steam production, release of carbon and sulfur and reaction of those elements with oxygen in the atmosphere may forming CO (g), CO_2 (g), SO_2 (g) and SO_3 (g). These gases may then combine with atmospheric moisture, forming aggressive substances such as H_2SO_4, and

H$_2$SO$_3$; these precipitate in the form of acid rain and are deposited on metallic structures, causing corrosion [4].

Other facts related to coal aggressiveness is the particulate matter from coal combustion may have large amounts of ash (up to 50%), which contain abrasive mineral species such as hard quartz, promoting the erosion propensity of coal [5]. The erosion is a serious problem in power generation equipment, in gas turbines for ships and aircrafts and in other energy conversion and chemical process systems and should be either totally prevented or detected at an early stage to avoid catastrophic failure [5].

According to several authors, corrosion is defined as the deterioration of a material, usually metallic, by electrochemical or chemical action of the environment, either associated or not associated with mechanical stress [4,6,7]. The deterioration caused by physical-chemical interaction between the material and the environment results in undesirable changes in the material, such as wear, chemical or structural changes, making the material unsuitable for use [4].

The corrosion of metallic structures may result in loss of material, interruption of processes, product contamination, and risks to human life and the integrity of the environment [7]. Therefore, it is fundamentally important to study materials and corrosive processes, including the causes and possible consequences of corrosion [4,6,8]. Exposure of metallic samples (called coupons) properly prepared, in atmospheres of interest, is an efficient technique for the study of atmospheric corrosion [9].

Many metal structures, mainly industrial pipes, are manufactured from carbon steel, due to favorable cost and strength, easy welding and shaping, high resistance to high and low temperatures, and resistance to major changes [10]. However, this metal is susceptible to corrosion processes because it contains impurities, such as non-metallic inclusions [4].

The non-metallic inclusions are known to be preferred sites for the nucleation of pits on steels [11-13]. Steel corrosion studies have been conducted using aggressive media, such as NaCl, HCl and H$_2$SO$_4$ at relatively high concentration. The distribution of inclusions plays an important role; apparently larger inclusions or regions with a higher density of inclusions are preferred for pit nucleation. Corrosion of inclusions in carbon steel samples has also been studied presence of solutions containing humic and fulvic acids extracted from soil and coal, both of which may also cause corrosive process on the non-metallic inclusions [8,14,15].

The main of the present work was to study the corrosion process in samples of carbon steel type API 5L Gr. B brought about by the action of particulate matter from Candiota coal. The study involved the characterization of the coal, a corrosion simulation process of carbon steel in coal, and electrochemical tests on aqueous solutions to evaluate any soluble compounds released by the coal.

2. MATERIALS AND METHODS

The coal sample used in the study was extracted from the Candiota mine, in Candiota City, RS. The weathered sample was transferred in large blocks solid. These blocks were fractionated into smaller pieces and milled to a fine particle size, for further characterization and leaching to achieve the electrochemical tests. The characterization of Candiota coal was performed by thermal analysis (TGA), morphological characterization by scanning electron microscopy (SEM), spectroscopic analysis by absorption spectroscopy in the infrared (FTIR) and Raman spectroscopy, and physical analysis particle by the BET method (Braunauer, Emmet and Teller) analysis and electrical conductivity (EC).

The thermogravimetric analyses were performed at a heating rate of 10 °C/min and the final temperature of 900 °C under air atmosphere to study the thermal decomposition of the material. Characterization by scanning electron microscopy was performed by acquiring images using secondary electrons, low voltage (5 keV), because to not change the morphological characteristics of the sample. This analysis was carried out to know the fine particles morphology of coal sample, then was not used energy dispersive x-ray (EDS) analysis. The analysis by absorption spectroscopy in the infrared region was performed on tablet obtained by mixing coal powder and KBr in a range from 4000 to 400 cm^{-1}. Raman spectroscopy was performed using a filter and laser wavelength of 785 nm. The pulverized coal sample had its surface area determined by the BET method [16] (Braunauer, Emmett and Teller), which employs adsorption isotherms. And the electrical conductivity of carbon was measured using to digital conductivity meter. This parameter is very important for the evaluation to coal corrosiveness.

The metallic material used for sample preparation was extracted from a section of pipe made of steel API 5L Gr. B, typical material used for the construction of industrial metal pipes for transporting different fluids. Table 1 shows the nominal composition of the sample according to the manufacturer COSIPA – "Companhia Siderúrgica Paulista" determined using energy-dispersion spectrometry (EDS).

Table 1: Nominal chemical composition of the API 5L Gr. B steel by EDS (wt%).

STEEL	C	Mn	P	S	Fe
API 5L Gr. B	0.27	1.15	0.03	0.03	Balance

The metal samples for the study were prepared by cutting, yielding a geometric area of about 0.7 cm^2. The sections were then polished using silicon carbide paper (until particle size of 2500) in water, for the removal of impurities and reduction of surface defects of metal. The samples were rinsed in ethyl alcohol, dried in an air jet at room temperature, weighed in analytical balance and stored in desiccators under vacuum. The morphology of the metallic samples prepared was characterized by optical microscopy in reflected light at different magnifications, and then forwarded to the corrosion simulation and electrochemical tests.

The corrosion tests were simulated by two different methods:

1. the steel samples were put in direct contact with dried coal particles, for a total time of 6 months exposure;
2. the steel samples were exposed outdoor to the weather in a coal combustion plant, receiving to particulate matter from a thermoelectric industry, in Candiota City, for 6 months.

In both cases the attack morphology on the steel samples was evaluated every month by optical microscopy and the variation of mass determined by weighing in an analytical balance. All tests were performed in duplicates.

For determining the corrosion rate at the end of the period of the corrosion tests, the samples were cleaned of the corrosion products that had been formed, following technical standard ASTM G1-90 entitled "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens", reweighing to determine the weight variation in the metal samples free of corrosion deposits.

The corrosion rate [4] was calculated according to the following equation (1):

$$Rate = \frac{(k * W)}{(A * T * D)}$$

(1)

in which: k is a constant for adjusting units (8.46 x 10^4 mm/year), W is the weight loss in grams, A is the area in cm^2, T is the exposure time in hours and D is the density in g/cm^3 of the metallic material; for carbon steel D is 7.86 g/cm^3.

For the realization of electrochemical tests the pulverized coal was leached with distilled water (pH 6.0 and electrical conductivity of 2.5 μS/m) for the extraction of soluble components in a ratio (coal/water) of 1:10, with agitation for about two hours. The leachate solution was filtered through filter, to eliminate any residual coal particles. The leachate solution was used as electrolyte to perform the electrochemical tests. This solution showed pH 7.5 and electrical conductivity of 290 μS/m. It was used a three-electrode electrochemical cell comprising: the reference electrode was Ag/AgCl, platinum as counter electrode and the sample of carbon steel API 5L Gr. B as working electrode. The results are showed in normal hydrogen electrode (NHE). The cyclic voltammetry tests were performed at scan rates of 1, 10 and 100 mV/s, varying the range of potential sweep. A first investigation was conducted by cyclic voltammetry in extensive potential sweep between -2000 to +1550 mV (NHE) at a rate of 100 mV/s. To observe the nucleation of corrosive attack was restrict the scan range between -1000 to +560 mV (NHE), at scan rates of 10 and 100 mV/s. The tests were performed in the presence of oxygen in an Autolab with potentiostat/galvanostat PGSTAT101, including differential electrometer amplifier. At the end of the tests, steel samples were analyzed by optical microscopy. By electrochemical tests is possible to evaluate the corrosion process in metal samples in aqueous solution content soluble compounds of coal, simulate the rain in coal mine.

3. RESULTS AND DISCUSSION

Microscopic analysis of pulverized coal particles revealed that these solids are composed of dense particles, relatively smooth surface, as shown in Figure 1. It is interesting to visualize the particles which are studied here. The particle size distribution is heterogeneous. Previous work has shown the mild steel corrosion rate was observed to increase with decreasing coal particle size distribution [17].
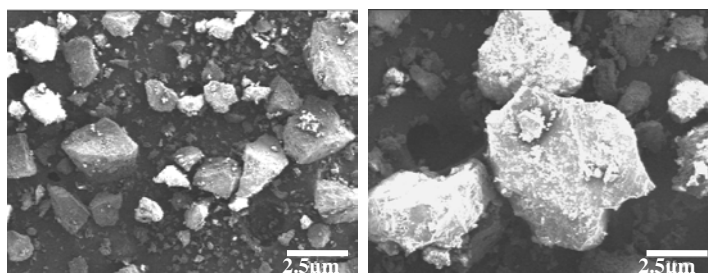

Figure 1: Scanning electron microscopy of pulverized coal.

Thermogravimetric analysis of the coal is shown in Figure 2, which allows observing that the sample has a first thermal decomposition in the range 190-428 °C, decomposing about 13 % of the mass of the whole sample and a second range of thermal decomposition about 428-561 °C, representing approximately 38 % of the sample mass.
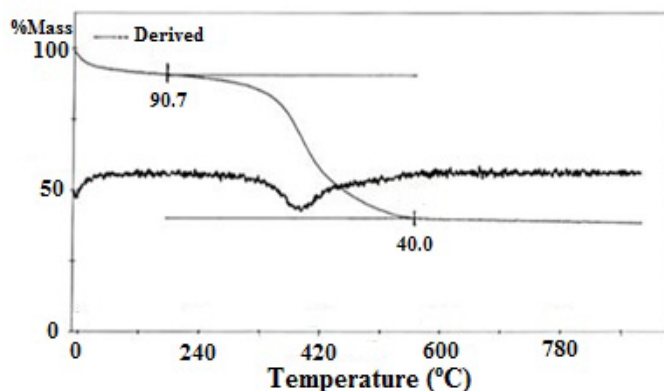

Figure 2: Thermogravimetric analysis of the pulverized coal.

For the surface area analysis of the coal particles, by the BET method, it was found that the particles have a surface area of 9,064 m^2/g. And the electrical conductivity was 0.1 μS.

The evaluation of the infrared spectrum, shown in Figure 3, indicates that the major compounds present in coal sample are relative to chemical bonds O-H, aliphatic C-H, carboxyl C=O, C-O and aromatic rings.
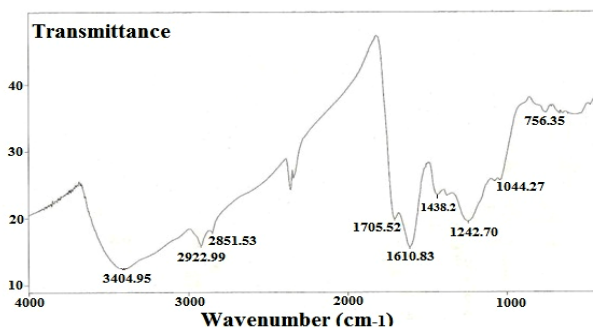
Figure 3: Absorption spectrum in the infrared region to the coal.

Analysis by Raman spectroscopy showed two peaks: one at 1587 cm^{-1} that indicates C-C vibration in aromatic structures, and another at 1350 cm^{-1}, which refers to different types of structural defects typical of coal [18]. This spectrum is shown in Figure 4.
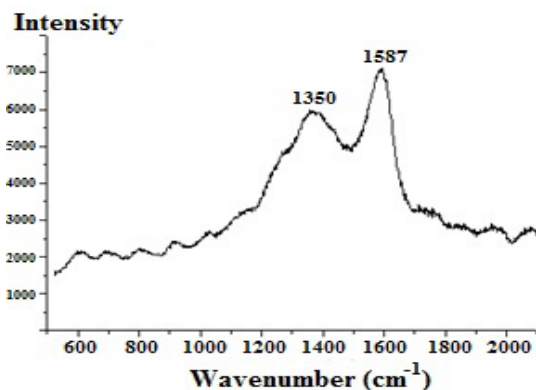
Figure 4: Raman spectrum of the coal.

For the corrosion simulated tests, the morphology of prepared metallic samples was analyzed by optical microscopy (Fig. 5). It is possible to visualize the presence of non-metallic inclusions of sulfur compounds (rounded dark small dots), typical for carbon steel type API, previously studied [8,14,15].
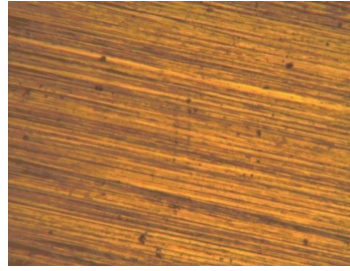

Figure 5: Surface morphology for the prepared sample of API 5L Gr. B.

After 60 days of the contact between the steel samples and coal particles, nucleation of the corrosion process was detected by microscopic analysis (Fig. 6). Apparently, this nucleation occurs from the non-metallic inclusions present in steel API 5L Gr. B, as already detected by other authors studied the corrosion of API steel in soil [5]. It is possible to detect the formation of metal oxides thin layers, by the occurrence of color formation in the samples. The green and red details around the inclusions showed in Fig. 6 indicated the formation of oxides [19].
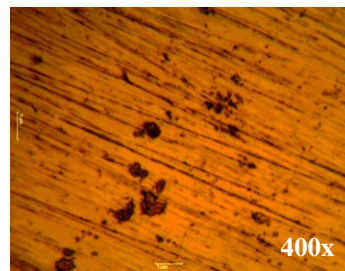
Figure 6: Nucleation of corrosive attack after 60 days exposure to pulverized coal.

After 90 days of exposure there is a greater amount of corrosion products on the metal surface, rounded, surrounding the inclusion, as shown in Figure 7.
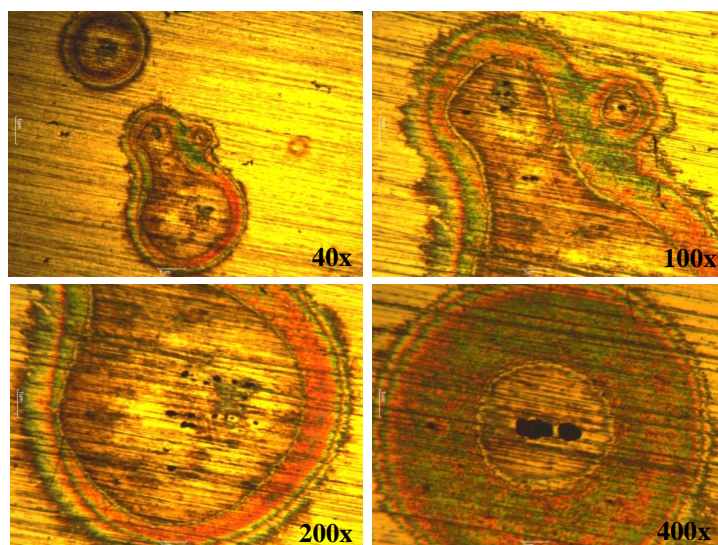

Figure 7: Formation of corrosion products after 90 days exposure to coal at different regions.

To investigate the corrosive attack were removed the deposits formed on the metal surface for micro-

scopic analysis. In the Figure 8 is possible to observe the attacks are nucleated on the non-metallic inclusions.
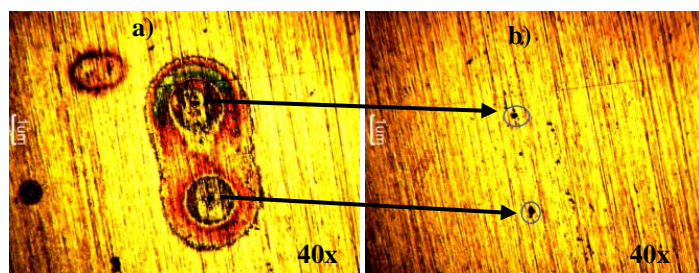

Figure 8: Attack morphology to metallic samples exposed to coal: a) before removal of the corrosion products from metallic surface; b) after removal, using the Clark solution.

Nucleation of the corrosion process was also detected, by optical microscopy after 150 and 180 days of exposure of the metal to the coal sample, as shown in Figure 9.
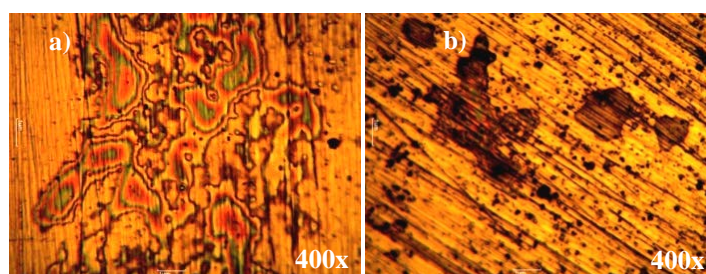

Figure 9: The formation of corrosion products after (a) 150 and (b) 180 days of exposure to coal.

In the simulation of corrosion in metallic samples exposed to an industrial atmosphere, rich in particulate matter from coal combustion, a thick layer of corrosion products was quickly generated on the sample surface. This dense film was difficult to analyze by metallurgical optical microscope, and the attack morphology was therefore evaluated from by digital images at low magnification, shown in Figure 10.
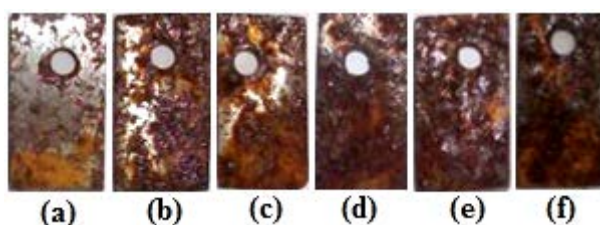

Figure 10: Metallic samples exposed to particulate material from the combustion of coal in thermoelectric power plant industrial atmosphere: (a) 30, (b) 60 (c) 90 (d) 120 (e) 150 and (f) 180 days of exposure by digital photo.

The average corrosion rate for the samples in direct contact to the pulverized coal was 0.15 mm/year, while in samples exposed to the atmosphere from industrial power plant was 0.30 mm/year, indicating that the latter was twice as more aggressive to API 5L Gr. B steel.

The Candiota coal sample was leached with distilled water to extract its soluble constituents, to check the influence of these constituents on the surface of the steel sample by electrochemical testing.

A first investigation was conducted by cyclic voltammetry in extensive potential sweep between -2000 to +1550 mV (NHE) at a rate of 100 mV/s. It is possible to observe the firing current density (Fig. 11). This electrochemical test caused severe corrosion by pits in steel sample (Fig. 12).

Restricting the scan range between -1000 to +560 mV (NHE) it was possible observe the nucleation of corrosive attack, which occurred on the non-metallic inclusions present in API 5L Gr. B steel and the formation of small precipitates on the sample (Fig. 13). It was performing this scanning potential at scan rates of 10 and 100 mV/s, to provide different times for the electrochemical reactions. It was observed the current density increases about 300 μA/cm^2 when the corrosion process is performed slower. The current peak was about 50 mV (NHE).
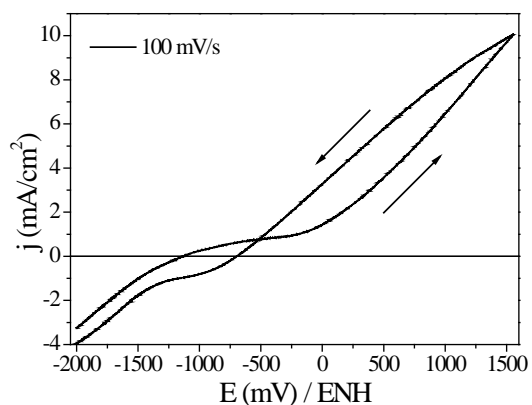
Figure 11: Cyclic voltammetry at potential sweep -2000 to +1550 mV (NHE), scan rate 100 mV/s.
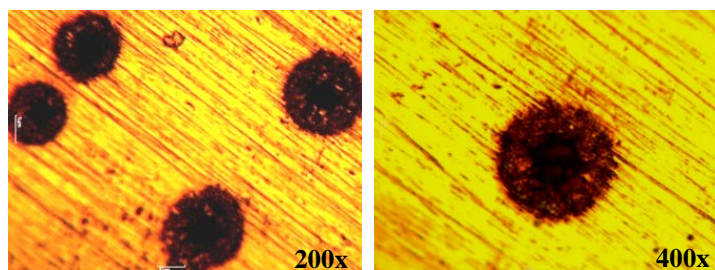

Figure 12: Corrosive attack on metal samples after electrochemical test at potential sweep -2000 to +1550 mV (NHE).
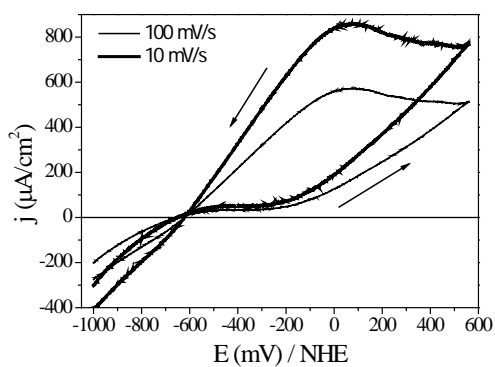

Figure 13: Cyclic voltammetry at potential sweep -1000 to +560 mV (NHE), scan rates 100 and 10 mV/s.

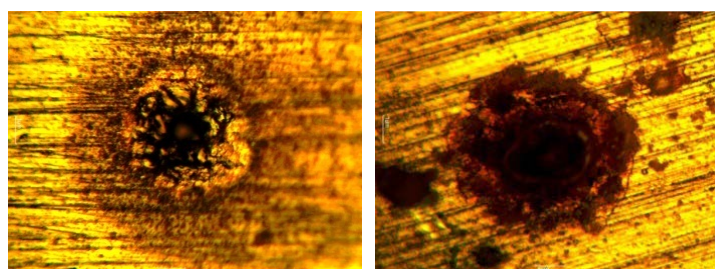Consequently, the formation of pits was observed over the entire length of the metal sample (Fig. 14).

Figure 14: Attack nucleation after electrochemical tests at potential sweep -1000 to +560 mV (NHE), scan rates (a) 100 and (b) 10 mV/s.

4. CONCLUSIONS

The coal of Candiota has aromatic groups and these in decompose above 400 °C, representing about 13 % of the integral mass of the sample and the functional groups simple aliphatic chains, decomposing around 280 °C is approximately 38 % of the sample.

The corrosive process simulated through the metallic samples in direct contact with Candiota pulverized coal indicates nucleation of attack after 60 days of exposure. After 90 days, the formation of corrosion products was observed in the vicinity of colored inclusions, indicating thin layers of metal oxides. Strong formation of corrosion products was further, observed after 150 and 180 days of exposure to the coal, indicating a localized attack on the sample.

The simulation of corrosion in metallic samples exposed to the industrial atmosphere indicated the formation of oxides and precipitation on the metal surface, causing a general corrosion of the samples. Even after the first 30 days of exposure, samples of carbon steel already showed signs of corrosion on its surface.

The first electrochemical tests performed indicate that the water soluble constituents of the coal promote the corrosion of carbon steel structures in contact with atmospheres rich in coal. Localized attacks were detected, such as the nucleation of the non-metallic inclusions in API 5L Gr. B steel.

It is concluded that metal structures in general, such as pipes, equipment, and storage tanks, exposed to atmospheres rich in Candiota coal and its derivatives, must be properly protected and monitored to avoid future damage caused by corrosion.

5. ACKNOWLEDGMENTS

6. BIBLIOGRAPHY

[1] PIRES, M, QUEROL, X, TEIXEIRA, E. C., "Caracterização do carvão de Candiota e de suas cinzas", *Geochimica Brasiliensis*, v. 15, n. 1/2, pp. 113-130, 2001.

[2] STEVENSON, F. J., Humus chemistry: genesis, composition, reactions, New York, John Wiley & Sons, 1994.

[3] FOUST, A. S., WENZEL, L. A., CLUMP, C. W., et al., Principles of unit operations, New York, John Wiley & Sons, 1980.

[4] GENTIL, V., Corrosão, 6 ed., Rio de Janeiro, LTC, 2011.

[5] CHAWLA, V., CHAWLA, A., PURI, D., et al., "Hot corrosion & erosion problems in coal based power plants in India and possible solutions – a review", *Journal of Minerals & Materials Characterization & Engineering*, v. 10, n. 4, pp. 367-385, 2011.

[6] GEMELLI, E., Corrosão de materiais metálicos e sua caracterização, Rio de Janeiro, LTC, 2001.

[7] ROBERGE, P. R., Handbook of corrosion engineering, New York, The McGraw-Hill Companies Inc., 1999.

[8] RODRIGUES, L. M., DICK, L. F. P., "Influence of humic substances on the corrosion of the API 5LX65 steel", *Corrosion*, Houston, v. 62, n. 1, pp. 35-43, 2006.

[9] ALMEIDA, N. L., PANOSSIAN, Z., Corrosão atmosférica 17 anos, São Paulo, IPT, 1999.

[10] TELLES, P. C. S., Tubulações industriais: materiais, projeto, montagem, São Paulo, LTC, 2010.

[11] BAKER, M. A., CASTLE, J. E., "The Initiation of pitting corrosion at MnS inclusions", *Corrosion Science*, v. 34, n. 4, pp. 667-682, 1993.

[12] PUNCKT, C., BÖLSCHER, M., ROTERMUND, H. H., et al., "Sudden onset of pitting corrosion on stainless steel as a critical phenomenon", *Science*, v. 305, n. 5687, pp. 1133-1136, 2004.

[13] STEWART, J., WILLIAMS, D. E., "The initiation of pitting corrosion on austenitic stainless steel: on the role and importance of sulphide inclusions", *Corrosion Science*, v. 33, n. 3, pp. 457-463, 1992.

[14] YASAKAU, K. A., WEBER, C. R., RODRIGUES, L. M., et al., "AFM study of the corrosion of pipeline steel in organic compounds extracted from soil", *ECS Transactions*, v. 11, n. 22, pp. 107-119, 2008.

[15] SCHÜTZ, P., CASTILHOS, E., RODRIGUES, L. M., et al., "The influence of inclusions and naphthenic acids on the corrosion of pipeline steels", *ECS Transactions*, v. 3, n. 13, pp. 173-179, 2007.

[16] BRUNAUER, S., EMMETT, P. H., TELLER, E., "Adsorption of gases in multimolecular layers", *Journal of the American Chemical Society*, v. 60, n. 2, pp. 309-319, 1938.

[17] GARDINER, C. P., MELCHERS, R. E. "Corrosion of mild steel by coal and iron ore", *Corrosion Science*, v. 44, n. 12, pp. 2665–2673, 2002.

[18] POTGIETER-VERMAAK, S., MALEDI, N., WAGNER, N., et al., "Raman spectroscopy for the analysis of coal: a review", *Journal of Raman Spectroscopy*, v. 42, n. 2, pp. 123-129, 2011.

[19] COLPAERT, H., Metalografia dos produtos siderúrgicos comuns, São Paulo, Blücher, 2009.