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High-temperature corrosion during the thermal treatment of footwear leather wastes

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ABSTRACT

The footwear leather waste (FLW) has shown some distinct features of a conventional biomass, among which high concentrations of sulfur and chromium. The paper presents the obtained experimental results from gasification and combustion of FLW performed in a semi-pilot plant (350 kW_{th}). The corrosion tests were carried out with one low carbon steel and three stainless steels at temperature around 500 °C. The obtained corrosion rates for all the tested alloys were significantly lower than those observed on other types of biomass. The presence of chromium oxide and sulfur dioxide in the flue gas was associated with reduction in the corrosion rate.

1. Introduction

The footwear industry contributes significantly to the Brazilian economy. In 2008, approximately 165 million pairs of shoes were exported with a turnover of about US$ 1.88 billion. Nevertheless the footwear industry has a high potential to generate solid wastes. These wastes are either disposed to an open dump which results in significant environmental impacts as a consequence of the skin forming leachate degradation, or are incinerated in an uncontrolled system [1]. In this case, the waste thermal treatment method can be considered as an alternative cost-effective one. A problem of the process that has to be overcome is connected with the corrosion of the equipment metal parts, which reflects in frequent maintenance and increased overall operational costs.

The footwear leather wastes contain chlorine concentration similar to that one found in other biomass, but sulfur and chromium concentrations are much higher [2]. The tannery wastes (raw materials for production of footwear) have high sodium concentration due to the use of NaCl for the skins preservation and during the pickle. Analysis [3] indicated the presence of some amount of potassium.

The suitability of an alloy for high temperature process performance (425 to 1, 100 °C) depends on inherent alloy composition properties and chosen operational conditions. Chromium is essential constituent of alloys which plays a key role in chemical process performance above 550 °C. It forms a tightly adherent oxide film that prevents the oxidation process [4].

The mechanism of high-temperature corrosion in sulfur and chlorine containing atmosphere is very complex which leads to the formation of layers with an exemplary structure presented in Fig. 1 [5,6]. In the case of low alloy heat-resisting steels, the first two layers contained iron hematite and magnetite oxides and the last layer (next to the material) is formed by iron chlorides and sulphides. In high alloy heat-resisting steels the layers are similar, with the exception of the last layer, where double chromic and ferric oxides (spinels) can be formed.

In order to understand the corrosion mechanism of alloys exposed to high temperatures, and in the presence of chlorine, a literature review analysis was done [7]. On the bases of this analysis it can be concluded that when steel is exposed to an oxidative environment at high temperatures, the metal is gradually oxidized to thermodynamically stable oxides and forms an oxide layer attached to the metal. This oxide layer is smooth and dense, and provides a barrier for further diffusion of oxygen and most other gaseous species to the metal. However, chlorine has the ability to penetrate through the protective oxide layer. The mechanism can be explained as follows: Cl_2 diffuses through the oxide layer, most probably through pores and cracks, to the layer–metal interface where it reacts with the metal alloys to form metal chlorides. Three forward reactions may take place. The Cl_2 may react with the metal according to Reaction (1) to form metal chlorides. Metals can also react directly with HCl according to Reaction (2). Metal chlorides have high vapor pressures

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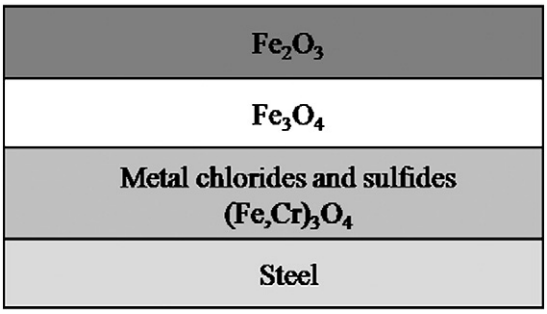

Fig. 1. Structure of layers formed on steel as a result of high-temperature chlorine–sulfur corrosion [6].

at the metal–layer interface, and continuous evaporation may take place, as well (reaction 3).

$$M(s) + Cl_2(g) \rightarrow MCl_2(s) \quad (1)$$

$$M(s) + 2HCl(g) \rightarrow MCl_2(g) + H_2(g) \quad (2)$$

$$MCl_2(s) \rightarrow MCl_2(g) \quad (3)$$

where: M = Fe, Cr or Ni.

These volatile metal chlorides may diffuse (in particular conditions) to the layer surface. The oxygen concentration proportionally increases with distance from the metal, leading to an oxidation of the metal chlorides to solid metal oxides. The resulting oxides precipitate from this gas-phase reaction and form a very loose metal oxide layer that provides no protection against further attack.

$$3MCl_2(g) + 2O_2(g) \rightarrow M_3O_4(s) + 3Cl_2(g) \quad (4)$$

$$2MCl_2(g) + 3/2\,O_2(g) \rightarrow M_2O_3(s) + 2Cl_2(g). \quad (5)$$

According to Reactions (4) and (5), chlorine is released and can diffuse to the bulk gas or back to the metal surface, thus forming a cycle of reactions. Fig. 2 shows a graphical representation of the corrosion mechanism.

Researchers have revealed two different mechanisms that play important role for the chemical break-down of the protective oxide (for FeCrNi alloys) in the presence of alkali metals, oxygen, hydrochloric acid, sulfur dioxide and water. The evaporation of chromic acid ($CrO_2(OH)_2$) and the chromate formation [8,9] can be explained as follows: chromic acid molecules are formed through hydrolysis of the chemisorbed chromate by water molecules; the evaporation of chromic acid decreases in the presence of small amounts of SO_2 [8]. This effect was attributed to the formation of

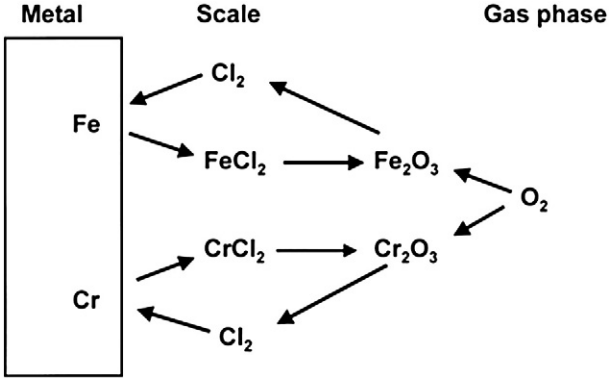

Fig. 2. Schematic drawing of the corrosion mechanism between $Cl_2(g)$ and solid metal [7].

adsorbed sulfate on the oxide surface. Sulfate is expected to compete for the same surface sites as chromate. The reaction of sulfate formation can be written as follows:

$$K_2SO_4 + 2HCl \leftrightarrow 2KCl + SO_2 + H_2O + \frac{1}{2}O_2. \quad (6)$$

Experiments showed that the corrosion of a 304 L stainless steel in the presence of KCl and K_2CO_3 (H_2O and O_2 in gas phase) was much more intense than in an only oxygen and water environment at the given temperature of 600 °C. A substitution of these salts by K_2SO_4 showed gain mass equivalent to experiments with oxygen and water. The slight corrosion effectiveness of potassium sulfate is explained by its relative thermodynamic stability. In contrast to the carbonate and the chloride (reaction 7), the reaction of potassium sulfate with the protective oxide to form potassium chromate is thermodynamically unlikely.

$$Cr_2O_3(s) + 4KCl(s) + 2H_2O(g) + \frac{3}{2}O_2(g) \rightarrow 2K_2CrO_4(s) + 4HCl(g). \quad (7)$$

The effect of sulfur dioxide (SO_2) on the system deposit/layer/low alloy steel was investigated [10]. Fly ash produced in a waste incineration plant was used as deposits. The fly ash is composed of Akermanit ($Ca_2MgSi_2O_7$), Langbeinit ($(K,Na)_2Ca_2(SO_4)_3$), K_2SO_4, $CaSO_4$, (K,Na)Cl. A slight increase of oxidation rate was observed due to a conversion of chlorides to sulfates and as a result some chlorine was liberated. In addition, the SO_2 converts sulfates to pyrosulfates, which may form a melt, attacking the layers.

The effect of atmospheric HCl on the oxidation beneath deposits is very deleterious. In the presence of HCl, deposit sulfates are converted to mixed chlorides, which react with the oxide layer under a chlorine formation, hence inducing active oxidation. Further, the combined effect of SO_2 and HCl (in low alloy steel) on the deposit, steel beneath corrosion deposit and layer was investigated. The mass loss of the deposit caused by HCl was clearly decreased by the SO_2 presented in the atmosphere. According to the author, the decrease has occurred by a shifting of the Reaction (6) towards a formation of HCl. Additionally, a sulfating of chlorides took place according to Reaction (8).

$$2KCl + SO_2 + O_2 \leftrightarrow K_2SO_4 + Cl_2. \quad (8)$$

According to this reaction mechanism, chlorine is generated within the deposit, but not at the deposit/layer interface, and thus most of it diffused to the atmosphere and only a small part of it retained into the layer and into the layer/metal interface, respectively. Thus, the active oxidation is less enhanced in the presence of SO_2 and HCl than in the presence of HCl alone. At the temperature around 500 °C the sulfates are more harmless compared to the chlorides. Finally, an increasing the SO_2-addition effectively decreases the mass gain by oxidation.

The goal of the present work was to assess the corrosion rate of different alloys exposed to high temperature in a semi-pilot plant (350 kW_{th}) where gasification and combustion of the footwear leather wastes took place. In particular, the study was focused to evaluate the impact of chromium particles on the corrosion rate.

2. Experimental set up

The methods usually used to measure corrosion rate are the gravimetry and the metallography [11], when the corrosive medium is a gas (high-temperature corrosion). In this research the corrosion rates were determined on the bases of mass loss after a removal of corrosion products.

During the experiments, samples in the form of square (≈40 mm × 40 mm) with average thickness of 2.9 mm were used. All the samples were designed with a 10 mm hole in the center and