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ANALYSIS OF CORROSION AND FOULING DEVELOPMENT IN A BIOMASS STEAM GENERATOR BURNING SLUDGE FROM A SLAUGHTERHOUSE EFFLUENT TREATMENT PLANT

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Abstract. *The objective of this work was to evaluate the impact of burning sludge mixed with eucalyptus woodchips in the development of corrosion and fouling in a biomass boiler used to generate saturated steam for a poultry slaughterhouse. In this regard, a probe was positioned at the exit of the furnace. This probe served as a support for the installation of ring specimens whose temperature was controlled by adjusting the flow of cooling water. Tests were performed for three sludge:woodchips mixtures (0, 5 and 10%), while the temperature of the specimens made of SA 178M GrA steel was maintained at 180°C. After experiments, specimens were prepared and SEM/EDS was performed. As results, a reduction in the amount of material deposited on specimens was observed with increasing sludge content. This trend is possibly due to the higher concentration of sulfur in the sludge, what may have caused the sulfation of species such as KCl. The higher sulfur and lower chlorine contents in the depositions seem to confirm this hypothesis. In general, the sludge combustion seemed to generate benefits regarding fouling in high temperature zones of the boiler, while no evidences were identified regarding aggravation or mitigation of corrosion.*

Keywords: *Co-firing, corrosion, fouling, wastewater treatment plants, woodchips*

1. INTRODUCTION

Brazil should end the year 2022 as the second largest producer of chicken meat in the world, with an expected production of 14,750 thousand tons. In this context, approximately 60% of this production takes place in the South region of the country, 20% in the Southeast region, and approximately 15% in the Midwest region (EMBRAPA, [s.d.]). In places where the meat processing plants are located there is no access to the natural gas network and the demand for process steam is associated with the use of low-pressure boilers equipped with furnaces for burning eucalyptus or pine chips on grates.

There is significant waste generation due to the operation of industrial units for poultry slaughtering. In this context, one example is the floated sludge, which is a waste generated in large quantities in the effluent treatment plants of slaughterhouses. The floated sludge normally goes through a centrifugation process, being separated in three phases: the clarified liquid phase (destined for biological treatment), the centrifuged oil (which can be destined for biodiesel production) and the centrifuged sludge (with humidity that usually varies between 60 and 80%, destined for composting).

It is estimated that the annual production of centrifuged sludge is around 500,000 tons per year, which generates a disposal cost for the sector that exceeds 45MR$/year (KUNH, 2022).

The centrifuged sludge presents significant energy content, but its high humidity when generated in the process and its chemical composition are factors that can make the combustion of this waste in boilers unfeasible. In this context, a number of studies are presented in the literature. As examples, Sena et al. (2007) e Virmond et al. (2011) investigated the properties of sludge samples produced using different coagulants with a focus on its energy recovery. Experimental combustion tests, however, were limited to pilot-scale burners. Fagnani (2017) performed the characterization of centrifuged sludge samples, as well as combustion tests of the sludge mixed with eucalyptus woodchips (sludge content of 10% on mass basis) in an industrial-scale boiler. The tests, however, were limited to quantification of biomass savings, steam line pressure stability, and gaseous emissions (NOx, SO_2, and CO_2). In the work developed by Mantovan (2022), in turn, promising results regarding the co-combustion of centrifuged sludge with eucalyptus woodchips in an industrial scale steam generator are presented, with special focus on the evaluation of thermal efficiency of the equipment and atmospheric emissions, which met the limits stablished by resolutions.

However, an important aspect that needs to be evaluated and that represents a gap in the specialized literature concerns the development of problems related to corrosion, fouling and slag in steam generating units operated by burning mixtures of centrifuged sludge and biomass. It is necessary to evaluate the composition of the inert portion of the fuels used and the interaction of these elements with the equipment structure, considering that the burning of this waste can eventually be unfeasible if the costs of repairing corroded parts are excessive or if operational problems resulting from the formation of incrustations and slag are aggravated.

Given this scenario, the objective of this study was to evaluate the impact of combustion centrifuged sludge mixed with eucalyptus woodchips on the occurrence of corrosion and fouling in a biomass boiler used to generate saturated process steam in a poultry processing plant.

2. STEAM GENERATING UNIT

A schematic representation of the steam generating unit that is the object of study in this paper is presented in Figure 1. The unit is installed in Palotina, Parana, and supplies the saturated steam demand of a poultry processing plant. It has a nominal capacity of 40 t/h of saturated steam at 15 bar (absolute pressure). It is equipped with a reciprocating grate and a furnace covered with water walls of finned tubes connected to a firetube boiler, through which the combustion gases pass in two stages. The flue gases then proceed to the heat recovery section, where they first pass through the primary air preheater. Next, the flue gases pass through the economizer, used to heat the boiler feedwater, and through the multicyclone, where part of the particulate material is retained. Preheated primary air is introduced into the furnace through the grate, while secondary air at room temperature is fed above the flame region. The probe used to monitor corrosion and fouling formation was positioned at the furnace exit, as indicated in Figure 1.

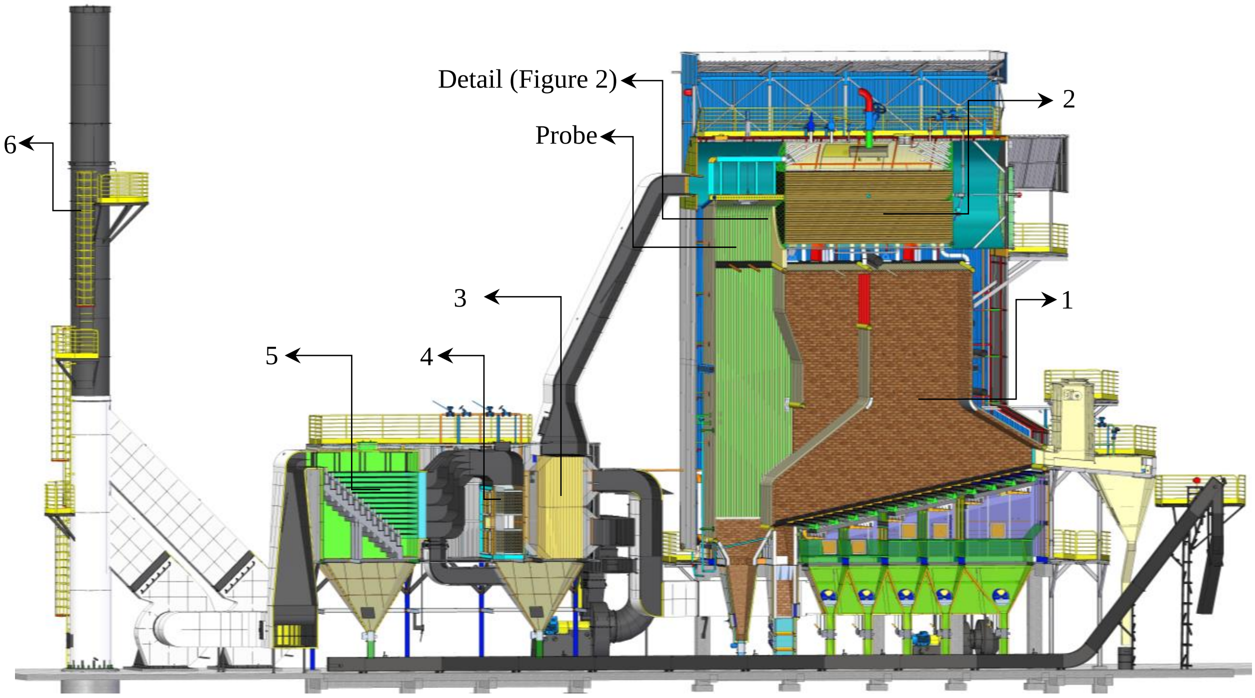


Figure 1. Schematic representation of the steam generator: 1) Furnace; 2) Drum with firetubes; 3) Air Preheater; 4) Economizer; 5) Multicyclone; 6) Chimney.

The main fuel used in the steam generating unit is eucalyptus woodchips – considered in the equipment design. Considering the generation of centrifuged sludge in the effluent treatment plant of the slaughterhouse, tests regarding the co-firing of this waste with the main fuel were performed. In this context, results regarding the characterization of fuels (Table 1) and the evaluation of thermal efficiency and atmospheric emissions of the steam generating unit are presented by Mantovan (2022).

Table 1. Properties of eucalyptus woodchips and centrifuged sludge (results obtained by Mantovan (2022)).

	Units	Sludge	Eucalyptus woodchips
Proximate analysis			
Volatiles	[wt%, db]	86.2	83.9
Ash	[wt%, db]	7.0	0.6
Fixed carbon	[wt%, db]	6.8	15.5
Moisture content*	[wt%, raw]	60-70	30-40
Elemental analysis			
Carbon	[wt%, db]	54.4	46.7
Hydrogen	[wt%, db]	8.6	7.2
Oxygen	[wt%, db]	22.5	45.4
Nitrogen	[wt%, db]	6.8	0.02
Sulfur	[wt%, db]	0.7	0.02
Chlorine	[wt%, db]	0.02	0.05
Ash composition			
Fe_2O_3	[mg/kg, db]	32882	167
CaO	[mg/kg, db]	3180	1700
MgO	[mg/kg, db]	635	394
Na_2O	[mg/kg, db]	1796	1152
K_2O	[mg/kg, db]	214	1357
SiO_2	[mg/kg, db]	3497	1008
Al_2O_3	[mg/kg, db]	1098	357
TiO_2	[mg/kg, db]	17	17
P_2O_5	[mg/kg, db]	45541	5
MnO	[mg/kg, db]	36	53
SO_4	[mg/kg, db]	172	50
Higher heating value			
HHV	[kJ/kg, db]	25,936	18,707

*Moisture of fuels during tests

Since the beginning of the steam generating unit operation, in 2017, problems regarding fouling at the inlet of the first pass of the firetube drum have occurred, as can be seen in Figure 2. In this context, there was also a demand for the analysis of the impact of sludge combustion in the eventual aggravation of fouling and corrosion development, which is the object of study of this work.

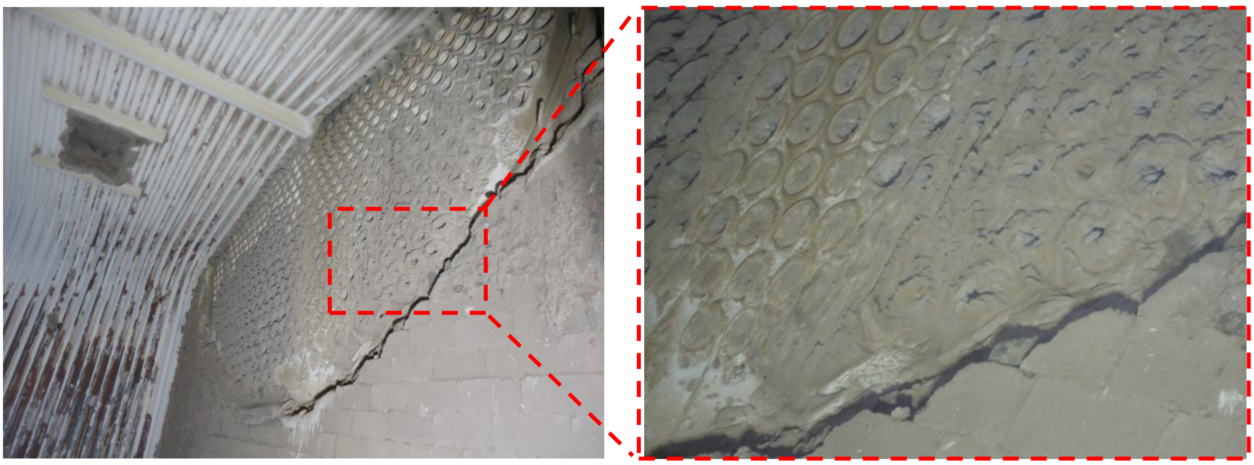


Figure 2. Formation of fouling at the entrance of the first pass of firetubes.

3. PROBE AND RING SPECIMENS

To evaluate the impact of burning centrifuged sludge mixed with eucalyptus woodchips on the development of corrosion and fouling, a probe was designed and manufactured, on which ring specimens were positioned for exposures to the gas flow in the boiler. The probe is based on the assembly of two concentric tubes, through which cooling water flowed to control the metal temperature. The temperature was monitored using a WIKA TC-59 v-pad thermocouple attached to the external surface of the probe, integrated with a WIKA T16 temperature transmitter and a WIKA DI10 digital display. Each ring specimen was tightly clamped at the tip of the probe, so that the temperature of the ring was close to the metal temperature of the probe. Figure 3 shows the mechanical design of the probe and a photo of it installed in the steam generator.

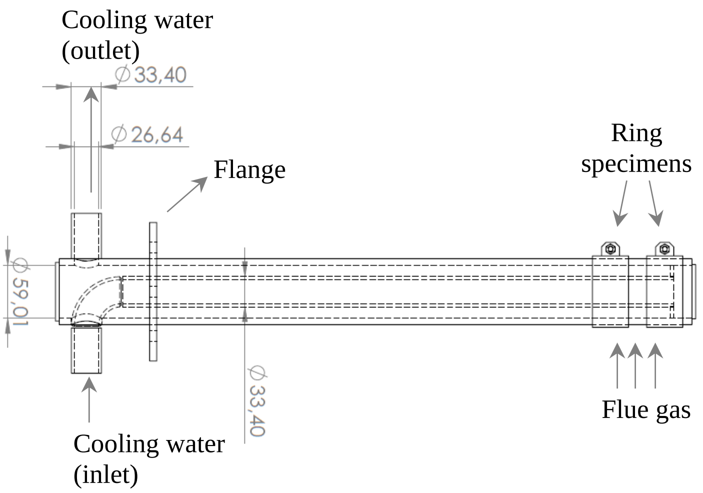


Figure 3. Mechanical design of probe (left) and probe installed on the steam generator (right).

4. EXPERIMENTAL DESIGN

The experimental field tests were performed considering the operation of the steam generating unit burning 0%, 5% and 10% of centrifuged sludge mixed with eucalyptus woodchips (in mass basis). For each mixture, a rapid test (3 hours) and a prolonged test (108 hours) was performed, totaling six tests.

Before the tests, each specimen made carbon steel SA 178M GrA - the same used in the manufacture of the firetube boiler - was washed with tap water and neutral liquid soap, passed through an ultrasonic bath with distilled water (20 minutes), was dried with paper towels and hot air, weighed, and then stored in an airtight container with a silica gel sachet until the day of the experiment.

The rapid tests were performed in duplicate. For each repetition, the probe containing one specimen was positioned in the gas flow and, after being removed from the boiler, the specimen was gently detached from the probe and placed in an airtight container with a silica gel sachet for further analysis. After that, each specimen was weighed to quantify the mass of adhered material, and a piece from one of the test samples was dry clipped and then the surface of the clipping (surface exposed to the gas flow) was examined by SEM-EDS to characterize the deposited material.

The extended tests, in turn, were performed in triplicate. For each repetition, the probe containing a specimen was positioned in the gas flow and, after being removed from the boiler, the specimen was gently detached from the probe and placed in an airtight container with a silica gel sachet for subsequent analyses. Afterwards, each specimen was weighed to quantify the mass of adhered material. Two specimens from two repetitions were bathed in HCl solution to remove adhered material and corrosion products (ASTM G1-03 2017), were washed in tap water, dried in paper towels and hot air, and weighed to assess the base metal loss due to corrosion. In addition, the specimen from the third repetition was dry cut to later perform SEM-EDS of the tube cross section to evaluate the evolution of the oxidation process of the base metal.

As a preparatory step for the SEM-EDS of the tubes cross-sections, the samples were subjected to a polishing step using an Arotec Aropol 2V polishing machine. The procedure followed a polishing sequence, starting with 80 mesh sandpaper and progressing up to 2500 mesh. The preparation time per sandpaper was around 4 minutes and the process was performed dry to avoid interaction with the material deposited on the ring surface. Aiming for a finish free of scratch marks, a dry polishing process was performed using a 4000 mesh grit sandpaper for about 15 minutes. To follow the characterization process of the steel microstructure after the metallographic preparation, the optical microscopy technique was used, using an Olympus BX60M microscope. It is important to point out that during the characterization process no chemical attack was used.

The SEM images were obtained using a HITACHI benchtop microscope model TM-3030. An EDS module coupled to the SEM was also used to evaluate the composition of the deposited material and base material. Images were acquired at magnifications of 100x to 3000x with an electron accelerating voltage of 15kV. Carbon tape was also used to reduce saturation and increase the quality of the micrographs.

The specimens were weighed using a Shimadzu UX6200H balance with a resolution of 0.01g.

5. RESULTS AND DISCUSSION

The results referring to the deposition of material (fouling) in the specimens for the rapid and prolonged tests and for the different sludge shares dosed to the eucalyptus woodchips are presented in Figure 4. In this regard, as the sludge content was increased from 0% to 10%, the mass of adhered material was slightly reduced, despite the higher ash content present in the sludge.

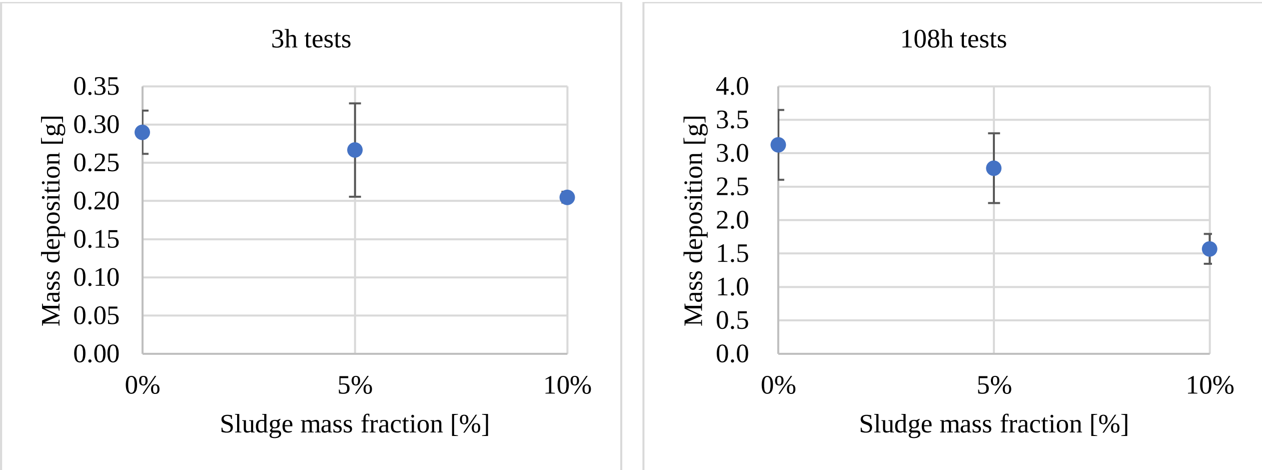


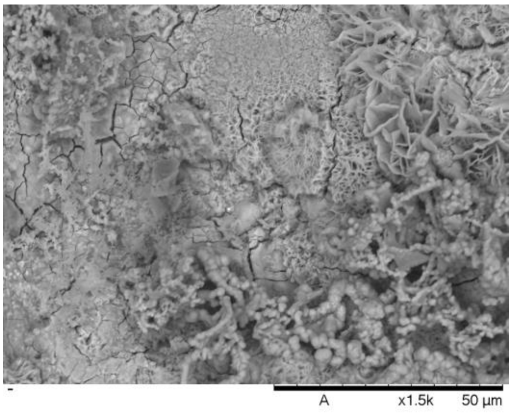
Figure 4. Results referring to the deposition of material on the specimens for the rapid and prolonged tests.

Results of SEM-EDS analysis of specimen surfaces used in rapid tests are shown in Figure 5. As important aspects to be observed, there was a reduction in the amount of chlorine and potassium and an increase in the amount of sulfur present in the deposits as the sludge share was increased from 0% to 10%. These results, considered together with the observed tendency for material deposition in the specimens, lead us to establish the hypothesis that sulfation of volatile salts based on chlorine and alkali metals (especially KCl) may have occurred as the sludge, with a higher sulfur content, was dosed to the woodchips.

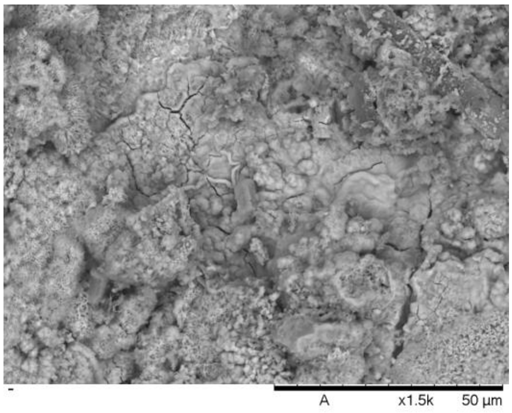
As described by Sandberg (2011), the presence of chlorine and alkali metals in the inert portion of the burned fuel intensify the deposition of fouling in steam generating units. Salts based on chlorine and alkali metals (especially KCl) are volatilized in the combustion chamber and condensate on the cold surfaces of heat exchangers and water walls, what in turn, provides the adhesion of particulate material carried by the combustion gases. This process is described and experimentally reproduced by Zhang et al (2020).

One way to mitigate this problem consists on the sulfation of the alkaline chlorides. In this regard, Broström (2010) carried out tests in a large-scale circulating fluidized bed (CFB) boiler firing biomass and compared two approaches to reduce fouling, one based on the addition of $(NH_4)_2SO_4$ in the flue gases (the ChlorOut® technique proposed to enable the urban solid waste combustion) and the co-combustion of biomass with peat (20% peat on energy basis), aiming to reduce the KCl content in the flue gases. Promising results are also presented by Carlberg (2008), indicating that adding $(NH_4)_2SO_4$ reduced KCl in the flue gas and also the chlorine content in deposits in the superheater region of a waste wood fired CFB boiler. The deposits were collected by using temperature-controlled steel rings on a deposit probe. Sandberg (2011), in turn, indicates that the fouling formation boosted by the deposition of volatile alkali chlorides is significantly mitigated in cases where the burned fuel has a sulfur to chlorine molar ratio S/Cl>4. It is worth mentioning that, in the present work, the eucalyptus woodchips presented an S/Cl=0.44 ratio, while the sludge presented an S/Cl=25 ratio.

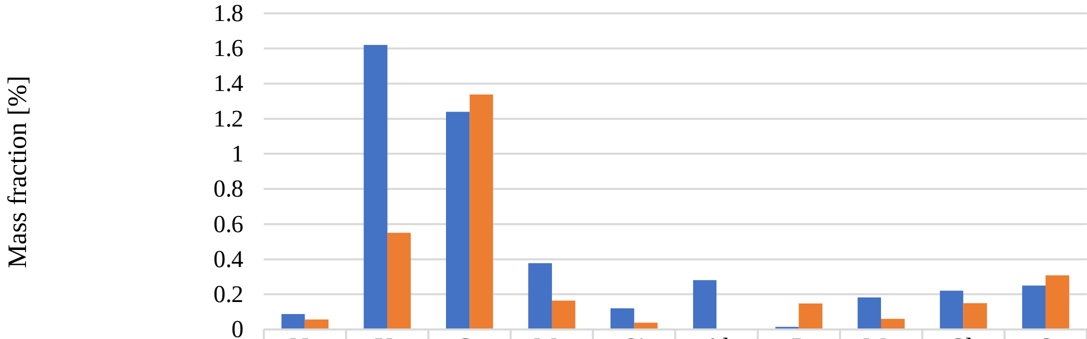
Furthermore, there is the presence of chlorine in the depositions arising from the condensation of compounds based on chlorine and alkali metals, which are related to the worsening of the corrosion of the base metal, especially for metal temperatures above 400ºC and in situations where melting of part of the deposited material occurs. This problem, called active corrosion (or chlorination), typically occurs in superheaters of boilers that burn fuels with high contents of chlorine and alkali metals, as some biomasses and urban solid wastes (NIELSEN et al., 2000; CARLBERG, 2008; BROSTROM, 2010; VIKLUND, 2013; LARSSON, 2016).



SEM of ring surface (1500x / 15eV) - 0% sludge



SEM of ring surface (1500x / 15eV) - 10% sludge



	Na	K	Ca	Mg	Si	Al	P	Mn	Cl	S
0% sludge (1500x)	0.088	1.62	1.24	0.378	0.12	0.28	0.015	0.183	0.221	0.25
10% sludge (1500x)	0.056	0.55	1.337	0.165	0.038		0.147	0.06	0.15	0.308

EDS results

Figure 5. SEM-EDS results for the 3h duration tests.

In this context, although the boiler studied in this work is not equipped with superheaters and the water walls operate with relatively low metal temperature (boiler operated at 9 bar), it was also the objective of the present study to evaluate the loss of base metal by corrosion as a function of the sludge content added to the eucalyptus woodchips (0%, 5% and 10%) - results shown in Figure 6. However, the variability associated with the results was high and the experiment inconclusive. Thus, it is not possible to conclude that the addition of sludge to the woodchips aggravated or attenuated the corrosion process. In any case, because the metal temperature is relatively low in the present application, it was already expected that the chlorination process would not be severe.

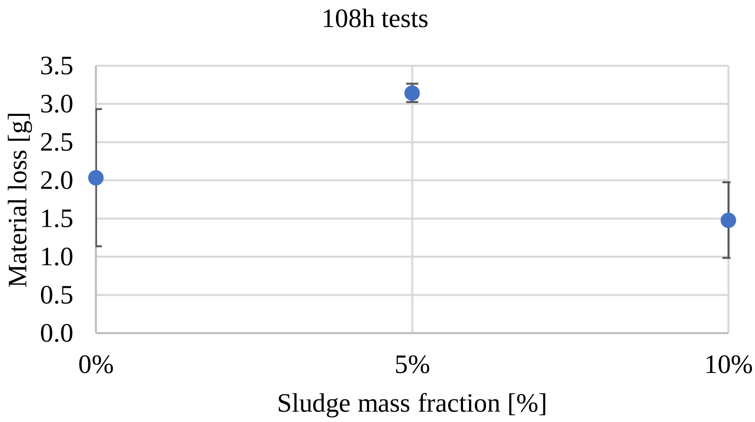


Figure 6. Loss of base material after prolonged tests for different sludge contents.

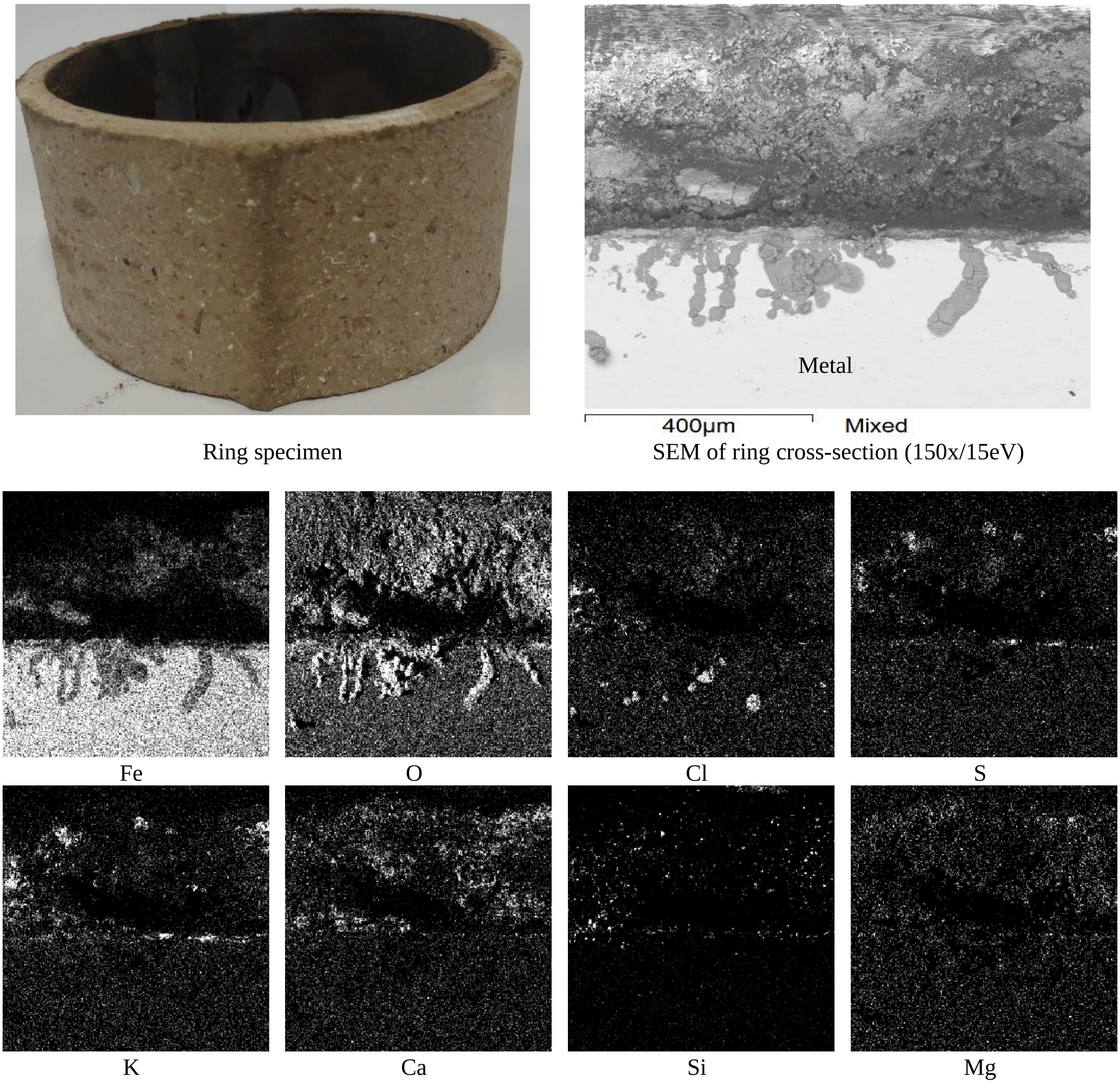


Figure 7. SEM-EDS of the cross-section of a specimen (0% sludge).

To generate additional insights regarding the problem of corrosion of the base metal, SEM-EDS analyzes were carried out on the cross-sections of the specimens used in the extended tests for the dosages of 0% and 10% of sludge added to the eucalyptus woodchips – results shown in Figures 7 and 8, respectively.

A characteristic of the chlorination or active corrosion process consists on the presence of chlorine at the interface between the base metal and the oxide layer (scale). The chlorine combines with the base metal to form metallic chlorides M-Cl. Metal chlorides, in turn, are unstable and the metal tends to combine with oxygen to form a non-protective porous layer of oxides, releasing chlorine to attack the base metal again. This process is cyclic and is aggravated with increasing temperature. A detailed description of this process is presented by Noguchi and Yakuwa (2017).

In this work, such characteristics were not evident. However, chlorine was observed at some points at the interface formed between the base metal and the scale in the specimen used in the combustion of pure eucalyptus woodchips. In the specimen referring to the 10% sludge test, in turn, the presence of chlorine was not identified, while the presence of sulfur was clearer.

In both specimens, regions of the base metal with iron depletion coinciding with the presence of oxygen were observed, indicating the formation of iron oxides resulting from the oxidation of the material. Through the analysis, it was also possible to observe the presence of other elements (eg, Ca, K, Si) related to the adhesion of particulate material.

It should be noted, however, that the analyzes were punctual and generated for a single specimen for each sludge content, so additional tests are recommended.

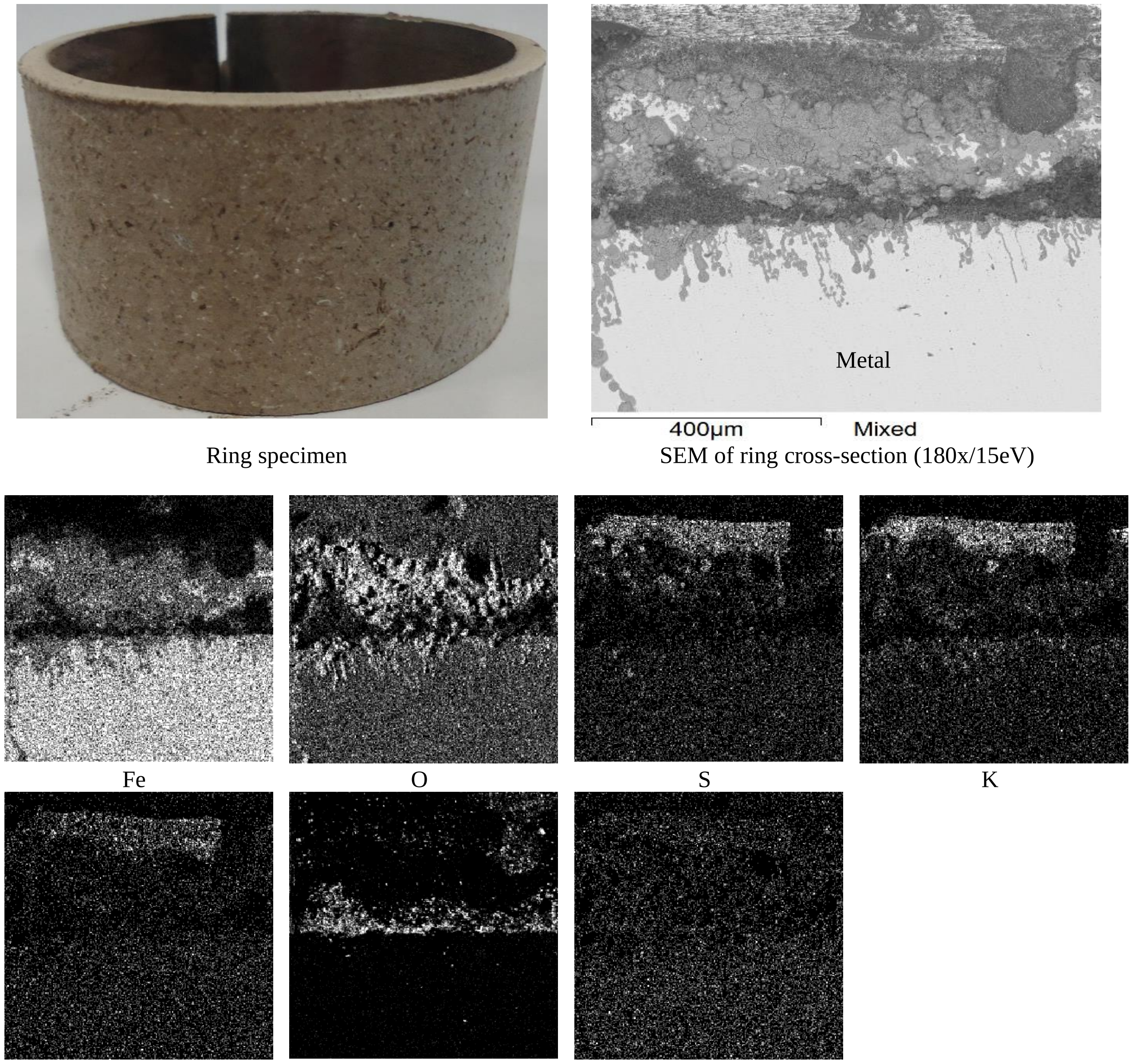


Figure 8. SEM-EDS of the cross-section of a specimen (10% sludge).

6. CONCLUSIONS

The co-combustion of centrifuged sludge obtained from the effluent treatment plant of slaughterhouse with Eucalyptus woodchips seems to have generated benefits in relation to the adhesion of particulate material to the specimens positioned at the exit of the furnace of the biomass steam generating unit. These results are possibly related to the sulfation of volatile salts based on chlorine and alkali metals (especially KCl) as the sludge was dosed to the eucalyptus woodchips.

The results were inconclusive, however, regarding the aggravation or attenuation of the corrosion of the specimens as sludge was dosed to the eucalyptus woodchips. Nevertheless, this result was somewhat expected due to the low metal temperatures inherent to the application in question, where water walls and fire-tubes are in contact with saturated steam at 9 bar (absolute pressure).

It is important to note that these are preliminary results and refer to the specific boiler design and operating conditions tested in this work. The results are also related to the sludge from a poultry slaughterhouse and produced in the effluent treatment plant using ferric chloride as the coagulating agent. More specimens must be tested, also considering runs of longer duration so that the corrosion process at a more advanced stage can be evaluated. The SEM-EDS analyzes here presented were punctual and generated for a single specimen for each sludge content, so additional tests are recommended.

Finally, the burning of centrifuged sludge mixed with eucalyptus woodchips seems to be a promising route, enabling the energy recovery of this waste generated in large quantities in slaughterhouses.

7. ACKNOWLEDGEMENTS

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8. REFERENCES

BROSTROM, M. **Aspects of alkali chloride chemistry on deposit formation and high temperature corrosion in biomass and waste fired boilers**. Sweden: Umea University, 2010.

CARLBERG, M. **Application of the ChlorOut concept in a Waste Wood fired CFB Boiler**. Sweden: Swedish University of Agricultural Sciences, 2008.

EMBRAPA. **Embrapa Swine & Poultry**. Disponível em: <https://www.embrapa.br/en/suinos-e-aves/cias/estatisticas/frangos/brasil>. Acesso em: 2 jun. 2022.

FAGNANI, K. **Comparison of the energy content of sludge generated in poultry industries using different coagulan agents**. Master Thesis—[s.l.] University of Parana, 2017.

KUNH, S. S. **Viabilidade técnica e econômica da produção de briquetes de lodo do tratamento primário de efluentes avícola e serragem**. [s.l.] Universidade Estadual do Oeste do Paraná, maio 2022.

LARSSON, E. **The Corrosive Effect of Chlorine Containing Species on Waterwalls and Superheater Materials in Waste and Biomass-Fired Power Plants**. Doctoral thesis—Sweden: Chalmers University of Technology, 2016.

MANTOVAN, F. DE M. **Estudo da queima de lodo flotado de estação de tratamento de efluentes em caldeira a biomassa**. Master Thesis—[s.l.] Universidade Federal do Paraná, 2022.

NIELSEN, H. P. et al. The implications of chlorine-associated corrosion on the operation of biomass-fired boilers. **Progress in Energy and Combustion Science**, v. 26, p. 283–98, 2000.

NOGUCHI, M.; YAKUWA, H. **Lecture on Fundamental Aspects of High Temperature Corrosion and Corrosion Protection. Part 3: high temperature corrosion and corrosion protection of the boilers in waste to energy plants**. Disponível em: <https://www.ebara.co.jp/en/jihou/no/list/detail/253-6.html>.

SANDBERG, J. **Fouling in biomass boilers**. Sweden: Malardalen University, 2011.

SENA, R. F. et al. Biofuel application of biomass obtained from a meat industry wastewater plant through the flotation process - A case study. **Resources Conservation & Recycling**, v. 52, p. 557–69, 2007.

VIKLUND, P. **Superheater corrosion in biomass and waste fired boilers - characterisation, causes and prevention of chlorine-induced corrosion**. Doctoral thesis—Sweden: KTH Royal Institute of Technology, 2013.

VIRMOND, E. et al. Organic solid waste originating from the meat processing industry as an alternative energy source. **Energy**, v. 36, p. 3897–906, 2011.

ZHANG, H.; YU, C.; LUO, Z. Investigation of ash deposition dynamic process in an industrial biomass CFB boiler burning high alkali and chlorine fuel. **Royal Society of Chemistry**, v. 10, p. 21420–6, 2020.

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