


Corrosivity study in Usiminas continuous casting machines segments

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Abstract

Volatile fluorine compounds are generated in continuous casting processes that use mold flux containing fluorine. The reaction of these compounds with the superheated steam from the secondary cooling system forms hydrofluoric acid, which is corrosive to the metallic structures of continuous casting machines (CCM), mainly in the first segments because there are greater contact between the steam and the fluorine compounds. To obtain knowledge about corrosivity in Usiminas's CCM and to support taking actions to reduce costs with maintenance, the characteristics of the secondary cooling water were evaluated (pH, alkalinity and ion concentrations) and corrosion coupons were exposed inside the CCM. From the results, it was verified that the water flows and mold flux used in the CCM, which are specific to each type of steel, have a great effect on the water parameters that comes into contact with the structures of the CCM. The corrosion products were characterized by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDS) and X-ray diffraction (XRD) techniques and. It was observed a predominance of alveolar corrosion and high corrosion rates in the first segments of the CCM. These results helped in the implementation of actions to minimize corrosion in CCM, such as pH monitoring during the process and strict control of sodium hydroxide used in the first segments.

Keywords: Continuous casting process; Corrosion; Fluoride ions; Mold flux.

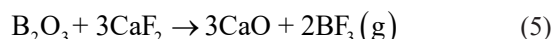
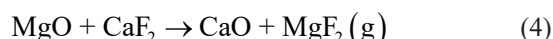
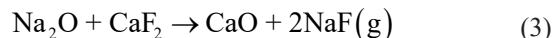
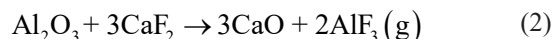
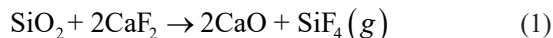
1 Introduction

Aiming to ensure mold lubrication and liquid metal protection in continuous slab casting, mold fluxes are used, which may contain fluorine in their composition. During the process, the mold flux is added above the mold and due to the high temperature of the liquid steel and the oscillating movement, it penetrates into the edges of the mold in continuous casting machines (CCM). In this equipment, two stages of steel cooling are carried out: primary and secondary. In the first one, the process occurs indirectly through the contact of liquid steel and mold flux with the cooled mold. In secondary cooling, air and water are sprinkled through sprays, directly over the entire surface of the plate, as shown in Figure 1.

The extreme conditions in which CCMs operate, such as high temperatures, humidity and the presence of corrosive agents, can result in severe corrosion of metallic structures. The reason for the high corrosivity of the environment, mainly in the first segments, is due to the presence of hydrofluoric acid in the secondary cooling region and the condensation of water steam enriched with this acid, which considerably reduces the pH of the water that comes into direct contact with the structures. Thus, the corrosion process is developed in CCMs structures, which operate using mold fluxes containing fluorine [2-7]. The main impacts generated by

corrosion are the increase in maintenance costs, the increase in stoppages and the consequent drop in steel production.

Volatile fluorine compounds can be formed from residual moisture in the mold flux, when it melts. However, they are generated more intensely during the continuous casting process, in the presence of superheated steam from the secondary cooling system, below the mold [8]. According to Wang [9], the main volatile fluorine compounds, formed under such conditions, are detailed in Equations 1 to 5. Subsequently, these compounds react with superheated steam and originate hydrofluoric acid (HF), whose dissociation results in the release of fluoride ions.



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At the beginning of 2022, during visual inspection, considerable corrosion was observed in the segments of the CCMs of Usiminas, mainly in places close to the curvature region, the corrosion was evidenced by the attack on the protection plates and tie rods that fasten the segments, as shown in Figure 2. This event boosted the monitoring of the parameters of the water used in the process and the development of the present work. In this context, the objective of this work is to support actions to neutralize the deleterious effect of fluoride ions and, thus, preserve the structures of the machines.

2 Methodology

2.1 Corrosion tests

Corrosion tests included the determination of the corrosivity of the environment, evaluations of corroded surfaces and characterization of corrosion products. Corrosion coupons of unalloyed carbon steel were made in 100 x 50 mm x 6 mm dimensions, pickled with HCl solution, dried and kept in a desiccator for 24 h. In sequence, the coupons were individually weighed and exposed at CCM#1 and #4 of Usiminas Ipatinga plant. As shown in Figure 3, the corrosion coupons were properly

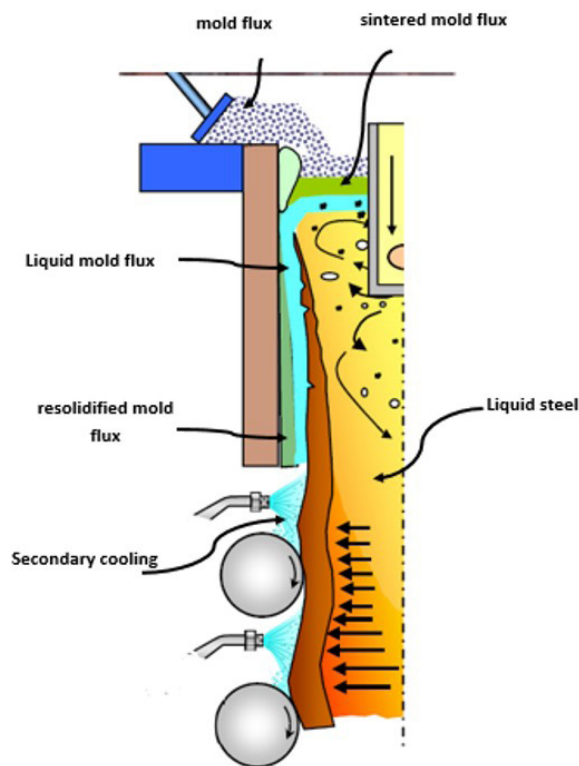


Figure 1. Mold flux operation mechanism [1].

fixed on a support, which was placed in segments 1, 2, 3 and 8 of the CCM. The first three segments are characterized by a greater corrosive attack on CCM structures, unlike segment 8, where the corrosion is not severe.

The corrosion coupons were exposed during the exchange of NaOH by Na₂CO₃ on the pH treatment of CRALIN and the exposure time of them was specified in 3 to 4 production campaigns for each CCM, which corresponds to the target times of 30, 60, 90 and 120 days approximately. After each exposure time, three corrosion coupons were removed and cleaned according to ASTM G1-03 [10]. The corrosivity was obtained in terms of corrosion rate (mm/year) and thickness loss (mm), using Equations 6 and 7 respectively. In these equations Δm is the mass loss, in g; A is the area of the coupon, in cm²; ρ is the density of the metal (carbon steel ≈ 7.86 g/cm³); and t is the exposure time, in years. Corrosion rate information from Ruy et al. [7], which is shown in Table 1, was used as reference values in this work. The corrosion products were characterized by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDS) and X-ray diffraction (XRD) techniques.

$$\text{Corrosion rate} = \frac{\Delta m}{A \cdot \rho \cdot t} \quad (6)$$

$$\text{Thickness loss} = \frac{\Delta m}{A \cdot \rho} \quad (7)$$

2.2 Water analysis

Water samples were collected from two different points: (i) at the CCM water recirculation center (CRALIN) and (ii) at the CCM spray system, where it was necessary to put a channel, positioned between the 2nd and 3rd segments, and an opening valve outside the machine, in order to generate a representative sample of the points most affected by corrosion, as are shown in Figure 4.

The samples were evaluated by ion chromatography to determine the concentration of fluorine and chloride ions. The pH was determined using a pHmeter and the total alkalinity was calculated in terms of calcium carbonate using the methyl orange indicator. These parameters were assessed considering the type of mold flux used during continuous casting.

3 Results and discussion

3.1 Assessment of the corrosive process in CCM

The results of the evaluations of coupons that were exposed after different times in CCM#1 and #4 can be seen

Table 1. Reference values for corrosion rate in CCM, mm/year [7]

Very low	Low	Acceptable	High	Critical
< 0.254	0.254 to 0.508	0.508 to 0.762	0.762 to 1.27	> 1.27

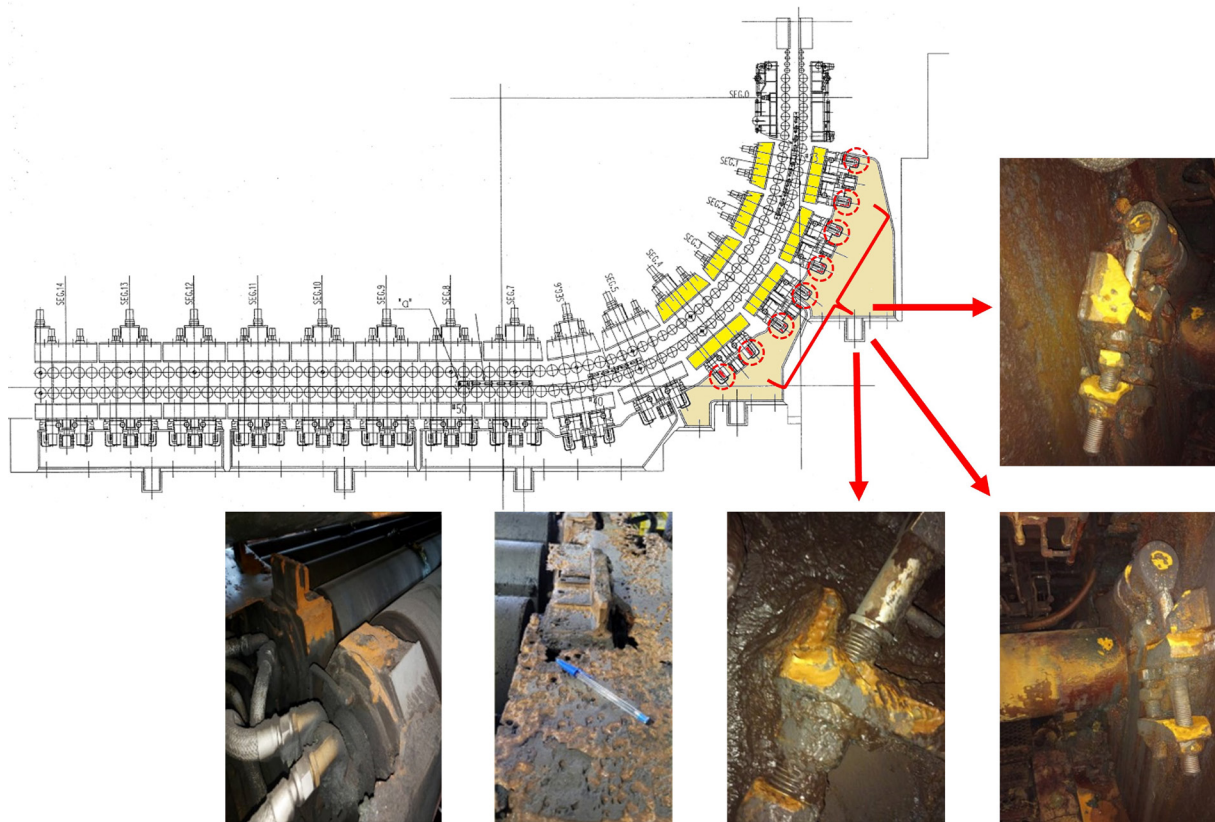


Figure 2. CCM structures with intense corrosive attack.

in Figure 5. The missing data in this figure correspond to coupons lost during the test, for example, coupons of 97 days of exposure in segment 1 of CCM#1. It is important to note that the corrosion rate can decrease over time due to the accumulation of corrosion products on the metallic surface, which slows down the corrosive process. If these corrosion products are not adherent, corrosion will continue and thus the thickness loss tends to increase over time, as shown in Figure 5.

From this figure, it can be observed that segments 1, 2 and 3 of both machines are characterized by the most aggressive environment. For the period of about 30 days of exposure, compared to the reference values in Table 1, segment 1 of CCM#1 presented the worst situation, with a corrosion rate near to 1.27 mm/year, a value considered critical. Segments 2 and 3 of this machine, as well as segments 1 and 2 of CCM#4, showed relatively high corrosion rates, around 0.8 to 1.10 mm/year. Low to acceptable levels (0.254 to 0.762 mm/year), were only obtained for segment 8 of CCM#1 and for segments 3 and 8 of CCM#4. It is desirable that the most critical segments, that is, 1, 2 and 3, present these levels for corrosion rate to avoid problems associated with structural corrosion of the CCM.

The visual aspect of corrosion coupons exposed for about 30 days in the different segments of the CCM is shown in Figure 6. Regardless of exposure time, a greater accumulation of corrosion products and residues was observed in the coupons exposed in the first three segments of both

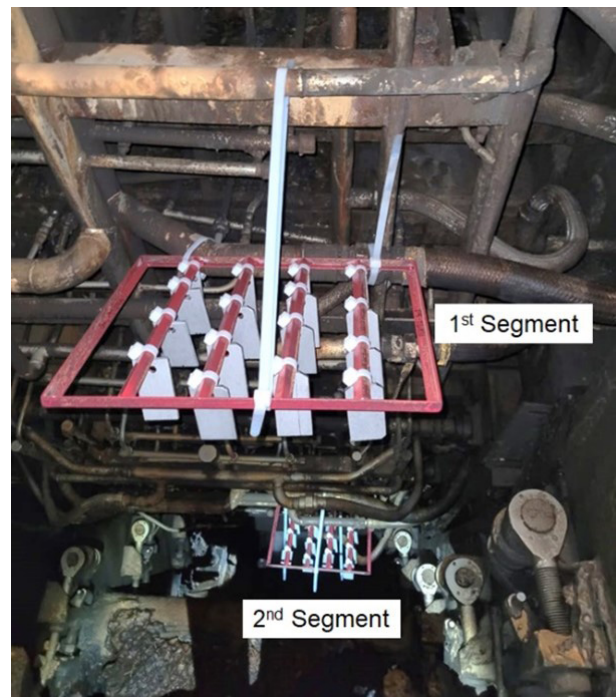


Figure 3. Arrangement of corrosion coupons inside the CCM.

CCM. The XRD analysis carried out on the surfaces of the coupons indicated the presence of magnetite, goethite, hematite and wustite iron oxides. The first three ones are



Figure 4. (a) Channel for water collection and (b) opening valve.

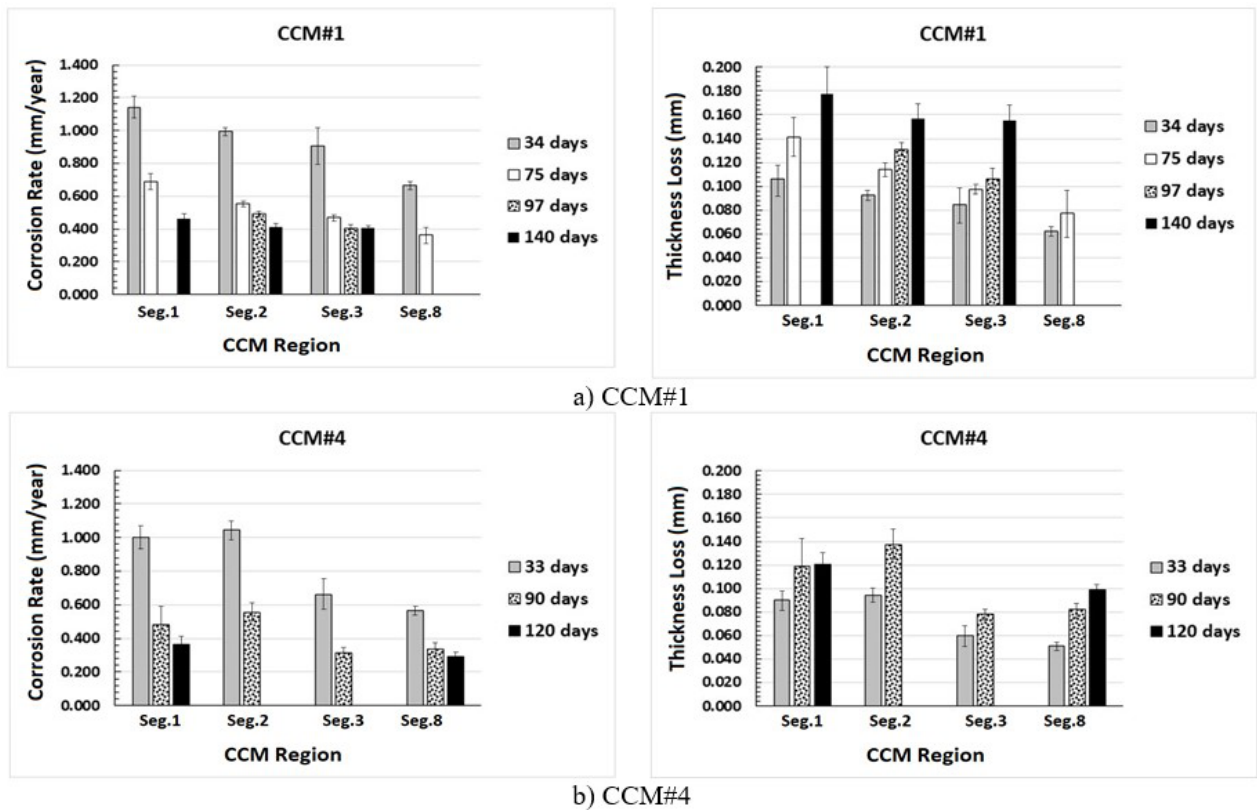


Figure 5. Corrosion rate and thickness loss of coupons exposed in CCM#1 and #4. a) Corrosion rate and thickness loss of CCM#1; b) Corrosion rate and thickness loss of CCM#4.



Figure 6. Typical appearance of coupons after corrosion test inside CCM.

normally observed in steel corrosion and the last one, wustite, usually forms at high temperatures [11]. Calcium fluoride (CaF_2) was also detected by DRX analysis, associated with these iron oxides. CaF_2 is a compound originating from mold flux and whose reaction with water, at high temperatures, forms hydrofluoric acid [12].

SEM/EDS analysis of the morphology and elemental chemical composition of the coupons surfaces in Figure 7. Higher intensities of counts for Ca and F predominate in the EDS spectrum of regions containing mold flux residues (Figure 7g). Iron oxides with different morphologies (Figure 7e), characterized by the highest intensities of O and Fe counts (Figure 7h), can be observed below the mold flux residue layer. Elements detected in residual in the EDS spectra, such as Al, Mg, Na, Si, S, P and K, are also related to the mold flux components.

Independently of the CCM segment where the corrosion coupons were exposed, the predominant form of attack by fluoride ions on the metal surface is the alveolar type.

It is typically caused by halogen ions and is associated with differential aeration. This type of corrosion is characterized by a rounded appearance (alveoli, craters or pit) with a depth lower than its diameter according to Frazão et al. [12], as shown in Figures 8c and 8d. As the corrosion process proceeds, these alveoli grow and/or coalesce, generating the appearance of cavities, which can perforate the metallic material. As shown in Figure 7f, fluoride ions can also promote intergranular corrosion. In Shokri's paper [13], this evidence was associated with fluoride ions adsorption in grain boundaries.

3.2 Water analysis

The CRALIN samples represent the water, duly treated, which is used in the secondary cooling of the continuous casting process. Therefore, in addition to cooling the CCM, the water from CRALIN must have characteristics that enable the neutralization of the HF generated in the first segments of the CCM. CRALIN water samples showed pH values within the recommended range, alkalinity above 50 mg/l and a low concentration of chloride ions, around 30 mg/l. However, the concentration of fluoride ions was close to 50 mg/l, a value considered high for issues related to corrosion problems in CCM [9]. These results suggest that only alkalinity, a measure of water's capacity to neutralize acids, was not effective in promoting a satisfactory reduction in the concentration of fluoride ions in water directed to the CCM.

The analysis of water samples collected inside CCM#1 and #4 are shown in Figure 8. Parameters like pH, alkalinity and concentration of fluoride and chloride ions are specified in this figure by type of mold flux used in steel production. From these results, it appears that the type of mold flux has an effect mainly on pH values, alkalinity and concentration of fluoride ions. For example, mold flux B and D resulted in water samples with fluoride ions concentration above 90 mg/l; low pH, between 5.8 and 3.8, and they were the only ones with zero alkalinity, as can be seen in Figures 8a, 8c and 8d. These results can be justified by the lower volume of water used in continuous casting when mold fluxes B and D are used. The highest concentrations of chloride ions, Figure 8b, were also obtained for the aforementioned mold fluxes, including mold flux C.

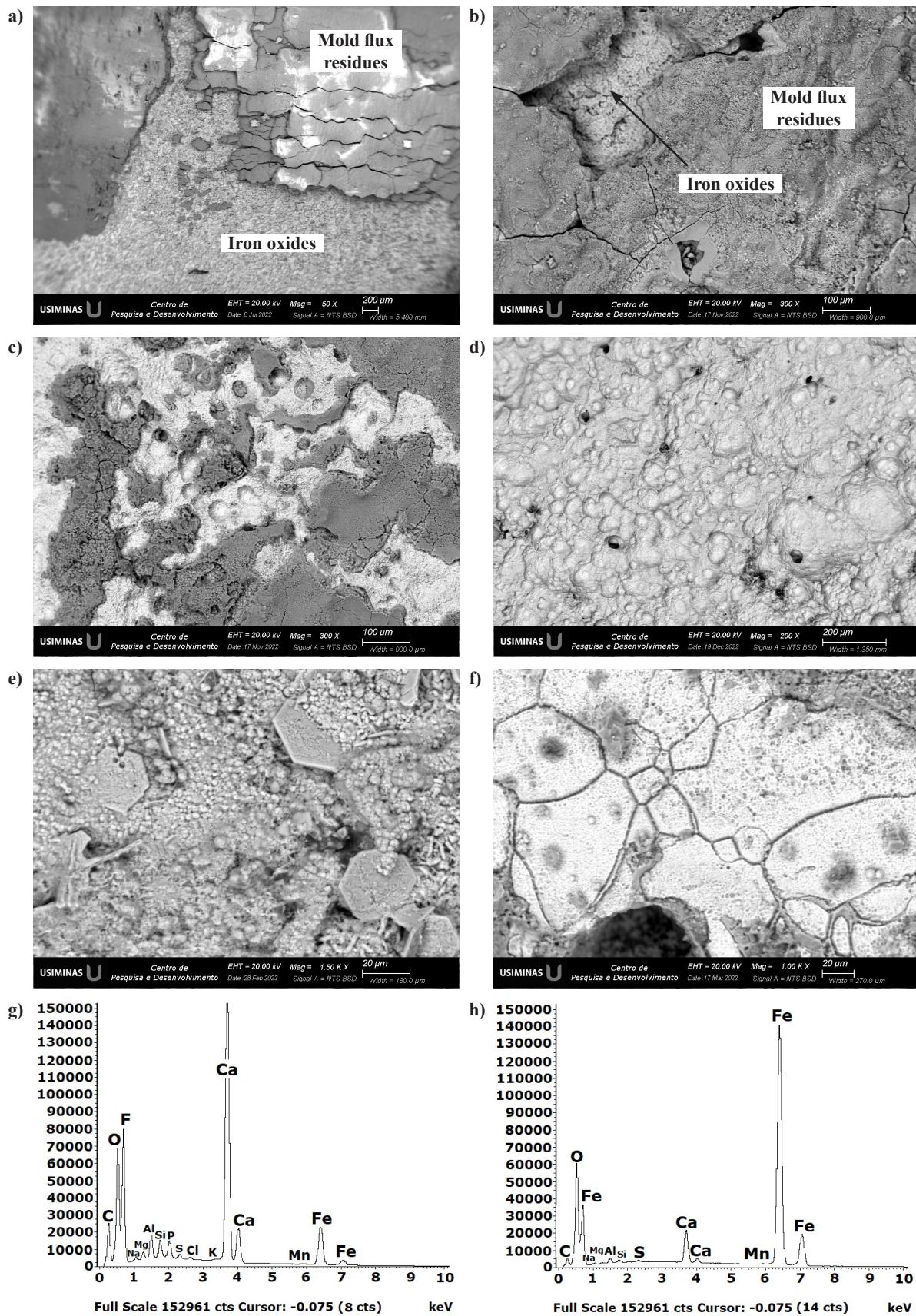


Figure 7. SEM/EDS analysis of corrosion coupon surfaces after exposure to CCM. a) Flux mold residues and iron oxides; b) Flux mold residues and iron oxides; c) Alveolar corrosion and flux mold residues; d) Alveolar corrosion - surface after pickled; e) Iron oxides with different morphologies; f) Intergranular corrosion; g) Typical EDS spectrum of flux mold sediments; h) Typical EDS spectrum of iron oxides.

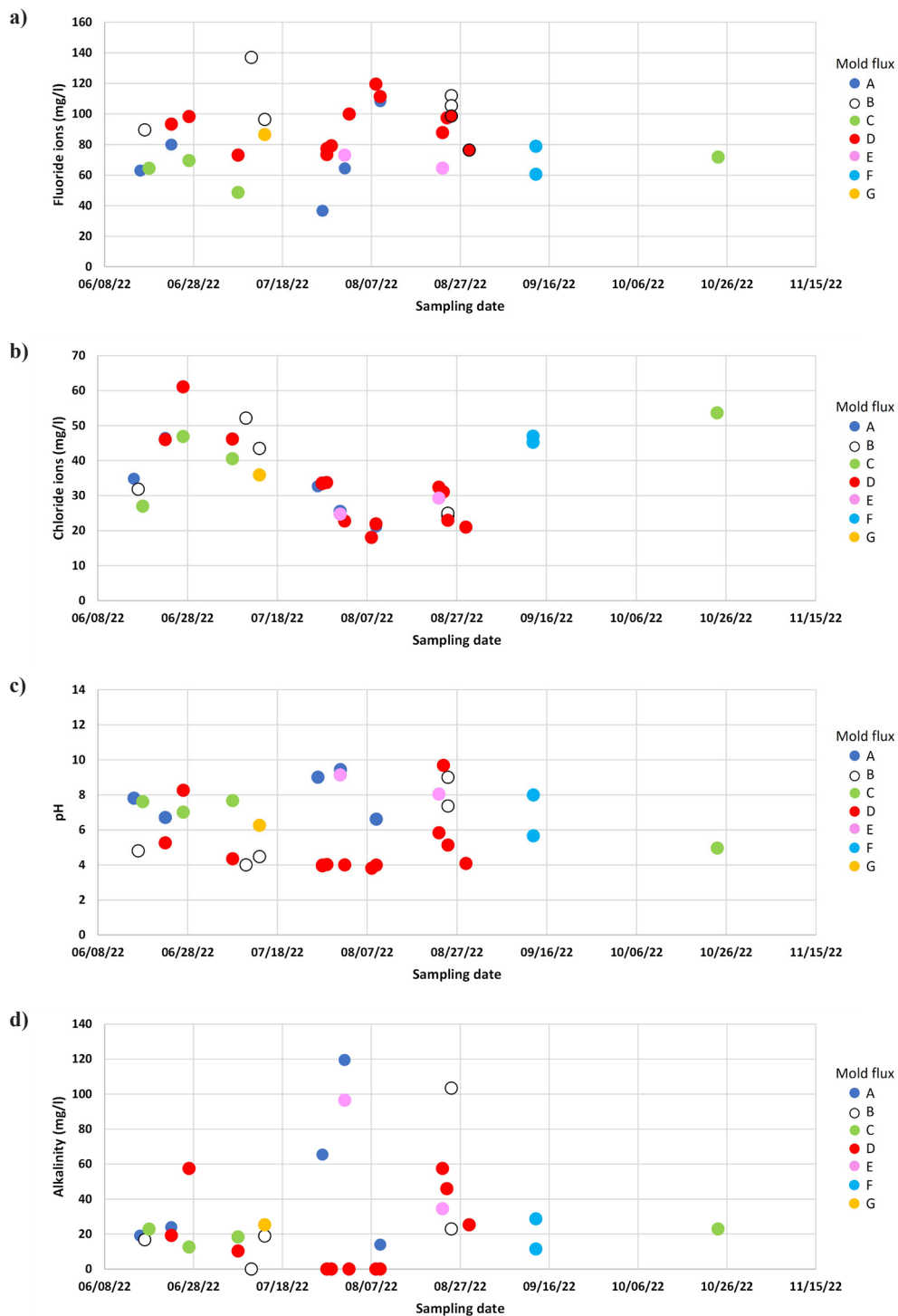


Figure 8. Secondary cooling water samples analysis specified by mold flux type. a) Fluoride ions concentration; b) Chloride ions concentration; c) pH; d) Alkalinity.

3.3 Actions to reduce CCM corrosion

In parallel with the studies on water quality and corrosion coupons, some actions were taken in the “*modus operandi*” in the continuous casting, as described below:

- Machine washing after interruptions in the process for removing any remaining acid residue;

- Increase the frequency of visual inspections on the CCM structures, with the taking of photographic records for comparison at each inspection;
- Replacement of NaOH by Na₂CO₃ in the water treatment in CRALIN, in order to increase the alkalinity of the water to a range of 50 to 90 mg/l and thus neutralize the acid.

Usiminas Ipatinga Plant has an operational peculiarity that does not allow alkalinity above 100 mg/L in the continuous casting water recirculation system to avoid fouling in pipes.

According to the results of this study, it was showed that alkalinity under 100 mg/L was not efficient to contain the corrosion. Since Na_2CO_3 has a higher cost than the previous treatment, it was decided to use NaOH for control of pH in CRALIN and not to use Na_2CO_3 anymore.

To increase the pH in the region of segments 1, 2 and 3 and neutralize the HF formed, an additional NaOH dosage system was designed during the process in these segments. The implementation of this system began at CCM#4 in February 2023 and it will be implemented at CCM#1 and CCM#2 after they have been overhauled. The NaOH is transferred from a storage tank directly to the water intake pipes of the most affected segments. In one second step, the dosage will be carried out only in situations of low pH during the process.

In the first month of implementation of the direct dosage of NaOH, it was possible to observe an increase in the pH of the water collected during the process for all types of steel manufactured by Usiminas. Currently, the pH results are above 7, thus indicating a reduction in the corrosivity of the CCM environment.

4 Conclusion

In this study, secondary cooling water samples were evaluated and corrosion tests were performed in the

CCM at Usiminas Ipatinga Plant. From the results, it was verified that the water flow rates used in the CCM, which is specific for each type of mold flux, have an effect on the pH, alkalinity and concentration of fluoride ions of the water that comes into contact with the structures of the CCM. Lower water flows are associated with acidic pH levels and fluoride ion concentrations above 90 mg/l, resulting in an intense corrosion process in the first segments of the CCM.

Corrosion was more intense in the first segments of both CCM, with rates above 0.7 mm/year, an alert value for problems associated with corrosion. The corrosion coupons surface exhibited an accumulation of residues from mold flux, mainly on those exposed in the first three segments of the CCM. Since mold flux is the precursor for the formation of HF and, consequently fluoride ions, the presence of residues from it on the metallic surface contributes to the corrosive process, whose predominant form of corrosion attack is alveolar.

To combat corrosion in the CCM, several actions were taken, such as the implementation of an additional NaOH dosage system during the casting process. Currently, the efficiency of this system is being monitored through analysis of water samples, exposure of new corrosion coupons, and visual monitoring of the CCM structures. In the first month of implementation, all water samples evaluated had a pH above 7, thus indicating a reduction in the corrosivity of the environment inside the CCM.

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