

# IMPACT OF FLUORINE FREE MOULD FLUX USE ON CONTINUOUS CASTING PROCESS<sup>1</sup>

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## Abstract

The characteristics of Mould fluxes have been improved in recent years, in order to meet the rigorous demands of the continuous casting of steel. The most important improvements in mould fluxes have been focused on the prime requirements of the continuous casting process, *i.e.*, better surface quality of the solid steel, higher productivity and minimum environmental impact. In order to keep abreast of these trends, a F- free mould flux has been developed and tested in a European steel plant<sup>(1)</sup>. In this paper, preliminary results obtained with this mould flux has recently been used in a Brazilian billet-casting machine and preliminary results are presented describing its impact on steel productivity.

**Key words:** Continuous casting of billets; Fluorine-free mould fluxes.

## IMPACTO DO USO DO FLUXANTE LIVRE DE FLUORETO NO PROCESSO DE LINGOTAMENTO CONTÍNUO

### Resumo

As características dos Fluxantes têm evoluído muito nos últimos anos para atender cada vez melhor, às necessidades do processo de lingotamento contínuo de aços, principalmente, em relação à melhoria de qualidade superficial do lingote solidificado, aumento da produtividade do processo, e ainda, menor impacto ambiental. De modo a atender a todos esses requisitos, foi desenvolvido um fluxante livre de fluoreto, avaliado primeiramente em uma usina siderúrgica européia<sup>(1)</sup>.

A proposta deste artigo é apresentar os resultados preliminares obtidos com o mesmo fluxante avaliado em uma máquina de lingotamento contínuo para fabricação de tarugos brasileira, bem como o seu impacto na produtividade de fabricação do aço.

**Palavras-chave:** Lingotamento contínuo; Fluxantes; Fluoretos.

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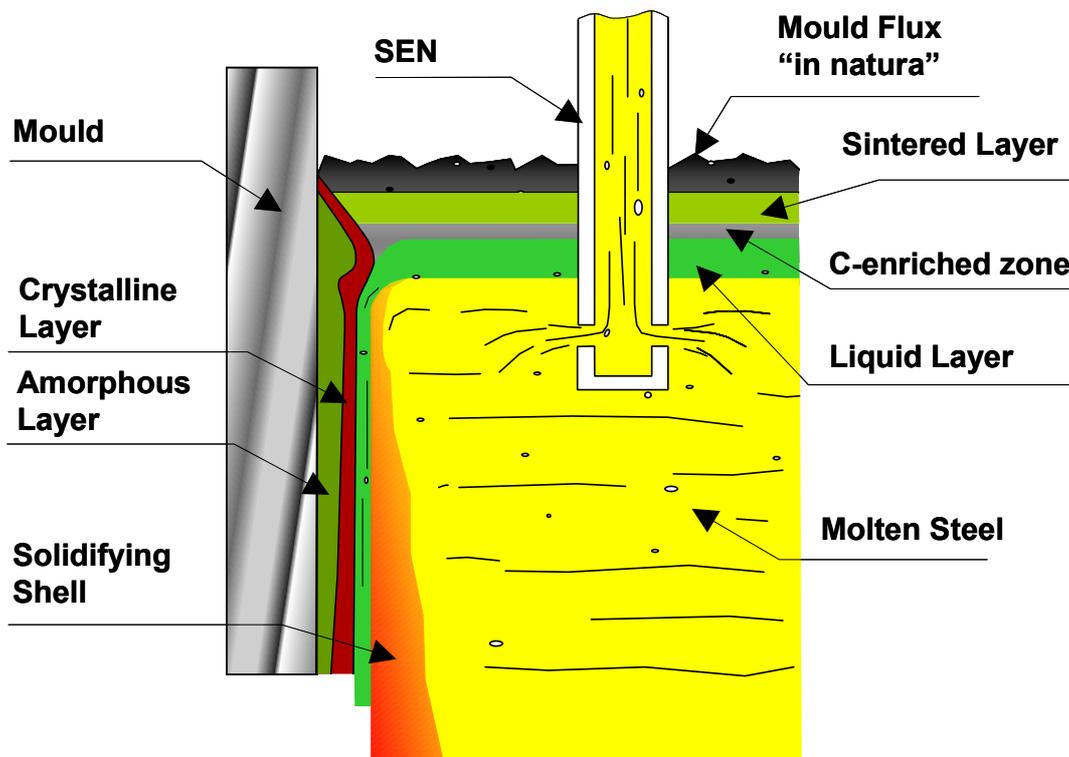
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# 1 INTRODUCTION

Mould fluxes are added to the top of continuous casting mould in order to cover the liquid steel. Since the molten steel is at a temperature of around 1550°C, a temperature is established across the mould powder layer and the carbon in the flux starts to burn off, it starts sintering and then melts to form a liquid pool of flux, which prevents oxidation of the steel. The liquid slag infiltrates into the gap between strand and mould (aided by the mould oscillation). The liquid flux partially solidifies leaving a slag film consisting of a solid slag layer (ca. 1-2 mm) and a liquid layer (ca. 0.1 mm), which provides lubrication to the newly formed shell.

The slag film controls the heat transfer between the shell and the mould (Figure 1<sup>(2)</sup>)



**Figure 1.** Schematic representation of the mould flux in the continuous casting mould (Adapted from Reference 2)

Mould fluxes are designed to meet the requirements for specific steel grades and different steel plant conditions. Table 1 shows the functions of mould fluxes and problems that can arise when mould flux is used improperly for different casting conditions.

**Table 1.** Functions of mould fluxes and problems caused by inadequate use of mould flux <sup>(3)</sup>

Functions	Problems due to inadequate mold flux
<ul style="list-style-type: none"> <li>• Insulation of molten steel</li> <li>• Prevention of molten steel re-oxidation</li> <li>• Absorption and dissolution of non metallic inclusion;</li> <li>• Lubrication between mould and strand;</li> <li>• Heat transfer between mould and strand.</li> </ul>	<ul style="list-style-type: none"> <li>• Occurrence of breakouts;</li> <li>• Occurrence of defects on slab surface as:               <ul style="list-style-type: none"> <li>- Pin / Blow hole;</li> <li>- Sub-surface inclusions;</li> <li>- Surface cracks.</li> </ul> </li> </ul>

Mould fluxes are silica based synthetic slags. Silica exists as a network composed of tetrahedra of Si surrounded by four oxygen ( $\text{SiO}_4$ )<sup>4-</sup> and consequently, are known as *network formers*. In contrast, basic oxides like CaO or MgO are *network breakers* since they break the  $\text{SiO}_4$ <sup>4-</sup> network formed by the slag.

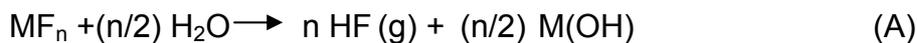
Oxides that do not fit clearly into either group are called amphoteric (ex.  $\text{Al}_2\text{O}_3$ )<sup>(4)</sup>

In general, slags with stronger bonds or large chain lengths result in high viscosities. When basic oxides are added, a weaker single bond between oxygen and silica is formed, lowering the activation energy and reducing the viscosity of the system. The single valence alkaline-earth oxides as  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Li}_2\text{O}$  or  $\text{Rb}_2\text{O}$ , behave in a similar manner, but their effects on the silica chain are greater than calcium oxide, and are mostly called *fluidizers*.<sup>(4,5)</sup>

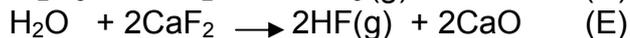
The behavior of fluorine is different since it replaces a bonding-oxygen ion, thereby breaking the silicate chains, and consequently lowers the viscosity and melting point.

Mould fluxes are designed to deal with specific steel grades and steel plant conditions. They are dependent on the raw materials used and the chemical composition obtained. Typical ranges for mould fluxes are: CaO: 25-45%,  $\text{SiO}_2$ : 20-50%,  $\text{Al}_2\text{O}_3$ : 0-10%,  $\text{Na}_2\text{O}$ : 1-20%, F<sup>-</sup>: 4-10% and C:1-25%.<sup>(2)</sup>

Fluorine can be added in form of NaF,  $\text{Na}_3\text{AlF}_6$  or  $\text{CaF}_2$  but the latter is generally used. Approximately 20 to 30% of fluoride from mould flux is dissolved into the secondary cooling water and it acidifies the cooling water by reaction (A)<sup>(6)</sup> where M= metal ion:



According reactions (B), (C), (D), and (E), the fluoride emissions as a gas are depended of the F<sup>-</sup> sources, caused by:



There are environmental concerns surrounding the continuous casting of steel because:

- (i) The fluorine gas emissions into the atmosphere contribute to acid rain;
- (ii) It can be leached from landfill sites into ground-water;
- (iii) Corrode plant equipment;
- (iv) Are possibly detrimental to staff health<sup>(1,3)</sup>.

Increasing fluoride contents are also thought to increase SEN erosion. Also, the slag containing F<sup>-</sup> can lodge in the oscillation marks and react with the secondary -cooling water (reaction A) and thereby decreasing the water pH. This fact contributes even more to the equipment corrosion.

Several studies have been made in order to develop F<sup>-</sup> free or low F<sup>-</sup> mould flux<sup>(1,3,6,7)</sup>. In order to remove the fluorine from the mould flux, it is necessary to find a replacement that can replicate the fluxing functions carried out by F<sup>-</sup>. The most obvious candidates are  $\text{B}_2\text{O}_3$  and  $\text{Na}_2\text{O}$ .

The F<sup>-</sup> free mould flux developed for billet casting has recently been tested in a Brazilian billet-casting machine and preliminary results are presented here.

## 2 EXPERIMENTAL

The F-free mould flux, LCB 426, was developed according to experimental section described on ref. 1. The chemical composition is given in Table 2.

**Table 2.** LCB 426 Typical Chemical Composition <sup>(1)</sup>

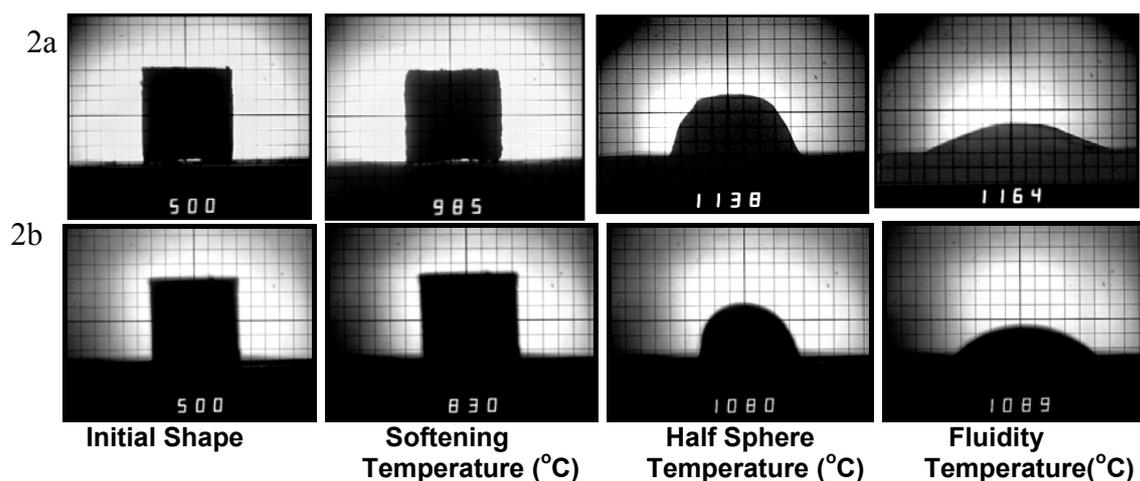
Components	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	MnO	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	F <sup>-</sup>	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>
Wt %	26,6	44,3	8,3	5,2	0,31	0,48	1,07	0	12,35	1,49

The performance of mould flux LCB 426 was compared against the standard mould flux, LCB 416, used continuously at Villares Sidenor, Mogi Plant. The typical chemical composition of LCB 416 is described on Table 3:

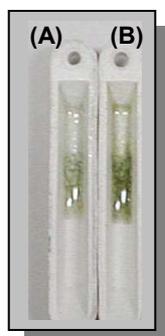
**Table 3.** LCB 416 (Standard Mould Flux) Typical Chemical Composition and Properties

Components	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	MnO	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	F <sup>-</sup>	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>
Wt %	19,5	31,0	4,5	2,0	-	0,5	0,5	3,0	9,5	0

The melting characteristics were determined by Hot Stage Microscope, (according DIN 51730, standard) and are shown at Figures 2a and 2b.



**Figure 2.** Melting Characteristics of LCB 426 (2a) and LCB 416 (2b) determined by Hot Stage Microscope.



**Figure 3.** Boat Test Evaluation - (A) LCB 416, (B) LCB426

The relative viscosities of the two fluxes were compared using the boat test method. Both mould fluxes were placed in boats, at then manipulated into an inclined position and were subject to the same conditions, are shown in Figure 3.

The performances of both mould fluxes were determined when casting high carbon billets. A typical steel chemical composition is given in Table 4.

**Table 4.** Chemical composition of the steel

Element	%	Element	%
C	0,56-0,64%	Al	0,015-0,040%
Si	0,75-1,10%	Cu	0,35% max
P	0,025% max	Sn	0,025% max
S	0,025% max	Nb	0,007% max
Cr	0,70 – 0,90	V	0,007% max
Ni	0,25% max	B	0,0015–0,0025%
Mo	0,06% max	Ca	0,001 max

The continuous casting parameters used on the trial is described on Table 5.

**Table 5.** Average of continuous casting parameters

Casting Speed (Average)	1,50 m/min	Billet Section	155x155mm
Steel <i>Liquidus</i> Temperature	1532°C	Water flow in the mould	1900 L/min
Superheat (Average)	52°C	Oscillation Mould Frequency	6,8Hz

The following items were evaluated in order to check the LCB 426 behavior:

- Slag pool thickness, using the wire system; <sup>(8)</sup>
- Mould Flux Consumption Rate (kg/t);
- Melting behavior in the mould;
- Quality surface of billets;
- SEN erosion rates by measurement of SEN external diameter, before and after cast.

At the end of casting, at the moment when the steel level was lowered in the mould, the solidified slag film automatically peeled away from the mould wall. Samples of slag film were taken at around 200 mm from the top of the mould. Chemical Analysis was carried out using X-Ray Fluorescence (Philips, Venus 100).

X-ray diffraction was used to determine the crystalline phases in the slag films. This was performed using RIGAKU equipment, MiniFlex model, with copper radiation, goniometer speeds of 0,02%/s and 0,7 count per step. The diffractograms were compared with ICDD-1996 standard, using a diffractometer at the National Research Council's Mineral Technology Centre (CETEM).

In order to check the F<sup>-</sup> content in the water-cooling, a water sampling was made from the scale pit of the continuous caster. The chemical analysis was carried out using the standard Anions EPA Method 300.1 - Determination of Inorganic Anions in Drinking Water by Ion Chromatography.

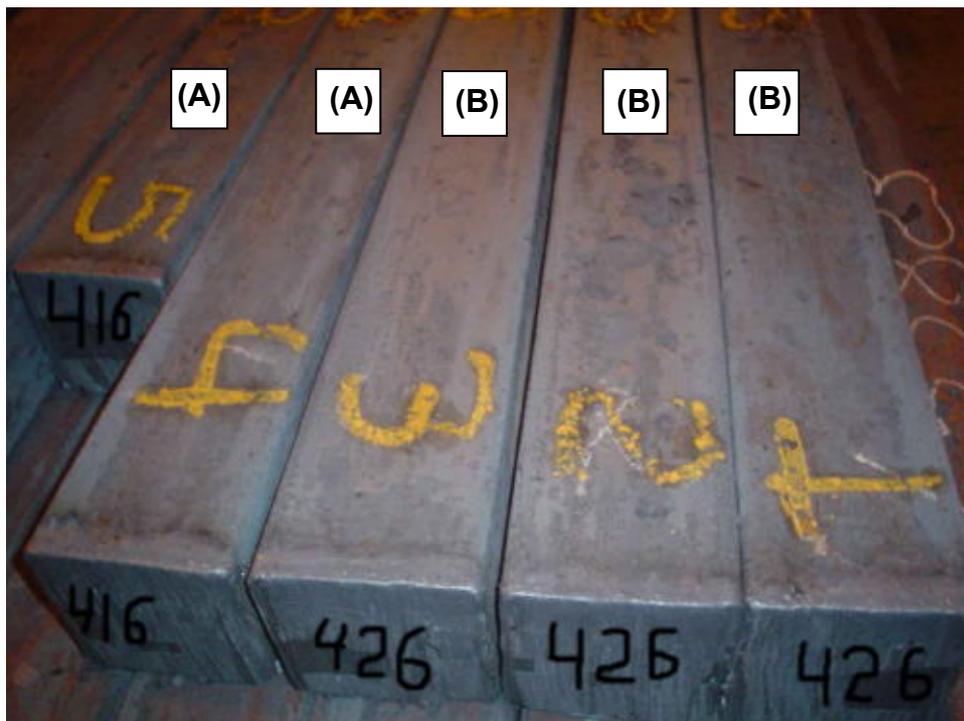
### 3 RESULTS

The behavior of LCB 426 was monitored over 40 heats, the average values obtained are given in Table 6 was obtained.

**Table 6.** Average of results obtained with LCB 426 use

Item evaluated	LCB 416 use	LCB 426 use
Fusion behavior in the mould	Good	Good
Slag pool thickness	12 mm	13 mm
Consumption Rate	0,23 kg/t	0,20 kg/t
SEN erosion Rate	1,2 mm/hour	0,63 mm/hour
Billets Quality surface	Good	Good

Figure 4, shows the surface of billets cast with LCB 416 and LCB 426, and Figure 5, shows details of the billet cast with LCB 426 mould flux. The surface quality of the billet cast with the F-free flux (LCB 426) was as good as that obtained with the original flux (LCB 416).

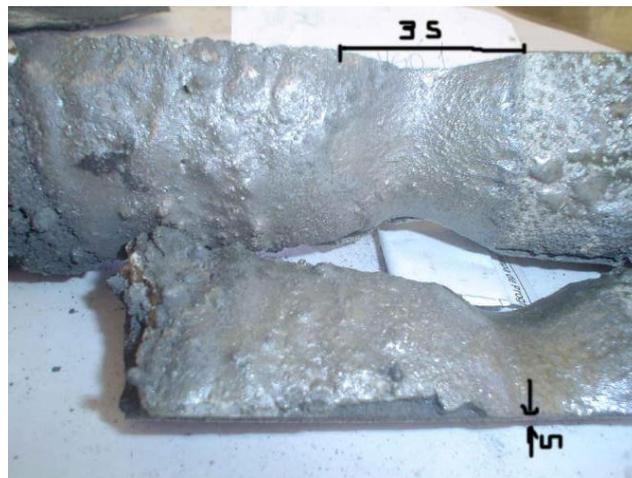


**Figure 4.** Surface of billets cast with LCB 416 (A) and LCB 426 (B)

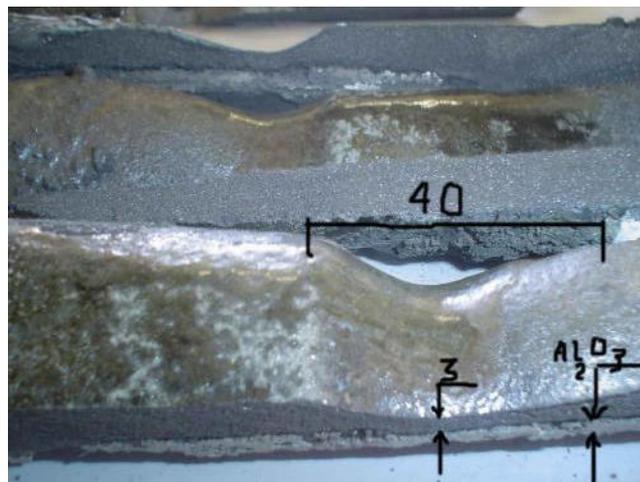
Figures 6 and 7 show the profile of SEN after 11 heats cast, using LCB 426 and LCB 416, respectively. The erosion rates were significantly lower for the F-free flux.



**Figure 5.** Detail of surface of billets cast with LCB 426 (B)



**Figure 6.** SEN profile after 5 heats using LCB 426 mould flux

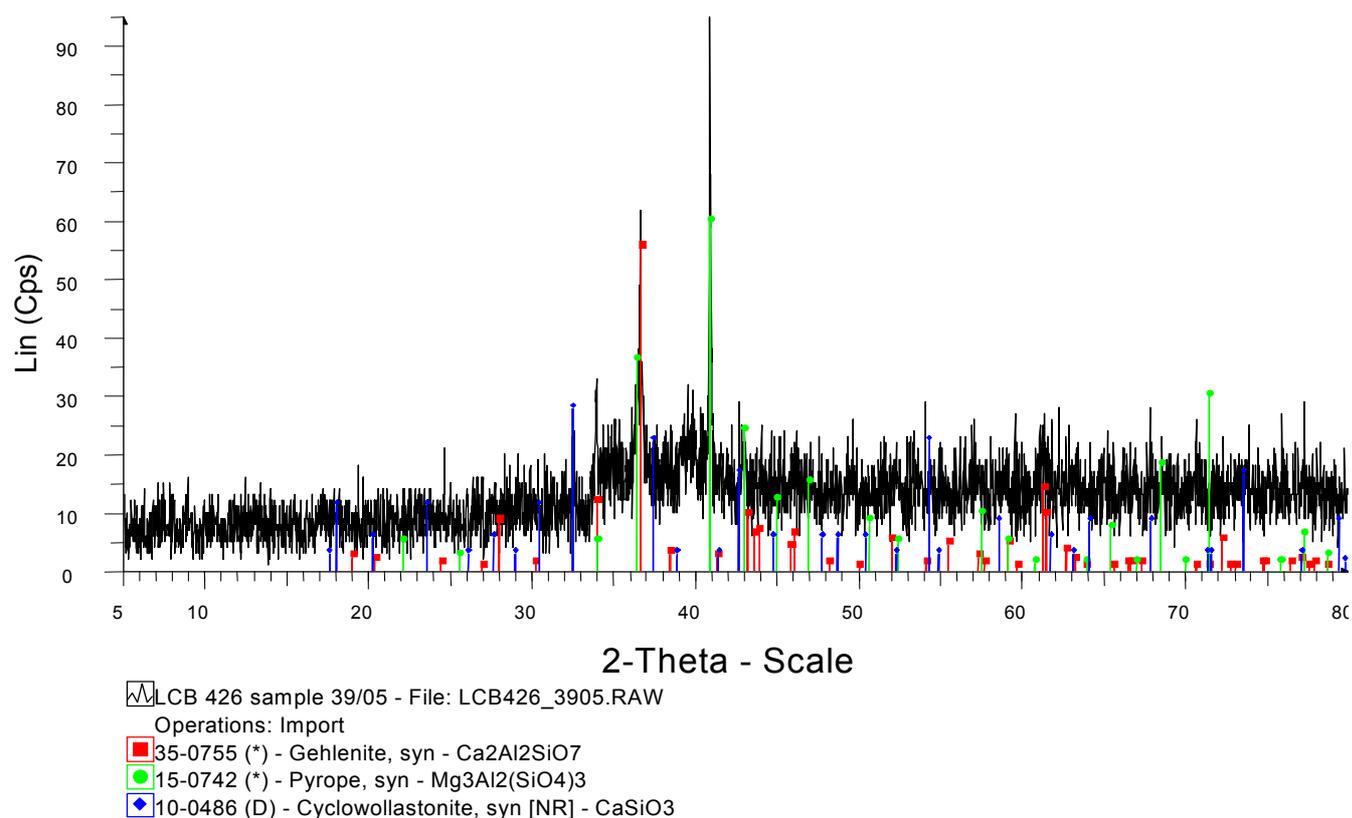


**Figure 7.** SEN profile after 5 heats using LCB 416 mould flux

Table 7 shows the chemical analysis, and Figure 8 shows the X-Ray Diffractograms of the slag film (LCB 426) collected at the end of casting

**Table 7.** Chemical Analysis (%) of slag film of LCB 426 standard and the slag film.

Description	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	F <sup>-</sup>	C free
LCB 426 Standard	33,39	21,02	6,70	3,71	0,65	8,80	0,09	0,0	18,40
LCB 426 Standard glass base	44,28	26,55	8,25	5,23	1,00	12,35	0,48	0,0	0,0
LCB 426 Slag Film	38,74	25,64	7,77	5,55	0,63	11,00	0,17	0,0	0,0



**Figure 8.** X-Ray Diagram of LCB 426 slag film, collected at casting end.

For the evaluation of the acidification of the cooling water, the comparison was made for the situation where LCB 426 was used in all strands, in order to avoid the interference of another mould flux that contains F<sup>-</sup>. The result obtained for the F<sup>-</sup> content in the water was 2,6mg/L. Typically, values obtained at Aços Villares, Mogi das Cruzes Plant, lie between 3,5 – 3,9mg/L. Thus the use of the F-free flux leads to considerably lower fluoride contents in the cooling water.

## 4 DISCUSSION

Regarding the behavior of mould flux in the mould, LCB 426 exhibited homogeneous fusion, with no formation of sintered material. The slag pool depth was very satisfactory, being very similar to that obtained for the original flux and falling within the recommended window for pool depth of 10 to 20 mm.<sup>(10)</sup>

The consumption rate obtained with LCB 426 was slightly less than that obtained with the standard mould flux, LCB 416. The powder consumption could be increased slightly for safer caster operation by adjusting melting rate and viscosity of LCB 426.

The chemical analysis of the LCB 426 slag film, showed no considerable changes in composition.

The X-Ray Diffraction indicated the presence of *Gehlenite*,  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ , *Pyrope*  $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$  and *Cyclo wolastonite*  $\text{CaSiO}_3$ . The most common phase found in traditional (F- containing) mould slag films, is *cuspidine*.  $(3\text{CaO} \cdot 2\text{SiO}_2 \cdot 2\text{CaF}_2)^{(11)}$ . As LCB 426 has no fluorine content, *cuspidine* was not found, but, it is important to note that the others phases formed (mentioned above), contribute for heat transfer control.

The replacement of the original powder with a F-free flux one, (LCB 426) led to significant reductions in the SEN erosion rate and F- content in the secondary cooling water evaluation.

## 5 CONCLUSION

The results obtained in these trials, showed that the use of fluorine –free mould fluxes led to the following benefits:

- Important reductions in SEN erosion rates which could lead to increased productivity for the continuous casting process;
- A significant decrease in the F- content in the cooling water (collected on scale pit)
- There was no reduction in the surface quality and the behavior in the mould, was similar to that obtained with the original mould flux.

As LCB 426 was used only in 40 heats, the trials must continue, in order to check the results and look to improve the billet surface quality and, mainly, productivity of continuous casting process.

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