DESENVOLVIMENTO DE PÓ FLUXANTE ISENTO DE FLÚOR PARA AÇO BAIXO CARBONO NA ARCELORMITTAL TUBARÃO*

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Resumo

O flúor é amplamente empregado em pós fluxantes usados no lingotamento contínuo de aços. Embora o flúor seja importante no comportamento de fusão, infiltração de escória e cristalização do filme de escória, ele fornece algumas desvantagens. O flúor reage dentro da escória, produzindo substâncias, como NaF e SiF, que, por sua vez, reagem com a água no resfriamento secundário, formando HF. Estes compostos levam a corrosão severa da câmara de exaustão, riscos para a saúde ocupacional e impacto ambiental. O pó fluxante isento de flúor, para lingotamento de placas, está em desenvolvimento como um resultado da parceria entre a Imerys Group e ArcelorMittal Tubarão. Matérias-primas alternativas para substituir F na composição dos pós foram investigadas. Pesquisas indicaram o B_2O_3 como substituto potenciai do flúor nas escórias de molde. Os testes industriais do fluxante sem flúor, realizados na ArcelorMittal Tubarão, foram com o objetivo de analisar a sua performance no molde, durante a produção de aços baixo carbono. Parâmetros tecnológicos como: fluxo de calor no molde, qualidade dos laminados, teor de flúor e boro na água de resfriamento secundário, absorção de boro pelo aço, consumo de pó fluxante, comportamento da detecção de alarme no molde, desgaste da válvula submersa (SEN), impacto ambiental e saúde ocupacional foram monitorados durante o lingotamento contínuo com o objetivo de avaliar o desempenho do fluxante desenvolvido e fornecer informações sobre a sua influência na qualidade dos laminados a frio e a quente. Os testes industriais de lingotamento do aço baixo carbono revelaram uma boa qualidade superficial, redução da erosão da válvula submersa, e não apresentou impacto na saúde ocupacional e ambiental da planta.

Palavras-chave: Pó fluxante; Lingotamento contínuo de placas; Pós fluxantes isentos de flúor.

DEVELOPMENT OF FLUORINE - FREE MOULD POWDER FOR LOW CARBON STEEL IN ARCELORMITTAL TUBARÃO

Abstract
Fluorine is widely employed in mold powders used in continuous casting of steels. Although fluorine is important in the melting behavior, slag infiltration and crystallization of the slag film, it provides some disadvantages. Fluorine reacts within the slag, producing substances, such as NaF and SiF, which, in turn, react with the water in the secondary cooling, forming HF. These compounds lead to severe machinery corrosion and risk for the plant's personnel health and environmental impact. Fluorine free mold powder for slab casting is under development as result of the partnership between Imerys Group and ArcelorMittal Tubarão. Regarding to this, alternative raw-materials to substitute F in the mold powders composition have been investigated. Researches have indicated B_2O_3 as potential substitutes of fluorine from mold slags. The industrial trials, performed in the Brazilian steelworks, ArcelorMittal Tubarão, were accomplished aiming to analyze its behavior during continuous casting operation of low carbon steel grade. Technological parameters like: heat flux in the mold, quality of coils, Fluorine and Boron contents in secondary cooling water, steel Boron pick-up, mould flux consumption, behavior of mold sticker detection, SEN wear, environmental impact and personnel health were monitored during continuous casting with the objective of evaluating the performance of mould powder and to provide information about its influence on the surface quality of the steel. The preliminary industrials trials of low carbon steel casting revealed a good surface quality and reduction in the SEN erosion, not impact of plant's personnel health and environmental.

Keywords: Mould powder; Slab casting; Fluorine-free mould powder.

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1 INTRODUCTION

Mould powders, Figure 1, are mineral mixtures that, in contact with liquid steel, must melt and generate a liquid slag used to lubricate the mold during the continuous casting, and thus generate a better finishing and surface quality of the casted steels [1].

Figure 1. Photo of Mould Powders
(Source: Imerys Steelcasting of Brazil)

Mold flux plays a crucial role in aspect of the efficiency of the continuous casting of steel and the surface quality of the steel product, avoiding defects such as longitudinal cracks and sticker alarms as well as contributing to the inclusion absorption in the region of the meniscus [2,3]. Especially, the surface quality depends on viscosity and heat transfer of the infiltrated mold flux between the mold wall and the solidified steel shell and the crystallization of mold flux, they strongly influences heat transfer because heat transfer is influenced substantially by the thermal resistance at the interface between mold flux film and copper mold [3]. Figure 2 shows a cross-section of the mold:

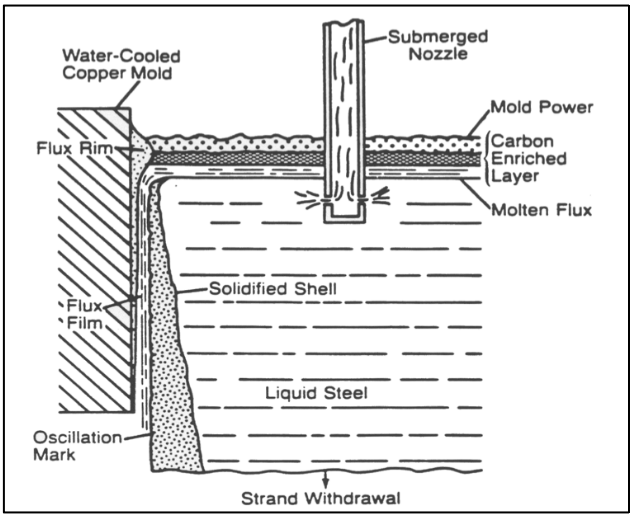


Figure 2. Cross-Section of the Mold [Brimacombe, 2018]

Fluorine is one of the main components of mould fluxes. Usually used in a range from 6 to 12% for flat products, it is used mainly to reduce the viscosity of the molten slag and also contributes to control the heat flux extraction in mold through a crystallizing slag film formation. The percentage of crystallinity is increased with the rise of fluorine through precipitation of cuspidine ($3CaO.2SiO_2.CaF_2$). However, the fluorine emissions lead to decrease cooling water pH that generates the erosion of the exhaustion chamber and continuous casting machine structure, besides being a potential for health and safety hazard. Another disadvantage of the fluorine is the increase of submerged entry nozzle wear [2].

So, the use of fluorine in mold fluxes has several advantages, such as [5]:

- Decreases the *liquidus* temperature and the slags viscosity of the system CaO-SiO_2-Al_2O_3
- Increases the crystallization tendency;
- Reduces the tendency to re-oxidations reactions between the liquid steel and the mold powder slag;
- Capacity to absorb non-metallic inclusions from steels.

However, the following reasons explain the huge interest in the research regarding the reduction of fluorine content in mold powders [5]:

- Fluorine evaporate easily from slags, producing gases that are harmful to health (such as fluoridrical acid);
- Fluorine causes excessive wearing of refractories and corrosion of the continuous casting machine (increase of maintenance cost);
- Problems related to storage and use of generated solid waste;
- Acidification of the cooling water.
- Environmental impact

Within this context, the elimination of fluorine in the composition of mold powder for casting of steel billets and slabs has become essential. Some oxides have been used to substitute the CaF_2, such as B_2O_3, Li_2O and Na_2O and must reproduce the same physical properties of the conventional powder based on fluorspar [6].

Some researchers have been made using B_2O_3 as potential substitute of fluorine, as [7]:

- It is a good flux because it presents a low fusion temperature;
- Reduces the solidification temperature (*break temperature*) of the flux powders without fluorine;
- Decreases the crystallization ability of the slags, therefore, the crystalline fraction will be reduced;
- B_2O_3 is a slags network forming oxide. Some studies show that the borate network can incorporate itself in the silicate network to increase the complexity of the network structure, this increase helps to increase the ability of vitreous formations of molten slag and reduces the crystallization ability of the slag;

Figure 3 shows the influence of B_2O_3 in the properties of mould powders

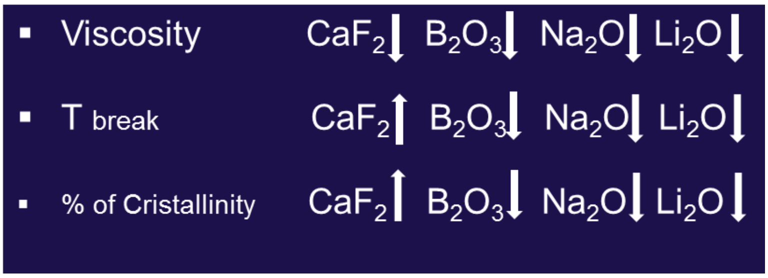


Figure 3. Influence of B_2O_3 in the properties [2, 7]

In the present paper, the preliminary results obtained from industrial tests made with the use of mold powder without fluorine are reported. Determined were: the results of heat flux in the mold, quality of coils, fluorine and boron contents in secondary cooling water, steel boron pick-up, mould flux consumption, plant's personnel health, environmental impact, behavior of mold sticker detection and SEN wear.

2 DEVELOPMENT

This paper was conducted by the evaluation of a mould powder without fluorine, used for the continuous casting of slabs for low carbon steel. Based on a conventional flux powder, with fluorine (8%), a product without fluorine was developed, searching for the same properties according to Table 1. The fluorine was substituted by a combination of B_2O_3 and Na_2O.

Table 1. Chemical Composition of Fluorine Free Mould Powder

Components	Flux Powder without Fluorine
SiO_2	35,0
CaO	28,0
$MgO + Al_2O_3$	7,0
$Na_2O + B_2O_3 + K_2O$	15,0
F	0,00
C free	2,50

At a Brazilian steel plant, ArcelorMittal Tubarão, industrial tests were performed during continuous casting of slabs of low carbon steel. During the casting, mold fluxes with fluorine and without fluorine were tested on two different strands simultaneously to compare the main process parameters in the mold during casting.

<u>Following the preliminary results with fluorine free mold powder:</u>

2.1. First trial (2 Tons)
The results were evaluated as being positive and promising regarding to the casting parameters. On the other hand, high occurrences of stickers (Figure 4) and slivers index were obtained, in spite of a very stable steel level. The irregular mold heat transfer was observed when compared with regular powder (Figure 5).

Figure 4. Sticker on slab (low carbon) with fluorine free powder

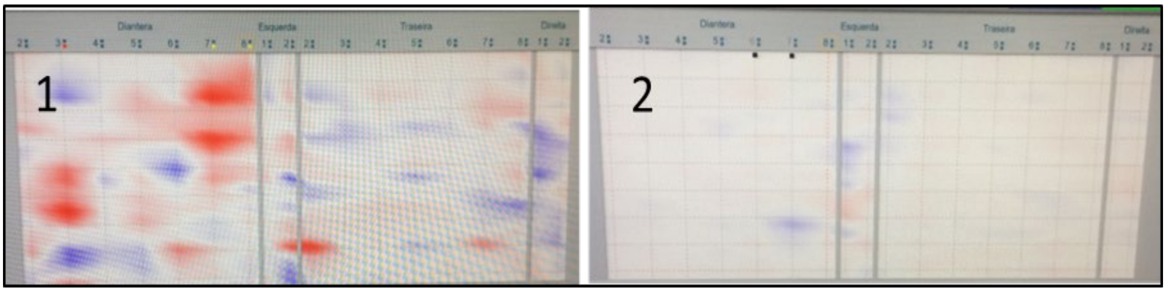


Figure 5. Thermography map: (1) fluorine – free powder; (2) standard powder with fluorine. Low carbon steel grade; casting speed= 1,5 m/min ; 1350x 225 mm

2.2. Second, third and fourth trials (20,8 Tons)

Some adjustments of the recipe were realized as Break-Point (Tbr) reduction, to improve the infiltration of liquid slag all along the mould and to keep it liquid as long as possible in order to improve the lubrication. The adjustment was done reducing the Basicity to avoid any crystallization and have a deeper infiltration of the slag in the mold (table 2):

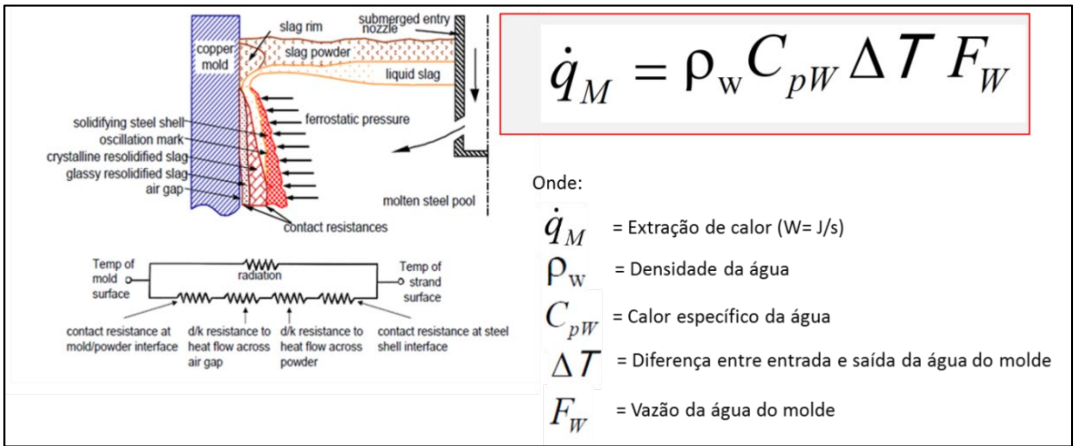
Table 2 shows the Basicity value of the 2 versions of Fluorine Free mould powder

	Material	
Characteristics	Fluorine Free1	Fluorine Free 2 (optimized recipe)
Basicity	0,93	0,80

The process and quality results are presented as follows, using the optimized fluorine free recipe.

a) Mould heat flux:

The main challenge of development regarding to the powder without fluorine is to control the mould heat flux. The percentage of crystallinity is increased with the rise of fluorine through precipitation of Cuspidine ($3CaO.2SiO_2.CaF_2$). Highest heat transfer in the mold will create the spot depression in slab and false sticker alarm. The Figure 6 shows the total mould heat flux obtained with fluorine free. The results are similar as regular powder without impact on slab surface quality.



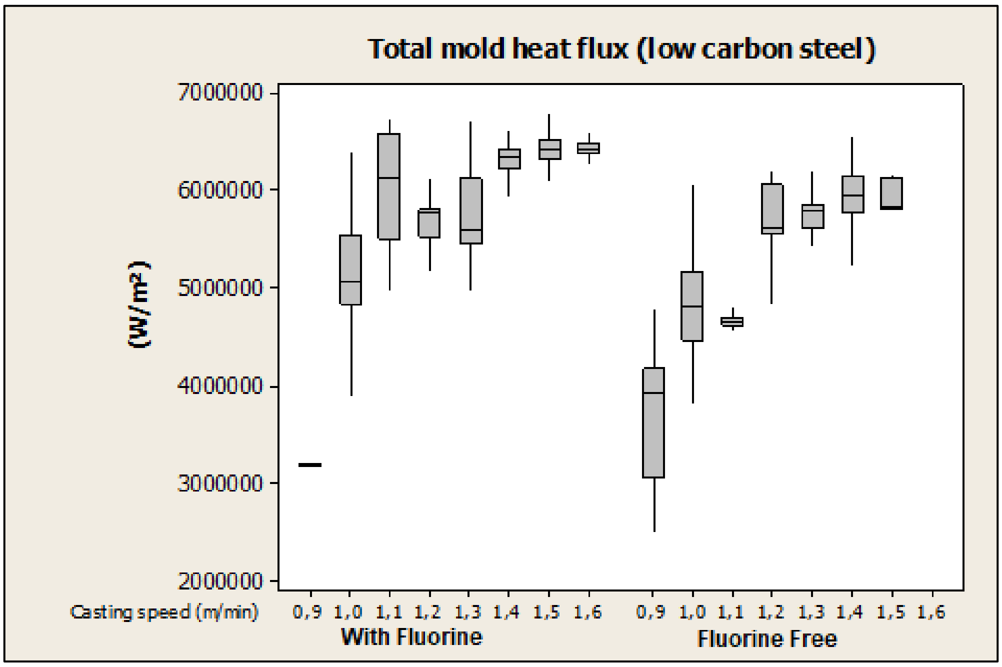


Figure 6. Total mold heat flux (low carbon steel) vs flux powder with fluorine and fluorine-free

b) Frequency of sticker alarms:

The results were with low frequency at the same level as flux powder with fluorine.

c) SEN wear:

The SEN wear with fluorine – free decreased ~ 18% when compared with regular powder (figure 7).

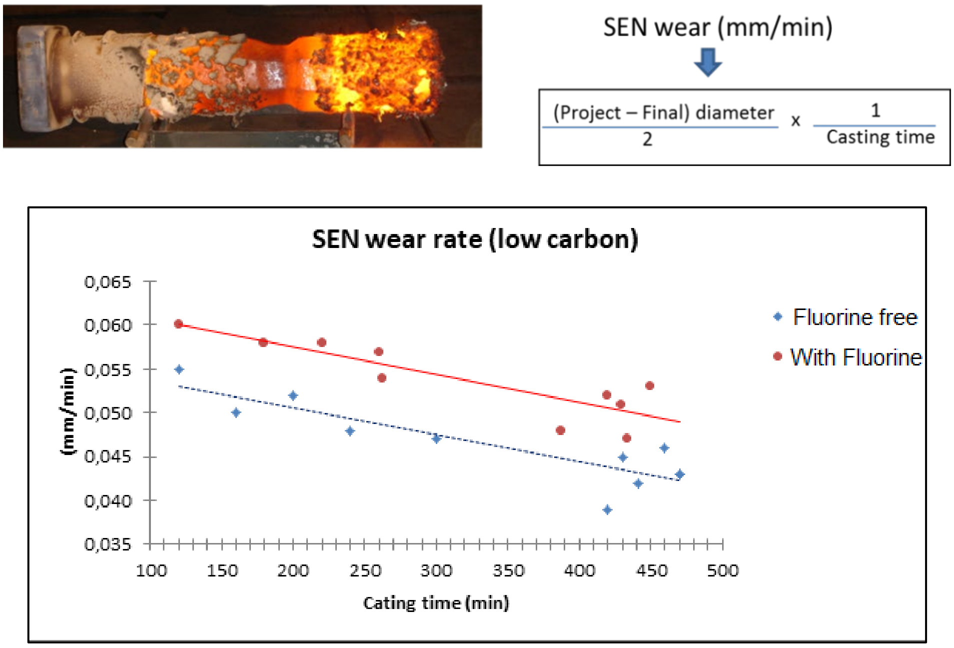


Figure 7. SEN wear rate: fluorine – free vs with fluorine

d) Steel boron pick-up:

The literature shows that the boron pick up in steel due to influence of powder slag is thermodynamically representative if (%) of B_2O_3 > 5% (Figure 8). To prove this statement was carried out chemical analysis of samples taken from the mold and refining for regular powder and fluorine – free. Statistical data demonstrated similar results between these fluxes (P value = 0.0189).

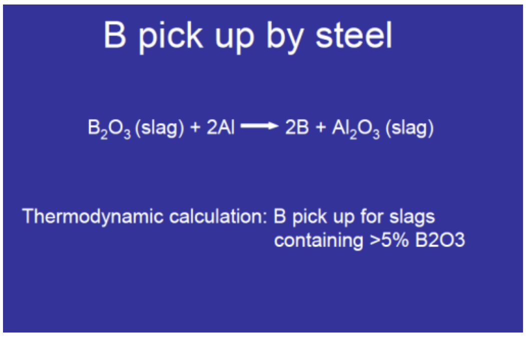


Figure 8. Thermodynamic calculation – B pick up by steel

e) Boron contamination in water

The boron values in the final effluent (water analysis) has no impact = 2 mg/l (acceptable=5mg/ l - CONAMA 430/2011) [8].

f) Powder consumption:

The consumption (kg/t) of fluorine-free powder was at the same level as the regular powder.

g) Exhaustion chamber corrosion:

When to add the (F) in mould powder will be created F- emissions in gaseous form and HF that increases the corrosion of caster. 20 to 30% of F- dissolves in the secondary cooling water reducing the PH and increases the environmental impact. Figure 9 shows the fluorine emissions in gaseous form during casting:

✓ F- emissions in gaseous form during the casting:

$Na_2O + CaF_2 \Rightarrow 2NaF(g) + CaO$

$Al_2O_3 + 3CaF_2 \Rightarrow 2AlF3\,(g) + 3CaO$

$H_2O + 2CaF_2 \Rightarrow 2HF(g) + 2CaO$

$SiO_2 + 2CaF_2 \Rightarrow SiF4(g) + 3CaO$

Figure 9. Thermodynamic calculation – F pick up by steel

Corrosion samples have been installed inside the exhaust chamber of the caster to evaluate the corrosion rate (Figure 10). The preliminary results referring to the fluoride in secondary cooling water (scale pit) is shown in Figure 11. The impact of fluoride depends on the production mix with fluorine free mould powder.

Figure 10. (1) – corrosion samples installed in exhaustion chamber to evaluate the corrosion rate

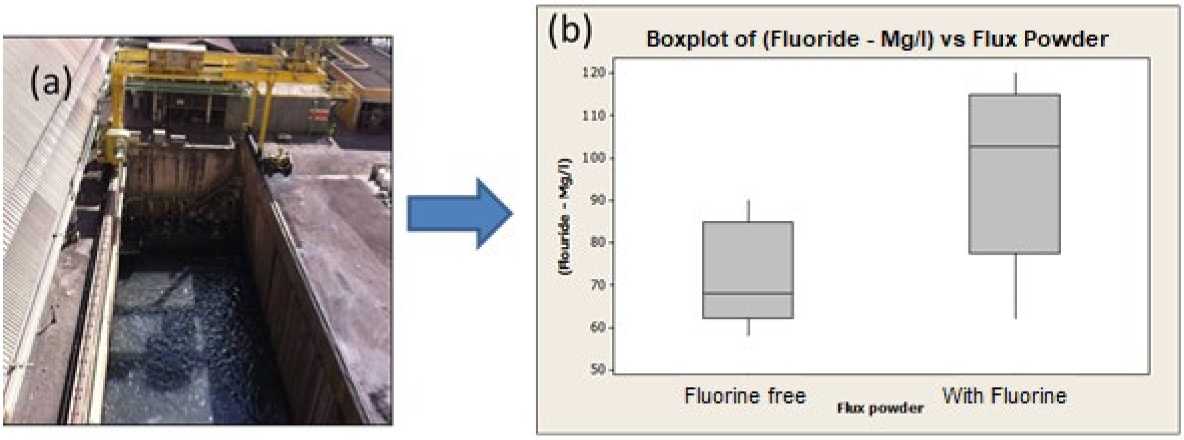


Figure 11. (a) – scale pit at caster 1; (b) – fluoride content in secondary cooling water

h) Safety hazard (boron impact):

Installed on the casting platform - Equipment (IOM sampler), Figure 12, to collect the ambient air with use of fluorine free. The results of the boron and components were smaller than maximum limit of standard ACGIH - American Conference of Governmental Industrial Hygienists - (table 3) [9].

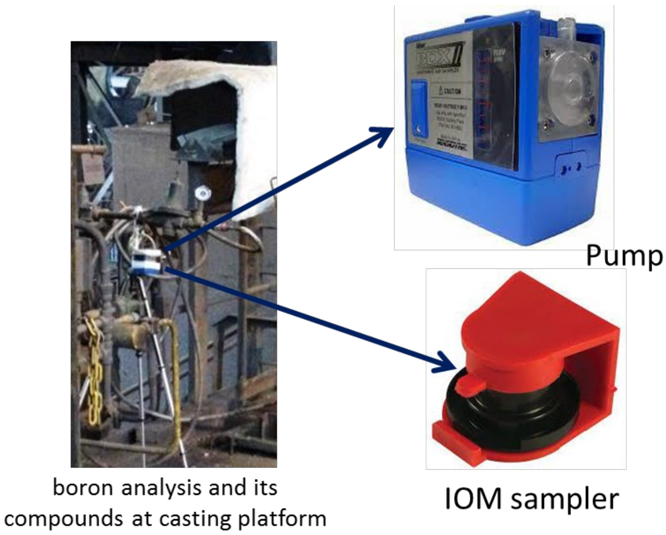


Figure 12. Equipment – IOM sampler installed on casting platform

Table 3. Results of boron and components in ambient air with use of fluorine free powder

Agent	Results	Tolerance limit (standard ACGIH - 2017) [9]	
		TWA (average values for 48 hours of exposure)	Stel/Teto (Short-term exposure limit)
	Mg/m^3	Mg/m^3	
Boron and components	< 0,1 - Fluorine free < 0,1 - With Fluorine	2	6

i) Slag rim and spots:

When to add B_2O_3 + Na_2O there is the possibility of creating steam in the mold with white color. During this trial wasn´t observed this phenomenon, but on the other hand some spots were created on the meniscus in the soft form (figure 13) but without impacts on quality.
With respect to the slag rim formation showed no abnormality during casting.

Figure 13. Agglomerate powder (spots) on the meniscus with fluorine – free

j) Quality – hot and cold coils:

Was processed 48kt of the low carbon steel using fluorine free mold powder. The sliver index in coils was on the same level as the powder with fluorine.

3. CONCLUSIONS

- ✓ Fluorine is widely used in continuous casting fluxes but is source of health and operational problems due to some gas generation at use (HF, SiF_4) and environmental impact;
- ✓ A fluorine-free flux has been developed to be used on low-carbon steels;
- ✓ Because of the Fluorine removal from the recipe, Boron has been added in order to be able to keep stable the viscosity and melting characteristics of the slag;
- ✓ Following a few adjustments, an optimized recipe has been defined and was tested in industrial conditions;

- ✓ The process parameters did not show any changes, and the steel quality index remained unchanged;
- ✓ Reduction in the SEN wear;
- ✓ The results of the boron and components in ambient air were smaller than maximum limit of standard ACGIH;
- ✓ Without boron pick up in steel;
- ✓ These first results are very promising and will follow a long-term evaluation period in order to evaluate the positive impact of Fluorine removal on machine corrosion and water pollution.

4. NEXT STEPS

- ✓ Evaluate the corrosion rate in exhaustion chamber.

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