Optimization of injection treatment with High Purity Calcium and High Purity Compacted CaSi 30/70 in Low carbon Al-killed and Al/Si-killed steels

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Summary

This work describes the optimization process of calcium treatment using High Purity Calcium (HPCa) on Low Carbon Aluminum killed steels (LCAK) and High Purity Compacted CaSi 30/70 (HPCaSi) on Low Carbon Aluminum-Silicon killed steels (LCAl/SiK). 51 heats of LCAK were treated with HPCa and 55 heats of LCAl/SiK were treated with HPCaSi in recognized steel mills in North Mexico to optimize treatment parameters modification of inclusions. Both wires were made with a 1.1 mm wall thickness sheet (welded seam). Their filling rates were 69 gr/m in case of HPCa (Calcium purity 98.5%), and 230 gr/m in case of HPCaSi (Calcium 30%-Silicon 70%). The optimized parameters were injection speed (m/min) and consumption of calcium per ton (kg Ca/ton). The degree of modification of inclusions in heats treated with HPCa was evaluated and compared versus heats treated with AlCaFe CCW (conventional cored wire). In the case of HPCaSi a similar study it was conducted. Both inclusionary states were characterized in steel samples obtained after injection treatment, in terms of chemical composition, morphology, number of inclusions and area fraction analysis by scanning electron microscopy (SEM/EDX) and Image analysis. Efficiency with High Purity Calcium was 32.6 % with an average of 22 ppm of Ca, whereas this efficiency with AlCaFe CCW varies between 24 and 25%. The optimum injection speed for HPCa ranged between 140 and 160 meters per minute (m/min) with an optimum Ca consumption of 0.065 kilograms per ton (kg Ca/ton). Efficiency with HPCaSi was average 33.7% with 20 ppm of Ca. The best injection speed and Calcium consumption were 122 m/min and 0.060 kg Ca/ton. The inclusionary state in heats treated with High Pure Calcium was characterized by liquid inclusions of type Al_2O_3-CaO with MgO content less than 20%, with size less than 10 μm and globular morphology while in heats treated with AlCaFe CCW the inclusionary state was characterized by inclusions unmodified Al_2O_3-MgO type of irregular morphology and smaller than 10 μm, similar to inclusions analyzed before treatment with calcium. Early inclusion modification with High Pure Calcium (HPCa) was observed compared with AlCaFe CCW. In case of inclusion analysis for heats treated with HPCaSi, inclusions before injection were characterized by Al_2O_3-Si_2O-MnO inclusions of globular shape and size larger than 20 μm. After injection inclusions present were mainly of Al_2O_3-CaO with MgO content lower than 10% wt, with globular morphology and smaller than 10 μm. In addition S.E.V. (Statistics of extreme variation) analysis has revealed an improvement in steel cleanliness levels in heats treated with HPCaSi compared with CaSi CCW.

Key words: Efficiency, Low Carbon, Al Killed steel, Al-Si Killed steels, inclusion modification.

Introduction

The growing demand in the production of clean steels has led to the development of new technologies in the treatment of inclusions modification that benefit the profitability of the injection process of cored wire. In this area the development of two alternatives (High Purity Calcium and High Purity Compacted CaSi wires) encapsulated with Hi-Core technology using a steel plate of 1.1 milimeter of thickness, promotes greater penetration of calcium in the bath of liquid steel increasing the residence time and favoring the reaction kinetics in the modification treatment inclusions. High Purity Calcium wire is often used in low carbon Al Killed steels with Silicon restricted, while the High Purity Compacted CaSi is used commonly in Calcium treatment of steels without Silicon restricted. The goal of this work was to study the parameters involved in the secondary metallurgy process that affects the efficiency of both Hi-Core wires and optimize their injection parameters and evaluation of inclusions modification degree.

Development

Trials with HPCa (High Purity Calcium) in LCAK

51 heats of steel LCAK (0.04 to 0.06% C) were treated with High Pure Calcium. It tested two coils of this Hi-Core wire, containing 0.069 kilograms of Calcium per meter. Injection parameters were determined according to the weight of heat and specification chemical analysis of calcium (Ca ppm) after treatment in the ladle furnace. To heats of 136.5 tons of steel, began injecting 130 meters of High Pure Calcium (8.97 kilograms of calcium) at a speed of 140 meter per minute. The objective of Ca ppm's was 22. These parameters (injection speed, kilograms of calcium per ton) were modified according to results. The steel sample obtained in the ladle furnace after injection of the wire, was analyzed to determine Ca ppm's obtained. With this result the efficiency of treatment using High Pure Calcium was calculated. Other process variables monitored to evaluate their impact on the calcium treatment of steel were Al and S contents in steel before injection. The steel sample analized was obtained in the ladle furnace between 3 and 5 minutes after the injection.

Results

Efficiency of injection treatment using High Pure Calcium

Table 1 presents average results obtained after treatment with High Pure Calcium. This table shows an average efficiency of 32.6 % for heats treated. Also shows a standard deviation of 5.9% and an average of 22 ppm's Ca, injecting 0.065 kilograms of calcium per ton.

RESULTS						
Injected meters	TLS	Average efficiency (%)	Standard deviation	Average PPM Ca at Ladle furnace	kg Ca / heat	kg Ca / ton
133.4	138.20	32.60	5.90	22	9.18	0.065

Table 1.

Injection speed effect on efficiency

Figure 1 shows the effect of injection speed on efficiency of treatment. At the start of test injection speed of wire was 140 meters per minute. With this parameter ensuring that the wire reaches a suitable penetration liquid metal bath before fusion of the sheet, obtaining an average efficiency of 33.4% (see Table 2). As the speed was increased to evaluate the effect of splashing, a slight decrease in efficiency was observed. Upon reaching the injection speed of 180 meters per minute this decrease became more prominent (30.02%) addition began to be observed a considerable increase in splashing. The above phenomenon is due to a higher injection speed, High Pure Calcium wire penetrates sufficiently before melting, causing that calcium is released in an area where stirring with argon benefits Calcium expulsion to the atmosphere decreasing the residence time in the steel and resulting in lower efficiency. With these results, injection speed was determined in a range of 140 to 160 meters per minute. Figure 2 shows the decrease of efficiency as the injection speed was increased.

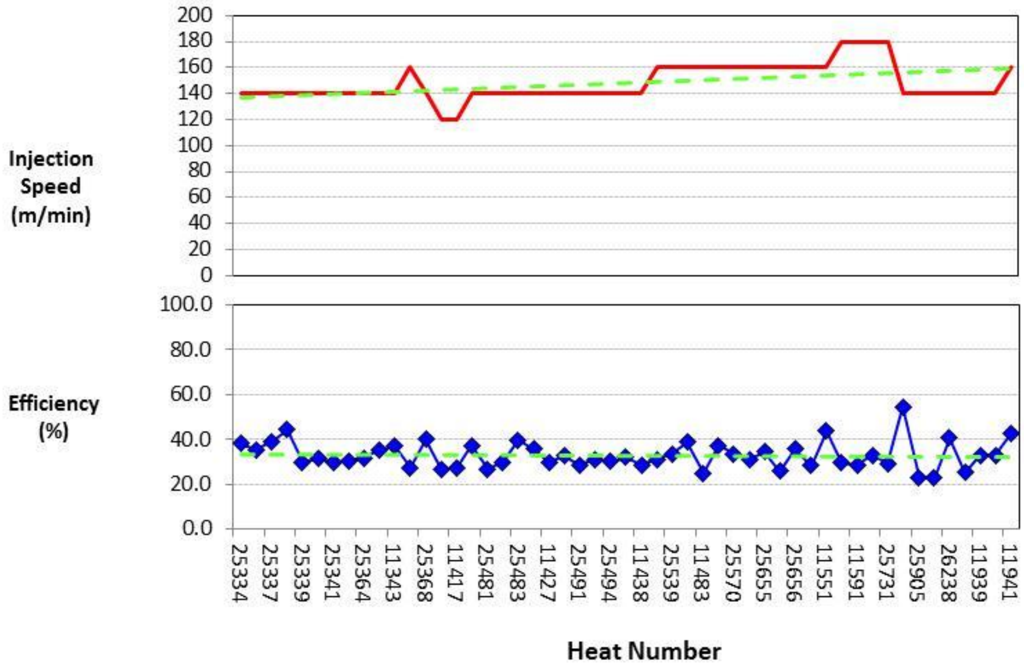

Figure 1.

RESULTS									
Injection Speed (m/min)	Treated Heats	meters injected	TLS	Average yield (%) LF	Standard deviation	Average Ca ppm LF	Standard deviation	kg Ca / heat	kg Ca / ton
120	2	152.5	141.9	26.87	0.4	20	2.1	10.49	0.073
140	32	133.4	138.4	33.40	6.4	22	2.9	9.18	0.065
160	13	129.2	136.5	32.63	5.4	21	3.3	8.89	0.064
180	4	137.3	140.2	30.02	2	20	2.2	9.46	0.067

Table 2.

Effect of consumption (kilograms of Ca per ton) on efficiency.

Figure 3 shows efficiency of treatment with consumption. In this figure an average efficiency of 32.9% was obtained with an average consumption of 0.065 kilograms of Calcium per ton. However, there were heats with efficiency higher than 40% where this consumption was lower than 0.060 kg Ca/ton. Table 3 contains results of average efficiency and consumptions. As the amount of calcium injected decreases (less than 0.065 kg Ca/ton) efficiency of High Pure Calcium increases due to dissolution of calcium in the steel was optimized.

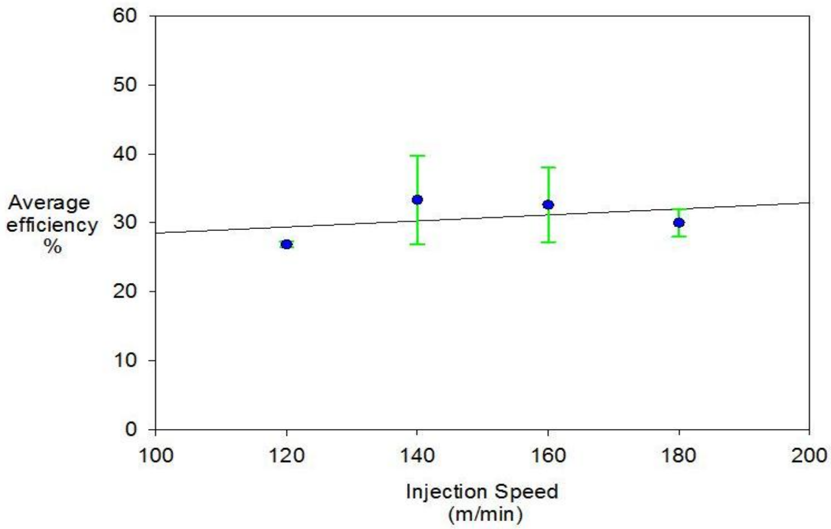

Figure 2.

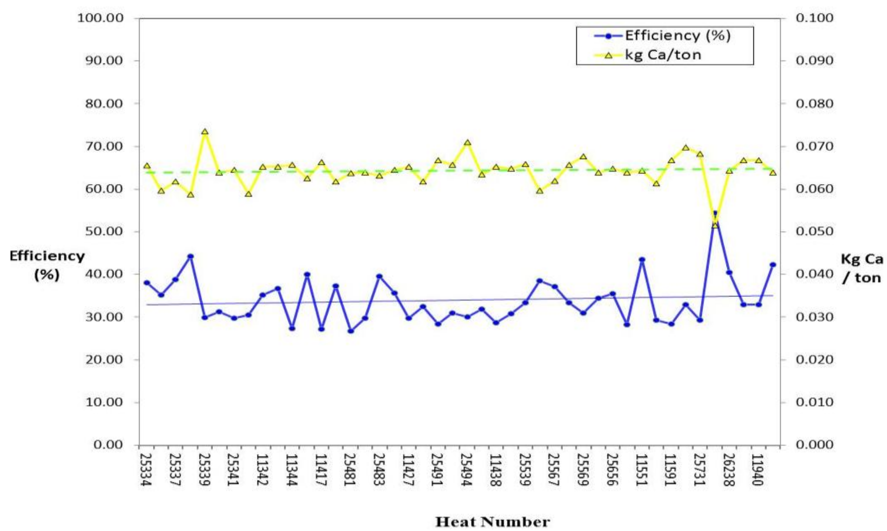

Figure 3.

Figure 4 shows a tendency to increase the average efficiency decreasing of kilograms of Calcium per ton. In this graph, the trend is affected by high variation of efficiency due to the shortage of heats treated with minor kg Ca/ton (7 heats treated with calcium less than 0.064 kilograms per ton), so that a greater number of tests with less amounts of calcium injected confirm this tendency.

RESULTS									
meters injected	Heats treated	Injection speed (m/min)	TLS	Average efficiency (%) LF	Standard deviation	Average Ca ppm LF	Standard deviation	kg Ca / heat	kg Ca / ton
100	3	140.0	134.6	34.9	17	20	6.7	6.88	0.050
120	2	140.0	140.2	31.0	3	21	4.2	8.26	0.058
125	2	160.0	139.5	32.2	9	20	4.9	8.60	0.061
130	38	145.8	138.0	32.9	5.1	21	2.8	8.95	0.064
>140	6	160.0	139.8	31.1	2.1	21	1.5	9.75	0.069

Table 3.

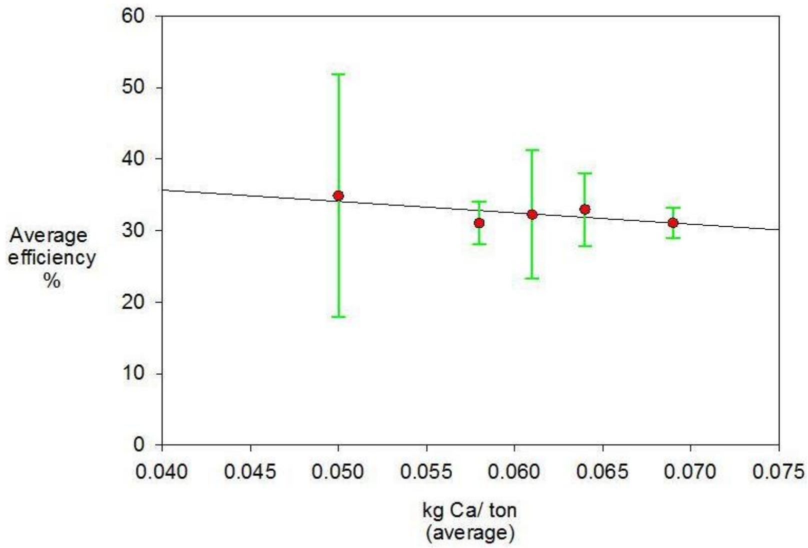

Figure 4

<u>Effect of Al and S contents on treatment efficiency</u>

Figure 5 shows the effect of Al and S contents in the steel before treatment with High Pure calcium on efficiency. It is observed that many heats with efficiency less than 30% showed high levels of Al and S. These heats had favorable levels of these elements to form solid calcium aluminates and CaS (curved line displayed in blue) and decreased efficiency on modification of inclusions. At high levels of Al in steel (from 0.025 to 0.035% wt. Al, represented by the vertical lines in yellow) amount of calcium required for inclusions modification is insufficient, so that poor efficiency is observed. Added to this behavior, levels of S higher than 0.0050% (specification represented by the red horizontal line) causes that High Pure Calcium injected reacts first with this element causing a desulfurization of steel and formation of CaS inclusions. Heats with efficiency ranged from 30 to 40% also were observed. In this figure a deoxidation practice improved is observed, resulting in better control of Al content in steel before treatment with calcium. As result a better steel desulfurization treatment prior High pure Calcium was achieved (S content less than 0.0050%) preventing that Calcium injected works as desulfurizer (reducing CaS formation). Finally those heats with Al and S contents before treatment within its specification had efficiency higher than 40%. In these heats Aluminum content before treatment was between 0.025 and 0.035%, while S content was less than 0.0050%.

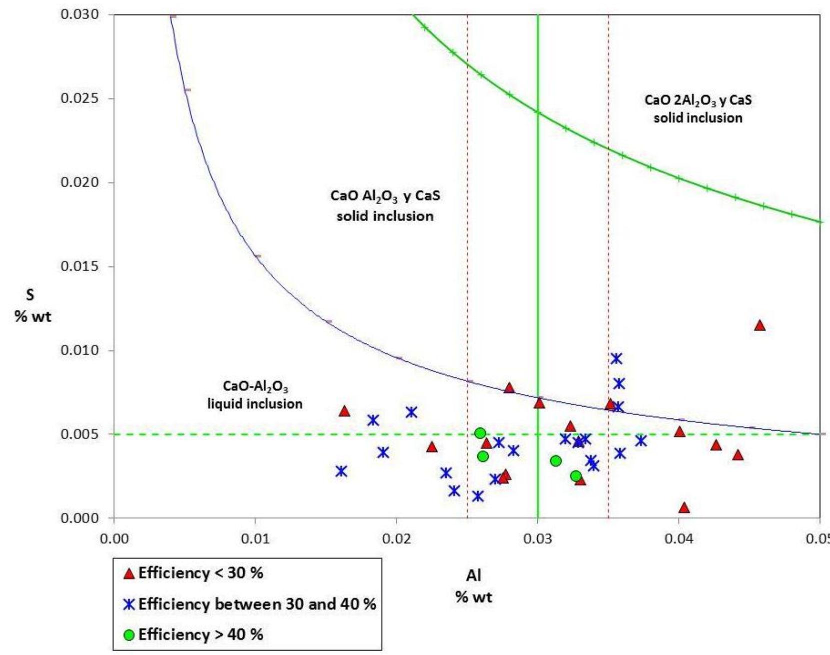

Figure 5

Trials with HPCaSi (High Purity Compacted CaSi 30/70) in LCAl/SiK

A total of 55 heats were treated with HPCaSi. The injection parameters were defined according to the weight of the heat and the chemical analysis specification Ca (ppm Ca) at the end of the treatment in the ladle furnace. The average weight of the heats was 152 ton and initially 152 m of HPCaSi (10.5 kg of Ca) at a velocity of 137 m/min were injected aiming for a ppm Ca target of 20. These parameters (injection velocity and kg Ca/ton) were modified according to the results obtained. A sample was taken from the ladle furnace after 3-5 minutes of the injection treatment for chemical analysis. Other process variables were monitored in order to evaluate their impact on the treatment yield, such as levels of Al and S dissolved.

Results

Trials at Steel shop

Results obtained after HPCaSi injection treatment is presented in Table 4. An average yield of 33.7% was accomplished with a standard deviation of 8.1% having as result 20 ppm Ca with 0.060 kg Ca/ton, and all heats treated were within the Ca ppm range specified (10-20 ppm Ca).

RESULTS						
Injected meters	TLS	Average Yield (%)	Std Deviation	Average ppm Ca	kg Ca per heat	kg Ca per ton
133	152	33.7	8.1	20	9.2	0.060

Table 4

Effect of injection speed and consumption kgCa/heat on the efficiency.

The evidence of the optimized parameters for the HPCaSi injection process vs efficiency is plotted in Figure 6. At the beginning of the tests, the wire was injected at 137 m/min to evaluate the penetration in the liquid bath. Five heats were injected at 137 m/min and 152 meters (10.5 kg Ca per heat) having an average yield of 25.3%. Subsequently the yield was improved reducing the consumption to 9.4 and 8.4 kg Ca per heat (137 and 122 m of wire length respectively). With the objective of evaluating the increase in the yield, injection speed was increased to 152 m/min. With this raise in velocity, a slight improvement in the yield occurred reaching levels of 28.5% and 30% with 10.5 and 9.4 kg Ca respectively. Nevertheless, steel splashing at this injection velocity was also higher. The next step consisted of reducing the injection velocity to 122 m/min to determine an adequate wire penetration that guarantees acceptable splashing levels and further increases in the yield obtained. The efficiencies obtained with the injection velocity reduction were 32.9, 35.8 and 43.4 %. This increase in efficiency was because at this low injection velocity (122 m/min), the HPCaSi wire goes deeper in the liquid bath before being melted. This causes the Ca to be liberated and react in a high ferrostatic pressure zone, raising the residence time in the steel and resulting in an adequate dissolution and an efficient inclusion modification.

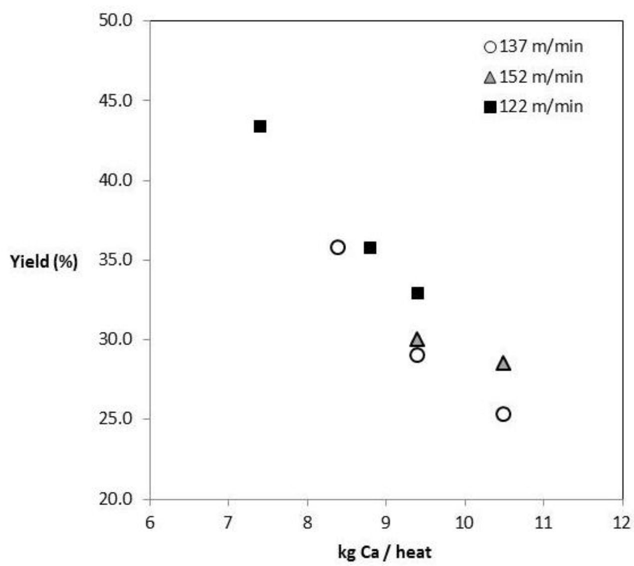

Figure 6

Al and S content before injection treatment.

In Figure 7 contents of Al and S in liquid steel before cored wire injection are presented. It was observed that most of the heats treated with HPCaSi (85% of the heats) were thoroughly deoxidized and desulphurized. This is evidenced by the S content before the Ca treatment below 0.0080% wt and Al levels which were within 0.025-0.045 %wt. With these adequate levels of Al and low S within the steel it can be guaranteed that the injected Ca would not act as desulphurizer or deoxidant.

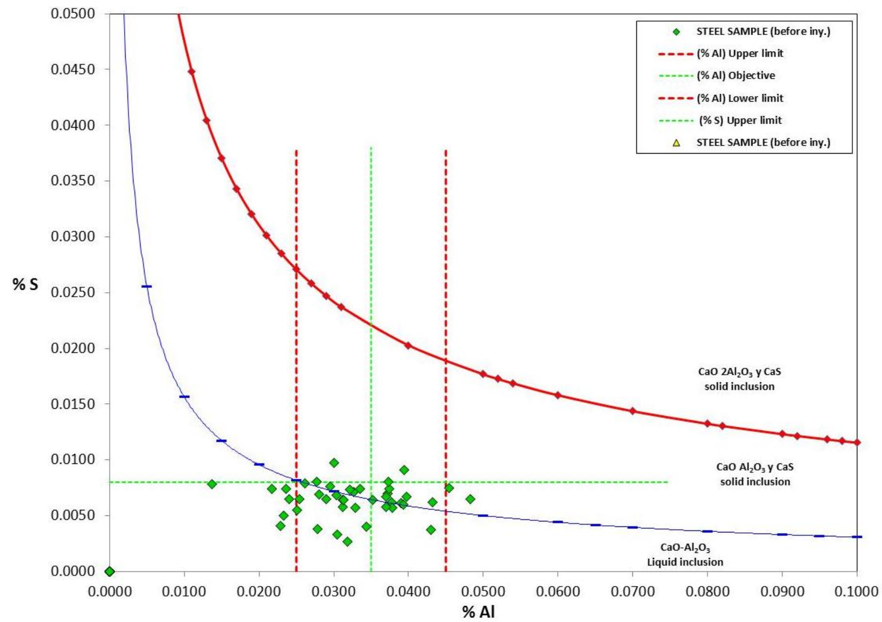

Figure 7

Effect of the injection speed on Ca recovery

The effect of injection speed on the Ca recovery in heats treated with HPCaSi, in the system Fe-Al-Ca-S-O at 1600 °C is shown in Figure 8. As it can be observed on the right side of Figure 8, Al dissolved content after injection treatment ranges in 0.030-0.050 % wt (300-500 ppm Al). At these Al levels, the content of Ca required to promote an adequate inclusion modification must be within 10-25 ppm Ca. With these Ca recoveries, a satisfactory inclusion modification has been reached having mainly liquid calcium aluminates (45-55% CaO). All heats treated with HPCaSi had ppm Ca within the specified range and as the injection speed was reduced from 152 to 137 and 122 m/min, the ppm Ca recovered increased. It is important to mention that at the optimum injection speed 122 m/min most of the heats HPCaSi treated recovered Ca contents higher than 20 ppm (above the superior limit specified) showing an important tendency of the inclusions to be enriched with CaO without being saturated with this oxide. In the left side of Figure 8 it can be observed the same tendency of increasing the Ca recovery with an injection speed reduction. In this part of the Fe-Al-Ca-S-O diagram, it can be noted that for steel grades Si killed, with Ca recoveries higher than 20 ppm, the S content in the metal after the injection was lower than 0.0080% wt (80 ppm) for most of the heats injected with HPCaSi, thus conditions for CaS formation were not met.

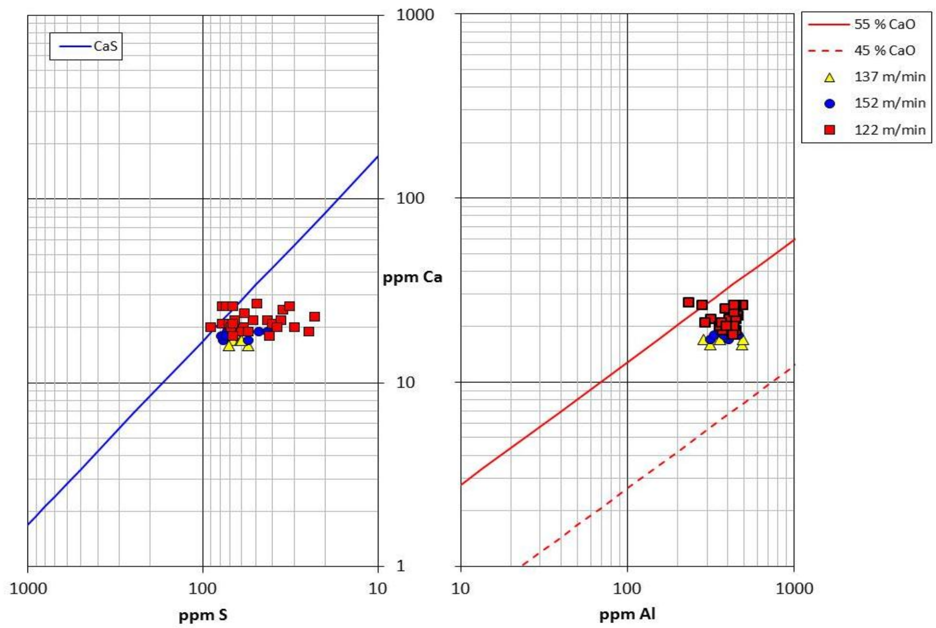

Figure 8

Evaluation of state inclusionary

Metallographic preparation and analysis by scanning electron microscopy

Steel samples obtained after treatment with High Purity Calcium (HPCa) were sectioned and metallographically prepared [1,2] and polish condition were observed in optical microscope to locate representative inclusions. In the case of High Purity Compacted CaSi 30/70 (HPCaSi) samples were obtained at the ladle furnace before and after the HPCaSi treatment as well as at the caster in three heats named A, B and C, which were treated at optimum Ca recovery injection parameters (7.4 kg Ca at 122 m/min) to characterize their inclusions. Table 5 showns the chemical composition and Ca ppm recovered of these heats.

HEAT	TLS				Chemical Composition after					% Recov LF
		primary (m)	primary kg Ca	real (m/min)	%C	%Si	% S	% Al	% Ca	LF
A	152	107	7.4	122	0.12	0.184	0.0066	0.045	0.0022	45.4
B	152	107	7.4	122	0.17	0.180	0.0068	0.037	0.0014	28.9
C	152	107	7.4	122	0.17	0.179	0.0073	0.039	0.0020	41.3

Table 5

Quantification of number of inclusions and area fraction was performed with an Image analyzer coupled to an optical microscope brand Olympus Vanox Mod. AHMT3. These estimates were made on polished surface. 50 fields were evaluated at 200 X. Figure 9 shows the scheme of preparation of samples. The samples were observed with a Scanning electron microscope brand Philips Model XL30ESEM equipped with a microanalyzer EDX for chemical inclusions analysis using an accelerating voltage of 20 kV and a time of 30 seconds.

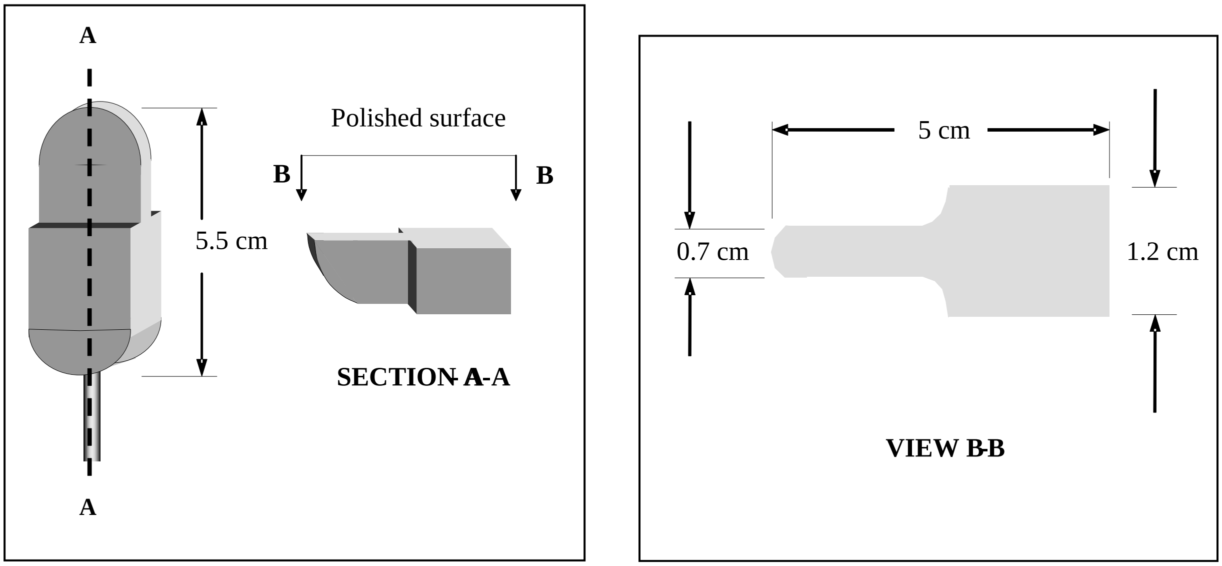

Figure 9

Results

<u>Heats treated with High Purity Calcium (HPCa)</u>

Figure 10 shows chemical composition of inclusions on ternary system Al_2O_3-CaO-MgO after treatment with High Pure Calcium at the end of refining treatment in the ladle furnace. Basically three types of particles are distinguished: a) few solid inclusions unmodified Al_2O_3-MgO type (Figure 10A) with a specific chemical composition of 70-75% Al_2O_3 and 25-30% MgO. Such inclusion is result of chemical association of alumina formed by deoxidation of steel and MgO formed by erosion of the refractory of ladle [3], b) Spinels with an incipient modification to calcium aluminate (Figure 10B), according Al_2O_3 inclusions and spinels (MgO-Al_2O_3) are enriched in CaO, decrease their melting point to become liquid at the temperature of steelmaking [4] (1590° C isothermal section, bounded area by dashed red line in ternary equilibrium diagram); and c) calcium aluminate inclusions Al_2O_3-CaO modified (Figure 10C) whose melting point is lower than the temperature steelmaking (1590 ° C) with size less than 7 microns and globular morphology. Such inclusions tend to agglomerate due to their lower surface tension favoring the formation of larger particles that facilitate their flotation to slag improving steel cleanliness.

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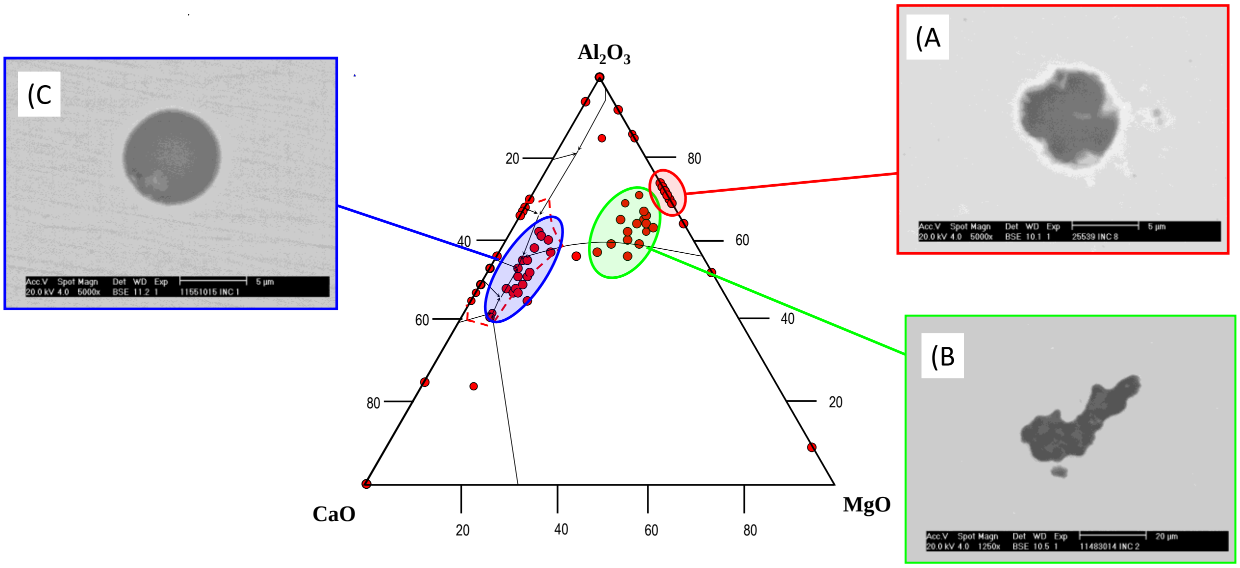

Figure 10

Figure 11 shows the chemical composition of inclusions analyzed in samples obtained in tundish of Continuous Casting for heats treated with High Pure Calcium. For these heats a large number of inclusions modified to liquid calcium aluminate (Figure 11A) are presented. Inclusions of type Al_2O_3-CaO-MgO (Figure 11B) who presented an incipient modification at the end of treatment in the ladle furnace, have reached thermodynamic equilibrium metal-inclusion so have migrated to liquid area in the ternary diagram enriching the population of these inclusions and subsequently they will float through to the slag improving cleanliness steel. This behavior is result of an efficient treatment of inclusion modification with High Pure Calcium.

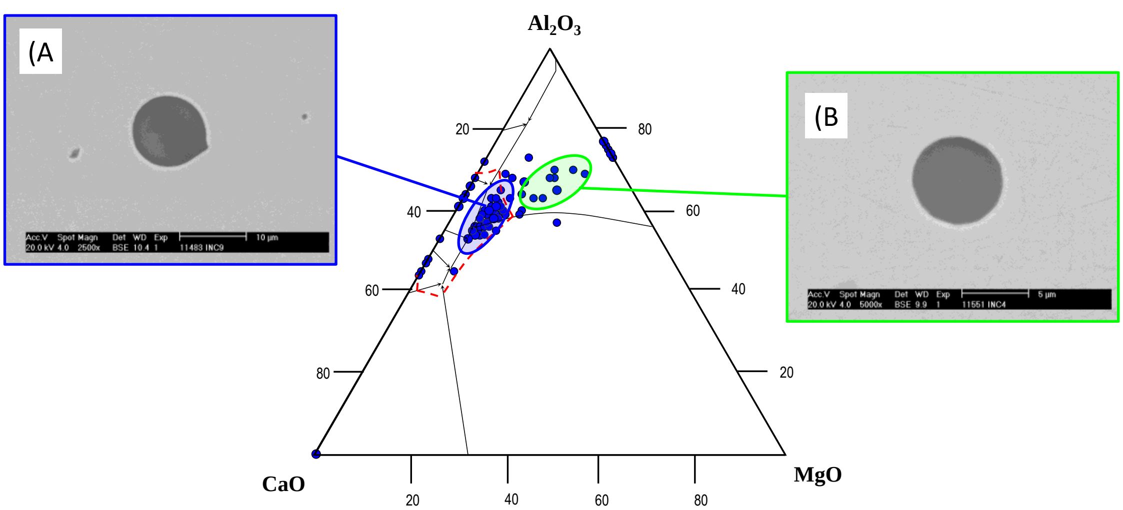

Figure 11

Heats treated with AlCaFe CCW

To compare the level of cleanliness steel obtained in heats treated with High Pure Calcium, same study was performed in heats treated with AlCaFe CCW. Some samples of heats treated with AlCaFe were obtained before injection, after injection of wire and in tundish of continuous casting. All these samples were obtained similarly to the samples obtained of heats treated with High Pure Calcium. Figure 12 shows the chemical composition of inclusions analized in samples obtained before treatment with AlCaFe. Generally these inclusions are spinels (Al_2O_3-MgO) with Al_2O_3 content between 70-75% and MgO content from 25 to 30%. Figure 13 shows the result of AlCaFe CCW injection where a null modifying to calcium aluminate inclusions was observed. At this stage of process inclusions should show an incipient modification with Calcium, however, in the case of these heats treated with AlCaFe this behavior was not observed.

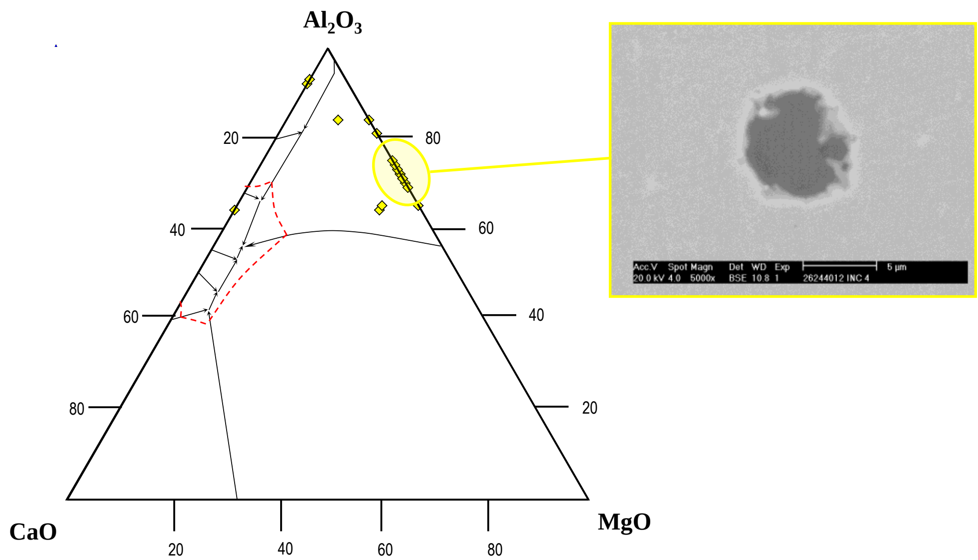

Figure 12

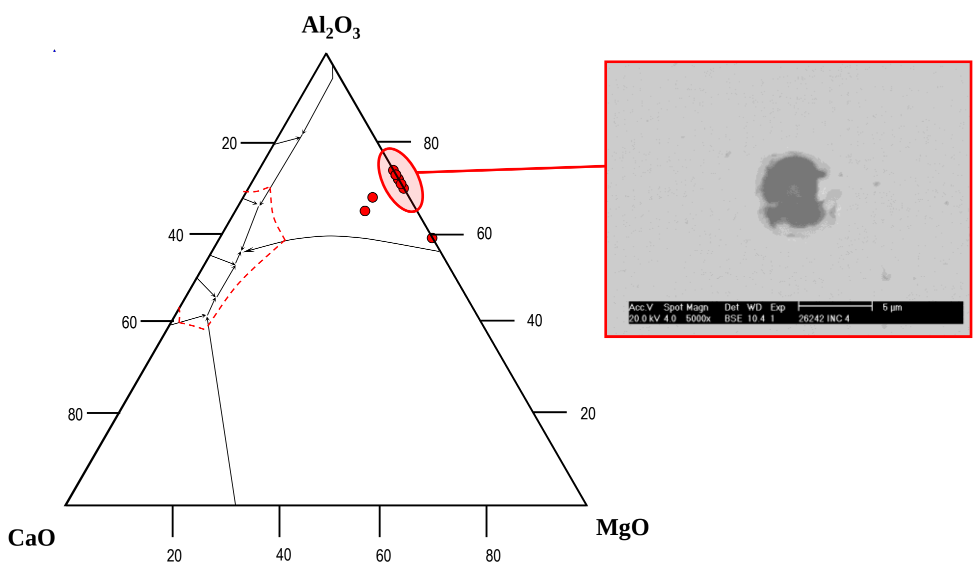

Figure 13

Chemical composition of inclusions analyzed in samples obtained in tundish is presented in Figure 14. Although in the samples obtained after AlCaFe injection at the end of treatment in ladle furnace were found only unmodified inclusions (Al_2O_3-MgO), generally calcium aluminate inclusions with variable MgO contents were analyzed in samples obtained in tundish (Figure 14A). This inclusions modification is result of equilibrium achieved of those inclusions with incipient modification with Calcium. This equilibrium is achieved by decreasing of temperature of steel in the continuous casting process. This decrease in temperature also promotes the enrichment of inclusions with MgO content (Figure 14B).

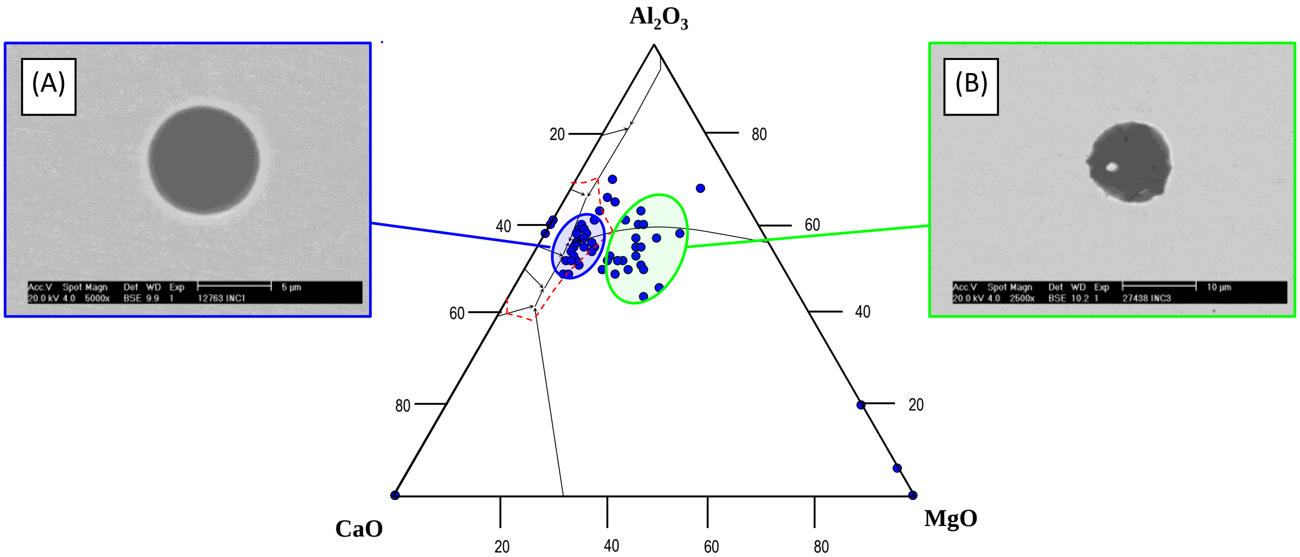

Figure 14

In general the reaction kinetics for inclusions modification with AlCaFe is lower than with High Pure Calcium due to the influence of Al injected into the wire. The addition of Al favored the formation of alumina-rich inclusions [5.6], thus delaying the modification process. Once consumed this Aluminum could occur modification process.

<u>Evaluation of cleanliness steel on heats treated with High Purity Calcium (HPCa) and AlCaFe CCW.</u>

The estimates made with image analyzer (Nonmetallic inclusions per square millimeter, NMI/mm^2 and area fraction x 10^3) on steel samples obtained from the tundish for heats treated with High Pure Calcium and AlCaFe CCW was plotted in Figure 15. This figure shows that heats treated with High Pure Calcium presented lower values of number of inclusions per mm^2 (1.1 - 1.5 NMI/mm^2) resulting in cleaner steel in this stage (mold). In case of heats treated AlCaFe this result was greater than 2 NMI/mm^2. This improvement of cleanliness steel was achieved by early inclusion modification after injection of High pure Calcium. When this wire is injected alumina inclusions quickly reached equilibrium, so they have enough time to float to slag. Figure 16 shows values obtained of area fraction analized.

Again heats treated with High Pure Calcium showed lower values of this parameter (less than 0.01 x 10^3) showing a better cleanliness for such heats. In the case of heats treated AlCaFe, this result was between 0.015 and 0.020 x 10^3.

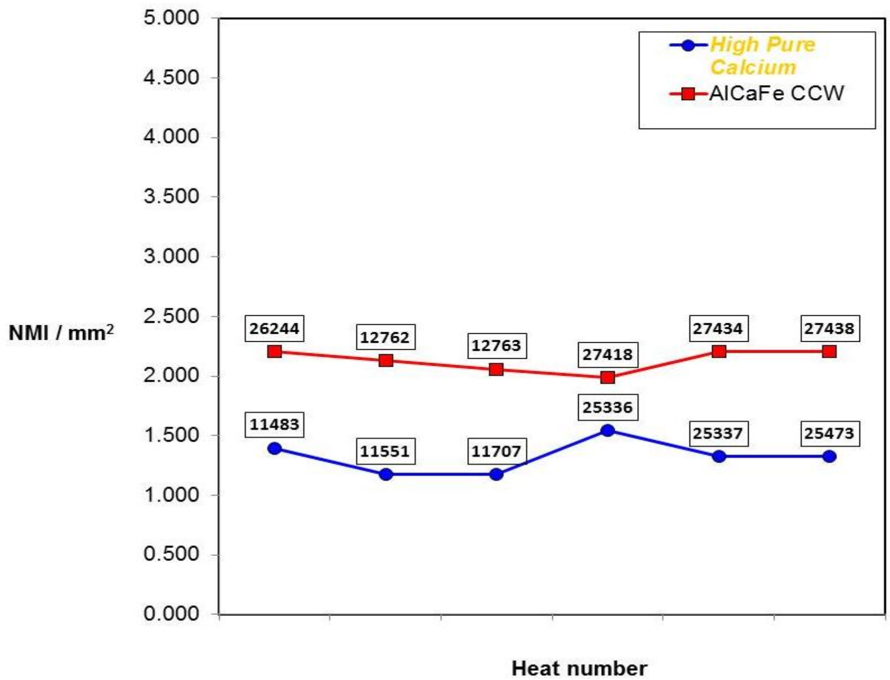

Figure 15

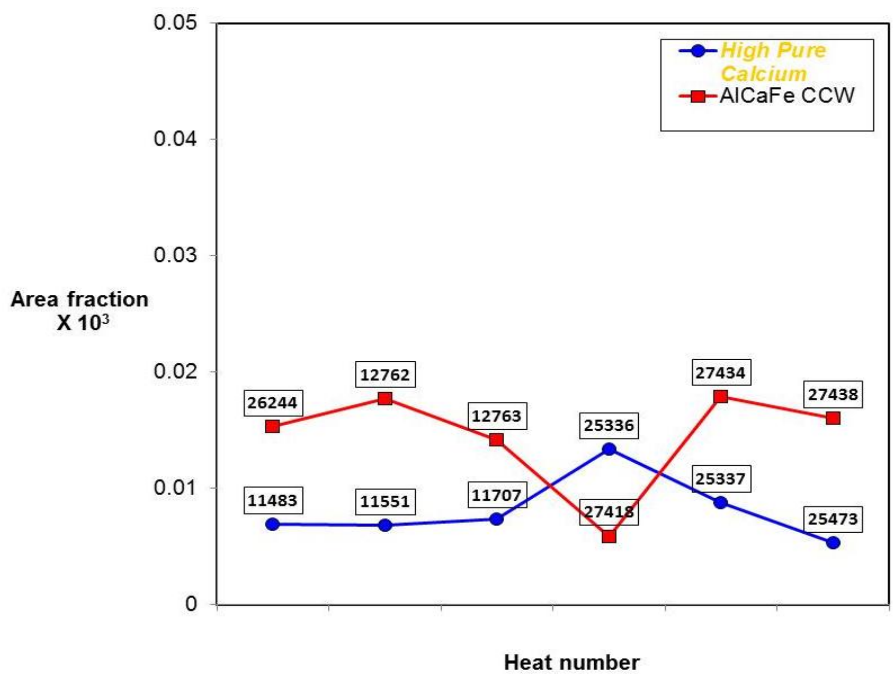

Figure 16

Heats treated with High Purity Compacted CaSi 30/70 (HPCaSi)

The chemistry of the analyzed inclusions in these optimally processed heats is presented in the ternary systems Al_2O_3 – SiO_2 – MnO (before treatment) in Figures 17 and Al_2O_3 - CaO – MgO after treatment in ladle Furnace in Figure 18. Before the Ca treatment the inclusions were mostly manganese-silico-aluminates with variable contents of alumina (40-100 % wt Al_2O_3). The morphology of such particles was mainly globular and their size was greater than 20 µm. As these inclusions become richer in SiO_2 and MnO, their melting points decrease becoming liquid at a temperature of 1600 °C (see Figure 17). These particles coalesce and form bigger inclusions enabling their flotation towards the slag. Those inclusions rich in Al_2O_3 which remain until CaSi injection are modified to liquid calcium aluminates.

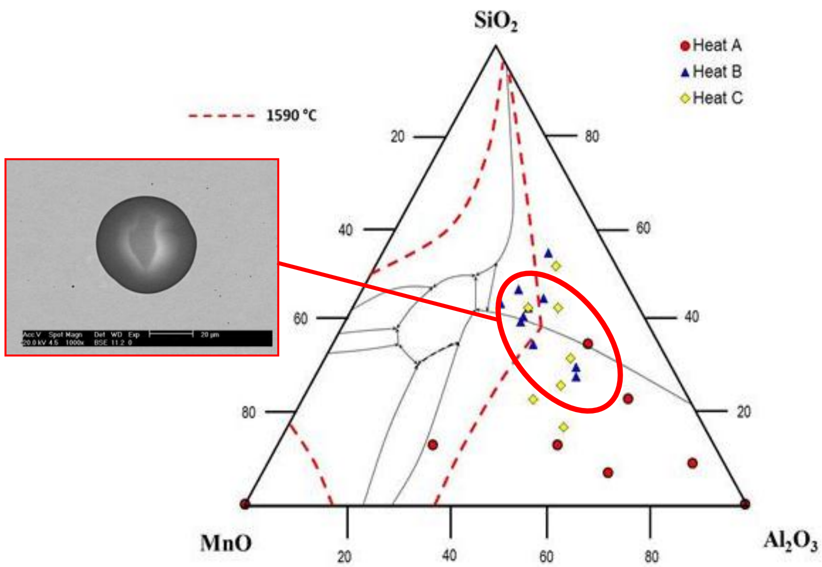

Figure 17

The chemical composition of the inclusions analyzed after Ca treatment with HPCaSi in ladle furnace is presented in the ternary system Al_2O_3 - CaO – MgO in Figure 18. The inclusions of these heats were mostly Al_2O_3-CaO (45-55 %wt) whose melting point is lower than steel making temperature (1590 °C). These inclusions were globular morphology and were bigger than 10 µm. It can be observed in this diagram, the inclusions were fully modified with an injection velocity of 122 m/min. At this velocity, the HPCaSi was released deep enough in the steel to overcome the ferrostatic pressure and reach deeper toward the ladle furnace bottom, such that it has more time to react in the steel before reaching the surface . This type of inclusion with lower surface tension, floats towards the slag improving the steel cleanliness.

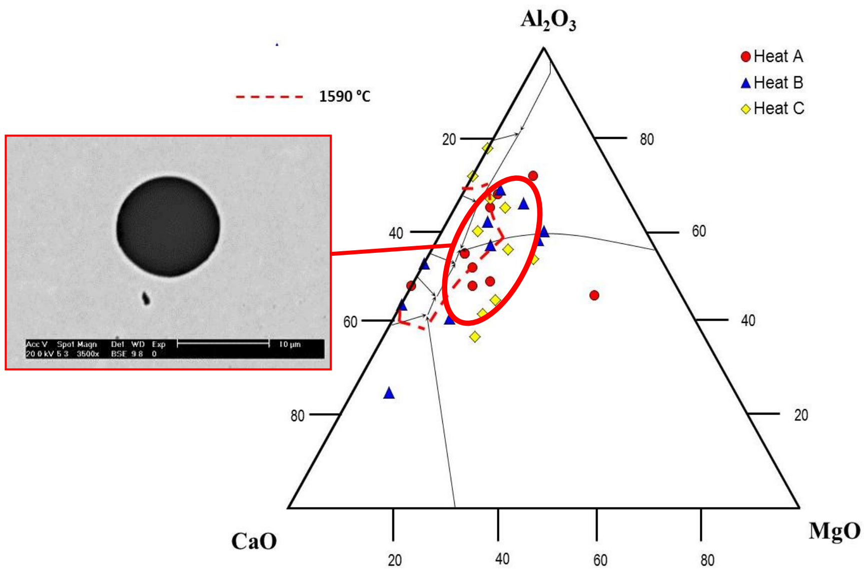

Figure 18

Heats treated with CaSi CCW 30/60

Figure 19 shows the inclusion chemical composition of two heats before Ca treatment with conventional cored CaSi CCW in the ladle furnace and similarly analyzed to compare their inclusion chemical composition and morphology. In figure 20 the composition of these inclusions analyzed is presented in the ternary system Al_2O_3 - CaO – MgO. The inclusions of these heats were mostly Al_2O_3-MgO (20-50 %wt) whose melting point is much higher than steelmaking temperature (1590 °C). These inclusions were irregular morphology. We can see that after the injection of CCW CaSi 30/60 the inclusions were only semi-modified toward the liquid calcium aluminate area of the ternary.

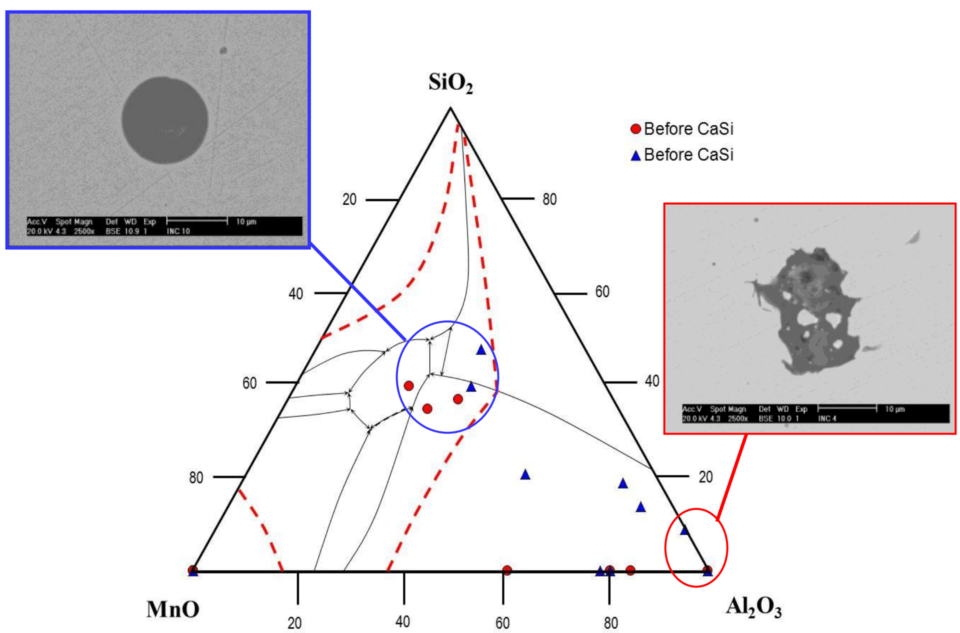

Figure 19

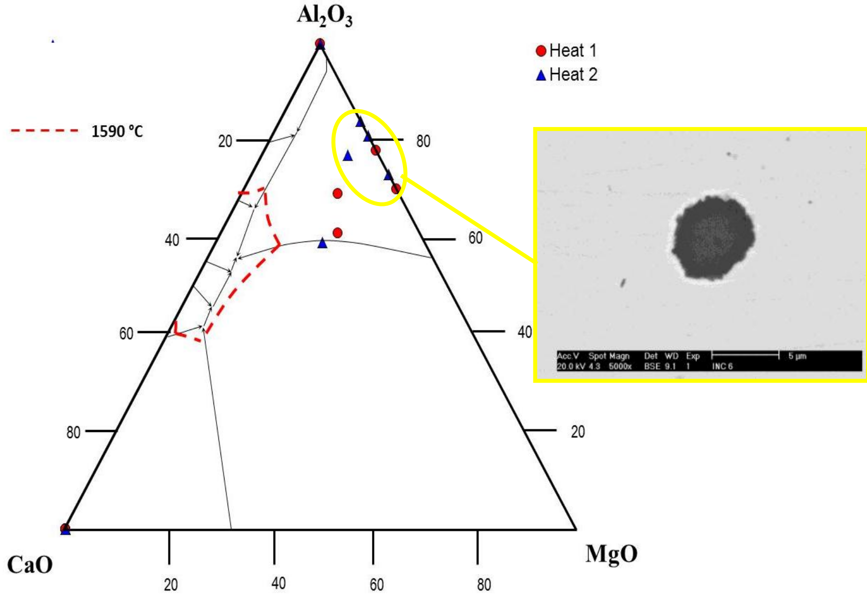

Figure 20

<u>Evaluation of cleanliness steel treated with HPCaSi by SEV method</u>

Samples obtained at the caster of treated heats with HPCaSi and CaSi CCW were evaluated. The level of steel cleanliness was expressed in terms of maximum inclusion size. This level of cleanliness was evaluated by the statistics of extreme values method (SEV) developed by Murakami et al [7]. In Figure 21 are plotted in ascending order in the horizontal axis the probability function [-Ln (-Ln (H))]) and on the vertical axis is plotted square root of the inclusion area measurement (*v*) Shi et al [8] used this method to compare different levels of cleanliness of steel by the slope of the linear relationship between the probability function [-Ln (-Ln (H))]) and the square root of the area of inclusion (inclusion size). In this paper we used this tool to discriminate between treated heats with HCP CaSi 30/70 and treated heats with CCW CaSi 30/60. The slope a in the case of heats treated with HCP CaSi 30/70 is smaller than those heats treated with CCW CaSi. A smaller slope will give a smaller calculated size of the "maximum inclusion in the same volume of steel"

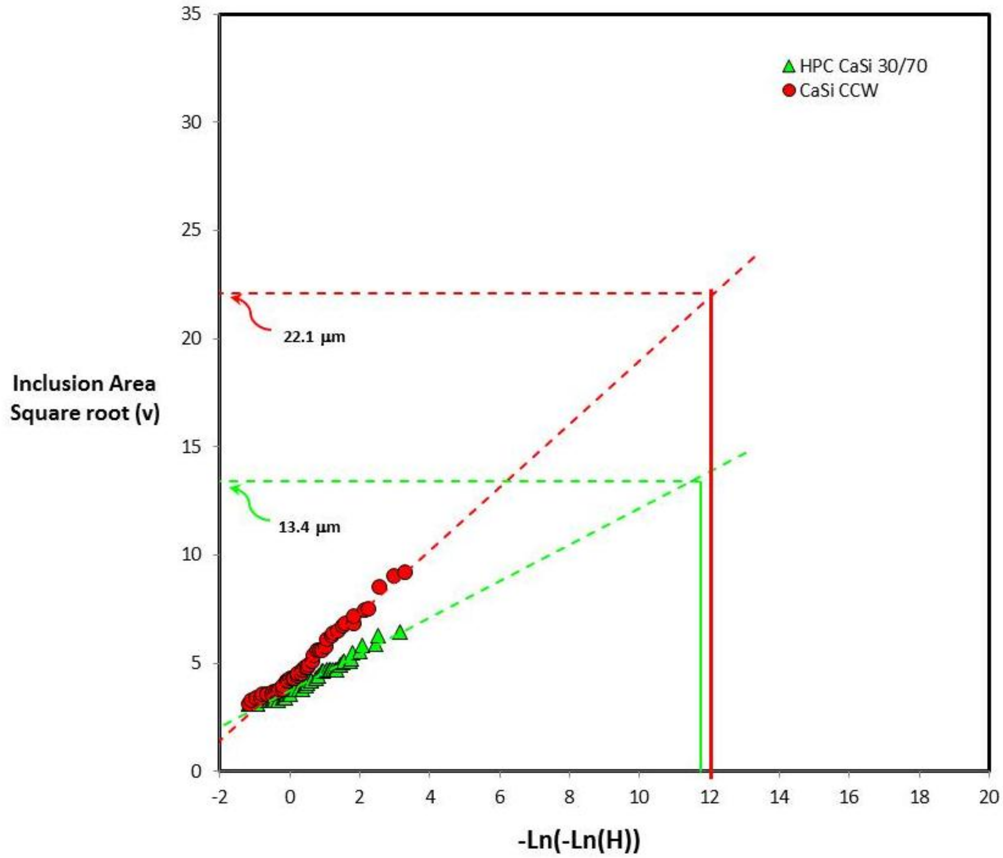
HPC CaSi 30/70
CaSi CCW
22.1 μm
13.4 μm
Inclusion Area
Square root (v)
-Ln(-Ln(H))
35
30
25
20
15
10
5
0
-2
0
2
4
6
8
10
12
14
16
18
20

Figure 21

Conclusions

Calcium treatment with High Purity Calcium (HPCa)

<u>Injection parameters and efficiency.</u>

From the results of tests performed with High Pure Calcium at plant, we conclude the following:

1. Best average efficiency in the treatment of steel with High Pure Calcium was obtained (32.6%) compared with AlCaFe (24-25%). Average consumption for this efficiency was 0.065 kg Ca/ton.
2. Injection speed was determined between 140 and 160 meter per minute to obtain the best results and significantly reduce the splashing.
3. The best efficiency (34.86%) was obtained injecting 100 meters of High Pure Calcium, recovering an average content of 20 ppm's of Calcium, similar value to those obtained with greater amounts.

<u>Cleanliness Steel</u>

Regarding to level of cleanliness steel achieved by treatment with High Pure Calcium we conclude the following:

1. Better inclusions modification with High Pure Calcium was obtained. This indicates better reaction kinetics caused by the injection of High Pure Calcium which favored inclusions modification early.
2. Appropriate inclusions modification is favored by suitable Al and S contents in steel before treatment with Calcium.
3. Better levels of cleanliness steel are associated with inclusions modification early (just after High Pure Calcium injection) favoring its flotation to the slag due to the longer time that they have for this phenomenon, obtaining a finished product of better quality and less rejections.
4. In general Hi-Core technology has the potential to modify inclusions correctly with lower amounts of calcium and with a consequent increase of efficiency.

Calcium treatment with High Purity Compacted CaSi 30/70 (HPCaSi)

Injection parameters and yield

From results obtained of the HPCaSi injection trials the following conclusions are presented:

1. An average yield of 33.7% was reached in the ladle with the HPC CaSi 30/70 injection treatment.
2. The average consumption to obtain such yield was 0.060 kg Ca/ton, that is, 9.2 kg Ca/heat.
3. Best yields (43.4 %) were reached in the ladle by injecting 7.4 kg Ca/heat with an average Ca of 20 ppm.

Steel Cleanliness

Regarding the steel cleanliness met with the HPC CaSi 30/70 injection treatment we can conclude the following.

1. An immediate modification of inclusions after treatment was met.
2. This successful inclusion modification is favored by the strict control in Al and S levels before Ca treatment.
3. Best inclusion levels are associated with an early modification of the inclusions (just after the HPC CaSi 30/70 injection), promoting the flotation due to the higher time available for this effect. With more flotation time a better quality finished product results. There are reduced rejects resulting from defects that are exposed during the lamination process due to the reduction of inclusions.
4. Inclusion levels via S.E.V. analysis are reduced with HPCaSi when compared to CaSi 30/60 CCW. Particularly for the long products SBQ makers, bearing steel producers and specialty steel producers this improvement will yield higher quality end products in your customer’s operations.

References

1. L. Hollappa, M. Hamalainen, M. Liukkonen and M. Lind: Ironmaking and Steelmaking, 2003, **30** 111-115.
2. M. Herrera, M. Castro, H. Solis and E. Guzman: *Scand. J. Metall.*, 1998, **27**, 233-239.
3. F. Castro, M. Herrera, M. Castro, H. Solis, M. Barbaro and A. Castella: Proc. 14th IAS Steelmaking Conf. , Argentina, 2003, 663-672.
4. K. Larssen and R.J. Fruehan: Calcium Modification of Oxide Inclusions," Iron and Steelmaker, 17(7) (1990), 45-52.
5. H. Tozawa, Y. Kato, K. Sorimachi and T. Nakanishi: ISIJ Int. 1999, **39**, 426-434.
6. *K. Wasai, K. Mukai and A. Miyanga: ISIJ Int. 2002, 42,459-466.*
7. Comparison of extreme value statistics methods for predicting maximum inclusion size in clean steels. G Shi, H.V. Atkinson, C.M. Sellars, C.W. Anderson Ironmaking and Steelmaking 1999 Vol 26 No. 4, 239 - 246.
8. Maximum inclusion size in two clean steels Part 1: Comparison of maximum size estimates by SEV and GPD methods. G Shi, H.V. Atkinson, C.M. Sellars, C.W. Anderson Ironmaking and Steelmaking 2000 Vol 27 No. 5, 355 - 360.