Injection Alloys México S.A. de C.V.

Evaluation of inclusions cleanliness of steels treated with Hi-CaSi at AHMSA (Altos Hornos de Mexico. S.A.B.)

August 2013

GOALS

- **Evaluation of steel inclusions cleanliness treated with CaSi wire produced with Hi-Core technology called Hi-CaSi with a content of 30% pure Ca and 70% pure Si powder mix, and 190 gr/mt powder filling rate**

- **Correlate level of steel cleanliness in terms of number, type and size of inclusions v.s Efficiency obtained during Calcium treatment made with this new Hi-CaSi wire technology.**

- **Evaluation of the impact of Aluminum and Sulfur content before Calcium treatment over the inclusions modification.**

DEVELOPMENT

- **6 steel samples were obtained from 6 different heats after Calcium treatment with Hi-*CaSi*® at the Ladle Furnace #2 station.**
- **500 ft/min was the speed used for all the 6 heats as well as different lenghts of Hi-CaSi wire accroding to the steel grade, to evaluate the impact of the Calcium recovery over the steel cleanliness in termns of number, type of size of non metallic inclusions by the technology of SEM (Scan electronic microscopy)**
- **2 samples were obtained for every steel grade (one with high Ca ppm recovery and one with low Ca ppm recovery).**
- **The next table show us the process conditions of every heat (steel Chemistry, length and Kg of injected wire, Ca ppm recovery and %Yield during Calcium treatment.**

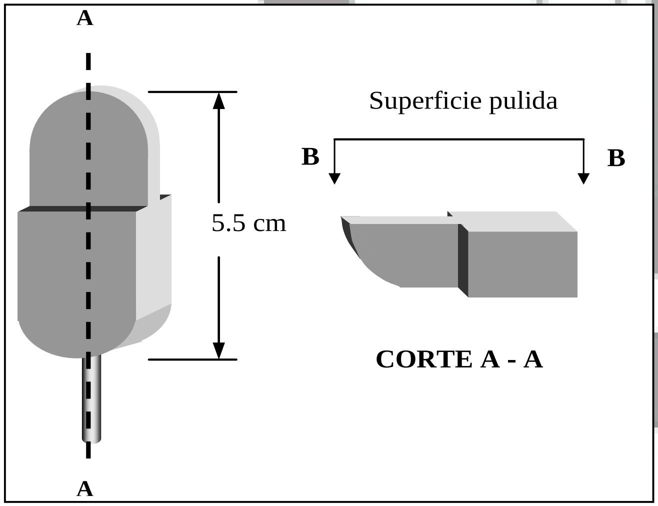
Datos de la colada			Comp. Quim. Acero antes de Hi-CaSi		Parametros y consumos					Comp. Quim. Acero despues de Hi-CaSi			
DATE	Colada	Familia de acero	% S	% Al	Longitud inyectada (ft)	kg Hi-CaSi / colada	kg Ca / colada	kg Ca/ton	Velocidad de inyección(ft/min)	% S	% Al	% Ca	Rend. % LF Final
08/07/2013	135458	10 a 20	0.0065	0.0356	450	26.1	7.8	0.051	500	0.0037	0.0302	0.0026	50.5
10/07/2013	235553	10 a 20	0.0090	0.0323	450	26.1	7.8	0.051	500	0.0055	0.0423	0.0018	35.0
10/07/2013	135552	20 a 40	0.0101	0.0307	850	49.2	14.8	0.097	500	0.0045	0.0392	0.0032	32.9
08/07/2013	135487	20 a 40	0.0060	0.0344	900	52.1	15.6	0.103	500	0.0041	0.0408	0.0028	26.6
09/07/2013	235516	gas amargo	0.0058	0.0354	900	52.1	15.6	0.103	500	0.0035	0.0409	0.0036	35.0
09/07/2013	135502	gas amargo	0.0035	0.0378	900	52.1	15.6	0.103	500	0.0023	0.0401	0.0022	21.4

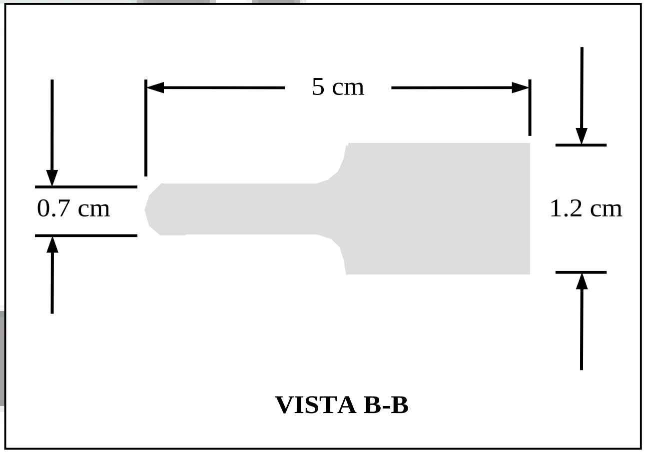
DEVELOPMENT

- These 6 samples were selected and metallographic prepared in the laboratory. Then they were observed in a optical microscopy to locate representative inclusions.

- Figure 1 presents the drawings for size and polished face of the samples to analyze

- Then samples were analyzed in a electronic microscopy PHILIPS model XL30ESEM equipped with a micro analyzer EDX for the chemical analysis of the inclusions using a acceleration voltage of 20 kV and 30 seconds of alive analysis
- COUNTING of number and fraction in area of inclusions was made with an image analyzer coupled to the optical microscopy OLYMPUS VANOX Model AHMT3. This estimations were made over the polished surface and 50 fields were evaluated at 200X





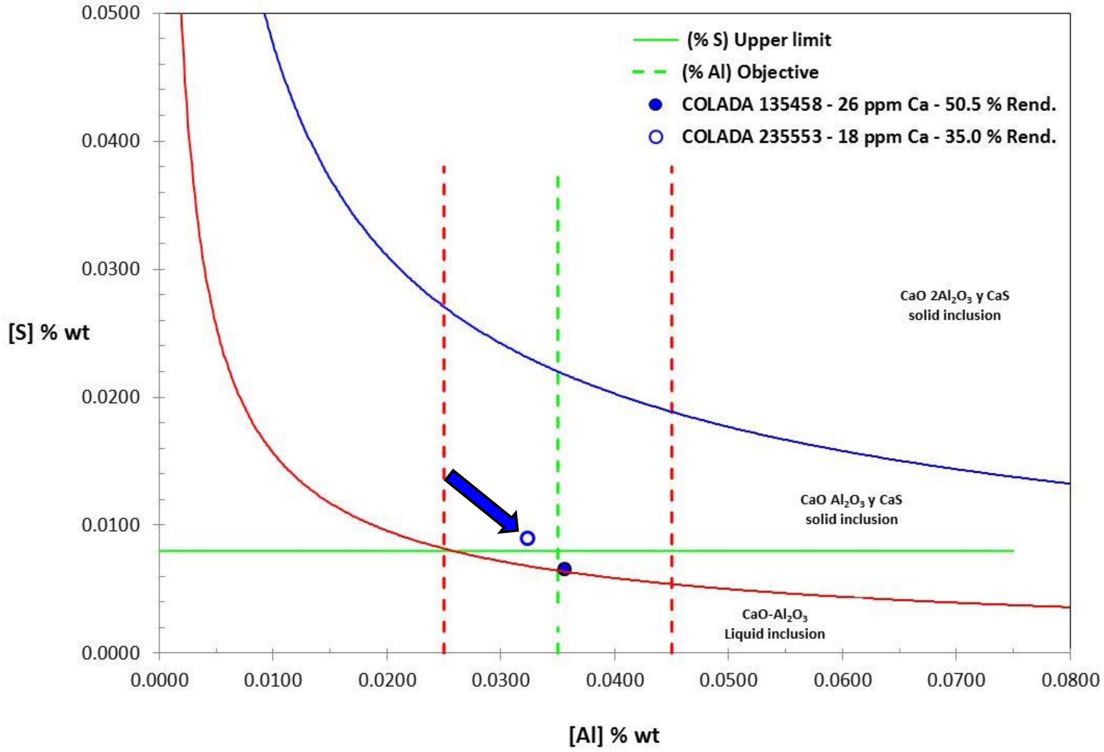
RESULTS

STEEL GRADES WITH 10 to 20 ppm Ca

RESULTS

Steel Grades with 10 a 20 ppm Ca

Content of Al y S in steel before Caclium injection

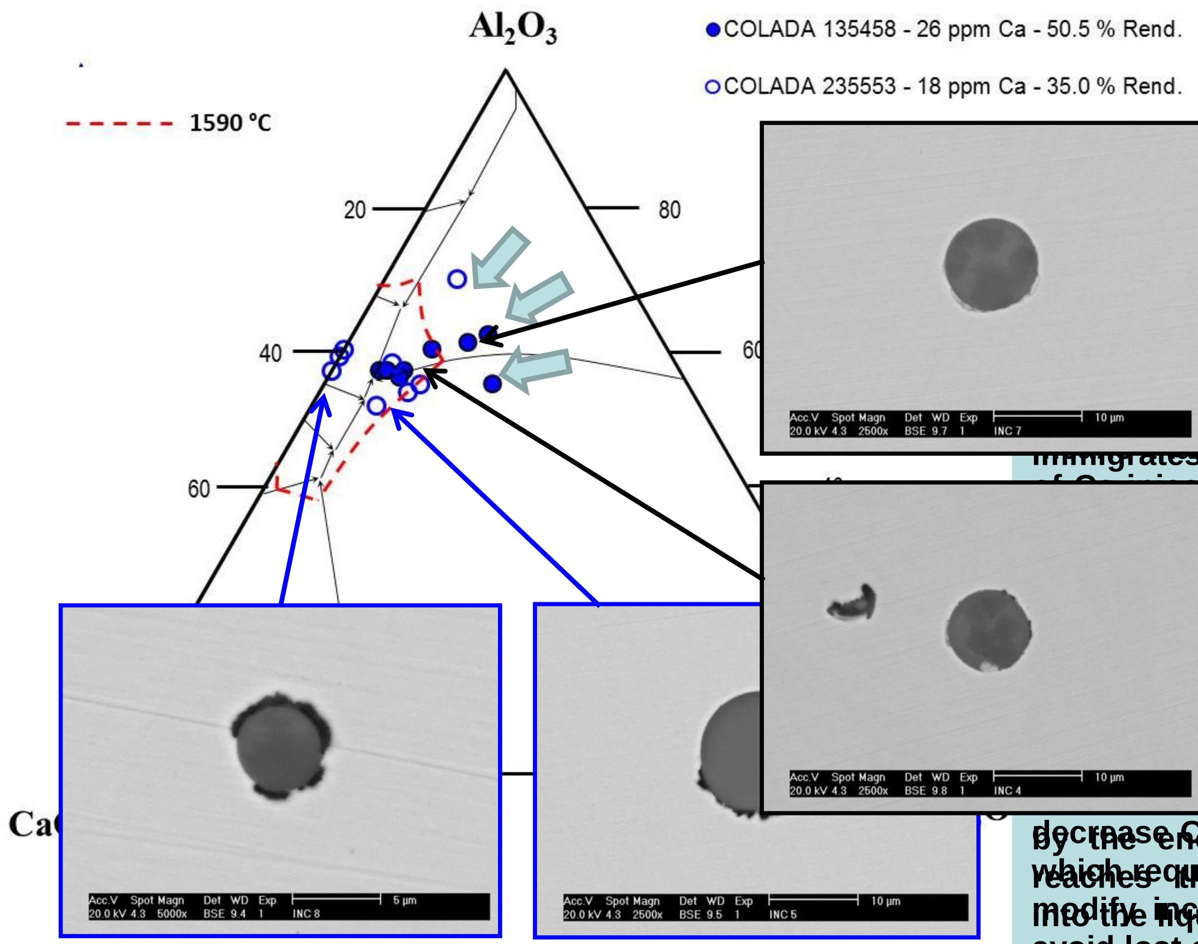


In this group of steel grades, both heats had content of Al and S favorable for CaS inclusions formation, nevertheless, only heat 235553 was affected with low yield (35%), due to sulfur content was higher than the upper limit specification of 0.008 weigh %

RESULTS

Grades (10 to 20 ppm Ca)

Grade of inclusions modification after Hi-CaSi injection



...t must be stand out for ... micrographs of typical ...minates analyzed are ...h are found in liquid ... 1590 °C globular ...nd 10 µm size

...ection of (50 ppm). heats immigrates to the liquid calcium ...(CA) region (red doted ...represents steelmaking ...e of 1590 °C. Previous ...stage shows an early ...modification to liquid ...minates promoted by ...ve reaction of Ca and Al_2O_3-MgO present into ... This reaction is favored by the enough penetration that reaches the cored Hi-CaSi wire into the liquid steel bath.

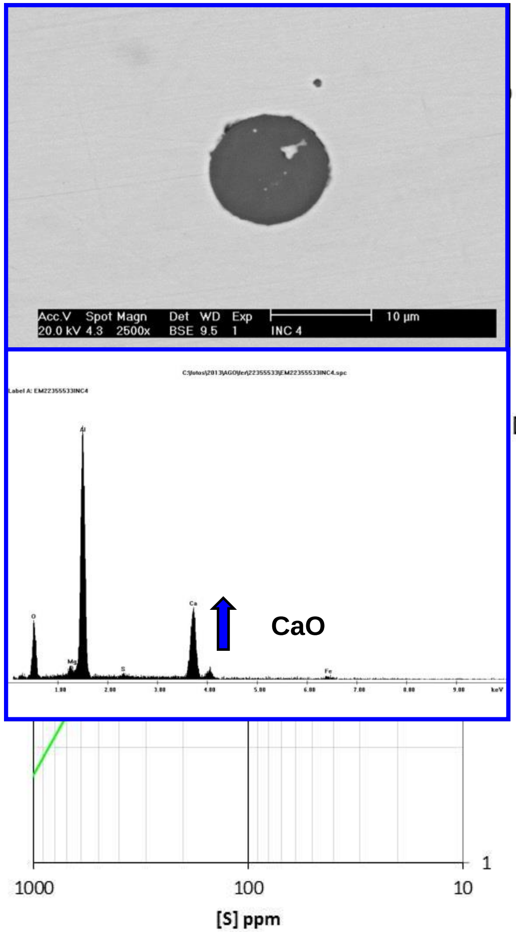
... with the same amount of Ca injected in both heats (51 gr ...he % Ca must react with ...of S desulfurazing the ...forming CaS. Even so ...Calcium was enough to ...*lumina and spinel* ...ins the hypothesis of decrease Ca in this group of steels which requires less than 20ppm to modify inclusions adequately and avoid lost of yield of Calcium wire

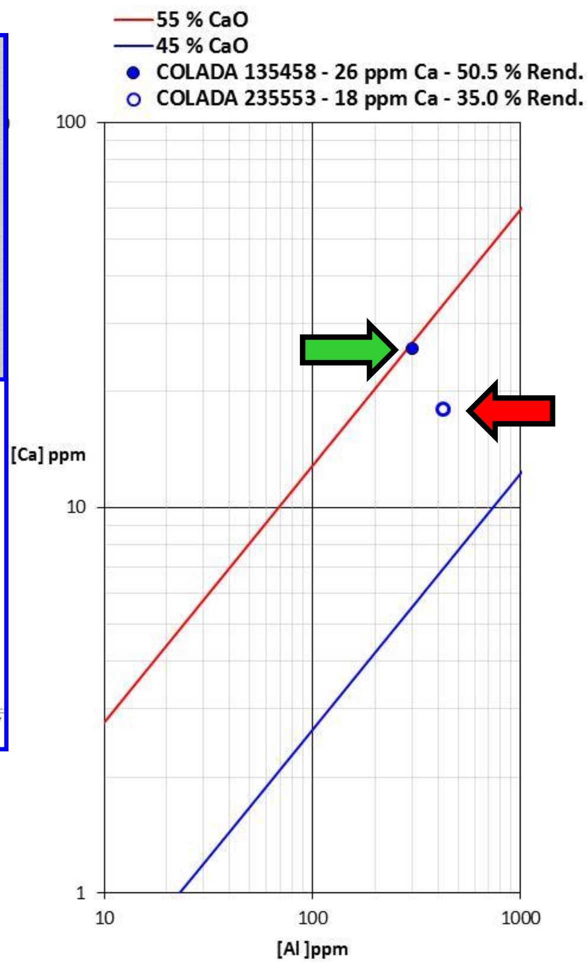
Sistema Ternario Al_2O_3 – CaO - MgO

RESULTS

Grades 10 a 20 ppm Ca

Contents of Al, S and Ca in steel after Hi-*CaSi*® injection





In the left side of figure (explained before) … This was due to Ca injected worked as desulfurizing agent, because sulfur content decreases from 90 to 55 ppm after Ca injection and still was near to the CaS formation line. This Calcium sulphides were trapped in the interface metal-slag by the effect of Argon stirring decreasing the Ca available in the steel to modify the inclusions. Nevertheless, it must be waited that traces of this desulfurizing process (CaS) some left in the steel and precipices over the surface of calcium aluminates inclusions recently modified.

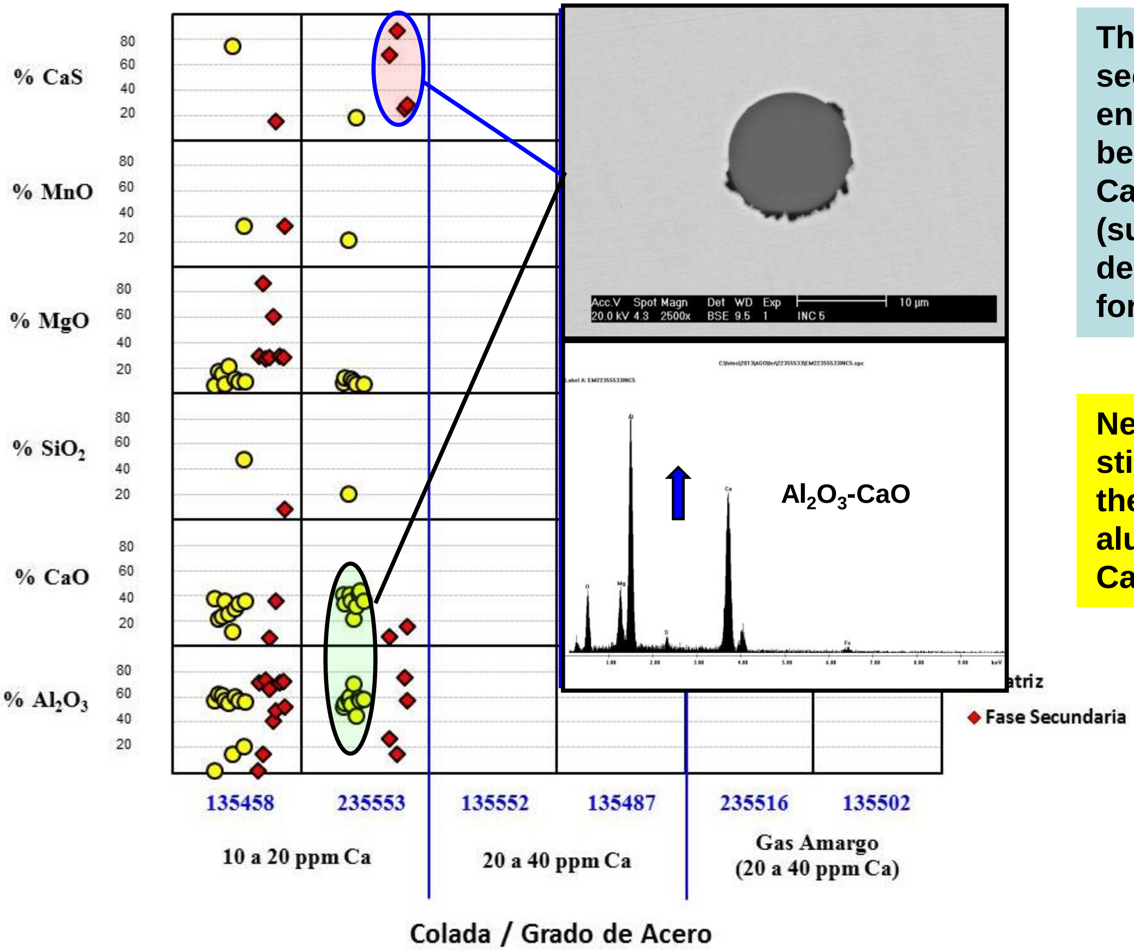
In the other hand, heat 235553 that had a recovery of 18 ppm Ca and 35% yield, with same Ca consumption (.051 kg Ca/ton), inclusions did not reach the saturation limit of 55% CaO (average 45-50%)

… high Ca recovery (26 ppm) and yield (50.5%), with .051 Kg/ton it was due to teoretically inclusion were very close to saturate of CaO. When they reached the saturation limit (55%CaO) with the excess of injected Ca, this inclusion starts to increase its melting point, which become viscous and difficult to floating to the slag, therefore a big population of this type of inclusions will remain in the steel increasing ppm Ca in the steel ..

RESULTS

Grades 10 to 20 ppm Ca

Chemical composition of inclusions after Hi-CaSi injection



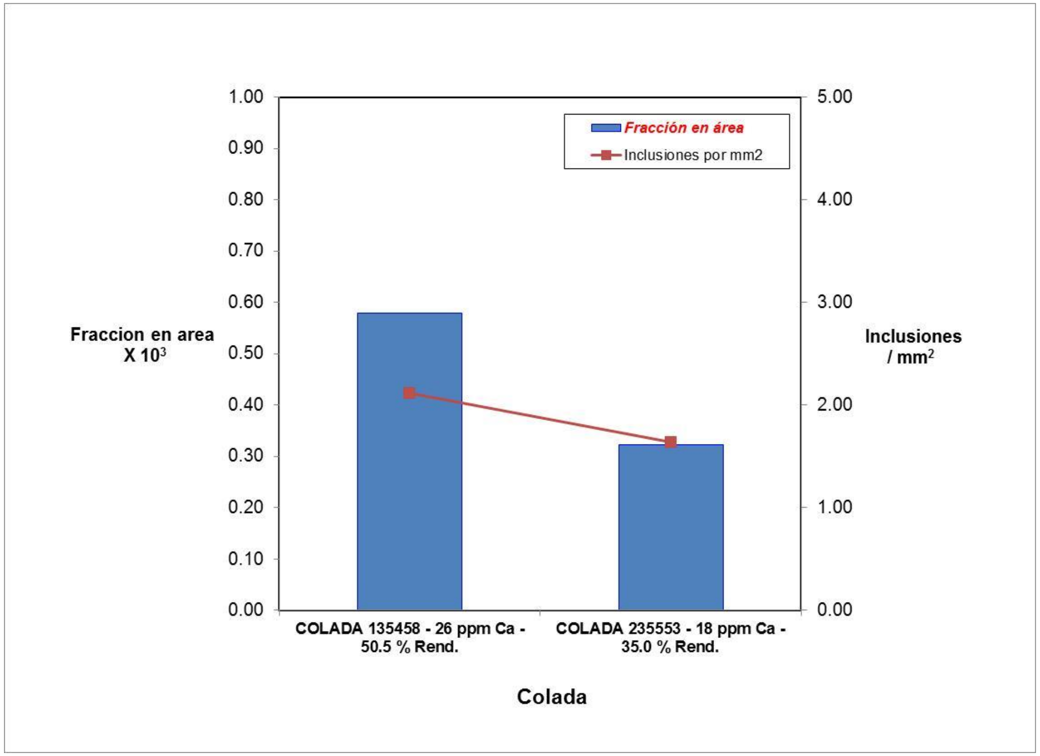
The appearance of inclusions with secondary faces rich on pure CaS encountered in heat 235553, confirms the behavior described before, where excess of Ca injected worked as desulfurizing agent (sulfur decrease from 90 to 55 ppm), decreasing at the same time Ca available for alumina inclusions modification.

Nevertheless the desulfurization of steel, still there was some Ca enough to modify the inclusions to liquid globular Calcium aluminates affecting mainly the yield of Calcium injected in the Hi-CaSi.

RESULTS

Grades 10 a 20 ppm Ca

Inclusions per mm^2 and fraction on area



The following graph show that heat 135458 with higher yield has more inclusions by mm^2 than heat 235553. Besides, the area occupied by inclusions was bigger, due to bigger inclusions. This confirms that inclusions of heat 135458 start to saturate with CaO which made them to grow up and remain them in the steel resulting in *a dirtier steel than heat 235553.*

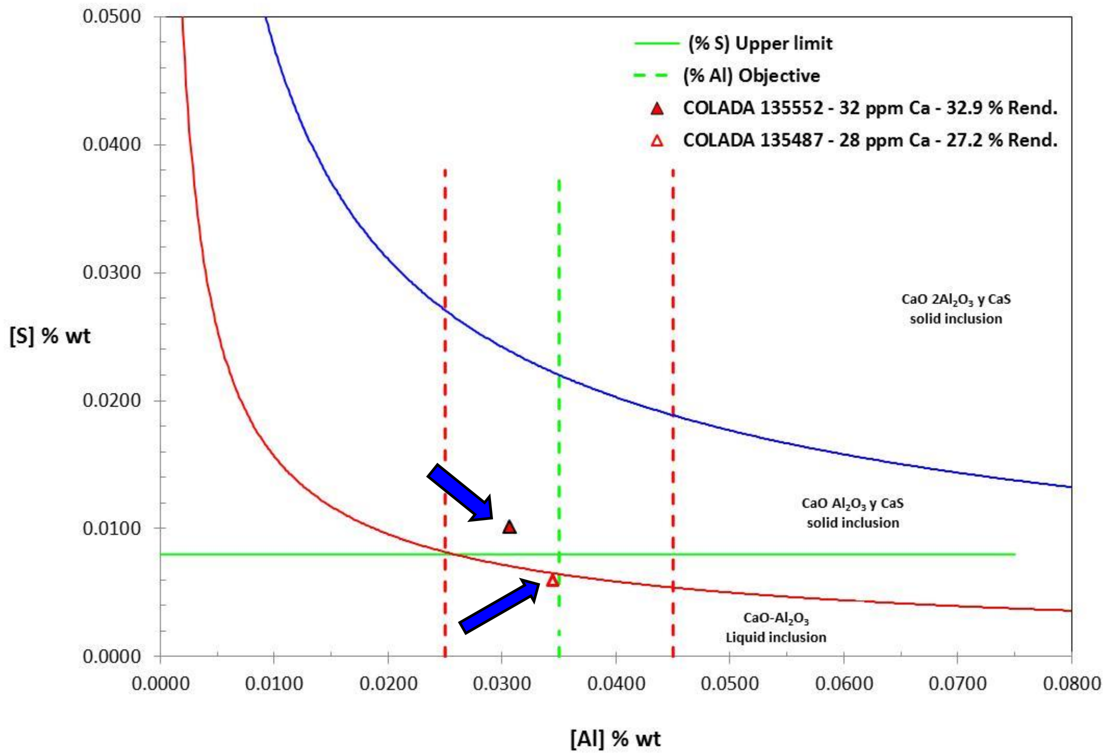
RESULTS

Steel grades 20 to 40 ppm Ca

RESULTS

Grades 20 a 40 ppm Ca

Contents of Al an S in steel before Calcium injection



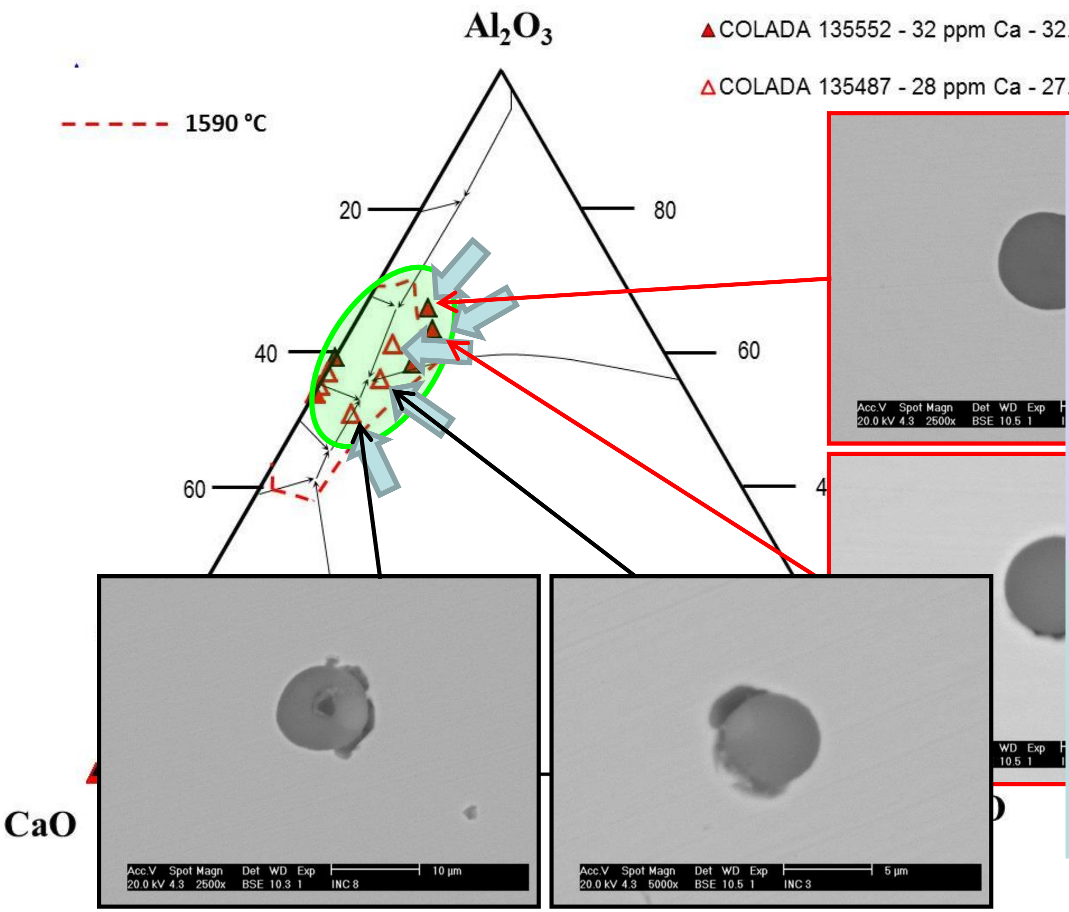
For the family of steels with 20 to 40 ppm Ca, heat 135552 was the one with higher content of S (0.0101 weight %) before Hi-CaSi injection

theoretically there were the conditions of chemical equilibrium for steel desulphurization and formation of CaS

RESULTADOS

Grados 20 a 40 ppm Ca

Grado de modificación de las Inclusiones después de la Inyección de Hi-CaSi



Sistema Ternario Al_2O_3 – CaO - MgO

Inclusions population of these two heats also showed **early modification to liquid calcium aluminates**, since they are found in the zone of 1590 ºC (delimited by red doted line).

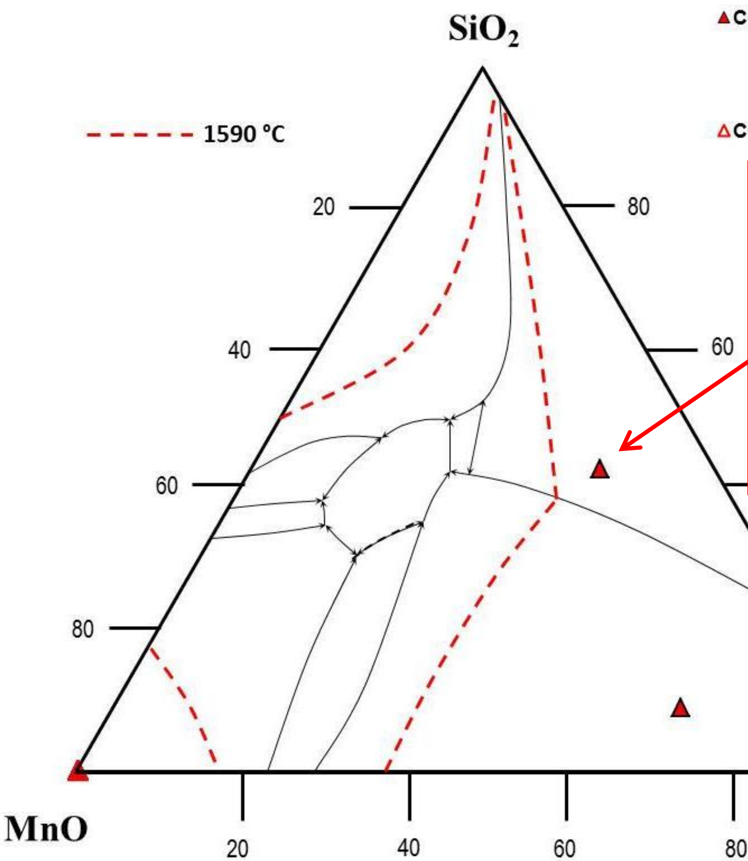
Typical calcium aluminates from both heats analyzed presented globular morphology and size below 10 µm.

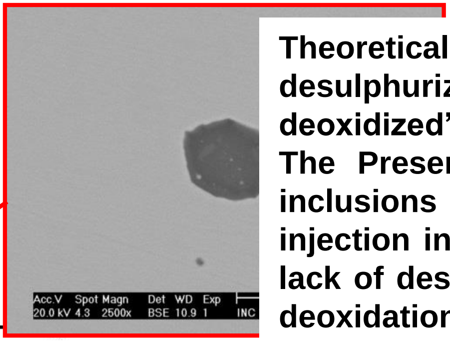
Less recovery of Calcium in this heat can be translated into a cleaner steel, due to early modification of inclusions with more time to float to the slag, decreasing its population

RESULTADOS

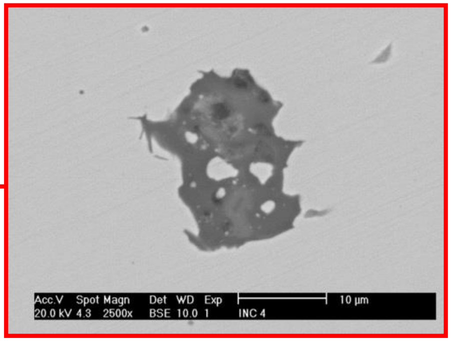
Grados 20 a 40 ppm Ca

Grado de modificación de las Inclusiones después de la Inyección de Hi-CaSi





Theoretically, "one steel not enough desulphurized its not enough deoxidized"
The Presence of silicoaluminates inclusions in the steel after Calcium injection in heat 135552 is shown in lack of desulfurization and tehrefore deoxidation

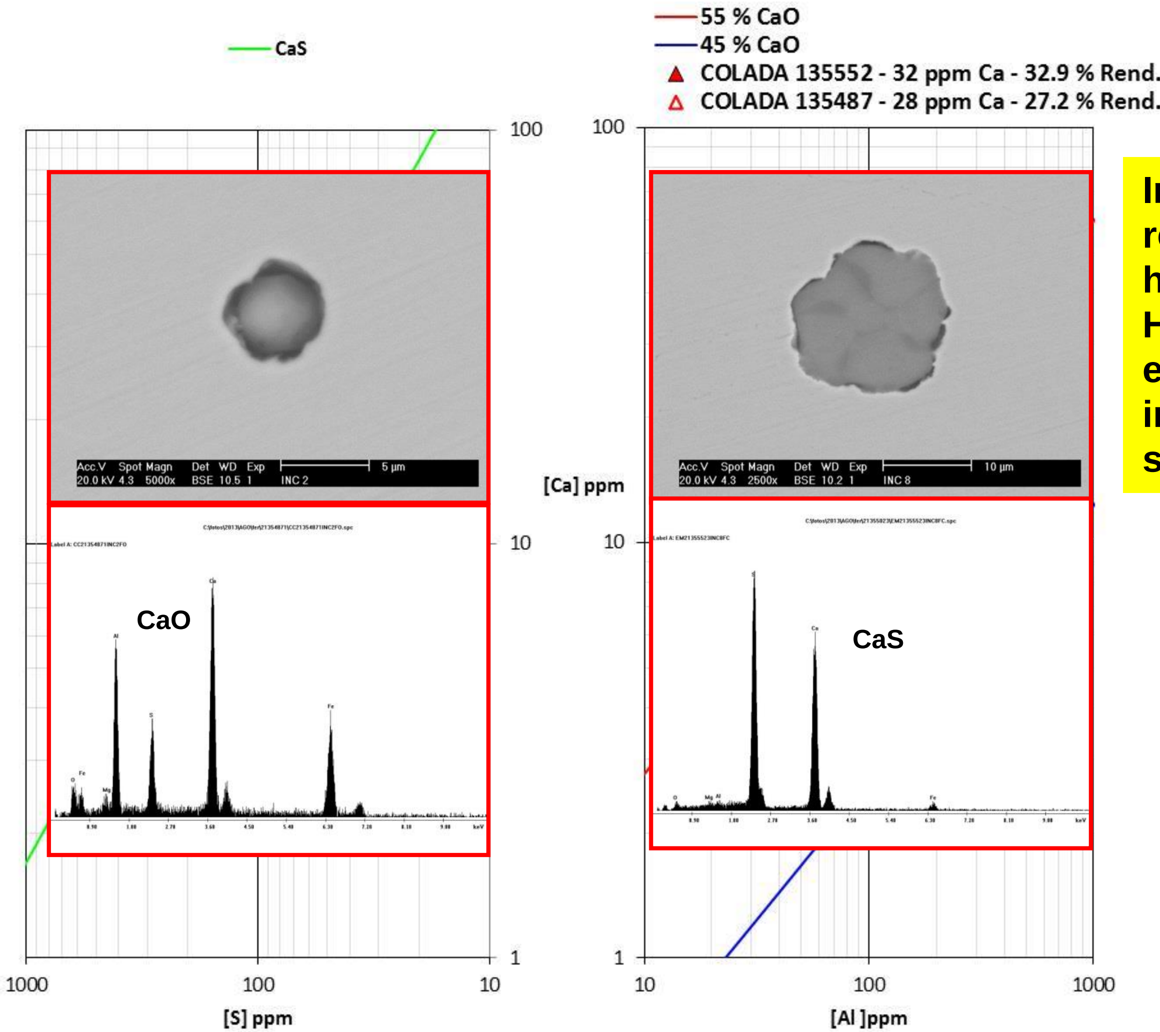


Sistema Ternario Al_2O_3 – SiO_2 - MnO

RESULTS

Grades 20 a 40 ppm Ca

Content of Al, S y Ca in steel after Hi-CaSi



In case of heat 135487, the recovery of 28 ppm Ca with higher a consumption (15.6 kg Hi-CaSi/heat) meant the enrichment of CaO in the inclusions near to the saturation limits (55% CaO)

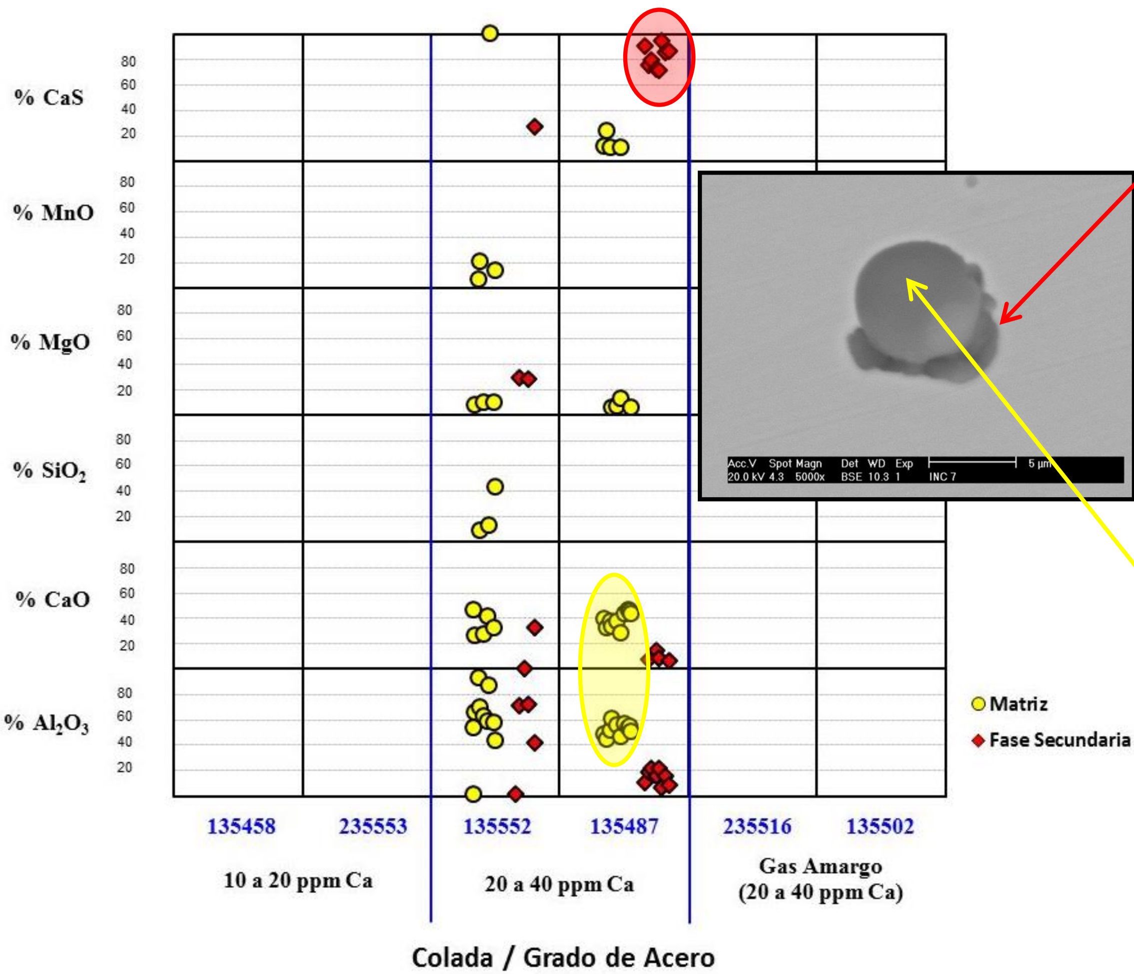
in ue nt g) m lts is found y form of sulphides, whose population must be big before trapped to the slag and much of these particles certainly precipitates over the liquid calcium aluminates preventing their flotation and decreasing the steel cleanliness.

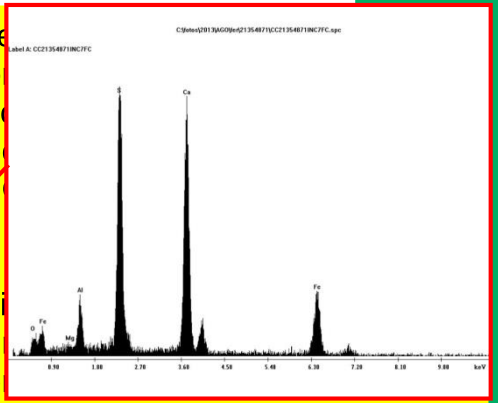
Therefore in this heat 135552 this good yield **was no translated into a cleaner steel**

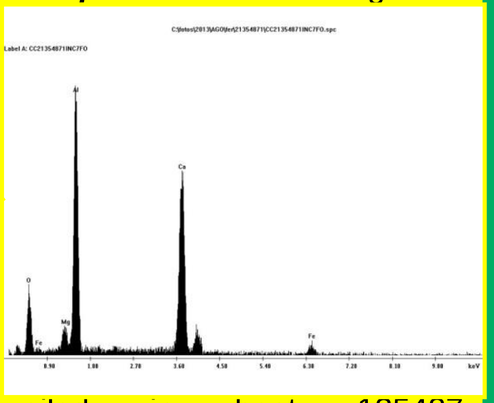
RESULTS

Grades 20 a 40 ppm Ca

Inclusions chemical composition after Hi-CaSi injection







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with values near to saturation (55%) by the excess of Calcium injected acting as ***slag in the liquid phase*** desulfurizing the
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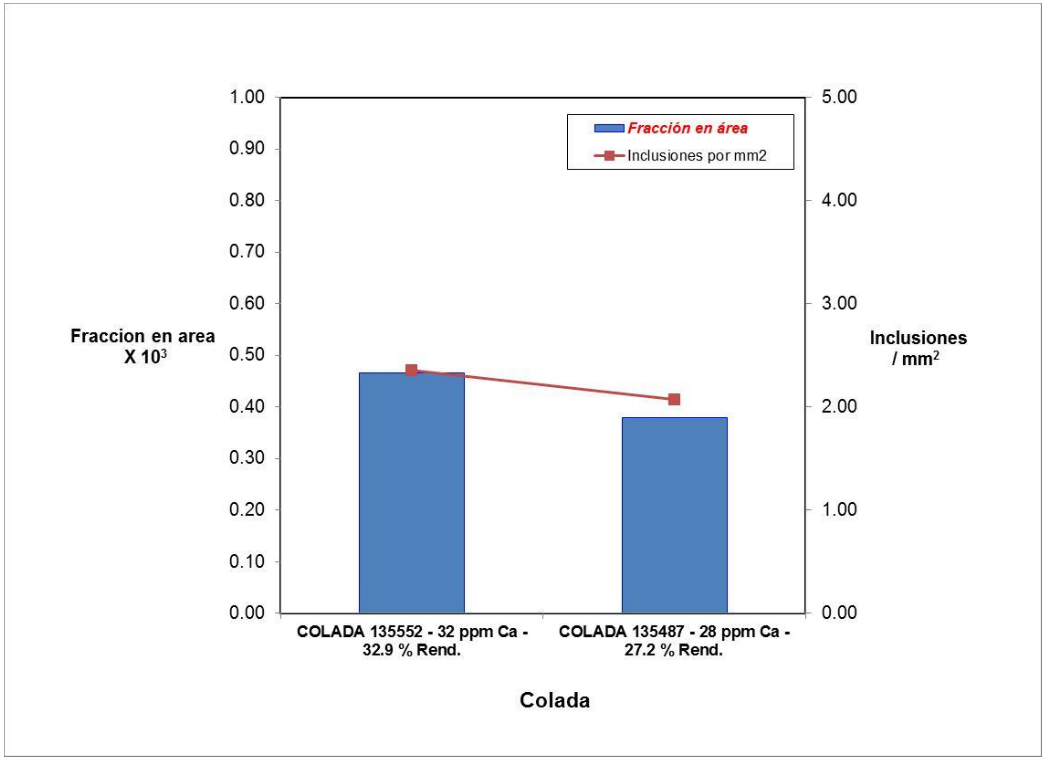
prevailed in heat 135487 demonstrating that excess of Calcium injected could desulphurize the steel, decreasing its yield.

RESULTS

Grades 20 a 40 ppm Ca

Inclusions per mm^2 and fraction on area



Steel cleanliness expressed with the number of inclusions per mm2 and the fraction per area, for the family of steels with 20 to 40 ppm Ca. Was slightly better in comparison with the family of steels with 10 to 20 ppm Ca.

Nevertheless, again with stand out a cleaner steel in the heat 135487 with less recovery, since the size of the inclusions must be lower (expressed in a lower fraction of area) and less particles per mm^2 compared with heat 135552 that had higher recovery.

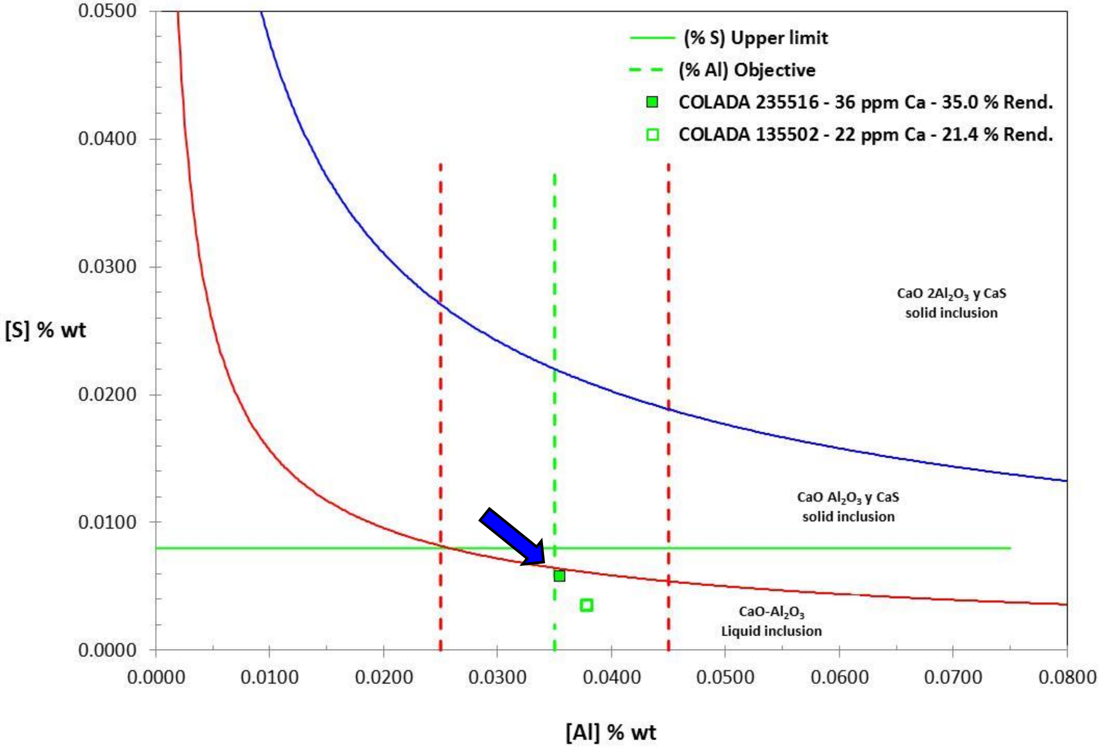
RESULTS

Grades Sour Gas

RESULTS

Sour gas steel grades

Content of Al and S in steel before Calcium injection



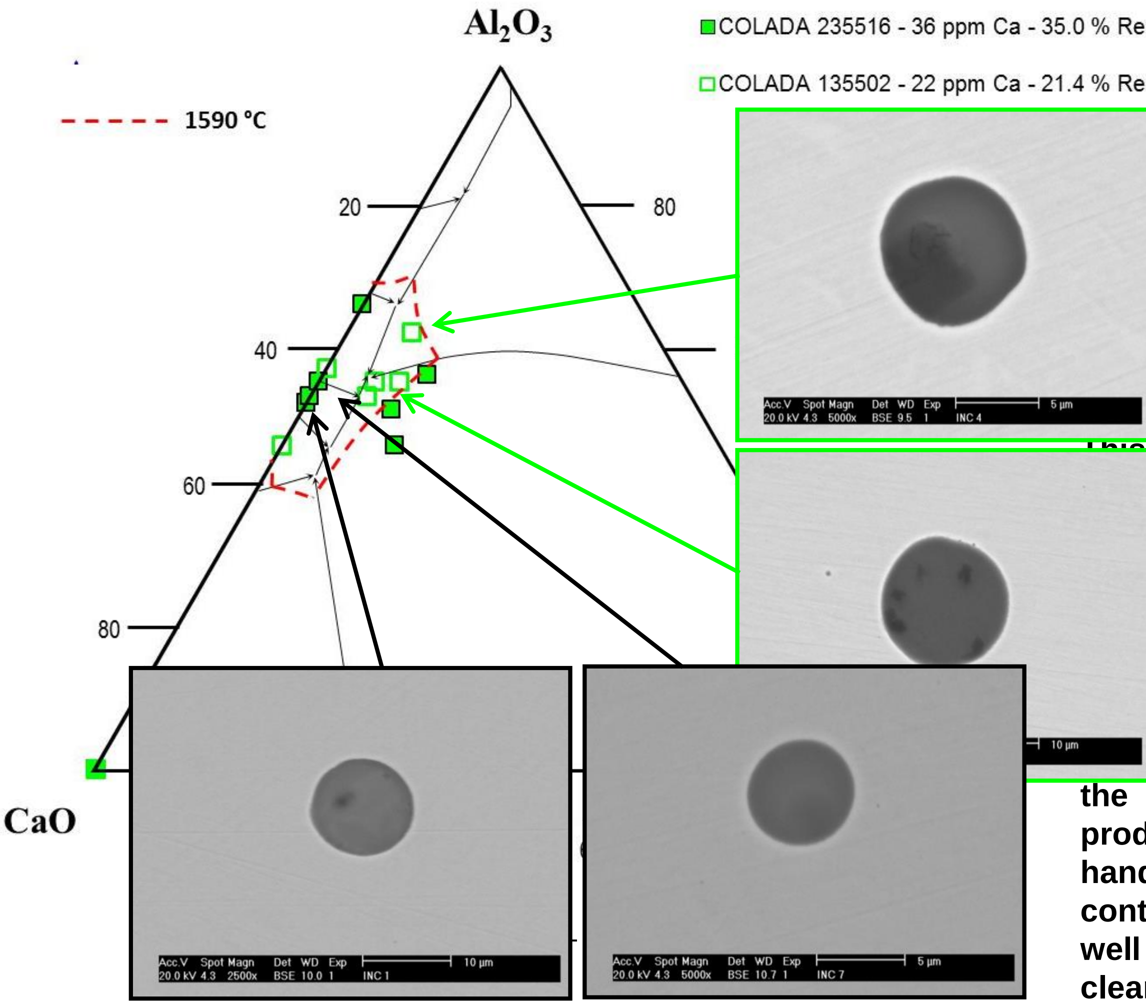
Heats with sour gas treated with Hi-CaSi were the ones with levels of Al and S before injection , *below de solid CaS formation curve*.

Heat 235516 with content of Al and S more closer to this formation curve (blue arrow) (0.0354%Al & 0.0058%S) was more susceptible to form this sulphides.

RESULTS

Sour gas steel grades

Inclusions modification degree after Hi-*CaSi* injection



ese 2 heats sour gas steel e, regardless Calcium very, inclusions

Inclusions analyzed in these heats, generally showed globular morphology and size below 10 μm

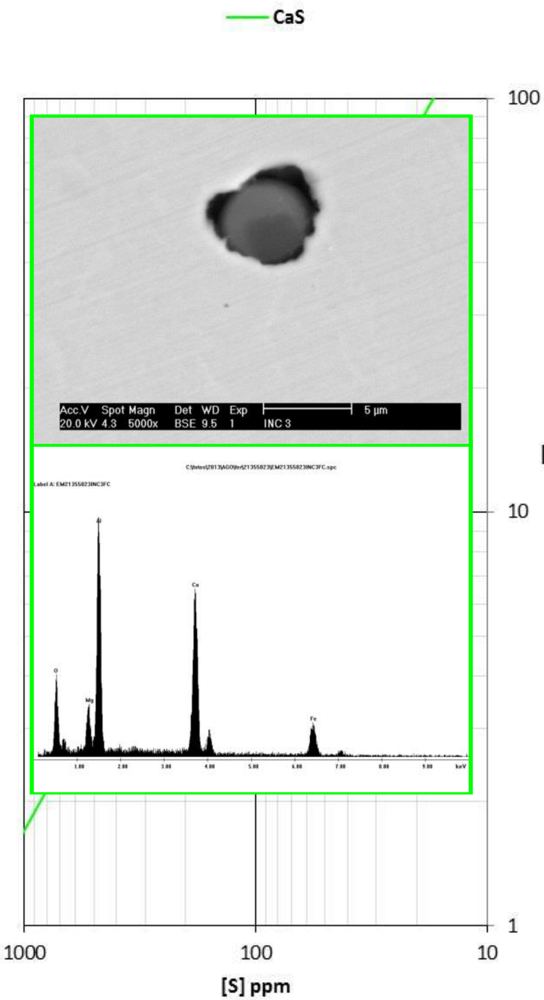
sions modification was to the steel had the idation and lfurization conditions ble before Calcium tion.

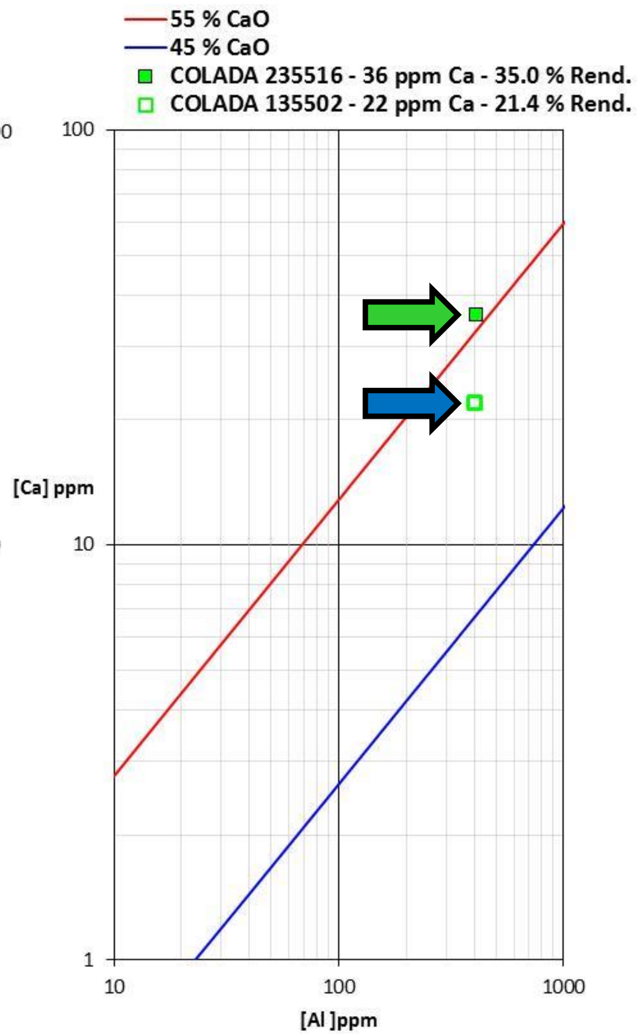
use steel grades used in the manufacture of tubular products applied to fluid handling, require special control of these elements as well as optimum levels of cleanliness.

RESULTADOS

Sour gas steel grades

Content of Al, S and Ca in steel after Hi-CaSi





But, In Heat 135502, 22 ppm Ca recovery was enough to modify the inclusions to calcium aluminates without saturation of CaO (blue arrow)

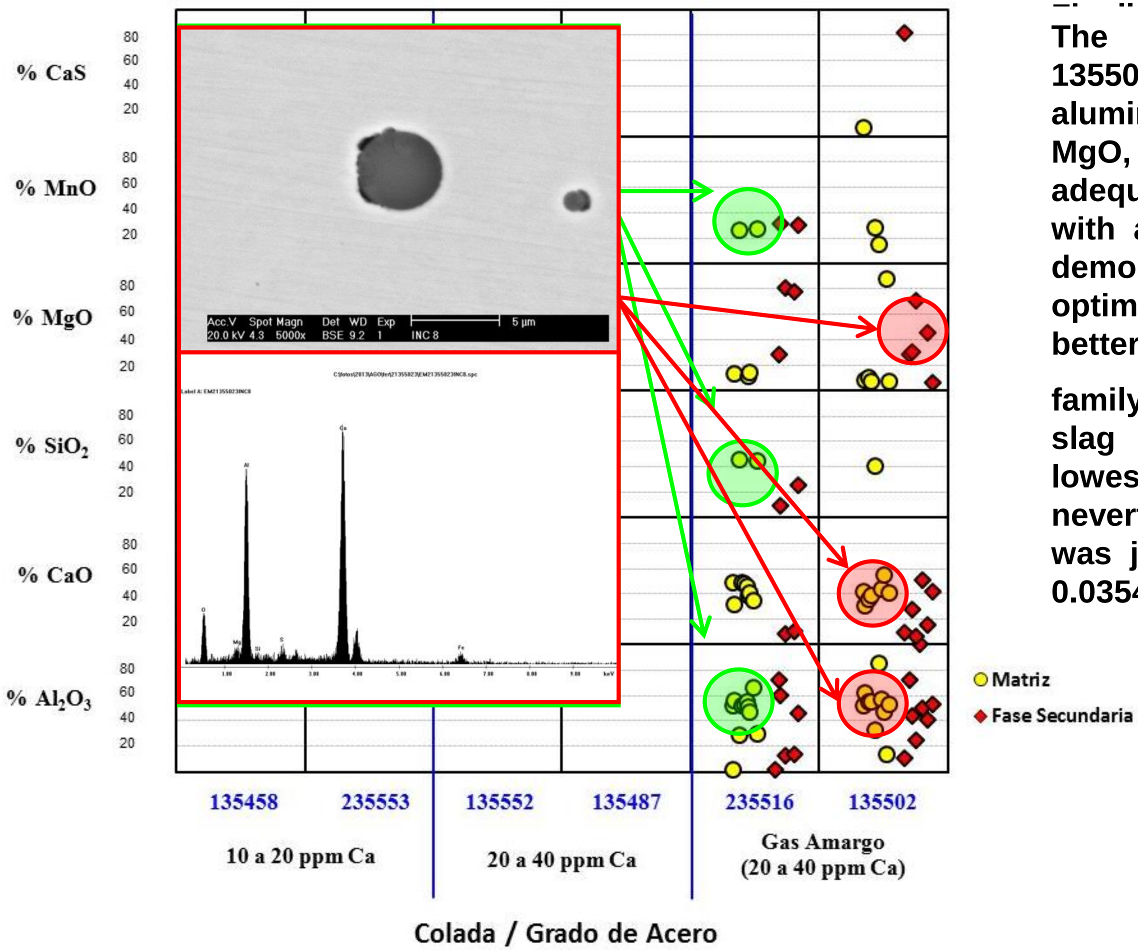
This lower ppm Ca recovery resulted in a improvement in the steel cleanliness after inclusion flotation stage

inclusions population and decreasing the cleanliness

RESULTS

sour gas steel grades

Inclusion chemical composition after Hi-CaSi injection



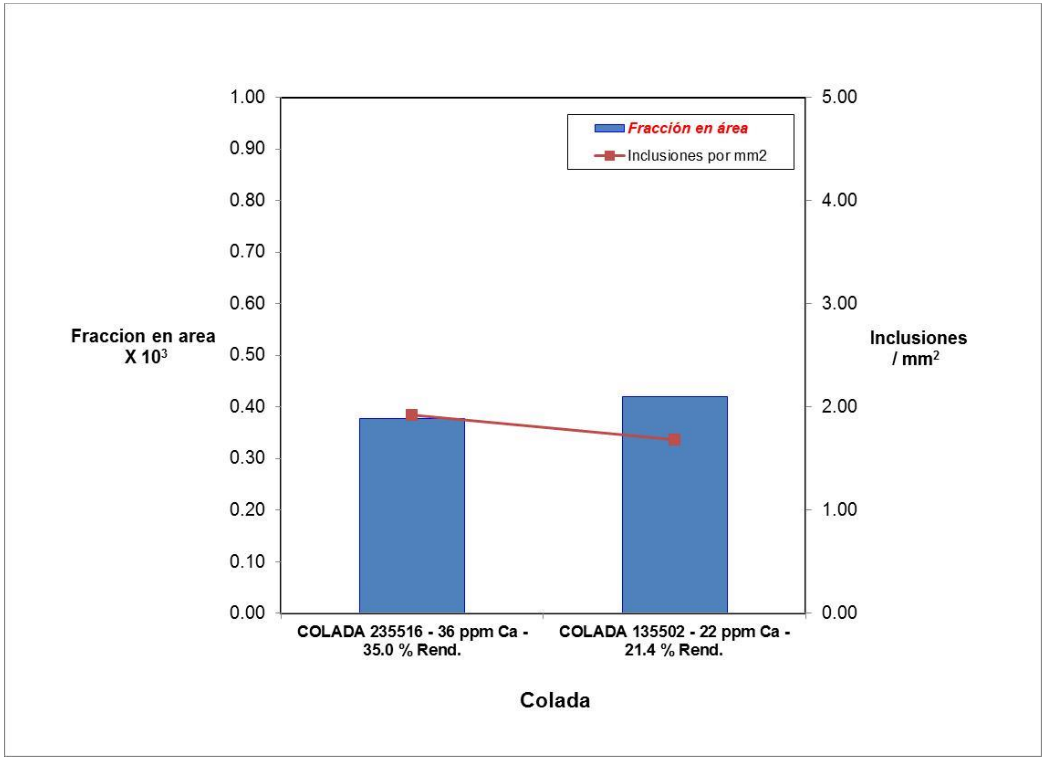
The particles present in heat 135502 were liquid calcium aluminate type with traces of MgO, which demonstrates an adequate inclusions modification with a recovery of 22 ppm Ca , demonstrating the possibility to optimize the use of Hi-CaSi to get better levels of steel cleanliness

family there is a special care in slag conditioning to reach the lowest levels of sulfur, nevertheless, in this heat sulfur was just 0.0058% and aluminum 0.0354%.

RESULTS

Sour gas steel grades

Inclusions per mm^2 and Fraction on area



As expected, this sour gas heats, were the ones with the best level of cleanliness, due to better slag conditioning and better steel desulphurization, which was beneficial for a better inclusion entrapment and as a consequence, less inclusions per mm^2 with less sizes (fraction on area)

CONCLUSIONS

CONCLUSIONS

From chemical analysis and morphology of inclusions it can be concluded the following:

1.The 6 heats analyzed showed an early and efficient inclusions modification and efficient for every steel grade family, that is, alumina was converted successfully to liquid calcium aluminates.

2.Consumptions of Calcium were excessive for the 3 families of steel grades to get an adequate inclusions modification.

3.High levels of sulfur before calcium injection, affects negatively the yield of the Hi-CaSi wire, due to formation of other product like CaS, that decreases the Ca available in the steel for the liquid calcium aluminates inclusions modification process

4.So the same, excessive Ca consumptions -under adequate desulphurization conditions-, enriched the liquid calcium aluminates inclusions with CaO, resulting in higher ppm recovery but low levels of steel cleanliness, due to this inclusion become solid and reamins in the steel final product.

THANK YOU