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INJECTION ALLOYS GROUP Injection Alloys Germany GmbH

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Optimization of injection treatment with High Purity Calcium (Hi-*Cal*[®])and High Purity Compacted CaSi 30/70 (Hi-CaSi [®]) in Low carbon Al-killed and Al/Si-killed steels

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Injection Alloys Group



Injection Alloys is a group of companies with manufacturing facilities and commercial offices in many locations across the globe. The head office is in Cambridge in the United Kingdom, where it was founded in 1985.

Injection Alloys Countries

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Key Parameters: Will Point Out



✓ Injection speed
✓ Injection quantity
✓ Cost savings
✓ Clean steel
✓ Ultra high yield
✓ Stable efficiency

Summary of the trials:

- Steel grades: Low-C AI-K steels
- Total: 51 heats
- Average Efficiency of HPCa: 32,6 %
- Average Ca ppm of HPCa: 22 ppm
- Optimum speed: 140 160 m/min
- Average quantity (Ca): 0,065 kg/ton (kg Ca/ton)
- Comparison with: AIFeCa CCW

Calcium purity: 98,5 % Low-C (0.04 to 0.06% C)



Inclusionary states were characterized in steel samples after injection treatment in terms of:

- Chemical composition
- Inclusion morphology
- Number of inclusions
- Area fraction analysis by scanning electron microscopy (SEM/EDX)
- Liquid inclusions Al₂O₃-CaO with MgO content
- Inclusion size and form



Efficiency of injection treatment using High Pure Calcium

51 heats of steel LCAK were treated with HPCa 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. (C: 0,04 to 0,06 %)

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		



Injection speed effect on efficiency

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%.



Heat Number



Injection speed effect on efficiency

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.

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

Injection speed effect on efficiency

Figure illustrates the decrease of efficiency as the injection speed was increased.



Effect of consumption (kg 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 the consumption was lower than 0.060 kg Ca/ton.



Heat Number



Effect of consumption (kg of Ca per ton) on efficiency

Table shows results of average efficiency and consumptions. As the amount of Ca injected decreases (less than 0.065 kg Ca/ton) efficiency of High Pure Ca increases due to dissolution of calcium in the steel was optimized.

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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



Effect of consumption (kg of Ca per ton) on efficiency

Figure illustrates a tendency to increase the average efficiency decreasing of kg of Ca 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 Ca less than 0.064 kg per ton), so that a greater number of tests with less amounts of Ca injected confirm this tendency.



Effect of AI and S contents on treatment efficiency



- Many heats with efficiency less than 30% showed high levels of Al and S
- At high levels of Al in steel (from 0.025 to 0.035% wt. Al, represented by the vertical lines in yellow) amount of Ca required for inclusions modification is insufficient
- S higher than 0.0050% (specification represented by the red horizontal line) causes that HPCa injected reacts first with this element causing a desulfurization of steel and formation of CaS inclusions
- As result a better steel desulfurization treatment prior HPCa was achieved (S content less than 0.0050%) preventing that Ca injected works as desulfurizer (reducing CaS formation)
- More than 40 % efficiency: Al 0,025 0.035, S: less than 0.0050 %

Trials with HPCaSi (High Purity Compacted CaSi 30/70) in Low – C Al/SiK

Summary of the trials:

- Steel grades: Low-C AI / Si -K steels
- Total: 55 heats
- Average Efficiency of HPCaSi: 33,7 %
- Average Ca ppm of HPCaSi: 20 ppm
- Optimum speed: 122 m/min
- Average quantity (Ca): 0,060 kg/ton (kg Ca/ton)
- Comparison with: AIFeCa CCW

Calcium purity: 98,5 % / Calcium 30 % - Silicon 70 % Low-C (0.04 to 0.06% C)

Trials with HPCaSi (High Purity Compacted CaSi 30/70) in Low – C Al/SiK

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		

Trials with HPCaSi (High Purity Compacted CaSi 30/70) in Low – C Al/SiK



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



5 heats at 137 m/min + 152m (10,5kg Ca) = Recovery 25,3 % at 152m/min + 137m &122m (9,4 & 8,4 kg) =Recovery 28,5 % slight improvement 10,5 kg and 9,4 kg = 30 % Recovery (spl)

At 122 m/min: 33 %, 35,8 and 43,4 % x Deeper Injection x Correct release zone x Longer residence time in the steel

Trials with HPCaSi (High Purity Compacted CaSi 30/70) in Low – C Al/SiK

Effect of the injection speed on Ca recovery

Heats were treated with HPCaSi, in the system Fe-Al-Ca-S-O at 1600 °C. As it can be observed on the right side of the figure, 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).





Heats treated with High Purity Calcium (HPCa)

After HPCa treatment at LF:

A: A few solid inclusions unmodified Al_2O_3 -MgO type with a specific chemical composition of 70-75% Al_2O_3 and 25-30% MgO.

B: Spinels with an incipient modification to calcium aluminate, according Al_2O_3 inclusions and spinels (MgO-Al₂O₃) are enriched in CaO, decrease their melting point to become liquid at the temperature of steelmaking.

C: Calcium aluminate inclusions Al_2O_3 -CaO modified whose melting point is lower than the temperature steelmaking (1590 ° C) with size less than 7 microns and globular morphology.





Heats treated with High Purity Calcium (HPCa)

After HPCa treatment at tundish:

A: Many inclusions modified to liquid calcium aluminate

B: Inclusions of type Al₂O₃-CaO-MgO, 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



Heats treated with AICaFe CCW

The same study to compare: HPCa vs AlCaFe

The figure illustrates the chemical composition of inclusions analised in samples obtained <u>before treatment with AlCaFe</u>. Generally these inclusions are spinels (Al_2O_3 -MgO) with Al_2O_3 content between 70-75% and MgO content from 25 to 30%.



Heats treated with AICaFe CCW

The same study to compare: HPCa vs AlCaFe

The figure illustrates the result of AICaFe CCW injection where a null modifying to calcium aluminate inclusions



Heats treated with AICaFe CCW

The same study to compare: HPCa vs AlCaFe

A: Although in the samples obtained after AlCaFe injection at the end of treatment at LF were found only unmodified inclusions (Al_2O_3 -MgO), generally calcium aluminate inclusions with variable MgO content.

B: 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



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

Before HPCaSi treatment:

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 SiO₂ and MnO, their melting points decrease becoming liquid at a temperature of 1600 °C. These particles coalesce and form bigger inclusions enabling their flotation towards the slag.



Heats treated with High Purity Compacted CaSi 30/70 (HPCaSi) After HPCaSi treatment at LF:





Conclusions



Calcium treatment with High Purity Calcium (HPCa) Injection parameters and efficiency

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

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

Conclusions

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

Injection parameters and efficiency

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

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



Thank you Injection Alloys Group



