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CALCIUM TREATMENT OF MOLTEN STEEL WITH AN INNOVATIVE NEW CALCIUM WIRE: Hi-*Cal*®[1]

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Abstract
Calcium treatment by injecting cored wire into molten steel is a fundamental technology applied in steel plants all over the globe. Castability is improved by modification of solid inclusions into liquid ones at normal molten steel temperatures. Typical calcium recoveries with conventional surface fed calcium containing cored wires vary between 8 and 15 %. Hi-*Cal*® can achieve recoveries of 25 to 55 %. Experience now demonstrates that the recovery has been typically 3 to 5 times better compared to conventional products.
Key words: Secondary metallurgy; Calcium treatment; Seamless cored wire; Ultra high yield; Repeatability.

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INTRODUCTION

Calcium treatment, its necessity and reaction kinetics have been discussed comprehensively in literature.[1-12] Since continuous casting has been introduced to steel industry, calcium treatment has become a step in secondary metallurgy as part of the steel making process of clean steels. The challenge centres on the low solubility of calcium in iron, which is described in literature with 0.030 % at 1600 °C and 10^5 Pa.[1,2]
Several methods have been developed to introduce calcium to molten steel - all with low recoveries and undesirable side effects. The most common technology to introduce calcium into molten steel is the cored wire application. Almost every treatment station as ladle furnaces and vacuum degassing units is equipped with cored wire feeding units, which are used for alloying, trimming and calcium treatment. For the least conventional calcium containing wires are used. This article will focus on the application of calcium treatment.

CONVENTIONAL CORED WIRE

Conventional cored wire is produced with profiling machines by forming a steel sheath to a half shell, filled with the required powder and then closed with a hook. The typical wall thickness is in the range of 0.4 to 0.6 mm, because it is limited by the kind of production. The hook that closes the wire is 4 times the sheath thickness. The wire is coiled and then caged for the use in a steel mill. Figure 1 shows the cross section of a conventional cored wire.

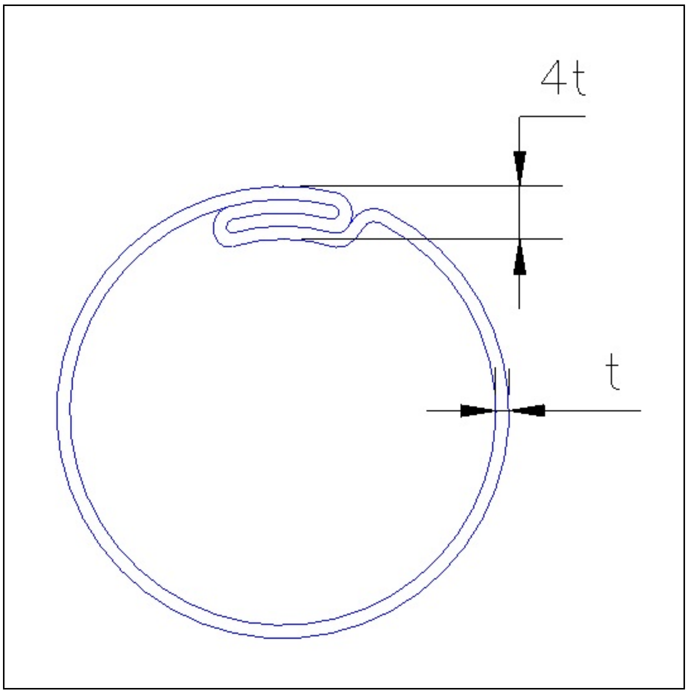

Figure 1: Cross section of conventional cored wire.

Investigations of the melting behaviour of conventional cored wires[3] lead to the conclusion that the injection speed of those wires used for calcium treatment must be very high to reach optimum depth in the ladle, where the ferro-static pressure is higher than the vapour pressure of calcium, in order to improve recoveries. In this

article recovery and yield are used as the percentage of total calcium after treatment against inbound calcium. Standard practice in steel plants where Hi-*Cal*® has been introduced so far is to stir with argon for 2 to 5 min after the end of calcium treatment. After the stirring process the sample is taken and analysed.
There are several conventional cored wire qualities which contain calcium available on the market. Non silicon restricted steel grades are normally treated with CaSi, a compound of approx. 30 % calcium and 60 % silicon. Silicon restricted steel grades are treated with pure calcium and blends of pure calcium with iron powder and aluminium powder. Typical calcium/iron wire compositions are CaFe 30/70, which consist of Ca 30 % and Fe 70 %. If aluminium is used the most common composition is AlCaFe 30/40/30. They include 30 % Al, 40 % Ca and 30 % Fe.

HI-*CAL*®

Hi-*Cal*® is the first wire in the new product family Hi-*Core*® from the Injection Alloys Group. It is a seamless pure calcium cored wire with a sheath thickness of 1.4 to 1.6 mm and therefore over 3 times thicker than conventional cored wire. Figure 2 shows the cross section of Hi-*Cal*®.

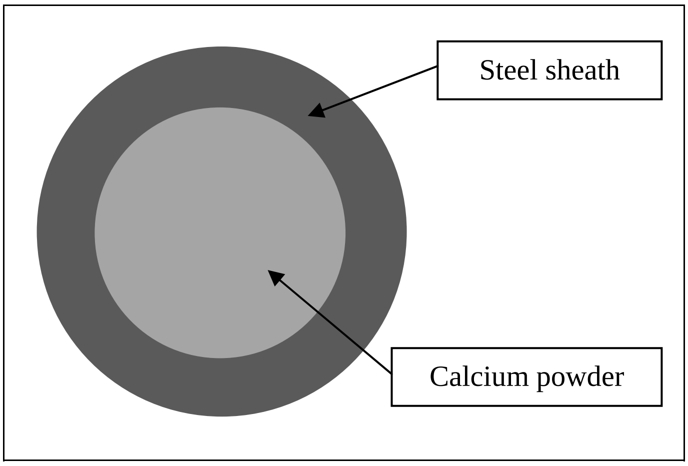

Figure 2: Cross section of Hi-*Cal*® (ratio of steel sheath and powder shown to scale).

It has a nominal outer diameter of 9.6 mm and a powder filling ratio of 54 g/m. It can typically be fed by any existing feeding equipment already installed in the plant and used for conventional cored wires. There is no need for expensive lance systems or other similar equipment which cause additional investment and consumable costs. Hi-*Cal*® is produced by a new, innovative production process in Germany and Mexico. Both, product and manufacturing process are patented and patent pending in every steel producing region. Hi-*Cal*® is a seamless cored wire which contains only pure calcium. The wire is produced by longitudinal welding and subsequent reduction down to final diameter. Due to the production process, the calcium powder is highly compacted and does not contain any atmospheric gases. Like conventional cored wire Hi-*Cal*® is coiled and caged for the application in steel plants too. Table 1 shows a summary of the most common conventional cored wires compared to Hi-*Cal*®.

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Table 1: Comparison of conventional calcium cored wires with Hi-*Cal*®

Cored wire type	CaFe 30/70	AlCaFe 30/40/30	Ca	Hi-*Cal*®	CaSi 30/60
Ca content	30 %	40 %	100 %	100 %	30 %
Powder weight	280 g/m	195 g/m	50 g/m	54 g/m	230 g/m
Ca weight	84 g/m	78 g/m	50 g/m	54 g/m	69 g/m
Wire diameter	13 mm	13 mm	9 mm	9.6 mm	13 mm
Sheath thickness	0.4 to 0.6 mm	0.4 to 0.6 mm	0.4 to 0.6 mm	1.4 to 1.6 mm	0.4 to 0.6 mm
Injection speed	160 to 300 m/min	160 to 300 m/min	160 to 300 m/min	70 to 130 m/min	160 to 300 m/min
Ca addition rate	80 to 140 g Ca/t x min	75 to 125 g Ca/t x min	45 to 80 g Ca/t x min	30 to 50 g Ca/t x min	65 to 110 g Ca/t x min
Ca recovery	12 to 18 %	14 to 21 %	9 to 15 %	25 to 55 %	10 to 18 %

COMPARISON OF CONVENTIONAL CALCIUM CORED WIRE WITH HI-*CAL*®

Conventional practice suggests a calcium addition of 100 to 140 grams per tonne of liquid steel and more to achieve acceptable inclusion modification. The use of Hi-*Cal*® completely invalidates this practice as just 40 to 80 grams of calcium additions are necessary for the same result.
The high injection speed that is required for conventional cored wires to reach optimum depth in the ladle causes the side effect of local supersaturation by offering a surplus of calcium. This effect has a negative impact on recovery. Both - the high speed requirement and the surplus of calcium - creates the paradox of calcium treatment with conventional cored wire. The sheath thickness of 1.5 mm of Hi-*Cal*® allows to add calcium in a range of 30 to 50 g Ca/t x min, which avoids the effect of supersaturation.
However, the use of Hi-*Cal*® significantly reduces the range of additions required, due to the excellent level of consistency and low standard deviation of Ca ppm result.
Today Hi-*Cal*® has been introduced to steel plants all around the world. As an example, at one major US customer, utilising a 200 tonne ladle capacity, the inbound calcium was reduced from 39 kg calcium (195 g/t) with conventional CaSi 30/60 wire to 15 kg calcium with Hi-*Cal*® (75 g/t). In a major European steel plant the calcium inbound of 10.6 kg (85 g/t) from 9 mm calcium cored wire was reduced to 6.5 kg calcium (52 g/t) from Hi-*Cal*®. Figure 3 shows a yield comparison of conventional cored wires with Hi-*Cal*®.
It must be mentioned that all introductions of Hi-*Cal*® were carried out without any changes to the equipment or the current practice at customers' site.

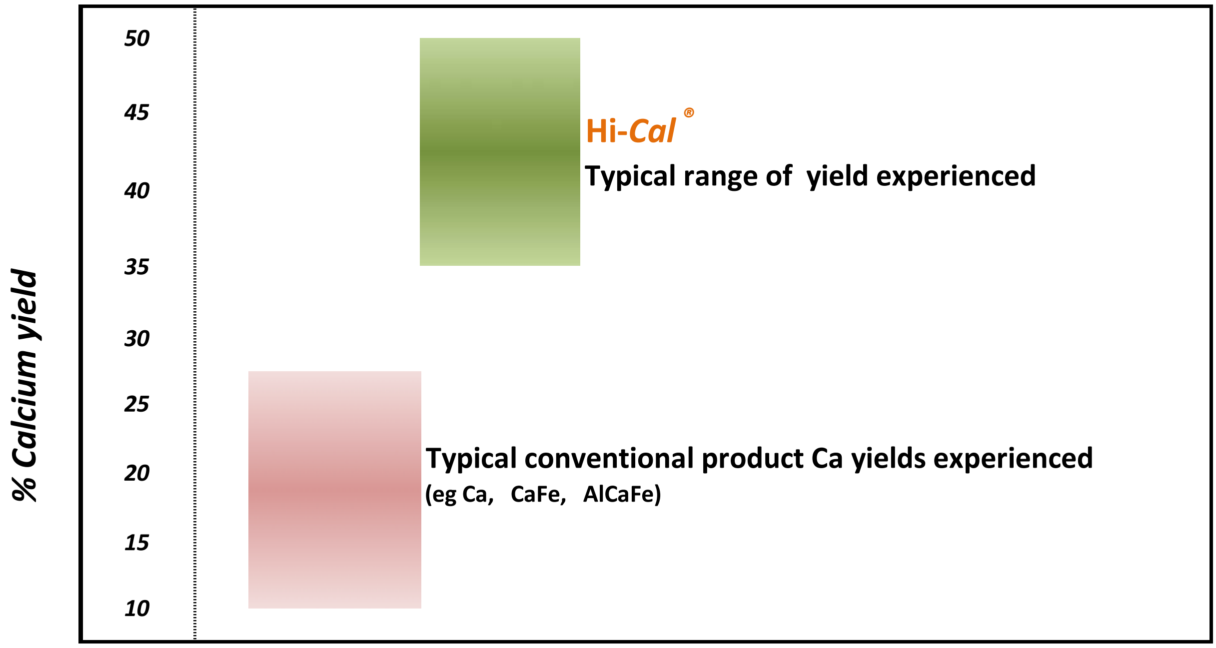

Figure 3: Yield comparison of conventional cored wire with Hi-*Cal*®.

A constant ultra high recovery with corresponding small deviation range is one of the major metallurgical advantages of this wire. Repeatable high recoveries of 3 to 5 times better than with surface fed cored wires are constantly achieved. The significantly lower splashing allows a better utilisation as the freeboard can be reduced. Consequently oxygen and nitrogen pick-up during calcium treatment is minimised as contact of liquid steel to atmosphere is avoided.
All this enables enormous cost savings to the customer based on less consumption of calcium, better usage of ladle capacity as the freeboard can be significantly reduced, less cored wire coil movements within the plant, less damaging impact on the environment by avoiding fumes and transportations. Furthermore less splashing and less transport makes life safer for the operational staff.

CONCLUSION

The seamless Hi-*Cal*® cored wire is the first true innovation in the past 25 years of steel treatment with injection cored wires. It is superior to all conventional calcium cored wires and can replace all surface fed calcium wires. It is the first product of the new Hi-*Core*® family, other powder qualities will follow soon. Additionally Injection Alloys can provide a complete solution to the demands of steel plants in cored wire technology - not only for calcium treatment.

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