ENHANCING RARE EARTH INOCULANT EFFECT IN COMPACTED GRAPHITE CAST IRONS AND INFLUENCE ON GRAPHITE SHAPE FACTORS

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The main objective of the present paper is to examine the possibility of enhancing CaRE-FeSi based inoculants efficiency and also reducing inoculant consumption for compacted graphite cast irons. In the surface layer of castings, for of all of the tested inoculant systems, inoculation increased graphite nodularity and shape factors. [OS-IE] proved to be a viable standalone inoculation solution promoting a high nodularity effect through the section of casting. Dual addition of CaRE-FeSi + [OS-IE] inoculant enhancer led to the highest compacted graphite formation sensitivity.

Keywords: compacted / vermicular graphite iron, in-mould inoculation, inoculant enhancer, rare earth, sulphur, oxygen

1. Introduction

Compacted graphite cast iron (CGI) is replacing grey cast iron (GCI) in applications where greater mechanical strength is needed without the loss of characteristics associated with fully spheroidal graphite. Of the present production, iron castings represent more than 70% of all castings worldwide mainly due to the package of physical and mechanical properties associated with competitive costs. While the manufacture of compacted graphite (CG) iron castings has seen significant expansion over the years, the nucleation and growth of (CG) during solidification is still not fully understood as is the effect of various commercially available inoculants combined with different enhancer solution on graphite morphologies and characteristics.

Inoculation in case of cast iron consists in changing the physico-chemical state of the molten iron. It is a mean of controlling the structure and properties of cast irons by increasing the number of nucleation sites available for the nucleation and growth of graphite flakes in grey irons (GCI) or graphite nodules in ductile

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irons (DI). The change is obtained by introducing to the cast iron of low graphite nucleation power a small amount of inoculant that contains a compound capable of increasing the number of active nuclei. The main criterion used in evaluation of the inoculation effects are changes in the metallic base microstructure, mechanical properties of cast iron along with graphite shape characteristics and chilling tendency. Inoculation has a vital role to play in the continuing progress of cast iron.

The purpose of inoculant is to assist in providing enough nucleation sites for the carbon to precipitate as graphite rather than iron carbide. Traditionally, inoculants have been based on graphite, ferrosilicon or calcium silicide. The most popular inoculant today is ferrosilicon containing small quantities of elements such as Al, Ba, Ca, Mn, Bi, Sr, Zr, Ce and RE (rare earths)[1]. Amongst these, Ba, Zr, Sr, Bi, Ce, RE (rare earths) are more powerful active elements than Al and Ca in FeSi based inoculants, this results in lower addition rates [2]. FeSi as a pure material has no inoculation effect.

The main objective of this paper is to examine and also understand the effects of in-mould inoculation treatment to a MgRE-FeSi treated CGI, at a relatively low anti-nodularizing potential of the base iron. One of the main aspects of this research focuses on reducing inoculant addition rates by enhancing the inoculant used with an oxy-sulphide inoculant enhancer [(OS-IE)]. The inoculant variants used consisted of three inoculant configurations: (a) CaRE-FeSi alloy, (b) [(OS-IE)] used as a standalone inoculant solution, (c) CaRE-FeSi alloy added alongside [(OS-IE)].

2. Experimental Procedure

A 150 kg, 2400Hz coreless induction furnace was used for melting the base iron. The charge mix contained 50 wt. % high purity pig iron and 50 wt. % cast iron scrap. Chemical composition of the iron was corrected by adding 520 g of graphite powder (Fig. 1). After the metallic charge was melted the thermal regime was as follows: superheat temperature Ts=1550ºC; Mg treatment temperature Tm=1530ºC; pouring temperature Tp=1350ºC.

Nodulizing treatment with FeSiMgRE alloy (Table 1) was conducted by tapping the base iron into a tundish cover ladle. After the nodulizing treatment the iron was poured into a specially designed test mould (Figure. 2), that maintains for each inoculant variant and contained samples the same thermodynamically / physical solidification conditions.

The mould has a central downsprue that feeds Mg-treated iron simultaneously into four separate ‘reaction’ chambers: (1) an un-inoculated reference; (2) 0.1wt.% CaRE-FeSi alloy; (3) 0.02wt.% oxy-sulphide inoculant enhancer [(OS-IE)]; (4) 0.04wt.% CaRE-FeSi alloy + 0.015wt.% ([OS-IE)] alloy.

The furan resin sand mould contained 3 different test samples that can be used to evaluate the treated iron chill wedge samples - W_3 (ASTM A367-85 specification, dimensions 19 x 38 x 100 mm, cooling modulus, CM = 3.5 mm), plate samples 4.5 mm thick used for chemical analysis and round bar samples 25mm diameter.

A 5 µm trap size for particle analysis was chosen eliminating all of the much smaller particles or very fine surface imperfections (e.g. scratches) and counted as graphite particles [3].

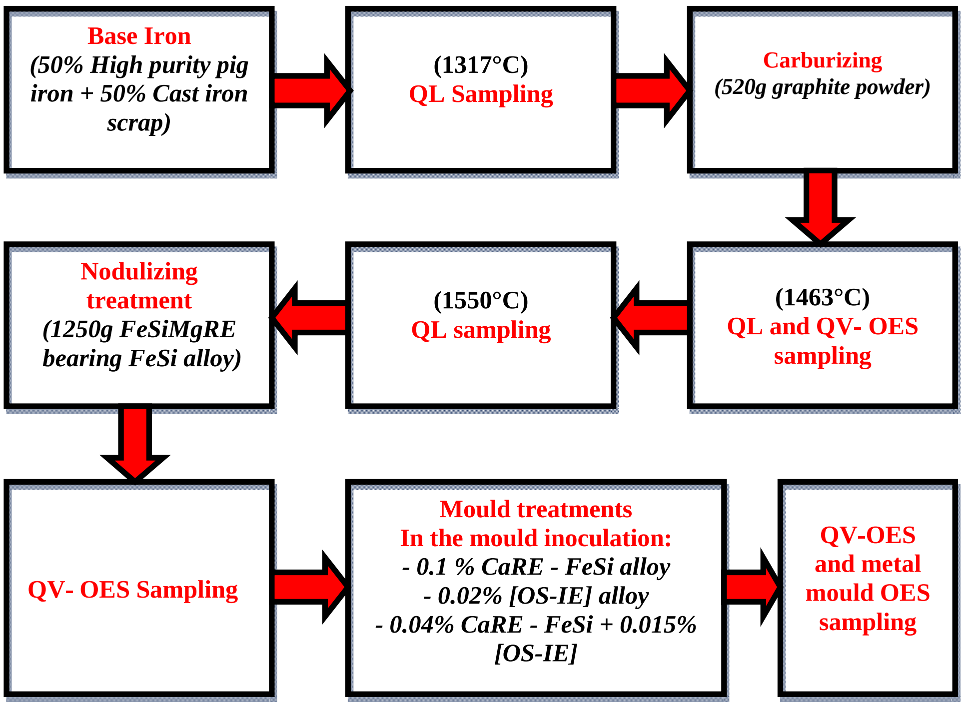


Fig. 1. Technical schedule [OES/QV- Optical emission spectroscopy; QL- Quick Lab]

The trap size is a feature offered by IA software which allows the user to eliminate particles smaller than a pre-defined size. On the bar samples 8 axes to be analyzed were chosen (Fig. 3). Every field analyzed was 1375 x 1030 pixels (886.87 x 664.35 µm).

The number of fields analyzed on each axis was equal to 19 (12.62265mm) for 25 mm round bar samples. For this research, the center of the sample was excluded from the analysis and also a number of fields where the graphite shape factors and graphite type were influenced by the sample's center during solidification. A number of 9 (5.97915mm) fields from the surface towards center, were analyzed for each axis, this included the first fields where the surface layer presents graphite degeneration.

Table 1

Chemical composition of the treatment alloys (wt. %)

Alloy	Si	Ca	Mg	Al	TRE	Ce	La	Ba	S	O
FeSiMgRE [Nodulizer]	44.71	1.02	5.99	0.91	0.25	0.15	0.10	0.035	-	-
CaRE-FeSi [Inoculant]	73.52	0.87	0.057	0.83	1.86	-	-	-	-	-
OS-IE [Enhancer]	36.90	16.29	1.96	5.74	-	-	-	-	8.11	2.67

*TRE-total rare earth element

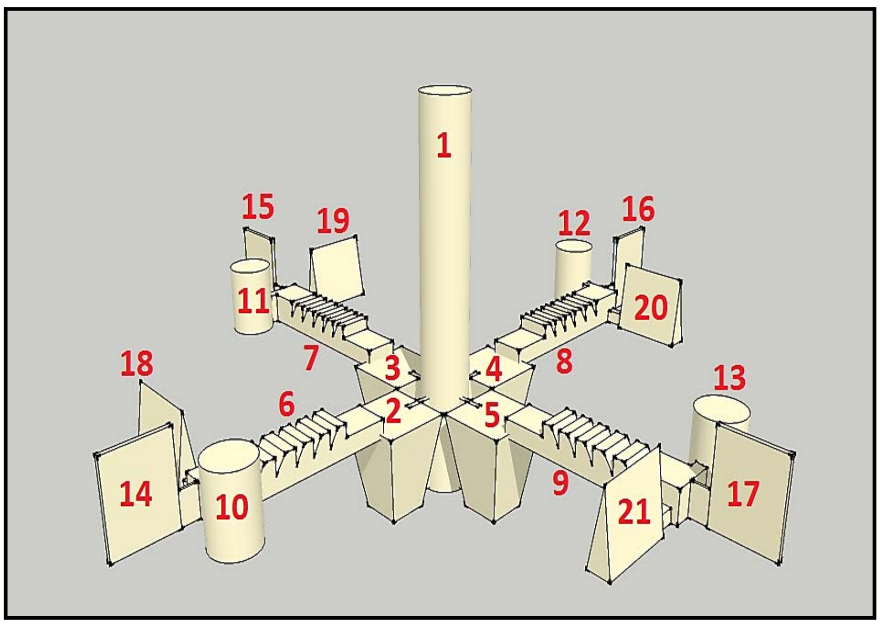


Fig. 2. Mould network - computer simulation. (1- central downsprue; 2, 3, 4, 5 – reaction chamber; 6, 7, 8, 9 – slag stopper; 10, 11, 12, 13 – round bar samples; 14, 15, 16, 17 – plate samples; 18, 19, 20, 21 – W_3 chill wedge samples, ASTM A 367)

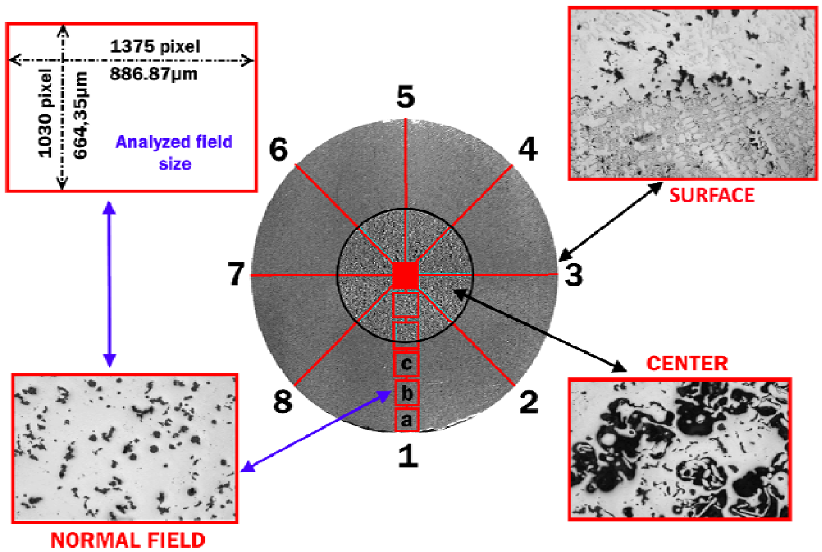


Fig. 3. Simulation of analysis made on 25mm round bar samples (1, 2, 3, 4, 5, 6, 7, 8 analysed axes; a, b, c examples of fields analysed on axes)

3. Results and discussions

For the plate samples, chemical analysis (Tab. 2.) obtained with Spectrolab M system the calculated (Eq. 1) carbon equivalent (CE) was found to be between 4.3 - 4.4%. The slightly hypereutectic treated irons are accompanied by a residual magnesium value Mg_{res}= 0.018% - 0.025%.

Cumulative influence of the pearlite forming elements P_x (Eq. 2) and anti-nodularizing elements K factor (Eq. 3) can be seen in Table 2 [4]. Anti-nodularizing elements in these Mg treated irons are at a low value with $K < 0.7$. Pearlite forming factor with a value of $P_x = 3.9 – 4.76$ indicates a medium forming pearlite tendency.

$$CE = \%C + 0.3(\%Si + \%P) - 0.03\%Mn + 0.4\%S \quad (1)$$

$$P_x = 3.0(\%Mn) – 2.65(\%Si - 2.0) + 7.75(\%Cu) + 90 (\%Sn) + 357(\%Pb) + 333(\%Bi) + 20.1(\%As) + 9.60(\%Cr) + 71.7(\%Sb \quad (2)$$

$$K = 4.4(\%Ti) + 2.0(\%As) + 2.4(\%Sn) + .0(\%Sb) + 90(\%Pb) + 370(\%Bi) +1.6(\%Al) \quad (3)$$

Analysis on micrographs taken for the 25 mm round bar samples (Fig. 4) show a typical, normal structure, for all the treated irons at the same solidification rate. In all the samples microscopic and statistical analysis that concerns graphite morphologies reveals a mixture of both compacted and nodular graphite structures, with a relatively high nodularity level between 0.66 – 3.96 mm - distance from the surface (Fig. 4. and Fig. 5.). Applied treatment influences graphite nodularity which is also influenced by the solidification rate (greater distance from the surface slower cooling rate). Between 0 – 3.3 mm from surface CaRE-FeSi inoculation choice has a visible effect on the graphite nodularity parameter.

Table 2

Chemical composition of cast irons

Inoculation Type	Chemical Composition wt.%							Control Factors	
	C	Si	Mn	P	S	Mg	CE	K	P_x
Un-inoculated	3.59	2.49	0.43	0.040	0.023	0.020	4.42	0.645	3.879
CaRE-FeSi	3.50	2.44	0.47	0.048	0.021	0.025	4.31	0.566	4.672
[OS-IE]	3.58	2.45	0.47	0.046	0.021	0.023	4.40	0.649	4.694
CaRE-FeSi + [OS-IE]	3.50	2.42	0.47	0.047	0.019	0.020	4.31	0.627	4.759

The lowest graphite nodularity less than 15% can be seen for the un-inoculated irons in the casting surface between 0 - 0.66 mm, where a high cooling rate during the solidification due to high metal to mould heat transfer leads to the formation of degenerated graphite. In general a higher solidification rate is beneficial by promoting greater graphite nodularity in Mg-treated irons, but in this case the surface of the casting is affected S-transfer from the mould especially when P-Toluol Sulphonic Acid (PTSA) is present. Combustion of PTSA in the resin sand during solidification process at casting temperatures can generate SO_2, which is dissociated into atoms and absorbed at the surface of the casting. This phenomenon can explain the reduction of graphite nodularity in the casting's surface layer. The most effective inoculant enhancer that influences graphite nodularity values in the analyzed fields, appears to be CaRE-FeSi inoculant solution followed by OS-IE standalone inoculant solution and CaRE-FeSi + OS-IE inoculation solution.

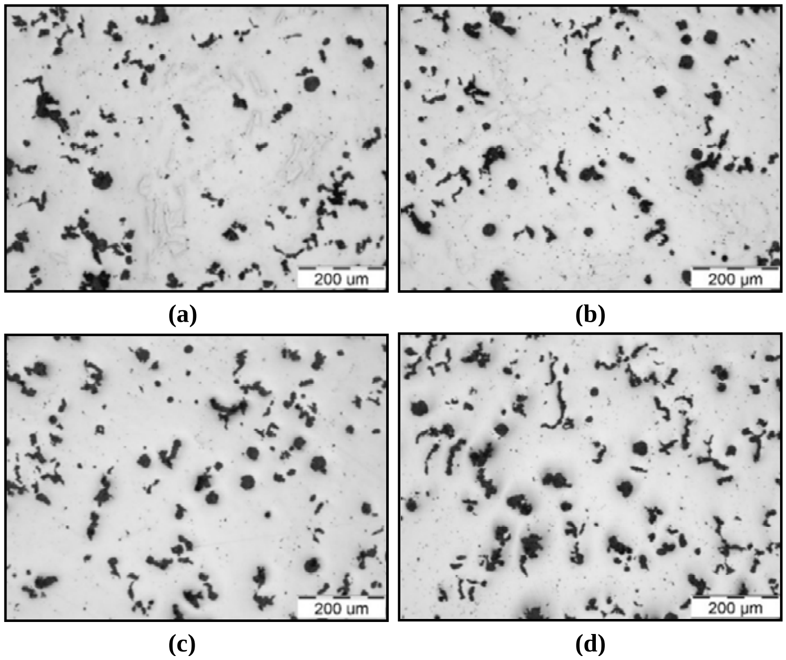


Fig. 4. Graphite structure at 3.96 mm distance from the surface of 25mm diameter sample: a) un-inoculated; b) CaRE-FeSi; c) OS-IE; d) CaRE-FeSi + OS-IE; [un-etched]

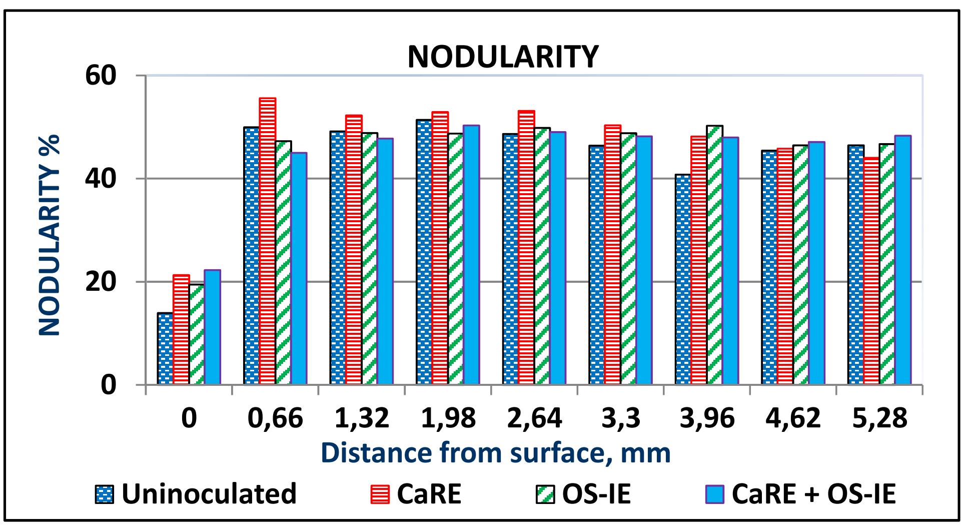


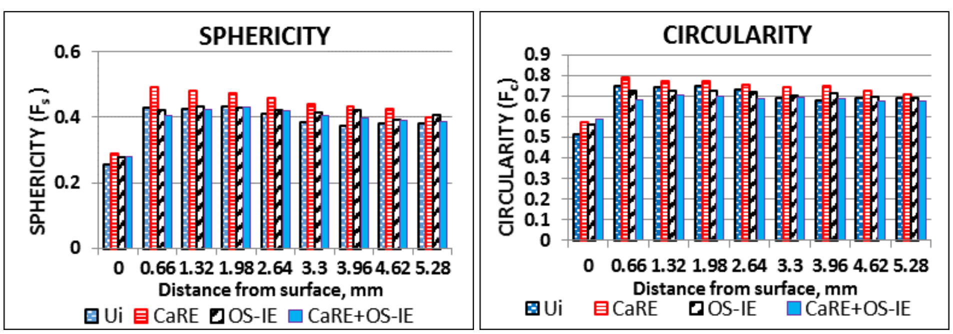
Fig. 5. Graphite nodularity at different distances from the sample surface and different inoculation treatments

Many studies have shown that furan resin PTSA moulding system has an important role in degeneration of the surface layer in Mg-treated iron castings. Sulphur content in the binder of FRS-PTSA moulds promotes graphite degeneration resulting in abnormal graphite morphologies specially in the case of compacted graphite iron which is more vulnerable to this type of phenomenon due to a more marginal nodularizing potential (lower Mg_{res} values) [5-7].

In the surface layer inoculation has a visible effect on graphite nodularity for all treatments tested. The highest nodularity values for the surface layer 22 % appeared in CaRE-FeSi + OS-IE treated irons followed in this order by CaRE-FeSi inoculant solution 21% and OS-IE inoculant enhancer 19% used as standalone inoculant solution. Values for surface layer nodularity are very close to one another and clearly show the beneficial effect of the inoculation treatments. After the superficial layer zone, graphite nodularity increases, with nodularity values between 45-55% with only limited influence from the cooling rate.

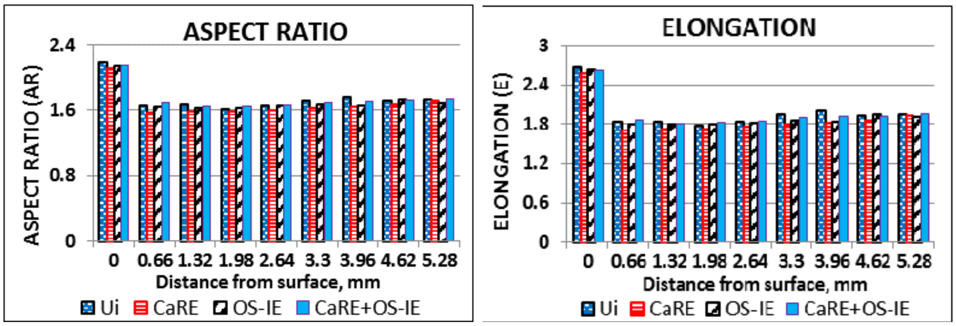
Shape factors used to characterize graphite morphologies in cast irons were also used in this experiment for the 25 mm round bar samples (Fig. 6 and Fig. 7).

The graphite characteristics were evaluated by Automatic Image Analysis [analySIS® FIVE Digital Imaging Solutions software] on micrographs taken with BX61 Olympus Optical microscope. Two representative categories of shape factors were considered: (1) Sphericity and circularity – describing graphite particle compactness. Circularity and sphericity are different approaches that describe the roundness of graphite. (2) Aspect ratio and elongation that define at lower levels a higher degree of particle compactness.



(a) **(b)**

Fig. 6. The main shape factors used for describing graphite particle compactness: (a) sphericity; (b) circularity;



(a) **(b)**

Fig. 7. The main shape factors used to evaluate the roundness of graphite:
(a) aspect ratio; (b) elongation

The graphite shape factors revealed a low degree of compactness in the surface layer in all inoculation treatment variants used. Graphite particles show an increasing decline of compactness at an increase of distance from the casting surface. Shape factors like circularity (F_c) and sphericity (F_s) decrease while the elongation (E) and aspect ratio (AR) increase.

A visible influence on graphite particle sphericity and circularity can be observed for the CaRE-FeSi inoculation solution and [OS-IE] standalone inoculation solution. In the casting surface layer, all inoculation solutions present a beneficial effect on graphite particle compactness. CaRE-FeSi has a more potent influence on graphite circularity and sphericity shape factors in the casting's superficial layer. For the rest of the analyzed casting body [OS-IE] standalone inoculation solution presents a potent influence on circularity and sphericity shape factors. Elongation and Aspect Ratio shape factors highlight the loss of compactness influence that CaRE-FeSi + [OS-IE] dual addition has on graphite parameters. Inoculation with CaRE-FeSi + [OS-IE] dual addition led to the formation of the highest compacted graphite formation. Oxy-sulphide inoculant enhancer standalone solution treatment created conditions for the formation of the second highest nodularity values. It can be assumed that the addition of complex [OS-IE] inoculant enhancer alloy as a standalone solution can support graphite nucleation during the solidification. This is due to the enhanced sulphur and oxygen levels in the inoculant which in combination with other active elements can create a nucleation and growth support for graphite in this types of cast irons.

4. Conclusions

- Inoculation has a visible influence on nodularity and shape factors in the surface layer of the casting and also in the casting body. At a smaller addition than CaRE-FeSi inoculant solution, [OS-IE] standalone inoculation solution proved to be a very viable alternative for inoculation triggering very similar effects on nodularity and shape factors.
- Enhancing CaRE-FeSi with [OS-IE] inoculant enhancer led to the highest compacted graphite formation tendency.
- For the 25 mm studied round bar samples the surface layer is visibly affected by the S content in the mould binder, this is highlighted by graphite nodularity of 13 – 22 % in the surface layer in contrast with 55 – 44% in the casting body for all inoculation variants tested.
- The surface layer of these MgRE-FeSi treated compacted graphite cast iron tests is strongly affected by S diffusion from the Furan resin – P-Toluol Sulphonic Acid (PTSA) binder. Values between Mg_{res}= 0.018% - 0.025% make these irons much more sensitive to graphite degeneration in the surface layer.

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