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In conjuction with ANKIROS / ANNOFER / TURKCAST fairs

«Inoculation Solutions Against Metallurgical Problems»

«Metalurjik Problemler İçin Geliştirilmiş Aşılama Çözümleri»

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7.Oturum / 7th Session
Oturum Başkanı / Session Chairman: Dr. Kazım Tur (Atılım Üniversitesi)

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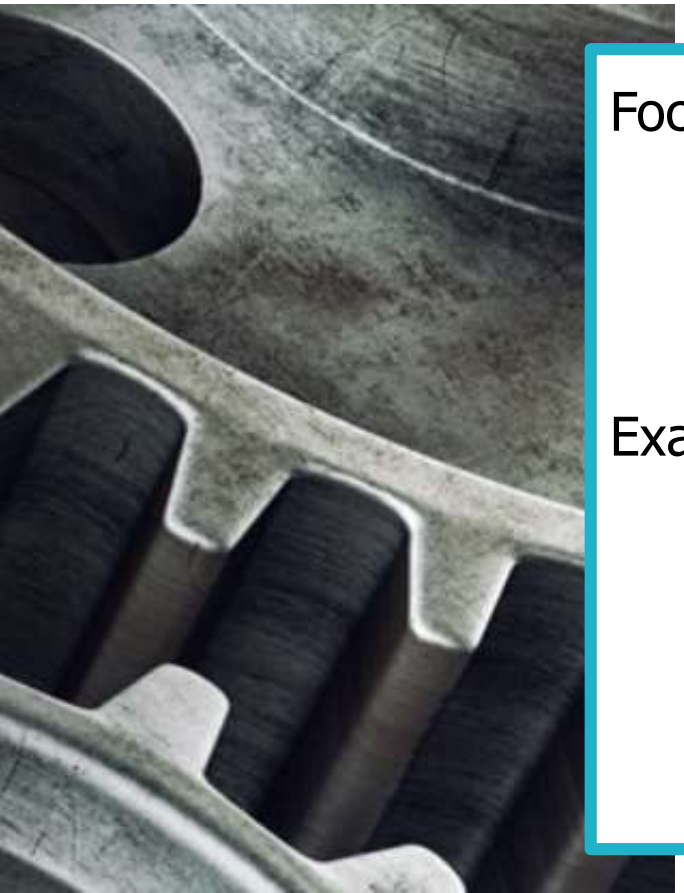
INOCULATION SOLUTIONS TO SOLVE METALLURGICAL PROBLEMS

OUTLINE



Focus on 3 elements in the Inoculation process:

- Barium (Ba)
- Bismuth (Bi),
- Antimony (Sb)

Examples of different applications:

1. Fighting chunky graphite in heavy-section castings
2. In Vertical Centrifugal castings
3. To modify Process Slag composition.

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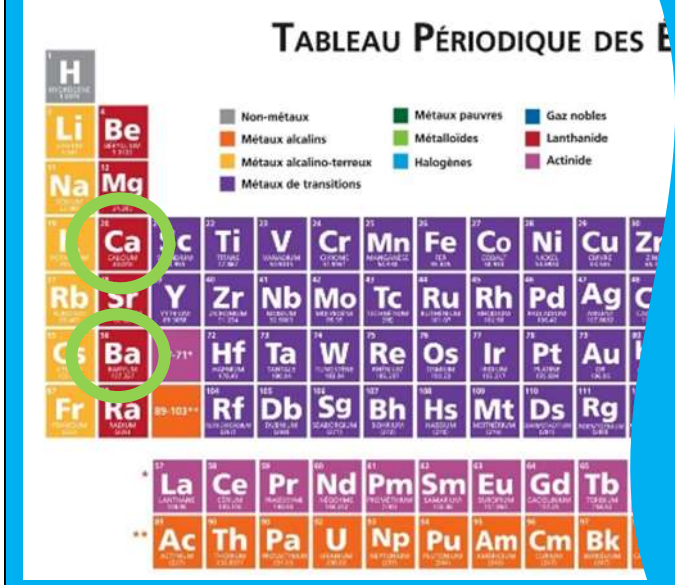
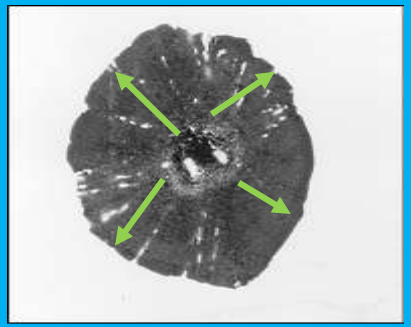
Inoculating with:
Barium, Bismuth & Antimony.

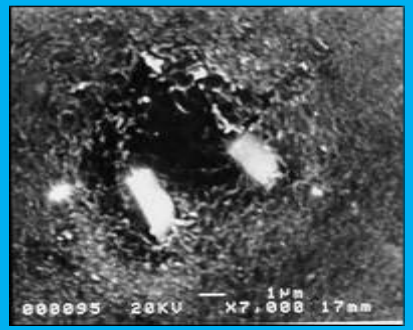
The Barium element compared to Calcium.



Barium acts in a similar way than Calcium:

- It has a strong nucleating effect.
- effect not soluble in iron.
- Higher density than Calcium.
- Vapor pressure 1MPa lower than Ca.



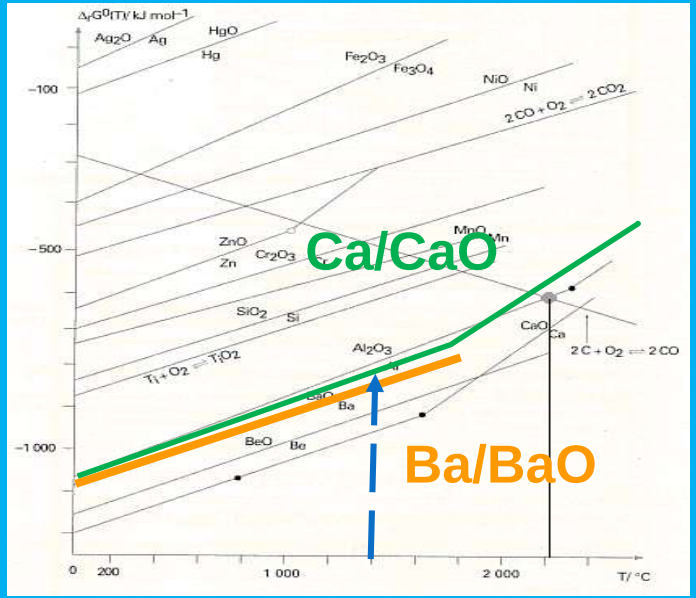


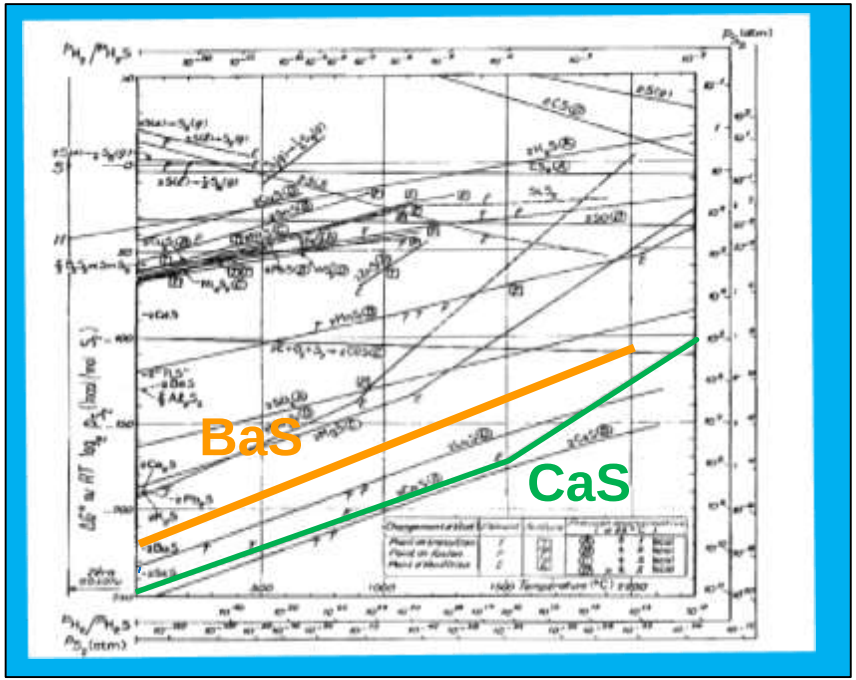
Square shape nuclei in SGI preconditioned with high-Ba grade inoculant - Atomic Ba content estimated at 40%.

Source: Internal reports.

Barium is a strong de-oxidizer & strong de-sulphurizer

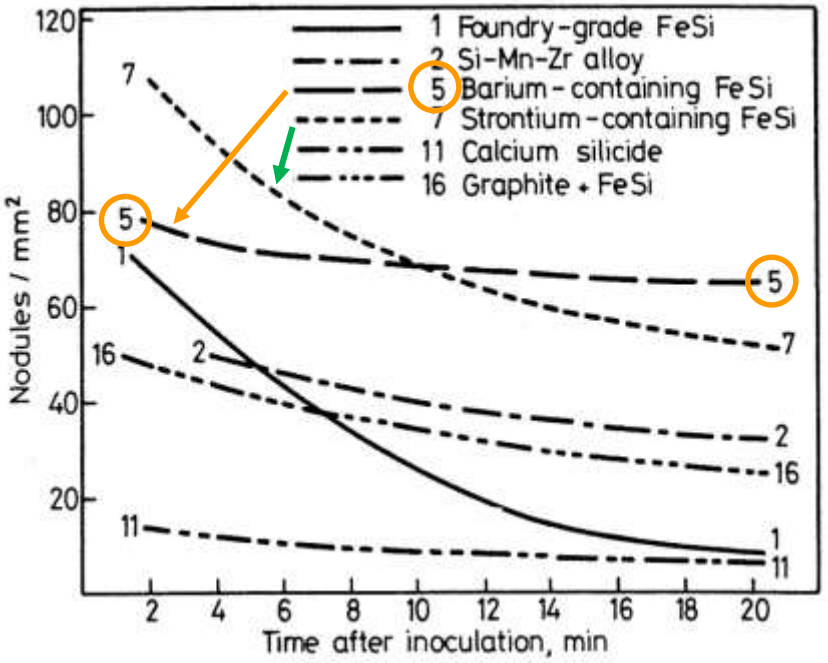
Ellingham Diagrams O /S





Those characteristics make it a strong inoculating element.

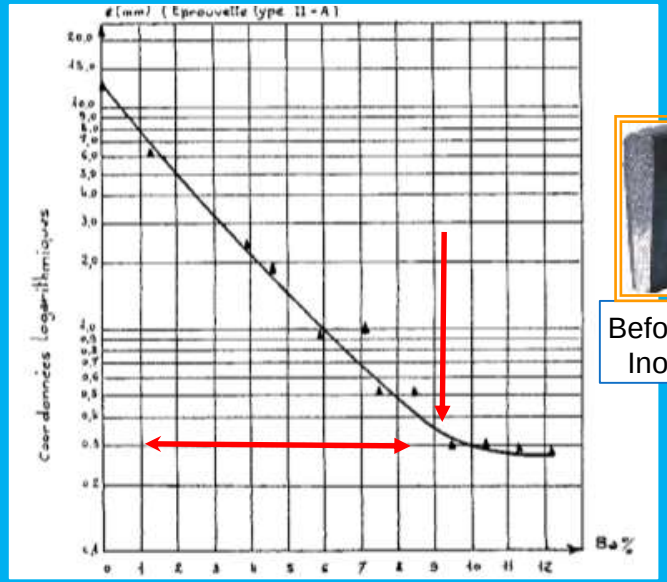
Benefits on fading time & nodule count with Inobar ®.



Fading time as compared for different kind of inoculants. The best compromise for the nodules/count vs. time after inoculation corresponds to inoculant with Barium.

Source: Communication Technique n°7 du Secrétariat International des Fontes, "Influence des impuretés sur la fonte à graphite Sphéroidal", Hommes et Fonderie, Morgan, Oct 1973

Benefits on Chill Depth

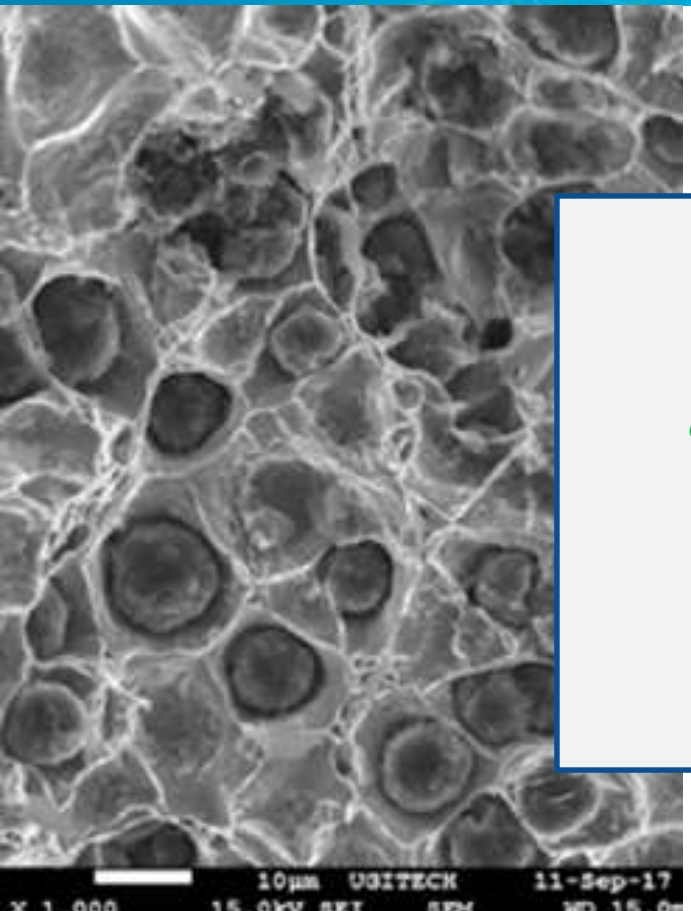


Before / After Inoculation

From 9% Ba in the alloy, Chill Depth stable at 0.3 mm

Source: "Influence of Ba on Chill Depth", JC Percheron.

A useful element in «pre-conditioning » or later in the process.



High-Ba grade inoculants Inobar ®:

65% Si, 9% Ba, 1.2% Al, 1.0% Ca

In the furnace or while tapping

In the ladle (sandwich)

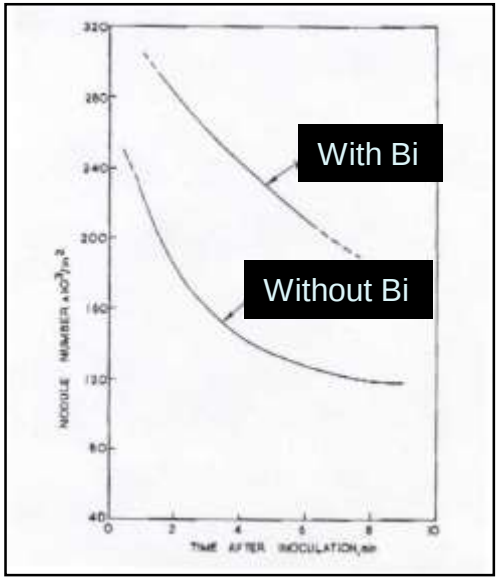
At the moulding machine (holding furnace)

Typical Sizing : 0,4 x 2 mm / 2 x 7 mm / 10 x 40 mm

Typical Addition rate : from 0,1% to 0,3% of iron.

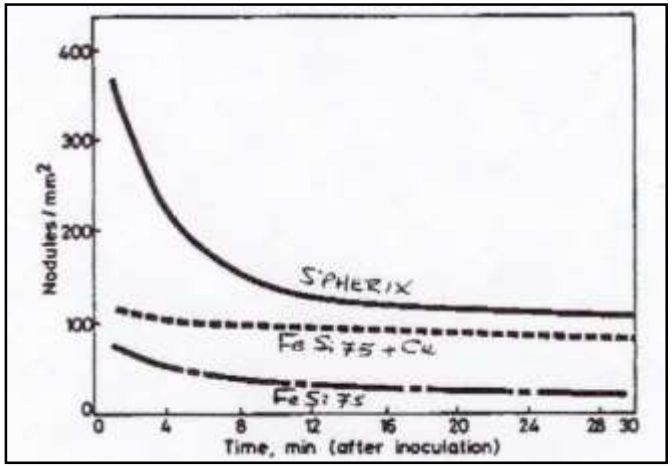
Using a Bismuth grade inoculant – Spherix ®.

Elements	Trace % /T Iron*	Main effects
Bi	> 0,002%	On it's own, it is a poison: Produces undesirable graphite forms.
	0,002% → 0,006%	With the presence of Cerium: Increases the nodule count Prevents from Chunky Graphite in thick section.

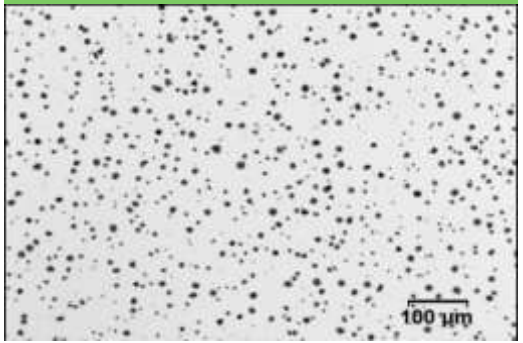


Benefits of Bi-grade inoculant on nodule count and fading in ductile iron

Source: Internal Reports.



FeSi**Bi**Re inoc – 3 mm



Using a Antimony grade inoculant – Spherix plus ®.

Sb - Amount % /T Iron*	Main effects
0,001% – 0,005%	Provided Ce is present, beneficial effect: - in promoting fully nodular structures in large-section ductile iron castings, - on the nodule count.
0,004 - 0,02%	Graphite degenerescence (without Rare Earth)
0,02 – 0,1%	Strong Pearlite promoter

Sb-grade inoculant:

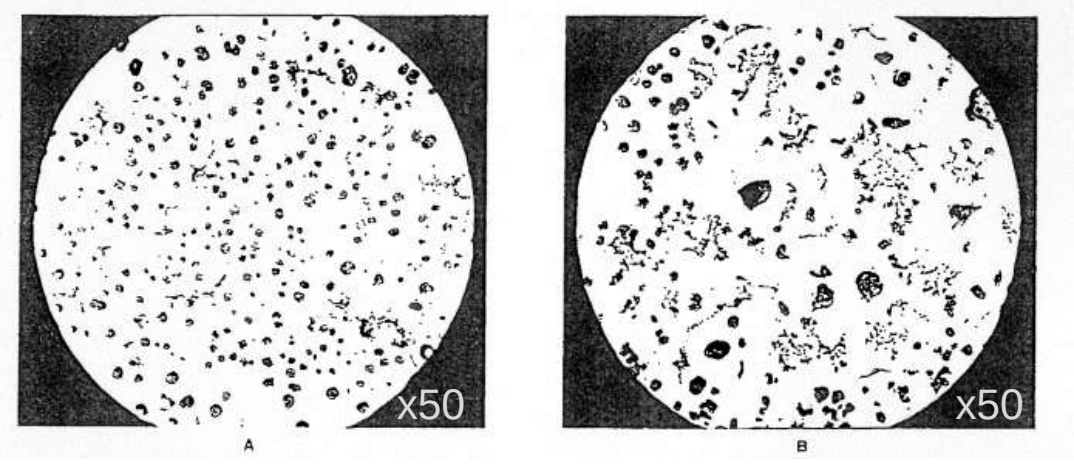
70% Si - 0,4-0,7%RE – 0,8-1,3% Sb

Typical grain sizes:

- ***0,2/0,7 mm (stream)***
- ***0,4/2 mm (ladle)***

Graphite particles in center of a cube 200 mm-side,

- ***A = 0,0005% Sb (presence of Ce)***
- ***B = no Sb (presence of Ce).***



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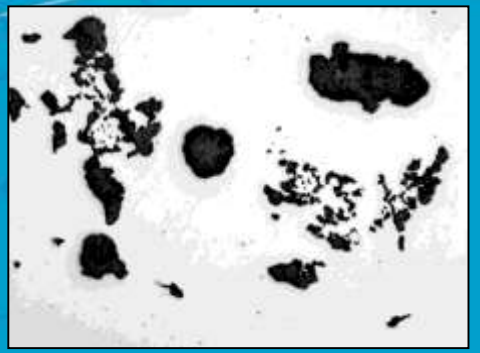
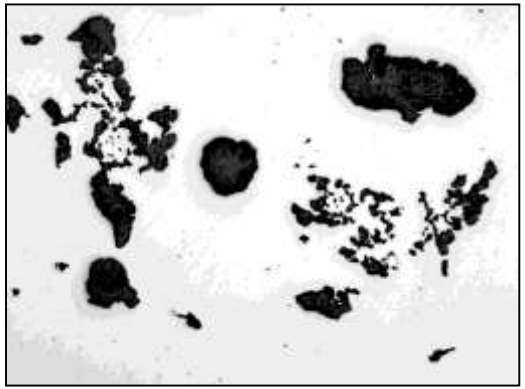
Inoculation solution against Chunky Graphite in heavy sections castings.



Fighting chunky graphite in heavy-section castings.



POSSIBLE DEFECT INITIATION:

- Castings with very slow cooling rate (ex: heavy sections castings >25 mm).
- Excess of Rare Earth in Iron, with high purity raw materials.
- High purity charge materials in hypereutectic compositions even when no Ce-Mischmetal is added.
- Possible in graphite flotation area.
- Possible after high rate of inoculation.

LOCATION:

- **Thermic center of heavy sections castings**
- **Non apparent defect**
- **Visible only after machining**

CONSEQUENCES:

Serious decrease of mechanical properties (tensile strength and elongation).

Fighting chunky graphite in heavy-section castings

The FOUNDRY

- Jobbing foundry
- Medium frequency Induction furnace.
- 7 tons-casting - Pump housing
- Grade EN GJS 600-18.

The PROCESS:

Nodulisation: Sandwich treatment with FeSiMg 7% Mg, 3% Ca , 1% RE.

The PROPOSED INOCULATION:

- Preconditioning: FeSi 65 bearing 10% Ba (0,3% of liquid iron weight) – Inobar ®
- Late inoculation: during mould casting with a Sb/RE-bearing inoculant (0,15% of the liquid iron weight). Spherix plus ®

- Heavy Section
- Presence of Chunky graphite.

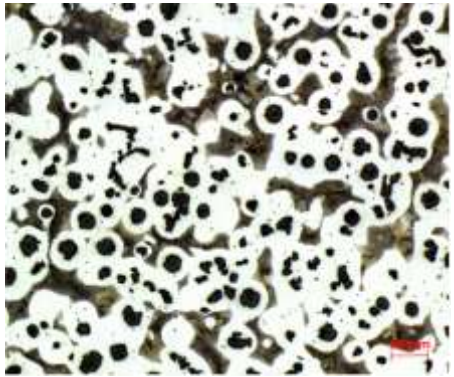
Microstructure checked on a vent attached to the castings.

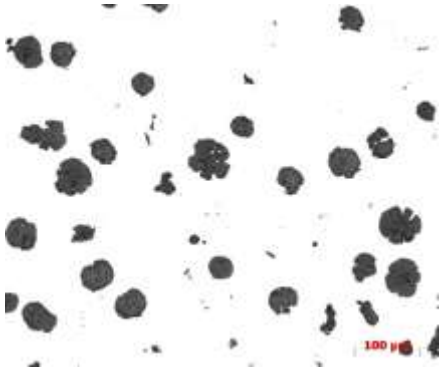
Before

Result after the use of:

- High-Ba grade inoculant – Inobar ®
- Sb/RE - bearing inoculant – Spherix plus ®

After





- Nodule count: 303 /mm²
- Nodularity: 91%
- No Chunky Graphite.

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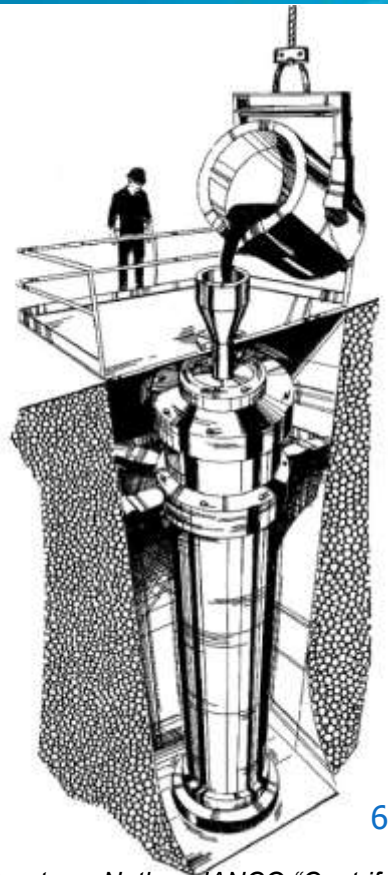
Inoculation Solution for Vertical Centrifugal Cast Iron

Vertical spincasting process of bi-metallic rolls for steel mills

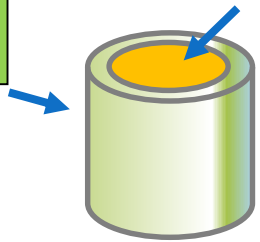


Courtesy: Nathan JANCO "Centrifugal Casting" AFS.

Finished weight: 15 to 40 tons
Roll diameter: 600 to 1200 mm

Shell metal: High Cr Iron or Steel

= Wear Resistance Properties



Nodular iron core

= Mechanical Properties

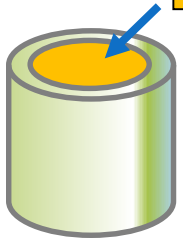
The Process in 3-steps:

1. Shell metal (high-Cr iron or steel) is poured at high-speed.
2. Shell metal starts to freeze under centrifugation.
3. Core metal is poured while shell metal is not completely freezed to have a correct bond at the interface.

A Process with Risks for Nodular Iron

Shell metal:
High Cr Iron or Steel

Nodular iron core



Process for the shell Iron:
Induction Furnace 20t

Process for the core iron:

- Electric Arc Furnace: Capacity 60t
- Nodulisation in the ladle: FeSiMg 5% (sandwich method)

Element in %	C	Si	Mn	P	S	Ni	Cr	Mg
Min	3,1	2,4	0	0	0	0	0	0,05
Max	3,2	2,5	0,2	0,035	0,015	0,5	0,01	0,07

Element in %	C	Si	Mn	Ni	Cr
Min	2,7	0,7	0,9	1,3	16,4
Max	2,8	0,8	1	1,4	16,6

The process gives difficult conditions for SG iron:

1. Heavy-thickness casting (1000mm)
2. Presence of Cr, Ni (rewashed elements from the shell)
3. Long pouring time: 20 min

Risk of degenerated graphite forms / Chunky graphite
Risk of Carbides formation in the center

Inoculation Practice – Before & After.

Previous inoculation Practice:

With a classical low Barium inoculant in ladle.

Split in two parts during heat treatment. Low mechanicle properties of the core.

Carbides in the core material (heart of the casting).
To be linked to the high Cr-content and poor inoculation practice.

Successful inoculation Practice:

1. Preconditioning in the treatment ladle with Inobar® high Barium (0,15% of liquid iron):
   - ✓ Long fading time
   - ✓ Will allow the inoculation effect to last

2. Stream inoculation with Spherix® Bi/RE-grade inoculant (0,15% of liquid iron):
   - ✓ Powerful inoculant
   - ✓ Fights carbide formation
   - ✓ Beneficial for graphite nodularity

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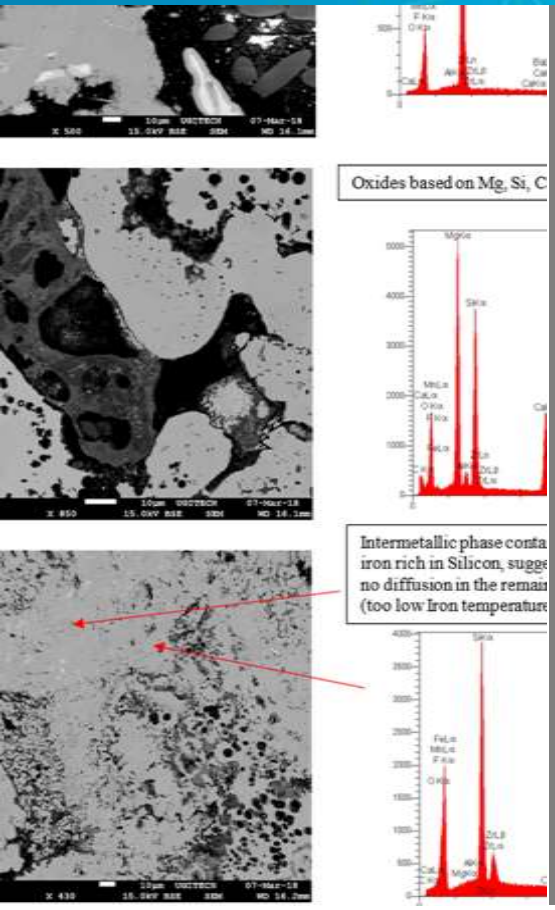
High-Ba Inoculation to modify Process Slag composition

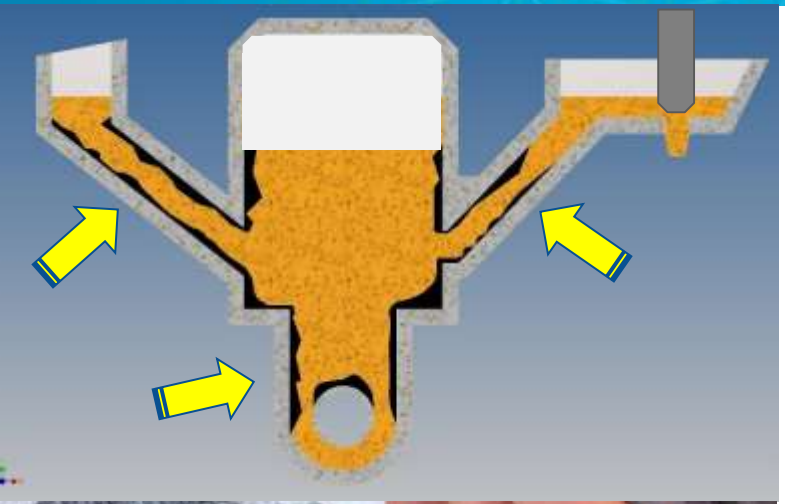
Why focus on Slag Buildups ?



- Slag will always be generated. It is a combination of FeO, SiO_2, Al_2O_3, MgO, CaO …
- Slag impacts:
  - Melting furnaces (coreless induction)
  - Cupolas (in the iron receiver)
  - Holding furnace
  - Ladles (tundish ladle pocket)
  - Pouring furnaces
- A pressure pour furnace can, in some cases, be stopped for 4 hours every 7 shifts.
  => 7% loss on Equipment Efficiency Ratio of the Moulding line.

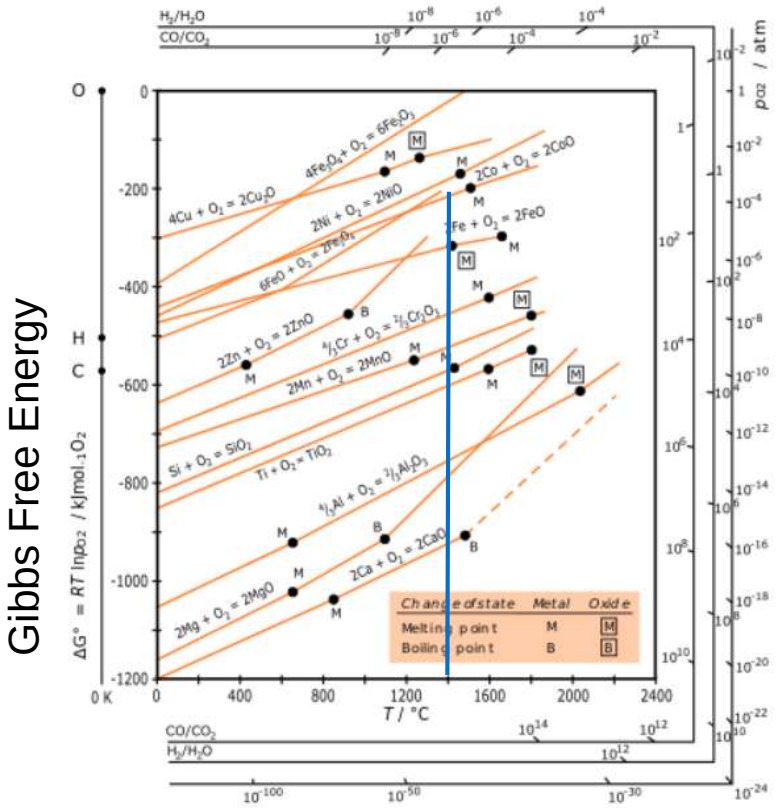
Shifts

How do Slag Buildups appear ?



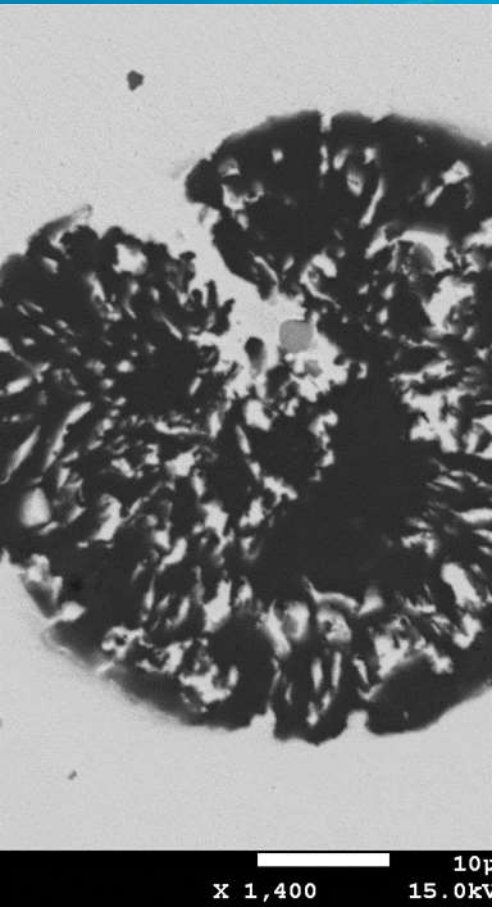
- We are focusing on the buildups, not the floating floating slag.
- Slag buildups appear when:
  1. The slag's temperature is lower than its melting point.
  2. When the compounds in the slag are the most stable.
  3. When the compounds are dense enough not to float quickly.

How to evaluate Stability of the Slag's Compounds ?



- The Ellingham Richardson diagram helps us to predict the oxides that are the most « stable » at a given temperature.
- This type of diagram is also available for sulfides and nitrides.

Density & Gibbs Free Energy of Slag Components



Density (kg/m³)		Gibbs Free Energy of formation at 1500°C
Ce_2O_3	7 220 kg/m3	-210 Kcal/mol
La_2O_3	6 510	-205
BaO	5 720	-205
FeO	5 240	- 60
Ce_2S	5 100	-180
Al_2O_3	3 950	-175
MgO	3 580	-180
CaO	3 350	-210
MgS	2 680	-100
CaS	2 580	-170
SiO_2	2 200	-140

The most heavy and most stable oxides and sulfides are to be controlled.

The Use of Barium in Iron Preconditioning

Barium has a higher **affinity for O and S** than Mg and Al.

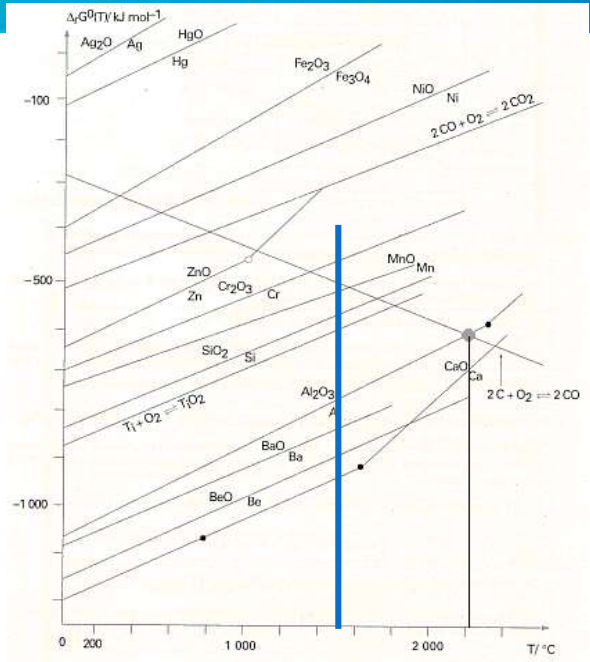
1. It reacts first !
2. **Decreases** the amount of **harmful compounds** such as MgO, Al2O3 in the slag.
3. Acts as a **fluxing agent.**

Resulting slag is easy to remove, it's the Pop-corn effect:

– « **dry** » and not liquid (better separation iron/slag),
– does not stick to the refractories walls
– Lower Specific Weight = will **float** on surface, easy to catch.

Preconisation of use:

Addition of **Inobar®** direct in the Furnace or on top of FeSiMg alloy (typical addition rate: 0,3-0,4%)



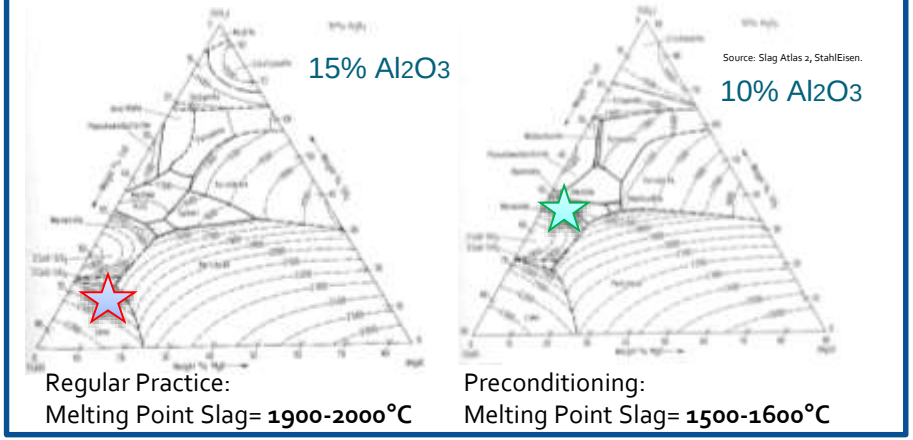
Slag sample with Ba-preconditioning

Slag sample without Ba-preconditioning

What happens when high Barium inoculant is added.

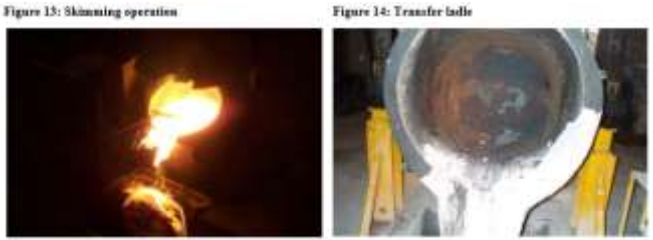
	Regular Practice			0,3% Ba-Preconditioning		
	A	B	C	X	Y	Z
Al_2O_3	17.2	13.3	17.2	8.3	7.6	7.4
BaO	1.05	0.8	0.7	9.8	11.9	10.5
BaS	0.9	1.1	1.8	1.7	1.6	2.1
CaO	11.6	11.8	14.1	14.9	13.7	13.3
MgS	2.61	2.61	3.16	1.31	0.7	2.75
MgO	14.7	14.1	11.3	8.3	8	9.7
SiO_2	15.1	11.7	11.3	31.6	31.8	29.6
La_2O_3	0.5	0.5	0.6	1	1.1	1.2
CeO_2	0.6	0.6	0.7	1.8	2.1	0.8
TR_2O_3	0.3	0.3	0.4	0.9	1	0.4
Fe_2O_3	8.4	12.7	12.3	6.7	7.8	7.1
K_2O	0.03	0.06	0.0542	0.4821	0.2892	0.0325
MnO	0.28	0.3	0.25	0.19	0.23	0.31
C	2.05	2.39	3.36	2.79	2.80	3.26
Iron	24.3	27.4	22.7	9.9	12.1	11.2
Sum	99.62	99.66	99.92	99.67	99.91	99.65
Slag %	75.32	72.26	77.22	89.77	87.81	88.45

Reference: Preconditioning Effect of Barium in Ductile Iron Production, J. Fourmann. Proceedings of the AFS Cast Iron Inoculation Conference.



Regular Practice:
Melting Point Slag= **1900-2000°C**

Preconditioning:
Melting Point Slag= **1500-1600°C**



When INOBAR ® is used:

- ✓ The % Barium oxides increase
- ✓ The % Alumina reduces
- ✓ The% MgO reduces

Leading to 400°C decrease in melting temperature.

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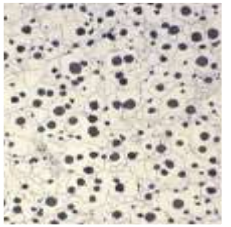
Conclusion.

Conclusion.



9% Barium inoculant: Inobar® – especially used as an iron preconditioner:

- Beneficial for consistency and fading time.
- Useful to guarantee a long lasting inoculation effect, even with long pouring and solidification times on heavy section rolls cast by spincasting process.
- Indirect but beneficial impact on slag nature modification to delay slag build-up formation.

Bismuth/RE: Sphérix® inoculation:

- Beneficial for graphite nodularity
- Beneficial to fight carbides in thin castings but also in the heart of the heavy section spuncast rolls.

Antimony/RE: Sphérix plus® inoculation:

- Usefull in heavy section ferritic castings for graphite nodularity & nodule count (windmill parts, pumps…).

Ferroglobe

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