Ferroglobe

# A NEW INOCULANT TO SOLVE MICROSHRINKAGE POROSITIES IN NODULAR IRON CASTINGS.

In collaboration with:

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METALLURGY RESEARCH CENTRE

# About Ferroglobe

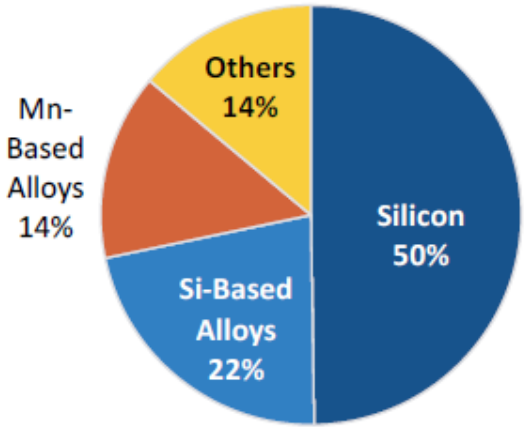
# ABOUT FERROGLOBE

## WHO WE ARE

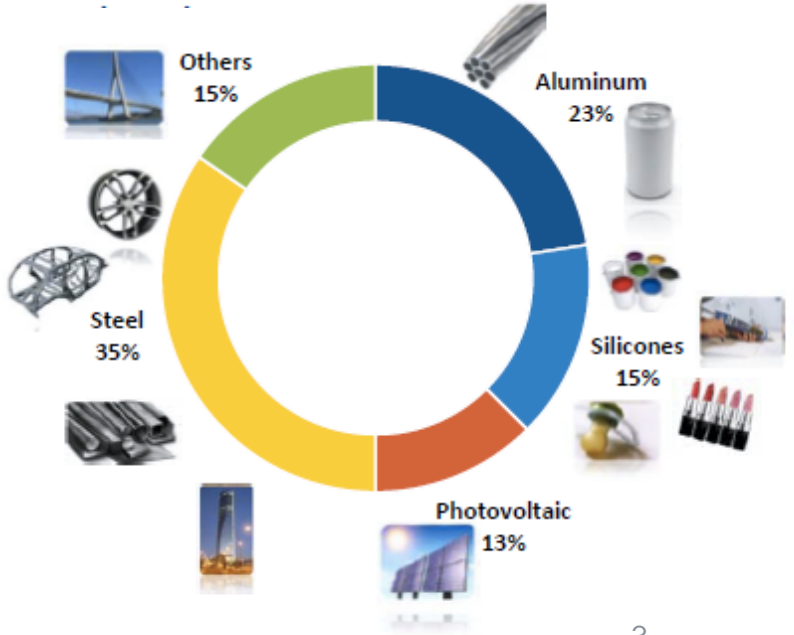
- The company is the largest merchant producer of **silicon metal** in the Western World, and a leading global producer of **silicon-based alloys** and **manganese-based alloys.**
- Ferroglobe PLC is **registered in London.**
- Listed on NASDAQ stoke market: **GSM**, with Market Cap. of $1.3B*.
- We **employ 3000 people.**

**as of 26/04/2022*

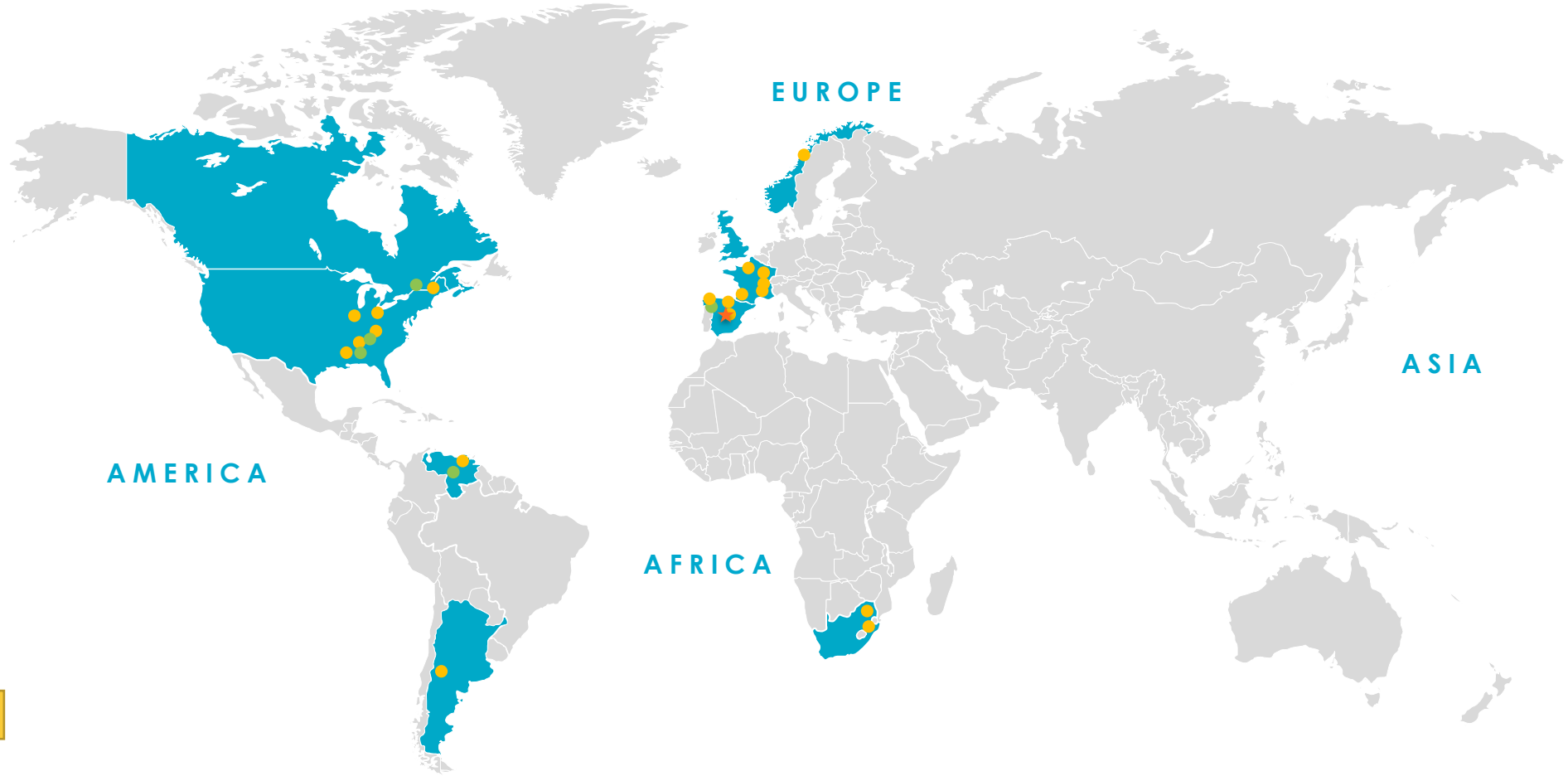
**Revenue by Product[1]**




**End Markets**



# FERROGLOBE
# INDUSTRIAL FOOTPRINT




- HQ
- Mine sites
- Metallurgy plants

- Leading manufacturer of **environmentally responsible metals** and materials with more than **120 years of experience.**
- We operate **25 electrometallurgy production centers** on four continents with **69 furnaces worldwide**.
- We serve our **customers worldwide**, providing prime quality, supply reliability and technical support around the world.

# Inoculation in Nodular Iron

# THE ROLE OF ACTIVE ELEMENTS

**Base metal** and the **type of inoculant** have a big influence on the castings.

They will have **an impact on:**

- Ferrite/perlite matrix %
- Carbides
- Nodule count
- Pinholes
- Shrinkage
- Mechanical properties.

The inoculant must be **chosen** according to the **goal to reach**.

| Product | Active Element | Features |
|---|---|---|
| **LMC® INOCAST® 175** | Ba | Universal inoculants for general use |
| **ZL 80® INOCAST® 125 ZIRCOGRAF® ZIRCOBAR®** | Zr | Universal inoculants, fade resistant, appreciated for medium and heavy sections |
| **INOCARB®** | Graphite | Avoids chill in grey iron castings, re-activating nucleation |
| **INOCAST® 100** | Al | Avoids chill |
| **SPHERIX®** | Bi + RE | High nodule count, reduces chill in thin wall castings, reduces chunky graphite in heavy sections |
| **SPHERIX® Plus** | Sb + RE | High nodule count, reduces chunky graphite in heavy sections |
| **AMERINOC®** | Bi + RE | High nodule count, reduces chill in thin wall castings, reduces chunky graphite in heavy sections |
| **INOSEL** | Se + S | Self-feeding ability, long lasting graphite expansion, reduces micro porosity |
| **CERINOC®** | Ce | Minimizes the risk of shrinkage, improves nodularity, recommended for compacted graphite iron |
| **FESILA®** | La | Against micro shrinkage |
| **WIN 4®** | Bi + La | High nodule count, reduces micro shrinkage |

# WHY SELENIUM ?

Those **active elements combine mainly** with:

- Oxygen
- Nitrogen
- Sulphur.

These **complex particles** will generate **starting points** for **graphite nodules.**

**Riposan & al.** in his paper shows the role of Sulphur in the melt to form various **sulfides.**[1]

But **Sulphur has some drawbacks** when it comes to Mg treatment and should be used with limited amount.

**Table 1.** Influence of %S in the base iron on the nuclei of SG for Mg-treated iron, adapt from [16].

| %S in Base Iron | Nucleus Shape | dia. (μm) | Main Compounds | Other Compounds |
|---|---|---|---|---|
| 0.0022 | rectangular | 0.5–1.0 | (Mg,Si,Al) N | MgS, MgO, (Ca Mg) S |
| 0.0052 | spherical | 0.5–1.0 | (Mg,Ca) S | MgO, (Mg,Si,Al) N |
| 0.013 | spherical | 0.5–1.0 | (Mg,Ca) S | MgO, (Mg,Si,Al) ON |
| 0.050 | spherical | 1.0–2.0 | (Mg,Ca) S | MgO, (La,Ce,Nd) S |
| 0.072 | spherical | 1.5–5.0 | (Mg,Ca) S | MgO, (La,Ce,Nd) S |
| 0.083 | spherical/faceted | 1.5–5.0 | (Mg,Ca,Mn) S | MgO, (La,Ce,Nd) S |

**Table 2.** Properties of some elements from group 16 of the periodic table.

| Properties | Sulfur | Selenium | Tellurium |
|---|---|---|---|
| Density (kg/m$^3$) | 1960 | 4790 | 6240 |
| Structure | orthorhombic | hexagonal | hexagonal |
| Melting Point (K) | 388.36 | 494 | 722.66 |
| Boling Point (K) | 717.87 | 957.8 | 1261 |
| Specific Heat (J/Kg·K) | 710 | 320 | 202 |
| Thermal Conductivity (W/k·m) | 0.269 | 2.04 | 2.35 |

We decided to **investigate** the inoculating properties of Selenium [2]

# The Selenium Inoculant

# THERMAL ANALYSIS 1/2.

An inoculant can be defined by its **ability to create graphite** (rather than carbides).

This is influenced by:

- The base metal **chemistry**
- The **inoculant** type
- The **metal's life**.

**Nodule count** is a good indication, but thermal analysis also gives **precious information.**

**Furnace holding time** has great influence on the **graphitization capacity.**

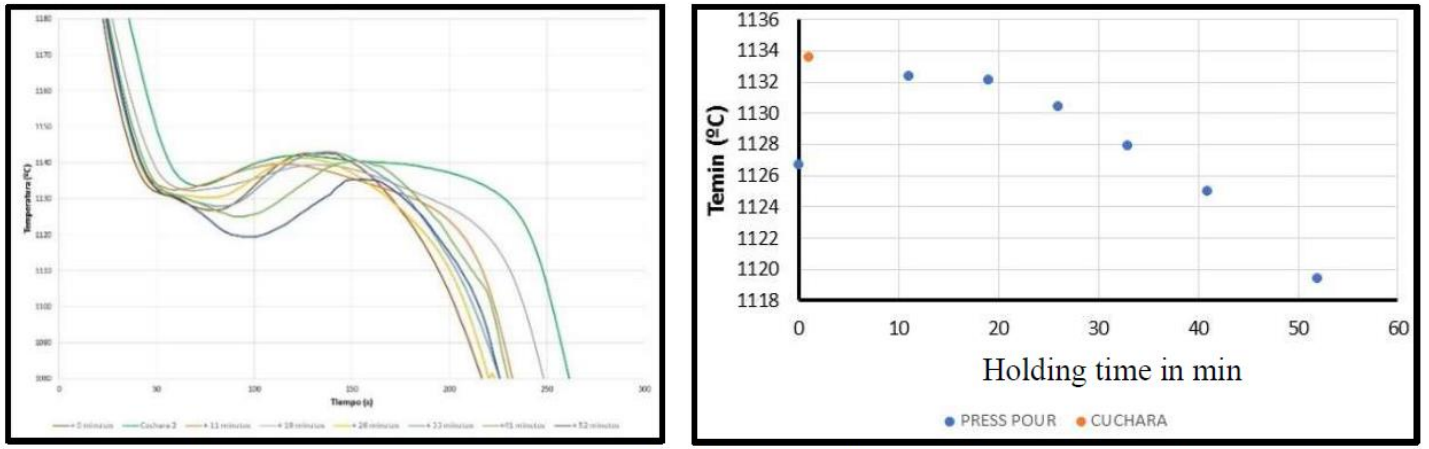



Figure 2. Variation of metallurgical quality of the metal and its evolution with the time inside the vessel.

As metal is maintained in a press pour furnace, **TEmin decreases** showing that the **graphitization potential weakens**.

# THERMAL ANALYSIS 2/2.

Running trials with selenium treated inoculant, we see that:

- The **solidification plateau** is longer,
- The **cooling rate after the plateau is steeper.** Meaning that **CR max (derivate value) is high** (3 degrees /sec 2).

This would indicate a **good ability to self-feed** any shrinkage or micro-shrinkage.

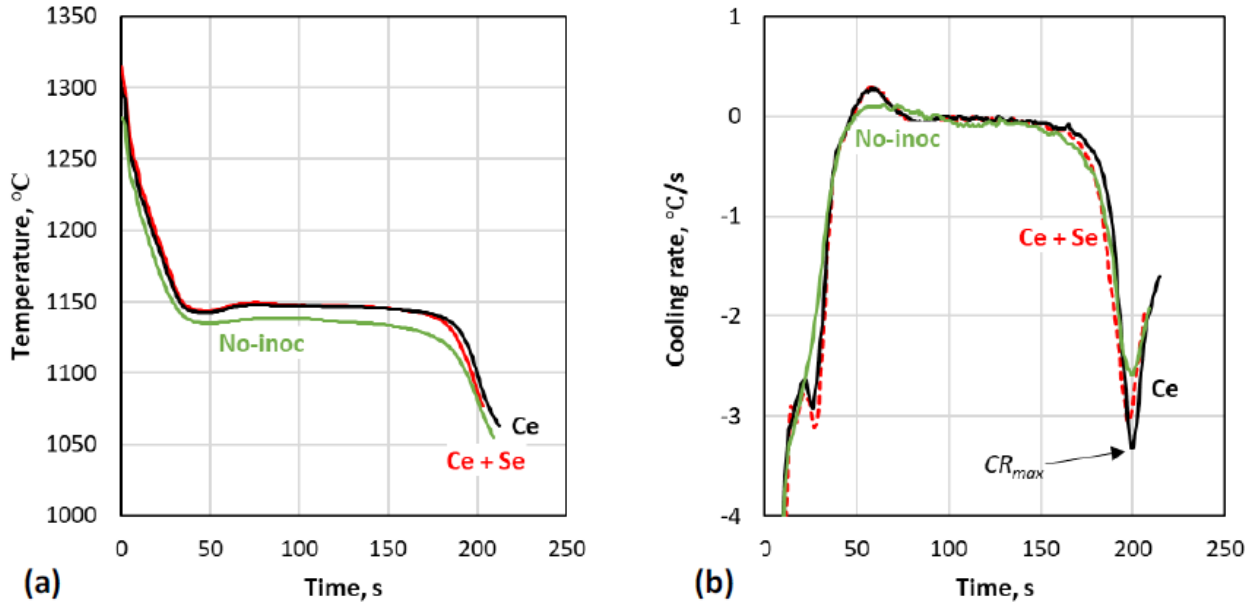



**Figure 2.** Cooling curves (**a**) and their first derivatives (**b**) from Heat 2 showing the effect of inoculation in increasing the maximum cooling rate, CRmax, at the end of solidification.

The Selenium provides self feeding ability.

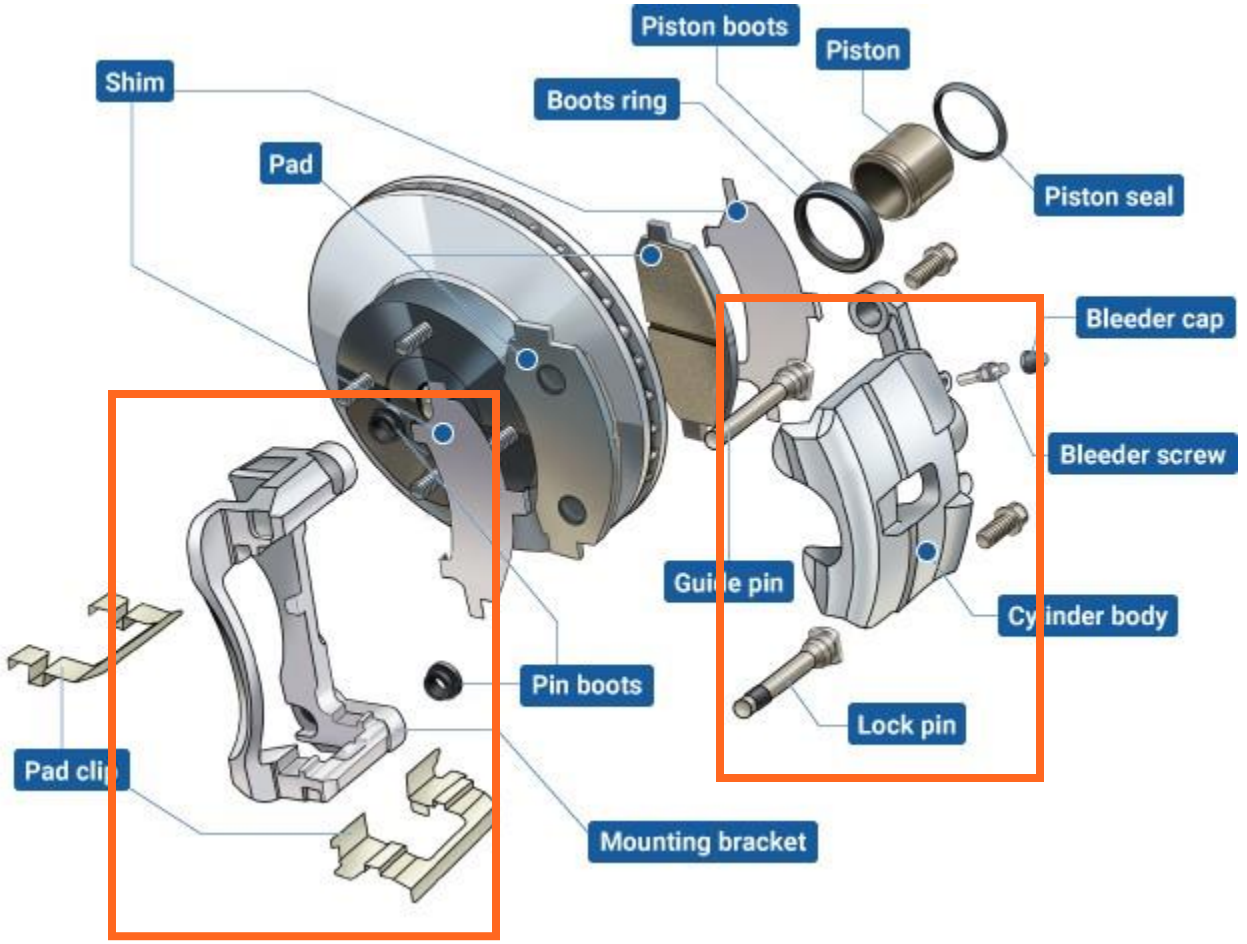
# Industrial Trials

# TWO TYPES OF SAFETY CASTINGS.

The chosen castings tend to show some **microshrinkage cavities in different areas.**

Those are caliper body and holder (fig.)

They are cast in **EN GJS 500-7 nodular iron** and are **safety parts.**



# PARAMETERS OF THE USUAL PROCESS (1/2).

The **base metal** before inoculation is as shown (table 1).

| C | Si | Mn | Mg | S | P | Cu |
|---|---|---|---|---|---|---|
| 3,70-3,8 | 2.0-2,4 | 0,3 | 0,035-0,04 | 0,003 | 0,017 | 0,35 |

Table 1. Chemical composition.

The inoculant used is a **Rare Earth based inoculant**.

The **magnesium treatment** is done with 12kg/MT of iron of a 6%Mg & 1,2% RE using sandwich method.

| | | | | |
|---|---|---|---|---|
| **Caliper body** | **Pouring Temperature** | **Pouring time** | **Flow rate** | **Stream Inoculation** |
| | 1390-1410ºC | 10 sec | 4Kgs/sec | 0,2% |
| | **Pouring Temperature** | **Pouring time** | **Flow rate** | **Stream inoculation** |
| **Anchor** | 1400 - 1420 | 7 sec | 3,5kg/sec | 0,2% |

Table 2. Production parameters.

The metal is cast from a **press pour induction furnace.**

Stream Inoculation 0,2% with an inoculant of these characteristics.

| Si | Ca | Al | Ba | Mn | Zr | Sr | TR |
|---|---|---|---|---|---|---|---|
| 70-75% | 0,75-1,25 | 0,75-1,25 | - | - | - | - | 1,5-2 |

Table 3. Stream Inoculant.

# RESULTS WITH THE USUAL PROCESS.

As already mentioned, **the X-ray controls** show some shrinkage in various part of the castings (fig 3).

**Cavities** represent **231** and **161 mm³** on each casting.

**Nodule count** are distributed as shown.

The **nodule size** are mainly from **15-25 microns.**

**Nucleus** are mainly MgO and complex Sulfides.

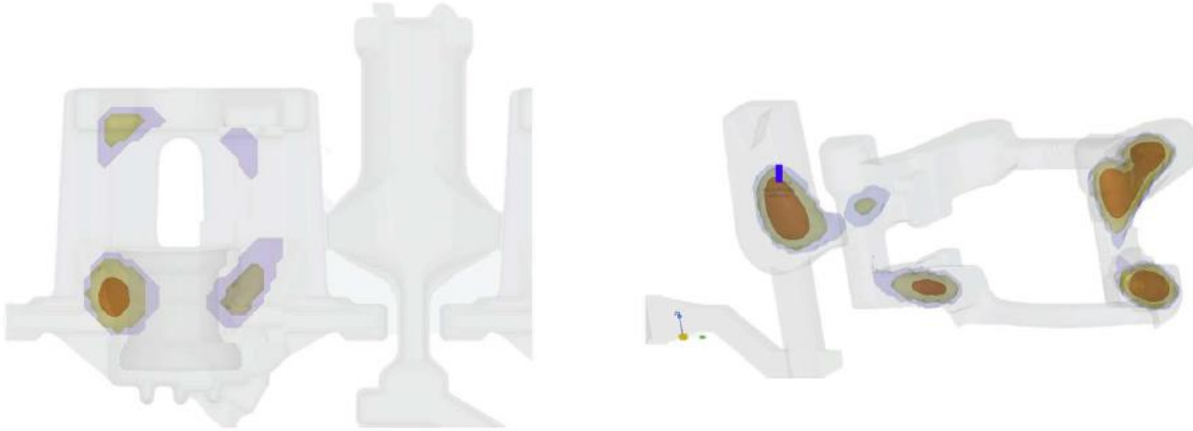
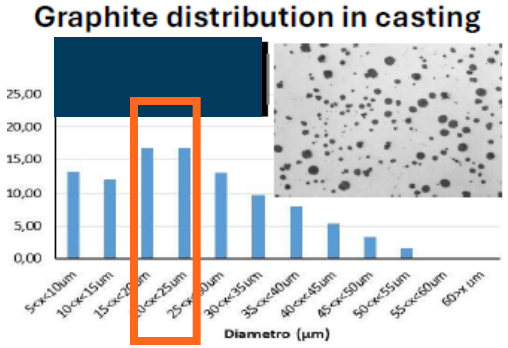
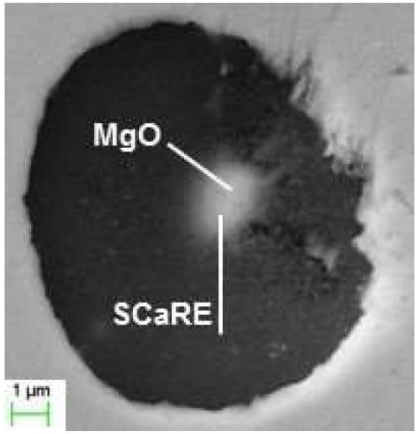


Figure 3. Cross section of a caliper and a holder in DI showing the different feeding isolated areas. Courtesy of Kasandra® software.




***100% RX DETECTABLE***

Nod/mm2: 220



# THE NEW INOCULANT.

We have seen that **Sulfur and Selenium** are important to :

- **create Sulfides and Selenides** (Ellingham chart),
- improve **self feeding** (plateau length & CR max).

**A new inoculant has been designed** with the usual Si, Ca, Al, Ce and **with S + Se** (table 4).

The **exact amount** of Sulfur and Selenium are **not disclosed**.

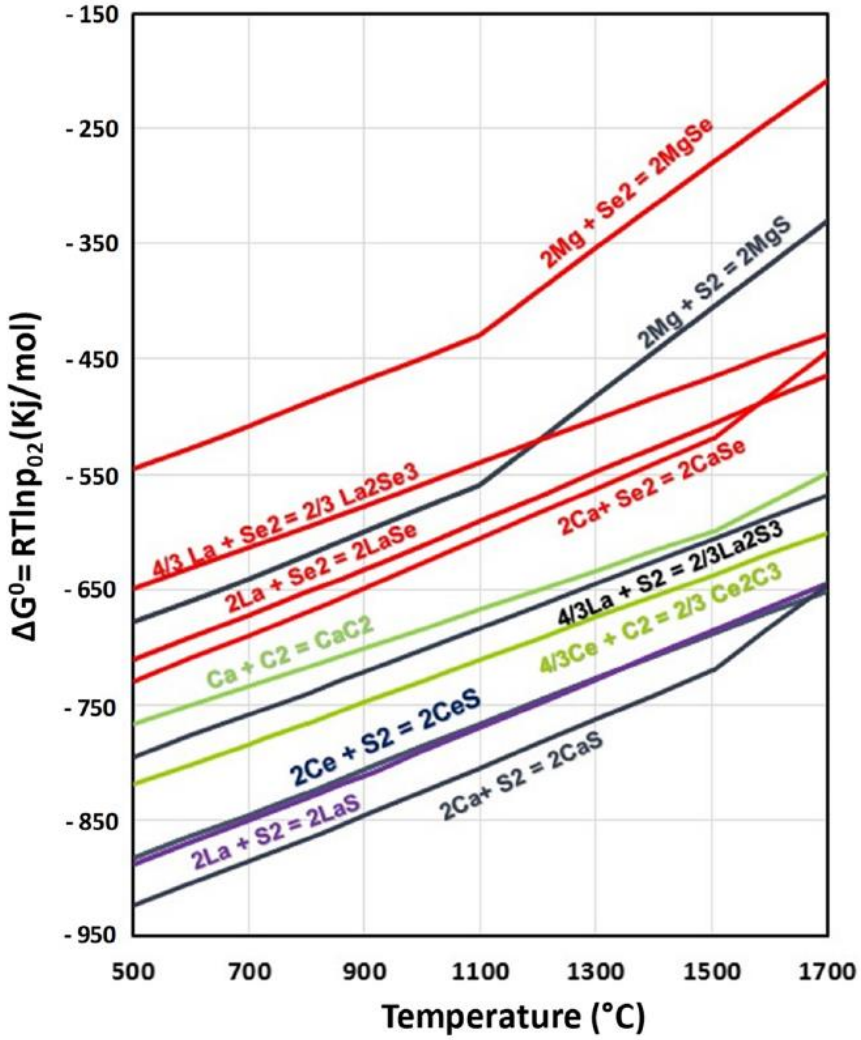



**Figure 9.** Standard free energy of formation of some selected sulfides and selenides.

| Si | Ca | Al | Ba | Mn | Zr | S | Se | RE |
|---|---|---|---|---|---|---|---|---|
| 70-75 | 0,75-1 | 0,7-1,2 | - | - | - | A | A/10 | 1,5-2 |

Table 4. Chemical composition of the new preconditioner/ inoculant (%).

# RESULTS WITH THE NEW PROCESS (1/3).

Total **shrinkage volume** reduction.

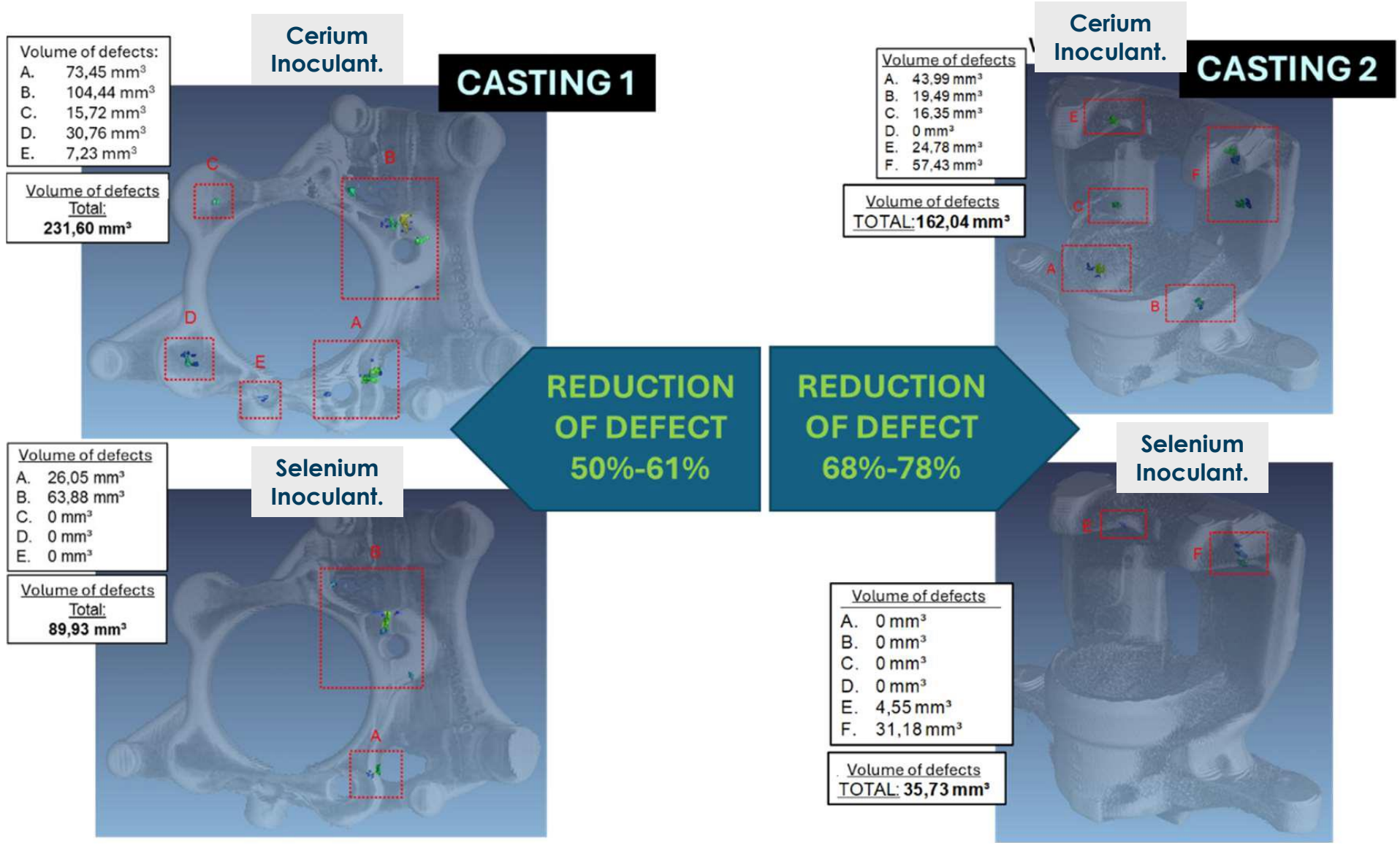
**Casting 1:**

- Dropped from 231 $mm^3$
- To 89 $mm^3$.

**Casting 2;**

- Dropped from 162 $mm^3$
- To 35 $mm^3$.

Some porosities have completely disappeared.



# RESULTS WITH THE NEW PROCESS (2/3).

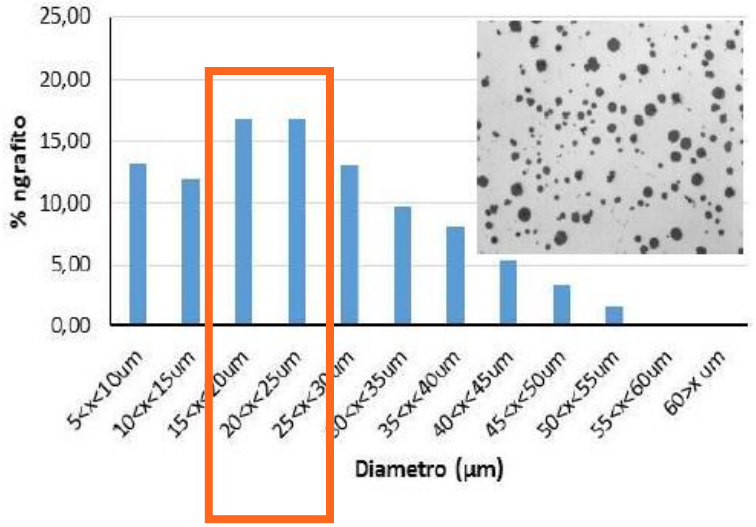
**Nodule count distribution** shows that most nodules have **reduced in size.**

This is linked to the **long graphitization plateau** seen on the thermal analysis.

Small size graphite nodules **appeared late** in the cooling stage.

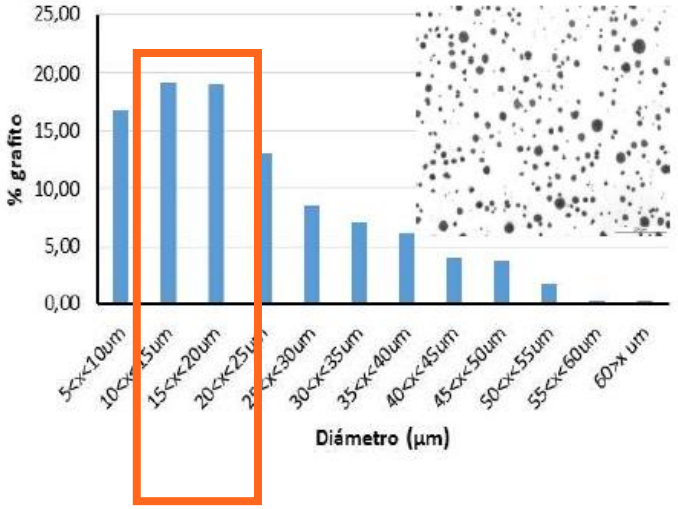
These will fight shrinkage with **graphite expansion.**

**Cerium Inoculant.**




The **nodules size** are mainly from **15-25 microns.**

**Selenium Inoculant.**




The **nodules size** are mainly from **10-20 microns.**

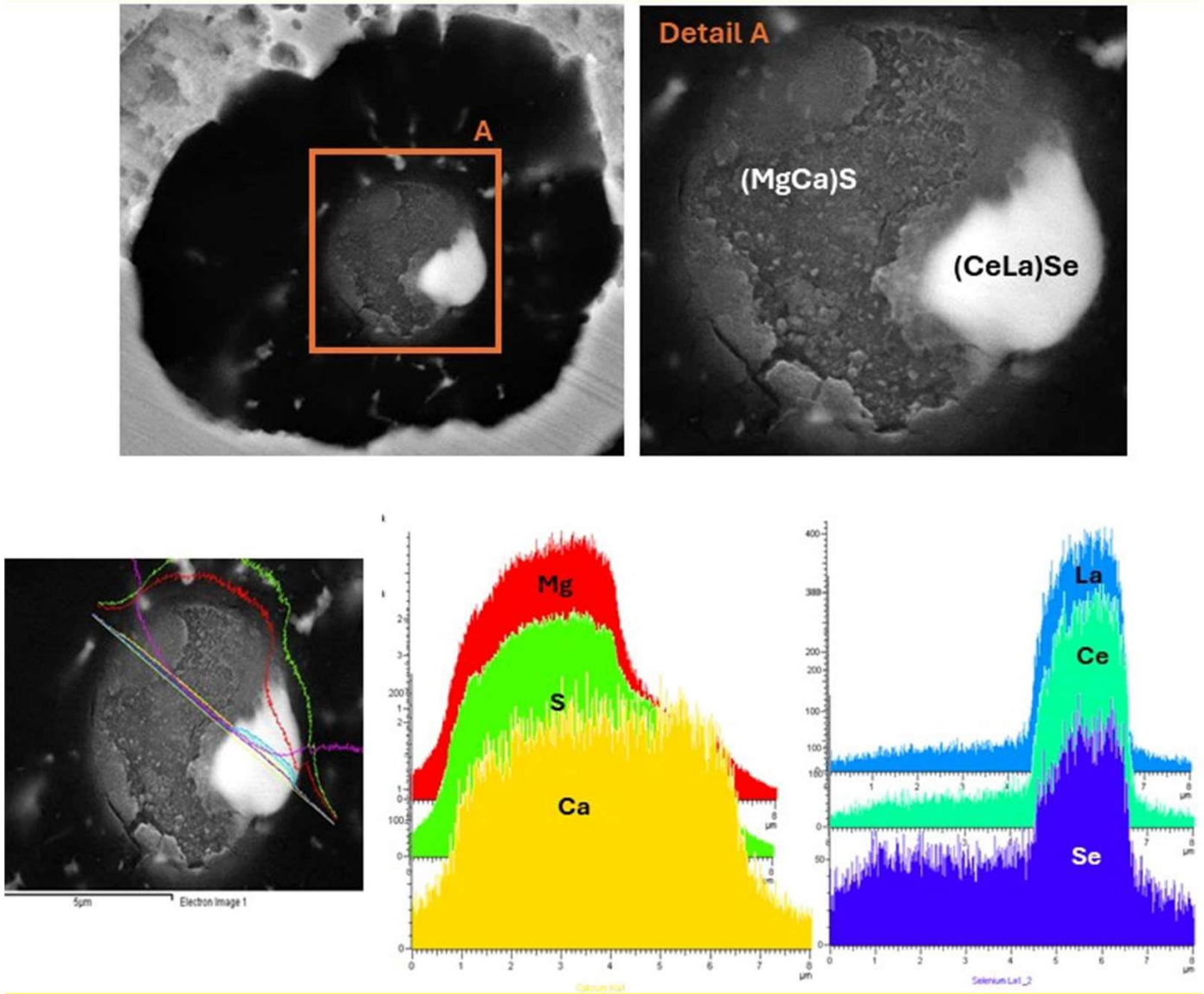
# RESULTS WITH THE NEW PROCESS (3/3).

The micrographs are obtained by looking at some nodules with a **SEM microscope.**

We see **complex nucleus formed** by:

- **Sulfides**
- **Selenides.**

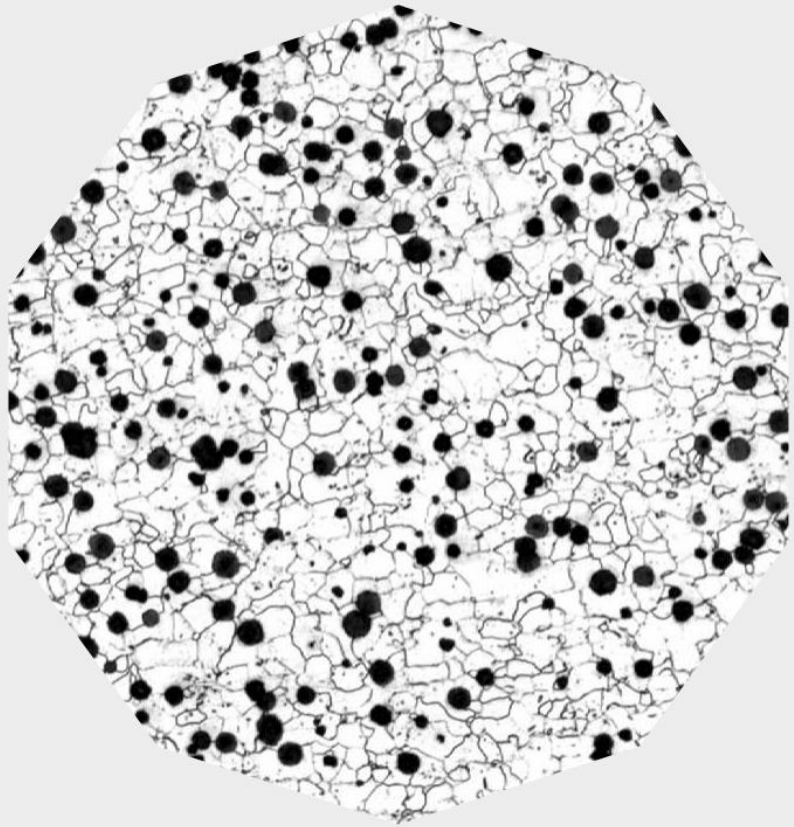
The **line scan** show that they both **play a role** in the graphite formation.



# OUR PRODUCTS

https://www.ferroglobe.com/static-files/f5c1fc51-59ff-447b-9ace-bbfe8833ad83

| Product | Grey Iron | Ductile Iron | Universal | Thin Wall | Heavy Section | Various Sections | Against Chill | Nodule Count | Against Shrinkage | Fading Time | Preconditioning | High Dissolution | Porosities N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GRAFIDIN® | | • | • | | | • | • | • | | • | • | • | |
| INOBAR® | • | • | • | | •• | • | ••• | •• | •• | ••• | ••• | | |
| INOSTRONG® | ••• | • | • | | | • | ••• | •• | •• | •• | | | |
| INOSTRONG® 50 | ••• | • | • | | | | •• | • | | | | | |
| LMC® | • | • | ••• | | • | | | • | | | | | |
| INOCAST® 175 | • | • | ••• | | • | | | • | | | | •• | |
| ZL 80® | • | • | •• | | | ••• | • | •• | | • | | | •• |
| INOCAST® 125 | • | • | ••• | | • | • | | • | | | | • | •• |
| ZIRCOGRAF® | • | • | • | | | • | • | • | | • | | •• | ••• |
| ZIRCOBAR® | • | • | • | | | • | | • | | • | | | • |
| INOCARB® | • | | | | | | ••• | ••• | | | •• | • | |
| INOCAST® 100 | • | • | •• | | • | | | •• | | | | • | |
| SPHERIX® | | ••• | | •• | ••• | • | ••• | ••• | | | | | |
| SPHERIX® Plus | | ••• | | | ••• | • | ••• | ••• | | | | | |
| AMERINOC® | | ••• | | •• | •• | | ••• | •• | | | | | |
| INOSEL | | ••• | | | | •• | | •• | ••• | | | | |
| CERINOC® | • | • | ••• | | | | | • | ••• | • | | | |
| FESILA® | | • | | | | | | | ••• | • | | | |
| WIN 4® | | ••• | | •• | • | | •• | •• | • | | | | |



# Conclusions.

- **Holding nodular iron** in an Induction furnace **can impact** the **graphitization potential** of iron.
- This **loss in graphitization potential** has a **bad effect on shrinkage** and micro shrinkage.
- An **inoculant containing Selenium and Sulfur** was shown to fight the shrinkage tendency by increasing the **graphitization plateau's length.**
- **This new Selenium based inoculant** has been tried and has shown **benefits versus difficult shrinkage cases.**

# OUR PARTNERS

**Designed** in collaboration with:

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METALLURGY RESEARCH CENTRE

**Tested** at:

Foundry Institute | RWTH AACHEN UNIVERSITY

**Distributed** in Turkey by:

AVEKS

Ferroglobe
Advancing Materials Innovation

# THANKS

➔ Ferroglobe