Rare Earths in Ductile Cast Iron
Minimizing Usage of These Metals For Cost Reductions and to Prepare for Reduced Supply

D. S. White, Technical Service Manager
Initial price increase Aug-Sept. 2010: $10 to $40/kg FOB China

La: 166$/kg
Ce: 169$/kg

Ce: 130 $/kg – La: 123 $/kg – Misch: 121 $/kg
RE Price Development 2009 - 2012

Source: metal-pages.com
Global Production REO

Source: USGS
Rare Earth Metals

Periodic Table of the Elements

<table>
<thead>
<tr>
<th>Period</th>
<th>Group</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>H, Li, Na, K, Rb, Cs, Fr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IIA</td>
</tr>
<tr>
<td>2</td>
<td>II</td>
<td>Be, Mg, Ca, Sr, Ba, Ra</td>
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<td></td>
<td></td>
<td>IIB</td>
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<tr>
<td>3</td>
<td>III</td>
<td>Al, Si, P, S, Cl, Ar</td>
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<td></td>
<td></td>
<td>IIIA</td>
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<tr>
<td>4</td>
<td>IV</td>
<td>C, O, F, Ne</td>
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<td></td>
<td></td>
<td>IVB</td>
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<tr>
<td>5</td>
<td>V</td>
<td>N, P, As, Sb, Bi</td>
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<td>VB</td>
</tr>
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<td>6</td>
<td>VI</td>
<td>O, S, Se, Kr</td>
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<td></td>
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<td>VIIB</td>
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<td>7</td>
<td>VII</td>
<td>F, Cl, Br, Kr</td>
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<td></td>
<td></td>
<td>VIIIA</td>
</tr>
<tr>
<td>8</td>
<td>VIA</td>
<td>Ne, Ar, Kr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VIA</td>
</tr>
<tr>
<td>9</td>
<td>VII</td>
<td>He, Ne</td>
</tr>
</tbody>
</table>

*Lanthanide Series*

- Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

*Actinide Series*

- Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr

Source: library.thinkquest.org
## Change in Chinese Export Quotas of REM

<table>
<thead>
<tr>
<th>Year</th>
<th>REM [tons]</th>
<th>Change [%]</th>
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<tr>
<td>2005</td>
<td>65.609</td>
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<tr>
<td>2006</td>
<td>61.821</td>
<td>-6</td>
</tr>
<tr>
<td>2007</td>
<td>59.643</td>
<td>-4</td>
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<tr>
<td>2008</td>
<td>56.939</td>
<td>-5</td>
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<tr>
<td>2009</td>
<td>50.145</td>
<td>-12</td>
</tr>
<tr>
<td>2010</td>
<td>30.258</td>
<td>-40</td>
</tr>
<tr>
<td>2011</td>
<td>30.184</td>
<td>-</td>
</tr>
<tr>
<td>2012</td>
<td>~30.000</td>
<td>-</td>
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</tbody>
</table>

- **54% reduction of export quota on REM from 2005 to 2010**
- **40% reduction of export quota on REM from 2009 to 2010**
World Demand of RE (tons/year)

Source: sgu.se
Effect of Rare Earths in Cast Iron

Possible Pros:

• Strong deoxidizing and desulphurizing elements: effective nodularizers.
• Forms stable nuclei that are less prone to fading.
• High boiling points: less violent reaction than Mg.
• With the correct RE addition, nodule count is higher than without RE.
• With the correct RE type and addition, nodule size distribution can be manipulated to reduce shrinkage.

• Neutralises subversive elements like Pb, Sb, Bi, As. There are no known substitutes for RE for this effect.
Effect of Rare Earths in Cast Iron

Possible Cons:
- Strong carbide promoters: Increases chill tendency if added in excess
- Deteriorated graphite morphologies (graphite flotation, exploded and chunky graphite) in case of unbalanced levels with tramp elements.
- Tolerance level of ductile iron to rare earths decreases with increasing casting thickness.
Effect of REM in ductile iron

Inoculation effect: increased nodule count.

0% TRE

1% TRE
Counteracting Increased RE Prices and Projected Reduced Supply

Minimizing Rare Earth Usage

1. Optimize the treatment process.
2. Lower RE-content MgFeSi.
3. Replace standard RE in MgFeSi with pure La metal (optimum nodule count at lower usage)
4. Use a RE-containing inoculant with a low or RE free type MgFeSi
   I. 1.75% RE or 1.75%Ce metal (75% FeSi - Ca,Al)
   II. S and O coated versions also available
Increase MgFeSi Treatment Efficiency

- Control base S (C raiser selection or desulfurize)
- Use thermal efficiency techniques to tap colder and increase Mg recovery to reduce MgFeSi usage. Use insulating ceramic paper behind working face linings and use ladle covers. Keep ladles covered when empty.
- Use tall pockets with reduced area for a longer reaction time.
- Fill treatment ladles quickly to minimize or avoid the use of cover metal
- Add treatment alloys from a dispensing system that avoids segregation of sizes and delivers the alloy totally into the treatment pocket
- Add treatment alloys just before the treatment – not sooner.
- Keep pockets clean so that MgFeSi and cover metal are totally contained
Change Treatment Processes?

- Flow – through treatment boxes – MgFeSi - low Mg with high RE content?
- Very thin carbide prone ductile castings - treated quite hot. MgFeSi with low Mg and high RE or Ce metal content. (3.25% Mg and 2% Ce for example)
- Use a covered treatment ladle or perhaps treat in the pouring ladle with low Mg type MgFeSi and eliminate the treatment ladle and associated temperature loss.
- Historically the most common MgFeSi grades contained 1% TRE, made with mischmetal. This has been changing to 0.4% La because of a reduced shrinkage effect. Now it is also the more economical approach, since the amount to achieve optimum nodule count is so much lower.
- Inmold – 0.9% by weight of iron with MgFeSi containing 0.4% La
  - No dust collector to buy or operate.
  - Reduced autopour maintenance costs with un-treated iron
  - No stream inoculant equipment or alloy – no carbides.
Optimizing RE-level in MgFeSi-alloy

![Graph showing nodule count in MgFeSi-alloy with varying RE levels.](image-url)
Change to MgFeSi with Lower RE

MgFeSi with 2% RE

MgFeSi with 0.5% RE

MgFeSi with 0.85% RE

MgFeSi with 0.65% RE
Change to La-containing MgFeSi

Misch-based MgFeSi 0.5% RE

Lanthanum-based MgFeSi 0.5% La
RE Containing Inoculant Technology

- Example: Ca + Al + 1.75% Ce metal grade of 75% FeSi - developed for continuous stream inoculation in cooperation with Grede Reedsburg.

- Concept: Why waste expensive RE elements on deoxidation and desulfurization with the Mg treatment? Why not add them within stream inoculant after the Mg treatment?

- How much RE is needed? Alternate alloys were tested with different RE types and RE contents. 1.75% mischmetal was selected. The pure Ce version provided superior nucleation, but was considerably more expensive than mischmetal.

- The design was later changed to the use of pure Ce due to far stronger chill reduction.

- When coated with readily reduced sulfide and oxide compounds a new highly potent alloy results which also minimizes shrinkage tendency results.
RE Weight and Cost Ranges - per ton of iron treated @
$54/lb Ce       $42/lb. La       $33/lb. mischmetal(TRE)

- 2% by weight of alloy with 2% TRE – 0.8 lb. mischmetal ($26)
- 2% by weight of alloy with 0.4% La – 0.16 lb. La ($7)

- 1.5% by weight of alloy with 1% TRE – 0.3 lb. mischmetal ($10)
- 1.5% by weight of alloy with 0.4% La – 0.12 lb. La ($5)

- 1.1% by weight of alloy with 1% TRE – 0.22 lb mischmetal ($7)
- 1.1% by weight of alloy with 0.4% La – 0.09 lb. La ($4)

- 0.9% by weight of alloy with 0.4% La – 0.07 lb. La ($3)

- RE free MgFeSi and 0.1% stream inoculant with
  - 1.75% Ce – 0.035 lb. Ce ($2)
Reducing RE-level in MgFeSi

- Standard MgFeSi typically contains around 1% RE
- RE levels increased when steel scrap quality was poor.
- Pb, Sb and As are generally lower today.
- A RE level of less than 1% may be sufficient for many foundries. In fact it may be mandatory in low S iron with low levels of tramp elements, to avoid inferior graphite shapes
- CAUTION: There may be a reduction in nucleation when reducing RE content

<table>
<thead>
<tr>
<th>Element</th>
<th>1967 Range</th>
<th>1998 Range</th>
<th>Max</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb ppm</td>
<td>2 – 90</td>
<td>80</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>As ppm</td>
<td>10 – 380</td>
<td>160</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>Pb ppm</td>
<td>– 50</td>
<td>43 ± 11</td>
<td>80</td>
<td>11</td>
</tr>
</tbody>
</table>

Lowering of Tramp Levels over time
Case study - RE reduction in MgFeSi

• A foundry in Denmark producing a range of different components for areas such as hydraulics, engineering, machines, trucks and busses, gears, pumps and valves, compressors, forest and agricultural machinery.

• The foundry has run trials where they changed from MgFeSi with 0.85% RE to 0.5% RE. Addition rate 1.4% The trial was successful and the foundry changed without any negative effects.
MgFeSi alloyed with Pure La Metal

- Sales of MgFeSi alloyed with small levels of pure La metal as the rare earth type have grown very rapidly in N. America.

- The initial growth in this type of MgFeSi was initially due to a reduction of shrinkage defects. Many foundries converted to this technology when La was far more expensive than mischmetal and the MgFeSi alloy cost more than traditional material. They switched because it was technically superior for them and reduced overall costs, not because it was cheaper per lb. to buy.

- The La-level is usually much lower than the typical mischmetal level in traditional MgFeSi. Also La metal prices have become more similar to mischmetal prices. Today this can allow a “purchased price” savings for MgFeSi due to the lower usage of La than mischmetal, in addition to the technical benefits.
Case Study

Objective:
Compare samples of ductile iron made by the “on-the-mould” process using:

1. Misch - MgFeSi
   - % Si: 47.0
   - % Mg: 4.5
   - % Ca: 0.3
   - % RE: 1.25
   - % Al: 0.8

2. La - MgFeSi
   - % Si: 46.0
   - % Mg: 5.5
   - % Ca: 0.5
   - % La: 0.35
   - % Al: 1.0

Both input 0.35% La
Graphite structure

Misch - MgFeSi

La - MgFeSi
## Microstructure

<table>
<thead>
<tr>
<th></th>
<th>Nodule Count (N/mm²)</th>
<th>Nodularity (%)</th>
<th>Graphite (%)</th>
<th>Ferrite (%)</th>
<th>Perlite (%)</th>
<th>Nodule Diamave (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La-MgFeSi</td>
<td>258</td>
<td>82</td>
<td>8</td>
<td>75</td>
<td>17</td>
<td>15.7</td>
</tr>
<tr>
<td>La-MgFeSi</td>
<td>299</td>
<td>89</td>
<td>9</td>
<td>81</td>
<td>10</td>
<td>16.4</td>
</tr>
<tr>
<td>Misch-MgFeSi</td>
<td>167</td>
<td>80</td>
<td>9</td>
<td>77</td>
<td>14</td>
<td>21.8</td>
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<tr>
<td>Misch-MgFeSi</td>
<td>176</td>
<td>81</td>
<td>9</td>
<td>79</td>
<td>12</td>
<td>21.9</td>
</tr>
</tbody>
</table>
Shrinkage Tendency

Misch-MgFeSi

La-MgFeSi
Microstructure in 5 mm Plates

Figure 2: Microstructure in 5 mm plate castings for the different nodularizer alloys.
(a) RE-free, (b) 0.5%La, (c) 1.0%La, (d) 0.5%Ce, (e) 1.0%Ce, (f) 1.0%MM.
Microstructure in 5 mm plates

FREE

0.1LA

0.2LA

0.3LA

0.4LA

0.5LA

Un-inoculated samples
Microstructure in 5 mm plates

FREE

0.1LA

0.2LA

0.3LA

0.4LA

0.5LA

Inoculated samples
Reduction of overall RE-consumption through use of RE-containing inoculant

Ca,Al,1.75%Ce - 75%FeSi

- Late stage addition for thick section D.I. for tight RE and tramp element balance, where the RE content in MgFeSi is being strongly reduced, or even eliminated.
- 0.2% addition with RE Free MgFeSi – replacing the RE in a 1.5% addition of MgFeSi containing 1% TRE

O and S coated version

- Similar attributes as the uncoated alloy, but even more efficient at very low addition rates.
- Improves and boosts nucleation state of iron and rejuvenates dead base iron.
- Excellent alternative for foundries with RE-free MgFeSi that need to boost the nucleation potential to avoid poor nodularity.
- Using 0.15% of the coated version with RE free Mg as an alternative to 1.5% by weight of MgFeSi containing 1% TRE
Case Study – Ce Containing Inoculant to Reduce RE Use

- A family owned old foundry in Germany producing about 10,000tpy finished castings grey iron and ductile iron. GI is produced in a cupola and DI in two 2 ton high frequent induction furnaces.
- The iron they make is very high in S (>0.1) but they do not wish to desulfurize.
- A test was conducted with RE-free Elmag® (2.1-2.2% addition rate) and Ce metal bearing inoculant.
- The result was higher quality ductile iron, with improved nodule count and nodularity.
O and S Coated Pure Ce Containing Inoculant – to Reduce RE Usage and Costs

- A foundry situated in Germany producing ductile castings for engineering and automotive industry.
- They have used MgFeSi containing 1% RE for a long time, but have been slowly replacing it with a RE free version.
- Trials have been run with a 0.3% addition of an O and S coated inoculant containing 1.75% Ce metal in combination with the RE-free MgFeSi.
- The trials have been successful.
- The cost reduction from this change is very worthwhile.
Success factors in changing RE-level

Field experiences and case studies have shown us a few critical factors when changing the RE-level.

1. Do not change too many variables at once!
2. Using a normal and RE-free version of the same nodularizer and then slowly mixing in higher proportions of RE-free version is a proven method of finding the threshold for RE-content.
3. In some cases the change to lower mischmetal content MgFeSi alloy will require more powerful inoculants. This is not the case with La alloyed MgFeSi alloys.
4. Patience is key, as it takes time for the RE-level in the system to settle at a lower level due to returns and residual RE in linings etc. To confirm a test result, the process should be monitored with the new RE-level over several days. Variations in trace element levels in raw materials might also cause unexpected results.
Fading characteristics: Mg vs RE

- Mg has a higher fading rate than RE.
- Reduced RE input = reduce holding time for good nodularity.
- This may be offset by:
  1) operating with a slightly higher Mg level
  2) making smaller more frequent additions to an autopour
  3) stream inoculating with a RE bearing inoculant.

![Graph showing Mg Fade vs. Ce+La Fade](image)

- Graph: Mg Fade vs. Ce+La Fade
- Equation: \( y = -0.0022x + 0.0326 \)
- Equation: \( y = -0.0008x + 0.0139 \)
How much RE is needed to neutralize tramp Elements?

Extensive research has been done on finding the proper amount of RE to counteract the negative impact of tramp elements. Javaid and Loper Jr\textsuperscript{5} gave a rule of thumb 1:1 (or added 1:1.5), Larranaga et al\textsuperscript{8} found the ratio Sb/Ce should be at least 0.8 and Diao et al\textsuperscript{9} found the ratio to be 0.7.

- Javaid and Loper Jr\textsuperscript{5} also gave some expressions to calculate the amount needed. These expressions are based on their own research as well as data reported in literature. Their expressions are as follows:
  
  \begin{align*}
    \text{Wt}\% \text{ RE} & = 1.1206\text{Bi} - 0.0029 \quad \text{Equation 1} \\
    \text{RE/Bi} & = 1.118 \\
  \\
    \text{Wt}\% \text{ RE} & = 0.840\text{Pb} + 0.0045 \quad \text{Equation 2} \\
    \text{RE/Pb} & = 0.845 \\
  \\
    \text{Wt}\% \text{ RE} & = 0.914\text{Sb} + 0.0042 \quad \text{Equation 3} \\
    \text{RE/Sb} & = 0.916
  \end{align*}
How Much RE When There are Multiple Tramp Elements?

- \( RE = 0.5037(Bi+Pb+Sb) + 0.0037 \)

- \( RE = (2.083 + 65.89P + 0.783Si - 39.09Mg - 1.963Ni - 0.176*\text{section size in inches})* (Pb+Bi+Sb) \)

(*For a 20 cm thick casting).
THANK YOU