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Magnesium-Sulfur Relationships in Ductile and Compacted Graphite Cast Irons as Influenced by Late Sulfur Additions

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ABSTRACT

The complex role of sulfur in magnesium treated iron was evaluated in both ductile and compacted graphite irons. At elevated levels, sulfur can act as a harmful element resulting in magnesium-neutralization and increased dross formation but is also beneficial and essential at lower levels because it promotes suitable nuclei for graphite precipitation. It also exercises graphite nodularity shape control at intermediate augmented sulfur levels.

Ductile and compacted graphite irons were prepared in an electric furnace with the same base iron melt chemistry for both the laboratory and production foundry trials. In the case of ductile irons, a late sulfur-addition during post-inoculation and after magnesium treatment produced high nodule counts, reduced occurrence of carbides, and provided excellent nodularity. These results were recorded with less than 0.01 weight percent of sulfur additions. Significant improvements in nodule count, nodularity and chill reduction were found when calcium, as a calcium silicon alloy, and iron pyrites (FeS_2) were employed together as a post-inoculant.

Re-sulfurizing a magnesium treated iron for compacted graphite iron production, in conjunction with knowing the initial base iron sulfur enables control of the graphite nodularity. Specially formulated iron sulfide briquettes (FeS_2), dissolved more rapidly than granular iron pyrites yielding sulfur recoveries in the range of 85 to 90 percent. With the advantage of little to no odor they were found to be an improved and more reliable sulfur additive in both compacted graphite and ductile irons.

INTRODUCTION

The current casting market is driving the need for stronger cast irons at lower weight than gray iron parts, but with improved machinability, thermal-fatigue resistance, damping capacity, casting mold yield, and castability compared to ductile iron parts. Compacted graphite cast irons (CGI) provide a cost-effective solution to meet these challenges**.** Automotive components, such as disc brake rotors, are prime candidates for conversion to compacted graphite production, especially where lighter weight and higher strength are important issues to design engineers. Unfortunately, producing consistent quality compacted graphite iron requires even more stringent controls than ductile iron production. Current popular methods of producing CG iron require the use of controlled titanium additions or complex thermal analysis techniques. In the former method, titanium contamination of casting returns and machinability issues remain a major concern while in the latter technique, the controls needed and licensing costs have prevented widespread use.

A review of worldwide research investigations and foundry experience involving different liquid metal treatment procedures to produce compacted graphite iron was the topic of the 2002 AFS Casting Congress Compacted Graphite Iron Panel. Various CG production methods included "High rare earth treatments" (Skaland), "Magnesium-Rare Earth Balance" (Burton), "Oxycast-Oxygen analysis control" (Bollen), "Thermal analysis control" (Dawson), "Varying Titanium Levels" (Knuckey), "Resulfurizing after Mg-treatment" (Kelley), and "Special In-Mold treatments" (Sillen).

From these panel discussions, Kelley generated a considerable amount of interest in the "Resulfurizing after Magnesium Treatment" presentation. Kelley showed that in a production environment, using a 0.015 to 0.025 percent sulfur addition (after magnesium additions) to denodulize magnesium treated iron, he was able to consistently produce acceptable CG irons with less than 20 percent nodularity. The key to Kelley's success was the employment of a new iron sulfide briquette, which allowed consistently high sulfur recoveries (85 to 90 percent). Prior to using the briquettes, granular iron sulfide (iron pyrites) were used with sporadic and inconsistent CG results. Recoveries of sulfur were 30 to 40 percent. Since sulfur was used to denodulize the irons, there was little concern about contamination of foundry returns. This is not the case when other antinodularizing elements such as titanium and aluminum are used in CG production. This production research was a response to the desire of many foundries to add alternative elements to “denodulize” magnesium treated ductile iron rather than elements that might contaminate other cast components being produced. (Chisamera 1986, 1988, 1994, 1995, 1996 1998 and 2002, Riposan 1991and 1998).

The simultaneous use of sulfur with inoculating agents is not a new concept. The use of sulfur added with potent oxy-sulfide forming elements was first demonstrated by Naro and Wallace (1970). Naro showed that balanced ratios of rare earths and sulfur, without the presence of ferrosilicon, provided drastic reductions in undercooling, completely eliminated chill and promoted favorable graphite shapes in gray irons. Strande (1984) showed that calcium silicide based inoculants along with increased sulfur additions provided vastly improved machinability in gray iron castings compared to proprietary ferrosilicon based inoculants and similar late sulfur additions.

It was further demonstrated by Riposan (1998) that a small sulfur addition (less than 0.010 percent), when added concurrently with calcium silicon based inoculants increased graphite nucleation potential in ductile iron, but without affecting graphite nodularity. Chisamera (1994, 1995, 1996, and 1998) and Riposan (1998) also showed that the strong sulfide forming tendencies of calcium and rare earths, when used in conjunction with controlled sulfur additions, strongly promoted the formation of sulfide compounds assisting their effectiveness as nodular graphite nuclei.

BACKGROUND

The amount of sulfur addition in magnesium-treated iron needed to obtain a critical nodular graphite / compacted graphite (NG/CG) ratio depends on the residual magnesium content after magnesium treatment as well as holding time prior to pouring. Other important factors are casting wall thickness, mold type and thermal gradient effects (Riposan 1991, Chisamera 1996).

Recently, it was pointed out that it is possible to produce both compacted graphite irons and ductile iron from the same base iron melt (suitable for ductile iron production) using cored wire containing a high magnesium containing ferrosilicon. Results showed (Kelley, et al.) that it was possible to use such a magnesium treated ductile iron, with low residual Mg levels (0.025 to 0.04 percent) but with an addition of “fresh” sulfur. The sulfur addition was in the form of a rapid dissolving iron sulfide briquette. Less than 0.02 weight percent sulfur was needed to “denodulize” the iron. Thus, it was possible to have the same furnace melt chemistry and have a controlled transition from ductile iron to compacted graphite iron in the same campaign.

Critical parameters for the process were holding final magnesium levels between 0.010 to 0.025 percent and adding fresh sulfur to obtain a final Mg/S ratio of 0.5 to 2.0. Thermal analysis software was adapted to monitor compacted graphite (CG) compared to nodular graphite (NG) formation conditions. The degree of under-cooling (DU) was found to be a critical factor for compacted graphite formation (DU equaled -40^{o}F to -60^{o}F), coral graphite (DU less than -60^{o}F) and nodular graphite (DU greater than 0^{o}F). (Chisamera 2002, Kelley 2002).

After magnesium-treatment, molten iron is depleted of both oxygen and sulfur causing a reduction of post inoculant efficiency or worse, inconsistent inoculant performance. It has been shown that the presence of sulfur is essential to form the core of a nodular graphite nucleus, while other active minor elements such as calcium, barium or strontium supplied by a proprietary post-inoculant, play an important role in the secondary stage developing a more complex nucleus. Skaland, (1993) described these relationships in his graphite nucleation model.

Sulfur relationships in Ductile and Compacted Graphite Iron: Sulfur can be both detrimental and beneficial element in ductile iron and compacted graphite iron. Sulfur’s harmful and beneficial effects are related to the amount present before magnesium treatment (nodularizing process) as well as its concentration during graphite nucleation.

A high base iron sulfur content is generally considered harmful because it will lower the magnesium efficiency and result in increased dross formation in both ductile and compacted graphite irons. However, in ductile iron, a minimum sulfur level of at least 0.005 to 0.008 percent is necessary after magnesium treatment to insure proper post-inoculation and reduce the risk of carbides. Thus, after magnesium treatment, the presence of critical sulfur levels is considered beneficial for the promotion of graphite nuclei. Further, the reaction of sulfur with sulfide forming elements such as rare earths and calcium enhance nucleation of graphite in ductile irons. In compacted graphite irons and after magnesium treatment, control of sulfur levels is critical for controlling graphite nodularity and promoting compacted formation. In summary,

- In ductile irons, if the residual sulfur content is increased late in the process by addition of small amounts of iron sulfide, graphitization is enhanced as measured by higher nodule count and fewer iron carbides. This is achieved without any adverse effects on graphite nodularity.
- In compacted graphite irons, a similar late sulfur addition at a higher level enables graphite nodularity control for the production of conventional compacted graphite structures with greater than 80 percent compacted graphite. A higher nodularity compacted graphite iron can also be produced (50 to 80 percent compacted graphite) with a very low risk of carbide formation.

Flow chart for Compacted Graphite Iron Production:

Figure 1 is an illustration of the three steps necessary to produce ductile irons and compacted graphite irons from the same furnace chemistry using controlled sulfur additions after magnesium treatment. The flow diagram illustrates the three steps necessary to produce ductile irons and compacted graphite irons from the same furnace chemistries.

I. Base iron production controls should maintain sulfur contents at 0.03 percent and lower.

II. Magnesium treatment by an appropriate technique for each foundry, targets a lower Mg range than for ductile iron, typically at a level of 0.025 to 0.04 percent Mg residual (Mg_{res}) for compacted graphite production.

III. The sulfur addition after magnesium treatment is to reduce the effective residual magnesium to the appropriate range for compacted graphite formation and for the casting weight and common section size (typically 0.010 to 0.025 percent final residual Mg after sulfur has been added).

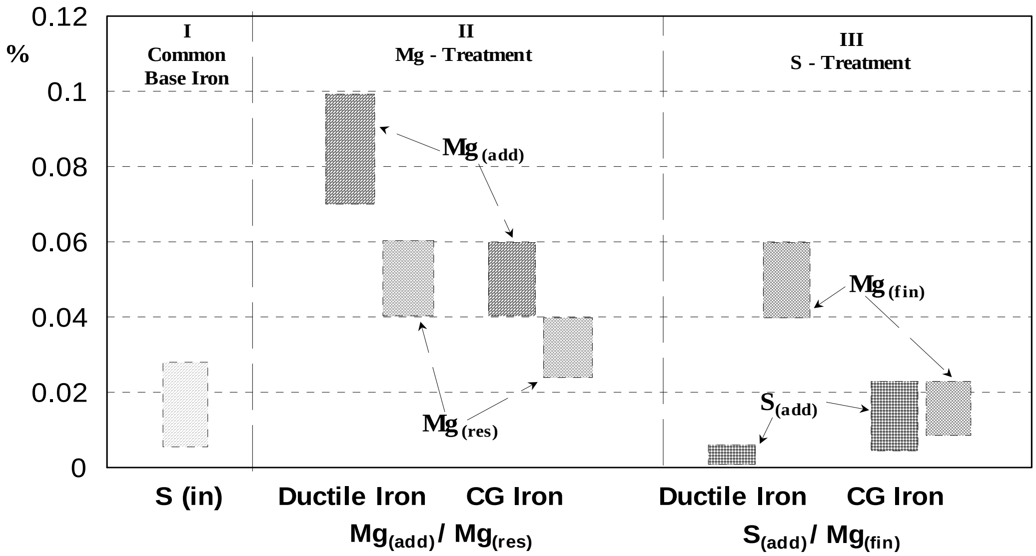

Figure 1: CG Iron vs. Ductile Iron production from the same base iron by Mg-treatment and late S-addition with the post-inoculation

Magnesium control: a magnesium addition to the base iron ($Mg_{(add)}$) is calculated to provide a residual magnesium after treatment ($Mg_{(res)}$), which then is reduced to a final residual magnesium after supplementary sulfur has been added ($Mg_{(fin)}$). The magnesium and sulfur levels are balanced to produce a compacted graphite structure.

Sulfur adjustment: from the initial sulfur level in a base iron either ‘as melted’ or after desulfurizing ($S_{(in)}$), sulfur content is reduced further sulfur after magnesium treatment ($S_{(res)}$), and subsequent sulfur additions ($S_{(add)}$), will control and affect the final sulfur level in compacted graphite cast iron ($S_{(fin)}$) .

The major difference between the supplementary sulfur route and a simple magnesium control technology to produce compacted graphite cast iron (without subversive elements like Ti), at the same lower level of final residual magnesium, is the introduction of two stages of magnesium control:

- Enough residual magnesium from a Mg addition that is high enough to avoid the appearance lamellar (flake) graphite, typical for a weak treatment, but not high enough to develop a fully ductile iron structure.

- Controlled neutralizing of the lower residual magnesium levels by a sulfur addition to ensure compacted graphite occurrence, according to the casting characteristics.

Foundry experience shows that this latter method is more attractive and economical than other technologies (Chisamera 2002, Kelley 2002).

Influence of initial sulfur content in CGI production:
In ductile iron technology, lower initial base iron sulfur contents allow lower magnesium additions to be used because less residual magnesium combines with sulfur. With base iron sulfur contents of 0.008 to 0.010 percent, excellent nodularity can be achieved with residual Mg levels as low as 0.018 percent. In those cases where the base iron contains 0.025 to 0.035 percent sulfur, approximately 0.04 percent Mg may be required. With a 0.085 percent sulfur base iron, a residual Mg level of 0.055 percent will be required (in this example, a separate desulfurization step would be more common practice prior to any magnesium addition). Base irons with very low sulfur content (less than 0.006 percent) are less responsive to the nucleation stage of graphite spheroidization, exhibit lower nodule count and have a greater tendency for carbide formation (Gundlach, 1992).

A recent survey of ductile iron practice pointed out a dramatic shift downward in sulfur levels in base irons. This survey found that in both larger and small foundries the more of the base iron sulfur levels fell in the lower 0.015 percent group. This trend appears to be associated with melting methods. The number of larger foundries melting in cupolas, with high base sulfur levels, has decreased. Conversely, the melting trend in smaller foundries has been toward induction melting, where higher quality charge materials are used, and correspondingly, lower sulfur levels result (Csonka, 2002).

Using Csonka's findings, a relationship exists between initial sulfur level in a base iron and the final sulfur level in compacted graphite iron produced by magnesium and sulfur additions. Several issues affect this possible relationship:

- Graphite nodularity after magnesium treatment is affected by low initial sulfur level and this in turn may lead to nodular graphite formation at lower residual magnesium in the treated iron.
- Dependence of final chemistry (residual magnesium and sulfur levels) and final structure (nodular graphite-compacted graphite ratio) on the initial sulfur content.
- The relationship of Mg-addition and / or S-addition to initial sulfur level or specific charge materials in electric furnace melting.

MATERIALS AND PROCEDURE:

Research Laboratory: Ductile irons having slight hypereutectic to hypoeutectic compositions were produced in a 10 kilogram capacity, 8,000 Hz frequency induction crucible furnace. The nodulizing treatment consisted of a tundish cover process ladle using standard magnesium ferrosilicon. This treatment method was chosen to ensure a high nodulizing effect in 25 mm wall thickness castings. Residual magnesium levels were varied between 0.055 percent to 0.065 percent. The post-inoculating treatment was made using different procedures, in the ladle, in the pouring basin and in an in-the-mold reaction chamber. Two conventional inoculants were used that included calcium bearing 75 percent ferrosilicon and calcium silicon. Iron sulfide was carefully blended in various percentages with these conventional inoculants to determine the mixture effect on inoculation. These same mixtures were also pressed under high pressure into an insert or tablet that was used for in-the-mold inoculation studies. Chill testing was conducted using a wedge that measured 125 mm long, 67 mm high and 25 mm width on the top section of the wedge and 4 mm on the bottom of the wedge. The depth of clear chill was carefully measured from the base of the chill in millimeters. The wedge was top gated and cast against a metal chill and a schematic of the chill mold is shown in Figure 2.

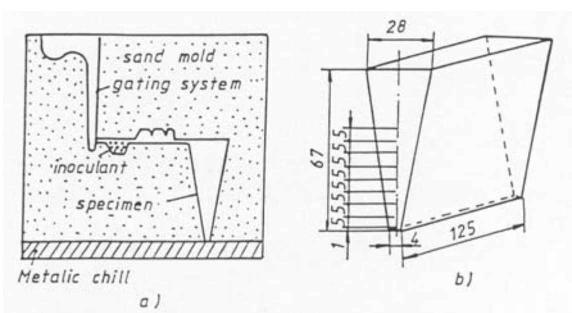

Figure 2. Schematic of a.) chill mold with in-mold chamber
b.) chill wedge dimensions used to assess chilling tendencies

The chemistry range of the ductile irons used for these tests is shown in Table 1.

Table 1: Composition of Ductile Irons

Element	Percentage
Carbon	3.45 to 3.75
Silicon	2.00 to 2.75
Manganese	0.45 to 0.50
Sulfur	0.007 to 0.015
Phosphorous	0.075 to 0.10
Magnesium residual	0.055 to 0.65

The compositions of the inoculating materials for the laboratory experimental study are shown in Table 2.

Table 2: Chemistry of Inoculants and Additives

Inoculant	% Silicon	% Calcium	% Aluminum	% Sulfur	% Iron
75% Foundry FeSi (FeSi75)	75.0 – 77.0	0.50 – 0.75	1.25 – 1.75	None	Balance
Calcium Silicon (CaSi)	62.0 – 65.0	28.0 – 32.0	2.25 – 2.50	None	Balance
Iron Sulfide (Fe_2S)	None	None	None	49.0 – 50.0	Balance

Iron sulfide was in the form of iron pyrites that typically contain 49 to 52 percent sulfur. The iron pyrites had a size distribution of 100 mesh by down. Cerium additions to selected heats were made by the addition of mischmetal while pure bismuth pellets (nominally 97 percent purity) were used for other experiments to determine effect.

The experiments were designed to assess the influence of various inoculants and inoculant blends with sulfur on graphite nucleation capacity as measured by the number and dimension of graphite nodules. Chill or carbide forming tendencies were measured as the ratio of carbides against the metallic chill area, and the size of the chilled areas.

Production Foundry Tests:

Ductile Iron Inoculation Trials: Inoculation trials with modified sulfur containing inoculants were conducted several production ductile iron foundries. The trials were run using both granulated and briquetted in-mold inserts. The modifications to the calcium silicon based inoculant listed in Table 2 incorporated proprietary blends (Naro 2001) of sulfur and oxygen containing (oxy-sulfide) ingredients.

Ductile and Compacted Graphite Production:

The U.S. production foundry casts both ductile iron and compacted graphite iron from the same base iron melt chemistry. Table 3 lists the base furnace charge. The aim is to use the same iron melt, produced from the same charge materials in order to have an easy transition from ductile to compacted iron production.

Table 3: Charge materials used for ductile and compacted irons

Material	Amount
Pig Iron	2.000 lbs
Ductile Returns	1,250 lbs
Steel scrap	1,300 lbs
Silicon Carbide	50 to 100 lbs
Carbon Raiser (low S)	35 to 50 lbs

Table 4: Composition of ductile base iron before nodulizing with cored wire

Element	Percentage
Carbon	3.65
Silicon	1.90
Manganese	0.20
Sulfur	0.011 to 0.03
Phosphorous	0.025

Table 4 lists the base iron chemistry before nodulizing with a 13 mm. cored wire containing nominally a 25 percent magnesium ferrosilicon alloy (nominally 25 percent magnesium and 45 percent silicon).

Melting at this Midwest jobbing foundry is done in two 9 ton medium frequency coreless induction furnaces. The base iron shown in Table 4 is typically tapped in 1,500 pound increments. The magnesium treatment employs a cored wire feed technique utilizing 13 millimeters (mm) Fe-Si-Mg diameter wire (25 percent magnesium, 45 percent silicon). The casting wall thickness varied between 13 to 25 millimeters (mm) using greensand molding (76 cm x 101.6 cm flasks). Representative CG iron housings are cast in the range of 50 lbs to 600 lbs. The tap temperature is in the range 2820 to 2870 ^{o}F and the pouring temperature 2540 to 2580 ^{o}F with a 5 to 8 minute ladle pour time.

The treatment conditions employed for producing compacted graphite irons at the jobbing foundry are shown in Table 5.

Table 5. Additions used to produce ductile iron and compacted graphite iron produced from the same base iron melt

Iron type	Amt Tapped (lbs.)	Mg-Wire (lbs.)	FeSi75 (lbs.)	Sulfur Addition (lbs.)
Ductile Iron	1200 - 1600	4.3 – 5.4	4 to 8	-
CG-Iron	1540 - 1840	2.9 – 3.5	4	1.0

Experimental work considered three characteristic ranges of initial sulfur content in induction melted ductile iron production with sulfur levels typically less than 0.03 percent. A higher range more typical of electric furnace melted gray iron was also selected to determine the effect and feasibility of converting gray base iron with a high sulfur level directly to CG iron. The ranges investigated are listed below.

I. 0.010- 0.015 percent sulfur, as optimum sulfur content in a base iron for ductile iron production.
II. 0.015- 0.018 percent sulfur, as a medium sulfur level, close to the optimum range.
III. 0.018 - 0.026 percent sulfur, as the upper level of sulfur, in normal ductile iron production.
IV. > 0.045 percent sulfur, as typical levels for induction melted gray irons.

Typically a 0.088 to 0.093 percent addition of a 25 percent magnesium containing magnesium filled 13 millimeter wire, depending on the initial sulfur level, is normally used to produce ductile iron (4.3 to 5.4 pounds of wire). This addition normally provides a final magnesium level of 0.040 to 0.055 percent. Post-inoculation is accomplished with 75 percent ferrosilicon added as a ladle treatment at the rate of 4 to 8 pounds per ton.

For compacted graphite production, an average 37 percent reduction in magnesium wire addition was used to obtain lower residual magnesium levels (%Mg_{res}) before sulfur additions. During the transfer of iron from the magnesium treatment ladle to the pouring ladle, one pound of iron pyrites was co-added with 75 percent calcium bearing ferrosilicon and both were added to the stream. Final magnesium content was usually targeted in the range of 0.015 to 0.030 percent. Magnesium content was determined by spectrometer analysis from a sample taken from the ladle after post-inoculation.

The sulfur additions were calculated from the base paper charts (Riposan 1998). Two sources of sulfur were used in the experiments to re-sulfurize the magnesium treated iron, (1) iron sulfide: powdery or granular iron pyrites containing 49 percent sulfur having a particle size of 100 mesh by down) and (2) a specially formulated 20 gram FeS_2 briquette containing 30 percent sulfur and designed with a rapid dissolution rate. The amount of sulfur addition was 1.0 pound of granular iron pyrites (0.49 pounds of contained sulfur) per 1550 pounds of treated metal, with a target of 0.03 percent $Mg_{residual}$, after Mg treatment. Iron sulfide briquettes were added at a rate of 0.75 pounds (0.225 pounds of contained sulfur) per 1500 pounds of metal.

RESULTS

RESEARCH LABORATORY STUDIES:

Sulfur effects on inoculation: The effects of blended iron sulfide additions to calcium bearing 75percent ferrosilicon (75FeSi) and calcium silicide alloys (CaSi) on magnesium treated ductile iron are shown in Table 6. The granulated inoculation blends were placed in the in-mold reaction chamber.

Table 6: Effect of granulated sulfur additions to silicon based post-inoculant alloys

Heat No.	Granular Inoculation System: Base Inoculant	Granular Inoculation System: Addition (in the mold reaction chamber)	Samples: Wall Thickness [mm]	Samples: Nodule Count [1/mm^2]	Samples: Chill Depth [mm]
1.1	No Inoculation	-	Chill Test 4 x 28 x 67 (Metallic Chill)	max.288	38
1.2	No Inoculation	0.015%S (as FeS_2)		max.299	34
1.3	0.30% FeSi75	-		max.468	14
		0.015%S (as FeS_2)		max.432	18
		0.015%S (FeS_2) + 0.02% Ce		max.494	19
		0.005% Bi		max.577	17
1.4	0.3% Calcium Silicon	-		max.379	21.5
		0.015%S (as FeS_2)		max.656	9
		0.015%S (as FeS_2) + 0.02% Ce		max.386	18

The addition of 0.015 percent iron sulfide to the ductile iron with a magnesium residual (Mg_{res}) of less than 0.05 percent had little to no inoculating effect. Thus, it appears that the formation of magnesium sulfide substrates from the iron sulfide additions have a low inoculating effect. A single addition of 0.30 percent calcium and aluminum bearing 75FeSi provided vastly improved inoculation. Nodule count increased significantly and chill depth was significantly reduced compared to post Mg "untreated" ductile irons melts.

The addition of 0.015 percent iron sulfide to the 75FeSi resulted in a slight increase in chilling tendency and slightly reduced nodule counts compared to unblended 75FeSi additions. However, adding 0.02 percent cerium to this same blend resulted in a increased in nodule counts, although chill depth increased slightly. The increased inoculation effect of cerium and sulfur blended with 75 percent ferrosilicon probably resulted from the creation of cerium sulfide substrates (Naro and Wallace, 1970). Other later works also pointed out the beneficial of sulfur inoculation of ductile irons (Skaland 2001, Suarez 2000 and 2002). The addition of 0.005 percent bismuth to the 75 percent ferrosilicon inoculant resulted in even further inoculation. A maximum nodule count of 577 was observed and chilled area was reduced to 17 mm.

Inoculation using only 0.30 percent calcium silicon (CaSi) resulted in increased nodule counts compared to "untreated" ductile irons and reduced chilling tendency. The calcium silicon addition by itself did not provide equivalent performance as using 75FeSi. However, blending 0.015 percent sulfur into CaSi inoculants provided the greatest nodule counts and largest chill reduction of the granulated mixtures tested. Adding 0.02 percent cerium to this same mixture impeded the inoculation process and did not produce the beneficial results found with the ferrosilicon blended inoculants.

The effect of using the same blends but in a pressed tablet form placed in the reaction chamber is shown in Table 7. The tablets weighed approximately 6.4 grams and were fabricated with a proprietary binder, which decomposed at very low temperatures.

Table 7: Effect of in-mold inoculation and sulfur additions on nodule count and chill reduction

Heat No.	Pressed Inoculation Insert Tablets		Samples		
	Base Inoculant	**Addition (in the mold reaction chamber)**	**Wall Thickness [mm]**	**Nodule Count [$1/mm^2$]**	**Chill Depth [mm]**
2.1	No-Inoculation	-	6.5	353	35
2.2	0.3% FeSi75	-	6.5	461	13
	0.3% FeSi75	0.005% S as (FeS_2)	6.5	430	6
	0.3% FeSi75	0.007%S as (FeS_2)	6.5	525	11
	0.3% FeSi75	0.01%S as (FeS_2)	6.5	535	11
2.3	0.3% Calcium Silicon	-	6.5	487	17
	0.3% Ca Si	0.005%S as (FeS_2)	6.5	580	14
	0.3% Ca Si	0.007%S as (FeS_2)	6.5	698	13
	0.3% Ca Si	0.01%S as (FeS_2)	6.5	670	13
	0.3% Ca Si	0.005%S as (FeS_2) + 0.02%Ce	6.5	430	6
	0.3% Ca Si	0.007%S as (FeS_2) + 0.02%Ce	6.5	609	11
	0.3% Ca Si	0.01%S as (FeS_2) + 0.02%Ce	6.5	636	12

Pressed inoculant inserts made with 75FeSi foundry grade and placed in the reaction chamber provided marginally improved results compared to granulated mixtures. Incorporating sulfur into the in-mold inoculation tablets again provided significantly improved inoculation. Nodule counts increased and chill depth was reduced compared to non-sulfurized in-mold tablets. Sulfur additions above 0.005 percent resulted in somewhat greater chilling tendencies, although nodule counts increased as the level of sulfur increased to 0.01 percent.

In-mold inserts made using calcium silicon as the primary inoculating agent provided improved nodule counts compared to 75FeSi inserts. However, although the same weight percentage of addition was used, the 75FeSi tablets provided marginally improved chill reduction. Incorporating 0.005 percent sulfur in the CaSi inserts provided significantly improved inoculation results. Chilling tendency was reduced and nodule counts increased as the sulfur level increased from 0.005 percent to 0.01 percent. Incorporation of 0.02 percent cerium to all of the sulfur-containing in-mold inserts tended to reduce nodule count somewhat. Cerium additions also reduced chilling tendencies at the same sulfur levels.

The results from Table 7 strongly suggest that the mixture of FeS_2 and calcium silicon based alloys, which intentionally contain active elements to form sulfides, achieves an important inoculation result demonstrated by an increased nodule number and reduced chill tendency. The inoculation effect is stronger when used as a late inoculation technique, in the mold as an insert, and is effective for thin section castings. As a ladle inoculation method, the effect was less marked.

Production Foundry Studies:

Effects of sulfur / oxygen on ductile iron inoculation: Table 8 shows the effect of adding sulfur and oxygen containing ingredients incorporated into a calcium silicide based inoculant. Both inoculating agents were added as a post-inoculant to the ladle after magnesium treatment. The inoculants were all in granular form.

Ductile iron production castings post-inoculated with standard 75 percent ferrosilicon containing a minimum 0.75 percent calcium exhibited acceptable ductile microstructures. Nodule counts were typically in the range of 125 to 150 nodules/mm^2 for the ½ inch thick castings.

Table 8: Effect of sulfur and oxygen additions on inoculation effect in ductile iron

Inoculant	Amount	Percentage	Nodule Count in ½ inch casting sections N/mm^2
75% Ca bearing FeSi	8 lbs / ton	0.53%	150
Calcium silicon with oxy/sufide modifications [1]	2 lbs / ton	0.13%	225

*1 38% silicon, and 32 percent oxy/sulfide forming elements

The results of tests run using the sulfur and oxygen modified calcium silicon additions showed significantly higher nodule counts than calcium bearing foundry 75 percent ferrosilicon. Nodule count increased to 225 nodules/ mm^2 in ½ inch wall thickness castings. Further, these results were obtained with significantly reduced inoculant levels; inoculant additions levels were reduced by 75 percent compared to the 75FeSi inoculant.

A briquetted in-mold insert consisting of the sulfur and oxygen enriched calcium silicide inoculant produced even more significant improvements regarding nodule count and graphite nodularity. Table 9 shows the effect of this potent inoculation employing the in-mold briquettes as a booster inoculant.

Table 9: Effect of sulfur and oxygen enriched calcium silicide in-mold inserts on inoculation

Inoculant	Amount	Casting Weight (lbs)	Section Size (in.)	Percentage	Nodule Count N/mm^2
75% Calcium bearing FeSi (no inmold inoculation)	8 lbs / ton	98	1 inch	0.53%	125 to 150
CaSi insert with oxy/sulfide elements	16 grams	55	½ inch	0.064%	225 to 300
CaSi insert with oxy/sulfide elements	43grams	98	1 inch	0.096%	225 to 300

1.) Insert nominally contains 35% silicon, and 35 percent oxy/sulfide forming elements

Use of the pressed inserts typically increased nodule counts 50 percent. Significant improved nodularity was also noted when these inserts were used for final late inoculation in the mold. Although the inserts were used as a supplementary inoculant, work at other foundries has shown similar or greater benefits when the inserts were used as the sole inoculant.

Production Foundry Trials - Compacted Graphite Iron Production

Effect of sulfur: Two sources of sulfur were used experimentally to resulfurize the magnesium treated iron. These included 1) iron sulfide or iron pyrites, which contained nominally 49 percent sulfur and was approximately 100 mesh by down and 2) the newly formulated FeS_2 briquettes. Excellent and consistent control of the sulfur recovery has been found to be an essential feature of this technology and it has been demonstrated in foundry conditions, for both ductile iron and compacted graphite iron.

The influence of initial sulfur level in the base iron was examined for several magnesium addition levels ($Mg_{(add)}$ additions of 0.04 to 0.05 percent as cored wire) and a late sulfur addition ($S_{(add)}$ additions were 0.031 percent) in the form of one pound of finely granulated FeS_2. Two specific types or forms of compacted graphite cast irons were obtained for these experiments. Irons designated conventional CG grade of iron contained 80 percent compacted graphite and less than 20 percent nodular graphite. High nodularity (HN) compacted graphite iron contained 50 to 80 percent compacted graphite iron and 20 to 50 percent nodular graphite. The aim of the research was to produce 80 percent conventional CG irons on a consistent basis, but data for less than 80 percent CGI is presented to show the effects of residual magnesium and sulfur levels. Since in recent years, there has been interest in HN compacted graphite iron production, so this data was also recorded.

Casting results for the lowest initial sulfur range of 0.010 to 0.015 percent are shown in Table 10. Table 10 shows that a sulfur addition to a base sulfur iron of 0.014 percent (average), after magnesium treatment, produced structures having an average of 69.5 percent compacted graphite. Final residual magnesium levels and final sulfur levels averaged 0.019 percent and 0.018 percent respectively. Although several heats exhibited conventional CGI levels above 80 percent, higher levels of conventional CG irons were sought.

Table 10: Magnesium and Sulfur Relationships in CG Iron – Granular Iron Pyrites

Initial $S_{(in)}$ [%]	**Heat No.**	**Mg Addition $Mg_{(add)}$ [%]**	**$Mg_{(add)}$ / $S_{(in)}$ Ratio**	**Final Magnesium $Mg_{(fin)}$ [%]**	**Final Sulfur $S_{(fin)}$ [%]**	**$Mg_{(fin)}$ / $S_{(fin)}$ Ratio**	**$Mg_{(fin)}$ / $S_{(in)}$ Ratio**	**CGI [%]**
0.011	1.1	0.039	3.57	0.021	0.015	1.40	1.91	50
0.011	1.2	0.036	3.30	0.022	0.019	1.16	2.0	70
0.013	2.1	0.048	3.69	0.022	0.011	2.0	1.69	60
0.013	2.2	0.048	3.69	0.028	0.012	2.33	2.15	60
0.014	3.1	0.044	3.13	0.012	0.020	0.60	0.86	85
0.014	3.2	0.045	3.20	0.010	0.026	0.38	0.71	85
0.014	3.3	0.045	3.20	0.014	0.022	0.64	1.00	80
0.014	4.1	0.041	2.93	0.023	0.024	0.96	1.64	85
0.015	5.1	0.045	2.98	0.021	0.018	1.17	1.40	50
0.015	5.2	0.048	3.17	0.020	0.017	1.18	1.33	60
0.015	5.3	0.046	3.09	0.020	0.015	1.33	1.33	80
Averages								
0.014		**0.044**	**3.27**	**0.019**	**0.018**	**1.20**	**1.46**	**69.6**

Increasing base furnace sulfur levels to the range 0.015 to 0.018 percent produced reduced levels of nodular graphite. Table 11 summarizes this series of experiments.

Table 11: Magnesium and Sulfur Relationships in CG Iron – Granular Iron Pyrites

% Initial $S_{(in)}$ [%]	**Heat No.**	**Mg Addition $Mg_{(add)}$ [%]**	**$Mg_{(add)}$ / $S_{(in)}$ Ratio**	**Final Magnesium $Mg_{(fin)}$ [%]**	**Final Sulfur $S_{(fin)}$ [%]**	**$Mg_{(fin)}$ / $S_{(fin)}$ Ratio**	**$Mg_{(fin)}$ / $S_{(in)}$ Ratio**	**CGI [%]**
0.016	6.1	0.046	2.89	0.028	0.013	2.15	1.75	50
0.016	7.1	0.043	2.68	0.022	0.013	1.69	1.38	90
0.016	7.2	0.041	2.56	0.017	0.018	0.94	1.06	90
0.016	7.3	0.041	2.56	0.021	0.018	1.17	1.31	80
0.016	7.4	0.040	2.50	0.021	0.014	1.50	1.31	90
0.016	8.1	0.049	3.03	0.025	0.029	0.86	1.56	70
0.016	8.2	0.049	3.03	0.021	0.018	1.17	1.30	50
0.016	9.1	0.041	2.58	0.017	0.010	1.70	1.06	85
0.016	9.2	0.039	2.44	0.017	0.014	1.21	0.88	85
0.017	10.1	0.048	2.79	0.012	0.026	0.46	0.71	90
0.017	11.1	0.047	2.75	0.021	0.014	1.50	1.24	80
0.017	11.2	0.047	2.75	0.021	0.015	1.40	1.24	90
0.018	12.1	0.049	2.69	0.015	0.019	0.79	0.83	70
0.018	12.2	0.049	2.69	0.019	0.021	0.90	1.06	80
0.018	12.3	0.049	2.69	0.020	0.013	1.54	1.11	55
0.018	12.4	0.049	2.69	0.023	0.023	1.0	1.28	55
Averages								
0.017		**0.045**	**2.71**	**0.020**	**0.017**	**1.25**	**1.19**	**75.6**

The results in Table 11 show that greater levels of compacted graphite form when the furnace sulfur level is increased from 0.013 percent to 0.017 percent and residual magnesium levels are also increased. A further increase in base furnace sulfur levels to 0.018 to 0.022 percent produced similar results. These results are shown in Table 12.

Increasing the base furnace sulfur levels incrementally to an average of 0.021 while adding slightly more magnesium (0.046 percent magnesium addition) produced essentially the same levels of compacted graphite irons. The microstructures still contained an average of 75.8 percent CG iron, somewhat less than the desired 80 percent minimum, normally considered as conventional CG iron.

Table 12: Magnesium and Sulfur Relationships in CG Iron – Granular Iron Pyrites

(%) Initial Sulfur $S_{(in)}$	**Heat No.**	**Mg Addition $Mg_{(add)}$ [%]**	**$Mg_{(add)}$ / $S_{(in)}$ Ratio**	**Final Magnesium $Mg_{(fin)}$ [%]**	**Final Sulfur $S_{(fin)}$ [%]**	**$Mg_{(fin)}$ / $S_{(fin)}$ Ratio**	**$Mg_{(fin}$ / $S_{(in)}$ Ratio**	**CGI [%]**
0.019	13.1	0.047	2.49	0.029	0.017	1.71	1.53	85
0.019	13.2	0.048	2.51	0.024	0.018	1.33	1.26	85
0.019	14.1	0.049	2.55	0.017	0.011	1.55	0.89	80
0.019	14.2	0.049	2.55	0.022	0.017	1.29	1.16	80
0.019	15.2	0.049	2.55	0.024	0.018	1.33	1.26	85
0.020	16.1	0.049	2.43	0.023	0.023	1.0	1.15	95
0.200	16.2	0.049	2.43	0.030	0.020	1.5	1.50	80
0.020	16.3	0.049	2.43	0.026	0.017	1.53	1.30	70
0.021	17.1	0.050	2.38	0.025	0.021	1.19	1.19	60
0.021	17.2	0.050	2.38	0.025	0.029	0.86	1.19	90
0.021	17.3	0.050	2.38	0.029	0.022	1.32	1.38	70
0.021	17.4	0.050	2.38	0.025	0.018	1.39	1.19	60
0.022	18.1	0.047	2.17	0.018	0.021	0.86	0.82	85
0.022	18.2	0.047	2.17	0.028	0.031	0.90	1.27	80
0.022	19.1	0.049	2.22	0.028	0.014	2.0	1.27	65
0.022	19.2	0.043	1.93	0.025	0.018	1.39	1.14	70
0.022	20.1	0.049	2.21	0.023	0.021	1.1	1.05	85
0.022	20.2	0.049	2.21	0.021	0.021	1.0	0.95	95
0.022	20.3	0.049	2.21	0.021	0.023	0.91	0.95	95
Averages								
0.021		**0.046**	**2.23**	**0.023**	**0.019**	**1.21**	**1.12**	**75.8**
Std. Dev.								
0.0012		**0.0016**	**0.163**	**0.0035**	**0.0045**	**0.303**	**0.185**	**10.8**

Final residual magnesium levels ($Mg_{(fin)}$), obtained after a sulfur addition during the post-inoculation stage is an important parameter that defines the graphite phase. Conventional CG Iron was obtained for a large range of final residual magnesium levels (where $Mg_{(fin)}$ ranged between 0.010 to 0.029 percent) while high nodule CG Iron is typically obtained when the $Mg_{(fin)}$ is greater than 0.02 percent. These results are shown in Figure 3.

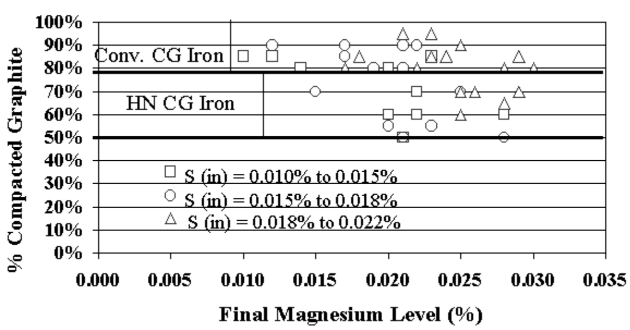

Figure 3: Influence of final residual magnesium $Mg_{(fin)}$ compacted graphite levels

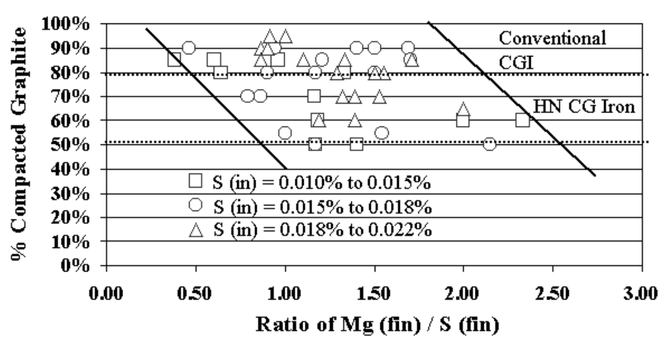

Figure 4: Influence of $Mg_{(fin)}/S_{(fin)}$ ratio on the compacted on graphite level in the final iron structure

A second control parameter identified as the ratio of $Mg_{(fin)}$ / $S_{(fin)}$ (Chisamera, 2002). This ratio also influences the final structure of the production castings. As shown in Figure 4, the higher this ratio becomes, lower levels of compacted graphite form and correspondingly, higher nodularity compacted irons tend to form. When this ratio falls in the range of 1.0 to 2.0, CGI iron forming tendencies are very high.

The final structure of compacted graphite irons is very dependent on the treatment method of the ductile base iron. The level of magnesium addition in relationship to initial sulfur level is extremely important, because the nodular graphite structure stability is not just determined by residual magnesium level but also by that initial sulfur relationship.

It was also observed that for the same magnesium addition rate over a relatively large range of initial sulfur contents, a linear relationship characterizes the ratio of $Mg_{(add)}$ / $S_{(in)}$, (magnesium addition rate to initial sulfur level) to the initial sulfur level.. Figure 5 shows this linear relationship for the two different categories of graphite nodularity, conventional compacted graphite (CG equal or greater than 80 percent compacted graphite) and high nodule compacted graphite (HN equal or greater than 50 percent compacted graphite).

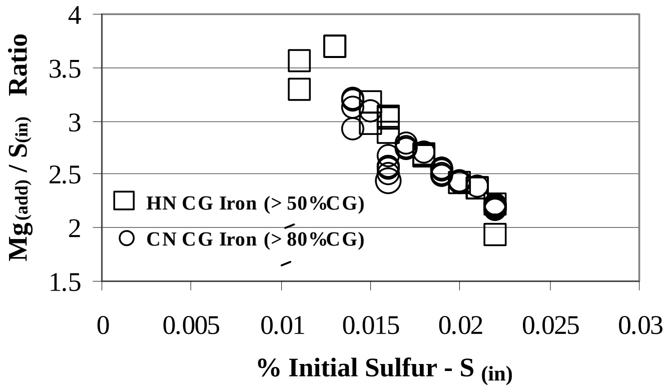

Figure 5: Effect of $Mg_{(add)}$ / $S_{(in)}$ ratio and on compacted graphite formation at varying initial sulfur ($S_{(in)}$) levels

It was also observed that as the ratio of $Mg_{(add)}$ / $S_{(in)}$ becomes greater than 3.2, high nodule compacted graphite formation is favored. However, when this ratio of $Mg_{(add)}$ / $S_{(in)}$ lies in the range of 2.0 to 3.2, both types of compacted graphite structures were obtained. $Mg_{(add)}$ / $S_{(in)}$ ratios greater than 3.2 favor increased graphite nodularity or decreased compacted graphite content in the final structure.

Initial sulfur level, before magnesium treatment, shows a complex influence on the resultant final structure. After an intentional sulfur addition, high graphite nodularity is mainly associated with a lower sulfur level base iron (sulfur less than 0.018 percent sulfur), while conventional compacted graphite iron (compacted graphite greater than 80 percent) is almost always obtained with higher residual final magnesium (greater than 0.022 percent $Mg_{(fin)}$) to compensate for the higher initial sulfur level (greater than 0.018 percent $S_{(in)}$). Other ratio relationships, such as the ratio of $Mg_{(add)}$ / $S_{(in)}$ and the ratio of $Mg_{(fin)}$ / $S_{(in)}$ to the percentage of compacted graphite formed are both very similar to the ratios of $Mg_{(fin)}$ / $S_{(fin)}$ (see Figure 4).

In all of the experimental heats, the sulfur level of the base iron had an important influence on determining the success rate for compacted graphite iron production. It was concluded that the entire magnesium line must respond to this most important parameter of base iron initial sulfur content. Two possibilities exist, especially for those melting processes that result in low initial sulfur contents (less than 0.018 percent sulfur). These are briefly outlined below:

- Lowering the magnesium addition, for the same sulfur addition.
- Increasing the sulfur addition, for the same magnesium addition.

The data shown in Tables 10 through 12 represent those heats where treatment with granular sulfur additions were, for the most part, successful. There were numerous heats in which there was little to no sulfur recovery. These data are not represented in Tables 10 through 12 because of the failures to recover sulfur. Some scatter in the data was also associated with the ladle design at the production foundry. Magnesium recoveries ($Mg_{(fin)}$) tended to have more variation because the treatment ladle did not have a desirable 2 to 2.5 ladle height to diameter ratio. A second source of variation in magnesium recovery was because the lid on the treatment ladle did not have a suitable guide to direct the magnesium wire to the bottom of the ladle.

Lastly, there was considerable scatter associated with adding the granular iron pyrites to the ladle. On several occasions, no sulfur pickup was observed. Often, there was considerable variation in final sulfur content ($S_{(fin)}$) because of poor recoveries. It was felt that the powdery, granular pyrites were difficult to get under the melt surface where consistent recoveries would have been possible. Another feature was the considerable odor associated with using granular iron pyrites. Consequently, a new sulfur additive was sought to provide a consistent and reliable method of increasing the sulfur content.

Briquetted FeS_2 results:

Based on the results of all the heats shown in Tables 10 through 12, it was established that the process of using sulfur to denodulize ductile iron is highly dependent on extremely close control of sulfur recovery. For this reason, a new and improved sulfur additive was evaluated in an effort to provide more stable results in an iron melt than available with powdered FeS_2.

Table 13: Magnesium and Sulfur Relationships in CG Iron – Iron Sulfide Briquettes

Initial $S_{(in)}$ [%]	Heat No.	% Mg Addition $Mg_{(add)}$	% Sulfur $S_{(add)}$ Briquettes	$Mg_{(add)}$ / $S_{(in)}$ ratio	Final Mag % $Mg_{(fin)}$	Sulfur $S_{(fin)}$ [%]	$Mg_{(fin)}$ / $S_{(fin)}$ Ratio	$Mg_{(fin)}$ / $S_{(in)}$ Ratio	[%] CGI
0.012	25	0.0317	0.020	2.64	0.026	0.019	1.37	2.16	95
0.012	26	0.0333	0.020	2.78	0.029	0.021	1.38	2.42	85
0.012	27	0.0305	0.0183	2.54	0.023	0.015	1.53	1.92	90
0.012	37	0.0300	0.024	2.50	0.034	0.020	1.70	2.83	80
0.012	36	0.0300	0.024	2.50	0.040	0.037	1.08	3.33	85
0.012	34	0.0300	0.024	2.50	0.033	0.028	1.18	2.75	85
0.013	28	0.0341	0.0177	2.62	0.028	0.014	2.0	2.15	80
0.013	29	0.0367	0.0180	2.82	0.029	0.016	1.81	2.23	80
0.013	30	0.0367	0.0180	2.82	0.039	0.023	1.70	3.0	80
0.013	23	0.0317	0.0180	2.44	0.025	0.015	1.67	1.92	85
0.013	24	0.0317	0.0180	2.44	0.036	0.020	1.80	2.77	90
0.013	25	0.0317	0.0180	2.44	0.023	0.022	1.05	1.77	90
0.013	27	0.0333	0.0163	2.56	0.036	0.021	1.71	2.77	80
0.013	32	0.0317	0.0198	2.44	0.038	0.032	1.19	2.92	80
0.016	25	0.0350	0.016	2.19	0.017	0.016	1.06	1.06	80
0.019	27	0.0383	0.016	2.02	0.017	0.014	1.21	0.89	85
0.019	28	0.0367	0.016	1.93	0.035	0.021	1.67	1.84	70
Averages									
0.0136		**0.0333**	**0.0186**	**2.48**	**0.0296**	**0.0209**	**1.463**	**2.24**	**83.75**
Std. Dev.									
0.0024		**0.0026**	**0.0024**	**0.0025**	**0.0072**	**0.0064**	**0.30**	**0.656**	**5.7**

Table 13 summarizes the iron sulfide briquette results in place of the powder grade used for all previous heats.
The use of iron sulfide briquettes provided significantly improved control of sulfur. The data shown in Table 13 resulted in 83.75 percent compacted graphite iron structures. Final magnesium levels and sulfur levels were 0.030 percent and 0.021 percent respectively. The ratio of $Mg_{(fin)}$ to $S_{(fin)}$ was 1.463 with a standard deviation of 0.30.

Sulfur additions rates for briquettes were reduced to an average of 0.019 percent compared to 0.031 percent for granular powder additions of iron pyrites. The briquetted iron pyrites appeared to provide the consistency for producing compacted graphite with 80 percent minimum compacted structures. The standard deviation for compacted graphite production decreased to 5.7 compared to 10.82 for granular additions (see Table 12).

CG production from gray base irons: Because of the favorable results obtained with the iron sulfide briquettes, a series of heats were made from a gray base iron having an initial sulfur content of 0.057 percent. The results of resulfurizing a gray base iron after magnesium treatment are shown in Table 14.

Table 14: Magnesium and Sulfur Relationships in CG Iron from gray base irons

Initial $S_{(in)}$ [%]	Heat No.	% Mg Addition $Mg_{(add)}$	% Sulfur Sulfur $_{(add)}$ Briquettes	$Mg_{(add)}$ / $S_{(in)}$ ratio	Final Mg % $Mg_{(fin)}$	Final Sulfur $S_{(fin)}$ [%]	$Mg_{(fin)}$ / $S_{(fin)}$ Ratio	$Mg_{(fin)}$ / $S_{(in)}$ Ratio	[%] CGI
0.057	29	0.037	0.016	0.64	0.024	0.013	1.85	0.421	80
0.057	31	0.038	0.016	0.67	0.029	0.014	2.07	0.509	75
0.057	30	0.037	0.016	0.64	0.024	0.016	1.50	0.421	90
0.058	34	0.035	0.016	0.60	0.018	0.017	1.06	0.310	85
0.058	33	0.037	0.016	0.63	0.024	0.012	2.00	0.414	75
Averages									
0.057		**0.037**	**0.016**	**0.64**	**0.024**	**0.014**	**1.70**	**0.410**	**81**

Table 14 shows that it was possible to produce compacted graphite iron from a gray iron furnace chemistry. The compacted graphite irons so produced exhibited microstructures containing an average of 81 percent compacted graphite. The ratios of

$Mg_{(fin)}$ to $S_{(fin)}$ to the percentage of compacted graphite formed increased somewhat to 1.7. This ratio is still well within the standard deviation calculated in Table 14, where the most consistent compacted graphite structures were obtained.

Briquetted FeS_2 to control sulfur recovery:

Precise control of sulfur recovery is an essential feature of this technology and it has been demonstrated to be easily achievable in foundry conditions, for both ductile iron and compacted graphite iron.

In the early stages of the investigation of sulfur additions after Mg-treatment in both Romania and the USA, iron pyrites were used to re-introduce sulfur (resulfurize) to an iron melt. Since iron pyrites are normally available only in very fine mesh sizes, difficulties are often encountered during the addition to ladles, resulting in inconsistent recoveries. The fine sized iron pyrite particles, when added to molten irons, tend to become airborne due to convection currents of super-heated air, leading to the generation of obnoxious fumes and odors. For all these reasons, it was necessary to improve and get improved control over the sulfur addition. After magnesium treatment, sulfur is usually added at a very low level (0.001 to 0.020 percent sulfur) and it was found that briquetted iron sulfide based materials can circumvent the inconsistencies of adding powdery iron pyrites. The "iron sulfide or iron pyrite briquettes" are formulated to go into solution rapidly without odor. A second and important benefit of these briquettes is that they supply a "fresh sulfur" source to the iron, which affects the surface activity and speculatively changes the graphite growth mechanism promoting the "compacted" growth mode.

Table 14: Physical and Chemical characteristics of FeS_2-Briquettes

Characteristics			
Physical Properties:	**Values**	**Chemical Composition:**	**Values**
• Appearance	A grayish-gold, briquetted alloy	• Sulfur	29.95-30.05%
• Bulk Density	3.83 grams/cc or 140 lbs./cu.ft	• Carbon	0.5 to 3.5%
• Dissolution Temperature	Starts to dissolve at 1,980 ^{o}F	• Iron	Balance
• Size	1 ¼ inch long pillow briquettes, 6.0 grams / contained sulfur		

Table 14 lists the typical physical and chemical characteristics of the FeS_2-briquettes.

The iron sulfide briquettes were designed to have the capability to increase the sulfur level by 0.001 percent sulfur, from one 20 gram briquette (which contains approximately 6 grams of sulfur) when added to 1,000 lbs. of molten iron. Practical results confirm the improved repeatability of this sulfur raiser addition. Iron pyrites in powder form afford only a 30 to 35 percent recovery, whereas, iron sulfide briquettes typically provide close to 90 percent recovery.

FeS_2 briquettes are also a very important source for very small sulfur additions in ductile iron to improve the graphite nucleation potential after Mg-treatment. Consistent sulfur recovery control in ductile iron is also of vital importance for promoting graphite nucleation without the risk of reduced graphite nodularity. In terms of both foundry and environmental performance, briquetted FeS_2 displayed vastly improved reliability than powdery or granular iron pyrites.

CONCLUSIONS AND RECOMMENDATIONS

1. Production foundry experience showed that it was possible to use controlled sulfur additions during a post-inoculation procedure to produce compacted graphite cast iron (without titanium additions). Controlled sulfur additions during post-inoculation of ductile iron also improved the nodule count with lower risk of carbides, due to the enhanced inoculant performance. Calcium silicide granular inoculants, incorporating oxy-sulfide containing enhancements, resulted in significantly higher nodule counts at a 75 percent addition reduction rate. Pressed inserts based on essentially this same chemistry and used as an in-mold inoculant also resulted in significant increases in nodule counts and with even further reduced addition rates.

2. By avoiding titanium additions, both compacted and ductile irons can be obtained from the same iron melt, using a two-step treatment process of sulfur and magnesium, but at different values:

By magnesium treatment methods: to obtain stable nodular graphite in ductile iron in a $Mg_{(final)}$ range of 0.04 to 0.06 percent and partially developed nodular or intermediate graphite structure for compacted graphite iron in a $Mg_{(final)}$ range of 0.025 - 0.04 percent.

By sulfur treatment methods: to improve graphite nucleation without affecting nodularity in ductile iron (S_{add} equals 0.005 to 0.007 percent) and to limit nodular graphite incidence in CG Iron (S_{add} equals 0.005 to 0.025 percent); conventional (greater than 80 percent CG) or high-nodularity (50 to 80 percent CG) compacted graphite irons could be obtained by this way.

3. Initial sulfur level, in base iron, is one of the prime factors that influences graphite shape and nodularity. Furnace sulfur levels not only affect graphite nodularity after magnesium treatment, but also affect graphite nodularity in the final structure after a supplementary sulfur addition. Low initial sulfur (especially less than 0.015 percent) require lower magnesium additions or higher sulfur additions to obtain conventional CG Iron, greater than 80 percent nodularity.

4. Increasing the $Mg_{(add)}$ / $S_{(in)}$ ratio will increase graphite nodularity in the final structure. With the same sulfur addition, high nodular compacted graphite (50 percent compacted graphite or more) can typically be expected to form when this ratio is greater than 2.85.

5. High nodular CG Iron typically formed when $Mg_{(final)}$ was more than 0.024 percent magnesium ($Mg_{(fin)}$) and final sulfur levels were in the range of 0.018 percent. Conventional CG Iron was obtained when the final magnesium level averaged 0.020 and final sulfur levels averaged 0.019. Higher final magnesium levels (greater than 0.022 percent) and high initial sulfur levels (greater than 0.018 percent) also promoted conventional CG formation.

6. Granular or powdery iron pyrites (FeS_2), initially used as the common source of sulfur additions, in both ductile and compacted graphite irons, produced inconsistent results. Because of the fine mesh size typical of iron pyrites, airborne losses during ladle additions lead to inconsistent recoveries and high odor levels.

7. Close and consistent control of sulfur additions were only achieved when briquetted iron pyrites were used. The FeS_2 briquettes were formulated to go into solution rapidly giving close to 90 percent recovery to increase the sulfur level by 0.001 percent from one 20g briquette (6g S) when added to 1,000 pounds of molten iron.

8. Conventional compacted graphite production, with greater than 80 percent compacted graphite structures, was possible using both gray and ductile base irons from the same furnace.

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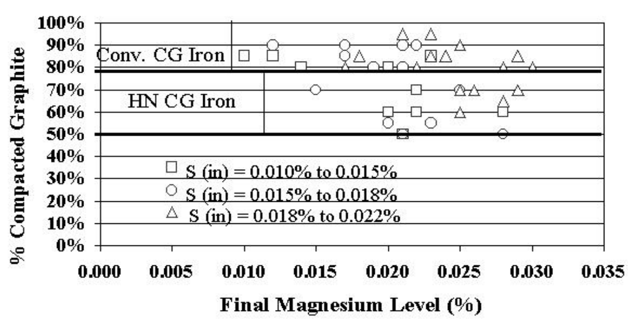

Figure 3: Influence of final residual magnesium $Mg_{(fin)}$ compacted graphite levels

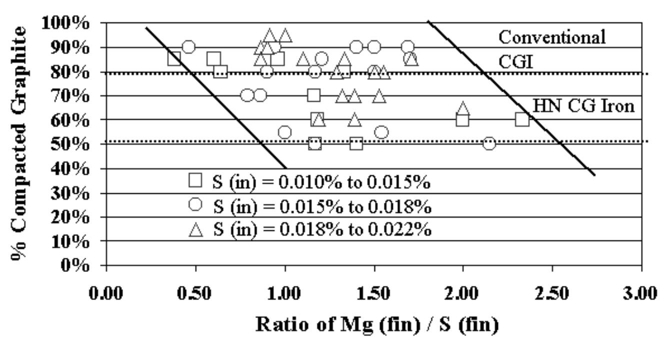

Figure 4: Influence of $Mg_{(fin)}/S_{(fin)}$ ratio on the compacted on graphite level in the final iron structure