# PRODUCTION ASPECTS OF SPHEROIDAL GRAPHITE IRON

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## INTRODUCTION

Spheroidal graphite cast iron, also referred to as ductile iron, nodular cast iron, spherulitic iron, is essentially cast iron in which graphite is present in the form of tiny balls of spherulites, rather than flakes as in normal grey iron or compacted aggregates (nodules) as in malleable iron. The elements present in the normal cast iron are carbon and silicon, together with manganese, sulphur and phosphorus. Moreover alloying elements such as copper, nickel, chromium, vanadium and molybdenum may be present in varying quantities. In addition, some unwanted elements like lead, titanium, tellurium, bismuth, antimony and arsenic may be present in cast iron in minute quantities which seriously interfere with graphite crystallisation. Finally certain gases, such as hydrogen, oxygen and nitrogen are also present in the normal cast iron. Such cast iron containing the above elements and gases will always precipitate their carbon as flake graphite. If such contaminated graphite is purified, a spheroidal cast iron will result in which the free carbon is present in a more or less spheroidal or nodular form in the metallic, steel like matrix. This purifying treatment of cast iron is accomplished primarily by desulphurising so that the sulphur content is reduced to 0.01-0.008% and at the same time degassing the starting melt.

Magnesium, cerium, yttrium, calcium and some other chemically similar metals have proved themselves eminently suitable for the deoxidation treatment which cause the normal flake graphite in cast iron to change to spheroids or nodules.

Of these reactive metals, magnesium is the most economical even though minute amount of magnesium is retained in the iron because of the violent reaction which occurs when added to the molten iron. To counteract the violence of this reaction, three general systems have been developed.

1. The magnesium is diluted by alloying with other less reactive metals. Of these magnesium-Ferro silicon and nickel-magnesium-silicon have gained commercial acceptance

2. The use of treatment ladle is constructed as an autoclave in the event of magnesium being introduced as the elemental metal. The violence of the reaction is controlled by using the pressure in the ladle higher than the vapour pressure of magnesium at the temperature of melt being treated i.e. 1400-1500°C
3. The injection of magnesium chips or powder below the surface of molten iron through graphite tubes with nitrogen or argon as a carrier. Whether pure or in the form of master alloys, the final contact of these elements in the spheroidal graphite iron is of the order of 0.02-0.08%Mg , 0.01-0.02% Ca or 0.02-0.03% Ce.

Each of the above method has a bearing on cost, and is influenced by processing problems or unwanted additions to the iron. In an attempt to reduce or eliminate these problems, a magnesium-impregnated coke was developed which was plunged into the iron to nodularize the graphite

## TREATMENT ADDITIVES FOR PRODUCTION OF SPHEROIDAL GRAPHITE IRON

The treatment for production of spheroidal graphite iron must be simple and safe; the media must dissolve and distribute themselves in the melt properly and should set up a movement to produce a kind of "self cleaning" action.

Since the origin of spheroidal graphite iron production, magnesium has proved itself eminently suitable as a treatment medium; it satisfies the above stated requirements both economically as well as technologically. This element vaporises at the treatment temperature of 1400-1500°C, lowering the partial pressure of the gases in the melt so producing a degassing effect-particularly on the oxygen content

## ADDITION OF MAGNESIUM TO IRON

The amount of magnesium required to be dissolved in molten cast iron to ensure the production of spheroidal graphite consists of that required to neutralise any sulphur present; (¾ of the %S) together with the necessary amount dissolved in the iron for spheroidisation i.e. 0.04 - 0.08%

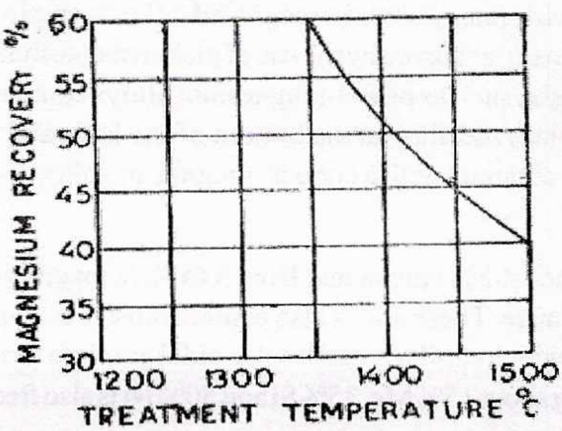


*Fig. 1 : Magnesium recovery from nickel magnesium alloy treatment at various treatment temperatures*

However, when magnesium is introduced to molten iron, only part of it dissolves to neutralise the sulphur and treat the iron, the remainder being lost by vaporisation and oxidation. The percentage of the added magnesium, which is dissolved and effective often called magnesium recovery. It depends upon many factors, 'principally the alloy used', method of addition and metal temperature. It has been established by Nicholls, higher the metal temperature lower is the magnesium recovery (Fig. 1). Furthermore, it has been found that the magnesium recovery increased sharply as the magnesium content of the treatment alloy drops below 10% (Fig. 2).

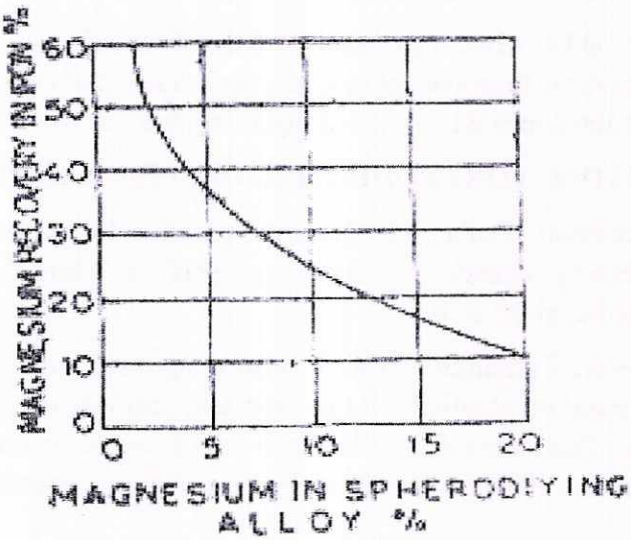


*Fig. 2 : The smaller the amount of magnesium in spheroidizing alloys, the higher the magnesium recovery*

Use of elemental magnesium in the foundry is basically possible, but it demands an equipment such that, it could not receive wide acceptance in the industry. Much better conditions are obtained when substances containing magnesium, viz., magnesium impregnated coke, is employed. In the foundry the addition of magnesium is mostly achieved by the use of nickel magnesium alloy. In the case of alloys of higher specific weight, such as nickel-magnesium alloys containing 15 to 20% Mg, the method of addition is to place the alloy at the bottom of the ladle and tap the metal onto it. Good results have also been obtained with a copper -magnesium alloy (85% Cu and 15% Mg).

The magnesium-silicon-iron alloy with about 55% silicon and from 5 to 35% magnesium has also gained considerable economic importance. These alloys also contain mostly calcium, rare earth and above all cerium and lanthanum, which similarly assist spheroidal graphite formation. Nickel-silicon-magnesium alloy containing about 15% Mg, 35% Si and 50% Ni is also frequently employed to put into the melt.

**Typical calculation of magnesium alloy additions :**

Nickel -Magnesium alloy (15% Mg)

Metal temperature 1425°C

Sulphur content of Iron- 0.08 % S

Magnesium to Neutralize Sulphur : 0.08 x 3/4 = 0.06%

Residual Magnesium required: 0.06%

Effective Magnesium required: 0.12%

Recovery of Magnesium at 1425°C ; 47.5 %

Total Magnesium addition

(100/47.5) x 0.12 = 0.253%

Amount of Ni-Mg alloy Required

(100/15) x 0.253 = 1.69 Ni-Mg

## ADDITION OF CALCIUM TO MOLTEN IRON

Calcium is the second element in order of importance, in the production of spheroidal graphite cast iron. In practice metallic calcium does not lend itself to spheroidal graphite formation and usually calcium silicon compounds containing rare-earth and occasionally magnesium as well are employed very frequently

Often, calcium is introduced as a reactive slag consisting of calcium-silicon for the major part, together with chlorides and fluorides of calcium, magnesium and cerium. The use of master alloys containing calcium instead of magnesium offers certain advantages, such as reduces susceptibility to shrinkage, produces clean as-cast surface, ensures less dross, shows less inclination to cementite formation, and more tendency towards production of ferritic Spheroidal graphite iron.

## COMMERCIALLY EMPLOYED METHOD FOR MAKING SPHEROIDAL GRAPHITE IRON

### Preconditioning

Conditioning a molten metal for treatment with spheroidizing agents include adjustment of temperature and adjustment of chemistry to desired level or Desulphurizing

### Temperature

Every effort should be made to keep the temperature as low as possible in the ductile iron process, since recovery of spheroidizing agent decreases with increase in metal temperature. The metal temperature range at treatment is 1400-1500°C

## Desulphurizing

One school of thought is to remove all the sulphur possible for best spheroidizing result. Others indicate that base iron having sulphur levels in the neighbour hood of 0.01% will produce better graphite structure than the base iron with sulphur levels below 0.005%. While feeling is also prevailing that base iron sulphur should be maintained at 0.02% for best results, particularly for thin section. Several methods have been employed for controlling sulphur level of iron used for making of S.G Iron. The most common method is basic cupola with sufficient fluxing agents like lime stone, fluorspar, dolomite to produce slag with high percentage of basic constituents. The final sulphur in basic cupola iron is in the range of 0.010-0.040%, the low sulphur cupola melt metal, however, often lacks the temperature of treatment and requires duplexing in conjunction with induction melting.

External treatment of iron with various Desulphurizing agents is used with varying degrees of success. For successful desulphurization, the following basic factors are desirable in the processes.

a) Intimate contact between molten metals and the Desulphurizing agent
b) Reaction duration
c) Simple removal of sulphur bearing slags after desulphurization
d) Temperature control
e) Fume control
f) Minimum refractory maintenance
g) Ease of handling and feeding of de-sulphurizing agent

There are various method employed for external desulphurization of iron. One of the oldest and simplest methods of desulphurization is the addition of soda ash to the molten metal when poured into the ladle. Injection has been used for Desulphurizing in a metal bath, yet found little use. The porous plug offers means of providing contact of metal and Desulphurizing agent by stirring action of the molten metal. In addition, various mechanical devices are available for achieving intimate contact between Desulphurizing agent and the metal through a stirring action. The Desulphurizing agents most commonly employed with these devices are calcium carbide or lime

## Treatment methodology

The addition of treatment alloys to molten iron is probably the most important single step in the production of spheroidal graphite iron. Results of a survey of various treatment techniques were published in 1967. That survey dealt with the relative popularity of various treatment methods in use at that time. At that time the most widely used method, based on the foundries responding to the survey, was the simple open ladle or transfer method.

A number of treatment methods are described in this write-up. However, not all of them are in common use. These are described to show how are many foundrymen have tried to economically alloy molten iron with a volatile, reactive metal that has low solubility in iron. Recovery of the treatment alloy is one of the most important considerations and yet probably it is the most inconsistent factor in the process. The variable that influence recovery include metal temperature, type and size of alloy material, quality of metal being treated, Rate of tapping and treatment method. Composition of ladle refractory has also has an effect on final residual magnesium. It has been demonstrated that magnesium loss is minimised by using refractory materials that do not react with it e.g. $Al_2O_3$ and MgO.

**Open ladle transfer method**

This method (Fig. 3) is the simplest in use. With this method a required amount of spheroidizing alloy is placed on the bottom of an open, heated ladle upon which a determined

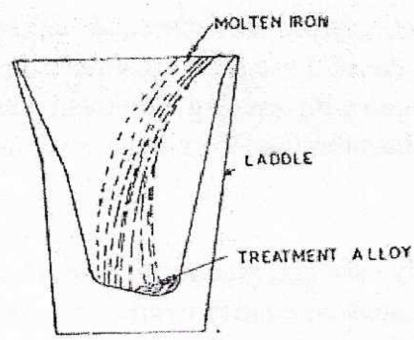


*Fig. 3 : Schematic diagram of the open ladle transfer method*

quantity of base iron, at the treatment temperature, is poured as rapidly as possible. Normal recovery of treatment alloy is about 20 to 30%. Denser alloy produces better recovery than the lighter alloys with this method.

**The sandwich method**

The sandwich method is an improved treatment technique of the described open ladle transfer (pour over) method. The ladle configuration almost the same as for ladle transfer, except at the bottom, which is modified to have a pocket (Fig. 4) to retain the treatment alloy.

The name is derived from the fact that to retard the start of alloy reaction, a covering material or sandwich layer is placed on top of spheroidizing alloy prior to the addition of molten iron. Both 50 % and 75 % Ferro-silicon are used as cover material to improve magnesium recovery. Resin-coated sand and calcium carbide are also occasionally used as sandwich covers in application requiring extended holding time.

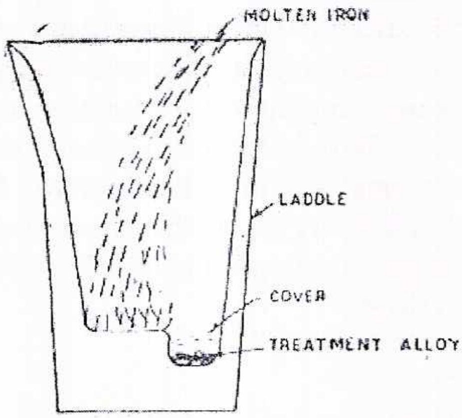


*Fig. 4: Schematic diagram of the sandwitch method*

Magnesium recovery is much improved with this treatment and may range upto 40 to 45 %. Advantages of the sandwich method are short treatment times, simplicity, flexibility and improved recovery of magnesium with less slag, fumes etc. The disadvantage is, a loss in melt temperature due to additional heat required to melt the cover material.

**Plunging method**

The plunging method is widely used and practically takes in all forms of treatment materials including magnesium impregnated coke and rare earth alloy combination. In this method, a bell shaped refractory device containing spheroidizing material is submerged deeply into the ladle of molten iron (Fig. 5) and thus prevents the material from floating. The material is usually held in the plunger by means of a sheet metal canister or other suitable container. Because of this,

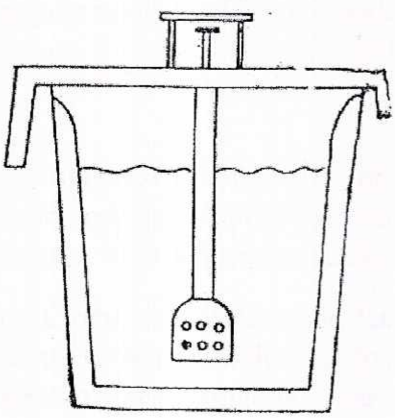

*Fig. 5 : Schematic diagram showing plunging method*

plunging method has the advantage of requiring less spheroidizing material than the open ladle or sandwich methods. The added cost of plunger bell assembly and labour may however, offset the reduced alloy cost, another advantage is that this method does not necessarily require a completely empty ladle for each treatment as do the open ladle and sandwich process. The recovery of magnesium from plunging method usually exceeds 50%.

The primary disadvantage is the greater temperature loss due to the mass of cold plunger assembly. In addition the cycle time is usually longer than the other methods.

The efficiency of an individual treatment process is determined by the reaction rate between molten iron and spheroidizing alloy. Though the two previously described methods work efficiently but in some instances the plunging technique is superior.

**Special treatment method**

A number of special treatment methods have been devised by foundrymen to increases the efficiency of particular treatment process or to take advantage of special treating materials.

*False or detachable bottom ladle*

False or detachable bottom incorporates a perforated refractory barrier in between two detachable ladles for treating molten iron with magnesium impregnated coke in particular, Fig. 6. The perforated barrier fitted at the bottom of upper ladle, prevents the magnesium-impregnated coke in the pocket of the attached bottom from floating, during the reaction. Each treatment requires a new sand rammed bottom.

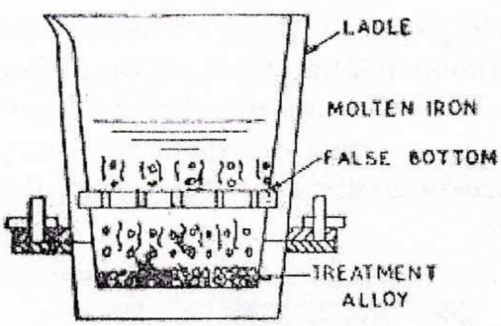


*Fig. 6 : Schematic diagram showing false or detachable bottom ladle for treating ductile iron.*

Magnesium recovery can be higher than the plunging and can exceed 50%. The advantages of the process include its adaptability to high capacity ladle treatments as well as its good efficiency. The most obvious disadvantage is the need for a newly rammed bottom for each treatment as well as the need to properly connect and seal the two ladle portions. Use of this technique is not widely accepted.

*The shelf ladle*

The shelf ladle is another method to trap or to hold down buoyant, reactive treatment material. The usual upright cylindrical ladle of the height to diameter ratio of 4:1 is used. A perforated refractory shelf or ledge is placed in the lower part of the ladle, Fig. 7. A slight angle will help to retain the coke beneath the shelf during the reaction. Recovery can be upto 50%.

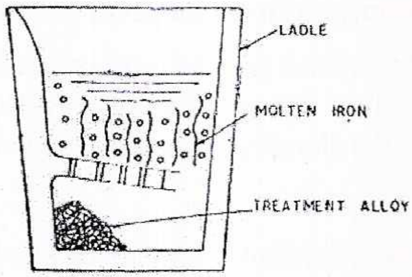


*Fig. 7 : Schematic diagram for showing shelf ladle method*

Advantages include the possibility of using low cost magnesium treatment material and the low evolution of magnesium oxide fume. Flexibility in batch size is also possible.

One disadvantage is, the necessity for using extremely accurate quantities of the material when using magnesium-impregnated coke.

*The hollow stream treatment process*

The hollow stream treatment process provides a means of introducing treatment alloy into the centre of molten stream of iron during transfer, Fig. 8. Once a 'head' of metal is established, the feed rate of the alloy must be synchronised with the flow rate of the iron. The purpose of this technique is to prevent air ingress during the magnesium-iron reaction. Inert gases can also be used to shield the reaction area to further increase the efficiency. Recovery in the inert atmosphere is reported as high as 80%.

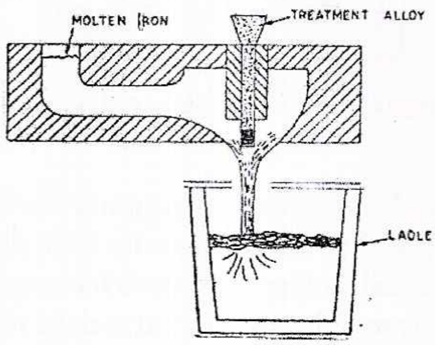


*Fig. 8 : Schematic diagram showing the hollow stream treatment method*

*Pressure ladle and pressure chamber*

The concept of using pressure tight devices to introduce low boiling point metals like magnesium to molten iron is not new. The practice was one of the early treatment techniques proposed but has not gained wide acceptance because of the cycle time and the handling mechanisms.

Two variations of the pressure system can be used. In one, a conventional ladle is placed inside a pressure chamber where the spheroidizing material is added, Fig. 9. In the second method, the treatment ladle is tightly sealed and pressurised as the spheroidizing material is introduced to the molten iron, Fig. 10. In both instances the pressure used is about 30 atmosphere. Pure

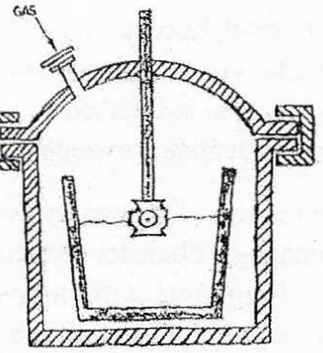


*Fig. 9 : Schematic diagram showing process chamber*

magnesium is used in both techniques with the magnesium being encased in a steel jacket or in alternatives arrangements fulfilling the condition. Magnesium shot can also be added and stirred under pressure.

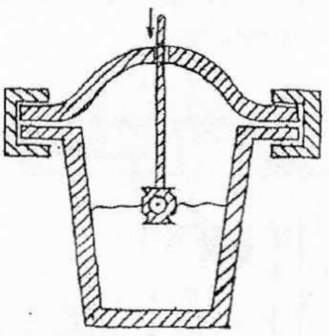

*Fig. 10 : Schematic diagram showing process ladle*

*Injection method*

Methods of injections of spheroidizing alloys were not widely used according to the 1967 survey. The principle of injection is to introduce a powdered or granular material to the molten iron

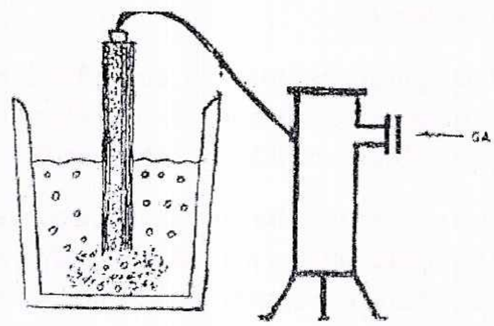


*Fig. 11 : Schematic diagram showing injection process*

beneath its surface to accomplish desulphurization and /or spheroidization. A hollow tube of refractory material, usually graphite is used with pressurised inert gas acting as a carrier (Fig. 11). In some instances, calcium carbide is injected to reduce the sulphur level followed by spheroidizing alloy. Recovery of about 50% is expected.

Advantages of injection include the use of pure magnesium and benefits derived from using elemental magnesium. Disadvantages include temperature loss that is considerably high and also tendency of the tube to be clogged-up with magnesium shot and dross. Recovery of magnesium is erratic and cost of magnesium shot is high.

*Mold treatment process*

Efforts have also been made towards spheroidization involving reaction between treatment alloy and the molten iron within the mould itself. A special reaction chamber is incorporated in the runner and gating system of the mould, Fig. 12. Treatment alloys are placed within the chamber and the reaction occurs during metal pouring.

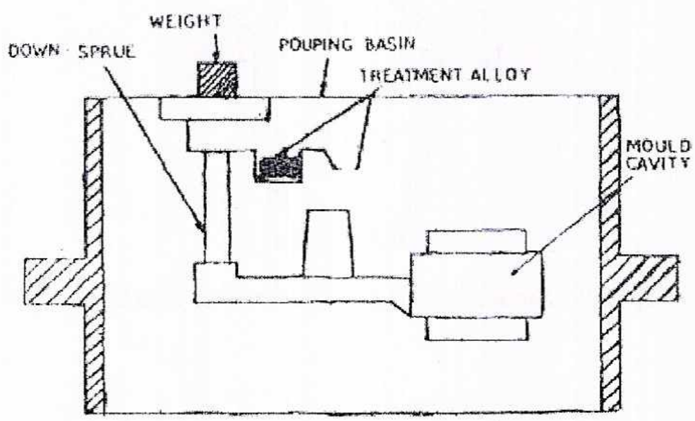


*Fig. 12 : Schematic diagram showing mould treatment process*

Magnesium recovery of as high as, 100 % has been reported in this process. The sulphur content requirement is below 0.010% before treatment. One variation of this process is to under-treat the molten metal using one of the other processes, then add the remaining quantity of spheroidizer, using mold treatment technique. Information lacks concerning the effectiveness of the process.

*Tiltable reactor (Converter)*

The Tiltable reactor is a cylindrical shaped vessel capable to rotate 180 degrees about a stationary axis. The process uses pure magnesium as the converter has the flexibility to seal by itself. A separate reaction chamber of perforated refractory is constructed and placed initially at the out of contact from the molten iron. Metal is drawn in to the converter, keeping it in the horizontal position. The reaction chamber at that time remains on the back and at a higher level than the metal level. As the converter is rotated to the vertical positions the reaction between the magnesium and the iron starts and builds up a pressure of 4 to 5 psi.

Recovery is reported as high as 50% to 60%. Advantages include the ability to simultaneous desulphurization and spheroidization.

*Direct Drop-in technique*

The direct dropping of the treatment alloy into liquid iron is based on the development of denser (compared to iron) magnesium containing alloy. The alloys are dropped directly into molten iron in a furnace, magnesium treatment ladle, transfer ladle or pouring ladle. More efficient use of alloy is achieved when the drop-in is done to the full weight of iron being treated. Low sulphur base iron is preferred to minimise alloy addition. The magnesium alloy addition may be preceded by a small addition of cerium, normally equal to the base iron sulphur content to further minimise magnesium alloy addition

These high density alloys may also be employed to recover nodularity in irons that have faded due to prolonged holding time. An alloy addition equivalent to 0.01 to 0.02 % Mg is dropped directly into the iron and is normally sufficient to fully recover nodularity. The alloys tried are:

60% Ni, 4.2 % Mg, balance iron for use upto a maximum of 1470°C treatment temperature.

95% Ni, 4.6% Mg, for use upto 1540°C treatment temperature; recovery is reported from 70 to 100%, and inversely proportional to the treatment temperature.

Advantages of this process are reduction in generated fumes, ease of handling, elimination of ladle skimming, and reduction in defects due to dross. The mentionable disadvantage is alloy cost.

**INTRODUCING REACTIVE SLAG**

The spheroidal graphite forming elements contained in reactive slags are placed on the surface of the melt and stirred mechanically during which the reaction with base iron takes place,

Fig. 13. The treatment element is a granular calcium-silicon coated with flux; besides 3% Mg it contains rare-earth elements to neutralise tramp elements in the melt.

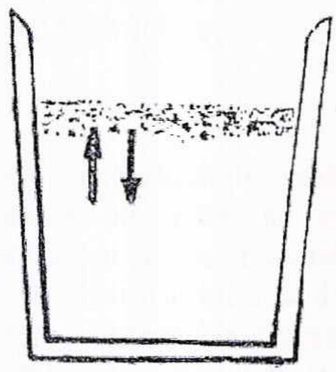

*Fig. 13 : Schematic of the method of introducing reactive slag*

Reactive slag, consisting of a mixture of calcium silicon with fluorides or halides of the rare-earths with or without magnesium is also eminently suited for production of small casting. When such slag is placed over the melt, calcium reacts with the halides of the rare earth, yielding calcium halides and rare-earth metals. The latter diffuse into the iron melt and favour the formation of spheroidal graphite. Because the reaction proceeds underneath the slag layer, losses of rare-earth metals are to a minimum extent. Further, since the slag reaction is exothermic, the temperature drop in the melt due to the treatment is very slight. By using a mixture of 50% of Ca, Si(75%) and 50% of addition media, a clean melt, free from inclusion is obtained. The magnesium recovery is claimed to be over 30%.

## SUMMARY

The choice of a treatment method for a unit foundry involves many a factors. The quality of the spheroidal graphite iron is greatly influenced by the method of production adapted. It should be clearly kept in mind that no single process described here can be regarded as the best to make spheroidal graphite iron under all circumstances. On the contrary, focus should be on selection of the master alloy and the treatment process to produce castings of predictable and consistent quality in a cost effective manner.

The criteria in the selection of a treatment method involve:

- Cost of treatment alloy and treatment method
- Temperature of treatment
- Reaction kinetics
- Simplicity of treatment method

- Considerations of Environment during treatment
- Batch size
- Composition of base iron
- Physical limitations of the plant

The processes, those have yielded the best results in practice are:

- The most simple open ladle transfer (Pour over) method
- The sandwich method
- The plunging method

For proper nodularization, it is necessary that the spheroidal graphite iron should contain 0.04-0.08% residual magnesium. The amount of spheroidizing alloy must be calculated accordingly, considering allowance for initial sulphur content of the base iron, treatment temperature and recovery. In practice, alloys amounting to 0.8-2.5% of the melt are added. Treatment time range and subsequent pouring should be fast enough to avoid fading.

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