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# Constructive Improvements in the In-Ladle Treatments - A Comparative Industrial Study

Imre Kiss

**Abstract:** Nodular gray cast iron having properties superior to conventional gray cast iron can be produced by treating the molten iron so that, when cast, the graphite will be compacted rather than in flake form. One such treatment involves the introduction of magnesium (Mg) into a molten iron bath of such composition. It is the principal object of the present industrial experiments to provide an improved process for the ductile cast iron production. Another object is to provide a process which permits the efficient use of the nodulizing agents, which results in the efficient production of an improved homogeneous nodular cast iron. Essentially such treatments result in the retention by the cast iron of small amounts of nodulizing agents, for example magnesium (Mg). Conventionally these agents are added to cast iron, usually in the form of pre-alloys and the efficiency of the process is illustrated by the high assimilation of the added nodulizer's constituents. Another object of this technological practice is to provide an improved method for introducing the nodulizing agents, using constructive improvements to the in-ladle equipment. Finding magnesium (Mg) using novel techniques is the first step to advance the understanding of the role of magnesium (Mg) in the formation of the nodular graphite, the mechanism behind nodular graphite formation due to the addition of Magnesium (Mg) being still relative unclear at present time. Moreover, this may advance new methods to improve the nodulizing treatment process. This study take into account the flexibility of the used technique, which describes the elasticity of the treatment process, by improvement or alternative to the existing one. As nodulizing agents magnesium-ferrosilicon (Fe-Si-Mg type) and cerium-magnesium-ferrosilicon (Nodulin type) are examples of materials containing nodulizing agents that have given excellent results in the mixture. This experiments relates to a process for the production of ductile iron (nodular gray cast iron) and particularly to a process for adding magnesium (Mg) to the melted iron.

**Keywords:** assimilation degrees; constructive improvements; ductile cast iron (nodular graphite iron); in-ladle treatments; magnesium (Mg); nodulizing agents; silicon-based pre-alloys

## 1 INTRODUCTION

Nodulization in cast irons is a process of controlling the structure and properties by changing the graphite shape from flakes to spheroidal, during the solidification process [1-6]. The nodularizers are added into the liquid iron to promote the formation of spheroidal (or compacted) form of graphite, specific for the ductile irons. Therefore, a certain quantity of nodularizing agent is necessary to obtain the spheroidal (or compacted) form of graphite [1-9]. So, production of ductile iron with consistent properties is generally accomplished by the addition of nodulizing elements in the iron alloys [1-9]. Nodulizers such as magnesium (Mg), cerium (Ce) and rare earth elements, alone or as pre-alloys, promote the formation of spheroidal graphite in iron. Among these, magnesium (Mg) is the most commonly used in the production of ductile iron [1-9].

Depending on the characteristics of each pre-alloy used as nodulizing agent, different treatment techniques are used. Among these, the most widely used are the in-ladle, the in-mould, and the flow-through methods, the first being the most used [3-9]. Most in-ladle treatments involve the use of pre-alloys (usually magnesium-ferrosilicon) in a specially prepared ladles, as in the open ladle (sandwich) and covered ladle (tundish) processes. In the practice of nodulization it is demonstrated that, compared to open ladle techniques, the use of a covered ladle gives better magnesium (Mg) assimilation with much less fume [4-9].

Nodular cast iron is made by adding to the cast iron under the proper conditions a quantity of a nodulizing agent and inoculating the cast iron [1-9]. The treatment results in a cast iron in which free graphite appears in compacted or nodular form rather than as flakes [1-4, 10-11]. Recent discoveries have established that certain advantages accrue when the elements necessary to nodulizing the cast iron's graphite are used by in-ladle treatment [4-9].

Over the years, in the history of nodular graphite irons, numerous and different treatment processes have developed. Some, the best performing, were accepted, others were rejected a long time ago. The first procedures used spear injection and ladle shaking to achieve the nodulization, and many of these can no longer be seen in the modern foundries, being out dated. Currently, the most widespread processes are those with in-ladle treatment, with ordinary bottom, or those with special construction, which use, in particular, silicon-based nodulizers (class of Fe-Si-Mg) [3-13].

**Figure 1** Silicon-based (light) master alloys as nodulizer
(a) magnesium-ferrosilicon lump; (b) magnesium-ferrosilicon granular;
(c) magnesium-ferrosilicon briquette; (d) magnesium-ferrosilicon powder

The properties of cast iron can be improved by the addition to it of nodulizing elements, commonly cerium (Ce), magnesium (Mg) or both, added, suitably, by various technological techniques [1-9].

In nodulizing of cast iron with the treating agent and according to the nodulizing process, the sulphur (S) content of the iron needs to be treated as an important factor [1-5, 9-13]. In general if a substantial amount of nodulization is to be obtained efficiently the sulphur (S) content of the iron prior to the adding of the treating agent should not exceed about 0.02%. For best results the sulphur (S) content should not exceed 0.01% [1-5, 9-13]. The reduction of the sulphur (S) content of cast iron to the indicated low values may be accomplished conveniently by the adding of nodulizing agent into the melted iron.

In view of the above–described problems, it is one objective to provide a method for producing nodular cast iron by using a nodulizer and a spheroidizing device that effectively solves problems of violent reaction and low adsorption rate of effective nodulizing elements [1-5, 9]. The treatment method need to be capable of accurately controlling the reaction time of the spheroidizing, improving the product quality, lowering the production cost, effectively using the resource, and obviously improving the manufacturing process of the nodulizer and the environment of the spheroidizing process [1-5, 9, 13].

Since the start of ductile iron production the simple ladle treatment has undergone various developments, all of them trying to improve the consistency of the nodulizing process and thus favouring adding as lesser magnesium (Mg) as possible [1-5, 9]. Thus have evolved the treatment procedures, from simply immersion with the plunging bell, to the in-ladle treatments, with a pocket or pockets [3, 4, 9]. These processes (i.e. Plunging, Sandwich/Over pouring, Trigger) are joined by those that introduce a cap on top of the treatment ladle into the nodulization technology. In this category of in-ladle treatments with cover, significant is the Tundish-Cover process. During cast iron treatment, such technique would ensure recovery of magnesium (Mg) reaction thanks to the pressure generated inside the ladle and to the contact of the magnesium (Mg) with the metal bath.

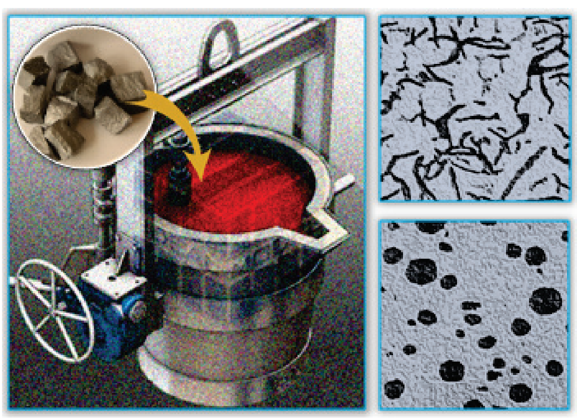

**Figure 2** In-ladle treatment

The Trigger process can be improved in order to increase the magnesium (Mg) assimilation. Thus, a proposed solution consists in the arrangement at the ladle bottom of two or more pockets, arranged equidistantly, in which the nodulizers (same nature or of different sorts) are introduced. The nodulizers can be protected with calcium carbide layers like in the conventional technologies (Sandwich or Trigger). This layers will be perforate, successively, triggering a series of change reactions, time–appropriated, lasting only a few tens of seconds [1-5, 9]. Theoretically, the nodulizing effect increases. And practically this has been experimented under foundry conditions, in special ladle with two or four pockets, arranged equidistantly and symmetrically.

## 2 IN-LADLE TREATMENT METHODS

A number of in–ladle treatment techniques have been developed to prepare ductile iron over the years [1-5, 9]. The most common treatment techniques in use today are the immersion (plunging) process, the open ladle process, the sandwich process (with special pocket), and covered ladle (tundish) process [1-5, 9]. Today, the majority of ductile iron castings made throughout the world are produced using ladle-metallurgy practices with Fe-Si-Mg alloys [1-5, 9].

In-ladle treatment is one of the most common technology used in foundries due to its simplicity. For in-ladle treatment, the magnesium-ferrosilicon is introduced into a pocket built into the bottom of the ladle and is then covered with either steel punching [1-5, 9, 13]. As a way of increasing the assimilation of magnesium (Mg) from the pre-alloy, in order to achieve the nodulization of the graphite of cast iron, changes made constructively to the treatment ladle were used [1-5, 9]:

- The classic Trigger method (Fig. 3) uses a ladle with a pocket, in which the agent is placed. This method is an improved variant of the open ladle process. In this process, the magnesium-ferrosilicon is introduced into pocket built into the bottom of ladle [1-5, 9].
- The Trigger method with covered pocket (Fig. 4) uses a ladle with a pocket, in which the nodulizer is placed, over which a layer of calcium carbide is placed [1-5, 9]. The liquid iron causes a layer of slag over the nodulizing alloy, which prevents, for the time being, direct contact between the iron and the nodulizer. After filling the treatment ladle, the slag layer is perforated with a steel bar, thus making contact between the iron and the nodulizing agent [1-5, 9].
- The Trigger method with 2 covered pockets (Fig. 5) uses a treatment ladle with two symmetrical pockets, in which the nodulizer is placed [1-5, 9]. After the nodulizing in two steps, the slag formed on the surface of the metal bath is removed, the cast iron is discharged into another ladle and before pouring into the mould, a post–nodulizing with FeSi75 is made.
- The Trigger method with 4 covered pockets (Fig. 6) uses a treatment ladle with four symmetrical pockets, in which the nodulizer is placed [1-5, 9]. After the nodulizing in four steps, the slag is removed and a post–nodulizing is made (with FeSi75).
- The Tundish-Cover process, based on Trigger classics (Fig. 7), is a further improvement of an open ladle by applying a special cover [1-5, 9].

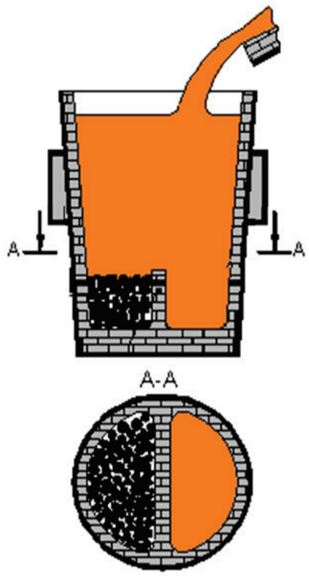


**Figure 3** The Trigger method (classic, uncovered pocket) - Trigger I

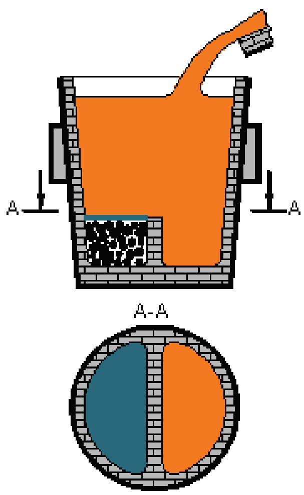


**Figure 4** The Trigger method with 1 covered pocket - Trigger II

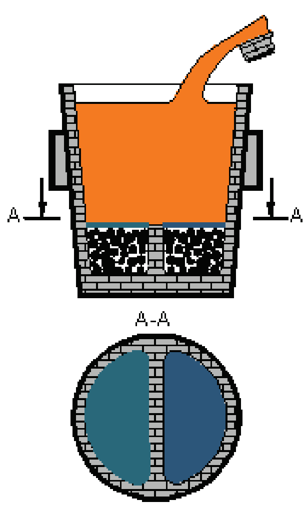


**Figure 5** The Trigger method with 2 covered pockets - Trigger III

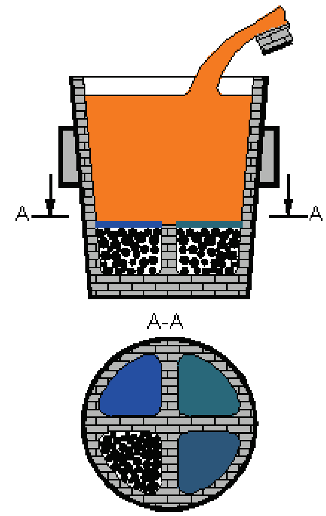


**Figure 6** The Trigger method with 4 covered pockets - Trigger IV

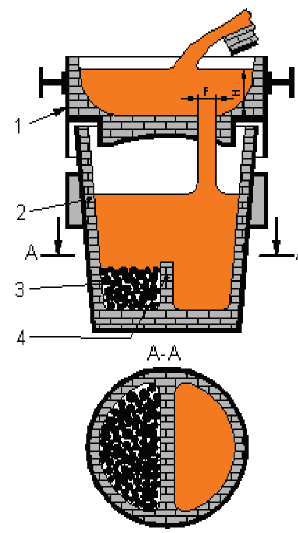


**Figure 7** The Tundish process based on Trigger classics (uncovered pocket) – Tundish-Cover I

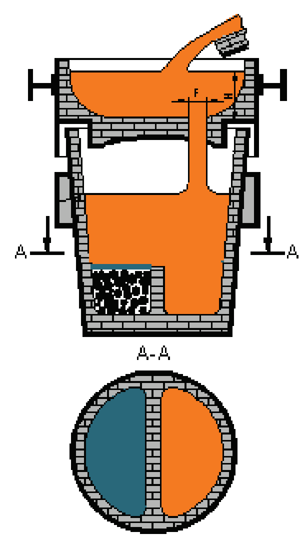


**Figure 8** The Tundish process based on Trigger method with 1 covered pocket - Tundish-Cover II

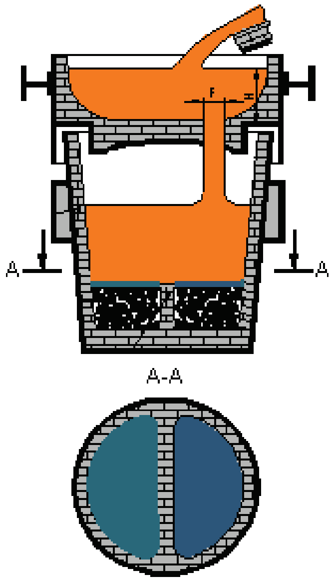


**Figure 9** The Tundish process based on the Trigger method with 2 covered pockets - Tundish–Cover III

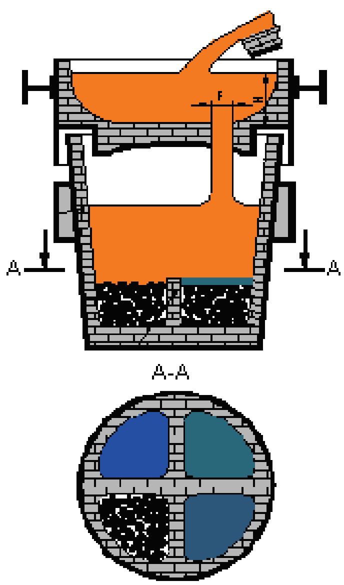


**Figure 10** The Tundish process based on the Trigger method with 4 covered pockets – Tundish-Cover IV

- A covering material is also possible in Tundish-Cover II (Fig. 8), though generally in lesser quantities than used in the classic technique. The classic version is also used, but the nodulizer is covered before the cast iron is fully discharged into the treatment ladle.
- In Tundish-Cover III (Fig. 9) the improved method of the Trigger process is used, with a special nodulizing ladle, having two pockets in the bottom, making a first step nodulizing, with two reactions, at small intervals.
- In Tundish-Cover IV (Fig. 10) another improved method of the Trigger process is used, with a nodulizing ladle with four pockets, making a step-by-step time-response nodulization at small intervals. In the modification ladle, four pockets were allocated in the bottom of it, in which the pre-alloy is deposited.

The foundries production capacity in ductile iron can determine the type of treatment or type of agent. Whereas numerous nodulizers are known, alloys based on magnesium (Mg) are usually preferred because of their effectiveness, availability and relatively low cost. Nowadays, most foundries use Fe-Si-Mg alloys for the treatment. The treating agent is defined as an essentially homogeneous solid cast block preferably containing alloying ingredients to treat the graphite's form. In order to treat these irons, developed in electric induction ovens (with the chemical compositions according to [14]), classical techniques - the Trigger and Tundish-Cover methods, and their variants described above - were used.

## 3 METHODOLOGY & MATERIALS

The iron melting is performed in induction electric furnace (12.5 t capacity, 2800 kW installed power) and is carried out with the maximum possibilities of the furnace, in order to reduce the duration of the charge [13]. Immediately after melting, the liquid iron contains a large quantity of coarse inclusions and remaining graphite, mainly from raw cast iron and from the carburizing process of cast iron with petroleum coke. In order to eliminate the coarse inclusions and the dissolution of the remaining large graphite, it is necessary to overheat the liquid iron in the temperature range of 1450-1550 °C, the higher the temperature being when the cast iron contains a greater amount of inclusions [9, 13]. Using an overheating between 1530-1550 °C, an advanced purification of liquid iron is obtained, overheating which will positively influence the mechanical properties. Keeping at overheating temperature is about 15 minutes [9, 13].

In the case of cast irons with nodular graphite, after de–charging, the nodulizing operation is followed, using a special ladle (Fig. 11). The treatment ladle must be clean, without scraps of slag or metal from the previous charges. The required amount of nodulizing alloy is placed in a special pocket. The nodulizing alloy has been placed as compactly as possible and then covered with a coating material, placed in such a way that the nodulizing reactions will begin only when the entire amount of iron has been filled in the ladle.

**Figure 11** Treatment ladles

In all cases, the same amount of iron, melted in electric induction ovens (12.5 t capacity), using one method or another, or one pre-alloy or another, has been modified. As nodulisers Fe-Si-Mg pre-alloys were used, with different percentages of magnesium (Mg) (5, 6 and 10%), but also a special silicon based pre-alloy, considered "light pre–alloy" (Nodulin type), with composition given by Tab. 1 (according to [9, 15]).

**Table 1** Silicon based pre–alloys – Chemical composition [9, 15]

| Used pre–alloys | Chemical composition (%) | | | | | |
|---|---|---|---|---|---|---|
| | Mg | Si | Ca | Al | Ce | Ba |
| Fe-Si-Mg 5 | 5 | 42 | 0.5 | 1.0 | 1.5 | 0.5 |
| Fe-Si-Mg 6 | 6 | 42 | 0.5 | 1.0 | 1.2 | 0.5 |
| Fe-Si-Mg 10 | 10 | 42 | 0.5 | 1.0 | 1.2 | 0.5 |
| Nodulin 5.8 | 5.8 | 48 | 1.5 | 1.0 | 2.0 | 1.2 |

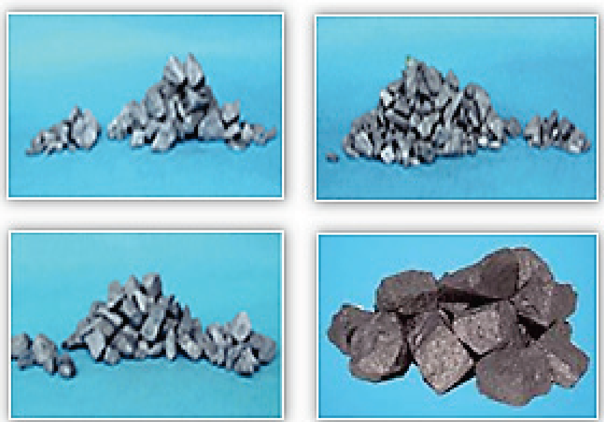

**Figure 12** Nodulizing pre-alloys
(a) Fe-Si-Mg 5; (b) Fe-Si-Mg 6; (c) Fe-Si-Mg 10; (d) Nodulin 5.8

The amount of pre-alloy used is between 1.2-1.8% of the quantity of treated iron, so that the remaining magnesium (Mg) must be between 0.03 and 0.06% [9, 13]. The most used in practice are those that use as a modifier metallic magnesium (Mg), in powder form, in the form of magnesium (Mg) pre-alloys, or magnesium (Mg) lighters. Once more, it is shown that magnesium remains the most common modifier. An increase in its efficiency can be done by using the magnesium (Mg) pre-alloy, with given and precise compositions in magnesium (Mg), or by using special construction of the nodulizing ladle. The treatment effect lasts between 5-30 min, during which time the casting of iron must be carried out at 1400-1450 °C [9, 13].

## 4 RESULTS & DISCUSSIONS

Different degrees of assimilation of magnesium into the iron were obtained, depending on the method and the type of nodulizing pre-alloy used in the experiments, rendered in a synthesized way in Tab. 2.

The experiments start from a given capacity of liquid iron (1000 kg), which has a temperature between 1350 and 1450 °C [9]. The pre–alloy are inserted in the ladle (granulation 20-40 mm), preheated in advance, to increase the degree of magnesium (Mg) assimilation.

**Table 2** Summary table on experiments

| Nodulizing technique/ method | Used Pre-alloys (-) | Quantity of nodulizer (%) | Treatment temperature (°C) | Degree of magnesium assimilation (%) |
|---|---|---|---|---|
| Trigger (I) | Fe-Si-Mg 5 | 1.8 | 1480 | 42 |
| | Fe-Si-Mg 6 | 1.8 | 1480 | 43 |
| | Fe-Si-Mg 10 | 1.8 | 1480 | 45 |
| | Nodulin 5.8 | 1.8 | 1480 | 50 |
| Trigger (II) | Fe-Si-Mg 5 | 1.8 | 1480 | 45 |
| | Fe-Si-Mg 6 | 1.8 | 1480 | 48 |
| | Fe-Si-Mg 10 | 1.8 | 1480 | 52 |
| | Nodulin 5.8 | 1.8 | 1480 | 58 |
| Trigger (III) | Fe-Si-Mg 5 | 1.8 | 1480 | 49 |
| | Fe-Si-Mg 6 | 1.8 | 1480 | 53 |
| | Fe-Si-Mg 10 | 1.8 | 1480 | 57 |
| | Nodulin 5.8 | 1.8 | 1480 | 62 |
| Trigger (IV) | Fe-Si-Mg 5 | 1.8 | 1480 | 51 |
| | Fe-Si-Mg 6 | 1.8 | 1480 | 54 |
| | Fe-Si-Mg 10 | 1.8 | 1480 | 60 |
| | Nodulin 5.8 | 1.8 | 1480 | 64 |
| Tundish– Cover (I) | Fe-Si-Mg 5 | 1.8 | 1480 | 45 |
| | Fe-Si-Mg 6 | 1.8 | 1480 | 47 |
| | Fe-Si-Mg 10 | 1.8 | 1480 | 51 |
| | Nodulin 5.8 | 1.8 | 1480 | 58 |
| Tundish– Cover (II) | Fe-Si-Mg 5 | 1.8 | 1480 | 49 |
| | Fe-Si-Mg 6 | 1.8 | 1480 | 53 |
| | Fe-Si-Mg 10 | 1.8 | 1480 | 56 |
| | Nodulin 5.8 | 1.8 | 1480 | 64 |
| Tundish– Cover (III) | Fe-Si-Mg 5 | 1.8 | 1480 | 52 |
| | Fe-Si-Mg 6 | 1.8 | 1480 | 56 |
| | Fe-Si-Mg 10 | 1.8 | 1480 | 60 |
| | Nodulin 5.8 | 1.8 | 1480 | 72 |
| Tundish– Cover (IV) | Fe-Si-Mg 5 | 1.8 | 1480 | 58 |
| | Fe-Si-Mg 6 | 1.8 | 1480 | 61 |
| | Fe-Si-Mg 10 | 1.8 | 1480 | 65 |
| | Nodulin 5.8 | 1.8 | 1480 | 82 |

The Trigger method, in its improved variants, by increasing the number of pockets in the ladle bottom and by applying a cover to the surface of the treatment ladle, has, in conclusion, a number of advantages. The following advantages have been observed as a result of these practical experiments:

- In the case of the use of the same pre–alloy, regarding to the nodulizing of cast iron graphite, however, to different methods, the degree of assimilation differs, depending on how the modification takes place, by casting the iron over the pre–existing nodulizer at the bottom of the ladle. Under the same method, the assimilation increases, with the increase of the reaction surface, following the application of the treatment in several consecutive steps;
- A saving of nodulizing agent is made, the nodulizing effect increasing if the same quantity of nodulizer is inserted in two or more pockets. Therefore, at the same effect, the consumption of the nodulizer decreases;
- Increased the effect of assimilation because the distribution of the nodulizer over a larger area leads to the shortening of the diffusion distances;
- It is observed an increase of the degree of the treated cast iron's homogenisation;
- If the treatment ladle is covered, like the Cover process, the assimilation is even higher, resulting in an optimal, favourable and economical process, to any medium technological foundry. By applying a cover to the

nodulizing ladle related to the Trigger process, it becomes a more efficient and economical process (Tundish-Cover). Therefore, applying the cover will significantly improve the process. Without a cover, smoke and flame emission results during the change reaction;

- The classical modification procedures provide relatively low degrees of assimilation of magnesium (Mg) embedded in the pre-alloys. For the purposes of increasing assimilation, practice shows that the Tundish–Cover process, based on the increased Trigger ladle with 2 and 4 pockets can be used at higher performance as alternatives to the classic techniques;
- The both basic methods (Trigger and Tundish-Cover) and their variants show good and conclusive results (Fig. 13, Fig. 14), and their application in practice, appreciably raises the degree of assimilation of magnesium (Mg), by a few percentage points, moreover, are always open to any subsequent perfections.

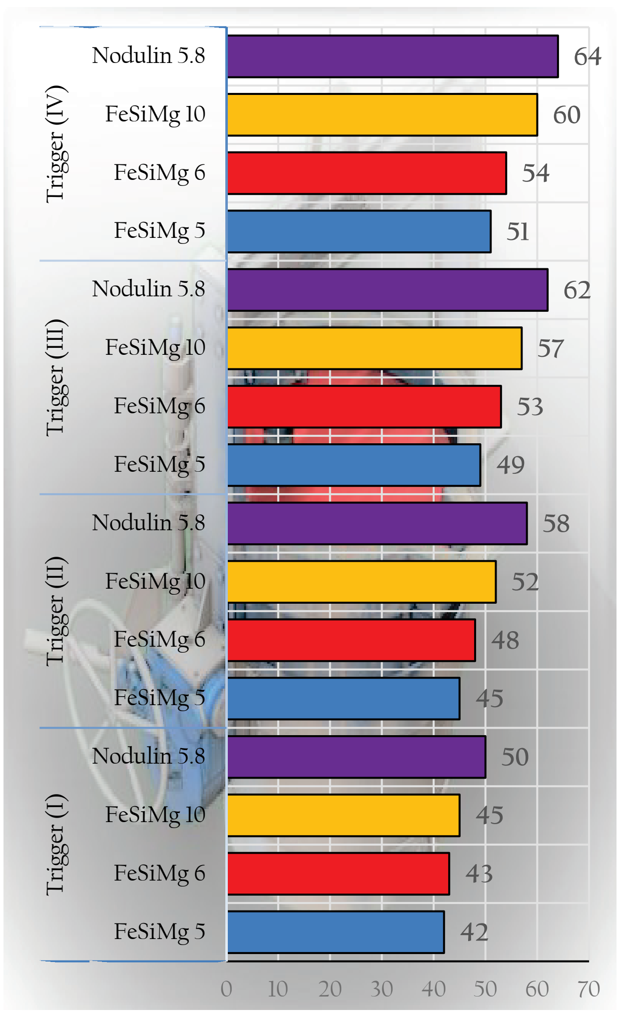


**Figure 13** Magnesium (Mg) assimilation in the Trigger methods (%)

For the purposes of the above, the Trigger method may undergo some improvements, which are worth stating, especially since during the experiments carried out, these methods have demonstrated their effectiveness. The purpose of the proposed process is to increase the efficiency of the nodulization process of the cast irons and is to make treatment ladles, of a special construction, with two or more pockets, in which the chosen nodulizer is then inserted. Thus, the nodulization is carried out in stages, practically achieving an increase in the degree of magnesium (Mg) assimilation.

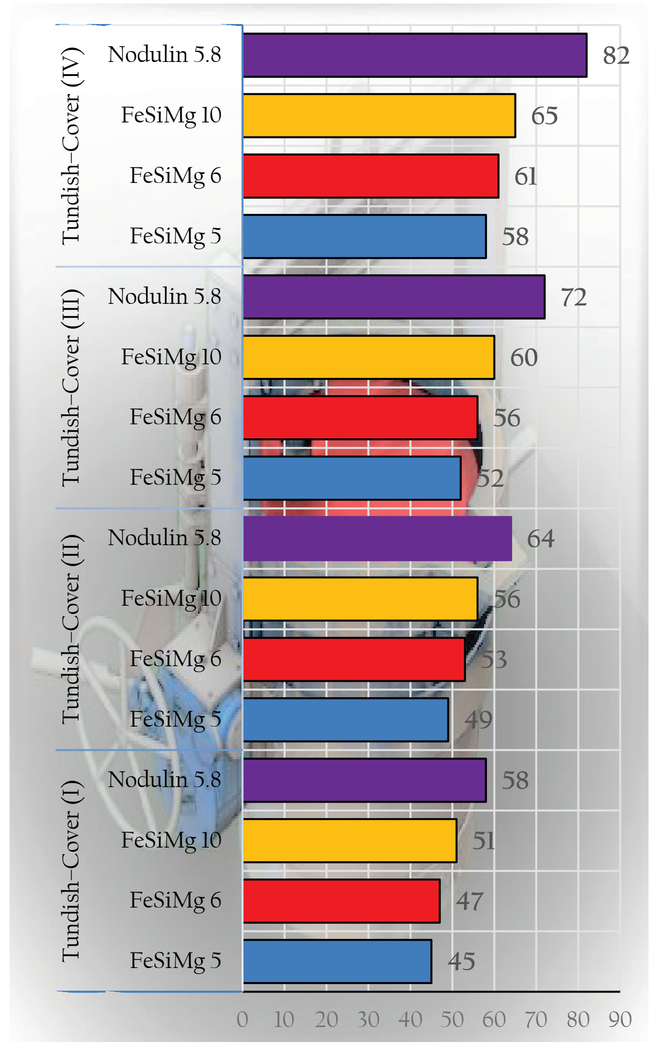


**Figure 14** Magnesium (Mg) assimilation in the Tundish-Cover methods (based on the Trigger methods) (%)

## 5 CONCLUSIONS

This study take into account the flexibility of the process, by improvement or alternative to the existing one. Some of most important variables, in the ladle treatment of irons, are:

- the nodulizer, which indicates the proper pre–alloy when several categories of agents (Fe-Si-Mg and Nodulin) are available;
- the nodulizing treatment temperature, which indicates the optimal range of temperature;
- magnesium (Mg) vapour steering in the ladle, which depends on whether the ladle is covered or uncovered;

These main factors should be taken into account when the method of introducing the pre-alloy into the treatment ladle is chosen. Also, the nature of the pre-alloy used according to the parameters of the process is a key-factor, having in view the risk of the silicon (Si) growth when the Fe-Si-Mg range is used. Magnesium (Mg) may be added directly to the ladle as nickel-magnesium, iron-silicon-magnesium or nickel-silicon-magnesium alloys. Higher magnesium (Mg) assimilation is obtained using the latter, as light pre-alloy.

If the treatment takes place at a temperature higher than 1480 °C, a Fe-Si-Mg pre-alloy with a high content of calcium (Ca) (1-2%) should be used, which will increase assimilation and calm the reaction. At lower temperatures, the reaction is less violent. Thus, if the temperature is below 1480 °C, pre-alloys with low calcium (Ca) (< 1%) content will be used.

One of the most advantageous methods of modifying the shape of cast iron graphite, applicable, without too much investment and in any foundry, is the Trigger method, and the improvements made to this method, only increase its industrial applicability.

It can be concluded that the effect of the nodulizing is high when number of pockets increases, increasing the reaction area between the nodulizer and the treated iron, thus ensuring all of the advantages outlined above. Above all, a nodulizer economy is achieved, a particularly important fact in a market economy, where production is always sought. It seeks the application in the foundries, in all ways, of the technologies that best ensure the savings of materials, increase productivity, efficiency of the production of ductile irons and alignment to a high standard. A simple nodulizing ladle shall be considered as a basis, plus the costs of adapting the technologies. Everyone can choose the system according to the facilities, possibilities and needs of this foundry sector.

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**Author's contacts:**

**Imre Kiss**, PhD, Associate Professor
University Politehnica Timisoara,
Faculty of Engineering Hunedoara,
Department of Engineering and Management
5, Revolutiei, 331128 - Hunedoara, Romania
E-mail: imre.kiss@fih.upt.ro