EFFICIENT PROCESS OF HOT METAL LADLE DESULFURIZATION WITH MAGNESIUM FOR LOW-SULFUR STEEL PRODUCTION

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ABSTRACT
Results of investigation of sulfur content decrease out-of-furnace desulfurization are provided. Various desulfurization methods are estimated and compared. Advantages of magnesium injection without additives are substantiated.

Production of hot metal with low sulfur content has always been a pressing problem in iron and steel industry [1–3]. The main peculiar feature is the strengthening of requirements of hot metal consumers to content of sulfur and technical process of low-sulfur hot metal production. Subject to prior information, the limit of sulfur in hot metal at the level of 0.030–0.035% met the demands of steel industry [1–4]. Since 1970-1990s the limit has reduced to 0.010–0.025%, and over the last 10–15 years the demand for hot metal with sulfur content not exceeding 0.005 or even 0.002% increased substantially [5–8].

Hot metal with sulfur content of 0.010-0.015% and above can be produced either by smelting in blast furnaces or by out-of-furnace desulfurization. Hot metal with sulfur content below 0.010-0.015% can be produced only by out-of-furnace desulfurization.

Technical processes of out-of-furnace desulfurization have become widely used throughout the world since 1970-1980s. Materials based on CaO, CaC₂, Na₂CO₃, Mg and compositions containing these elements and compounds were used as desulfurizing agents. The analysis of the flowing processes shows that the use of non-magnesium containing agents is most often accompanied with involvement of additional partners into the exchange processes, and desulfurization processes are associated with high consumption of materials, which even stoichiometrically exceed the amount of sulfur being bound by the reaction 2-4 times or more.

Interaction reactions of various agents with sulfur in hot metal in the basis of reactions are as follows:

CaO

\[ \text{CaO}_n + [S] + n \cdot B = \text{CaS}_n + B_nO \]  (1)

\[ 2\text{CaO}_s + [S] + \frac{1}{2} [\text{Si}] = \text{CaS}_s + \frac{1}{2} (2\text{CaO} \cdot \text{SiO}_2) \]  (2)

\[ \text{CaO}_s + [S] + 2/3 [\text{Al}] = \text{CaS}_s + 1/3 \text{Al}_2\text{O}_3s \]  (3)

\[ \text{CaO}_s + [S] + \text{Mg} = \text{CaS}_s + \text{MgO}_s \]  (4)

CaC₂

\[ \text{CaC}_2 + [S] = \text{CaS} + 2\text{C}_s \]  (5)
\[ \text{Na}_2\text{CO}_3 \]

\[ \text{Na}_2\text{CO}_3_{(aq)} + [S] + 2[C] = \text{Na}_2\text{S}_{(aq)} + 3\text{CO}_2 \]  
(6)

\[ \text{Na}_2\text{CO}_3_{(aq)} + [S] + [\text{Si}] = \text{Na}_2\text{S}_{(aq)} + \text{SiO}_2 + \text{CO}_2 \]  
(7)

\[ \text{Mg} \]

\[ \text{Mg}_g + [S] = \text{MgS}_s \]  
(8)

\[ [\text{Mg}] + [S] = \text{MgS}_s \]  
(9)

**Agents for hot metal desulfurization:**

– \text{CaO}; \text{CaO+Mg}; \text{CaO+Al}; \text{CaO+Na}_2\text{CO}_3; \text{CaO+CaF}_2.

– \text{CaC}_2.

– \text{Na}_2\text{CO}_3; \text{Na}_2\text{CO}_3 + \text{D}.

– \text{Mg}; \text{Mg + CaO}; \text{Mg +CaC}_2.

Extensive industrial use of non-magnesium containing agents shows [2-4,6,8] that there exists a number of essential disadvantages, the main of which are as follows:

1. High consumption rate of agents (6 – 20 kg/t of hot metal).
2. Large slag bulk formed additionally (up to 10 – 40 kg/t of hot metal).
3. Essential losses of hot metal with ladle slag formed (on average 45% of the slag bulk).
4. Restricted possibilities of hot metal deep desulfurization.
5. Long process duration (usually over 10 min.).
7. Negative impact upon environmental and water basin.
8. High expenses and economic costs caused by industrial application of desulfurization processes.

In this regard the use of magnesium shall be deemed advantageous: the amount of magnesium required stoichiometrically shall make 0.76 of amount of sulfur being bound (reaction (8), (9)). Moreover, the unique property of magnesium to dissolve in liquid hot metal (Fig. 1) – up to 0.3-1.3% (in real parameters of the zone of injection of magnesium into the melt) – enhances the potential of magnesium of ensuring hot metal desulfurization that is economical and efficient at the same time.

Scientists and engineers from Ukraine take leading positions in the development and application of magnesium agents for industrial out-of-furnace hot metal desulfurization. Since 1960s they have developed and practically tested various processes of magnesium injection in form of ingots, briquettes, different compositions, flux-cored wire, liquid magnesium, special rods and dispersed magnesium [2, 3, 5-8, 10-18]. In the context of large-scale industrial steel making, major changes of initial and final sulfur content in hot metal, high intensity of feed of ladles with hot metal for further treatment, continuous increase of proportion of deep-desulfurized hot metal, the injection processes of hot metal desulfurization with dispersed magnesium, its injection in pure form or in form of mixture with high-quality lime became the priority ones [2,4-8,16].

A particular advantage of injection desulfurization technologies is a reliable supply of hot metal with extremely low sulfur content under conditions of intensive work of converter plants - not more than 0.002% [5-8], with a weight of metal in the ladles amounting to up to 350 tons. That became the main reason for almost universal spreading of injection technologies and equipment for
desulfurization of hot metal with dispersed magnesium and various non-magnesium containing mixtures in industrial practice worldwide [5-8] that happened to replace non-magnesium containing agents.

![Graph showing dependence of hot metal saturation with magnesium (\([\text{Mg}]_{\text{sat}}\)) at steady state upon temperature (t) of refined melt.](image)

Fig. 1 Dependence of hot metal saturation with magnesium (\([\text{Mg}]_{\text{sat}}\)) at steady state upon temperature (t) of refined melt.

Numbers by the curves – absolute pressure in mass-exchanging zone, MPa.

Shaded area – values of \([\text{Mg}]_{\text{sat}}\) at characteristic (temperature, pressure) parameters in the zone of injection of magnesium into the melt.

The Ukrainian steel workers were the first to use magnesium for industrial out-of-furnace hot metal desulfurization [2-4, 8, 10, 13, 14, 17]. They performed a number of extensive studies of various technological processes and were the first to show [2, 8] that additives administered into magnesium are not involved in desulfurization process, they only passivate the magnesium injected from the tuyere into the refined melt. These fillers deteriorate the conditions for heat and mass-exchanging processes between magnesium and hot metal in the hot metal melt. Moreover, the consumption of magnesium for interaction with carbonates (incompletely burned materials), moisture and hydrates of these additives is inefficient, that results in increase of magnesium losses. As a result, the process of hot metal desulfurization by injection of magnesium-containing mixtures turns out to be far less economical. The available actual data of practical application of various injection processes of hot metal out-of-furnace desulfurization with magnesium-containing agents [2, 5-8, 19] suggest that the pure magnesium by injection should be recovered 1.5-2 times faster than a mixture of magnesium with lime and calcium carbide (Fig. 2). The latter, in its turn, is accompanied with the lowest level of magnesium consumption when it is injected in pure form. The industrial experience of hot metal desulfurization by injection of powder magnesium-containing mixtures revealed the following defects of this technology [2, 5-8, 19, 20]:

1. Low (20-50%) magnesium recovery level.
2. Necessity to apply several agents.
3. Increased (1.3-1.5 times) magnesium consumption.
4. Substantial (up to 3-4 kg/t of hot metal) consumption of agents.
5. Substantial (up to 6-10 kg/t of hot metal) additional ladle slag formation.
6. High (2.5–4.5 kg/t of hot metal) losses of hot metal with the slag.
7. Lack of stability of desulfurization results.

Fig 2. Dependence of magnesium recovery degree ($K_{Mg}^{S}$) on sulfur from initial sulfur content in hot metal ($[S]_{init}$) at final sulfur content upon desulfurization 0.005 ± 0.001%.

Weight of hot metal in ladles makes 160–280 t. Technologies compared: injection of granulated (grain) magnesium – Mg (the Ukrainian process); injection of magnesium and calcium carbide mixture – Mg + CaC$_2$ (ESM process, USA); injection of magnesium and lime mixture – Mg + CaO (ESM processes, Kroupp Polisisus, Rossborough, Hoogovens, Remacor).

8. Difficulties in hot metal desulfurization in ladles with weight of metal below 80-100 t and low ladle bath depth (below 1.8-2.0 t).
9. Complexity of equipment scheme and desulfurization plant, great number of equipment units and high capital expenses.
10. Unreliability of dosage and control system in actual industrial conditions.
11. Compliance of the plant model with special requirements to explosion and fire safety.
12. Essential current and operation costs.

All the above made the basis for active development and spreading of hot metal out-of-furnace treatment process by injection of magnesium without passivating additives. The technological basis for the developed process includes the following:

1. Magnesium is injected into hot metal without passivating, diluent or other additives.
2. The agent injected is grain or granular magnesium (or magnesium alloy), which does not contain any explosion-hazard magnesium fractions (<0.1 mm); the material is highly fluid and flowable, it does not need to be fluidized.
3. Magnesium is injected in a jet of noncorrosive gas with high magnesium concentration in the gas. High partial pressure of magnesium in the mass-exchanging zone is ensured.
4. Magnesium is injected with a controlled, smooth, regulated and guaranteed dosed material feed with tolerance of actual agent weight being below 0.5% as compared to the given one and actual intensity of magnesium injection (magnesium weight per time unit, including instantaneous) varying within the range of 2% as compared to the given one.
5. The conditions of dispersed evaporation of all the magnesium injected at the ladle bottom followed by active (over 80% of injected magnesium) saturation of refined iron with magnesium.
6. The guaranteed conditions excluding the return of sulfur to the iron from the slag, even if the contents of sulfur in desulfurized hot metal makes <0.00-0.002%, are ensured. If necessary (in certain cases), the physicochemical properties of ladle slag can be adjusted. 
7. Operations are held and the set parameters are maintained in automatic mode. 
8. Specific costs of materials, agents, energy products and expenses for desulfurization are the lowest (as compared with all the other analogues).

Depending on the conditions of refining (depth of the melt bath in the ladle, weight of hot metal, melt temperature, initial and final sulfur content etc.) magnesium can be injected in 2 ways:-- through the immersed tuyere with vaporization chamber at the output (if the flow rates in the tuyere channel does not exceed 30 m/s);-- through the immersed tuyere without any vaporization chamber at the output (but without special construction of tuyere tip and with the special injection modes). The represented technological developments can be widely used: in ladles of different sizes – 20 to 450 t, with initial content of sulfur in hot metal of up to 0.15%, with temperature of cast of 1220 to 1450°C, final required sulfur content down to <0.001 - 0.002%, degree of magnesium recovery up to 95% and above, the full cycle of ladle processing of 25-20 minutes. 
To increase the capacity of desulfurization complex, reduce its energy and material consumption, expand the guarantees, the technological magnesium injection process was upgraded [8], the intensity of magnesium injection was twice increased and the duration of injection process was shortened to 3-6 minutes, while the bubbling of melt in the ladle was calmed and stabilized. In order to exclude the possibility of sulfur returning to the melt (at a durable hold of hot metal with extremely low sulfur content of \( \leq 0.001-0.002\% \) in the ladle with slag) and improve the conditions for removal of sulfuric slag after desulfurization, the adjustment of content of the ladle slag was provided for with low (1.5-2 kg/t of hot metal) addition of non-deficient and low-cost waste from refractory and metallurgical industries to the melt surface. 
Hot metal desulfurization by injection of grain magnesium was mastered for the purpose of hot metal refining in blast transportation and casting ladles. An algorithm for control of hardware and manufacturing complex of deep hot metal desulfurization was developed, including all the components of technology and operations – from the agent administration to magnesium injection and slag removal. The developed hardware and process flow scheme allows to control the process either in a fully automatic or semi-automatic operation mode. The automation system provides control of operation of either separate desulfurization complex or as part of a unified system of the plant’s ACS. Hot metal is desulfurized with the lowest consumption of materials and agents. 
The developed process of hot metal desulfurization by magnesium injection was industrially inspected and mastered as part of desulfurization complexes with capacity of up to 6 million t/yr, providing in such a way the specified reduction of the sulfur content in hot metal. This process became widely applied as part of modernized and new facilities for steel smelting of metallurgical enterprises of the PRC [21]. As of the mid-2009, over 60 complexes for hot metal desulfurization by magnesium injection with total capacity over 70 mln. t/yr were constructed and put into operation in the PRC with the use of the Ukrainian technology. Several proposals on construction of similar complexes for metallurgical enterprises of China, Taiwan, India and Ukraine were developed and delivered to the customers. 
Comparison of the developed process of deep and extra-deep desulfurization of hot metal by injection of magnesium with the most effective world analogues shows that the injection of pure magnesium provides for the highest absorption of magnesium and its lowest consumption. The hot metal processing costs according to the Ukrainian technology are less than those for the most economical foreign analogue that is 1-2 USD/t of hot metal (Table). 
Thus, the technological process of hot metal refining by pure magnesium injection ensures the required desulfurization of hot metal in the context of large-scale industrial steel making.
Reliability, efficiency and effectiveness of the process prove its extreme efficiency and prospective for further wide application. The project was tested in the industry practice and is recommended for wide application in iron and steel companies.

Table. Comparison of main indices of hot metal desulfurization in heavy (200-300 t) hot-metal ladles by injection of magnesium-lime mixture (ESM process) into the ladles of Severstal OJSC [21] and injection of pure granulated magnesium (the Ukrainian process) with the reduction of sulfur content in hot metal, for instance, from 0.020 to 0.002%.

<table>
<thead>
<tr>
<th>№</th>
<th>Indices</th>
<th>Injection of CaO + Mg mixture (ESM process), Severstal OJSC (Cherepovets, Russia) [21]</th>
<th>Injection of granulated magnesium (Ukrainian technology), metallurgical complexes of China</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Specific consumption of agents, kg/t of hot metal:</td>
<td>0.49</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>– magnesium</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>– ground lime</td>
<td>1.55</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>– total agent consumption</td>
<td>2.04</td>
<td>0.30</td>
</tr>
<tr>
<td>2</td>
<td>Consumption of agent for processing, kg/ladle (300 t of hot metal in a ladle)</td>
<td>612</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>Magnesium injection duration, min</td>
<td>6.5</td>
<td>7.5</td>
</tr>
<tr>
<td>4</td>
<td>Hot metal temperature reduction, °C</td>
<td>6.72</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>Additional hot metal losses with the slag formed, kg/t of hot metal</td>
<td>1.84</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>Desulfurization costs, USD/t of hot metal:</td>
<td>1.470</td>
<td>0.900</td>
</tr>
<tr>
<td></td>
<td>a) magnesium</td>
<td>0.295</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>b) ground lime</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>c) hot metal losses with the slag formed</td>
<td>0.736</td>
<td>0.100</td>
</tr>
<tr>
<td></td>
<td>d) hot metal temperature losses</td>
<td>0.134</td>
<td>0.100</td>
</tr>
<tr>
<td></td>
<td>e) tuyeres</td>
<td>0.080</td>
<td>0.040</td>
</tr>
</tbody>
</table>
<pre><code>| Aggregate costs in points “a”, “b”, “c”, “d”, “e”                        | 2.715                                                                                    | 1.148                                                                                    |
</code></pre>
<p>| 6  | Profit (cost saving) from use of the Ukrainian technology of granulated magnesium injection as compared to injection of mixture of lime and magnesium (ESM), USD/t of hot metal | –                                                                                         | 1.567                                                                                    |</p>

References: