Hot metal desulphurisation: benefits of magnesium lime co-injection

The evolution of external hot metal desulphurisation has been driven by the ever-increasing consumer demand for higher quality steels. Currently, deep co-injection of magnesium and lime is a proven successful method of desulphurising hot metal that offers steel producers a reliable, repeatable and economical means of meeting their production requirements.

Over the past few decades the demand for steel around the world has been increasing at a rapid rate, coupled with an increase in steel quality. Steel producers are required to maximise throughput, minimise production outages and maintain high quality standards while all the time minimising costs.

One major technique for improving the quality of steel is to reduce its sulphur content. Sulphur is one of the most detrimental impurities in the steelmaking process, affecting both internal and surface quality. Unlike other impurities that are removed from the hot metal by oxidation in the converter, the most economic method of removing sulphur from the hot metal is by reduction before being charged into the converter.

There are a variety of methods that have been developed but all require a reagent and a method of mixing.

The differences between the technologies used are the properties of the reagents, the reagent effectiveness to remove sulphur and the effectiveness of the mixing method used to get the reagent into solution.

REAGENTS

Although the methods of addition may be different, reagents currently used are lime, calcium carbide and magnesium.

Lime Lime has always played a role in steelmaking desulphurisation. Its low cost and availability make it an attractive consumable, however, there are some critical disadvantages. During the desulphurisation process lime particles are continuously being covered by two precipitates: calcium sulphide (CaS) and calcium silicate (CaSiO₃). These compounds impede the desulphurisation reaction by surrounding the lime (CaO) and forming thick barriers at the lime – hot metal interface (see Figure 1). In order to reduce this growth, the grain size of the lime must be restricted to 45μm maximum.

Another method of avoiding the retardation of the reaction is to keep the hot metal temperature high in order...
Due to its relative low boiling point (1,090°C), magnesium vapourises as it enters the hot metal. This vapour is under high pressure which is directly related to solubility. Once in the ladle, the magnesium vapour forms bubbles which rise through the hot metal, dissolve and react with the sulphur in solution, forming magnesium sulphide (MgS). The MgS then floats to the top of the ladle and settles in the slag layer, which is later skimmed off. The lime that is injected with the magnesium assists in dissolution by reducing the diameter of the bubbles as well as providing precipitation sites for the MgS.

Magnesium has a high affinity for both oxygen and sulphur. Unlike lime, magnesium is not accompanied by oxygen when it is introduced to the hot metal, therefore, it can rapidly react with sulphur to form magnesium sulphide. Magnesium in solution that does not react with sulphur may also react with any oxygen in the hot metal, so removing excess oxygen.

**Calcium carbide** Once the most dominant of all desulphurising reagents, calcium carbide is now less prevalent. Complicated material handling issues as well as stringent environmental requirements associated with the disposal of slag have negatively influenced its use. Calcium carbide is also subject to precipitate layer formation similar to lime, which impedes the desulphurisation reaction.

**Magnesium** Although some earlier desulphurisation techniques involved mono-injection of magnesium, these practices have become less common due to the violence of the reaction and the relatively complicated equipment required. Magnesium is the only one of the three desulphurisation reagents that is soluble in hot metal and reacts with the sulphur in solution. Typical magnesium desulphurisation reactions are as follows:

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\begin{align*}
\text{Mg}_{(l)} &\rightarrow \text{Mg}_{(g)} \\
\text{Mg}_{(g)} &\rightarrow \text{Mg} \\
\text{Mg} + \frac{1}{2} \text{S} &\rightarrow \text{MgS}_{(s)}
\end{align*}
\]

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**Blended injection** The injection of pre-blended magnesium/lime or magnesium/calcium carbide combinations has also become less widespread. By blending reagents prior to treatment steelmakers sacrifice the ability to adjust individual injection rates of materials. Also, blended reagents are prone to material segregation in transport and storage vessels.

**Reagent ability to remove sulphur** It is important to realise that all reagents are not equal when it comes to the ability to remove sulphur. Magnesium, although more
expensive, has approximately 20 times the capacity for removing sulphur as lime. Calcium carbide has eight more times the potential to remove sulphur than lime; however, if injected into hot metal on its own it must be blended with volatiles in order to increase bath agitation.

**REAGENT DELIVERY INTO HOT METAL**

The two methods of introducing desulphurising reagents into hot metal are mechanical stirring and deep reagent injection. While both methods are used in different parts of the world, there are inherent advantages and disadvantages in each.

**Mechanical stirring** There have been many variations on the concept of mechanical stirring of hot metal during desulphurisation. The best known method, the Kambara Reactor (KR) Process, was developed in 1963 by Nippon Steel in response to restricted availability of magnesium in Japan. With the exception of a few locations in Asia and Europe, the process never gained wide acceptance.

In all instances, either calcium carbide or lime is introduced onto the surface of the hot metal in the transfer ladle. A paddle or impeller is lowered into the ladle and rotated by overhead motors, so mixing the reagent into the hot metal. Once completed, the impeller is removed and the slag is skimmed off the surface of the ladle.

**Deep reagent injection** Deep reagent injection can be defined as the introduction of desulphurising reagents deep into a hot metal bath by means of a pneumatic injection system and refractory coated lance. The reagents can be injected in mono-injection or co-injection form. The mono-injection process can be used for lime and calcium carbide, however, magnesium can only be successfully mono-injected through a bell-type vapourising lance. Typically, mono-injection of magnesium with a bell-type evaporation lance is a relatively old process. It was applied using salt-coated magnesium in steel plants of the former Soviet Union. In North America, a few plants did use mono-injection with salt-coated magnesium through a standard port lance, however, due to operational problems caused by the violence of the reaction the practice was soon abandoned.

One of the major problems with mono-injection of magnesium was the potential for sulphur reversion and, due to the absence of lime, there was a lack of precipitation sites. The lime also makes slag more basic which decreases the amount of iron held in the slag. With the advances that were made to the injection equipment, mono-injection of blended reagents evolved further to become co-injection.

Modifications to the process in order to improve production requirements as well as environmental and safety restrictions have all played critical roles in its evolution.

Co-injection has the flexibility to meet production demands as well as quality standards in any steelmaking process. Magnesium can be injected with either lime or calcium carbide without modification to the equipment. Due to the prevalence of co-injection with magnesium and lime in China, references to co-injection for the remainder of the paper will cite lime.

**Hot metal co-injection facility** Figure 2 shows a typical plant schematic. Hot metal desulphurisation facilities that employ co-injection can be divided into four major areas: reagent storage, reagent injection, slag removal and environmental control.

**Reagent storage** The most efficient method of supplying desulphurisation reagents to a steel plant is in transport trailers or rail cars. The reagents are unloaded by pneumatic means to the site storage silos which are located either at the injection site or close to the hot metal desulphurisation facility. Granulated magnesium can also be unloaded manually from one tonne fibreglass bags via a hopper on top of the site storage silos.

**Reagent injection** Delivery of reagents into the hot metal is facilitated by a pair of dispensing vessels and a refractory coated injection lance. One dispensing vessel is used for lime and the other for granulated magnesium. Both dispensers are identical, however the piping is arranged in such a manner that the granulated magnesium is metered into the lime flow.

The reagent transfer in the injection line is under dense flow conditions. Depending on the specific condition (line configuration and operating pressure), the gas : solid ratio...
Hoods can be installed to capture fumes during both reagent injection and slag skimming. The captured fumes are typically cleaned in a pulse jet type baghouse, designed for metallurgical applications.

**Cost of Desulphurisation**

**Reagent Costs**
The reagent consumption costs change with the market prices of magnesium and lime. Lime prices also change based on particle size. Residual lime that is recycled from other lime processes has a coarser particle size as well as a cheaper price. Based on current market values, lime prices vary from ¥300/t for recycled lime up to ¥1,200/t for ground lime specifically prepared for the desulphurisation process. It is true that the cost of reagent consumption for co-injection (magnesium/lime) is marginally higher than KR (lime), as illustrated in Figure 4 and Table 1.

The following assumptions were used:

- Mg cost ¥20,000/t
- Co-injection CaO cost ¥1,400/t
- KR 2mm CaO cost ¥300/t
- KR WISCO 2006 CaO cost ¥600/t
- KR 45μm CaO cost ¥1,190/t
- Reagent ratio $(1\text{CaO}/8\text{CaC}_2/2\text{Mg})$
- Mg unit consumption 0.6 kg-Mg/tHM
- Co-injection ratio (Mg/ CaO) 1:4

Magnesium has a greater potential than lime to remove sulphur from hot metal, which means that less magnesium is required to treat the same amount of hot metal than lime. By adding less material, steelmakers can realise greater savings in temperature loss, treatment time, refractory wear and iron loss.

Slag generation and iron loss

One of the major operational costs is iron loss. During the treatment
cycle, iron units become trapped in the slag and are pulled out of the transfer ladle during the slag skimming process. In North America iron loss is about 1% for co-injection desulphurisation. It is also well recognised that desulphurisation slag contains typically 50% iron. Therefore, under regular operating conditions, desulphurisation of 150 tonnes of hot metal generates approximately 3 tonnes of slag. Due to the absence of KR process facilities in North America, no data is available for a market to market comparison.

The generation of slag during desulphurisation is proportional to the amount of reagent added to the hot metal. The KR process, as well as other mechanical stirring methods, generates a high volume of slag due to the fact that large amounts of lime must be added to achieve the same low final sulphur levels as co-injection. Depending on lime particle size and operational practice, iron loss for a KR process operation could range from 2% to 3%. Co-injection iron losses are low in comparison because less magnesium is required due to its high desulphurising potential.

Iron loss is a direct cost of desulphurisation operation. Assuming 2.5% as iron loss for the KR process, 1% as iron loss for co-injection and hot metal cost of ¥1,960/t, then the iron loss cost difference is significant, as shown in Table 1.

By conserving the sensible heat of the hot metal and keeping slag levels to a minimum, co-injection reduces the risk of losing iron units during skimming. The lime that is injected with the magnesium is enough to keep the slag foamy which allows operators to remove it from the surface of the ladle in a timely and efficient manner.

**Temperature loss** The sensible heat of the hot metal is one of the main sources of energy in the steelmaking process, hence loss of temperature is a major operational cost of the desulphurisation process. The three primary sources of heat loss are radiation from the surface of the hot metal, addition of cold reagents and the introduction of cold injection lances or stirring impellers into the hot metal. The largest temperature loss occurs during injection or stirring operations rather than skimming.

As a supplier of co-injection systems, Danieli Corus can guarantee a maximum temperature loss of 1.2°C per minute during injection. Considering an injection time of 5-10 minutes, plus other losses due to operations such as skimming, the overall temperature loss of co-injection operation can range from 10 to 20°C.

The design figures for the KR process temperature loss are 25 to 50°C. Most operations can manage to keep the temperature loss less than 30°C by using lime instead of calcium carbide. The reasons for the higher temperature loss with the KR process are larger hot metal surface area during stirring, the addition of larger quantities of reagent and large size of stirring impellers.

It is predicted that 10°C temperature loss/tHM results in a 0.88% decrease in the scrap charge to the converter. This decrease in scrap would require more hot metal charged into the converter in order to maintain production rate. This increase in hot metal consumption would result in a ¥2.14/tHM cost increase.

Predictions can be made using electrical and chemical reheating models to estimate the cost of recovering the energy lost due to the drop in hot metal temperature. Each of these methods adds ¥1.39/tHM and ¥2.74/tHM, respectively for a 10°C gain.

Following assumptions were made for the above calculation and Table 1.

- Co-injection temperature loss 20°C
- KR Process temperature loss 30°C
- Electricity costs $US 0.07/kWh
- Silicon Carbide cost $US 938/t

**Cost summary** At first glance desulphurisation techniques that employ cheaper reagents, such as lime, may seem to be the answer to lower operational costs. However, closer analysis indicates that the gain in inexpensive reagents is actually surpassed by the expenses of iron loss, temperature loss and the potential loss of production throughput.

In this comparison a 2mm lime price of ¥300/tonne was used. For optimal sulphur removal, high quality 45μm ground lime should be used. If a higher grade lime is used for the KR process then the difference in reagent costs between the two systems would be much closer.
The hot metal that is displaced by the impeller as well as the increased hot metal height in the transfer ladle due to the vortex created by stirring. To account for this level change, steelmakers have either to decrease the amount of hot metal in their transfer ladles, which decreases throughput, or increase the size of the transfer ladle, which means a retrofitting cost and higher refractory costs.

With co-injection, the reagent addition occurs sub-surface. Injection rates and speeds are customised to meet the requirements of each specific installation so that volatility on the surface of the hot metal is minimal and transfer ladle freeboard requirements kept to a minimum.

Installation and retrofitting Co-Injection desulphurisation facilities have the flexibility and adaptability to accommodate for limited space in existing steel plants. Because the reagents are pneumatically transported to the facility, stations can be designed to fit within tight space requirements by locating reagent silos up to 100m away from the station.

Mechanical stirring facilities are limited in their flexibility because of their large impeller size. In plants with large ladle capacities, increased vertical height of the building may be required to ensure clearance on the vertical movement of the larger impeller.

CONCLUSIONS
Elevated customer quality requirements continue to drive steelmakers to refine their processes to make better and cleaner steel. Reducing sulphur levels in hot metal is one of the critical steps to satisfying this demand. With the desulphurisation process, as in many other areas of steelmaking, there is more than one approach to achieve the same end result. Limiting constraints such as space, budgets, availability of consumables, environmental requirements, and operational costs are all factors to be considered. The final goal, however, is to purchase the most advanced technology with the best return on investment and operational costs.

Deep co-injection of magnesium and lime is commonly used worldwide because it provides cost-effective desulphurisation of hot metal. Although it may use more expensive reagents, the process uses those reagents effectively and efficiently. The end result is a versatile, consistent and economical method of removing sulphur from hot metal.

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