

Comparison of Kanbara reactor, magnesium mono-injection and lime – magnesium co-injection for hot metal desulphurisation

Three main methods are used for hot metal desulphurisation in hot metal ladles in the steelmaking process. These are the Kanbara Reactor (KR) process (using only lime as a reagent), the magnesium mono-injection process (using only magnesium as a reagent) and the co-injection process (using magnesium and lime as reagents). These three desulphurisation methods were studied based on metallurgy, performance and operational costs. For this study both literature and the experience of Danieli Corus engineers and clients was used.

In conclusion, it depends on the circumstances of the steel plant when deciding which process is the best and most economical solution. In practice, co-injection with magnesium and lime is the most efficient and economical option for most steel plants, since it combines the speed of the magnesium mono-injection process and the reliability of the KR process. Therefore, co-injection is, worldwide, viewed as the standard practice.

Authors: Frank Schrama and Bart van den Berg
Danieli Corus

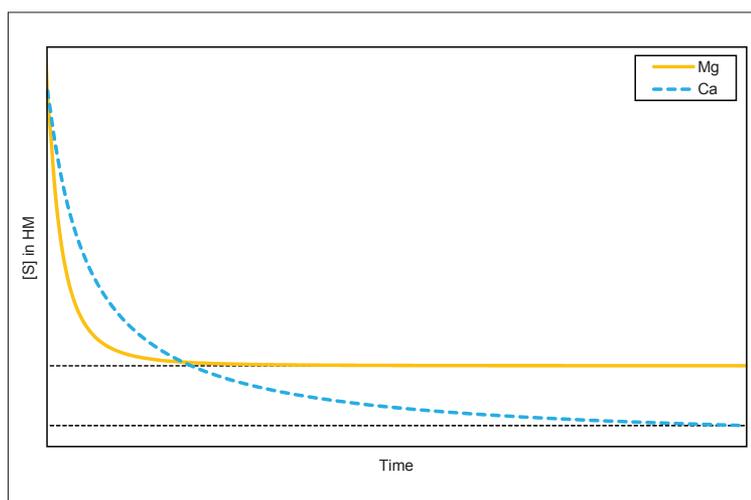


Fig 1 Qualitative graph of the equilibrium of magnesium and calcium with sulphur

Due to quality demands from the market and increasing sulphur content in hot metal, the vast majority of basic oxygen furnace (BOF) steel plants desulphurise at least a part of their liquid iron/steel. Although it is possible to desulphurise steel after the converter process, from an economic point of view, it is preferable to remove the sulphur from the hot metal before charging it to the

converter. Worldwide, a whole range of methods for hot metal desulphurisation exist. However, three methods are currently used on a larger commercial scale:

- Kanbara Reactor (KR) process, with lime as a reagent
- Magnesium mono-injection process (MMI), with magnesium as reagent (also referred to in literature as the Ukraina-Desmag process[1])
- Co-injection process, with magnesium and lime as reagents (in older plants calcium carbide is used instead of lime; in some plants all three reagents are used together).

REAGENTS

The reagents used in all three processes are lime and magnesium, with the following chemical reactions:



Reaction (2) is 20 times faster than reaction (1). This means that magnesium is a much faster desulphurising agent than lime. After the reactions between the reagent and the dissolved sulphur, the formed CaS and MgS (which have a lower density than the liquid iron) rise to the surface to form a slag layer so, when this layer is skimmed off, the sulphur is effectively removed from the hot metal. However, when the

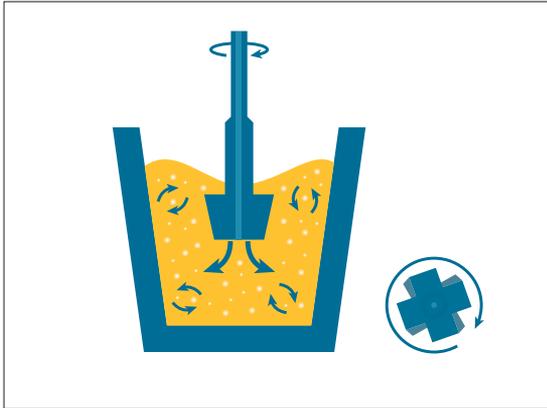


Fig 2 Kanbara reactor, with on the right, a top view of the rotor blades



Fig 3 Magnesium mono-injection process, with evaporation chamber

MgS reaches the surface it can get in contact with oxygen, which results in the following reaction:



Thus the unbounded sulphur re-dissolves in the liquid iron. This is called resulphurisation and can be prevented in two ways. The first is to avoid contact between MgS and air, which leads to practical problems (the injection and skimming should take place in an inert environment), the second is to bind the sulphur with calcium to form the more stable CaS:



The formed CaS and MgO will remain as stable solids in the slag[2,3].

Due to the reaction kinetics, magnesium is a faster reagent than the calcium-based alternatives, but lime has a lower equilibrium with the sulphur in the hot metal than magnesium. This is qualitatively depicted in *Figure 1*. For the desulphurisation process this means that magnesium is required for a fast process, but that lime or calcium carbide is required to reach low sulphur concentrations. The CaS formed in reaction (1) will remain attached to the reagent particles, which will rise to the slag layer within a minute due to upward pressure. Reaction (2) is a homogeneous reaction, which means that the magnesium first needs to dissolve in the hot metal before it reacts with the sulphur. The formed MgS starts, therefore, as a single molecule and takes much longer to cluster and rise to the slag (about 5-8 minutes). In practice, this means that for effective desulphurisation the skimming cannot be stopped earlier than 8 minutes after the last magnesium particles are injected[2,4].

KANBARA (KR) REACTOR

The KR process was developed in Japan by Nippon Steel in 1963. Low availability of magnesium in Japan meant alternatives were needed. Current KR stations can be found mainly in (east) Asia and in a few plants in Europe.

In the KR process, lime is used as the main reagent. Sometimes also calcium fluoride (CaF₂, about 10%) and/or aluminium oxide (Al₂O₃) are mixed with the lime. The reagent is usually added from the top, but sometimes it is injected through the rotating lance (typical speed is 100-120rpm) together with a carrier gas (usually nitrogen). The lance is equipped with four massive rotor blades, which create turbulence in the hot metal (see *Figure 2*).

Due to the created turbulence, the bubble size of the transport gas is smaller and the residence time of the lime in the hot metal is longer than during static injection. The increased residence time is of major importance to the process, since lime is a relatively slow reagent. The lime is used more efficiently in the KR process, which means less is required and lime of a lower (thus cheaper) quality can be used. The stirring process, however, also means that the hot metal needs to be skimmed prior to desulphurisation in order to remove high SiO₂ containing blast furnace slag, which decreases the efficiency of the lime. Also, the impeller and refractory of the ladle suffer from increased wear. Finally, the created turbulence requires a larger freeboard (typically 1m more than co-injection) in the hot metal ladle[3, 5-7].

MAGNESIUM MONO-INJECTION

Between 1969 and 1971, the magnesium mono-injection (MMI) process was developed at the Ukrainian Academy of Sciences. The Ukraina-Desmag process, as it is sometimes called, is today still used mainly in Russia and Ukraine, as well as in a few plants in China. Tests with this method in North America failed as a result of the violence of the ▶



Fig 4 Co-injection process, with T-shaped lance exit

process and in Finland, MMI was used in one steel plant, but later replaced by calcium carbide mono-injection because it was not stable.

With the MMI process, salt-coated magnesium is injected into the hot metal via a bell-shaped lance (see Figure 3). The bell at the end of the lance is used as an evaporation chamber for the magnesium (boiling point 1,107°C) to stabilise the process. However, there are also plants with larger ladle sizes, where a straight lance without an evaporation chamber is used. In both cases the evaporation of the magnesium causes enough turbulence to ensure a good reagent distribution in the hot metal.

Supporters of the MMI process often state that lime does not add significantly to the desulphurisation efficiency of magnesium. This is correct. Because magnesium is a 20 times faster reagent than lime, an equal amount of lime would contribute less than 5% to the desulphurisation. Furthermore, it is also claimed that lime actually decreases the efficiency of magnesium, especially in cases where the lime is not very well burnt. This leads to the following reactions:



However, when only magnesium is used as a reagent, resulphurisation is a major problem. Another problem is the thin slag layer (compared with KR and co-injection), which leads to an increased iron entrainment loss during skimming. In order to stabilise the slag and retard the resulphurisation, in most steel plants lime, flux and/or coagulant is added on top of the slag[1,3,8].

CO-INJECTION

The co-injection of magnesium and lime combines the advantages of the reagents. Magnesium makes it possible

to desulphurise rapidly and lime makes it possible to reach low sulphur concentrations without resulphurisation. Co-injection stations are used worldwide and the process is viewed as the standard practice.

The reagents are stored in different dispensers and are only mixed inside the injection line. The reagents are injected into the hot metal via a straight lance with one opening at the bottom or two or four openings at the side (see Figure 4). A transport gas (usually nitrogen) is used to ensure a smooth injection.

The turbulence in the hot metal is created by the carrier gas and the magnesium that evaporates. This turbulence ensures a sufficient distribution of reagent throughout the ladle. An advantage of co-injection is that the ratio between magnesium and lime can be modified if the situation requires or allows it. For example, if more time is available, more lime and less magnesium can be injected, which makes the process more flexible and cheaper.

In some older plants calcium carbide (CaC_2) is used instead of lime. Although CaC_2 is about three times more expensive (per kg), it is an eight times faster reagent than lime. Co-injection with magnesium and CaC_2 is faster and cheaper than co-injection with magnesium and lime. Another advantage of CaC_2 is that it can also be used without magnesium. Industrial calcium carbide, however, contains toxic compounds like phosphine and hydrogen sulphide and in contact with water highly explosive acetylene gas is formed. CaC_2 (or CaC_2 rich slag) therefore has major safety and environmental issues. A further disadvantage is that calcium carbide is abrasive, resulting in faster wear of equipment.

Lime has no major safety issues and is relatively easy to purchase worldwide. Due to the safety issues co-injection stations with magnesium and CaC_2 are usually no longer installed in new plants. Exceptions are the so-called tri-injection stations, where magnesium, lime and CaC_2 are all used, combining the advantages of the different reagents.

TECHNICAL AND METALLURGICAL COMPARISON

The aforementioned desulphurisation methods all have their strong and weak points. It depends on the specific circumstances and requirements of a plant, which points are more important, however, the three methods can be compared for a few important technical and metallurgical issues of hot metal desulphurisation.

TIME The process time depends on how fast the reagents can react with sulphur. Since magnesium is a much faster reagent than lime, MMI and co-injection are faster than KR. The KR process has an extra time delay since skimming prior to injection is often required. On average, KR requires 10-20% more time than co-injection.

The MMI process generally has a shorter injection time than co-injection (10-20% faster). However, the gained time is limited, since in both processes skimming can only be ended when all MgS particles reached the slag layer (which can take 8 minutes). Still, in general, the MMI process is faster than co-injection with magnesium and lime (about 5%; co-injection with magnesium and calcium carbide is, in general, even faster than MMI). The KR process is the most time consuming[1,3,9].

IRON LOSS DURING SKIMMING This is a major problem and iron is lost in two different ways. During slag formation, iron droplets get trapped in the slag, thus forming an emulsion with the slag. Then, when the slag is skimmed, the trapped iron is lost with it: this is emulsion loss. In general, about 50wt% of the slag is iron in emulsion. This means that emulsion loss can be lowered by reducing the total amount of slag. The other major contribution to iron loss is the entrainment loss. When slag is skimmed off, some iron can come with it. The entrainment loss can be reduced by more careful skimming or by a thicker, more viscous slag, which is easier to rake off.

Due to the high amount of slag created in the KR process and the required extra skimming prior to desulphurisation, the total iron loss is generally 2-3 times more than for co-injection. The MMI process has the lowest iron emulsion loss, since only little slag is created (about 7 times less than with co-injection). However, due to the lower basicity, MMI slag can contain more iron in emulsion than slag that contains calcium. The entrainment loss of iron for MMI is higher than for co-injection or the KR process, since skimming is more difficult due to the thin slag layer and skimming needs to be done more thoroughly due to the higher sulphur concentration of the slag and the high risk of resulphurisation later in the process.

Nevertheless, in some literature very low iron losses are claimed for the MMI process (as low as 0.03% total iron loss or 45kg for a 150 tonne ladle) that seem impossible when taking entrainment loss into account. In reality, the iron loss of the MMI process is similar to co-injection: around 1% total iron loss. For the KR process the total iron loss is 2-3%[1,3,9].

REFRACTORY AND LANCE WEAR Ladle refractory and lance wear is caused mainly by the high temperatures and corrosive composition of the hot metal and the slag. For the KR process the turbulence created by the rotating impeller is a major contributor, but also the impeller itself is more vulnerable to wear, since the blades can even break off. Worn impeller blades generate less turbulence and are therefore less efficient. Because of the wearing problems, a lot of research is done on refractories, especially of KR systems. The MMI process has fewer wear problems due

to less turbulence, however, since magnesium is used instead of lime, the basicity of the slag is lower, leading to increased corrosion wear. The co-injection process has less turbulence than the MMI process and a higher basicity in the slag, which explains why the refractory and lance suffer the least from wear in this process. However, even for co-injection, wear remains an issue[3,7].

TEMPERATURE LOSS During desulphurisation, the temperature of the hot metal decreases. The temperature of the hot metal when it is charged to the converter has an influence on the amount of coolant (scrap) that can be added or the blowing time of the converter. Colder hot metal means less scrap can be added or the longer the blowing time will be. When the hot metal temperature is already too low before desulphurisation, the desulphurisation process has to be omitted completely. This happens more often for the KR. It depends on the circumstances if temperature loss in the desulphurisation process is a problem or not. In Europe and North America, an increased scrap to hot metal ratio is very beneficial, since hot metal is more expensive than scrap.

Higher temperature losses are caused by longer process times, more turbulence, less slag (slag acts as an insulation material) and the use of reagents that lead to less heat. Magnesium causes an exothermic reaction in the hot metal whereas lime does not. The KR process involves longer process times, high turbulence and no major exothermic reactions, which leads to a temperature loss that is on average three times higher than for co-injection or MMI. As stated above, injection during co-injection takes, in general, longer than injection in the MMI process. On the other hand, co-injection is a less turbulent process and has a thicker slag layer. Therefore, the temperature losses for co-injection and MMI are, in general, comparable[1,3].

LOW SULPHUR Nowadays, hot metal with a sulphur concentration of only 10-20ppm can be demanded. Due to magnesium-sulphur equilibrium and the resulting resulphurisation, a magnesium-only reagent will not be sufficient to reach these low sulphur concentrations. In the literature, low sulphur concentrations using only magnesium are claimed, but measurements were taken only directly after injection (so before resulphurisation shows its effect). In practice, the MMI process delivers hot metal with a minimum sulphur concentration at the converter of around 60ppm. Lower concentrations are practically impossible to achieve with this process, however, this can be compensated a little by adding fluxes to the ladle top.

Co-injection is capable of reaching stable low sulphur concentrations in hot metal. However, since magnesium is not efficient at low sulphur concentrations, only the ▶

	KR	MMI	Co-injection
Process time	-	++	+
Iron loss	--	++	++
Equipment wear	--	-	+
Temperature loss	-	+	+
Low sulphur	++	--	+
Flexibility	-	-	++
Safety	++	--	+

Table 1 Qualitative comparison between the desulphurisation processes

injected lime has a contribution to the desulphurisation as soon as the low sulphur concentrations are reached. Due to the lower turbulence during the co-injection process, reaching the desired low sulphur concentration takes longer and costs more reagent than for the KR process. Where consistent low sulphur concentrations are required, the KR process is most suitable[1,3,10].

FLEXIBILITY A desulphurisation station that can respond to changing circumstances, like scarce reagents or lack of time, is beneficial to the overall flexibility of a steel plant. The KR is not flexible concerning the process time, since the optimal lime flow and stirring speed are already applied, so KR can only reduce the time by relaxing the sulphur aim. Availability of reagents are, under normal circumstances, not a problem for the KR process. Magnesium for the MMI process can become scarce though, leading to a sudden increase in the operational costs of the system or even a production stop. The co-injection system has a high flexibility for both process times and reagent scarceness, since both rate and ratio can be adjusted. Calcium carbide can be injected as an alternative reagent[3,12].

SAFETY Magnesium is a hazardous flammable compound. Spilled magnesium can catch fire and is not easy to extinguish. In contact with water it can form the explosive gas hydrogen and so for desulphurisation it is therefore coated in order to reduce its hazards. Nevertheless, coated magnesium remains a more hazardous reagent than burnt lime. In the MMI process (and sometimes in the KR process as well) calcium fluoride is often added to stabilise the process. When calcium fluoride reacts, the highly toxic gas fluorine is created, which, together with the violence during injection (due to vapourising and oxidising of the magnesium), makes the MMI process a relatively unsafe process for human health and the environment. This was also one of the causes why the MMI process was abandoned in North America. Co-injection is also considered to be less safe than the KR process, provided

no calcium fluoride is used in the KR process, due to the use of magnesium. When calcium fluoride is used in the KR process, co-injection can even be considered as a safer option[3,11].

ECONOMIC COMPARISON

When considering CAPEX, the KR system is the most expensive due to the large structure and support for the lance and motor system. The MMI process is probably slightly cheaper than co-injection because only one dispenser is required. Often the operational costs (OPEX) of a desulphurisation system are considered the most important factor. The most significant contributions to the OPEX are described below.

IRON LOSS Iron loss is the most important contributor to the costs of a desulphurisation system. It is estimated that the value of hot metal is €300/t. As described above, the hot metal loss for MMI and co-injection is about 1%. For KR the hot metal loss is 2-3% (so 2.5% is used in the calculations). In general, the costs for iron loss can be reduced when considering recycling treatment of slag, but this is not taken into account here[12].

REAGENT COSTS To make an estimate for the reagent costs, it is assumed that magnesium costs €2,500/t, lime for co-injection €175/t and lime for the KR process (lower quality) €50/t. It is estimated that for both MMI and the co-injection, 0.5kg magnesium is injected/tHM. With an average ratio of 1:4 (Mg:CaO) co-injection also requires 2kg lime/tHM. In general, the KR process injects 10kg lime/tHM. For KR and MMI, often flux and/or coagulant is also added (approximately 500kg/heat, which costs around €80/t). The costs for this are estimated at €0.20/t HM[1,3].

EQUIPMENT WEAR The major costs for equipment wear are the lances and the ladle refractory. Maintenance on the rest of the equipment is not taken into account since the differences are considered negligible. The complete lance of the KR system treats on average 30,000 tHM (150 heats of 200t) and costs around €8,000. The lance of the MMI system treats on average 10,000tHM (50 heats of 200t) and costs around €1,500. The lance of the co-injection system also treats on average 10,000tHM (50 heats of 200 t) and costs around €800. The average lifetimes of the lances also include the fact that some lances break or block during their first heat.

To replace the refractory of a hot metal ladle costs around €12,000 (including labour). Since MMI and KR require more freeboard (at least an extra 50cm), the amount of required refractory is about 10% more (thus total costs of €13,200). For a KR system, refractory needs to be replaced on average per 18,000tHM (90 heats of 200t).

The refractory of a ladle in a MMI system needs on average to be replaced every 24,000tHM (120 heats of 200t). For the co-injection system, the refractory of a ladle needs to be replaced per 36,000tHM (180 heats of 200t)[7].

TEMPERATURE LOSS Temperature loss of hot metal means that less scrap or more hot metal are added to the converter (simplified). The costs of this extra hot metal minus the costs of the scrap are estimated at 0.025/°C·tHM. The temperature loss for co-injection and MMI have an average temperature loss of 10°C per heat. KR has a temperature loss that is on average three times higher at 30°C per heat[3].

Certain costs are assumed for using nitrogen gas and electrical power. Initial figures show values of around €0.05/t of steel which has no major impact on the total OPEX. However, it is clear that KR requires much more electricity than the other processes, while MMI requires 5-6 times more nitrogen than co-injection. Also the influence of spare parts costs are neglected, since they are roughly €0.05/t HM.

CONCLUSIONS

In this study, an attempt was made to compare the three major desulphurisation techniques based on metallurgical performance and costs. The numbers mentioned in this study should not be considered solid, as most of them are averages and estimates based on experience and literature (of which most are unrealistically positive about the performance of their own installation or method). Local circumstances and fluctuations are not taken into account. However, based on this study some conclusions can be drawn.

- Considering the performance and the operational costs, the KR Reactor is only a viable option for hot metal desulphurisation when the main target is to produce low sulphur steel and when process times, temperature loss and hot metal loss are not an issue.
- When a steel plant has zero demand for low sulphur steels, resulphurisation is not considered a problem and short processing times are required, magnesium mono-injection is the most effective method.
- Co-injection with magnesium and lime is the most flexible and reliable option. For a wide range of steel grades (including both low sulphur grades and normal grades), co-injection is the most effective and economically most attractive method.
- It depends on the circumstances, focus and targets of a steel plant which of the hot metal desulphurisation methods is optimal. **MS**

	KR	MMI	Co-injection
Iron loss	7.50	3.00	3.00
Reagent costs	0.70	1.45	1.60
Equipment wear	1.00	0.70	0.41
Temperature loss	0.75	0.25	0.25
Total	9.95	5.40	5.26

📌 **Table 2 Most important contributions to the OPEX of the desulphurisation processes, €/tHM**

Frank Schrama and Bart van den Berg are with Danieli Corus, Velsen-Noord, the Netherlands

CONTACT: comms.office@danieli-corus.com

REFERENCES

- [1] Bol'shakov et al., 'Rational Ladle Treatment for Desulfurization of Hot Metal', in *Steel in Translation*, 39, 4, 2009 pp326-333
- [2] Sun, Liu and Lu, 'Behaviour of Ar-1%Mg Bubbles in Desulfurization of Hot Metal by Magnesium Injection', in *Steel Research Int.*, 80 (3), 2009, pp209-217
- [3] Filbri and Berg, 'Pre-treatment for steelmaking – benefits of magnesium lime co-injection, Kolkata, India, s.n., *Steel Tech.*, 2011, pp163-170
- [4] Cho et al., 'Hot metal desulfurization by CaO-SiO₂-CaF₂-Na₂O slag saturated with MgO, in *ISIJ International*, 50(2), 2010, pp215-221
- [5] Seshadri et al, 'A study of desulfurization in a Kanbara reactor through physical and mathematical modelling and plant assessment', in *AISTech.*, 1, 2009
- [6] Liu et al., 'Mechanical stirring for highly efficient gas injection refining', in *Transactions of Nonferrous Metals Society of China*, 21, pp1,896-1,904, 2011
- [7] Isoo et al, 'Improvement of durability of castable for desulfurization impeller', in *Journal of the Technical Association of Refractories*, 30(3), pp194-199, 2010
- [8] Magnesium. [Online] [Cited: April 3, 2014] www.lenntech.nl/periodiek/elementen/mg.htm
- [9] Saxena, 'Recent trends on desulphurisation of hot metal for mass production of quality steels in oxygen steelmaking furnace', in *Metal & Metallurgy China*, May 1997
- [10] Li et al, 'Improved slag skimming performance at hot metal desulphurisation station by using recycled materials as slag modifying agent', in Luleå (Sweden): s.n., *Proceedings of Scanmet IV*, 2, 2012
- [11] Yoshida, Wade and Kishigami, 'Improvement of productivity of refining process to make high purity steel at No.3 Steelmaking Shop in Yawata Works, Nippon Steel', *ICS 2008*, pp295-298
- [12] World Steel Prices. [Online] [Cited: September 17, 2014.] www.worldsteelprices.com