

THE LEADING HOT METAL DESULFURIZATION METHODS: A COMPARISON BETWEEN KR, MMI AND CO-INJECTION*

Frank Schrama¹
Guido van Hattum²
Bart van den Berg³

Abstract

Steelmakers worldwide agree that the most efficient and cost-effective solution in BOF steelmaking is to desulfurize the hot metal between the blast furnace and converter. Various methods are currently in use, among which the Kanbara Reactor (KR, using only lime as a reagent), Magnesium mono-injection (MMI, using only magnesium; also known as the Ukraina-Desmag process) and co-injection (using magnesium and lime/CaC₂) are leading. These three hot metal desulfurization methods are compared based on metallurgy, efficiency, costs and overall performance. Both available data from literature and experience from Danieli Corus engineers is used for this study. The KR process is able to reach low sulfur concentrations (> 10 ppm) in hot metal and has lower reagent costs. However, due to higher Fe-loss and heavy wear the KR process has the highest operational costs. The Magnesium mono-injection process is very fast due to the use of the reactive magnesium as reagent. Major problems with resulfurization (sulfur levels below 50 ppm cannot be reached) and the violence of the process made that this process could never get a firm foothold in the western steel industry. The co-injection process with magnesium and lime proves to be able to combine the best of both worlds. It can reach low sulfur concentrations and desulfurize fast. Co-injection is also the most flexible and cost effective.

Keywords: Hot metal desulfurization; Co-injection; Kanbara reactor; Magnesium mono-injection.

¹ MSc, process engineer, Danieli Corus, Velsen-Noord, the Netherlands.

² Sales manager, Danieli Corus, Velsen-Noord, the Netherlands.

³ MSc, senior process engineer, Danieli Corus, Velsen-Noord, the Netherlands.

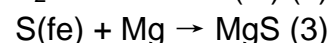
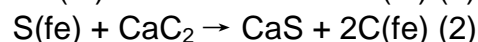
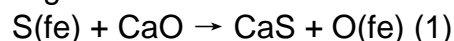
1 INTRODUCTION

Due to the quality demands from the market and increasing sulfur contents in hot metal, the vast majority of the Basic Oxygen Furnace (BOF) steel plants worldwide desulfurize at least a part of their steel. Although it is possible to desulfurize steel after the converter process, it is preferred from an economical point of view to remove the sulfur from the hot metal before charging it to the converter.

Worldwide a whole range of methods for hot metal desulfurization exists, however three methods are currently used on a larger commercial scale: the Kanbara Reactor (KR) process, with lime as a reagent, the Magnesium mono-injection process (MMI), with magnesium as reagent (also referred to in literature as Ukraina-Desmag process [1]) and the co-injection process, using magnesium and lime or calcium carbide (sometimes all three of them) as reagents.

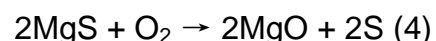
2 REAGENTS

The reagents that are used in KR, MMI and co-injection are lime, calcium carbide and magnesium. All processes are based on the following chemical reactions:

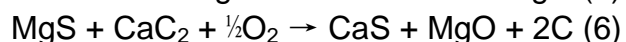
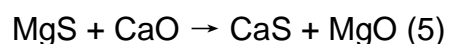


Reaction 3 is three times as fast as reaction 2 and 20 times as fast as reaction 1. This means that magnesium is a much faster desulfurizing agent than calcium carbide or lime.

After the reactions between the reagent and the dissolved sulfur, the formed CaS and MgS (which have a lower density than the liquid iron) rise to the surface to form a slag layer on top. When this layer is skimmed off, the sulfur is effectively removed from the hot metal. When the MgS reaches the surface it gets in contact with oxygen, which results in the following reaction:



The unbounded sulfur dissolves back into the liquid iron. This is called resulfurization. The resulfurization via reaction 4 can be prevented in two ways – to avoid contact between the MgS and air, which leads to practical problems (the injection and skimming should take place in an inert environment), or bind the sulfur with calcium to form the more stable CaS:



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

Due to the reaction kinetics, magnesium is a faster reagent than the calcium based alternatives, but lime and calcium carbide have a lower equilibrium with the sulfur in the hot metal than magnesium. This is depicted in Figure 1. For the desulfurization process this means that magnesium is required for a fast process, but that lime or calcium carbide is required to reach low sulfur concentrations.

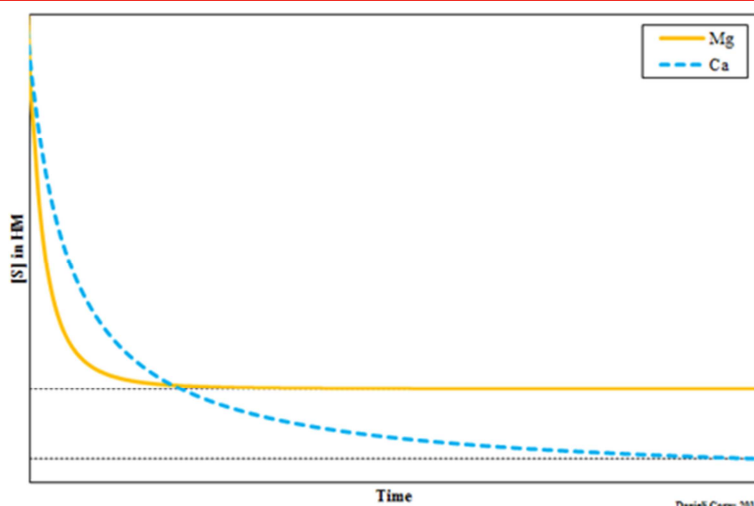


Figure 1. Qualitative graph of the equilibrium of magnesium and calcium with sulfur.

The CaS formed in reactions 1 and 2 will remain attached to the reagent particle, which will rise to the slag layer due to the upward pressure within a minute. Reaction 3 is a homogeneous reaction, which means that the magnesium first needs to dissolve in the hot metal before it reacts with the sulfur. The formed MgS therefore starts 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 desulfurization the skimming cannot be stopped earlier than 8 minutes after the last magnesium particles are injected [2,4].

3 KANBARA REACTOR

The KR process was developed in Japan by Nippon Steel in 1963. The low availability of magnesium in Japan was the reason to look for alternatives. Current KR stations in use can mainly be found in (east) Asia and in a few plants in Europe and South America.

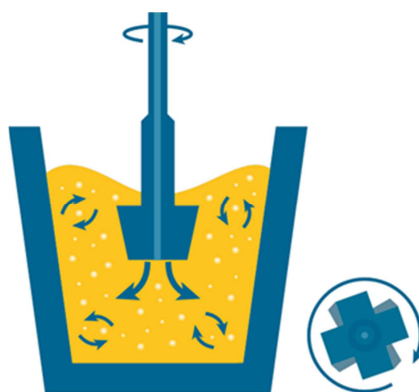


Figure 2. Kanbara Reactor, with on the right a top view of the rotor blades.

In the KR process lime is used as the main reagent. Sometimes also CaF_2 (about 10% of the flow) and/or Al_2O_3 are added. The reagent is either injected into the hot metal through a rotating lance (typical speed is 100-120 rpm) together with a carrier gas (usually nitrogen) or, alternatively, the reagent is added from the top. The stirring lance is equipped with four massive rotor blades, which create turbulence in the hot metal. Due to the 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 in the KR process is used more efficiently, which means less lime is required and lime of a lower (thus cheaper) quality can be used. The stirring however also means that the hot metal needs to be skimmed prior to desulfurization as well, in order to remove high SiO₂ containing slag from the blast furnace, which decreases the efficiency of the lime. Also the impellor and refractory of the ladle suffer from increased wear. Finally the created turbulence requires a larger freeboard (typically 1 meter more than co-injection) in the hot metal ladle [3,5-7].

4 MAGNESIUM MONO-INJECTION

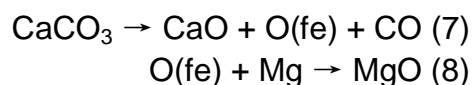
Between 1969 and 1971 the magnesium mono-injection (MMI) process was developed at the Ukrainian Academy of Sciences (in the former USSR). The Ukraina-Desmag process, as it is sometimes called, is today still mainly used in former USSR states Russia and Ukraine, as well as in some plants in China and Taiwan. Tests with this method in North America failed as a result of the violence of the process. In Finland the MMI process was abandoned after some years due to unreliability of the process.



Figure 3. Magnesium mono-injection process, with evaporation chamber.

With the MMI process, salt coated magnesium is injected via a bell shaped lance into the hot metal. The bell at the end of the lance is used as an evaporation chamber for the magnesium (which has a boiling point of 1107 °C) to stabilize 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 desulfurization efficiency of magnesium. This is correct, since magnesium is a 20 times faster reagent than lime, an equal amount of lime would contribute for less than 5% to the desulfurization. In contrary it is 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:



When only magnesium is used as a reagent, resulfurization 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 stabilize the

slag and retard the resulfurization, in most steel plants lime, flux and/or coagulant is added on top of the slag [1,3,8].

5 CO-INJECTION

The co-injection of magnesium and lime is a method that combines the advantages of both reagents. Magnesium enables fast desulfurization while lime allows for low final sulfur concentrations. In the past the lime was sometimes replaced by calcium carbide, which is more efficient, but due to safety issues this option is hardly used in new steel plants anymore. Co-injection stations are used worldwide and the process is considered standard practice.

The reagents are stored in different dispensers and are only mixed inside the injection line. The reagents are injected in the hot metal via a straight lance with one opening at the bottom or two or four openings at the side. An inert 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 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 more cost effective.

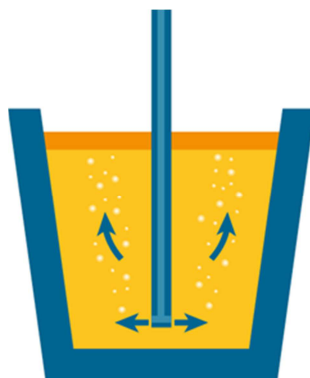


Figure 4. Co-injection process, with T-shaped lance exit.

6 TECHNICAL AND ECONOMICAL COMPARISON

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

6.1 Time

The process times depends on how fast the reagents can react with sulfur. Since magnesium is a much faster reagent than lime, the MMI process and co-injection are faster than the KR process. The KR process has an extra time delay, since skimming prior to injection is often required, in order to prevent the return of impurities from the blast furnace slag into the hot metal during the mixing. According to literature the KR process takes on average 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 for the MMI process, 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 CaC_2 is in general even faster than MMI). The KR process is the most time consuming process [1,3,9].

6.2 Iron Loss During Skimming

Iron loss during skimming is a major problem in steel plants. Iron is lost in two different ways. During the slag forming, iron droplets get trapped in the slag, thus forming an emulsion with the slag. When the slag is skimmed, the trapped iron is lost with it; the so called emulsion loss. In general about 50 wt% of the slag is iron in emulsion. This means that emulsion loss can be minimized by reducing the total amount of slag. The other major contribution to iron loss is the entrainment loss. When slag is raked 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 skim.

Due to the high amount of slag created in the KR process and the required extra skimming prior to the desulfurization, 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 co-injection). However, due to the lower basicity, MMI slag contains more iron in emulsion than slag that contains calcium. The entrainment loss of iron for the MMI process is higher than for co-injection or the KR process, since skimming is more difficult due to the small slag layer and skimming needs to be done more thoroughly due to the higher sulfur concentration of the slag and the high risk of resulfurization 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 45 kg for a 150 t 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].

6.3 Refractory and Lance Wearing

Wear of the refractory and the lance is mainly caused by the high temperatures and corrosive composition of the hot metal and the slag. For the KR process the turbulence created by the rotating impellor is a major contributor to the wear. Also the impellor itself is more vulnerable to wear, since the blades can even break off. Decrease of the blades of the impellers then leads to less turbulence and thus less efficiency. Because of the wearing problems, a lot of research is done on refractory of especially KR systems. The MMI process has less wearing problems than the KR process, 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 wearing in this process. However, also for co-injection wearing remains an issue [3,7].

6.4 Temperature Loss

During the desulfurization process, the hot metal loses temperature. 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 on the blowing time of the converter. The colder the hot metal, the less scrap can be added or the longer the blowing time in the converter will be. When the hot metal temperature is already too low before desulfurization, the desulfurization process has to be omitted completely. This happens more often for the KR. It depends on the circumstances if temperature loss in the desulfurization 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 there more expensive than scrap.

Higher temperature losses are caused by longer process times, more turbulence, less slag (slag acts as an isolation material) and the use of reagents that lead to less heat. Magnesium causes an exothermic reaction in the hot metal and 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 for MMI. On the other hand co-injection is a less turbulent process and has a thicker isolating slag layer. Therefore the temperature losses for co-injection and MMI are in general comparable [1,3].

6.5 Low Sulfur

Nowadays hot metal with a sulfur concentration of only 10-20 ppm can be demanded. Due to magnesium-sulfur equilibrium and the resulting resulfurization, only magnesium as a reagent will not be sufficient to reach those low sulfur concentrations. In literature low sulfur concentrations with the use of only magnesium are claimed, but only measurements are taken directly after injection (so before resulfurization shows its effect). In practice hot metal that is desulfurized by MMI never has a sulfur concentration below 0.006% when it is charged to the converter. This can be compensated a little by adding fluxes from the top.

Co-injection is capable of reaching stable low sulfur concentrations in hot metal. However, since magnesium is not efficient anymore at low sulfur concentrations, only the injected lime has a contribution to the desulfurization as soon as the low sulfur concentrations are reached. Due to the lower turbulence during the co-injection process, reaching the desired low sulfur concentration takes longer and costs more reagent than for the KR process. In case consistent low sulfur concentrations are required, the KR process is most suitable [1,3,10].

6.6 Flexibility

A desulfurization station that can respond to changing circumstances, like scarce reagents or lack of time, is beneficial to the overall flexibility of the steel plant. The KR is not flexible concerning the process time, since the optimal lime flow and stirring speed are already applied. The KR can only reduce the process time by releasing the initial sulfur 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. Even CaC_2 can be injected as an alternative reagent [3,11].

6.7 Safety

Magnesium is a hazardous flammable compound. Spilled magnesium can catch fire and is not easy to extinguish. In contact with water magnesium can form the explosive gas hydrogen. Magnesium for desulfurization is therefore coated, in order to retard 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) also often CaF_2 is added to stabilize the process. When CaF_2 reacts, the highly toxic gas fluorine is created. This, together with the violence during injection (due to vaporizing and oxidizing of the magnesium), makes the MMI process a relatively unsafe process for human health and the environment. This was also one of the reasons why the MMI process was abandoned in North-America. Co-injection is also considered as less safe than the KR process, provided no CaF_2 is used in the KR process, due to the use of magnesium. Due to safety reasons, CaC_2 (which can form the explosive gas acetylene when in contact with water) is only very seldom used for new co-injection stations. When CaF_2 is used in the KR process, co-injection (using lime) can even be considered as a safer option [3,11].

Table 1. Qualitative comparison between the desulfurization processes.

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

7 ECONOMICAL COMPARISON

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

7.1 Iron Loss

Iron loss is the most important contributor to the costs of a desulfurization 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 an average of 2.5% is used). 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].

7.2 Reagent Costs

In order to make an estimate for the reagent costs, it is assumed that magnesium costs 2500 €/t, lime for co-injection 175 €/t and lime for the KR process (lower quality) 50 €/t. It is estimated that for both the MMI process and the co-injection process 0.5 kg/t HM magnesium is injected. With an average ratio of 1:4 (Mg:CaO) co-injection also requires 2 kg/t HM lime. In general the KR process injects 10 kg/t HM lime. For KR and MMI, often flux and/or coagulant is added as well (approximately 500 kg/heat, which costs around 80 €/t). The costs for this are estimated at 0.20 €/t HM [1,3].

7.3 Equipment Wear

The most important equipment wear for the comparison is that of 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 t HM (150 heats of 200 t) and costs around € 8000. The lance of the MMI system treats on average 10,000 t HM (50 heats of 200 t) and costs around € 1500. The lance of the co-injection system also treats on average 10,000 t HM (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 labor). Since MMI and KR require more freeboard (at least 50 cm), the amount of required refractory is about 10 % more (total costs: € 13,200). For a KR system, refractory needs to be replaced on average per 18,000 t HM (90 heats of 200 t). The refractory of a ladle in a MMI system needs on average to be replaced every 24,000 t HM (120 heats of 200 t). For the co-injection system, the refractory of a ladle needs to be replaced per 36,000 t HM (180 heats of 200 t) [7].

7.4 Temperature Loss

Temperature loss for the hot metal means that less scrap or more hot metal can be added to the converter (simplified). The costs of this extra hot metal minus the costs of the scrap are estimated at 0.025 €/°C·t HM. 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, so 30°C per heat [3].

Table 2. Most important contributions to the OPEX of the desulfurization processes.

Per t HM	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

Certain costs are made for using (nitrogen) gas and electrical power. However no clear figures are known to compare this. Initial figures show values of around 0.05 €/t HM which has no mayor 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.

8 CONCLUSION

In this study an attempt was made to compare the three leading desulfurization 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 Kanbara Reactor is only a viable option for hot metal desulfurization when the main target is to produce low sulfur steel and when process times, temperature loss and hot metal loss are not an issue.

When no steel grades with a low sulfur concentrations need to be made, resulfurization is not considered a problem and short processing times are required, the 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 sulfur 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 desulfurization methods is optimal.

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