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EFFECT OF KAIF₄ ON THE EFFICIENCY OF HOT METAL DESULPHURISATION WITH MAGNESIUM

Frank N.H. Schrama - Delft University of Technology, Netherlands and Tata Steel, The Netherlands

Elisabeth M. Beunder - Tata Steel, The Netherlands

Fuzhong Ji - Materials Processing Institute, United Kingdom

Rhian Woolf, Chris Barnes - Tata Steel, United Kingdom

Jilt Sietsma, Rob Boom, Yongxiang Yang - Delft University of Technology, The Netherlands

At the hot metal desulphurisation (HMD) stations of Tata Steel's BOS plant in Port Talbot (UK), KAIF₄ is injected together with magnesium in order to increase the fluidity of the slag and thus to decrease the iron loss. Although KAIF₄ is successfully contributing to a lower iron loss during HMD, it also has a negative effect on the desulphurisation efficiency of magnesium. Analysis of slag samples from the plant and FactSage calculations showed that the fluorine in KAIF₄ reacts with the magnesium, thus preventing the magnesium from reacting with the sulphur.

KEYWORDS: HOT METAL DESULPHURISATION, SLAG MODIFIER, MAGNESIUM EFFICIENCY, FLUORINE, POTASSIUM CRYOLITE

INTRODUCTION

As is common practice in most modern European steel plants, at the BOS plant of Tata Steel in Port Talbot (UK) the hot metal from the blast furnace (BF) is desulphurised before it is charged to the steelmaking converter. Two hot metal desulphurisation (HMD) stations are available to desulphurise the hot metal by co-injection of magnesium and lime. This HMD process is required to meet Tata Steel's quality demands regarding sulphur concentration in the steel.

In the co-injection process the injected reagents react with the dissolved sulphur to form sulphides that end up in the slag. The slag is skimmed off after the injection so that the sulphur is removed from the hot metal. One of the major costs in the HMD process is the iron loss during slag skimming. Iron can get trapped in emulsion in the slag and then removed together with the slag (so called emulsion loss) or during skimming it can be entrained with the slag (so called entrainment loss). In order to decrease the emulsion loss, the slag viscosity and its solid fraction need to be lowered [1]. In Port Talbot KAIF₄ (sometimes referred to as "(potassium) cryolite") is injected together with the magnesium to successfully decrease the iron losses during skimming.

In practise iron losses during HMD significantly decreased since the introduction of KAIF₄, which led to lower costs for the process. However, since the introduction of KAIF₄ the magnesium reagent consumption also increased by roughly 20%. The increased magnesium consumption could only partly be explained by changes in hot metal composition and temperature and the fact that when adding KAIF₄ to the magnesium, the Mg concentration in the reagent decreases by 7% (from 97% to 90% pure Mg content), leading to an expected consumption increase of about 8%. It seemed that KAIF₄ has an undesirable effect on the desulphurisation efficiency of magnesium.

THEORY

Background

In the HMD co-injection process, the injected magnesium dissolves in the metal and reacts with the dissolved sulphur (reaction 1). The formed MgS clusters and ascends to the slag, where it reacts with lime to form the

more stable CaS (reaction 2). About 5% of the sulphur is removed via direct (heterogeneous) reaction with lime (reaction 3) [2], [3].



When measuring the efficiency of desulphurisation with magnesium, the specific magnesium consumption (\dot{m}_{Mg}) is used [3]:

$$\dot{m}_{Mg} = \frac{M_{Mg}}{M_{\Delta S}} \quad [4]$$

Here M_{Mg} and $M_{\Delta S}$ are the mass of injected magnesium and the mass of removed sulphur respectively. Although equation 4 neglects the effect of lime on the desulphurisation, this simple equation proves to be effective in plant conditions. Typical industrial values for \dot{m}_{Mg} are close to 1 (where the stoichiometric optimum for pure magnesium is 0.76) [3].

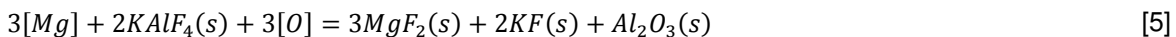
When $KAlF_4$ is injected into the hot metal, it breaks down in various compounds, of which CaF_2 , SiF_4 and various oxides of Al and K are formed most. The HMD slag is fluidised by $KAlF_4$ via both the fluorine and the potassium. The fluorine is the most important. It increases the fluidity of the HMD slag by lowering its viscosity and solid fraction. For that reason fluorspar (CaF_2) is also often used as slag modifier [4]–[6]. Potassium (in the form of K_2O) also lowers both the solid fraction of the slag and its viscosity [7].

Hypothesis

The observed increased magnesium reagent consumption cannot be fully attributed to the changes in hot metal composition and temperature and the fact that when adding $KAlF_4$ to the magnesium reagent, the reagent is diluted and contains 7% less pure magnesium. This means that $KAlF_4$ has another effect on the desulphurisation.

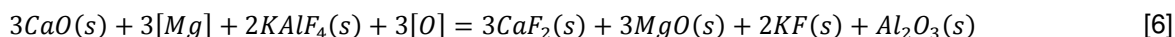
In theory $KAlF_4$ could have an effect on the efficiency of lime (reactions 2 and 3), which would lead to lower desulphurisation or even resulphurisation. CaO reacts with the fluorine in $KAlF_4$ to form CaF_2 . Addition of CaF_2 (via $KAlF_4$) decreases the basicity of the slag, albeit not as much as Al_2O_3 or SiO_2 which have a lower optical basicity (Λ), 0.61 and 0.46 respectively, as compared to 0.67 for CaF_2 ; MgO has a Λ of 0.78 [8]. Also the amount of added $KAlF_4$ compared to the amount of lime (roughly 1:40) suggests a negligible effect of $KAlF_4$ on lime efficiency.

The other possibility is that $KAlF_4$ directly or indirectly reacts with magnesium. According to calculations using FactSage [9], potassium and aluminium do not react with magnesium or MgS . In fact they do react with oxygen, which decreases the oxygen activity in the metal, and thus should have a beneficial (albeit insignificant) effect on \dot{m}_{Mg} . Fluorine in $KAlF_4$ does react with magnesium. Many different reactions between $KAlF_4$ and magnesium are possible and reaction 5 gives one potential route:



The dissolved magnesium will react with the available fluorine from the $KAlF_4$, which decomposes to F, K and Al. K and Al need to react with an oxidant, which can be oxygen, fluorine or sulphur. This means that besides KF also K_2O , K_2S and more complex products are formed, while aluminium will also react to Al_2S_3 and AlF_3 . However, according to FactSage calculations, most potassium forms a gas and most aluminium dissolves in the hot metal. With high excess of magnesium the less stable MgF is formed as well. However, according to FactSage even with high excess of magnesium under HMD conditions the MgF formation is small compared to the MgF_2 formation. Therefore MgF formation is neglected in this research.

When adding lime to reaction 5, the following reaction can occur:



The effect of $KAlF_4$ on \dot{m}_{Mg} via reaction 6 is the same as via reaction 5. Per two F atoms one Mg atom becomes unavailable for the desulphurisation reaction (reaction 1).

MEASUREMENTS

$KAlF_4$ is already mixed with the magnesium reagent when supplied to the plant. A sample from the magnesium silo was analysed with X-ray fluorescence (XRF). Table 1 shows that the magnesium reagent contains roughly 7% $KAlF_4$, which is according to the reagent specification. The higher amount of potassium is because the reagent contains a small amount of K_2O as well. XRF is less accurate for measuring fluorine, but the reagent specification indicates about 2% CaF_2 , so the expected total amount of fluorine in the reagent is 4.75%, which matches the XRF analysis.

Tab. 1 - XRF analysis of magnesium reagent used at HMD of Port Talbot BOS plant in wt%.

Ca	Si	Al	Mg	K	Na	Cr	S	F	Total
1.05	0.20	1.32	90.25	2.33	0.05	0.06	0.06	4.69	100

According to Table 1, 90% Mg and 4.7% F are present in the magnesium reagent that is used in the plant, which is equivalent to a Mg:F molar ratio of 15:1. According to reaction 5, 2 mol of fluorine is required to react with 1 mol magnesium. Therefore, if all available fluorine would react with magnesium, 3.3% of the injected magnesium would not be available for desulphurisation.

The XRF analysis also detected a small amount of sulphur in the magnesium reagent. However, even when assuming all sulphur in the reagent can be attributed to the addition of $KAlF_4$, this would lead to an efficiency loss of around 0.05%, which is negligible.

Sometimes "potassium cryolite" refers to K_3AlF_6 as well. It is possible that at room temperature part of the $KAlF_4$ is actually K_3AlF_6 , because both are stable under room temperature conditions. The assumption that all fluorine is in $KAlF_4$ or CaF_2 during HMD is not affected by that, since K_3AlF_6 under HMD conditions decomposes into $KAlF_4$ and KF [9]. X-ray diffraction (XRD) analysis of the reagent showed only the presence of metallic magnesium and $KAlF_4$ (see Figure 1). It is therefore unlikely that a significant amount of K_3AlF_6 is present in the reagent.

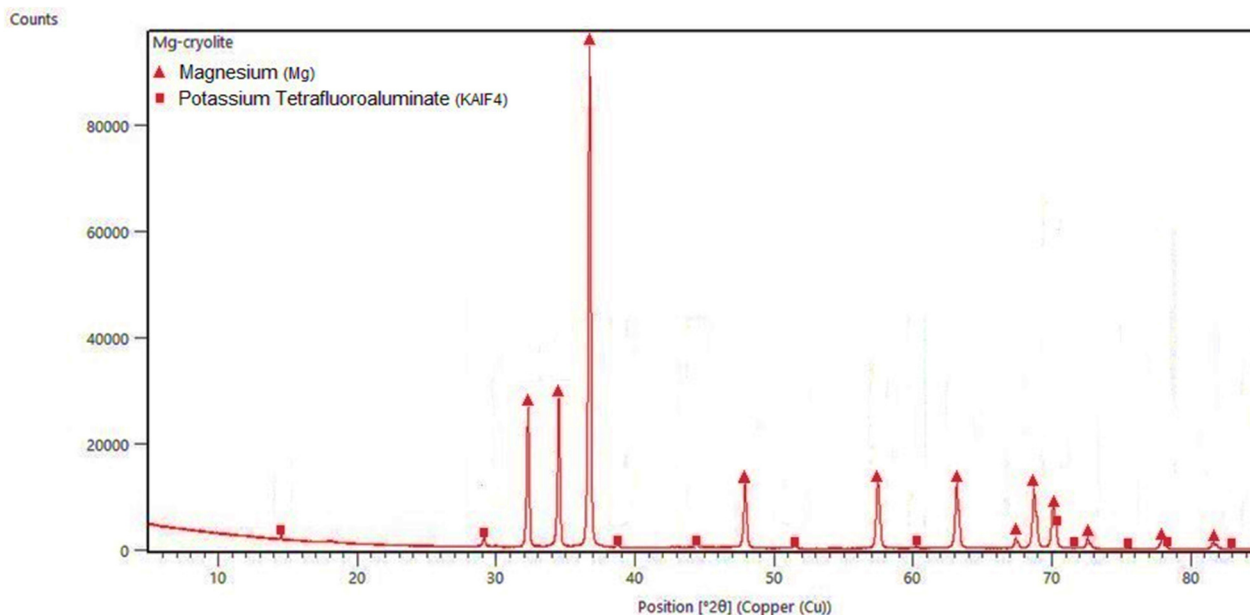


Fig. 1 - XRD analysis of magnesium reagent used at the HMD station of the BOS plant in Port Talbot. No other minerals were identified at a significant level.

Due to the safety standards of Tata Steel, it is not possible to take slag samples directly from the ladle. Instead slag samples were taken from the place where the (cooled) HMD slag is collected for processing and recycling. Therefore samples could not be traced back to a single heat. The slag samples were analysed with XRF in two different labs: at the Materials Processing Institute (MPI) in the UK and at the Analytical Lab of Tata Steel (ANA) in the Netherlands.

Tab. 2 - HMD slag XRF analysis by Materials Processing Institute (MPI) and Analytical lab of Tata Steel in IJmuiden (ANA).

	Fe	CaO	SiO ₂	MnO	Al ₂ O ₃	MgO	P ₂ O ₅	K ₂ O	TiO ₂	Na ₂ O	Cr ₂ O ₃	V ₂ O ₅	S	F
MPI	16.1	44.5	14.3	2.1	2.8	7.1	1.3	0.01	0.71	0.15	0.16	0.57	0.32	0.69
ANA	19.6	44.4	14.0	2.34	2.62	7.85	1.21	0.025	0.79	0.034	-	-	0.295	0.045

The two analyses of the same slag sample give comparable results, except for sodium, potassium and especially fluorine. Reason for the different results could be the time between the measurements. At MPI the sample was analysed 1-2 days after the sample was taken, while at ANA the sample was analysed more than a month later. At room temperature stable fluorine compounds (like KAIF₄, CaF₂ or MgF₂) do not react with oxygen or form gases, so it remains unclear what could have caused the decrease in fluorine in the sample. Another explanation could be the inhomogeneity of the slag. Accuracy of the measurements can play a role, but will not explain the large difference between both measurements of fluorine. Because with XRF analysis the elements (reported as oxides) rather than the products in the slag are found, the difference between MgF₂ and MgO cannot be found with it. Therefore, XRF analysis of the slag will not give an answer on what causes the higher \dot{m}_{Mg} after the introduction of KAIF₄.

The slag was also analysed with XRD at MPI. Cold XRD did not provide any clues on what had happened with the magnesium during the HMD process. Therefore a hot stage XRD analysis was carried out at three different temperatures: 500 °C, 750 °C and 950 °C (higher temperatures were not possible). This is shown in Figure 2, where the red arrows indicate the peaks for MgF₂.

MgF₂ is clearly detected in the slag by the hot stage XRD analysis between 500 °C and 950 °C. However, the analysis does not give a reliable quantitative analysis of MgF₂ in the slag.

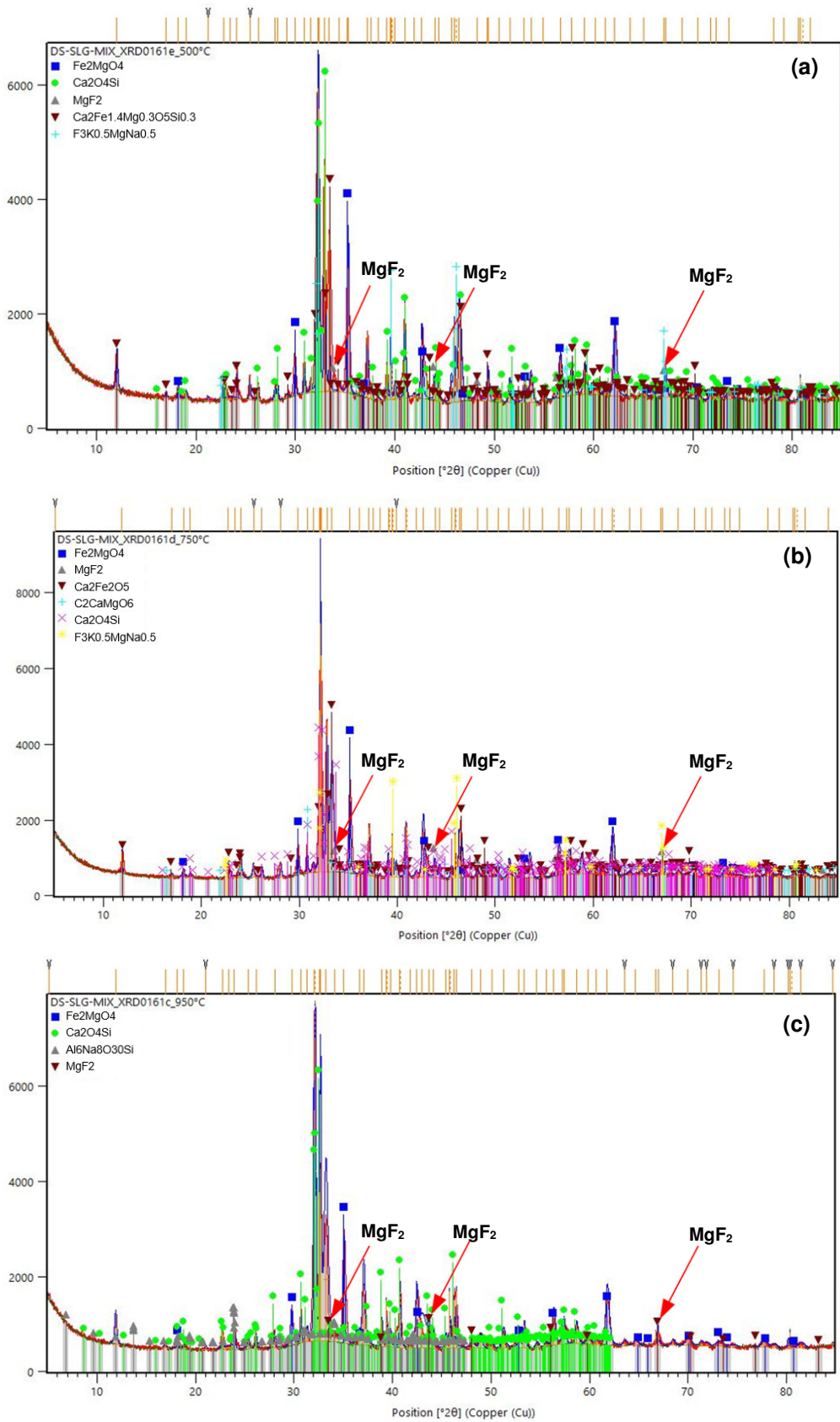


Fig. 2 - XRD analysis of an HMD slag sample at 500 °C (a), 750 °C (b) and 950 °C (c). Red arrows indicate MgF₂ peaks.

FACTSAGE CALCULATIONS

With FactSage thermochemical software [9], the injection of magnesium with KAIF_4 at HMD is simulated. With this calculation the influence of KAIF_4 on the formation of MgS (reaction 1) can be analysed. For the calculation hot metal containing only carbon (saturated; 4.85%) and sulphur (0.03%) is used, with a temperature of 1350 °C. Because FactSage calculates the thermodynamic equilibrium, no CaO or O_2 is added to the calculation, otherwise thermodynamically the formation of CaS and MgO are favoured over the formation of MgS [3]. A fixed amount of Mg is added (0.045%, which is 0.45 kg/tHM), which is a typical figure in HMD co-injection, while the addition of KAIF_4 is varied. Figure 3 shows the result of the FactSage calculation.

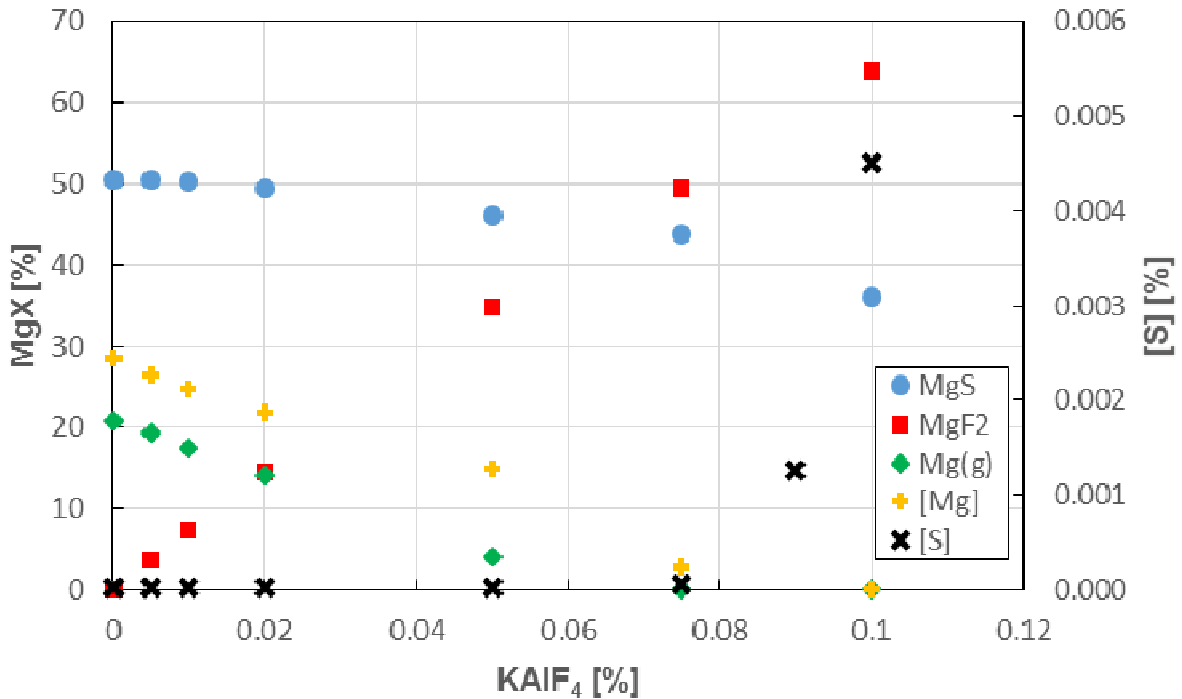


Fig. 3 - FactSage calculation of the effect of adding KAIF_4 to HMD with Mg (0.045%). MgX represents the percentage of Mg being converted to MgS , MgF_2 , Mg gas or $[\text{Mg}]$.

The FactSage simulation shows that when more KAIF_4 is added, more MgF_2 is formed. Over 90% of the added fluorine (in KAIF_4) reacts with magnesium to form MgF_2 . Because there is a stoichiometric surplus of magnesium present, the MgS formation, which is the desulphurisation of the Fe-phase (representing the hot metal), is not influenced significantly at lower KAIF_4 values. At these lower KAIF_4 values the surplus of magnesium dissolves in the hot metal or leaves the system as a gas. When more KAIF_4 is added, magnesium becomes scarce and desulphurisation of the hot metal decreases. To see the effect on desulphurisation when just enough magnesium is added to stoichiometrically desulphurise the hot metal (with 0.03% S), another FactSage simulation is done with 0.023% Mg (see Figure 4).

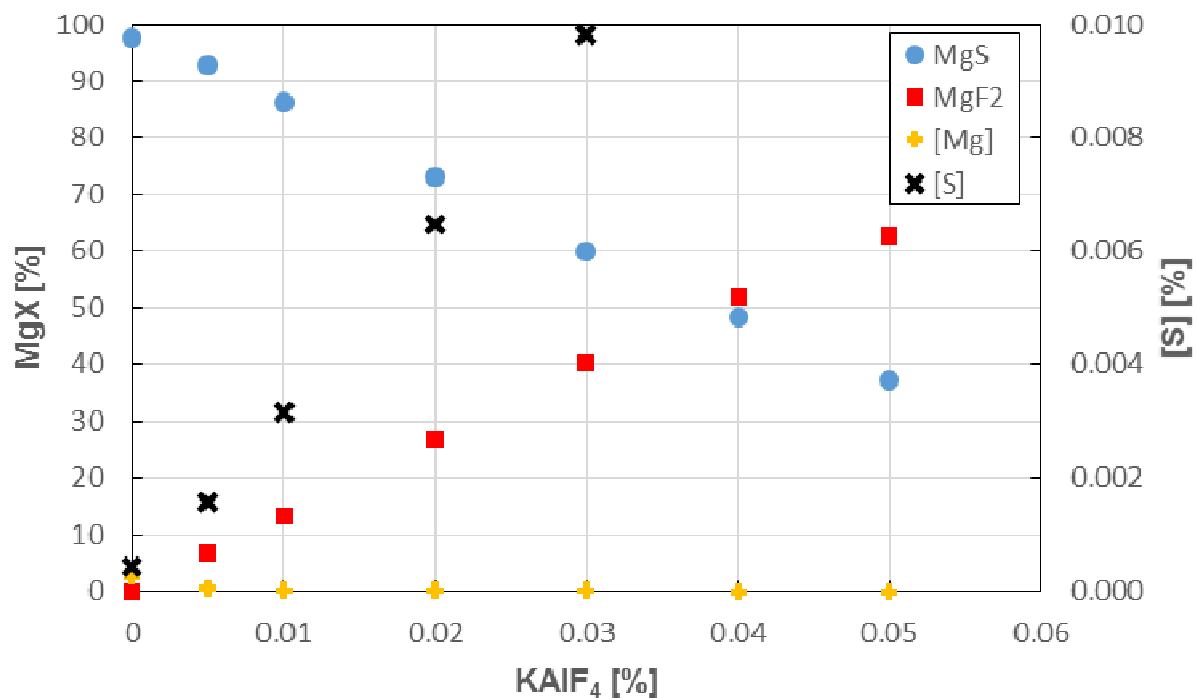


Fig. 4 - FactSage calculation of the effect of adding KAIF₄ to HMD with Mg (0.023%). MgX represents the percentage of Mg being converted to MgS, MgF₂ or [Mg].

In the FactSage simulation with only just enough magnesium present to desulphurise the HM, it becomes clear that KAIF₄ directly starts competing with the dissolved sulphur to react with the available magnesium. Even the smallest amount of KAIF₄ lowers the MgS formation. During a typical HMD heat, roughly 0.005% of the full hot metal weight is added as KAIF₄. Figure 3 shows no significant effect on the MgS formation at 0.005% KAIF₄, because there is enough magnesium available. However, with FactSage the thermodynamic equilibrium is calculated for the full ladle, assuming constant ideal mixing, which is not the case in the actual HMD co-injection process. The KAIF₄ concentration in and near the bubble plume will be much higher than 0.005%. Since KAIF₄ (or fluorine) does not dissolve in hot metal and its density is roughly half of that of the hot metal, ideal mixing of KAIF₄ will never be reached. Furthermore the FactSage calculation did not take the effect of CaO, O₂ and impurities in the hot metal into account, meaning that no representative slag is formed. The low final sulphur concentrations can be explained by not taking kinetics into account and by the simplification of the FactSage calculation. The outcome of the FactSage calculation should therefore be considered as qualitative and not quantitative.

The FactSage simulation was repeated with hot metal that, besides C and S, also contains Si, Mn and P. Addition of these elements to the simulation did not significantly change the MgS and MgF₂ formation. When doing a calculation without sulphur, the same amount of MgF₂ is formed, while most of the remaining magnesium becomes a gas.

DISCUSSION

The introduction of injecting KAIF₄ together with the magnesium led to a higher specific magnesium consumption that could not be explained by changing process conditions or by the lower pure magnesium concentration in the magnesium reagent.

The specific magnesium consumption depends only on the amount of magnesium injected and the amount of sulphur that is removed from the hot metal. This means that \dot{m}_{Mg} will also increase if the desulphurisation efficiency of lime decreases. However, possible reactions between KAIF₄ and lime are not likely to have a

significant effect on the overall desulphurisation process, since the amount of added KAIF_4 is very small compared to the amount of available lime per heat (the ratio is at least 1:40). There is always enough lime available for the MgS to react with (reaction 2) and due to the small influence of direct desulphurisation via lime (reaction 3), any effect on the overall desulphurisation is negligible. The injected KAIF_4 will also not decrease the slag basicity significantly.

A chemical reaction between KAIF_4 and magnesium can only be a reaction between fluorine and magnesium (reaction 5), since potassium and aluminium do not react with magnesium or MgS under HMD conditions, as was found by FactSage calculations. FactSage calculates thermodynamic equilibrium under certain conditions, but since it does not take kinetics and mass transfer into account, it will not predict how much MgF_2 will be formed in an industrial HMD process. Since MgF_2 can no longer be found in cold slag and no hot slag samples can be taken during the HMD process, analysis of the slag did not give insight on what might cause the increased \dot{m}_{Mg} .

When considering the HMD process as an ideally stirred reactor at thermodynamic equilibrium, the FactSage simulation shows that at the KAIF_4 amounts that are added to the process at the BOS plant in Port Talbot (~0.005%), the desulphurisation of hot metal by magnesium is not significantly influenced by the KAIF_4 . However, the results of Figure 3 and 4 also indicate that magnesium favours a reaction with fluorine from KAIF_4 (reaction 5) over a reaction with sulphur (reaction 1). Although the concentrations of KAIF_4 and Mg in the bubble plume are unknown, they will be much higher in the plume than in the rest of the ladle. As KAIF_4 does not dissolve in the hot metal, mass transfer limitations will ensure local high concentrations of KAIF_4 near the plume. Thermodynamically over 90% of the available fluorine in KAIF_4 will react with magnesium. This makes it likely that most KAIF_4 will react with magnesium during the HMD process.

Lime is present in the plume as well and it is likely that, even though the reaction is slower, some of the KAIF_4 will react with lime instead of with magnesium. Via reaction 6 this can still consume some of the magnesium and thus hamper the desulphurisation reaction. However, the oxygen from the lime could also react with dissolved silicon or carbon.

The predicted final sulphur concentrations in the hot metal by FactSage are much lower than what is achieved in an industrial HMD. This is because no oxygen is taken into account in the calculation. Higher oxygen activities in the hot metal lead to lower sulphur concentrations in the slag. Also oxygen from the air can react with MgS to form MgO , which leads to resulphurisation [3], resulting in a higher sulphur concentration in the hot metal.

The FactSage simulations show that when adding KAIF_4 to the HMD process, MgF_2 will be formed instead of MgS , but it cannot show how much magnesium reacts to MgF_2 , even though FactSage shows that MgF_2 formation is thermodynamically favoured over MgS formation under HMD conditions. Based on the stoichiometry of reaction 5 (and reaction 6) and the amount of added KAIF_4 , a maximum of 3.3% of the magnesium is inhibited from contributing to the main desulphurisation reaction (reaction 1) because of reacting with fluorine. This 3.3% of magnesium should be subtracted from the magnesium that is capable of reacting. Under plant conditions typically only 50-70% of the magnesium reacts with sulphur. Some magnesium will not dissolve and leaves the process as a gas. The fluorine will react with the dissolved magnesium, which means that the decrease in available magnesium for desulphurisation is higher. Considering all this, the reaction between magnesium and fluorine can contribute to 3-6% of the increased \dot{m}_{Mg} . This means that of the total observed 20% increase in magnesium reagent consumption, 11-14% can be explained by the lower magnesium concentration in the reagent and the reaction between magnesium and fluorine. The remaining 6-9% could be the result of changing process conditions and measurement errors. Table 3 gives this overview.

Tab. 3 - Overview of reasons of increased magnesium reagent consumption.

Reason	Effect on reagent consumption
Lower Mg concentration	8%
Reaction with fluorine	3-6%
Changing process conditions & measurement error	6-9%
Total	20%

Based on the available data it is not possible to quantify exactly how large the influence of the reaction with fluorine is on the desulphurisation efficiency of magnesium, but the effect is significant.

CONCLUSION

Injecting KAlF_4 (potassium cryolite) during the HMD co-injection process increases the specific magnesium consumption. The fluorine in KAlF_4 reacts with the injected magnesium to form MgF_2 , which decreases the amount of available magnesium for the desulphurisation reaction. The effect of MgF_2 formation on the specific magnesium consumption is significant, but the exact impact is still unknown.

KAlF_4 also decreases the viscosity and solid fraction of the HMD slag, leading to lower iron losses during the process.

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