# Reaction Mechanism of Hot Metal Desulfurization in the KR Process and Application of Red Mud as an Additive to Desulfurization Flux

*Soon-Jong* Jung[1,2], *Kang-Ho* Bang[1,3], *Baek-Kyoo* Jeong[1,4], *Michael* Bernhard[1,5], and *Youn-Bae* Kang[1,6]

[1]Graduate Institute of Ferrous and Energy Materials Technology, Pohang University of Science and Technology, Pohang, Republic of Korea
[2]Steelmaking Department, Gwangyang Works, POSCO, Gwangyang, Republic of Korea
[3]Thickplate Department, Gwangyang Works, POSCO, Gwangyang, Republic of Korea
[4]Steelmaking Department, Pohang Works, POSCO, Pohang, Republic of Korea
[5]Chair of Ferrous Metallurgy, Montanuniversitaet Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria
[6]Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, Republic of Korea

**Abstract.** The successful removal of sulfur (S) from hot metal is exemplified by the Kanbara Reactor (KR) process. However, a clearer understanding of its operating mechanism is needed. This study investigates the role of lime as the primary desulfurization agent, considering its chemical and mechanical aspects. Lime was found to not only chemically remove S but also facilitate the fragmentation of the desulfurization flux, which is crucial for enhancing the interfacial reaction area during vigorous mechanical stirring in the KR process. Fragmentation depends on the liquid-solid volume fraction in the flux. Traditionally, fluorspar has been used as an additive to aid in lime melting, but due to its environmental toxicity, alternative additives have been proposed. In this study, red mud, an industrial waste from alumina production, and spent MgO-C refractory, were used as additives to lime, creating a novel desulfurization flux for hot metal in steelmaking. Laboratory-scale tests were conducted with mechanical stirring. A "DeS Index" was introduced to quantitatively assess desulfurization efficiency, considering extent, rate, and cost. The industrial waste-containing flux showed comparable efficiency to commercially used fluxes, indicating its potential as an effective alternative. This study contributes to a better understanding of the desulfurization process and offers an environmentally friendly option for desulfurization in steelmaking.

## 1 Introduction

In ferrous processing, the molten iron is produced by reducing ore with coke, mainly in blast furnaces. The molten iron is called hot metal (HM) and dissolves substantial amounts of S originating from the coke. Hot metal desulfurization (DeS) is an essential process step in which nearly 90 % of the S from the blast furnace is removed [1]. Thus, its harmful effect on product properties of the steel can be reduced.

### 1.1 Ironmaking process and desulfurization

Commonly used reagents to remove S from the HM are lime (CaO) with fluorspar ($CaF_2$), calcium carbide ($CaC_2$), MgO or soda ($Na_2CO_3$). The basic equation of DeS is given by [2]

$$[S] + (O^{2-}) = (S^{2-}) + [O] \quad (1)$$

where, in case of CaO as DeS agent, the electroneutrality is obtained by the presence of the ($Ca^{2+}$) cation. Hence, **Reaction (1)** is reformulated as

$$[S] + (CaO) = (CaS) + [O] \quad (2)$$

The dissolved [O] reacts with C or Si in the HM and the DeS can be considered as an electrochemical reaction.

The general DeS reaction mechanism is illustrated in **Fig. 1**. A specific mixture of solid lime, CaO(s), and liquid flux is required to successfully remove S from the HM. CaO(s) supplies ($Ca^{2+}$) and ($O^{2-}$) ions to the liquid flux. At the interface liquid flux/HM, ($O^{2-}$) passes electrons to [S] form ($S^{2-}$). ($Ca^{2+}$) ions binds ($S^{2-}$) in the form of (CaS) in the slag. The fraction of liquid flux ($f_L$) is an essential parameter adjusted in the DeS process by adding other reagents, e.g. $CaF_2$. The liquid flux acts as (i) a pathway for the ions, (ii) a medium to dissolve CaO(s) and CaS(s), (iii) volume to absorb S, and (iv) a site for the reaction given in **Reaction (1)**.

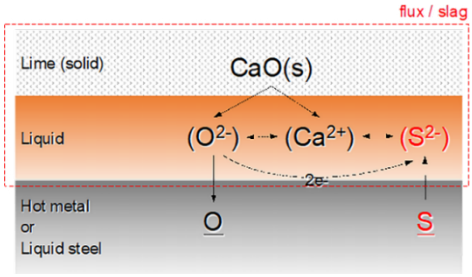


**Fig. 1.** General DeS reaction mechanism between HM/steel, liquid flux, and solid lime, CaO(s).

From a technological point of view, two different methods are used for DeS. In Europe, America, and India, lance injection into torpedo cars or into HM transfer ladles is the predominant practice today. In the 1960s, the Kanbara Reactor (KR) process was developed in Japan by Nippon Steel, which is nowadays widely used in the East Asian steel industry. The KR process is based on the principle of mechanical stirring with the simultaneous addition of the flux via the HM bath (**Fig. 2**). The flux consists of a mixture of CaO, and additives, e.g., $CaF_2$. In the KR process, low S contents can be consistently achieved, which represents a significant advantage compared to the lance injection.

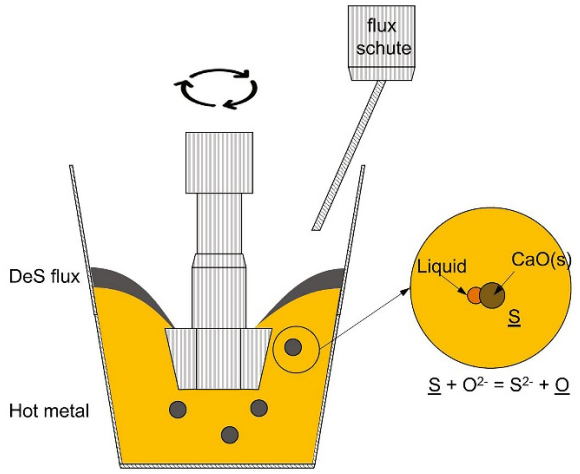


**Fig. 2.** Schematic illustration of the KR process and the DeS reaction between flux and hot metal [3].

### 1.2 Recycling spent industry wastes

Due to the toxicity of $CaF_2$, recent research activities focus on its substitution by other reagents. Further, excess amounts of CaO(s) in the KR process should be minimized with respect to cost-efficiency. The requirements on competitive additives in the KR process are (i) low costs at appropriate availability, (ii) the melting of CaO and (iii) increasing the interfacial reaction area between the flux and the molten HM.
Red mud (RM) is an industrial waste which is separated during the production of alumina from bauxite (Bayer process). It mainly consists of $Al_2O_3$, $Fe_2O_3$, $SiO_2$, $TiO_2$, $Na_2O$ and CaO. [4] The red colour results from the high $Fe_2O_3$ content of approximately 5 - 50 pct. [5], depending on the chemical composition of the bauxite. RM is classified as hazardous waste residue and its recycling in the cement industry and in building materials [4] has been investigated. Only a few authors studied the recycling possibility in the metallurgical field, e.g. [6, 7], in which RM was identified as a candidate to substitute fluorspar. RM serves as a source of $Na_2O$ and $Al_2O_3$, which lower the melting point of the lime. However, the high content of $Fe_2O_3$ may increase the activity of O in the molten HM, thus, DeS according to **Reaction (1)** will be shifted to the left reaction side. For the purpose of possible use in the KR process, it was shown that the reduction of $Fe_2O_3$ is a prerequisite step to reach highest DeS rate under a mechanical stirring [8].
In the present study, it was attempted to use recycled MgO-C refractory linings along with RM and CaO as a flux mixture. The aim was to provide a reducing atmosphere by C addition and to minimize excess CaO(s) in the KR flux by unreacted solids (MgO-C) to strengthen the dispersion and to increase the interfacial area between the solid/liquid flux and the HM.

## 2 Desulfurization mechanism in hot metal pre-treatment

Extensive studies have been conducted in the literature to investigate the basic mechanism of HM desulfurization, for example see [9, 10]. In general, one can distinguish between studies with static flux/HM interface (without stirring) and more technological studies with active mechanical stirring. Under static conditions, a high slag/flux sulfide capacity ($C_S$) combined with low viscosity and high temperatures showed a more efficient DeS in the experiments. It was further concluded [11, 12] that the DeS rate is high, when a large fraction of liquid flux ($f_L$) has been formed. These conditions were generally not confirmed in examinations under mechanical stirring. Based on a recent study in the authors' research group [3], the fundamental mechanism of DeS under the two different conditions will be discussed in the following chapters.

### 2.1 Experimental

Electrolytic Fe (Blyth & Co. Ltd, Japan, 99.9 pct.), FeS powder (Kanto chemical, > 70 pct.) were melted in a graphite crucible to produce carbon-saturated HM samples. The initial S content ($[pctS]_0$) was approximately 0.10 pct. in the alloys. The Des flux

consisted of various ratios of CaO and $CaF_2$. CaO was produced by calcinating $CaCO_3$ (Kanto chemical, > 99.5 pct.) at 1250 °C for 300 min under air in an alumina crucible and was mixed with $CaF_2$ powder (Junsei chemical, > 98 pct.) according to the defined experimental conditions. Based on the content of CaO and $CaF_2$ in the DeS flux, different proportions of liquid phase ($f_L$) are stable at a constant temperature. The values of $f_L$ in **Table 1** were calculated with FactSage thermochemical software [13] for the CaO-$CaF_2$ system at 1400 °C.

**Table 1.** Experimental conditions for investigation on the different DeS mechanisms depending on mechanical stirring and Des flux composition. $f_L$ was calculated by FactSage thermochemical software [13].

| No. | $m_{flux}$ [g] | CaO [pct.] | $CaF_2$ [pct.] | $f_L$ [pct.] | Stirring [Y/N] |
|---|---|---|---|---|---|
| 2-1 | 20 | 90 | 10 | 11 | No |
| 2-2 | 20 | 70 | 30 | 35 | No |
| 2-3 | 20 | 50 | 50 | 56 | No |
| 2-4 | 12 | 50 | 50 | 56 | No |
| 2-5 | 12 | 50 | 50 | 56 | Yes |
| 2-6 | 20 | 70 | 30 | 35 | Yes |

All tests were carried out in a high-frequency induction furnace with a mechanical stirrer. The equipment is shown schematically in **Fig. 3**, including detailed geometric dimensions. An outer graphite crucible was used, which contained the HM samples. Another inner graphite crucible ensured that no DeS flux was trapped during sampling. The experiments were conducted at a temperature of 1400 °C. The temperature was controlled by a B-type thermocouple, which was installed at the bottom of the outer crucible. 500 g of HM were melted and the time for thermal and chemical equilibration of the HM samples was 40 min, after which the first sample was taken using a quartz tube. The time step corresponded to the initial time of DeS (t = 0 s). DeS flux (20 g or 12 g) was added and samples of the HM were taken continuously over the 40 min period. The S content was then analysed using an infrared absorption combustion method (LECO CS-844, St-Joseph, MI USA). In total, stirring was used in 2 experiments, while 6 experiments were performed without stirring (see **Table 1**). In the experiments with stirring, the impeller was rotated at a constant speed (50 rpm). For more details, the authors refer to the corresponding article [3].

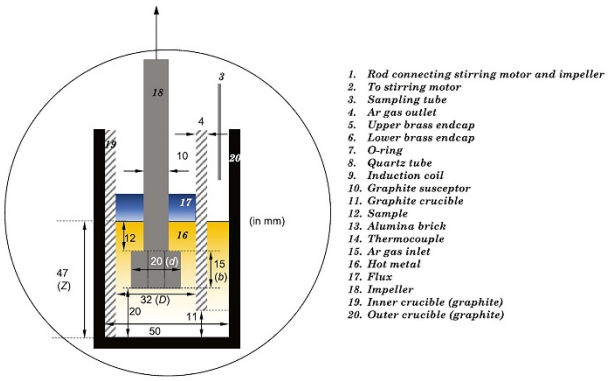


**Fig. 3.** Detailed illustration of the reaction crucible in the experimental apparatus used in the present study. [3]

## 2.2 Results

**Fig. 4** shows the results for with different compositions of CaO and $CaF_2$ when mechanical stirring is not applied. The mass of DeS flux was constant ($m_{flux}$ = 20 g). Flux No. 2-1 (10 pct. $CaF_2$, $f_L$ = 11 pct.) has the worst performance in terms of the final [S] content and the DeS rate. No. 2-2 (30 pct. $CaF_2$, $f_L$ = 35 pct.) shows better DeS rate when compared to flux No. 2-1. However, the best results are obtained with sample 2-3, where the DeS flux consists of equal proportions of CaO and $CaF_2$ and the liquid fraction is 56 pct. In this case, the final [S] content is lowest, simultaneously the DeS rate is highest and already at the initial stage, a significant amount of S can be removed from the molten HM. For experiments "without stirring", it can be therefore concluded that (i) increasing $f_L$ in the flux results in higher DeS rate and the overall DeS performance is improved, (ii) the early formation of a liquid phase is beneficial for a faster DeS rate and (iii) excessive amount of CaO(s) does no always guarantee highest DeS rate.

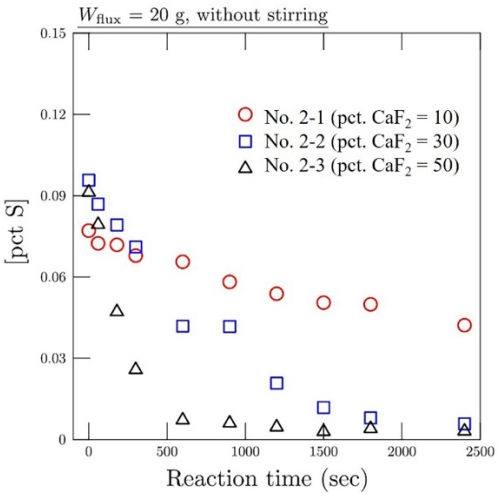


**Fig. 4.** Change of S content in HM by different amount of $CaF_2$ in the CaO-$CaF_2$ flux. No stirring was applied. [3]

If the DeS is assumed to be controlled by mass transfer, then, the change of [S] per time can be formulated as [14]

$$\frac{d[\text{pct S}]}{dt} = -k_S \frac{A}{V_{HM}} [\text{pct S}] = -k_S \frac{A\rho_{HM}}{m_{HM}} [\text{pct S}] \quad (3)$$

where $k_S$, A, $V_{HM}$, $\rho_{HM}$ and $m_{HM}$ denote the mass transport coefficient of S (m $s^{-1}$), interfacial reaction area ($m^2$), volume ($m^3$), density (kg $m^{-3}$) and mass (kg) of the HM.
Integrating of **Eq. (3)** from $t = 0$ ([pct S]$_0$) to $t = t$ ([pct S]) yields

$$\log \frac{[\text{pct S}]}{[\text{pct S}_0]} = -\left(\frac{k_S A}{2.303}\right)\left(\frac{\rho_{HM}}{m_{HM}}\right) t = -k'_S t \quad (4)$$

where the logarithm of the S ratio ([pct S]/ [pct $S_0$]) and the time $t$ are in a linear relationship, connected by the apparent DeS rate ($k'_S$).
In **Fig. 5** the S ratio is plotted over time on a logarithmic scale for the two cases when mechanical stirring is executed. In flux No. 2-6, the total mass of CaO(s) was higher ($m_{CaO}$ = 14 g) and $f_L$ was lower (35 pct.) than in flux No. 2-5 ($m_{CaO}$ = 6 g, $f_L$ = 56 pct.). However, utilizing flux No. 2-5 resulted worse DeS effectiveness. Hence, increasing $f_L$ is not always beneficial under conditions of mechanical stirring, instead more use of CaO(s) is favourable. These findings are in contrast to **Fig. 4**.
For all experimental conditions, the determined $k'_S$s are shown over $f_L$ in **Fig. 6**. The data points were taken up to $t$ = 600 s. When no stirring was applied, the DeS rate was sensitive to the liquid flux fraction and the DeS effectiveness continuously increased by increasing $f_L$. Mechanical stirring significantly improved the DeS rate at low $f_L$ (35 pct.) but was not effective compared to static conditions when $f_L$ increased (56 pct.).

### 2.3 Kinetic analysis

Chemical reactions occur rapidly at elevated temperatures and are therefore rarely the limiting factor for the overall reaction rate. In this case, the mass transport of S in the metal, from bulk to the reaction interface, usually limits the reaction kinetics. On the one hand, the mass transport can be positively influenced by smaller droplet sizes, and on the other hand, there is the possibility of partially increasing the reaction rate in the KR process through the mechanical stirring effect itself. The latter effect is clear in the apparent DeS rate in **Fig. 6** for fluxes no. 2-2 and no. 2-6 with a liquid fraction of 36 pct.

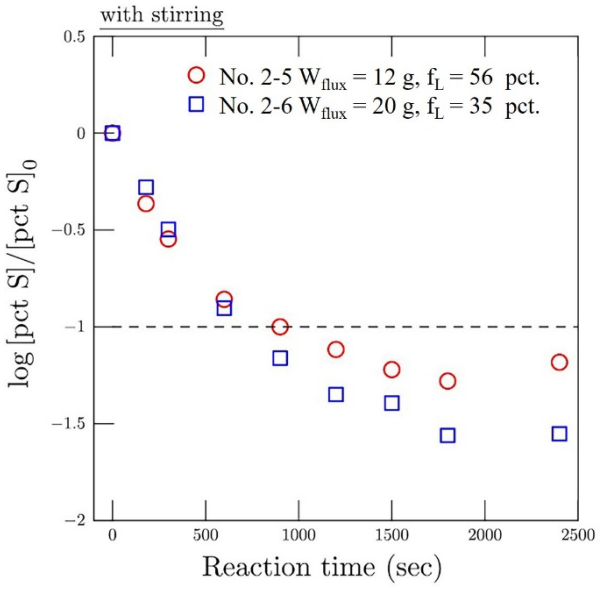


**Fig. 5.** Change of S content in HM by different [pct.] $CaF_2$ in the CaO-$CaF_2$ flux. Stirring was applied. [3]

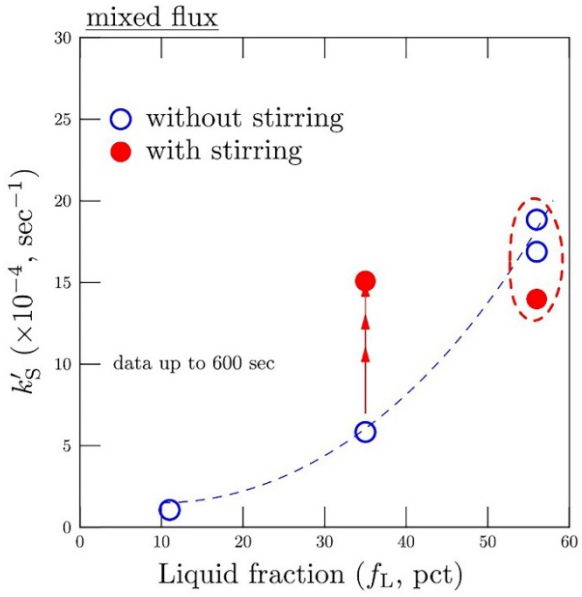


**Fig. 6.** Influence of $f_L$ on the apparent DeS rate constant for experiments with stirring and without stirring. Data points were taken up to 600 s. [3]

To gain a deeper understanding of the differences in reaction kinetics between the experiments with and without mechanical stirring, the experiments of equal amount liquid flux (No. 2-2 and 2-6 in **Table 1**) were examined in detail. The DeS data is compared in **Fig. 7**. Without mechanical stirring, the desulfurization process can be described by **Eq. (3)**. In this case, $A_{non\text{-}stir}$ was used simplified as the cross-section area of the inner crucible (**Fig. 3**). The density of the HM was assumed to be 7000 (kg $m^{-3}$) at 1400 °C, the mass of the HM ($m_{HM}$) is 0.5 kg according to **Sec. 2.1**. Thus, using the least squares method, the value $k_{S,non\text{-}stir} = 1 \times 10^{-4}$ (m $s^{-1}$) is obtained. The results are shown graphically

in **Fig. 7 (a)** to **(d)**. Since both the interfacial reaction area and the mass transport coefficient are constant, the term ($A_{non\text{-}stir} \times k_{S,non\text{-}stir}$) also remains constant during the DeS reaction (~ $10^{-7}$ $m^3$ $s^{-1}$). Under the effect of mechanical stirring, the model of Nakai *et al.* [15, 16] was used. In this model, A and $k_S$ change during the reaction considering the mean diameter of the flux particle. A detailed description of this model and the parameters used can be found in the recent article by Jeong *et al.* [3]. From **Fig. 7 (e)** mechanical stirring has a significant effect on the progress of the DeS reaction. Compared to the experiment without stirring, a [pctS] content of 10 % of the initial value [pct$S_0$] is already reached after 800 s, whereas this value is only observed after 2000 s in experiment No. 2-2. During DeS, the interfacial reaction area was significantly higher. With increasing time, the mean particle diameter of the flux increased due to aggregation, thus $A_{stir}$ and $k_{S,stir}$ decreased. The product ($A_{stir} \times k_{S,stir}$) is clearly higher at the beginning of the DeS than without stirring, which is the main reason for the accelerated desulfurization.

The outcomes of this section can be summarized as follows. A specific amount of $f_L$ is mandatory for the DeS reaction (**Sec. 1.1**), but, in general, increasing $f_L$ is not appropriate to enhance the DeS efficiency under "mechanical stirring" such as in KR process. Further, excess CaO(s) is required to enlarge the reaction surface area of the solid/liquid flux. From this point of view, other materials, can be selected to (i) substitute toxic $CaF_2$ to lower the melting point of lime, (ii) form a liquid flux and (iii) reduce the amount of excess CaO(s) for acting as non-reacted solid flux dispersion.

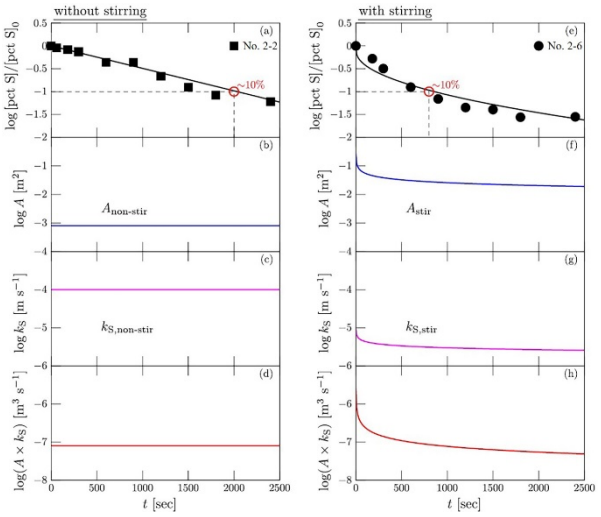


**Fig. 7.** DeS model calculations for the two experimental cases: (a) - (d) without stirring and (e) - (h) with stirring. [3]

## 3 Application of red mud as an additive to desulfurization flux

This section deals with the evaluation of RM as an additive to lime to find a sustainable and cost-effective alternative to toxic $CaF_2$. The focus is particularly on the role of $Fe_2O_3$ in the RM, which can affect DeS from a metallurgical point of view.

### 3.1 Experimental

The molten HM and the lime were similarly prepared as described in **Chapter 2.1**. In the present case, Si powder was added (RND Korea, 99.9 pct.) to the HM. The initial contents of S ([pctS]$_0$) and Si ([pctSi]$_0$) in the HM samples were 0.11 and 0.40, respectively.

The RM (KC Corp., Korea) had to be dried in an oven to remove residual moisture. It was then crushed with a milling machine and the chemical composition was determined by X-ray fluorescence (XRF, D8-DAVINCI, Bruker, USA) (see **Table 2**). The dried RM was sieved to obtain powders with particle size less than 250 µm. Selected experiments were performed with reduced RM to minimize the $Fe_2O_3$ content. For this purpose, the RM was mixed with C powders in a mass ratio of 5:1 and the mixtures were kept at 1100 °C for 3 hours in an induction furnace. The chemical analysis of the reduced RM is listed in **Table 2**.

**Table 2.** Composition of the RM provided by KC Corp. obtained by Bang and Kang [8] (XRF).

| Analysis | $Al_2O_3$ [pct.] | $Fe_2O_3$ [pct.] | $SiO_2$ [pct.] | $TiO_2$ [pct.] | $Na_2O$ [pct.] | CaO [pct.] |
|---|---|---|---|---|---|---|
| RM non-reduced | 15.4 | 47.5 | 12.9 | 7 | 10.6 | 3 |
| RM reduced by C | 31.1 | 2.1 | 27.4 | 14.8 | 18.4 | 6.1 |

The DeS flux was prepared by adjusting certain mixing ratios of CaO and RM ($\Phi_{RM}$, $\Phi_{RM\text{-}R}$). The values of $\Phi_{RM}$, $\Phi_{RM\text{-}R}$ are given by mass percent in **Table 3**, where “RM” refers to “RM” and “RM-R” refers to “pre-reduced RM”. All experiments were carried out in the same apparatus as shown in **Fig. 3** at a temperature of 1400 °C. Also, the procedure was identical. In each experiment, mechanical stirring was applied. Note that compared to experiments in **Sec. 2**, the impeller was rotated at a fixed speed of 80 rpm. Further details can be found in the corresponding study [8].

**Table 3.** Experimental conditions in the assessment of RM as additive to lime. [8]

| No. | $\Phi_{RM}$, $\Phi_{RM\text{-}R}$ [pct.] | RM reduction | Stirring [Y/N] |
|---|---|---|---|
| 3-1 | 20 | No | Yes |
| 3-2 | 40 | No | Yes |
| 3-3 | 60 | No | Yes |
| 3-4 | 20 | Yes | Yes |
| 3-5 | 40 | Yes | Yes |
| 3-6 | 60 | Yes | Yes |
| 3-7 | 0 | Yes | Yes |

### 3.2 Results

**Fig. 8 (a)** illustrates the change in [S] when a mixture of CaO(s) and non-reduced RM were used as flux. An increasing content of RM does not lead to a significant improvement in the DeS rate. Although at the beginning of the experiment, the [S] content decreases slightly faster at $\Phi_{RM}$ = 60 pct. compared to the experiments with $\Phi_{RM}$ = 20 to 40 pct.; the differences are, however, marginal. The final [S] content after a test time of $t$ = 2400 s is approximately the same in all experiments. A pre-reduction of the RM lead to a significantly improved DeS rate compared, see **Fig. 8 (b)**. With increasing content in the flux ($\Phi_{RM\text{-}R}$ = 20 - 60 pct.), the DeS rate is raised at the beginning. It should be noted that the final [S] content is identical in all experiments (3.1 - 4.1 ppm), independent of $\Phi_{RM\text{-}R}$.

The improved DeS with pre-reduction of RM can be explained as follows [8]: $Fe_2O_3$ in the non-reduced RM can form lower oxides, possibly even resulting in metallic Fe. The corresponding reactions are given by **Reactions (5)** and **(6)**:

$$(Fe_2O_3) = 2(FeO) + \tfrac{1}{2}O_2(g) \quad (5)$$

$$(FeO) = Fe(l) + \tfrac{1}{2}O_2(g) \quad (6)$$

For a favourable desulfurization effect, the [O] content in the HM must be low. Although the formed O is immediately bound by C and Si, the release by the decomposition of $Fe_2O_3$ can lead to an elevated O potential near the reaction interface and thus negatively affect the DeS.

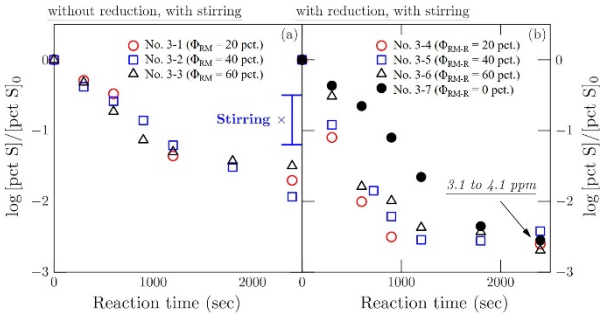


**Fig. 8.** Chang of S content in HM by the CaO-RM mixed flux under mechanical stirring conditions: (a) non-reduced RM and (b) reduced RM. [8]

$k'_S$ was again determined according to **Eq. (4)** from the changing [S] content in **Fig. 8 (b)**. Supplementary tests [8] to **Table 3** were added ($\Phi_{RM\text{-}R}$ = 10 and 15 pct.) to the evaluation. The plot of $k'_S$ versus $\Phi_{RM\text{-}R}$ in **Fig. 9** shows that even with a minor amount of reduced RM the DeS rate is significantly better. $k'_S$ reaches a plateau value already at low $\Phi_{RM\text{-}R}$, confirming that reduced RM is a suitable additive to CaO in the desulfurization flux when mechanical stirring is also used in the experiments. It must be noted that the reduction of RM is a prerequisite for successful use.

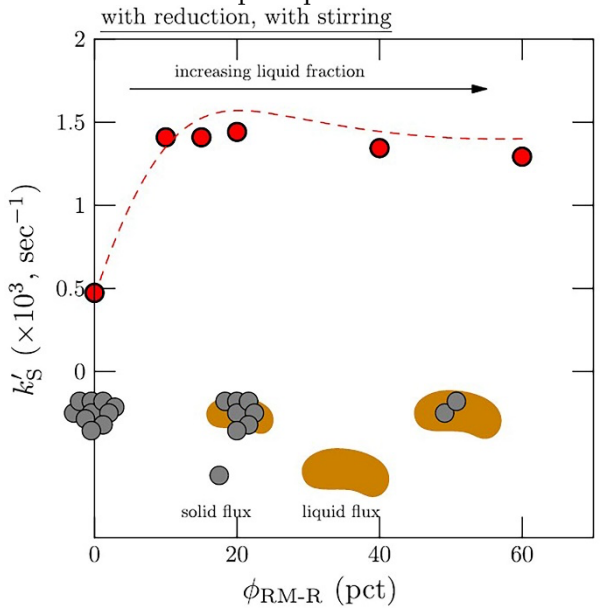


**Fig. 9.** Correlation between the apparent desulfurization rate constant ($k'$) and the mass fraction of reduced RM in the flux ($\Phi_{RM\text{-}R}$). [8]

## 4 Addition of spent magnesia-carbon refractory to the lime and red mud-based desulfurization flux

The recycling of MgO-C from spent refractory bricks of the converter is investigated. C can provide a reducing environment and residual MgO and C increase the solid fraction and substitute excess CaO(s). Together with a mixture of CaO, RM and MgO-C bricks, a highly sustainable design of the DeS

fluxes in the KR process could be achieved in the future.

### 4.1 Experimental

The experimental apparatus, procedure as well as the preparation of HM, CaO and non-reduced RM was identical as described in **Secs. 2.1** and **3.1**. The flux was prepared by mixing 20 g of powdered CaO, RM, MgO (Kanto Chemical, 98 pct.) and graphite (Alfa Aesar, 99 pct.) in various proportions. As in the previous study, the rotation speed was lower than here, one experiment was designed to check the DeS performance of CaO-RM mixture. The mixtures of CaO-RM with C or MgO were prepared according to calculated solid fractions using FactSage thermochemical software [13]. From the trials with only MgO-RM or C-RM addition, the optimum DeS composition was derived for MgO-C-RM mixtures. Two commercially available DeS fluxes were considered in the evaluation to compare the competitiveness of the developed DeS flux mixture. The ratio of RM was fixed in the majority of the fluxes (40 pct) but was reduced in one case (20 pct), according to the results in **Sec. 3**, where a low fraction of RM lead to the fastest DeS rate. The experiments were conducted at a temperature of 1400 °C.

The concept behind minimizing the RM content in the flux used is schematically illustrated in **Fig 10**. With a lower amount of RM in the flux, the total percentage of $Fe_2O_3$ in the mixture decreases from 19 pct. to 9 pct. By that, less oxygen potential is achieved and the RM reduction speed is higher. Simultaneously, the solid fraction in the flux is higher (83 pct.) compared to other experiments. It was demonstrated in **Sec. 2** that a higher solid fraction is advantageous if mechanical stirring is applied during the DeS process. Hence, optimum conditions for an excellent DeS performance should be achieved with the lower RM fraction.

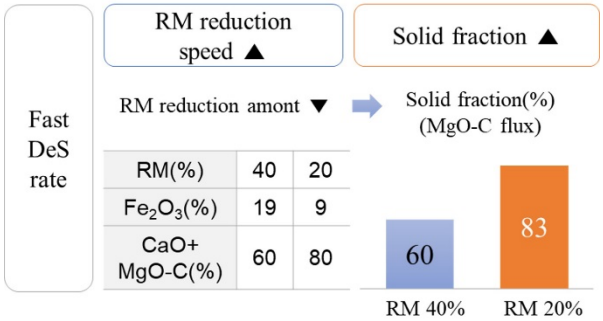


**Fig. 10.** Schematic illustration of the effect on DeS performance by reducing the RM amount from two experiments.

The results of the DeS rate achieved in selected experiments are presented in **Fig. 11**. As expected, the CaO-RM mixture shows the poorest DeS performance. Though a liquid flux is formed by adding RM, no additive is present to reduce $Fe_2O_3$ and the O potential is higher than in the other DeS trials. By adding C to the mixture, similar [S] contents over time are obtained in comparison with the flux containing 30 pct. MgO-C and 40 pct. RM. The best DeS rate can be achieved by reducing the amount of RM to 20 pct. along with 40 pct. MgO-C and 40 pct. CaO. At the initial stage, the DeS rate was almost the same, however, the [S] content rapidly decreased later at $t = 7$ min. The reason can be explained by the lower amount of RM in the mixture, although the amount of $Fe_2O_3$ is decreased in RM, also $f_L$ decreases, resulting in a slower overall formation of liquid flux. After $t = 7$ min, the DeS finally increases due to the solid flux dispersion effect after RM reduction.

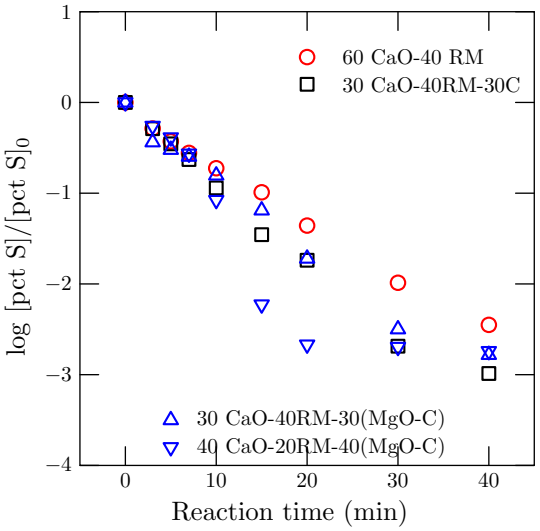


**Fig. 11.** Influence of RM ration and MgO-C content on the DeS rate.

### 4.2 Discussion

The influence of MgO and C on the flux aggregation and dispersion is explained by means of the illustration in **Fig. 12**. Under stirring conditions, appropriate fractions of solid and liquid flux are important for a high DeS rate. It was shown in the literature [17] that a high solid fraction is accompanied by a lower bonding force between the solid particles, which is advantageous for dispersion. MgO and C are stable in solid state at the temperature of 1400 °C. The addition of MgO and C increase the solid fraction and reduce the sintering of CaO. Thus, the flux particle size decreases, the interfacial area increases and the DeS rises.

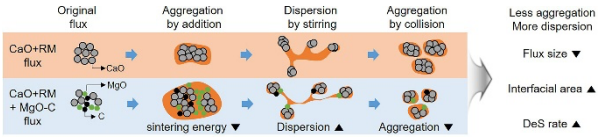


**Fig. 12.** Effect of MgO and C on flux agglomeration and dispersion.

Finally, a desulfurization index is used for quantitative assessment of the DeS capabilities for fluxes **used in this section**. The DeS index was formulated by Bang and Kang [8] according to **Eq. 7**:

$$\text{DeS Index} = \log\left[\left(\frac{[\text{pctS}]_f}{[\text{pctS}]_0}\right)^{-1} \times (k_S') \times \left(\frac{W_{CaO}}{S}\right)^{-1}\right] \quad (7)$$

The three terms on the right-hand side represent the extent of the reaction (equilibrium), the reaction speed (DeS rate) and the cost-efficiency of the flux mixture, The costs are related to the CaO used ($W_{CaO}$) and the mass of S ($W_S$) in the HM, which has to be removed. Hence, the DeS index becomes high, if the extent of the reaction is high, the reaction is fast and the amount of excess CaO is reduced.

**Fig. 13** summarizes the results of experiments with flux no. 4-1 to 4-13. In the calculation of the DeS index, two different final [S] contents after 15 min and 40 min were considered. A shorter DeS time in the KR process is highly relevant for steelmaking plants. In case of DeS index ($[S]_{f,40min}$) the flux with 30 pct. and 36 pct. C showed the highest values. However, $k_S'$ up to 15 min is lower than in case of commercial fluxes (no. 4-12 and 4-13). The highest DeS index ($[S]_{f,15min}$) is observed for the flux with 40 pct. MgO-C and 20 pct. RM, even though less CaO and dried, non-reduced RM was used as additive. This result proofs CaO(40pct)-MgO-C(40pct)-RM(20pct) to be a suitable flux under real DeS mechanical stirring conditions in the KR process.

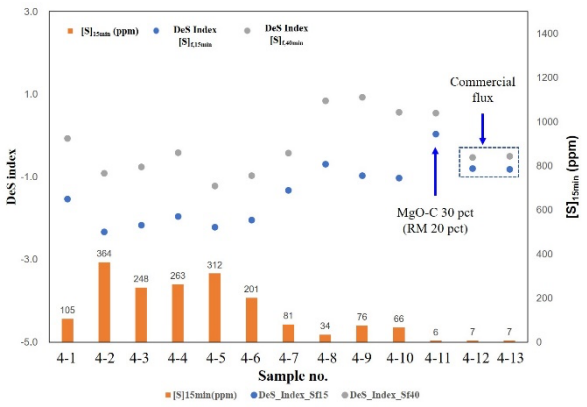


**Fig. 13.** Assessment of DeS flux by defining a "DeS index".

## 5 Conclusions

The present work introduces the concept of substituting excess CaO and $CaF_2$ in the KR process by spent industry wastes. For a fast DeS rate under mechanical stirring, a high liquid flux fraction is not always beneficial. Solid particles are required to increase the reaction surface area by forming a suspension. To adjust the liquid fraction in the flux, RM is a suitable candidate to substitute toxic $CaF_2$. It must be noted that the introduced amount of $Fe_2O_3$ should be considered in the fundamental thermodynamics and kinetics of the DeS reaction. $Fe_2O_3$ increases the oxygen potential and affects the DeS reaction. The pre-reduction or reduction of RM during the KR process is a prerequisite for a high DeS rate. It was shown, that spent MgO-C material from refractory linings can be used in the flux to reduce the amount of unreacted excess CaO and to develop a cost-saving process in the Kanbara Reactor. The flux containing CaO-RM-MgO-C showed the same level of desulfurization rate and final [S] content as a commercial flux within 15 minutes of KR treatment time, even though CaO was reduced by 50 %.

## References

[1] F. Schrama, E. Beunder, B. Van den Berg, Y. Yang and R. Boom, "Sulphur removal in ironmaking and oxygen steelmaking," *Ironmaking and Steelmaking,* vol. 45, pp. 333-343, 2017.

[2] C. Fincham and F. Richardson, "The behaviour of sulphur in silicate and aluminate melts," *Proceedings of the Royal Society A,* no. 223, pp. 40-62, 1954.

[3] B.-K. Jeong, G.-H. Bang and Y.-B. Kang, "Role of liquid and solid particles in solid-liquid mixed fluxes on sulfur removal from molten iron under centrifugal stirring by an impeller," *Powder Technology,* vol. 396, pp. 1-12, 2022.

[4] P. Tsakiridis, S. Agatzini-Leonardou and P. Oustadakis, "Red mud addition in the raw meal for the production of portland cement clinker," *Journal of Hazardous Materials,* vol. 116, pp. 103-110, 2004.

[5] W. Liu, X. Chen, W. Li, Y. Yu and K. Yan, "Environmental assessment, management and utilization of red mud in," *Journal of Cleaner Production,* vol. 84, pp. 606-610, 2014.

[6] T. Jeong and J. Park, "Effect of Fluorspar and Industrial Wastes (Red Mud and

Ferromanganese Slag) on Desulfurization Efficiency of Molten Steel," *Metallurgical and Materials Transactions B,* vol. 51, pp. 2309-2320, 2020.

[7] B. Zhang, C. Liu and M. Jiang, "A new method of red mud recycling in the process of hot metal pre-treatment," *Materials Research and Technology,* vol. 117, p. 115, 2020.

[8] K.-H. Bang and Y.-B. Kang, "Recycling red mud to develop a competitive desulfurization flux for Kanbara Reactor (KR) desulfurization process," *Journal of Hazardous Materials,* vol. 440, p. art. no. 129752, 2022.

[9] D. Lindström and D. Sichen, "Study on Desulfurization Abilities of Some Commonly Used Desulfurization Agents," *steel research international,* vol. 86, pp. 73-83, 2015.

[10] Y. Nakai, I. Sumi, N. Kikuchi, K. Tanaka and Y. Miki, "Powder Blasting in Hot Metal Desulfurization by Mechanical," *ISIJ International,* vol. 57, pp. 1029-1036, 2017.

[11] K. Takahashi, K. Utagawa, H. Shibata, S.-y. Kitamura, N. Kikuchi and Y. Kishimoto, "Influence of Solid CaO and Liquid Slag on Hot Metal Desulfurization," *ISIJ International,* vol. 52, pp. 10-17, 2012.

[12] R. Pezzifi, A. Berger, F. Grillo, E. Junca, H. Furtado and J. Oliviera, "Analysis of the influence of solid and liquid phases on steel desulfurization with slags from the CaO-Al2O3 systems using computational thermodynamics," *Journal of Materials Research and Technology,* vol. 9, pp. 838-846, 2020.

[13] C. Bale, E. Belisle, P. Chartrand, S. Decterov, G. Eriksson, A. Gheribi, K. Hack, I.-H. Jung, Y.-B. Kang, J. Melancon, A. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer and M.-A. Van Ende, "FactSage thermochemical software and databases, 2010-2016," *Calphad,* vol. 54, pp. 35-53, 2016.

[14] B. Deo and R. Boom, Fundamentals of Steelmaking Metallurgy, Hertfordshire, UK: Prentice Hall International, 1993.

[15] Y. Nakai, I. Sumi, H. Matsuno, N. Kikuchi and Y. Kishimoto, "Effect of flux dispersion behavior on desulfurization of hot metal," *ISIJ International,* vol. 50, pp. 403-410, 2010.

[16] Y. Nakai, I. Sumi, N. Kikuchi, Y. Kishimoto and Y. MIki, "Aggregation behavior of desulfurization flux in hot metal desulfurization with mechanical stirring," *ISIJ International,* vol. 53, pp. 1411-1419, 2013.

[17] M. van Deen, T. Betrand, N. Vu, D. Quere, E. Clement and A. Lindner, "Particles accelarate the detachment of viscous liquids," *Rheologica Acta,* vol. 52, pp. 403-412, 2013.

## Acknowledgment

This work was partially supported by the National Research Foundation of Korea (NRF-2021R1F1A1049973).