

USING OF CALCIUM MAGNESIUM ALUMINATE FLUX WITH HIGH MGO CONTENT TO IMPROVE SECONDARY STEEL LADLE LIFE TIME

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Abstract

One of the most corroded zones in the secondary steel ladle is the contact area between the metallurgical slag and the refractory lining. The slag zone, even with specially designed Magnesia-Carbon and Doloma-Carbon bricks, is in many cases the life time limiting factor for the whole steel ladle. This makes repairs by gunning or intermediate slag zone replacements necessary. During the slag zone replacement the ladle has to be cooled down with further negative effect on the other parts of the ladle due to thermally induced stresses and consequently crack formation. In order to improve the life time of the slag zone, the impact of OPTIMET™ RG (FLUX B) and OPTIMET™ HM (FLUX C), novel synthetic Calcium Magnesium Aluminate Fluxes (CMA) with high MgO-content, has been studied. Thermodynamic simulations with the FactSage® software and laboratory experiments have been conducted. A traditional slag fluxing practice with fluorspar (CaF₂) has been compared with Calcium Aluminate (CA), LDSF® RG (FLUX A), and with these novel synthetic fluxes with different MgO-contents. Calcium Magnesium Aluminate Fluxes (CMA) allow a quick formation of a homogeneous and liquid slag with a high capacity to absorb sulphur and oxide inclusions from the steel bath, very similar to Calcium Aluminate (CA). Calcium Magnesium Aluminate Fluxes (CMA) bring the MgO-content in the slag, right after tapping, close to the saturation concentration and minimise the dissolution of Magnesia-Carbon or Doloma-Carbon bricks in the slag. Life time increase of the slag zone can be expected. Calcium Magnesium Aluminate Fluxes (CMA) help to reduce the specific ladle costs per tonne of steel. The efficiency of high quality steel production can be increased which supports the efforts to reduce the CO₂-emissions per ton of produced steel.

Key words: Synthetic slag; Calcium aluminates; Refractory wear; Secondary steel ladle.

I INTRODUCTION

Refractory linings in steel ladles are exposed to steel, slag and air at temperatures up to 1650°C. Especially the contact zone between refractory material and the metallurgical slag has been studied by many authors with the objective to improve the refractory life.⁽¹⁻³⁾ Combinations of different degradation phenomena occur in this zone which are a mix between thermochemical degradation and thermophysical stresses.^(4,5) Thermochemical reactions are seen as a major degradation cause since the slag compositions are typically under-saturated in MgO which creates a chemical gradient between the MgO-containing bricks and the slag. As consequence dissolution reactions occur.⁽⁶⁾

This study is designed to improve refractory life and thus reduce operational costs by modifying the slag by adding different flux materials such as LDSF® RG (Flux A from now on) based on Calcium Aluminates and OPTIMET™ RG (Flux B from now on) and OPTIMET™ HM (Flux C from now on) which are based on Calcium-Magnesium Aluminates. The objective is to increase the MgO-content in the slag as early as possible and to reduce the driving force for the MgO-dissolution from refractories. In some cases, Doloma for example, is added directly to the slag as an external source for MgO⁽⁵⁾, practice that can result in crust formation and inhomogeneous slag since homogeneous dissolution of MgO or (Ca, Mg)O takes time.

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2 MATERIALS AND METHODS

2.1 Calcium Magnesium Aluminate Flux – The New Synthetic Fluxing Materials

Traditionally, CaF_2 was used to create a fluid steel works slag in mixes for example with bauxite and lime. But due to the environmental restrictions with Fluorine and furthermore due to the strong corrosion effect as consequence of the formation of a very low viscosity slag, synthetic Calcium Aluminate Fluxes have become part of modern steel works practice especially where clean steel production is required.^(7,8) Calcium Aluminate Fluxes combine the advantage of creating quickly a homogeneous and sufficient liquid slag with the capacity to absorb a large variety of non-metallic impurities from the steel bath and support for example the desulphurization process. The rapid modification of the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio by pre-reacted Calcium Aluminate phases plays an essential role in this regard.

The new synthetic Calcium-Magnesium Aluminate, FLUX B and FLUX C, contain MgO in microcrystalline phases and can be added to the slag in form of dust free aggregates in the same way as classical Calcium-Aluminate Fluxes, FLUX A. As can be seen in Table 1, FLUX B has a MgO -content of about 12% and FLUX C of about 21%. Both are free of impurities like Fluorine, Carbon and humidity. The increased MgO content compared to FLUX A has no negative impact on the metallurgical refining process, for example on desulphurization step.⁽⁹⁾

Table 1. Chemical Composition of synthetic CMA- and CA-Fluxes (wt.%)

	CMA- Flux		CA-Flux
	FLUX C	FLUX B	FLUX A
	Pre-reacted	Pre-reacted	Pre-reacted
CaO	32.9	37.0	50.5
MgO	21.3	12.5	0.6
Al_2O_3	40.9	43	41.5
SiO_2	3.6	3.6	3.4
FeO	1.7	1.7	1.7
TiO_2	2.2	2.2	2.3
CaF_2	0.0	0.0	0.0
H_2O	<0.15	<0.15	<0.15
CO_2	<0.1	<0.1	<0.1
Total	100	100	100
$(\text{CaO}+\text{MgO})/\text{Al}_2\text{O}_3$	1.3	1.2	1.2

The melting behaviour of FLUX B is almost equal to FLUX A as can be seen in Figure 1. At 1345°C it is almost liquid and starts to flow at 1360°C. FLUX C has the same melting behaviour. It takes only 1 minute at 1600°C

to create a homogeneous liquid top slag (Figure 3). This has the advantage of having an increased MgO -level in the slag right from the beginning compared to a normal CA-Flux or a CaF_2 practise.

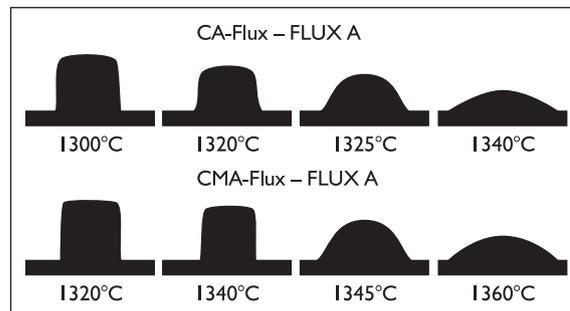


Figure 1. Melting behaviour of CA- and CMA-Flux (test method as described in DIN 51730, heating rate 10 K/min).

2.2 Thermochemical Calculations

After tapping steel into the ladle and having added traditional fluxing materials to it the initial slag composition at the beginning of the ladle treatment contains often between 3 and 7% MgO . The MgO -saturation concentration of model slag compositions, as shown in Table 2, has been calculated using the FactSage[®] software.⁽¹⁰⁾ From the analyses of the effects of slag basicity, temperature, FeO -and CaF_2 -content for the range of the considered compositions with basicity B between 0.7 and 1.5 with

$$B = \text{CaO} / (\text{Al}_2\text{O}_3 + \text{SiO}_2) \quad (1)$$

and temperatures between 1500°C and 1620°C the following Equation 2 is derived which describes the MgO -saturation of the slag:

$$\begin{aligned} (\% \text{MgO})_{\text{sat}} = & 8.2 / B + 0.06 (\% \text{FeO}) \\ & + 0.2 (\% \text{CaF}_2) + 0.019 (T - 1550) \end{aligned} \quad (2)$$

The results of this equation are in good agreement with experimental results from Reisinger et al.⁽⁶⁾ As shown by Equation 2. the levels of basicity and temperature have a strong impact on the MgO saturation concentration followed by the CaF_2 content in the slag. It shows that all considered initial slag compositions, unless No. 5, are under-saturated with MgO and have the potential to dissolve the lacking MgO -content from MgO-C or Doloma-C bricks.

With the Calcium Magnesium Aluminate Flux the gap between the initial MgO -concentration and the MgO -saturation will be reduced very fast and homogeneously throughout the whole slag mass on top of the liquid steel in the ladle. Especially the rapidity and homogeneity of

Table 2. Slag chemical compositions used for thermodynamic simulations of MgO-saturation (FS = FactSage®; E2 = Equation 2)

	1	2	3	4	5
CaO	44.0	44.9	41.6	35.0	50.0
MgO	6.0	6.1	5.7	7.0	6.8
Al ₂ O ₃	34.0	34.7	32.2	39.5	25.0
SiO ₂	9.0	9.2	8.5	10.4	10.2
FeO	7.0	5.0	12.0	8.1	8.0
CaF ₂	0.0	0.0	0.0	0.0	0.0
Basicity B	1.02	1.02	1.02	0.70	1.42
(MgO) _{sat} 1550°C (FS)	8.6	8.5	8.9	12.0	5.8
(MgO) _{sat} 1550°C (E2)	8.4	8.3	8.7	12.2	6.3
Liquidus (°C) (FS)	1395	1406	1366	1372	1614
	6	7	8	9	10
CaO	38.7	46.9	42.7	40.5	37.8
MgO	5.3	6.4	5.8	5.5	5.2
Al ₂ O ₃	42.0	36.2	33.0	31.3	29.2
SiO ₂	7.9	3.0	8.7	8.3	7.7
FeO	6.2	7.5	6.8	6.4	12.0
CaF ₂	0.0	0.0	3.0	8.0	8.0
Basicity B	0.78	1.20	1.02	1.02	1.02
(MgO) _{sat} 1550°C (FS)	11.0	7.3	9.2	9.9	10.1
(MgO) _{sat} 1550°C (E2)	11.0	7.3	9.0	10.0	10.3
Liquidus (°C) (FS)	1373	1495	1339	1322	1347

introduction of MgO into the slag is much more difficult to achieve by separate MgO-additions in form of Magnesia or Doloma. In order to verify this and to estimate the impact of kinetics practical experiments have been carried out.

2.3 Slag/Refractory Experiments Methodology

To simulate the conditions in the steel ladle slag line a laboratory induction furnace as described by Wöhrmeyer et al.⁽¹¹⁾ has been chosen as test vessel in which MgO-C bricks or (Ca,Mg)O-C bricks build the side wall.

The employed MgO-C brick material contains 12% carbon. The oxide components are 97% MgO, 1.7% CaO, 0.6% SiO₂, 0.5% Fe₂O₃ and 0.2% Al₂O₃. The density is 3.01 g/cm³ and open porosity 4.0%. Segments with trapezoidal cross section have been cut from this brick material. Eight of these segments build the side wall of the furnace. The furnace is charged with blocks of 15 kg of steel (0.1% C, 2.65% Si, 1.65% Mn, 0.014% P, 0.0006% S, 0.035% Al) which are heated up by induction under Ar/H₂ atmosphere required to the test temperature of 1600°C. Then 480 g of a slag (579 g in case of slag D) is formed on top of the liquid steel to which then 120 g of the fluxing materials (21 g in case of CaF₂ for slag D) as grains of 3-6 mm are added (Table 3). Slag compositions as can be found in Al-killed steel production have been targeted to compare the different fluxing practises. Slag A-1 and A-2 uses an addition of 20% FLUX C and 20% FLUX B to the total slag mass and slag C the same amount of FLUX A. Slag B has also been fluxed with FLUX A but 2% of sintered Magnesia in the grain size of 3-6 mm have been added supplementary. In case of Slag D 3.5% fluorspar has been used as fluxing agent. In preliminary trials with a holding time of 60 minutes it was found that the MgO-concentration reaches almost its saturation level after 30 minutes already so that it was preferred to run cycles of 30 minutes only to achieve a maximum of corrosion effect during a 6 hours trial.

Every 30 minutes the total slag mass has been removed and replaced by fresh slag and Flux. A total holding time of 6 hours, thus 12 slag cycles (heats) have been applied with the same slag practice. During this time the steel remains at 1600°C. Only the slag has been replaced after each heat. After the 6 hours trial the eight MgO-C segments have been cut and the corrosion depth measured. For a modified slag practice the furnace has been newly equipped with fresh segments of the same MgO-C material and fresh steel of the same quality has been charged. During all tests slag samples have been taken with a steel rod to follow the evolution of the

Table 3. Chemical composition of the liquid part of the slag 1 minute after Flux addition (wt.%)

	Slag A-1	Slag A-2	Slag B	Slag C	Slag D
Fluxing with	FLUX C	FLUX B	FLUX A + MgO	FLUX A	CaF ₂
Flux in slag	20.0%	20.0%	20.0%FLUX A + 2.0% MgO	20.0%	3.5%
CaO	53.5	54.1	56.8	57.4	53.3
MgO	7.0	5.8	4.1	3.9	3.8
Al ₂ O ₃	27.2	27.6	27.2	26.9	25.9
SiO ₂	9.2	9.4	9.0	9.2	9.9
FeO	3.1	3.1	2.9	2.7	3.4
(CaF ₂)	0.0	0.0	0.0	0.0	(3.5)
Basicity B	1.47	1.46	1.57	1.59	1.49
MgO _{liq.+sol.} After 1 minute	8.1	6.3	6.3	3.9	3.8
MgO _{sat}	6.8	6.8	6.3	6.3	7.4

chemical composition of the slag as a result of the refractory corrosion. During the short slag sampling process, the slag surface was exposed to normal air. Slag samples were analysed by semi-quantitative XRF.

3 RESULTS

3.1 Magnesia-C Brick in Contact with Slag from Al-killed Steel

Some of the different slag practices that have been tested are shown in Table 3 with their initial composition (liquid part of the slag after 1 minute of Flux addition). The values are average analyses from the first 2 (in some cases 3) heats. The theoretical MgO-saturation has been calculated from Equation 2 for 1600°C. As can be seen in Figure 2, Calcium Magnesium Aluminate Flux creates rapidly a liquid slag (e.g. slag A-2) in which the total MgO concentration is increased by 2% compared to Flux A (slag C) at an addition rate of 20%. Almost all MgO is already after 1 minute inside the liquid phase while in case of slag B practically none of the added MgO has been transferred into liquid at this stage. Based on the average of the inner diameter of the eight MgO-C segments during one run, it becomes obvious that CaF₂ creates the strongest corrosion (Figure 3).

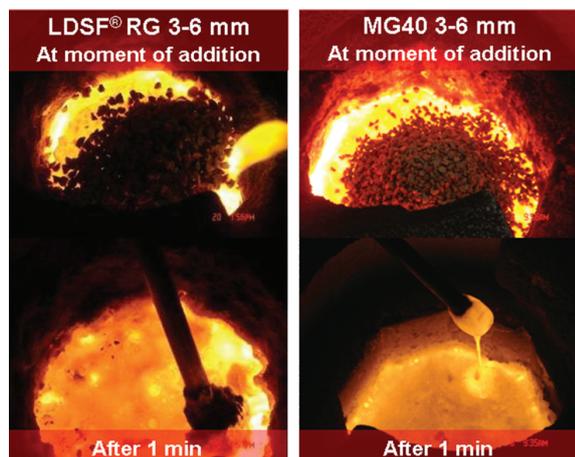


Figure 2. Fluxing behaviour of FLUX A (slag C; left) and FLUX B (slag A-2; right) at 1600°C.

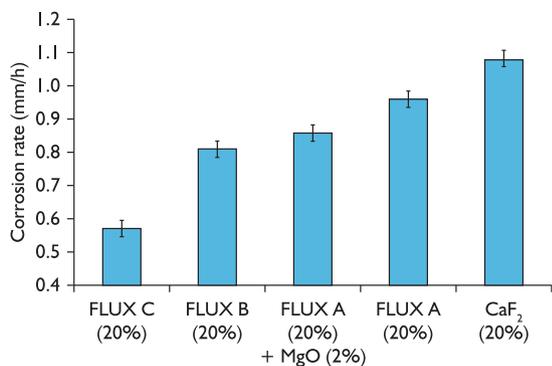


Figure 3. MgO/C-brick corrosion rate with different slags.

FLUX A represents an improvement compared to CaF₂. Significantly better is the use of FLUX B and FLUX C which causes by far the lowest corrosion. In case of the slag practice with FLUX B a high initial MgO level could be achieved (Figure 4) and consequently only a small MgO content increasing has been observed after 30 minutes which is related with the low corrosion rate. With FLUX C the initial MgO content in the slag reaches very early the MgO saturation limit (Figure 5) which explains the very low corrosion rate when FLUX C is employed. The most significant increase in MgO was observed with the CaF₂ practice which explains the strongest corrosion in that case. On the other hand a FLUX A practice shows a similar MgO dissolution but a lower corrosion rate. Here it has to be mentioned that the corrosion profile in case of CaF₂ is different due to the low slag viscosity which more strongly attacks the bonds of the MgO-C brick. As consequence MgO grains from the brick can more easily be removed from the brick structure by mechanical movements of the slag.⁽⁷⁾

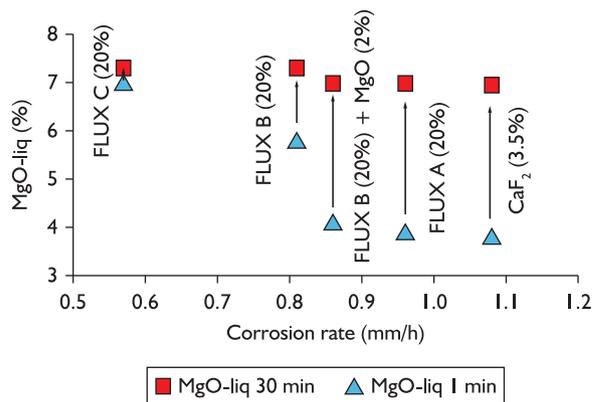


Figure 4. Measured initial MgO content in slag and after 30 minutes treatment time versus MgO-C corrosion rate.

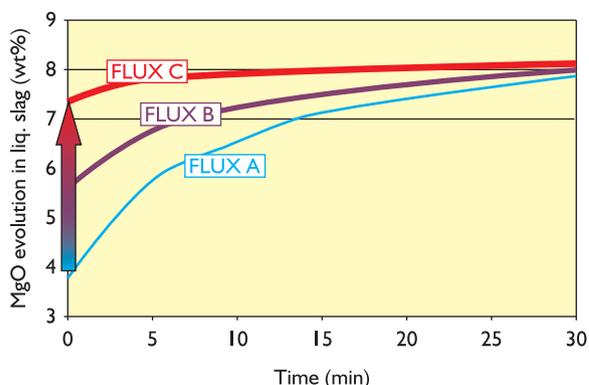


Figure 5. Evolution of MgO content in slag in contact with MgO-C bricks as function of flux material.

These MgO grains can float as solid particles in the slag when slag becomes saturated with MgO. During slag sampling with a steel rode, solid grains attached to

Table 4. Slag chemical composition before and after fluxing and corrosion rates of Doloma-C bricks at 1600°C (wt%)

	Slag E-0	Slag F	Slag G	Slag H
	Slag before flux addition	Slag E-0 plus 7% FLUX C	Slag E-0 plus 7% FLUX A	Slag E-0 plus 3.5% CaF ₂
FeO	10.4	9.8	9.8	10.0
CaO	56.0	54.4	55.7	54.0
Al ₂ O ₃	9.2	11.4	11.5	9.0
SiO ₂	20.8	19.6	19.6	20.0
MgO	3.6	4.8	3.4	3.5
CaF ₂	0.0	0.0	0.0	3.5
Σ	100	100	100	100
Corrosion rate (mm/h)		0.33	0.68	1.02

the liquid slag sample were observed. This phenomena explains why the MgO content after 30 minutes was close to 7% in all cases, corresponding to the MgO saturation limit. Although FLUX B and FLUX A + MgO bring theoretically the same total amount of MgO in the slags A-2 and B, the faster dissolution of MgO in Calcium Magnesium Aluminate Flux creates an advantage over an external MgO addition. Due to the slow dissolution rate of the added MgO grains corrosion is consequently stronger than in case of Calcium Magnesium Aluminate Flux. Chen, Brooks and Nightingale⁽¹⁾ observed that a dense MgO grain of 20 mm in diameter attacked in different slags is loosing only between 0.6 mm and 2.2 mm of its diameter in 15 minutes.

It has also been tested how a reduced addition rate of Calcium Magnesium Aluminate Flux behaves. By adding only 10% of FLUX B thus approximately 1% MgO the corrosion was found in the same range as with slag B with 20% FLUX A + 2% MgO. This indicates again that the MgO from the Calcium Magnesium Aluminate grains dissolves more rapidly in the slag than the externally added MgO-grains.

3.2 Dolomag-C Brick in Contact with Slag from Si-killed Steel

Similar positive effects on refractory life time have been found when Calcium Magnesium Aluminate is used as metallurgical flux for Si-killed ladle slags in contact with Dolomag-C bricks. While CaF₂ flux caused a corrosion rate of 1 mm/h it could be reduced by the use of FLUX A down to 0.7 mm/h and even to 0.3 mm/h when FLUX C was used as metallurgical flux.⁽¹¹⁾ The different slag practices that have been tested are shown in Table 4.

4 SUMMARY AND OUTLOOK

Calcium Magnesium Aluminate Flux additions to steel ladle slags allow a quick formation of a homogeneous liquid metallurgical slag with a high initial MgO-content. The elevated and microcrystalline MgO content inside

Calcium Magnesium Aluminate Flux compared to FLUX A improves the refractory life of the slag zone due to the fast gap closing between the initial MgO and the saturation concentration in the slag. This gives an advantage over the separate addition of Magnesia or Doloma as MgO source. Compared to CaF₂-practices an improvement of 25% and compared to a FLUX A practice of 15% has been measured in laboratory tests with Magnesia-Carbon bricks when FLUX B is used. FLUX C brings further significant improvements of the slag zone durability both in case of Magnesia-C and Doloma-C bricks. Based on simulations with the FactSage[®] software a simplified calculation equation has been proposed which allows very rapidly to estimate the real gap between initial MgO content in the metallurgical slag and the saturation concentration. This helps to select the most adapted Calcium Magnesium Aluminate Flux version for each steel ladle configuration and to adjust the necessary amount of flux addition in an easy and economical way. By applying the synthetic Calcium Magnesium Aluminate Flux in the secondary steel ladle process a significant reduction in specific production costs via the reduction of the specific refractory consumption per ton of steel can be expected. First results from large scale trials in steel ladles have confirmed this positive trend. The metallurgical efficiency of Calcium Magnesium Aluminate Flux enables to achieve rapidly the targeted high quality steel composition. This rapidity helps to save energy in the steel production process. The reduced specific refractory consumption helps to save resources. All together Calcium Magnesium Aluminate Flux supports the efforts to reduce specific CO₂ emissions per ton of produced steel.

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