CALCIUM MAGNESIUM ALUMINATE FLUX WITH HIGH MGO CONTENT: A NEW APPROACH OF SECONDARY METALLURGY TO IMPROVE STEEL QUALITY AND LADLE LIFE TIME[1]

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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 and OPTIMET™ HM, novel synthetic Calcium Magnesium Aluminate Fluxes (CMA) with high MgO-content, have been studied. Thermodynamic simulations with the FactSage© software and laboratory experiments have been conducted. A traditional slag fluxing practice with fluorspar (CaF_2) has been compared with Calcium Aluminate LDSF® RG (CA) and with these novel synthetic OPTIMET™ fluxes with different MgO-contents. OPTIMET™ allows 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 LDSF®RG. OPTIMET™ brings the MgO-content in the slag right after tapping close to the saturation concentration and minimises the dissolution of Magnesia-Carbon or Doloma-Carbon bricks in the slag. Life time increase of the slag zone can be expected. OPTIMET™ helps 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 CO_2-emissions per ton of produced steel.

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

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1 INTRODUCTION

Refractory linings in steel ladles are exposed to steel, slag and air at temperatures up to 1650℃. Especially the contact zone between refractory material and the metallurgical slag have been studied by many authors with the objective to improve the refractory lining.(1-3) Combinations of different degradation phenomena occur in this zone which are a mix between thermochemical degradation and thermophysical stresses.(4,5) The 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)

Significant progress has been made in recent years with respect to the life time of refractory materials in the slag zone. Highly sophisticated Magnesia-Carbon (MgO-C) and Doloma-Carbon bricks [(Ca,Mg)O/C] are widely used in steel ladle slag lines. Their high purity fused or sintered Magnesia or Doloma grains, surrounded by Graphite, creates a brick matrix which is well protected against penetration of liquid steel and slag. The Graphite is protected against oxidation by additions of small amounts of antioxidants like metal powders.(3) However, at the brick surface, where MgO or (Ca,Mg)O grains are in direct contact with the slag, a chemical reaction with the slag occurs which leads to dissolution since the slag is typically not saturated with MgO at the beginning of the ladle treatment.

This study is designed to improve refractory life time and thus reduce operational costs by modifying the slag with the new fluxing materials OPTIMET™ RG and OPTIMET™ HM 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 steel works add for example Doloma directly to the slag as an external source for MgO.(5) But this can make slag formation more difficult since dissolution of MgO or (Ca,Mg)O takes time and homogenisation in the slag is difficult which can create crust formation and an inhomogeneous slag.

2 MATERIALS AND METHODS

2.1 OPTIMET™ RG and OPTIMET™ HM – 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 problematic with Fluorine and furthermore due to the strong corrosion effect as consequence of the formation of a very low viscose 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 desulphurisation process. The rapid modification of the Al_2O_3/SiO_2 ratio by pre-reacted Calcium Aluminate phases plays an essential role in this regard.

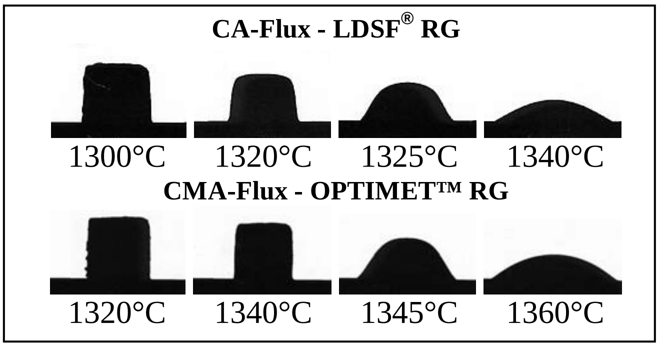

Figure 1. Melting behaviour of CA- and CMA-Flux (test method as described in DIN 51730, heating rate 10K/min).

The new synthetic Calcium-Magnesium Aluminate Fluxes OPTIMET™ RG and OPTIMET™ HM 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. As can be seen in Tab.1 OPTIMET™ RG has a MgO-content of about 12% and OPTIMET™ HM of about 21%. Both are free of impurities like Fluorine, carbon and humidity. The increased MgO content compared to LDSF® RG has no negative impact on the metallurgical efficiency, for example the de-sulphurization effect.(9)
The melting behaviour of OPTIMET™ RG is almost equal to LDSF®RG as can be seen in Figure 1. At 1345℃ it is almost liquid and starts to flow at 1360℃. OPTIMET™ HM has the same melting behaviour. It takes only 1 minute at 1600℃ 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.

Table 1. Chemistry of synthetic CMA- and CA-Fluxes

	CMA- Flux	CMA-Flux	CA-Flux
	OPTIMET™ HM	OPTIMET™ RG	LDSF® RG
	Pre-reacted	Pre- reacted	Pre- reacted
CaO	32.9	37	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
H_2O	<0.15	<0.15	<0.15
CO_2	<0.1	<0.1	<0.1
Total	100	100	100
$(CaO+MgO)/Al_2O_3$	1.3	1.2	1.2

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 Tab. 2 have 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

$$B = CaO / (Al_2O_3+SiO_2) \qquad (1)$$

and temperatures T between 1500 and 1620℃ the following equation (2) derived which describes the MgO-saturation of the slag:

$$(\%MgO)_{sat} = 8.2/B + 0,06(\%FeO) + 0,2(\%CaF_2) + 0.019\ (T-1550) \qquad (2)$$

The results of this equation are in good agreement with experimental results from $^{(6)}$. As can be seen from the equation (2) the levels of basicity and as well the temperature have a strong impact on the MgO-saturation concentration followed by the amount of CaF_2 present in the slag. The FeO concentration is of lower importance. The values from the FactSage© simulation for each single slag at 1550℃ and the values found by applying the equation (2) are in good agreement and all in the range of 6-11% MgO for 1550℃ and 7 to 12% at 1600℃. It shows that all considered slags with the exception of No.5 are under-saturated with MgO and have the potential to dissolve the lacking MgO-content from MgO-C- or Doloma-C-bricks.

Table 2. Slag compositions that have been 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_2O_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℃ (FS)	**8.6**	**8.5**	**8.9**	**12.0**	**5.8**
$(MgO)_{sat}$ 1550℃ (E2)	**8.4**	**8.3**	**8.7**	**12.2**	**6.3**
Liquidus (℃) (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_2O_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℃ (FS)	**11.0**	**7.3**	**9.2**	**9.9**	**10.1**
$(MgO)_{sat}$ 1550℃ (E2)	**11.0**	**7.3**	**9.0**	**10.0**	**10.3**
Liquidus (℃) (FS)	1373	1495	1339	1322	1347

With the OPTIMET™ fluxes 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 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 set up.

2.3 Test Methods

To simulate the conditions in the steel ladle slag line a laboratory induction furnace has been chosen as test vessel in which MgO-C bricks or (Ca,Mg)O-C bricks build the side wall (Figure 2).

2.4 MgO-C Bricks and Al-killed Slag with OPTIMET™-Flux

The employed MgO-C brick material contains 12% carbon. The oxide components are 97% MgO, 1.7% CaO, 0.6% SiO_2, 0.5% Fe_2O_3 and 0.2% Al_2O_3. The density is 3,01g/cm^3 and open porosity 4.0%. Segments with trapezoidic 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/H_2 atmosphere to the test temperature of 1600℃. Then 480g of a slag (579g in case of slag D) is formed on top of the liquid steel to which then 120g of the fluxing materials (21g in case of CaF_2 for slag D) as grains of 3-6mm are added (Tab.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% OPTIMET™ HM and 20% OPTIMET™ RG to the total slag mass and slag C the same amount of LDSF®RG-Flux. Slag B has also been fluxed with LDSF®RG 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.

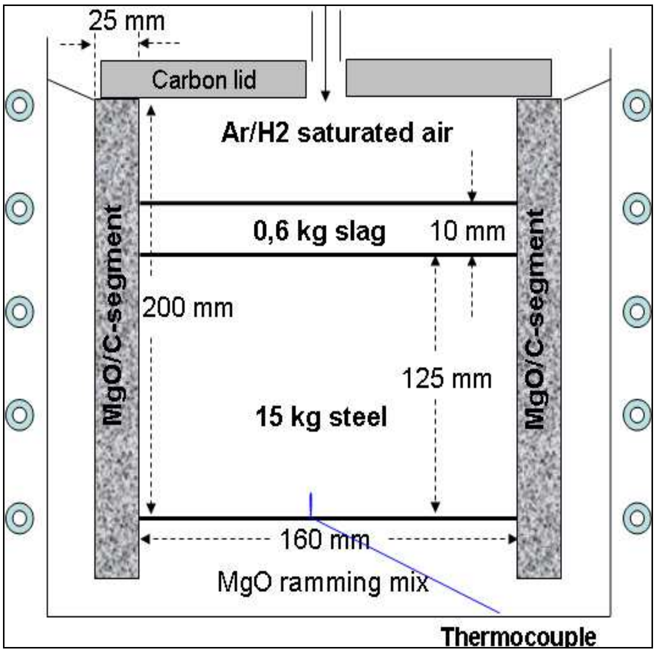

Figure 2. Induction furnace to quantify refractory dissolution.

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 6h 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 inside the vessel at 1600℃. Only the slag has been replaced after each heat. After the 6h-trial the 8 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 chemical composition of the slag as a result of the refractory corrosion. During the short slag sampling process, the slag surface is exposed to normal air. Semi-quantitative XRF-analyses have been conducted on pressed powder samples.

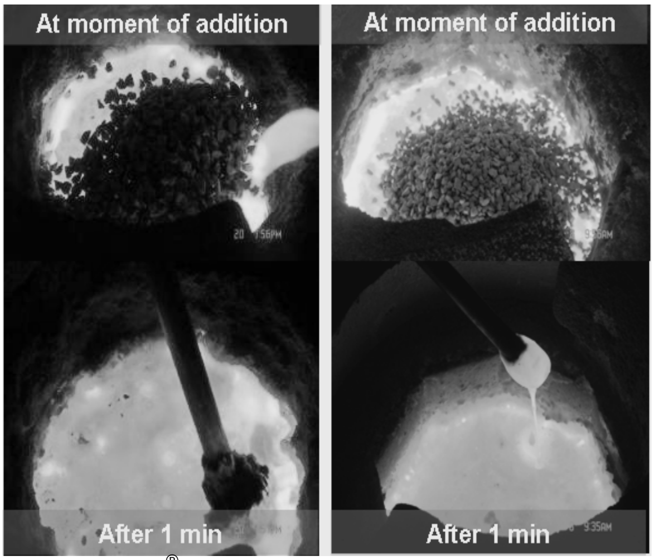

Figure 3. Fluxing behaviour of LDSF®RG (slag C; photos left) and OPTIMET™ RG (slag A-2; photos right) at 1600℃.

2.5 Doloma-C Bricks and Si-killed Sag with OPTIMET™ Flux

A magnesia enriched Doloma-C brick with a composition close to that mentioned in Schacht,(11) with around 36% CaO and 60% MgO for the oxide compounds and a content of 6% carbon has been selected. The bulk density is 2.95 g/cm^3 and the open porosity accounts for 12%. Since the Doloma is quite sensitive to humidity special care had to be taken for the sample preparation and it was decided to cut rectangular Doloma-C segments from the bricks and place only four of them as side wall in the induction furnace which forms a square in that case. The furnace has been charged here with 4 kg of steel only and a total of 400g of slag including the amount of fluxing material (7% for LDSF®RG and OPTIMET™, 3.5% in case of CaF_2). The steel contains 0.03% C, 0.03% Si, 0.3% Mn, 0.02% P, 0.02% S and 0.005% Al. The tests have been conducted here as well at 1600℃ and Ar/H_2 atmosphere. Every 30 minutes the slag has been replaced by a fresh slag. The total slag contact time was 3 hours (6 cycles). For each fluxing practice fresh bricks and steel of the same composition have been placed in the furnace.

3 RESULTS

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

Some of the different slag practices that have been tested are shown in Tab.3 with their initial composition (liquid part of the slag after 1 min 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 formula (2) for 1600℃. As can be seen in Fig.3 OPTIMET™-Flux creates rapidly a liquid slag (e.g. slag A-2) in which the total MgO concentration is increased by 2% compared to LDSF RG (slag C) at an addition rate of 20%. Almost all MgO is already after 1 min inside the liquid phase while in case of slag B practically non of the added MgO has been transferred into liquid at this stage. The corrosion profiles of the same MgO-C brick material in contact with slags A-2, C and D are shown in Fig.4. Taking the average of the lost diameter for the 8 MgO-C segments of one test run it becomes obvious that CaF_2 creates the strongest corrosion (Fig.5).

Table 3. Slag chemistry 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	OPTIMET™ HM	OPTIMET™ RG	LDSF®RG +MgO	LDSF® RG	CaF_2
Flux in slag	20%	20%	20% LDSF 2% MgO	20%	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_2O_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	(3.5)
Basicity B	1.47	1.46	1.57	1.59	1.49
$MgO_{liq.+sol.}$ After 1min	8,1	6,3	6,3	3,9	3,8
MgO_{sat}	6,8	6.8	6.3	6.3	7.4

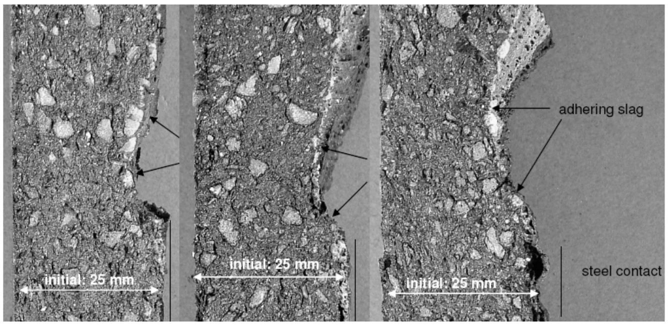

Figure 4. MgO-C brick after 6h at 1600℃ in contact with steel and slag A-2 (left), slag C (middle) and slag D (right).

LDSF®RG represents already an improvement compared to CaF_2. Significantly better is the use of OPTIMET™ RG and OPTIMET™ HM which causes by far the lowest corrosion. In case of the slag practice with OPTIMET™ RG a high initial MgO level could be achieved (Fig.6) and consequently only a small increase of MgO has been observed after 30 minutes which translates into the low corrosion rate. With OPTIMET™ HM the initial MgO-content in the slag reaches already at this very early moment the MgO-saturation limit which explains the very low corrosion rate when OPTIMET™ HM is employed into the slag. The biggest increase in MgO was observed with the CaF_2 practice which explains the strong corrosion in that case. On the other hand a LDSF®RG -practice shows a similar MgO dissolution but a lower corrosion rate. Here it has to be mentioned that the corrosion profile in case of CaF_2 is different (Figure 4). Slag viscosity is lower compared to the CA-Flux which more strongly attacks the bond 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)

These MgO grains can float as solid particles inside the slag when slag is already saturated with MgO. During slag sampling with a steel rode it is unlikely that a solid grain will be taken together with the liquid part of the slag. This explains why the measured MgO concentration after 30 minutes is in all cases close to 7%, the MgO saturation limit. Although OPTIMET™ RG and LDSF®RG + MgO bring theoretically the same total amount of MgO into the slags A-2 and B, the faster dissolution of MgO in OPTIMET™ 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 OPTIMET™. It was discovered by (1) that a dense MgO grain of 20 mm in diameter immersed in different slags is loosing only between 0.6 and 2.2 mm of its diameter in 15 minutes.

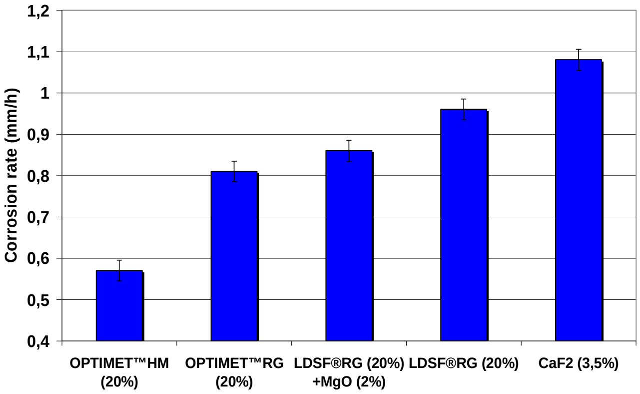

Figure 5. MgO/C-brick corrosion rate with different slags.

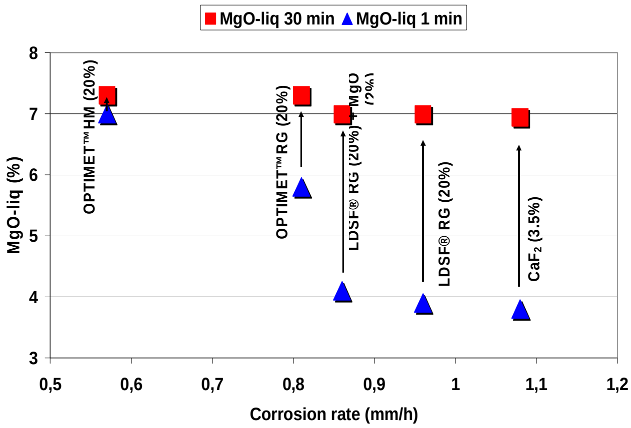

Figure 6. Measured initial MgO content in slag and after 30min treatment time versus MgO-C corrosion rate.

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

3.2 Doloma-C-brick in Contact with Si-killed Steel Slag

The following slag composition was used as the basis for the comparison of the different fluxing practices (Table 4). After being in contact with the Doloma-C brick during 3h at 1600℃ with slag replacements every 30 minutes by fresh slags F, G or H the remaining thickness of the Doloma-C segments have been measured at the thinnest section und the corrosion rate calculated accordingly (Table 5). Also in case of Doloma-C bricks and slags more closely to Si-killed steel production the positive effect of OPTIMET™ HM is very visible. Since only a low amount of Flux has been added to the slag the high amount of rapid soluble MgO inside OPTIMET™ HM plays a crucial role in this regard and saturates right from the beginning the slag with MgO. However it has to be mentioned in case of Doloma-C bricks that not only the MgO-saturation but also the lime saturation of the slag is crucial to prevent fast dissolution of the bricks in the slag.

Table 4. Slag composition before and after fluxing

	Slag E-0	**Slag F**	**Slag G**	**Slag H**
	Slag before Flux addition	Slag E-0 plus 7% OPTIMET™ HM	Slag E-0 plus 7% LDSF®RG	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_2O_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
CaF2	*0*	0	0	3.5
Σ	*100*	100	100	100

Table 5. Corrosion rates of Doloma-C bricks in contact with different slags at 1600℃

	Slag F	**Slag G**	**Slag H**
Flux content in slag	7% OPTIMET™ HM	7% LDSF®RG	3.5% CaF_2
Initial thickness of each of the 4 Doloma-C segments (mm)			
(mm)	25.0	25.0	25.0
Remaining thickness after 3h (mm)			
Segment 1	24.05	22.91	21.81
Segment 2	23.97	23.04	22.03
Segment 3	23.92	22.89	21.92
Sebment 4	24.08	22.99	21.97
Average	24.01	22.96	21.93
Std. dev.	0.07	0.07	0.09
Corrosion rate (mm/h)			
	0.33	**0.68**	**1.02**

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4 SUMMARY AND OUTLOOK

OPTIMET™-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 OPTIMET™ RG and especially in OPTIMET™ HM compared to LDSF®RG improve the refractory life of the slag zone due to the fast closing of the gap between the initial MgO and the saturation concentration. This gives an advantage over the separate addition of Magnesia or Doloma as MgO source. Compared to CaF_2-practices an improvement of 25% and compared to a LDSF®RG-practice of 15% has been measured in laboratory tests with Magnesia-Carbon bricks when OPTIMET™ RG is used. OPTIMET™ HM 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 formula has been developed 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 OPTIMET™ version for each steel ladle configuration and to adjust the necessary amount of OPTIMET™ flux addition in an easy and economical way. By applying the synthetic OPTIMET™ 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 already this positive trend. The metallurgical efficiency of OPTIMET™ flux enables to achieve rapidly the targeted high quality steel composition. This rapidity helps to safe energy in the steel production process. The reduced specific refractory consumption helps to safe resources. All together OPTIMET™ supports the efforts to reduce specific CO_2 emissions per ton of produced steel.

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