Novel Fluxing Agents for Ladle Slags to Improve Refractory Life Time and Steel Quality

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To improve the life time of ladle slag zone bricks the impact of novel synthetic pre-reacted Calcium Magnesium Aluminate Fluxes (OPTIMET™ RG and OPTIMET™ HM) has been studied. They bring the MgO content in the slag immediately after tapping steel from converter or electric arc furnace into the ladle throughout the whole slag mass close to the saturation concentration. That minimises the chemical dissolution of MgO from Magnesia-Carbon or Dolomag-Carbon bricks. Longer refractory live time is the positive effect. OPTIMET™ forms very rapidly a homogeneous and liquid slag with a high capacity to absorb sulphur and oxide inclusions from the steel bath, a prerequisite for efficient clean steel production. This new fluxing practice with Calcium Magnesium Aluminate helps to reduce the specific costs per tonne of steel. The efficiency of high quality steel production can be increased and production capacities be optimised. These novel fluxing agents support the efforts to reduce the CO_2-emissions per ton of produced steel.

1 Indroduction

Refractory linings in steel ladles are exposed to steel, slag, and air at temperatures up to 1650 °C. Especially the contact zone between the refractory material and the metallurgical slag have been studied by many authors with the objective to improve the refractory lining [1–3]. Different degradation phenomena occur in this zone which are combinations of thermo-chemical and thermo-physical processes [4, 5]. The thermo-chemical reactions are seen as a major degradation cause since the slag compositions are typically under-saturated in MgO. That 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 time and thus reduce operational costs by modifying the slag with the novel fluxing materials OPTIMET™ RG and OPTIMET™ HM. They are based on pre-reacted synthetic 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 steelworks add for example doloma directly to the slag as an external source for MgO [5].

But fusion and homogenisation of coarse MgO or (Ca, Mg)O grains takes time while dissolution of the fine grains from the matrix of the bricks is already in progress. Addition of powders of magnesia and doloma to the slag should be avoided to prevent dust formation and introduction of humidity into the system since both doloma and magnesia powders tend to hydrate in humid air [7].

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 steelworks 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
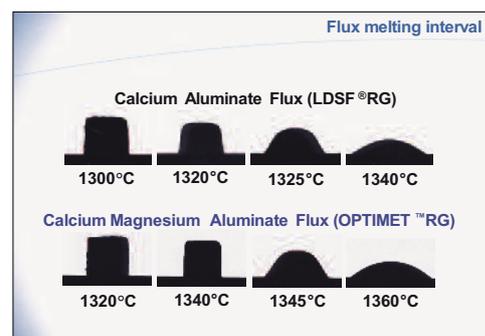

Fig. 1 Melting behaviour of Calcium Aluminate flux and Calcium Magnesium Aluminate flux (test method as described in DIN 51730, heating rate 10K/min)

as consequence of the formation of a very low viscose slag, synthetic calcium aluminate fluxes (LDSF® RG) have become part of modern steelworks practice especially where clean steel production is required [8, 9]. Calcium aluminate fluxes combine the advantage of creating quickly a homogeneous and sufficient liquid slag with the chemical capacity to absorb a large variety of non-metallic

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Tab. 1 Chemistry of synthetic calcium magnesium aluminate flux (OPTIMET™) and calcium aluminate flux (LDSF® RG)

	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

impurities from the steel bath and support as well the de-sulphurization 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.

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 [10].

The melting behaviour of OPTIMET™ RG is almost equal to LDSF® RG as can be seen in Fig. 1. At 1345 °C it is already almost liquid and starts to flow at 1360 °C. OPTIMET™ HM has the same melting behaviour. It takes only 1 minu at 1600 °C to create a homogeneous liquid top slag (Fig. 2). This has the

advantage of having an increased MgO-level in the slag right from the beginning compared to a normal calcium aluminate or a CaF_2 practise.

2.2 Thermo-chemical 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 [11]. The MgO-saturation concentration is dependent on the slag basicity, temperature, FeO- and CaF_2-content. For the range of the considered compositions (Tab. 2) 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 °C 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. It shows that all considered initial slag compositions 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 Dolomag-C bricks. 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. 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

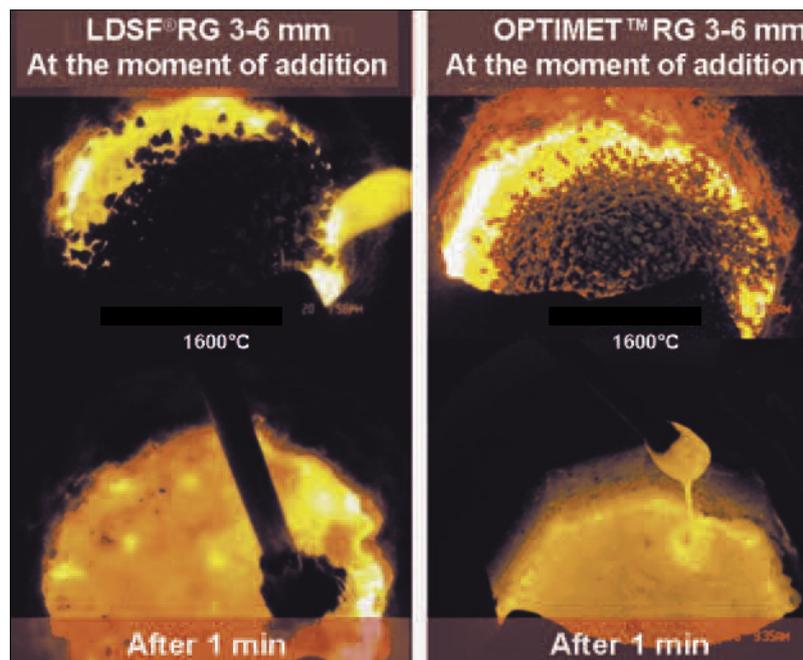To simulate the conditions in the steel ladle slag line a laboratory induction furnace

Fig. 2 Fluxing behaviour of LDSF® RG (slag C; left) and OPTIMET™ RG (slag A-2; right) at 1600 °C

Tab. 2 Slag compositions that have been used for thermodynamic simulations of MgO-saturation (FS = results from FactSage© simulations; E2 = results from 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 °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_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 °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

as described in [12] 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 % SiO_2, 0,5 % Fe_2O_3 and 0,2 % Al_2O_3. 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 (with 0,1 % C, 2,65 % Si, 1,65 % Mn, 0,014 % P, 0,0006 % S and 0,035 % Al) which are heated up by induction under Ar/H_2 atmosphere 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 CaF_2 for slag D) as grains of 3 – 6 mm are added (Tab. 3). Slag compositions as can be found

in Al-killed steel production at the beginning of the steel treatment in the ladle have been targeted to compare the different fluxing practises.

Slag A-1 and A-2 use an addition of 20 % OPTIMET™ HM respectively 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. In preliminary trials with a holding time of 60 min it was found that the MgO-concentration reaches almost its saturation level after 30 min already so that it was preferred to run cycles of 30 min only to achieve a maximum of corrosion effect during a 6 h trial.

Every 30 min the total slag mass has been removed and replaced by fresh slag and flux. A total holding time of 6 h, thus 12 slag cycles (heats) have been applied with the same slag practice. During this time the steel remains inside the vessel at 1600 °C. Only the slag has been replaced after each heat. After the 6 h-trial the 8 MgO-C segments have been cut and the corrosion depth was measured.

Since the doloma is quite sensitive to humidity special care had to be taken for the sample preparation and it was decided to dry-cut rectangular Dolomag-C segments from the bricks. Here only four segments build the wall in the induction furnace. The furnace has been charged with 4 kg of steel only and a total of 400 g of slag including the amount of fluxing material (7 % for LDSF® RG and OPTIMET™, 3,5 % in case of

Tab. 3 Slag chemistry of the liquid part of the slag 1 min after flux addition [mass-%]

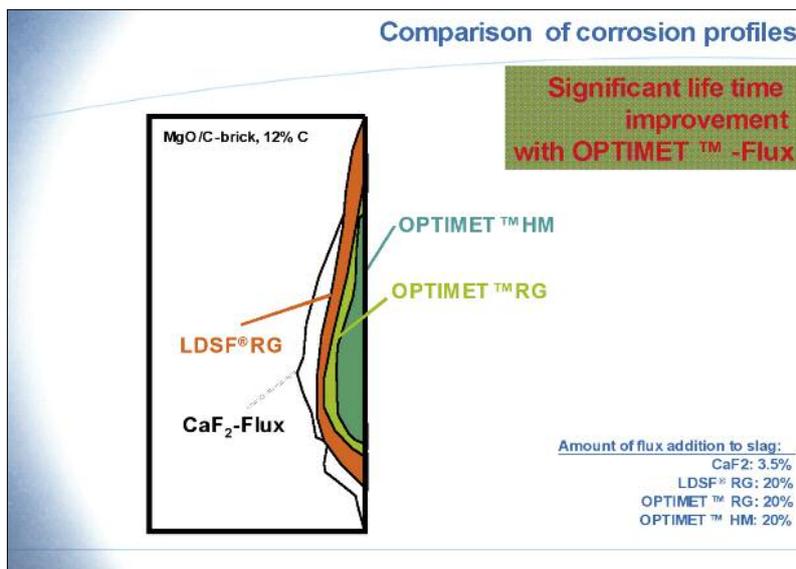|	Slag A-1	Slag A-2	Slag B	Slag C	Slag D
Fluxing with	OPTIMET™ HM	OPTIMET™ RG	LDSF®RG + MgO	LDSF® RG	CaF_2
Flux in slag	20 %	20 %	20 % LDSF 2 % MgO	20 %	3,5 %
CaO	53,5	54,1	56,8	57,4	53,3
MgO	7,0	5,8	4,1	3,9	3,8
Al_2O_3	27,2	27,6	27,2	26,9	25,9
SiO_2	9,2	9,4	9,0	9,2	9,9
FeO	3,1	3,1	2,9	2,7	3,4
(CaF_2)	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

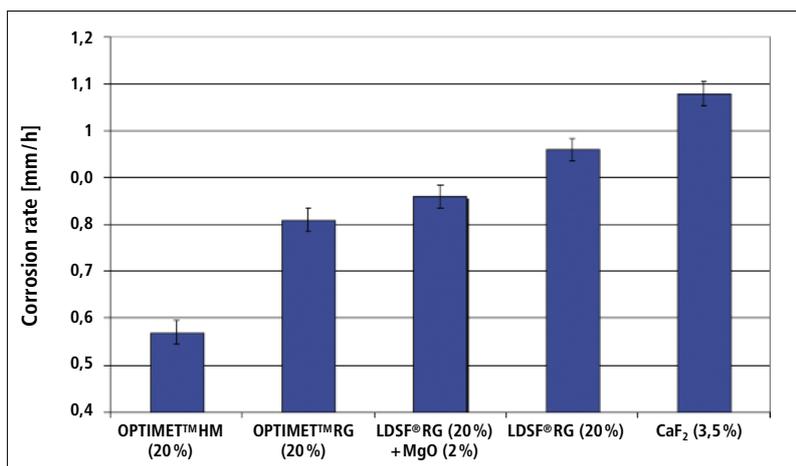**Fig. 3** MgO-C-brick corrosion profile as function of slag fluxing practise

Fig. 4 MgO-C-brick corrosion rate as function of slag fluxing practice

CaF$_2$). The steel is containing 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 °C and Ar/H$_2$ atmosphere. Every 30 min the slag has been replaced by fresh slag. The total slag contact time was 3 h (6 cycles).

For each slag practice the furnace has been newly equipped with fresh segments of the same MgO-C or (Mg, Ca)O-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.

3 Results
3.1 Magnesia-C brick in contact with Al-killed ladle 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 °C.

As can be seen in Fig. 2 OPTIMET™ flux creates rapidly a liquid slag (e.g. slag A-2) which increases the amount of MgO in the liquid phase almost instantaneously by 2 % compared to LDSF RG (slag C) at an addition

rate of 20 % in both cases. 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 yet into liquid at this stage. By measuring the average of the lost diameter for the 8 MgO-C segments employed in the furnace wall of one test run it becomes obvious that CaF$_2$ creates the strongest corrosion (Figs. 3, 4).

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. 5) and consequently only a small increase of MgO has been observed after 30 min 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 (Fig. 6) 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 with LDSF® RG a similar MgO dissolution but a lower corrosion rate was observed.

Here it has to be mentioned that the corrosion profile in case of CaF$_2$ is different due to the low slag viscosity which more strongly attacks the bond of the MgO-C brick (Fig. 3). As consequence MgO grains from the brick can more easily be removed from the brick structure by mechanical movements of the slag [8]. 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 min 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 case of 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 im-

mersed in different slags is loosing only between 0,6 and 2,2 mm of its diametre in 15 min.

It has also been tested how a reduced addition rate of OPTIMET™ behaves. By adding only 10 % of OPTIMET™ RG flux thus approximately 1 % additional 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 employed in the OPTIMET™ grains dissolves more rapidly in the slag than the externally added MgO-grains.

3.2 Dolomag-C brick in contact with Si-killed ladle slag

Similar positive effects on refractory life time have been found when OPTIMET™ was used as metallurgical flux for a Si-killed ladle slag in contact with the Dolomag-C bricks (Tab. 4).

While the slag H with CaF_2 caused a high corrosion rate of 1 mm/h it could be reduced by the use of LDSF® RG down to 0,7 mm/h and even to 0,3 mm/h when OPTIMET™ HM was used. The rapidly soluble MgO inside OPTIMET™ HM plays here as well a crucial role. However it has to be mentioned in case of Dolomag-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.

4 Conclusion

OPTIMET™ flux additions to steel-ladle slags allow a quick formation of a homogeneous liquid metallurgical slag with a high initial MgO-content in the liquid phase. The elevated and microcrystalline MgO content inside OPTIMET™ compared to LDSF® RG 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 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 Dolomag-C bricks.

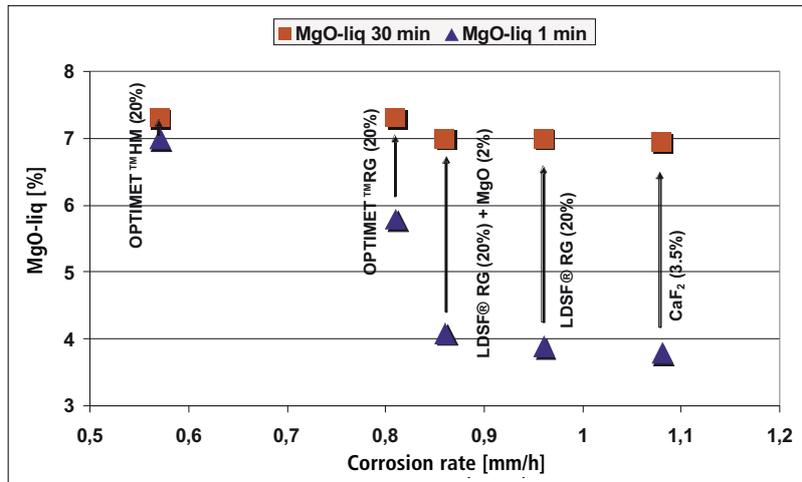The trials with fluorspar show as well, that further to chemical corrosion effects also

Fig. 5 Corrosion rate and MgO content in the liquid phase of the slag 1 min and 30 min after flux addition
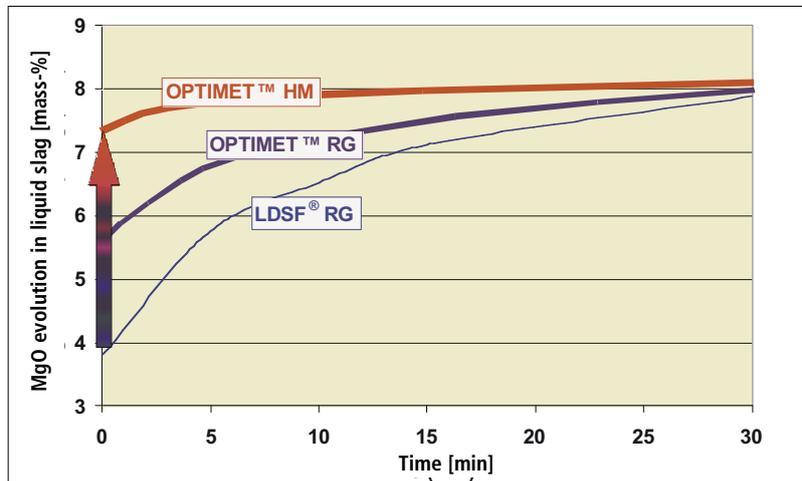

Fig. 6 Evolution of MgO content in slag in contact with MgO-C bricks as function of flux material

other aspects like mechanical and thermo-mechanical effects play a role in the degradation process of the refractory materials. 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 sat-

Tab. 4 Slag composition before and after fluxing and corrosion rates of Dolomag-C bricks at 1600°C

	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
CaF_2	0	0	0	3,5
Σ	100	100	100	100
Corrosion rate [mm/h]		0,33	0,68	1,02

uration 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. Results from applications in steel ladles have confirmed this positive trend. The metallurgical efficiency of OPTIMET™ flux enables to achieve rapidly the targeted high quality steel compositions. This rapidity helps to safe energy and to optimise capacities of existing steel production processes. The reduced specific refractory consumption helps to safe natural resources. All together OPTIMET™ supports the efforts to reduce specific CO_2 emissions per ton of produced steel.

Acknowledgement

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