

# Influence of calcination condition on the dissolution behaviour of lime in synthetic slags

## Author(s) Name(s) and Affiliations(s)

S. Lesiak, E. Cheremisina, J. Rieger, K1-MET GmbH, Austria; J. Schenk, Department of Metallurgy, Chair of Ferrous Metallurgy, Montanuniversität Leoben, Austria; F. Firsbach, T. Chopin, M. Nispel, Lhoist Business Innovation Center (BIC), Belgium; W. Johnson, Lhoist North America (LNA), United States of America

## Contact data

Stefanie Lesiak, K1-MET GmbH, Franz-Josef-Str. 18, 8700 Leoben, Austria, +43 (0) 3842 402 2279, stefanie.lesiak@k1-met.com

## Summary

The calcination of limestone leads to the decomposition and transformation of calcium carbonates to calcium oxides. The resulting material properties, such as microstructure, porosity, and reactivity, influence the dissolution performance of this flux material in the slag during steelmaking. The ability to saturate slag with CaO within the required time during the oxygen blowing operation in the Basic Oxygen Furnace (BOF) or the scrap melting in the Electric Arc Furnace (EAF) affects the refining reactions and the process productivity. The dissolution behaviour of different lime qualities (i.e. raw limestone, soft-burned and hard-burned lime) was examined in a static high-temperature experiment. Material samples were immersed into synthetic pre-melted liquid EAF and BOF slags at 1,450 °C and 1,400 °C, respectively. After the predetermined holding times in the range between 5 and 20 minutes, the crucible containing the CaO sample and the slag was quenched with liquid nitrogen. After quenching, the crucibles including slag were cut into cross-sections for mineralogical examinations. Scanning Electron Microscopy with Energy Dispersive X-Ray spectroscopy (SEM/EDX) analyses were applied to investigate slag chemistry in periodical distances along the cross-sections. Based on the derived concentration profiles of slag components, the dissolution behaviour of the investigated lime materials was assessed.

## Key Words

Calcination influence, basicity, driving force, in-situ decomposition, semi-quantitative analysis, relative basicity ratio

## Introduction

Due to economic and ecological reasons, the investigation of dissolution kinetics of CaO carriers in steelmaking slags has been of interest over the last decades. A rapid and complete dissolution of lime is favoured for an effective utilisation of additives. The fast dissolution of lime improves the capability to entrap impurities, lowers the consumption of refractory lining and changes the slag composition, which is relevant for process control either. <sup>[1–6]</sup>

Conventionally, lime is produced by calcination in rotary or shaft kilns at 900–1,300 °C. The calcination of limestone leads to the formation of pores and cracks. These artefacts enhance the slag penetration into the lime. The higher the contact area of slag and lime, the faster is the dissolution. Thus, the disintegration of sample as well as a high specific surface force the dissolution of lime. The calcination

process of burned lime for the steelmaking industry is intensive in fossil energy. Thus, to lower this demand, the direct applicability of limestone has been investigated. It is assumed that the in-situ decomposition of limestone under steelmaking conditions leads to a high reactivity and rapid dissolution; however, the in-situ calcination conditions may result in a dense layer of CaO at the lime surface as well as a low overall porosity. These properties immensely decrease the dissolubility. In contrast, raising the temperature leads to increasing dissolution rate, whereas the transformation of CaCO<sub>3</sub> into CaO shows highly endothermic character and causes an extensive drop of slag temperature during the procedure. Hence, a sufficient heat supply is required to prevent slag solidification. <sup>[4, 5, 7, 8]</sup>

The lime dissolution process shows multi-stepped mechanisms. The dissolution path of CaO in phase diagram enables the prediction of possible phases.

Firstly, there is a CaO increase in slag next to the lime. Subsequently, CaO and SiO<sub>2</sub> react under formation of 2CaO·SiO<sub>2</sub> (C<sub>2</sub>S). The formed solid precipitates may dissolve again and lead to the transport of calcium in liquid bulk slag. If the precipitates dissolve or accumulate, depends on the concentration range in multiphase region. The smaller it is, the lower is the accumulation to precipitates and the faster these are redissolved. If there are no turbulences in slag, dispersed 2CaO·SiO<sub>2</sub> particles change into a continuous layer. The thickness of the layer increases up to a maximum and shows a concentration gradient from particle to slag. As the FeO concentration in remaining liquid slag is elevated (CaO and SiO<sub>2</sub> consumed by high-melting precipitates), iron ions preferentially diffuse into the lime sample. The higher the iron oxide content in bulk slag, the higher is the depth of infiltration. Consequently, a CaO-FeO layer forms next to the sample and calcium ions need to diffuse across both layers to the bulk slag. Thus, the thickness growth of CaO-FeO layer sinks with 2CaO·SiO<sub>2</sub> layer formation and finally stops. The effective diffusion coefficient for Ca<sup>2+</sup> via 2CaO·SiO<sub>2</sub> layer is much lower than for the liquid slag because it must diffuse via the solid crystal lattice of C<sub>2</sub>S. The end of dissolution is marked by the precipitation of calcium monoxide in bulk slag. [1, 5, 7-10]

Typical steelmaking slags comprise SiO<sub>2</sub>, CaO and FeO. The driving force for additive dissolution is the difference between CaO content in the slag and the intersection of liquidus line with the connection of start slag composition and CaO corner. Thus, the dissolution of CaO is fastest if there is no CaO in slag, which results in a high concentration gradient as driving force. In contrast, the increasing slag basicity lowers the dissolution rate. In fact, the dissolution becomes faster by adaption of slag chemistry and increasing temperature, as the additives affect the driving force for dissolution but also the slag properties, such as diffusivity and viscosity. Because of the negative impacts of fluorspar, generating fluorine containing emissions and affecting the refractory lining, the oxides of transition metals, such as FeO or MnO, are commonly added to increase the diffusivity of CaO and to lower the viscosity of slag. In contrast, SiO<sub>2</sub> increases the viscous behaviour by formation of chained structures and hence, impedes the diffusion of CaO. However, the mentioned additives lower the activation energy of diffusion, whereas the effect of FeO<sub>x</sub> is even higher than of CaF<sub>2</sub>. Besides, elevated FeO contents in slag

(45 wt.-%) force the dissolution of lime due to the separation of calcium silicates from the interface and formation of calcium ferrites with low melting point promoting early slag formation. [1-5, 7, 8]

Test methods applying rotating cylindrical samples are commonly used to prevent an impact of natural convection and simultaneously simulate the agitation of slag due to turbulences in steelmaking processes. Under turbulent conditions an eventual C<sub>2</sub>S film ruptures and allows the FeO penetration into gaps. The dicalcium silicate disperses in the molten slag and cannot be observed in microscopic images. Due to the layer next to or at the surface of the particles, the dissolution is strongly different under static or dynamic conditions. More in detail, there is an exponential correlation of rotation speed and raising dissolution. However, it is reported that the samples removed from slag and cooled on air collapse after some seconds, which impedes any characterisation. [1, 2, 5] Hence, static tests to avoid the mitigation of calcination condition influences with samples remaining in bulk slag are selected for semi-quantitative comparison of dissolution kinetics.

This study focuses on the experimental investigation of lime dissolution in two synthetic slags. The aim is to point out the differences based on reaction time, initial slag composition as well as on calcination condition. More in detail, cylindrical samples of raw limestone, soft-burned and hard-burned lime are tested.

## Experimental

To evaluate the dissolution behaviour, a static experimental setup using the high-temperature vertical furnace HTRV 200-250/17 from Gero under protective N<sub>2</sub> atmosphere was selected. Applying a heat ramp of 300 °C/h, the target temperatures of 1,450 °C in case of EAF slag testing and 1,400 °C for BOF slag were reached and kept for 30 min. Simultaneously, oxide powder mixtures according to the chemistries in **Table 1** were prepared from chemically pure materials. The selected slag compositions were typical for EAF and BOF processes prior to CaO dissolution. The defined mass of 70 g was weighted for each experiment and molten within a pure iron crucible (60 mm in diameter, 50 mm height), ensuring the stabilisation of Fe<sup>2+</sup> cations in the slag. After 30 min of slag melting, the specimen was inserted and submerged within

Slag type	Oxide contents in start slag [wt.-%]					Slag basicity [-]
	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MnO	FeO	
EAF	10.0	25.0	25.0	8.0	32.0	1.00
BOF	–	35.0	20.0	–	45.0	0.57

Table 1: Compositions of representative, synthetic EAF and BOF slags and their basicity

some seconds. As sample materials raw limestone as well as soft-burned and hard-burned lime discs were utilised. The testing duration in EAF-type and BOF-type slags was altered between 5 min and 20 min for soft-burned lime. For the other specimens, the isothermal reaction period was fixed to 10 min. The end of the dissolution test was marked by the removal of the crucible containing slag and partial undissolved sample from the furnace and quenching with liquid nitrogen to avoid further reactions. As the position of the immersed specimens was unclear, the crucibles were cut twice in longitudinal direction and the chosen quarter, including some disc material rest, was embedded in resin. Due to the hygroscopic character of CaO, the cutting as well as the metallographic grinding and polishing were executed water-free with an organic lubricant. The bulk slag composition was determined by SEM/EDX analysis using FEI QUANTA 200 in low vacuum mode. In periodical distances of 2 mm with the crucible as start point reference images were taken. Subsequently, the slag matrix was analysed in multiple small areas of constant size (270  $\mu\text{m}$  by 200  $\mu\text{m}$ ) on every image. The mean oxide contents per image were plotted against the distance to crucible wall and resulted in concentration profiles. In the calculations of mean values areas of completely altered morphology, such as areas of remaining lime sample or single-phase analyses, i.e.  $2\text{CaO}\cdot\text{SiO}_2$ , were excluded. The total mean value determined from the points in concentration profile represented the total mean bulk slag composition after static dissolution trial. Moreover, the theoretical target values (see **Equation (1)**) under assumptions of complete limestone/lime sample dissolution and without iron uptake from crucible were calculated.

$$w_{\text{ox., target}} = \frac{m_{\text{slag}} \cdot w_{\text{ox., slag}} + m_{\text{sample}} \cdot w_{\text{ox., sample}}}{m_{\text{slag}} + m_{\text{sample}}} \quad (1)$$

$w_{\text{ox., target}}$  marks the target concentration of selected oxide at completely dissolved sample in wt.-%,  $m_{\text{sample}}$  represents the initial mass of sample material in g and  $m_{\text{slag}}$  the weighted slag mass input in g with  $w_{\text{ox., slag}}$  as the predetermined content of oxide in start slag in wt.-% as well as  $w_{\text{ox., sample}}$  as the concentration of oxide in sample material in wt.-%.

Due to the unsteady iron uptake from independent crucible dissolution, the slag basicity ( $B_2$ ) was examined as the ratio of CaO to  $\text{SiO}_2$  content (cf. **Equation (2)**) for the individual trials and compared with the theoretically possible basicity increase.

Finally, the dissolution behaviour of limestone-based specimens in EAF and BOF slags was evaluated in dependence on calcination condition as well as on reaction time for soft-burned lime.

$$B_2 = \frac{w_{\text{CaO}}}{w_{\text{SiO}_2}} \quad [-] \quad (2)$$

## Results

The experimental setting of static dissolution tests without extraction of sample at the test end led to fluctuations in the concentration profile. However, the analysis method using multiple small area SEM/EDX measurements along the cross-section of slag was advantageous as fields of undissolved sample or interfacial layers could be easily removed; hence, the composition of bulk slag was determined with minimised artefacts. Consequently, some gaps in the oxide concentration profile were observed (see **Figure 1**). Moreover, at positions where the slag crumbled out, no measurements were possible.

Due to the high temperatures of 1,450 °C and 1,400 °C, respectively, in dissolution experiments, the FeO content in some trials was extensively elevated (cf. **Figure 1**), suppressing the other oxides. Thus, the oxide contents in semi-quantitative SEM/EDX analysis could not be directly interpreted. However, the distances between yellow crosses ( $\text{SiO}_2$ ) and blue diamonds (CaO) were a first indicator if the sample dissolution was sufficient. In EAF slag the concentrations of  $\text{SiO}_2$  and CaO started at the same level of 25 wt.-%; thus, the CaO should be above the  $\text{SiO}_2$  caused by limestone/lime dissolution. In contrast, the BOF slag comprised a higher starting content of 35 wt.-%  $\text{SiO}_2$  and the CaO was 20 wt.-%. Consequently, a decrease of  $\text{SiO}_2$  and CaO levels' distance was demanded. In case of raw limestone dissolution, the mentioned criteria were reached in both slags. In some sections, the CaO was still above  $\text{SiO}_2$  in dissolution tests of soft-burned lime in EAF slag. In BOF slag differences with reaction time were visible. Enlarging the dissolution period from 5 min to 10 min led to lowered distances between CaO and  $\text{SiO}_2$  concentrations, whereas a further decline after 20 min was not observed. A possible explanation might be that an extended contact time to air prior to testing resulted in lower reactivity of the specimen. The CaO amount in trials with hard-burned lime in EAF slag was significantly lower than  $\text{SiO}_2$ , which might be caused by a not yet dissolved layer of CaO-FeO (layers excluded from bulk slag determination).

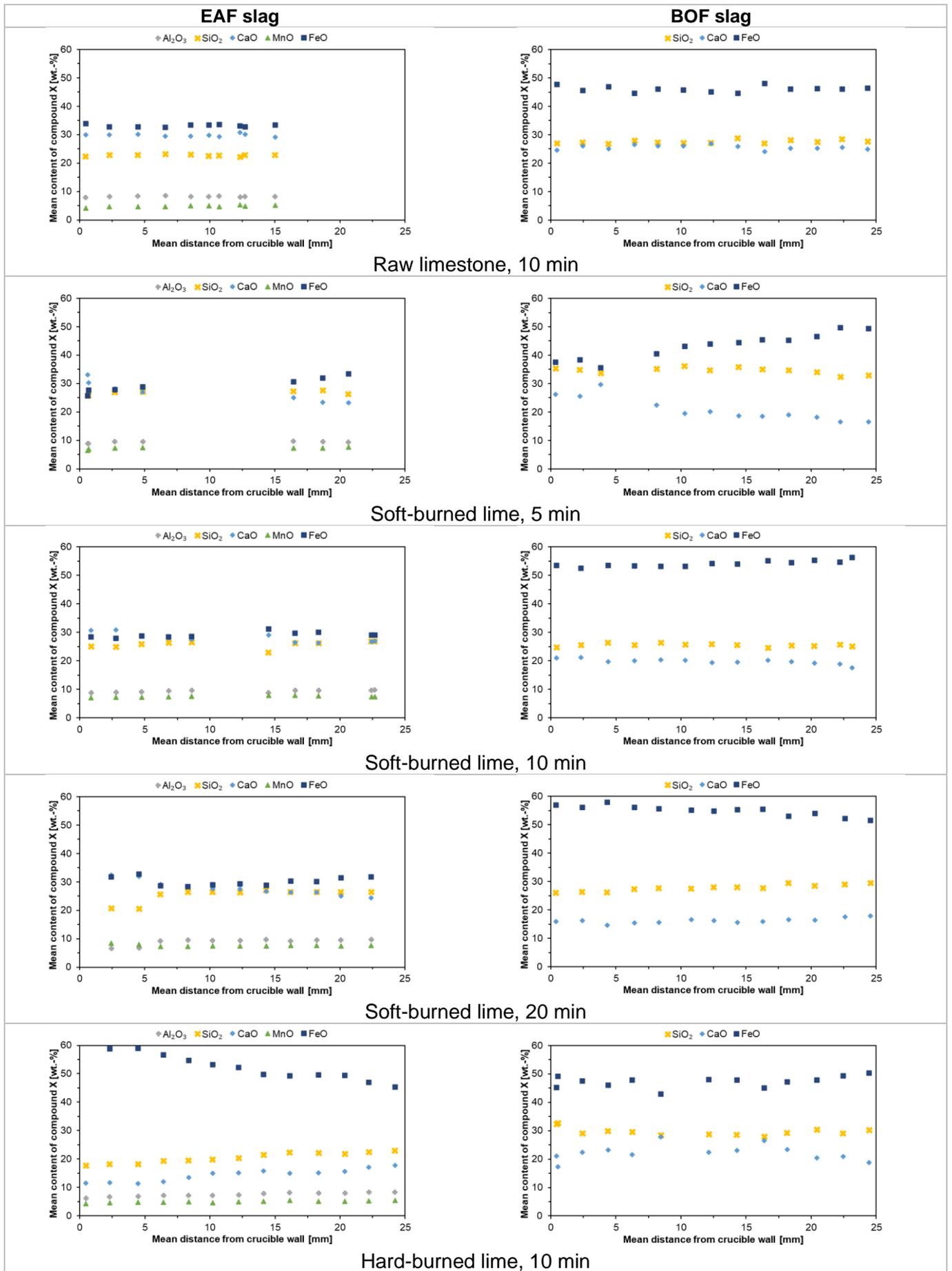


Figure 1: Concentration profiles of the slag oxides  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{MnO}$  and  $\text{FeO}$  along the cross-section after dissolution tests of limestone and lime samples

Material	Reaction time [min]	EAF slag		BOF slag	
		$B_2$ , actual [-]	$B_2$ , target [-]	$B_2$ , actual [-]	$B_2$ , target [-]
Raw limestone	10	1.32	1.48	0.93	0.92
Soft-burned lime	5	1.03	1.46	0.60	0.92
Soft-burned lime	10	1.10	1.46	0.78	0.90
Soft-burned lime	20	1.10	1.46	0.59	0.89
Hard-burned lime	10	0.71	1.53	0.75	0.95

Table 2: Calculated slag basicity of analysed and target compositions

In BOF slag test with hard-burned lime, the CaO was lower than SiO<sub>2</sub>; however, the difference was not as high as for soft-burned lime at the lower reaction time of 5 min. For better comparability of dissolution test results, the slag parameter basicity was introduced because of its independency of FeO. **Table 2** summarised the basicity values  $B_2$  of all tests as well as the related theoretical target basicity, which was calculated based on the composition of sample, its mass as well as under the assumption of complete material dissolution (cf. **Equation (1) and (2)**).

**Figure 2** visualised the slag basicity after the high-temperature dissolution experiments in EAF and BOF slags, whereas the height of the bars represented the ratio of actual to target basicity. As estimated by the distance of CaO and SiO<sub>2</sub> levels in concentration profiles of raw limestone samples, high amounts of the samples dissolved in EAF and BOF slags, since 89 % and 102 % of the target basicity were reached. In fact, more than 100 % were not possible but it resulted from the uncertainties in EDX analysis of oxide contents with i.e. lowered contents of MnO and Al<sub>2</sub>O<sub>3</sub> in this experiment. Due to the calcination to soft- and hard-burned lime the relative basicity decreased. As postulated by Chen et al. [8], CO<sub>2</sub> bubbles generated by limestone decomposition could improve the CaO dissolution because the rate of mass transfer-controlled reactions was enhanced by stirring. With increasing reaction time, the basicity ratio of EAF slags after soft-burned lime dissolution raised. However, there was a kind of plateau reached

after 10 min as no significant rise between 10 min and 20 min was determined. Regarding the BOF slag experiments, the difference in CaO uptake between 5 min and 10 min was even more considerable. As mentioned before, the results of the soft-burned lime in BOF slag and 20 min dissolution period were not reliable. Thus, a decline in basicity ratio compared to 10 min reaction time was observed. Concerning the dependency on calcination condition, an explicit trend of the basicity ratio decreasing from raw limestone, via soft-burned lime to hard-burned lime was determined for both slags. Nevertheless, the basicity of the EAF slag after hard-burned lime specimen dissolution was too low, even lower than the start basicity resulting in the relative ratio of 46 %. As the drop of the relative basicity ratio between raw limestone and soft-burned lime was quite the same in EAF and BOF slag (delta of 14 % and 15 %), the theoretical ratio for hard-burned lime in EAF should be somewhere between 66 % and 68 %; hence  $B_2$  would range from 1.01–1.04. With a start value of 1.00 in EAF slag, there would have been quasi no lime dissolution in the static test setup. Additionally, differences in the dissolution behaviour were recognised due to slag compositions. Deng et al. [4] assumed, that an increasing basicity forced a higher CaO saturation limit and thus, the better limestone/lime dissolution in the slag. Thermodynamic calculations of ternary and pseudo-ternary phase diagrams using FactSage™ 7.3 showed that the manganese and aluminium oxide additions shifted the boundaries of solid precipitates

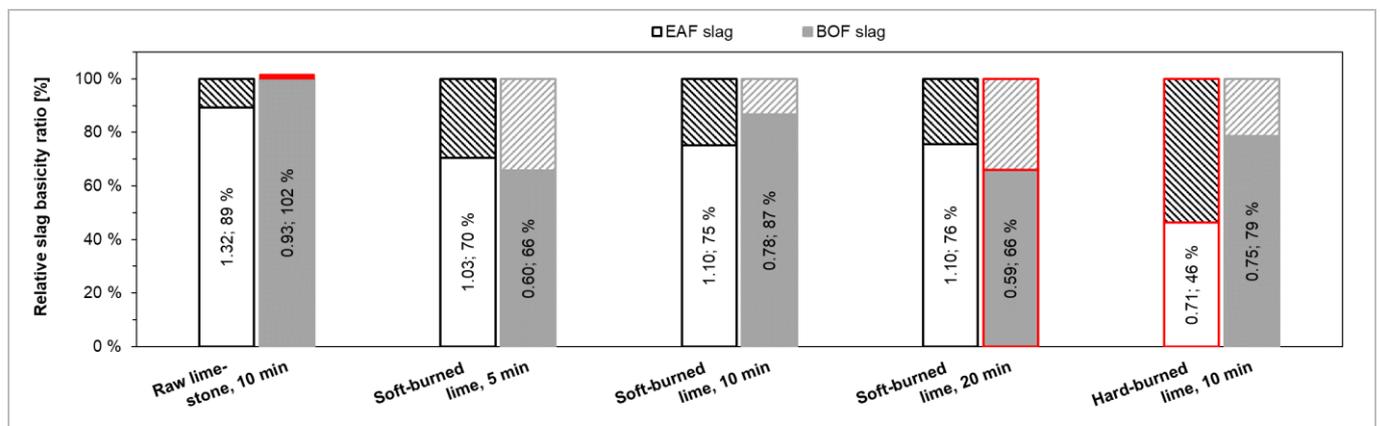


Figure 2: Comparison of relative basicity ratios in EAF and BOF slags; labels showing the calculated actual basicity  $B_2$  as well as the percentage of target basicity

towards the CaO corner in phase diagram. Hence, there should have been a higher driving force for limestone/lime dissolution in EAF slag. Nevertheless, FeO and MnO, acting as fluxing agents and infiltrating the pores and cracks of samples, influenced the dissolution of specimens. The start FeO concentration of BOF slag was higher than the sum of FeO and MnO in EAF slag. Furthermore, the lower start concentration of CaO in BOF slag resulted in higher CaO uptake by dissolution and thus, higher relative basicity ratios. The effect of the lower temperature in experiments with BOF slag (1,400 °C) compared to the EAF slag (1,450 °C) was negligible.

## Conclusion

In static high-temperature experiments utilising EAF and BOF slags, the influences of calcination condition on dissolution of limestone-based specimens were tested. The reaction time variations with soft-burned lime indicated the significant increase of relative basicity ratio from 5 min to 10 min, whereas the dissolution stagnated or even decreased after 20 min. Thus, the reaction time was fixed to 10 min for raw limestone and hard-burned lime.

The most significant increase in CaO content by sample dissolution was observed in trials of raw limestone, resulting in the highest relative basicity ratios. The CaO dissolution of soft-burned lime specimens was on medium levels, whereas the additional CaO uptake from hard-burned lime was low. The differences were caused by the in-situ decomposed calcium carbonates which led to a local stirring effect when raw limestone was immersed. In contrast, the higher porosity of soft-burned lime compared to hard-burned lime (particle sintering during calcination procedure) was beneficial regarding the infiltration of specimens with slag.

The initial slag composition effected the sample dissolution in opposite direction than expected from thermodynamic calculations, since the increment of CaO content in bulk slag and liquidus line as the driving force for dissolution was higher in EAF slag than in BOF slag. Hence, the enhanced relative basicity ratios in BOF slag resulted from the lower initial CaO amount and the higher fraction of fluxing FeO in slag, infiltrating the specimens.

## Abbreviations

B <sub>2</sub>	Basicity [-]
BOF	Basic oxygen furnace
C <sub>2</sub> S	Dicalcium silicate
EAF	Electric arc furnace
EDX	Energy dispersive x-ray spectroscopy
m <sub>sample</sub>	Initial sample mass [g]

m <sub>slag</sub>	Start slag mass [g]
SEM	Scanning electron microscopy
W <sub>ox., sample</sub>	Oxide content in specimen [wt.-%]
W <sub>ox., slag</sub>	Oxide content in start slag [wt.-%]
W <sub>ox., target</sub>	Target concentration of oxide in slag after complete dissolution [wt.-]

## Acknowledgments

We thank the Lhoist Business Innovation Center for funding the research and preparation of testing samples. Further financial support is gratefully acknowledged by K1-MET. The research programme of the K1-MET competence center is supported by COMET (Competence Center for Excellent Technologies), the Austrian programme for competence centers. COMET is funded by the Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology, the Federal Ministry for Digital and Economic Affairs, the Federal States of Upper Austria, Tyrol and Styria as well as the Styrian Business Promotion Agency (SFG) and the Standortagentur Tyrol. Furthermore, Upper Austrian Research gives continuous support. Beside public funding from COMET, K1-MET is partially financed by company and scientific partners.

## References

- [1] Sun, Z. H. I. et al.: Phase evolution and nature of oxide dissolution in metallurgical slags; *AIChE J.*, Vol. 59, No. 8 (2013), P. 2907–2916
- [2] Amini, S. H. et al.: Effects of Additives and Temperature on Dissolution Rate and Diffusivity of Lime in Al<sub>2</sub>O<sub>3</sub>-CaO-SiO<sub>2</sub> Based Slags; *Metall Mater Trans B*, Vol. 37B (2006), P. 773–780
- [3] Hamano, T.; Horibe, M.; Ito, K.: The Dissolution Rate of Solid Lime into Molten Slag Used for Hot-metal Dephosphorization; *ISIJ Int.*, Vol. 44, No. 2 (2004), P. 263–267
- [4] Deng, H. et al.: Dissolution behaviour of limestone in converter slag: evolution of microstructure and reaction interface; *Ironmak. Steelmak.*, Vol. 30, No. 2 (2019), P. 1–7
- [5] Umakoshi, M.; Mori, K.; Kawai, Y.: Dissolution rate of burnt dolomite in molten FeO-CaO-SiO<sub>2</sub> slags; *ISIJ Int.*, Vol. 24, No. 7 (1984), P. 532–539
- [6] Nispel, M. et al.: Successful Application of Lhoist's Innovative Lime Based Slag Conditioner in the BOF Process at Dillinger. Proceedings of 4<sup>th</sup> ESTAD, (2019)

[7] Martinsson, J.; Glaser, B.; Sichen, D.: Lime Dissolution in Foaming BOF Slag; Metall Mater Trans B, Vol. 49, No. 6 (2018), P. 3164–3170

[8] Chen, M. et al.: Limestone Dissolution in Converter Slag: Kinetics and Influence of Decomposition Reaction; ISIJ Int., Vol. 58, No. 12 (2018), P. 2271–2279

[9] Hamano, T.; Fukagai, S.; Tsukihashi, F.: Reaction Mechanism between Solid CaO and  $\text{FeO}_x$ –CaO–

$\text{SiO}_2$ – $\text{P}_2\text{O}_5$  Slag at 1 573 K; ISIJ Int., Vol. 46, No. 4 (2006), P. 490–495

[10] Deng, T.; Gran, J.; Sichen, D.: Dissolution of Lime in Synthetic 'FeO'- $\text{SiO}_2$  and CaO-'FeO'- $\text{SiO}_2$  Slags; Steel Res. Int., Vol. 81, No. 5 (2010), P. 347–355

## Copyright

Copyright of all material published in the 5<sup>th</sup> ESTAD 2021 Proceedings passes over to Jernkontoret.