Static dissolution evaluation of dolomite-based materials in EAF-type slag

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K1-MET at a glance

Motivation - Development of resource intensive processes

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K1-MET – Competence Center for Excellent Technologies in Advanced Metallurgical and Environmental Process Development
➔ Austrian funded research program

Current funding phase 2019–2023
Budget of this phase: 22.7 M€

Financing: 45 % public funding

- **30 % Governmental funding**
- **15 % Federal states Upper Austria, Styria, Tyrol**
- **5 % Scientific partners**
- **50 % Industrial partners**

Currently 75 employees

- **Thereof 65 researchers (master and PhD students, post-docs, Senior Experts)**

Locations

- **Linz**
- **Leoben**

K1-MET at a glance

Research Areas

Four symbiotic areas:

- **Area 1: Raw Materials and Recycling**
  Endeavours the best possible utilisation of all resources and searches for residue treatment and recycling solutions
- **Area 2: Metallurgical Processes**
  Unites the core topics of metallurgical process developments
- **Area 3: Low Carbon Energy Systems**
  Is dedicated to the developments of carbon-lean steel production
- **Area 4: Simulation and Analyses**
  Represents the enveloping area for numerical developments and data analyses

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Introduction

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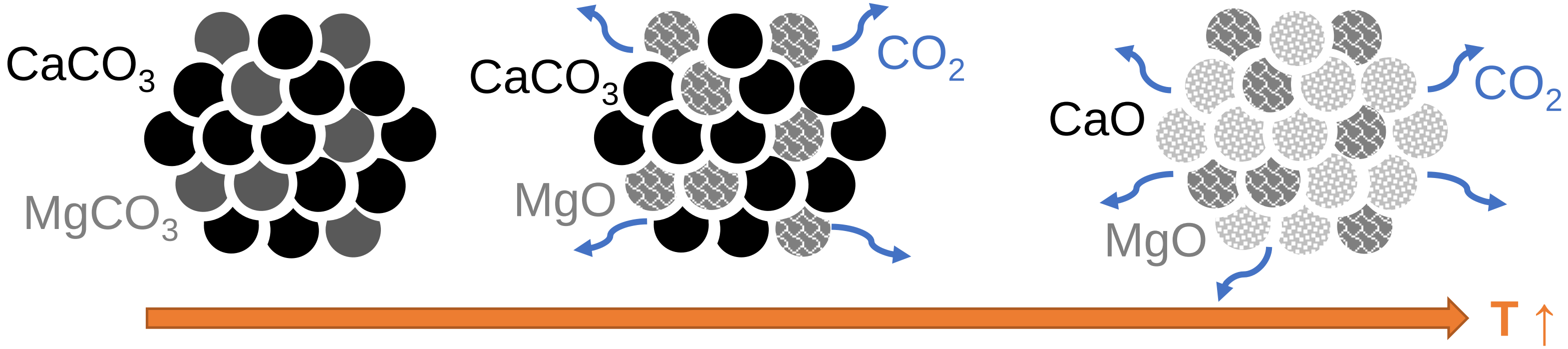
- **Basic additives to adapt slag chemistry and enable refining**
- **Advantages of dolomite-based materials due to MgO saturation**

- **Stepwise calcination of $CaMg(CO_3)_2$ to MgO (600–700 °C) and CaO (700–900 °C)**



- **Cracks and pores resulting from decomposition**
- **Heat losses because of transport to steelmaking industry**

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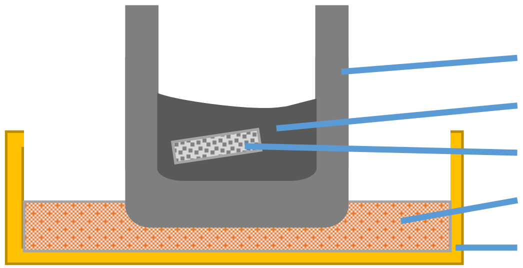
Experimental setting

High-temperature static dissolution investigation

- **Heating of Gero vertical high-temperature furnace to 1,450 °C under N_2 atmosphere**
- **Mixing of chemically pure oxides according to target composition**
- **Melting of EAF slag at target temperature in the pure iron crucible**
- **Insertion of dolomite-based samples of varying composition and calcination condition**
- **Isothermal reaction duration fixed to 10 min**
- **Disc sample not extracted at the end of dissolution test**
- **Quenching of crucible, slag and immersed sample in liquid nitrogen**

EAF slag	MgO	Al_2O_3	SiO_2	CaO	MnO	FeO
Oxide [wt.-%]	–	10	25	25	8	32

	Raw 1	Raw 2
	Soft-burned 1	Soft-burned 2
	Hard-burned 1	Hard-burned 2



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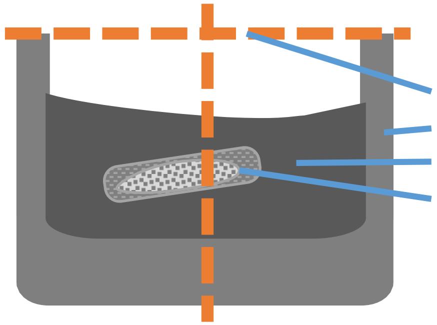
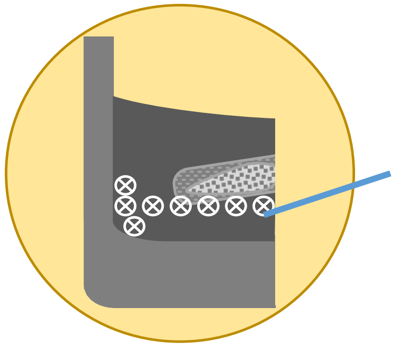
Methodology of slag chemistry determination

From EDX analysis to oxide profiles and bulk slag chemistry

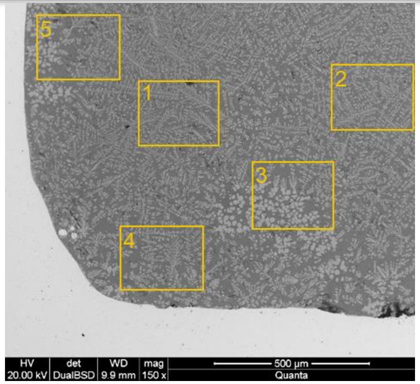
- **Water-free cutting and metallographic preparation of embedded slags**
- **SEM/EDX analysis using FEI QUANTA 200 in low vacuum mode**
- **Pure iron crucible as reference position**
- **Multiple small area analyses (270 µm by 200 µm) of bulk slag on images in periodical distances of 2 mm**
- **Exclusion of interfacial layers and remaining undissolved sample pieces**
- **Calculation of mean oxide composition per image and plot of concentration profile**
- **Brittle behaviour of slag and thermal stresses cause material losses during cutting and grinding → cracking and crumbling of slag**
- **Total mean value of all chemistries in the plot for examination of dissolution behaviour dependent on calcination condition**



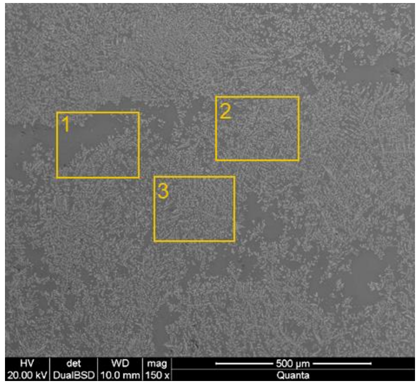


Extract from SEM/EDX analyses of raw dolomite 1

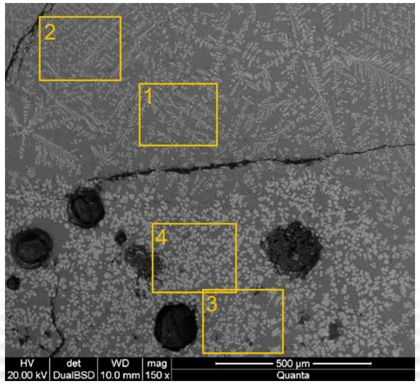
Selection of bulk slag areas without morphology changes



Oxide [wt.-%]	MgO	Al_2O_3	SiO_2	CaO	MnO	FeO
1	4.3	8.3	23.6	26.9	5.3	31.5
2	4.2	8.5	23.7	26.1	5.7	31.7
3	5.8	7.9	20.5	21.9	6.0	37.8
4	4.5	8.3	22.5	24.5	5.2	34.9
5	4.8	8.0	22.3	25.0	5.2	34.8



Oxide [wt.-%]	MgO	Al_2O_3	SiO_2	CaO	MnO	FeO
1	3.7	9.2	26.3	27.8	5.3	27.7
2	4.2	8.2	23.0	24.3	6.1	34.2
3	4.0	8.2	23.9	25.0	6.0	32.9



Oxide [wt.-%]	MgO	Al_2O_3	SiO_2	CaO	MnO	FeO
1	5.1	8.4	24.3	26.2	5.9	30.1
2	4.7	8.5	24.1	27.0	5.2	30.4
3	9.3	7.7	21.3	22.3	6.1	33.3
4	10.5	6.6	19.1	19.0	6.5	38.3

Pic.	Distance to wall	MgO	Al_2O_3	SiO_2	CaO	MnO	FeO
	[mm]	[wt.-%]					
1	0.7	4.5	8.3	23.0	25.6	5.4	33.2
2	0.5	4.2	8.7	23.3	26.4	5.8	31.5
3	2.6	4.3	8.6	23.8	27.5	5.6	30.2
4	4.4	4.0	8.7	24.1	25.7	6.0	31.5
5	6.5	3.8	9.1	25.4	27.4	5.7	28.6
6	8.6	3.9	8.6	24.4	25.7	5.8	31.6
7	10.6	4.2	8.3	23.7	25.2	5.9	32.8
8	12.5	4.2	8.5	23.6	25.8	6.0	32.1
9	14.6	4.3	8.5	23.5	26.0	5.9	31.7
10	16.7	4.4	8.5	24.1	27.0	5.6	30.4
11	18.6	4.5	8.4	23.6	27.3	5.7	30.5
12	20.6	4.3	8.6	24.4	28.4	5.6	28.7
13	22.5	4.4	8.5	23.6	27.1	5.8	30.6
14	14.5	4.1	9.3	25.2	27.0	5.4	29.0
15	14.3	4.9	8.6	23.0	24.2	5.3	34.0
16	14.6	4.8	8.6	23.6	27.8	5.5	29.7
17	14.2	4.8	8.2	24.0	27.4	5.5	30.2
18	6.2	4.9	8.6	24.7	26.4	5.7	29.7
20	5.0	5.2	8.4	24.0	25.9	5.8	30.8
22	6.5	4.9	8.5	24.2	26.6	5.5	30.3
Total mean value		**4.4**	**8.6**	**24.0**	**26.5**	**5.7**	**30.8**
Standard deviation		**0.4**	**0.2**	**0.6**	**1.0**	**0.2**	**1.5**

Original slag: $0MgO-10Al_2O_3-25SiO_2-25CaO-8MnO-32FeO$

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Bulk slag oxide concentrations

Distribution profiles as well as average amounts of MgO and CaO

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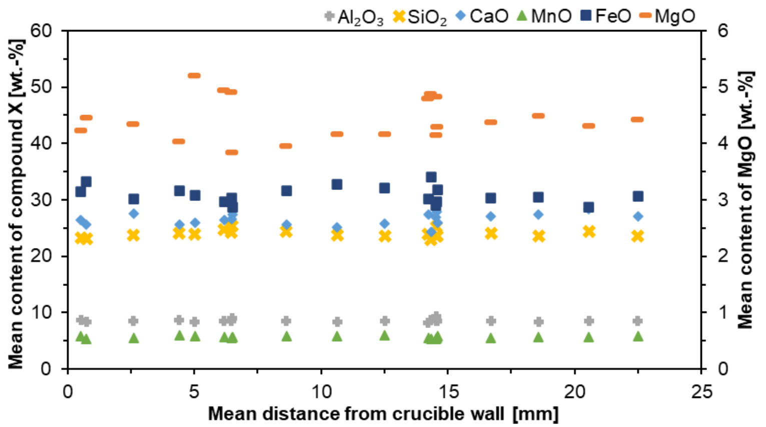
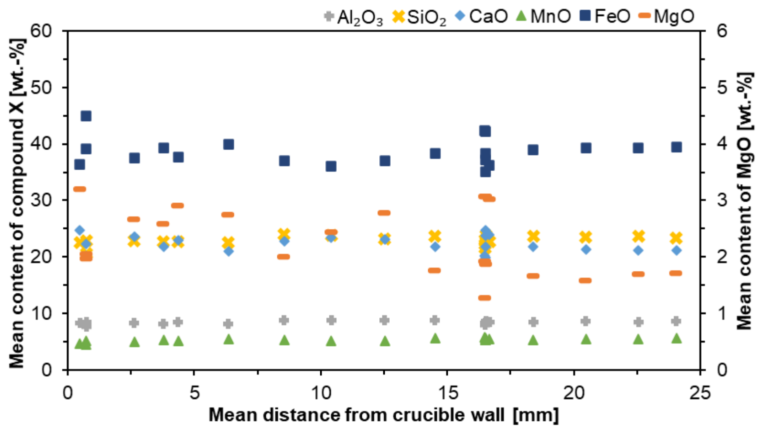


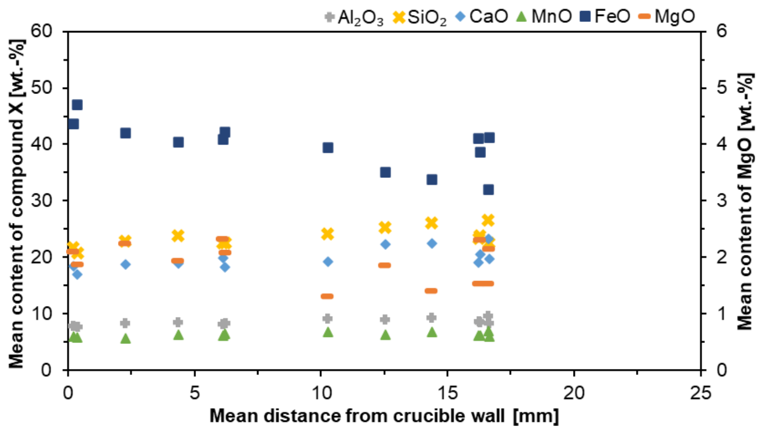
Raw dolomite 1

4.4 wt.-% MgO; 26.5 wt.-% CaO



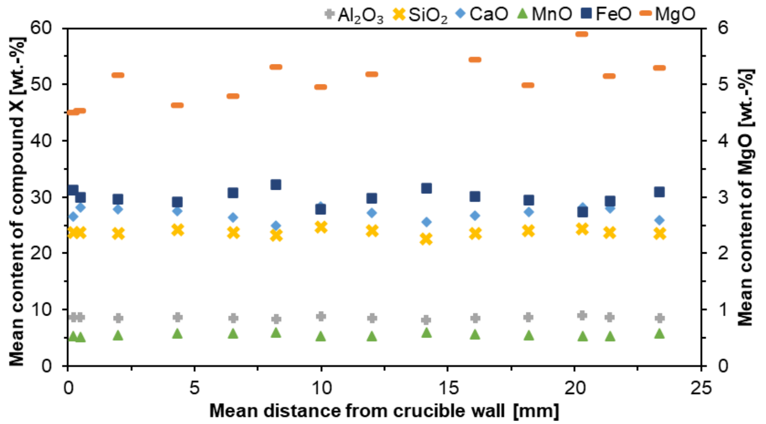
Soft-burned dolomite 1

2.3 wt.-% MgO; 22.3 wt.-% CaO



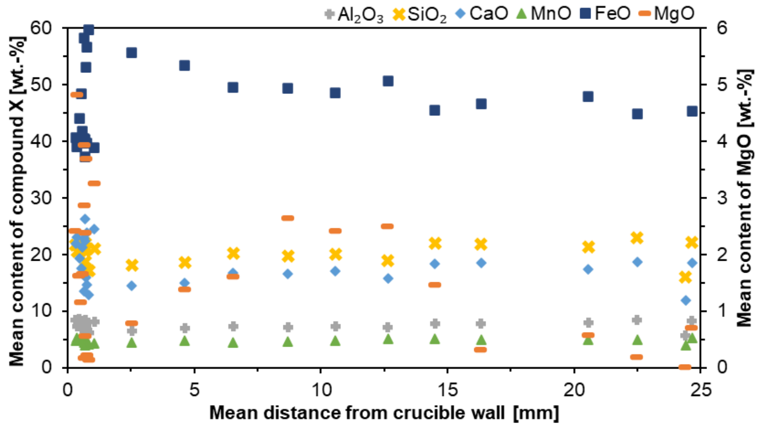
Hard-burned dolomite 1

1.9 wt.-% MgO; 19.8 wt.-% CaO



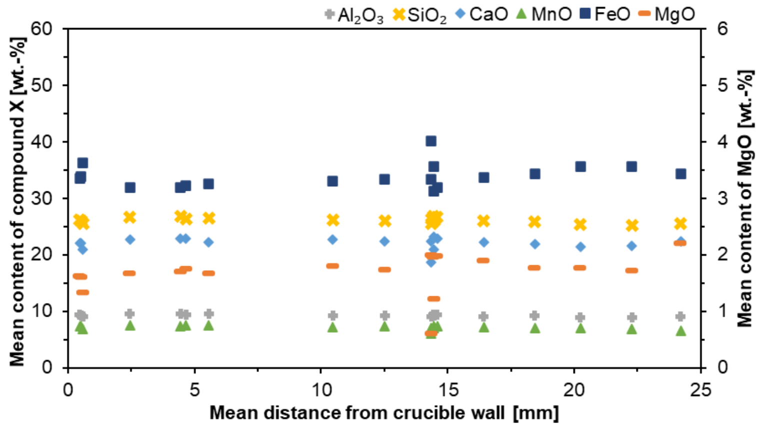
Raw dolomite 2

5.1 wt.-% MgO; 27.0 wt.-% CaO



Soft-burned dolomite 2

1.6 wt.-% MgO; 18.4 wt.-% CaO



Hard-burned dolomite 2

1.7 wt.-% MgO; 22.0 wt.-% CaO

Original slag: $0MgO-10Al_2O_3-25SiO_2-25CaO-8MnO-32FeO$

Comparison of dolomite dissolution

Influences of calcination conditions raw, soft- and hard-burned

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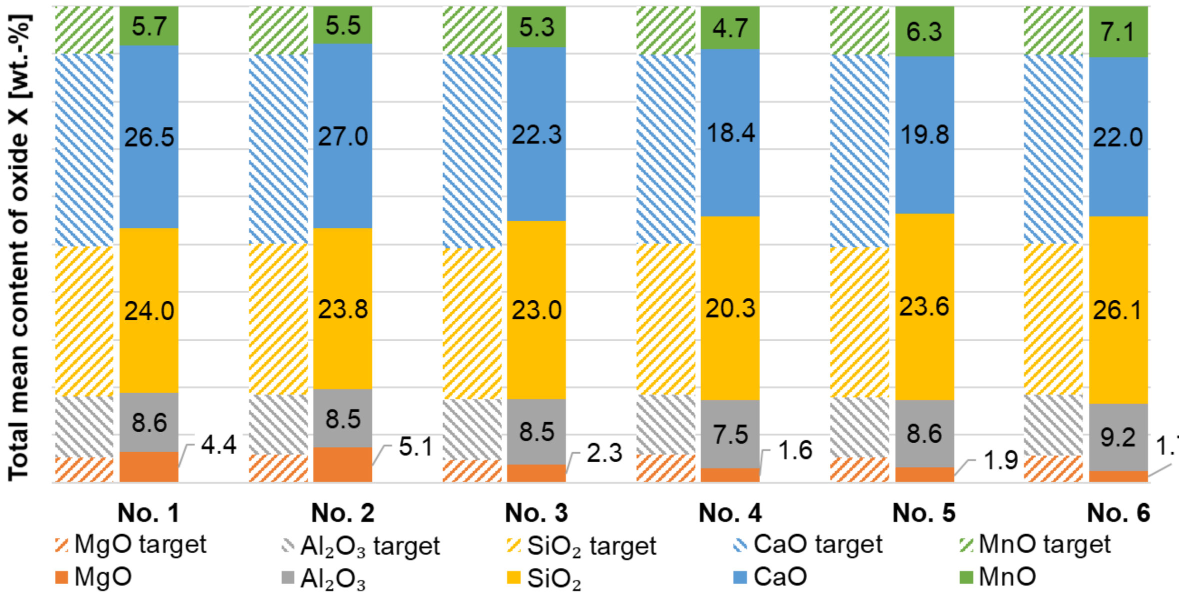
- **Excluding the FeO for comparison of dissolution behaviour**
- **Raw dolomite samples exceeded the MgO target and more than 95 % of CaO dissolved**
- **Decrease to relative levels of 78 % MgO and 89 % CaO for soft-burned dolomite 1**
- **Very high FeO content in test no. 4 suppressed other oxides in analyses (cf. Al_2O_3 and MnO; 52 % MgO and 88 % CaO dissolved)**
- **MgO level of hard-burned dolomite 1 higher than of hard-burned dolomite 2 (60 % vs. 44 %), opposite effect for CaO (81 % vs. 84 %)**



No.	Dolomite condition	Target content of oxide X [wt.-%]					
		MgO	Al_2O_3	SiO_2	CaO	MnO	FeO
1	Raw 1	3.8	9.0	22.5	28.8	7.2	28.7
2	Raw 2	4.2	9.0	22.5	28.3	7.2	28.8
3	Soft-burned 1	3.4	9.0	22.6	28.9	7.2	28.8
4	Soft-burned 2	4.2	9.0	22.5	28.3	7.2	28.8
5	Hard-burned 1	3.7	9.0	22.5	28.9	7.2	28.7
6	Hard-burned 2	4.1	9.0	22.6	28.2	7.2	28.9

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Conclusions

- The raw dolomite materials dissolved quickly, as the resulting MgO concentrations were high (no MgO in starting slag composition).
- Additionally, the CaO contents were above the SiO_2 amounts, indicating additional CaO uptake from specimens.
- It was assumed that in-situ decomposing carbonates caused local stirring effects.
- The fluctuations in tests of soft- and hard-burned dolomites could indicate a slower dissolution with missing time for concentration balancing.
- The dissolution of soft-burned dolomite 1 was on a medium level, whereas the massive amount of FeO in trial with soft-burned dolomite 2 impeded a comparable evaluation of dissolution behaviour.
- The hard-burned dolomite materials showed reduced MgO and CaO dissolution, which might be caused by lower sample porosity due to sintering of particles during calcination.

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