Utilization of recovered refractory material as slag additive and experimental determination of liquid sla properties

Alexander Halwax [a], Irmtraud Marschall [a], Nina Schlemmer [a],

Florian Kek [b], Christian Weiß [c], Simon Moll [c], Jan Eisbacher-Lubensky [d]

[a] K1-MET GmbH
[b] RHI Magnesita
[c] Chair of Process Technology and Industrial Environmental Protection, Montanuniversitaet Leoben
[d] Chair of Ferrous Metallurgy, Montanuniversitaet Leoben

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PRIMETALS TECHNOLOGIES

Introduction

To meet the European Commission's Green Deal climate target:

Existing processes need to be optimized to reduce greenhouse gas emissions

Slag metallurgy is a key factor, as slags have a significant influence on process efficiency.

State of the art:

addition of usually CaO- and MgO-containing slag additives allows adjustment of the slag composition for optimum process operation

To save resources and reduce CO_2 emissions:

use of secondary metallurgical additives (recycled refractories)

Investigated properties:

- Diffusion coefficient
- Activity
- Dissolution behaviour of secondary metallurgical additives in the slag
- Viscosity
- Electrical conductivity

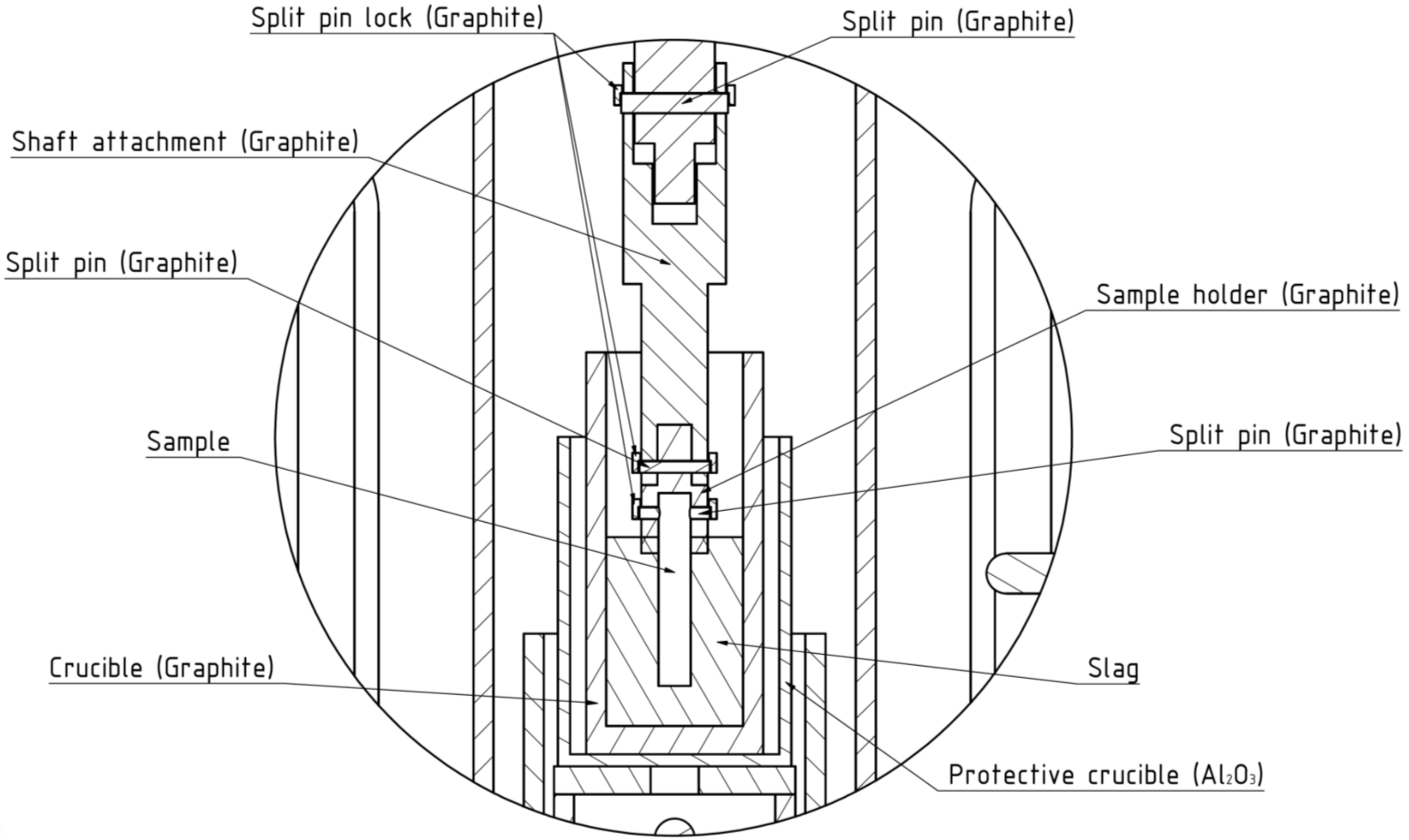
Determination of diffusion coefficients

Method

Rotating cylinder method

- Post-mortem analysis
- Effective boundary layer thickness defined and adjustable
- Experimental conditions are exactly reproducible

Experimental setup for dissolution tests in FeO-free slags



A. Halwax, Measurement of diffusion and activity coefficients in slags. PhD Thesis, Leoben (2024).

Determination of diffusion coefficients

Calculation model

metallurgical competence center

$$0.42 \cdot l \cdot \left(\frac{R_1}{\nu \cdot (R_2 - R_1)}\right)^{\frac{1}{4}} \cdot D_{eff}^{\frac{3}{4}} + 0.62 \cdot \frac{R_1}{\nu^{\frac{1}{6}}} \cdot D_{eff}^{\frac{2}{3}} - \bar{j}_{tot} \cdot \frac{2 \cdot l + R_1}{\omega^{\frac{1}{2}}} \cdot \frac{1 + 0.566 \cdot B}{\rho_s \cdot B} = 0$$

$$B = \frac{w_s - w_0}{1 - w_s}$$

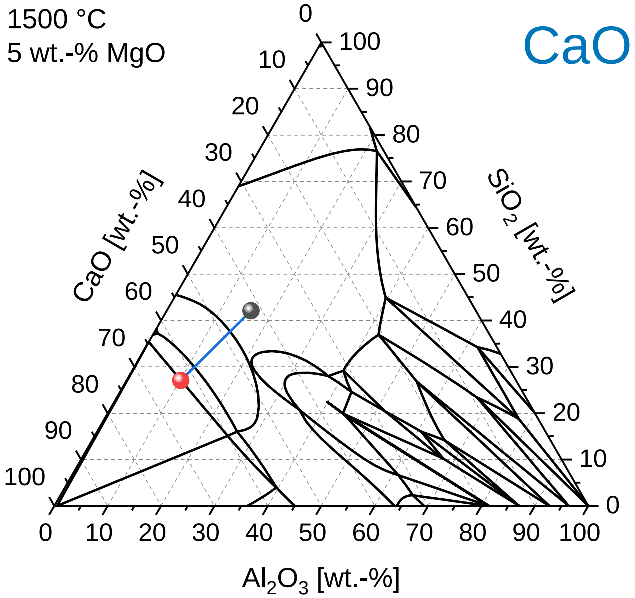
l	immersion length of sample	$\bar{j}_{tot}$	average mass flow density
R_1	radius of sample	ρ_s	slag density
R_2	inner radius of crucible	B	mass transfer parameter
D_{eff}	effective binary diffusion coefficient of dissolving substance	w_s	saturation concentration of slag for dissolving oxide
ν	kinematic viscosity of slag	w_0	concentration of slag for dissolving oxide

A. Halwax, Measurement of diffusion and activity coefficients in slags. PhD Thesis, Leoben (2024).

Results

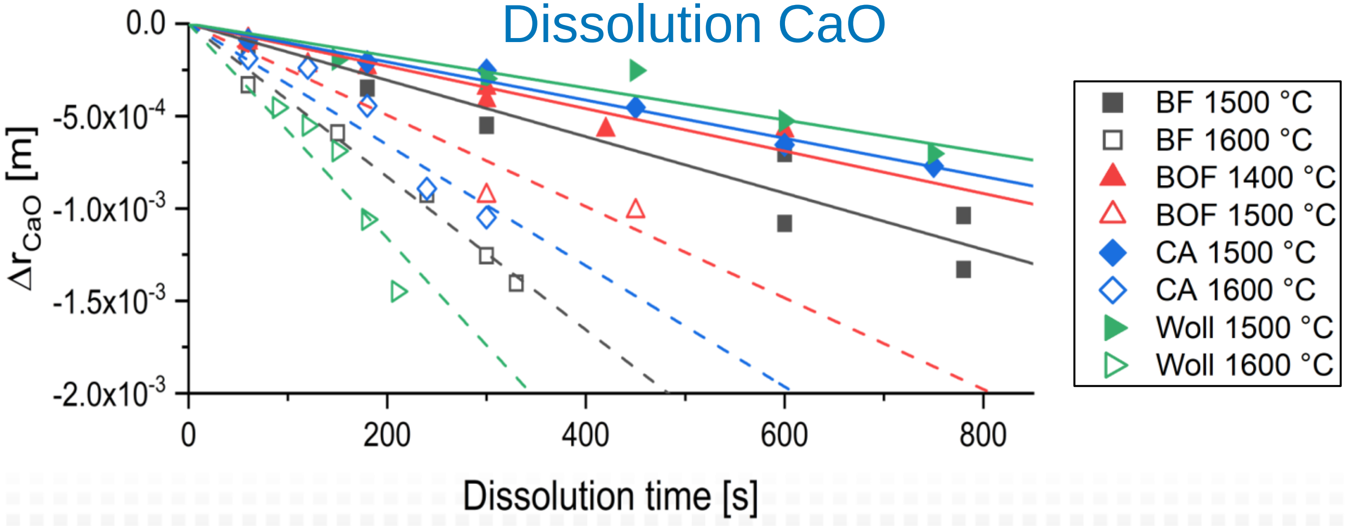
Diffusion coefficient

Slag	Composition [wt.-%]				
	SiO_2	CaO	Al_2O_3	MgO	FeO
BF	40	40	15	5	-
BOF	30	30	-	-	40
CA	5	50	45	-	-
Woll	45	40	15	-	-



CaO saturation (BF)

Dissolution CaO



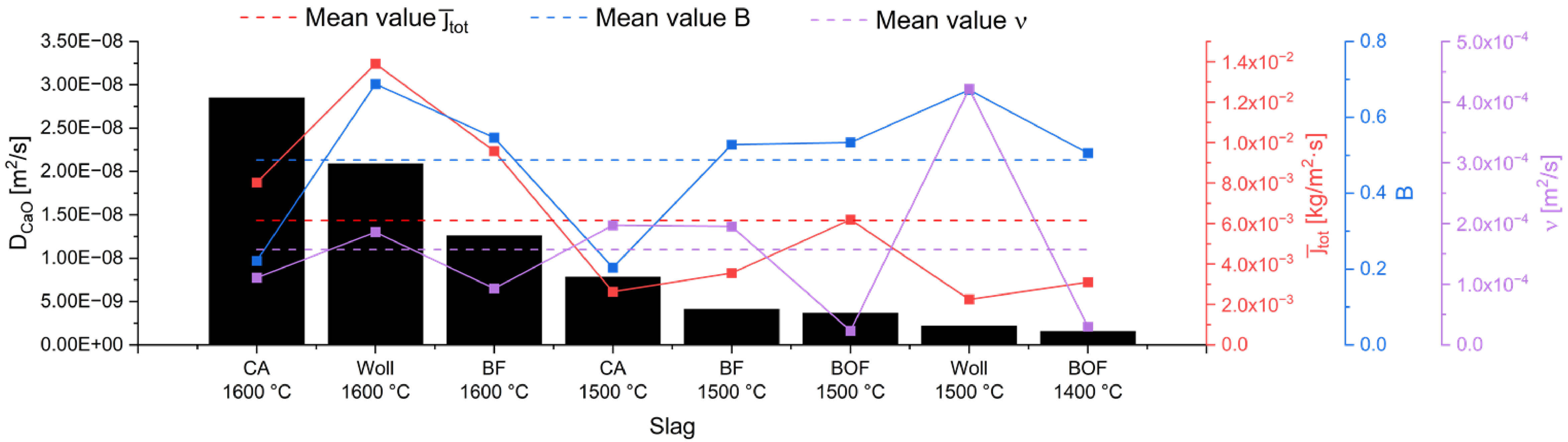
- Dissolution experiments of CaO provided these radius decreases as a function of the dissolution time,
- which were then used to calculate the mass flow densities.
- Dissolution rate in a slag increases with increasing temperature due to
  - decrease in slag viscosity
  - increasing saturation concentration

A. Halwax, Measurement of diffusion and activity coefficients in slags. PhD Thesis, Leoben (2024).

Results

Diffusion coefficient

CaO



- The general correlation is:
  - diffusion coefficient is high if
  - a high mass flow density is achieved at a low mass transfer parameter and a high slag viscosity.

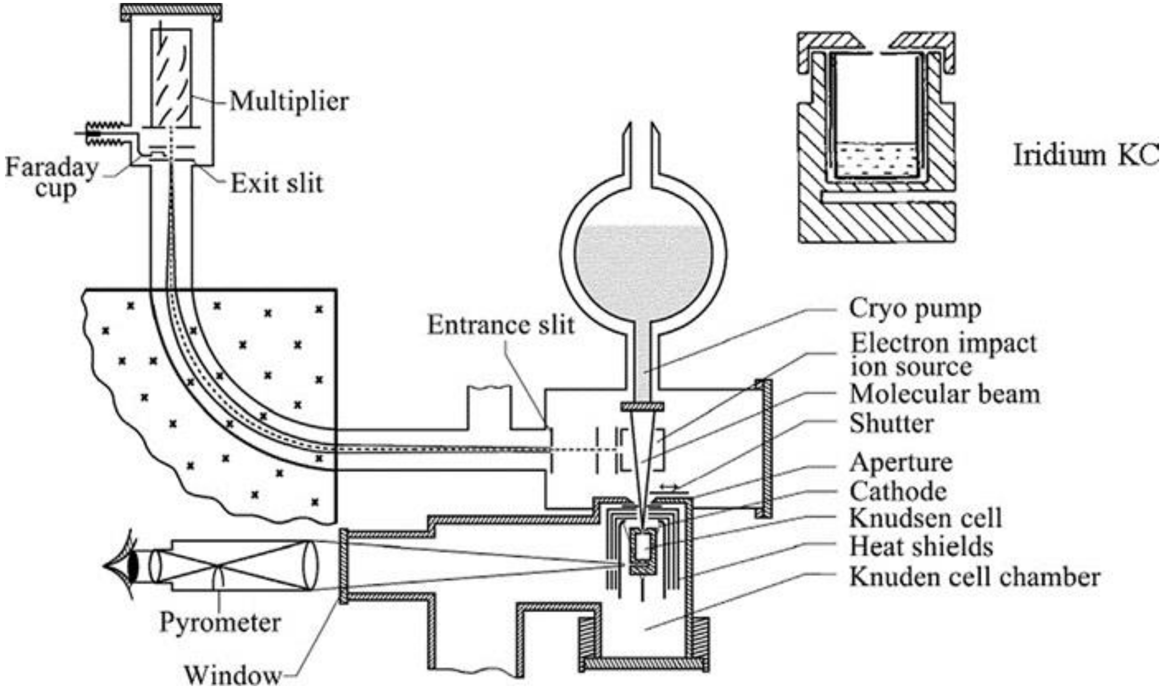
A. Halwax, Measurement of diffusion and activity coefficients in slags. PhD Thesis, Leoben (2024).

Determination of activities

Method

Knudsen Effusion Mass Spektrometry (KEMS)

Schematic setup of a KEMS]



$$a_i = \frac{p_i}{p_i^\circ} \qquad p_i = \frac{k I_i T f_i}{n_i \gamma_i \sigma_i}$$

a_i	activity of component i in a solution
p_i / p_i°	partial pressure of component i in solution / standard state
k	pressure calibration factor
I_i	ion intensity of species i
T	temperature
f_i	ratio of M^+ to $\sum M^+$
n_i	isotopic abundance
γ_i	multiplier factor
σ_i	ionization cross-section of species i

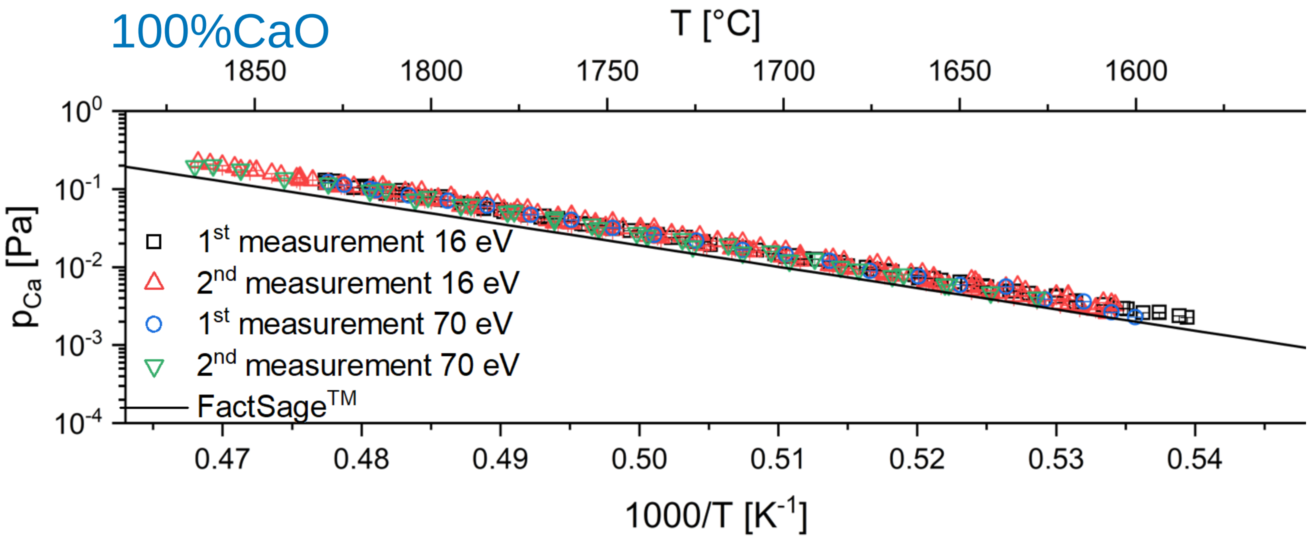
D. Kobertz, M. Müller and A. Molak, Vaporization and caloric studies on lead titanate. Calphad 46 (2014), pp. 62–79. doi:10.1016/j.calphad.2014.02.001

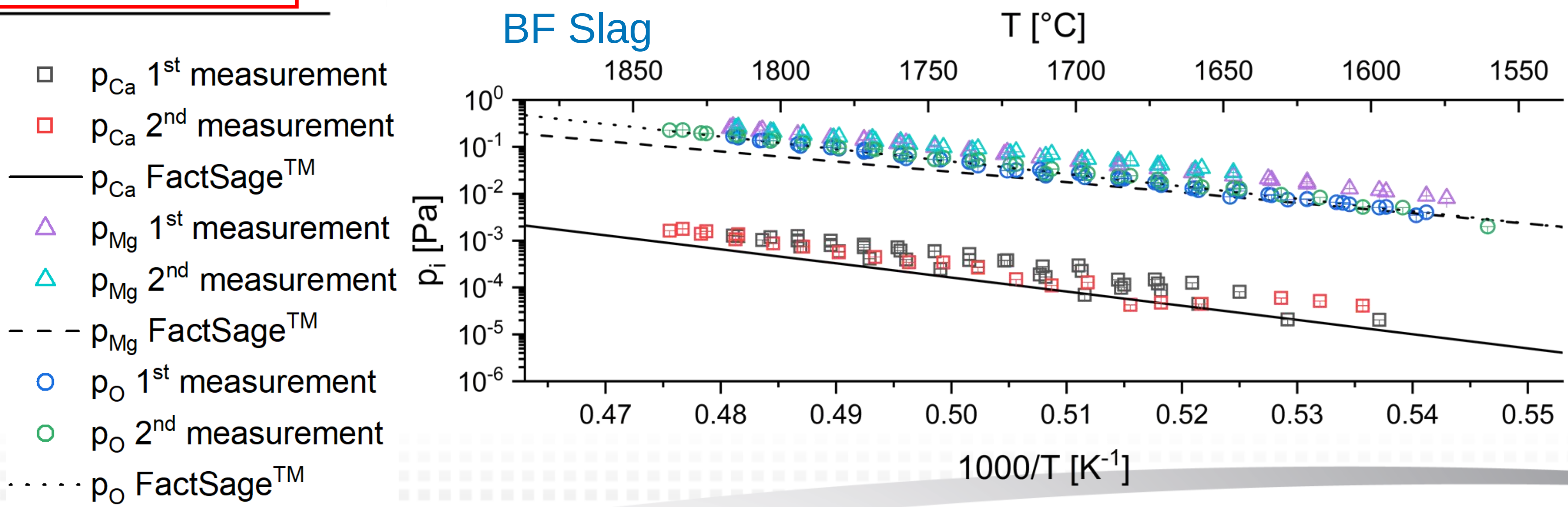
Results

Activity

Slag	Composition [wt.-%]				
	SiO_2	CaO	Al_2O_3	MgO	FeO
BF	40	40	15	5	-
BOF	30	30	-	-	40
CA	5	50	45	-	-
Woll	45	40	15	-	-
DS	15	50	30	5	-
DS sat.	12.8	56.7	25.5	5	-

$$a_i = \frac{p_i}{p_i^\circ}$$





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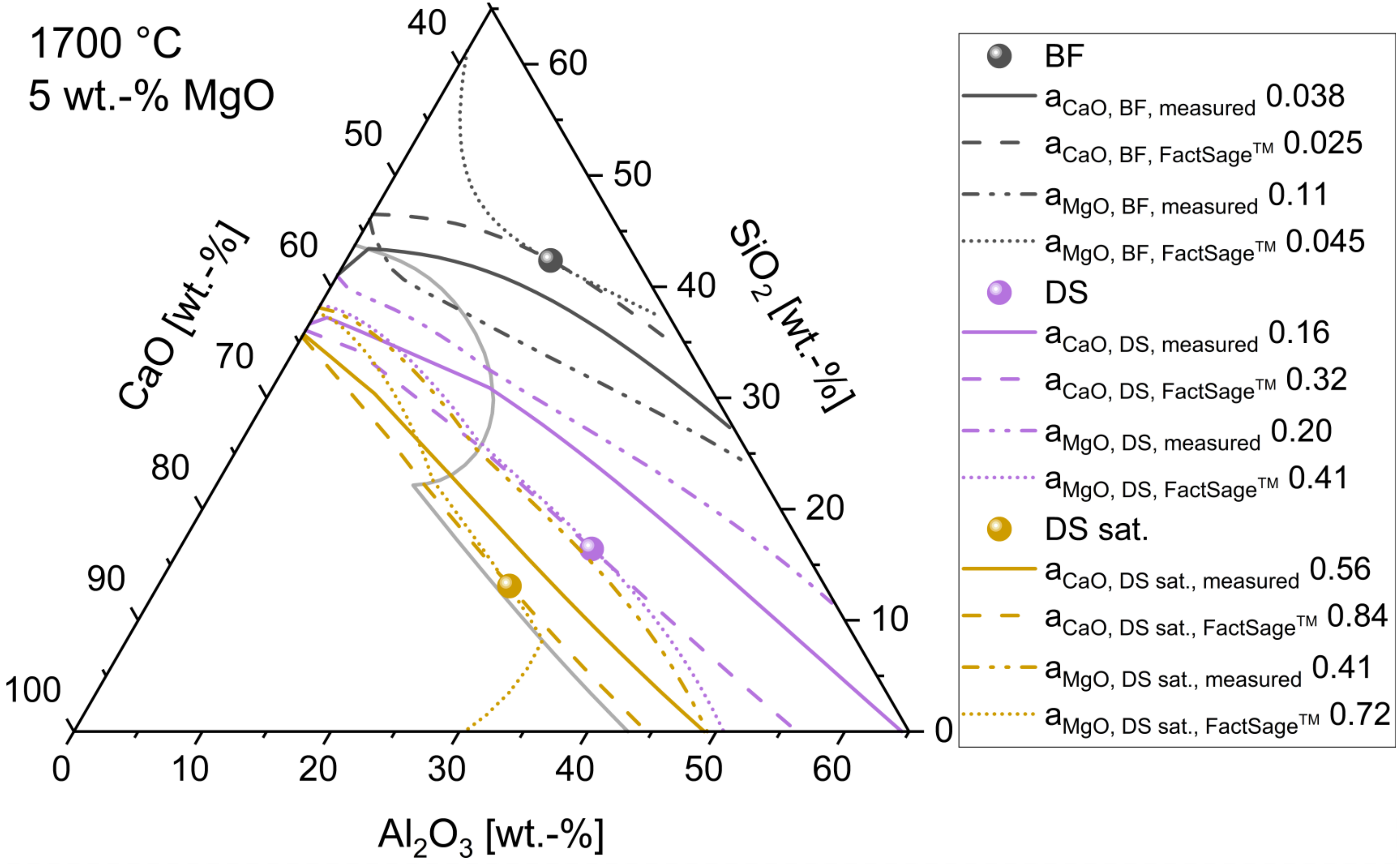
Results

Activity

Calculated isoactivity lines using FactSage



Δ Measured and FactSage values

Slag	Species	T range [°C]	Δa_i [-]	Δa_i [%]
BF	CaO	1500-1900	-0.0128	51
BF	MgO	1500-1900	-0.0643	149
BOF	CaO	1500-1900	0.0066	33
CA	CaO	1500-1900	0.0992	23
Woll	CaO	1500-1900	-0.0236	178
DS	CaO	1500-1900	0.1615	51
DS	MgO	1500-1900	0.2128	51
DS sat.	CaO	1600-1900	0.2944	38
DS sat.	MgO	1600-1900	0.2946	49

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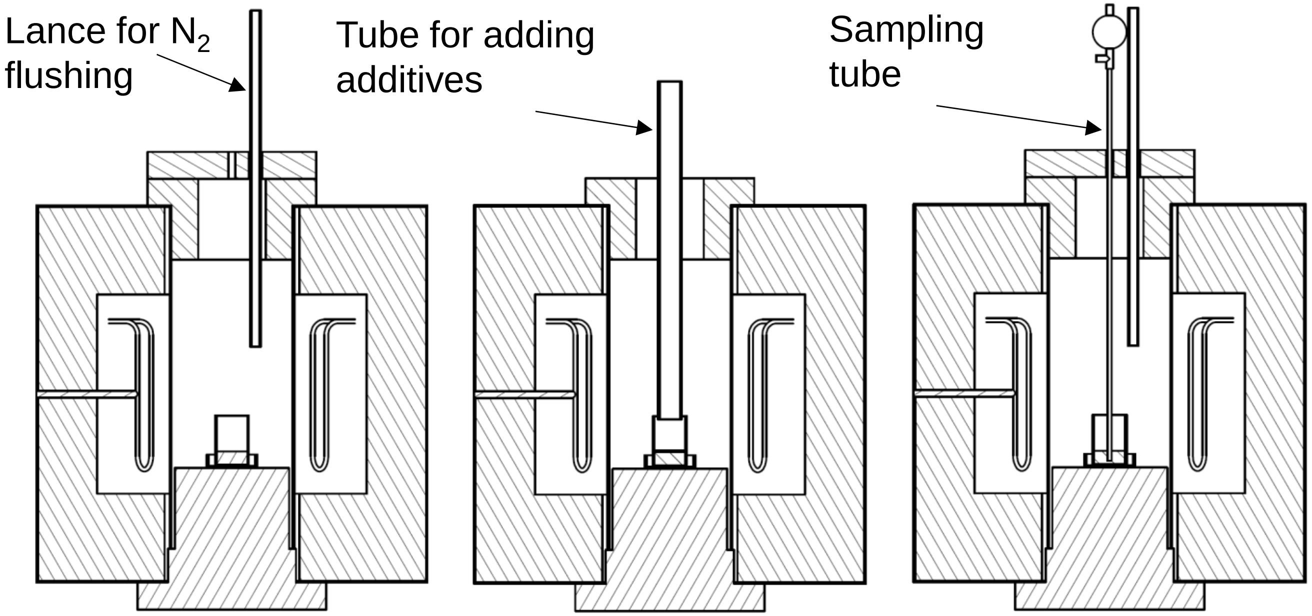
Determination of dissolution behaviour

Method

Melting of slag → Addittion of additive → Sampling



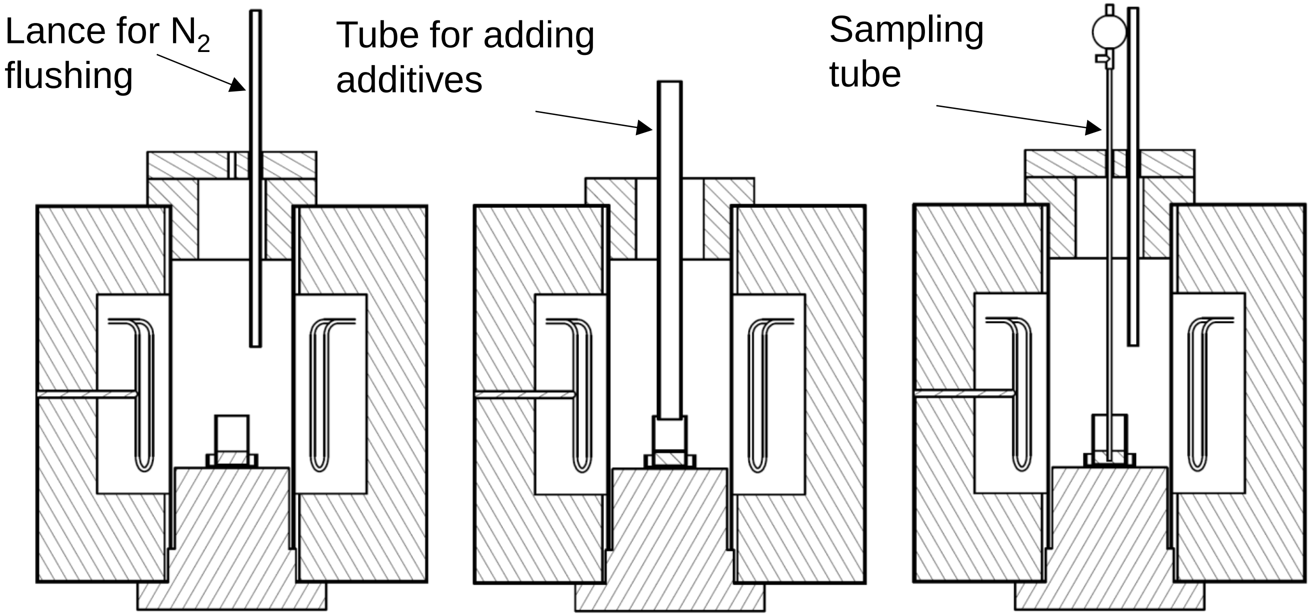
Slag	Composition [wt.-%]					
	SiO_2	CaO	Al_2O_3	MgO	FeO	MnO
BOF_1	15	43	0	4	30	7
BOF_2	23	36	32	6	1	1
Smelter	44	40	12	3	1	0

Additive	Composition [wt.-%]					
	SiO_2	CaO	Al_2O_3	MgO	FeO	TiO_2
CaAl-slag	1	25	71	3	0	0
TE80+Lime	9	21	64	3	2	2
Dololime	2	58	1	39	1	0
MgO75+Lime	2	56	2	39	2	0

Determination of dissolution behaviour

Method

Melting of slag → Addittion of additive → Sampling



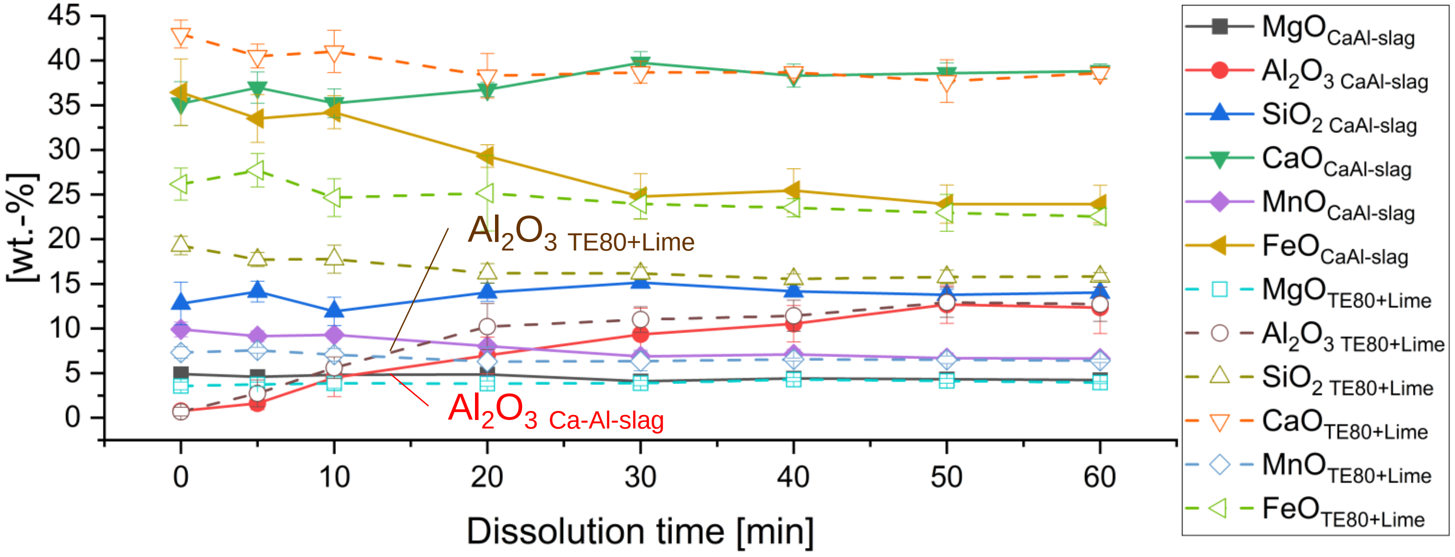
Slag + additive	Composition [wt.-%]					
	SiO_2	CaO	Al_2O_3	MgO	FeO	MnO
BOF_1+CaAl-slag	13	40	12	4	25	6
BOF_1+TE80+Lime	14	39	11	4	25	6
BOF_2+CaAl-slag	20	35	39	6	0	0
BOF_2+TE80+Lime	22	35	38	6	0	0
Smelter+Dololime	40	44	9	7	0	0
Smelter+MgO75+Lime	44	40	12	3	1	0

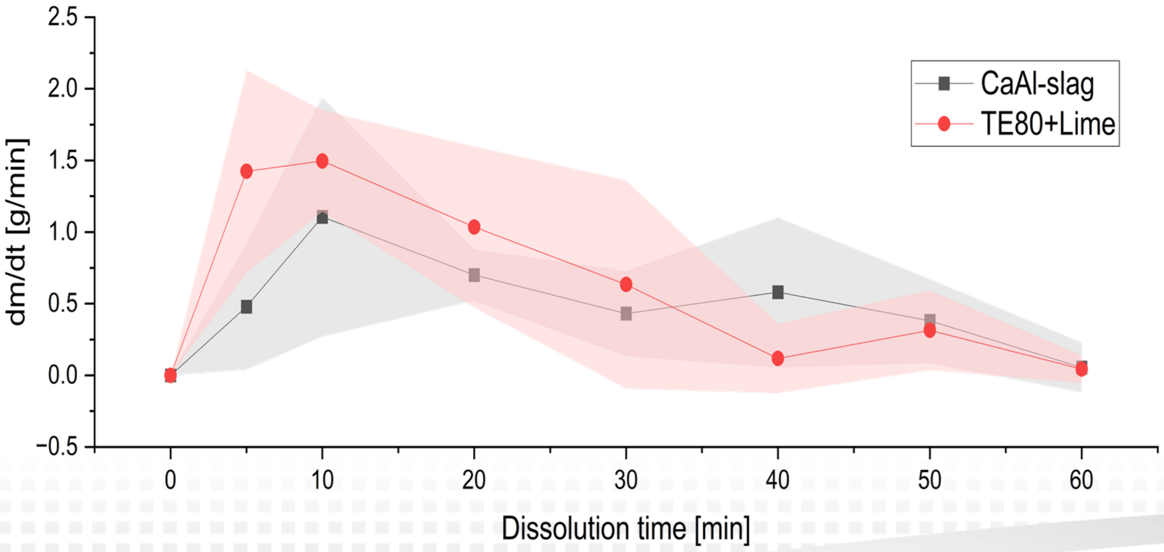
Results

Dissolution behaviour

BOF_1

- T_{exp} = 1650 °C
- $m_{slag, 0}$ = 200 g
- $m_{additive}$ = 40 g





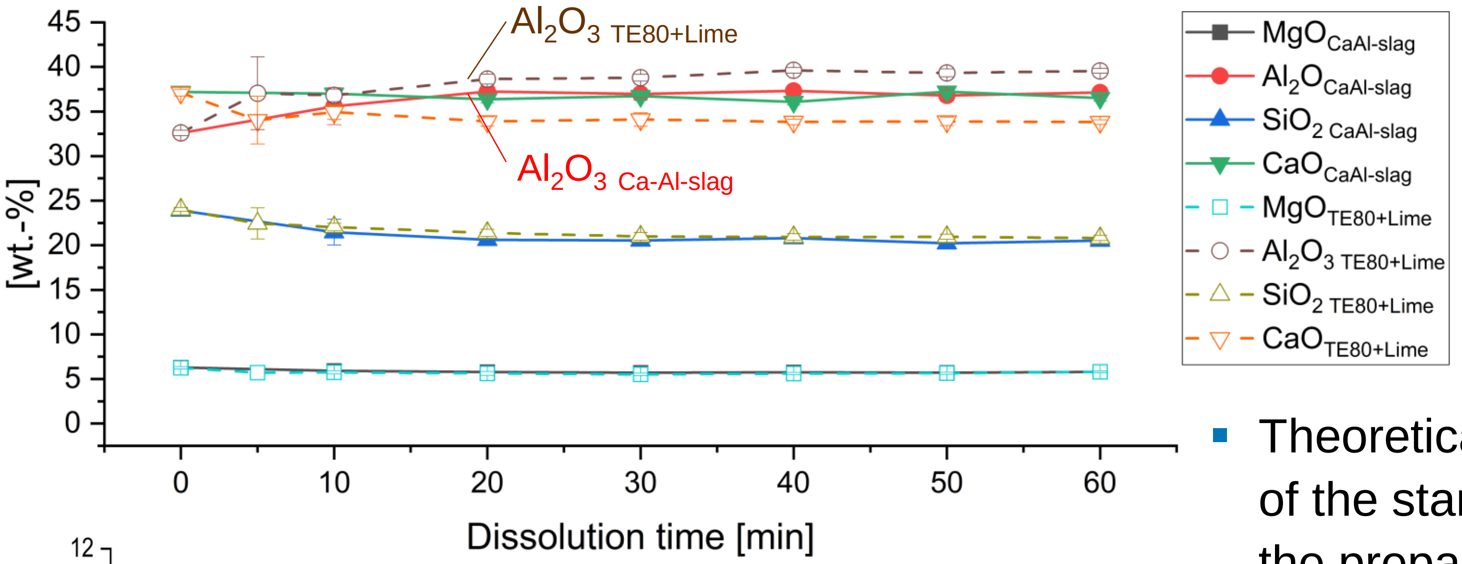
- The standard additive and the prepared refractory material show an almost identical trend in the BOF_1
- Recycled refractory materials mixed with lime represent an alternative to the standard additives.

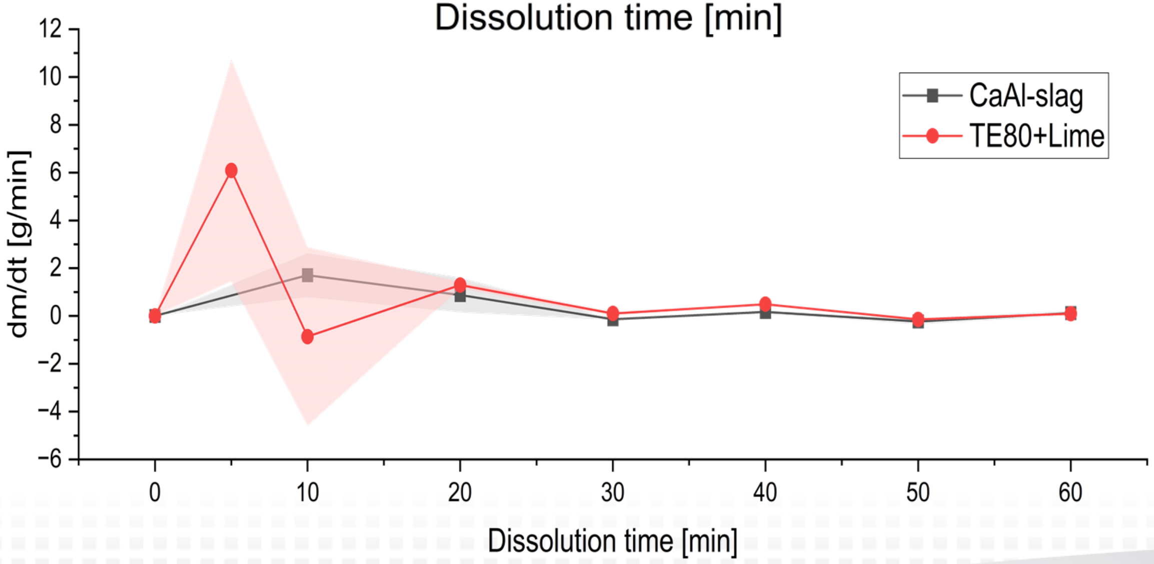
Results

Dissolution behaviour

BOF_2

- T_{exp} = 1600 °C
- $m_{slag, 0}$ = 200 g
- $m_{additive}$ = 40 g





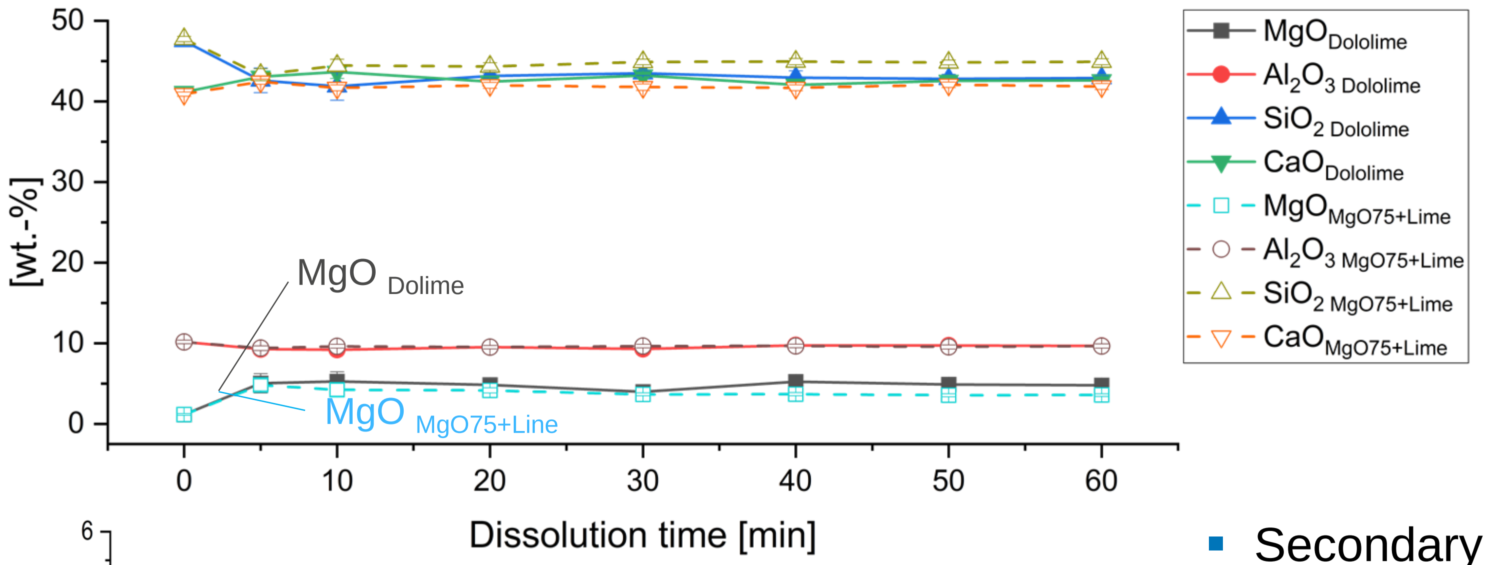
- Theoretical dissolution rates of the standard additive and the prepared refractory material show also an almost identical trend.
- Recycled refractory materials mixed with lime represent an alternative to the standard additives.

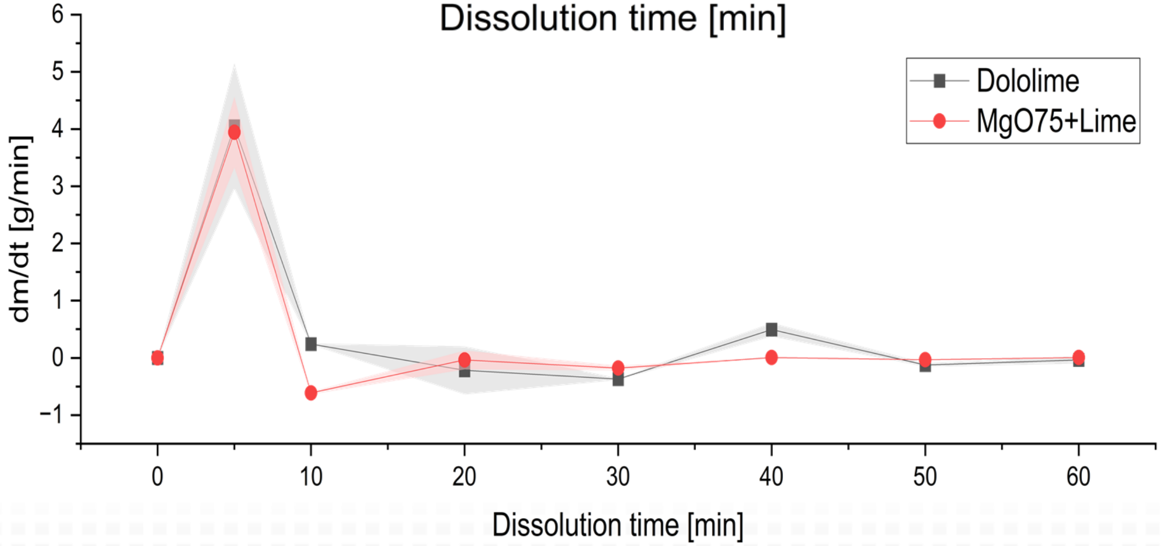
Results

Dissolution behaviour

Smelter

- T_{exp} = 1550 °C
- $m_{slag,\ 0}$ = 200 g
- $m_{additive}$ = 40 g





- Secondary slag additive in the smelter slag also show almost the same trend.
- Recycled refractory materials mixed with lime represent an alternative to the standard additives.

Viscosity measurement

Method

Motivation

- Impact of viscosity on dissolution behaviour:
  - visocity $\downarrow \rightarrow$ dissolution rate $\uparrow$
- Many calculation models in literature
- Model is considered good if the error is less than 30%.

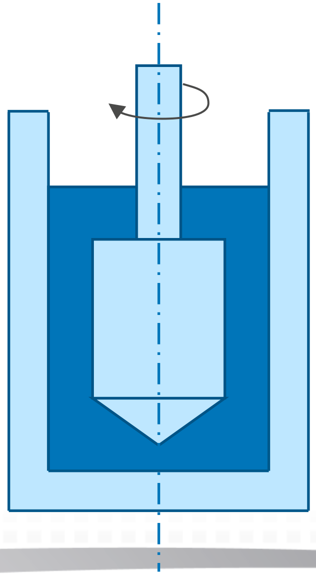
Rheometer FRS 1800 Anton Paar

Rheometer Head:
Air bearing system

Furnace:
max sample temperature:
1730°C

Sealing of the working tube

Methode of concentric cylinder



Viscosity measurement

Method

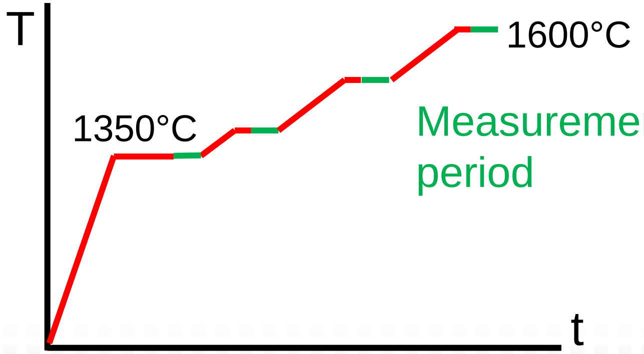
Chemical composition slag [wt.-%]

	Smelter Slag
SiO_2	40.3
CaO	43.7
Al_2O_3	8.5
MgO	7.4
CaO/SiO_2	1.08
Calculated liquidus temperature	1372 °C

Experimental

- Molybdenum system
  - Dimensions:
    - Crucible inner Ø 23 mm
    - inner height 80 mm
  - Bob: Ø 17 mm
    - hight 25 mm

- Shear rate 5, 10,15,20 and 30 s^{-1}
- Argon purging
- Heating regime
  - Rapid heating to 1350°C and 20 min dwell
  - Temperature Steps: 1350, 1400, 1500 and 1600°C

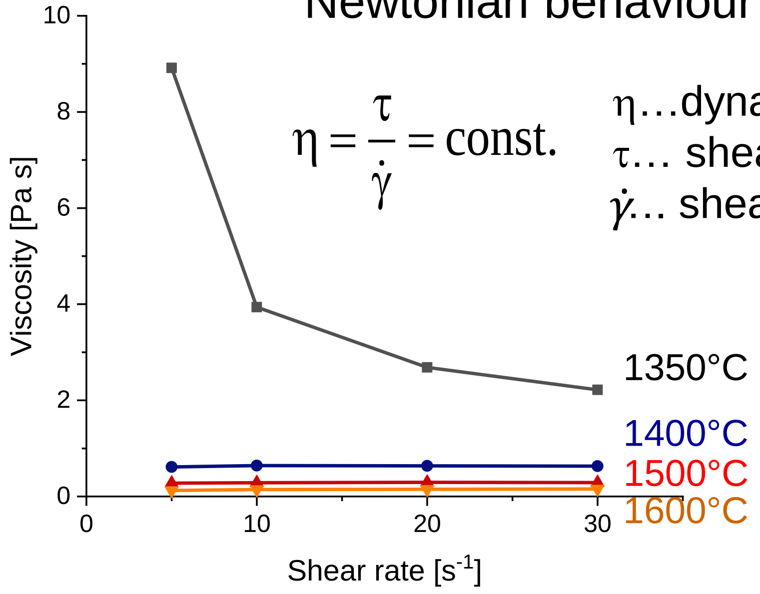


Results

Viscosity

Viscosity in dependance on the shear rate

Newtonian behaviour

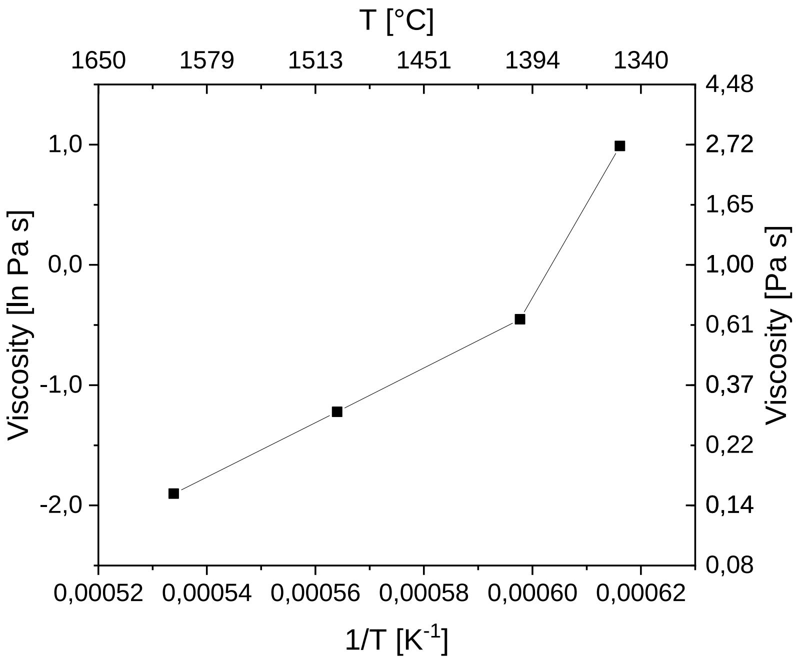


$$\eta = \frac{\tau}{\dot{\gamma}} = \text{const.}$$

η…dynamic viscosity
τ… shear stress
$\dot{\gamma}$… shear rate

- Above liquidus temperature: Newtonian behavior
- Below liquidus lemperatur: shear- thinning behavior due to solids

Viscosity in dependace on the temperature at a constant shear rate (20 s^{-1})



Arhenius Approach

$$\ln \eta = A + \frac{E_A}{RT}$$

A …constant
E_A ..activation energy
R…gas constant
Here A= -14.032 [ln (η) [Pa s]]
E_a = +188861 [J/mol]

- Above liquidus temperature: viscosity follows Arhenius approach
- Below liquidus temperatur: additional increase in effective viscosity due to solids

Electrical conductivity measurements in iron- and steelmaking slags

metallurgical competence center

Method

- Describes the current flow caused by an applied voltage
- Current flow results in the movement of electrons (electronic conduction) or the migration of cations and anions (ionic conduction)

Intensive material property

- Accessible via electrical resistance measurement
- Different measurement setups/electrode arrangements and evaluation methods

$$\sigma = \frac{1}{R} * \frac{L}{A}$$

A … current-carrying area
L … mean current path length
R … electrical resistance

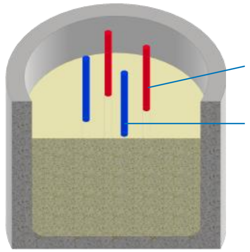
Moll, S: Vergleich impedanzspektroskopischer Methoden zur Leitfähigkeitsmessung an Schlackeschmelzen, Master Thesis July 2023

Electrical conductivity measurements in iron- and steelmaking slags

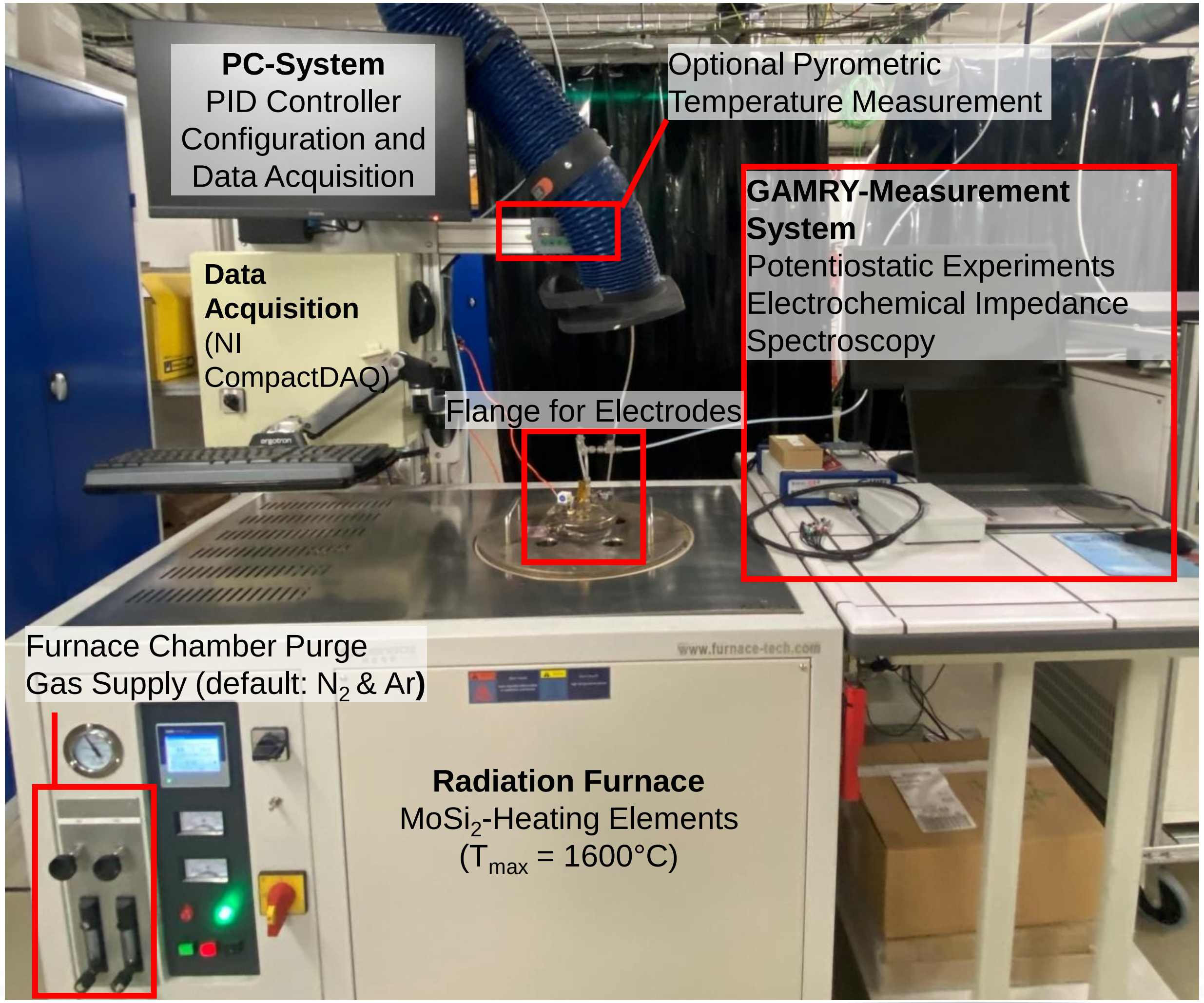
Method

Measurement

- Four electrode setup (Van der Pauw setup)



- Vacuum radiation furnace under argon atmosphere
- Measurements at different immersion depths with additional variation of the current and voltage path



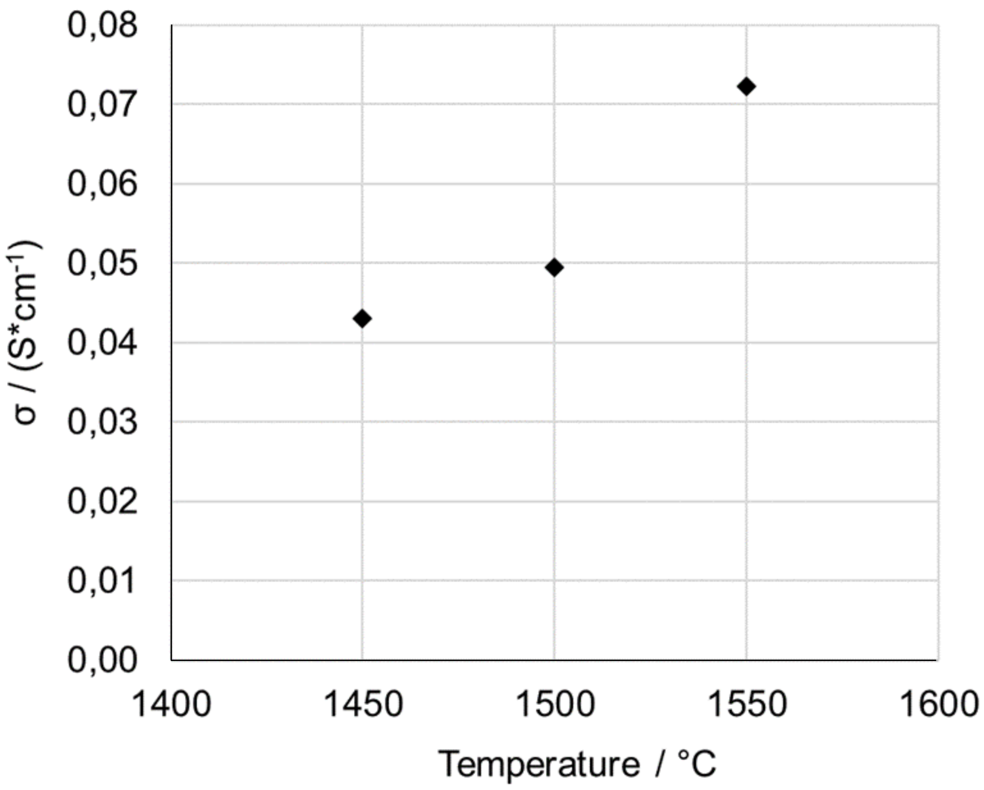
Results

Electrical conductivity

Evaluation:

- Several impedance spectra per immersion depth
- Equivalent circuit approximation
- Calculation electrical conductivity

Electrical conductivity of smelter slag



- Increase of of electrical conductivity with increasing temperature

Conclusion

- Investigated properties:
  - Diffusion coefficient
  - Activity
  - Viscosity
  - Electrical conductivity

- Dissolution behaviour of secondary metallurgical additives in the slag
  - Recycled refractory materials mixed with lime represent an alternative to the standard additives.

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Linz, 30. Oct. 2024

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