Technische
Hochschule
Nürnberg

Miaoli University

“Redox of Glass Melts”

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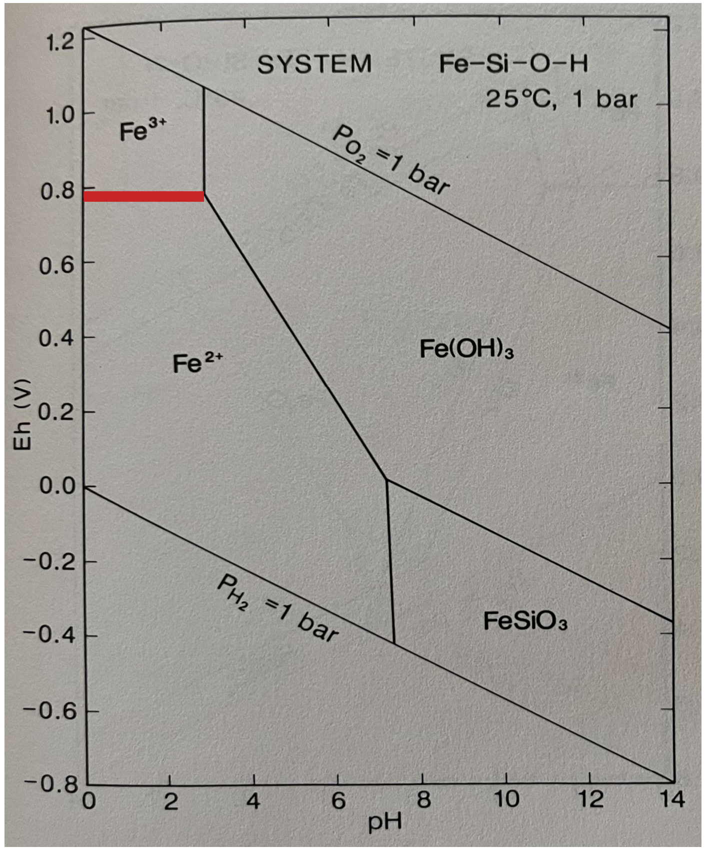
Presentation Structure

1. Redox in Glass – Definition / Influence on Properties
2. Influencing factors on redox
3. Starting conditions
4. Redox number concept

Definition / Influence on Properties

Definition



Chemistry of water
Redox is related to:

- Potential Eh
- Partial pressure of oxygen
- Boundaries of Fe^{3+} and Fe^{2+}
  Ratio of Fe^{3+}/ Fe^{2+} is 1 at red line
- Ratio of Fe^{3+}/ Fe^{2+} is related to Eh
  (Nernst-Equation)

[Brookins D.: Eh-pH Diagrams for Geochemistry. Springer 1987. ISBN 3-540 -18485 -6]

ohm

Definition / Influence on Properties

Definition

Redox $\simeq \frac{c_{Fe2+}}{c_{Fe-tota}}$ or $\frac{c_{Fe3+}}{c_{Fe-total}}$ or $\frac{c_{Fe2}}{c_{Fe3+}}$

Redox is a term to describe the oxidation state of the glass. (How much Oxygen is available.)

What is the main equation?

$$Fe^{2+} + \frac{1}{4}O_2 \Leftrightarrow Fe^{3+} + \frac{1}{2}O^{2-}$$

K= $\frac{a(Fe^{3+})}{a(Fe^{2+})\cdot(a_{O_2})^{1/4}}$

Note the activitiy of the oxygen! Partial pressure of physical dissolved oxygen is a very important factor for redox discussion.

$$a_{O_2} = \frac{p_{O_2}}{p_{O_{2,Ref}}}$$

We use Fe – Iron, because it could be measured easily. It is not always the best choice!

$$As^{3+} + \frac{1}{2}O_2 \Leftrightarrow As^{5+} + O^{2-}$$

K= $\frac{a(As^{5+})}{a(As^{3+})\cdot a(O_2)^{1/2}}$

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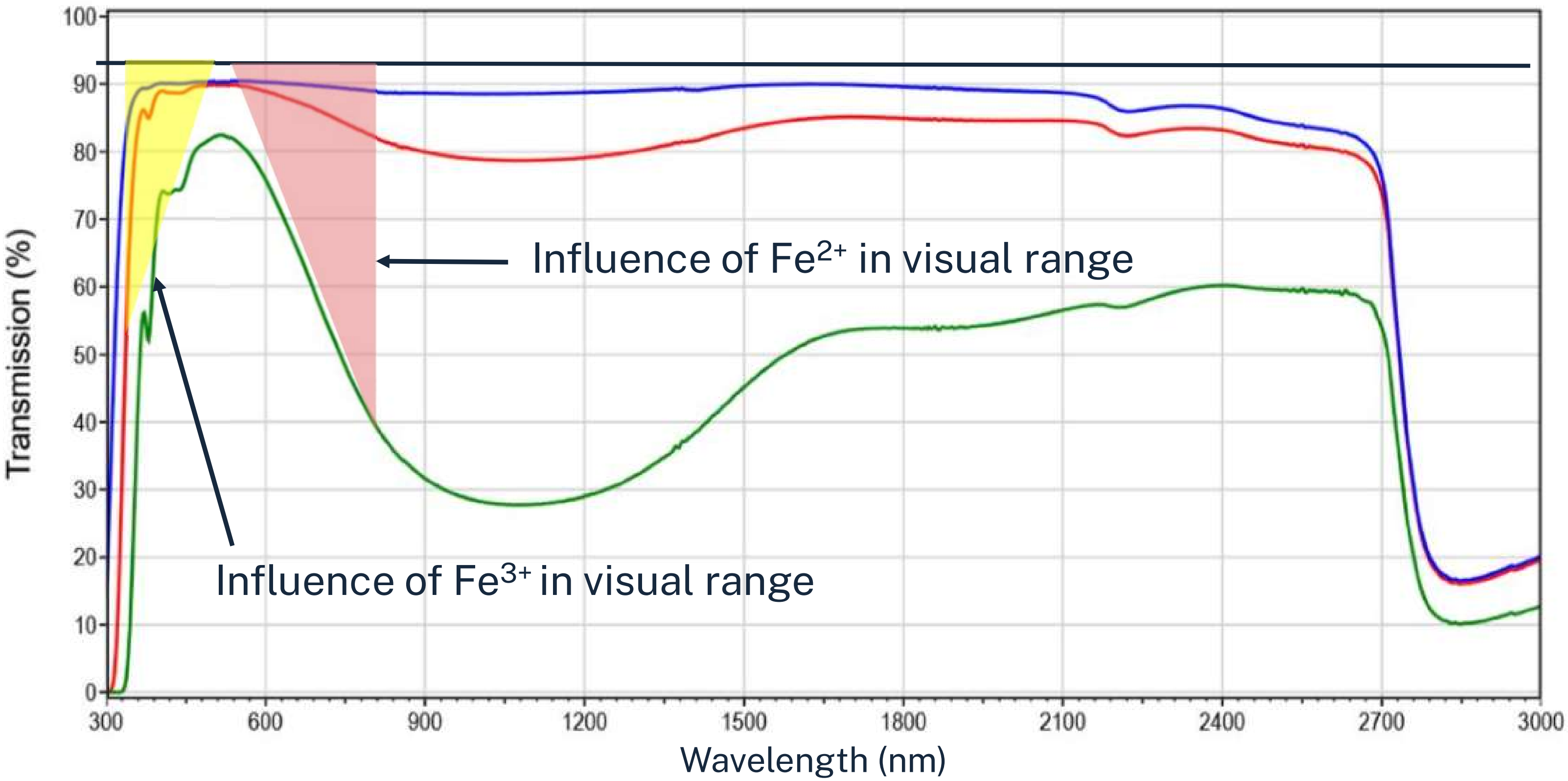
Definition / Influence on Properties

Influence on Properties

- **Colour of glass** – change of colour process
- Chemical stability
- **Seed / Bubble quality - Fining**
- Homogeneity
- Surface tension (indirectly)
- Heat transfer in glass melts – temperature distribution in the glass melt
- Corrosion (indirectly) of refractory
- Corrosion of platinum tube systems
- Corrosion of molybdenum electrodes
- (Oxygen) bubble formation at later stages of the process

Definition / Influence on Properties

Influence on Properties – colour of glass



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Definition / Influence on Properties

Influence on Properties – Seed / Bubble quality

Fining using redox pair ions – Redox is a main factor

$$As^{3+} + \frac{1}{2} O_2 \Leftrightarrow As^{5+} + O^{2-}$$

$$K = \frac{a(As^{5+})}{a(As^{3+}) \cdot a(O_2)^{1/2}}$$

→ CeO_2, Sb_2O_3, Fe_2O_3

$$a_{O_2} = \frac{p_{O_2}}{p_{O_{2,Ref}}}$$

Fining using phase change or chemical reactions with gas formation – Redox is unimportant

NaCl(s) → NaCl(g) (1400 °C partial pressure of NaCl for pure NaCl is 1 bar)

$2{*}CaF_2 + SiO_2 \rightarrow 2{*}CaO + SiF_4$

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Influencing factors on redox

What is your main question?

→ Do you have a colour problem? → K= $\frac{a(Fe^{3+})}{a(Fe^{2+})\cdot(a_{O_2})^{1/4}}$

→ Do you have a fining problem? → K= $\frac{a(Fe^{3+})}{a(Fe^{2+})\cdot(a_{O_2})^{1/4}}$

First specifiy your challenge – Partial pressure of oxygen and / or activities of redox pair ions!

Influencing factors on redox

Main parameters (?)

→ Atmosphere of the furnace

→ Batch composition

→ Temperature of the glass melt

→ Other redox pairs

→ Glass melt process (T(t))

new batch

old batch

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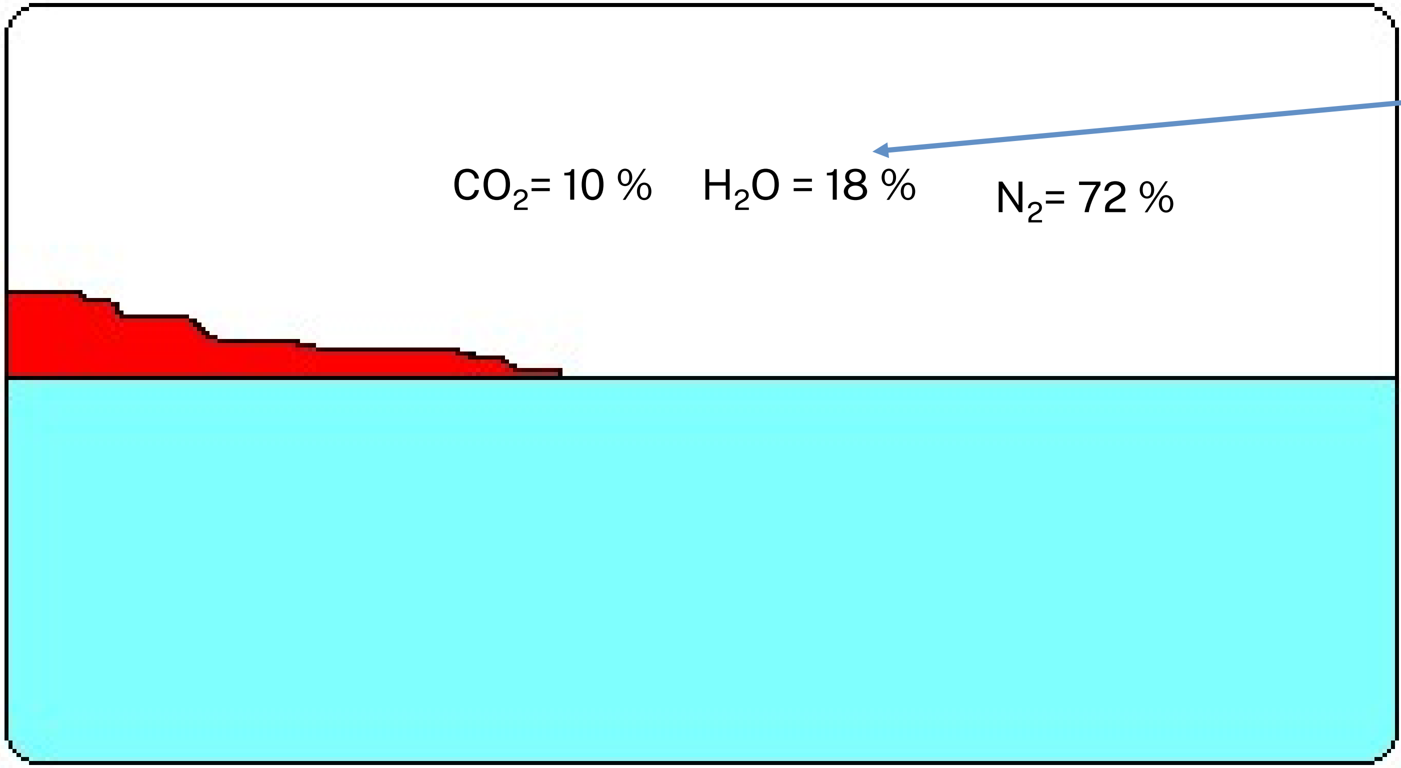
Influencing factors on redox



Atmosphere of air / natural gas-fired furnace

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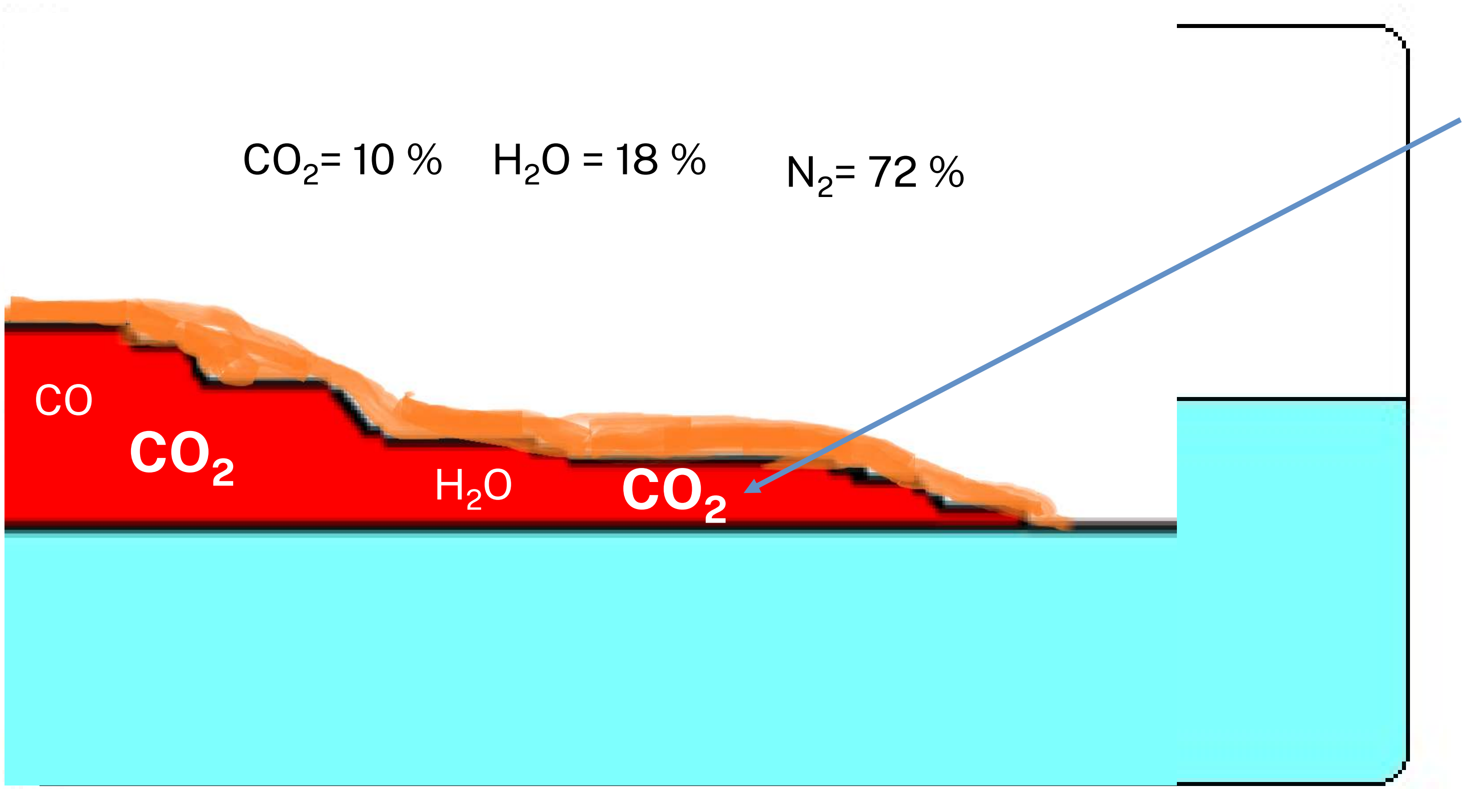
Influencing factors on redox



Batch has an own atmosphere.

Furnace atmosphere has a minor Influence on batch atmosphere.

Minor components of Batch have the main influence on Redox (C, $NaNO_3$, Na_2SO_4)

Batch influences both – Redox pair ions and partial pressure of oxygen.

Influencing factors on redox

Main parameters (?)

→ Atmosphere of the furnace

→ **Batch composition**

→ Temperature of the glass melt

→ Other redox pairs

→ Glass melt process (T(t))

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Influencing factors on redox

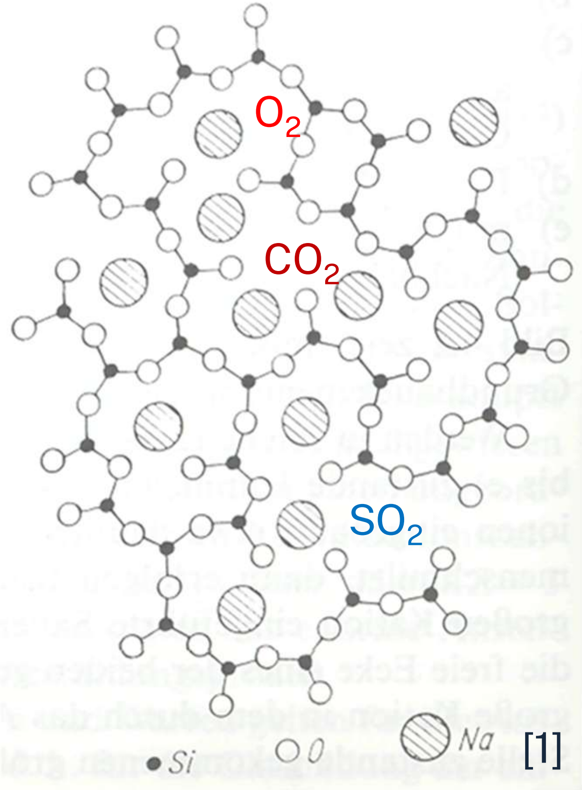
One redox pair / temperature

$$K = \frac{a(Fe^{3+})}{a(Fe^{2+}) \cdot (a_{O_2})^{1/4}}$$

$$Fe^{2+} + \frac{1}{4} O_2 \Leftrightarrow Fe^{3+} + \frac{1}{2} O^{2-}$$

$$\frac{chemical\ dissolved\ oxygen}{physical\ dissolved\ oxygen} = 1.000 - 10.000$$

Small change of activities of Fe^{2+} / Fe^{3+} strongly influence physical dissolved oxygen.

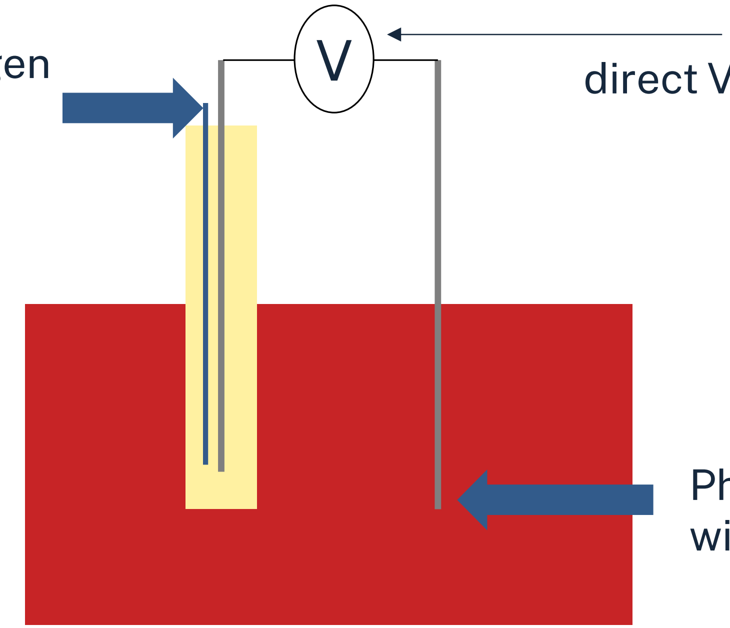


[1]

[1] Vogel W.: Glaschemie 1. Auflage. VEB Deutscher Verlag für Grundstoffindustrie Leipzig. VLN 152-915/99/79 1979

Influencing factors on redox

Oxygen partial pressure of glass melts measured with ZrO2 probes (lambda probe)



$$\Delta U = -\frac{R \cdot T}{4 \cdot F} \cdot \ln \frac{p_{O2,dissolved}}{p_{O2}}$$

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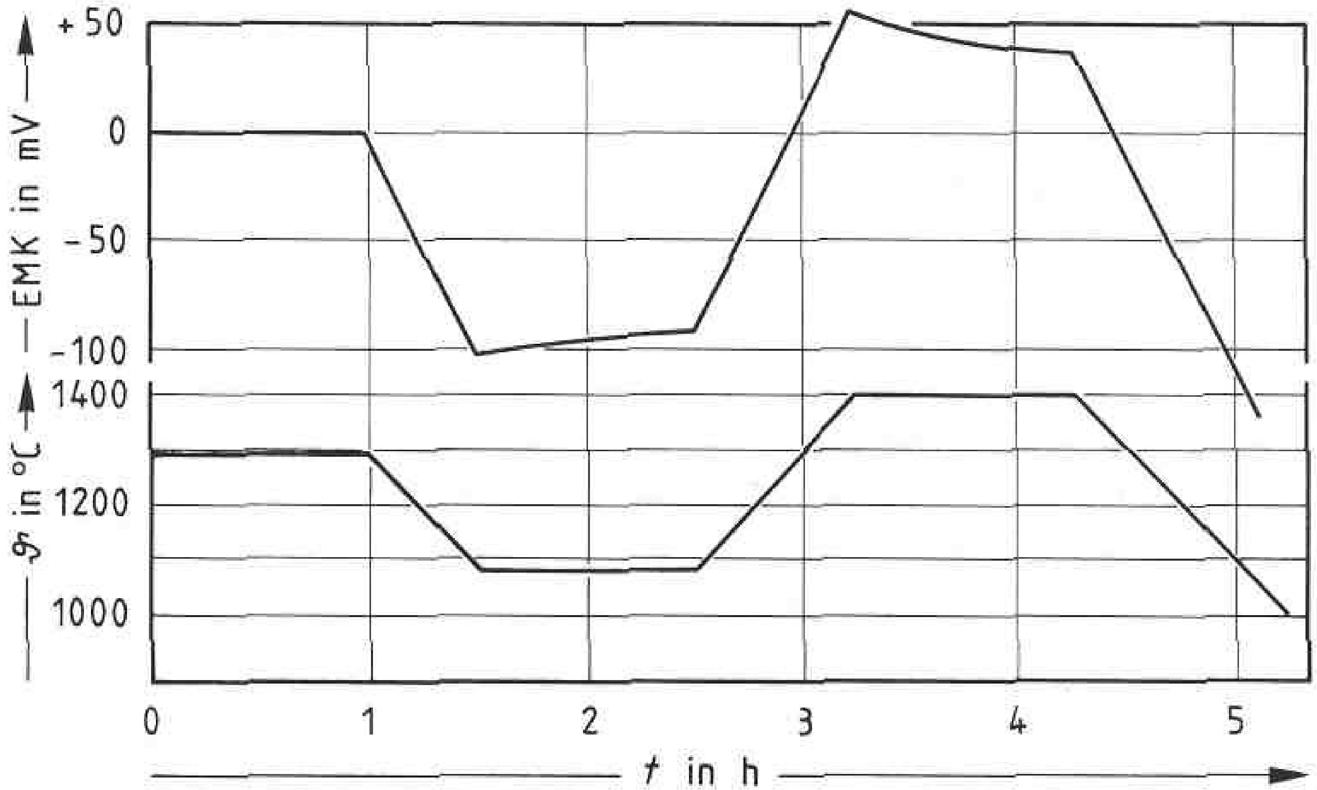
Influencing factors on redox

One redox pair / temperature

Change of temperature changes the partial pressure of oxygen.

Temperature has not a direct influence on redox pair ions (!), but on partial pressure of oxygen. (one redox pair ion only.)

$$K = \frac{a(Fe^{3+})}{a(Fe^{2+})\cdot(a_{O_2})^{1/4}}$$



[2]

[2] Lenhart A.: Untersuchung des Redoxverhaltens polyvalenter Elemente in Glasschmelzen unter Einsatz elektrochemischer Messverfahren. Dissertation an der Technischen Fakultät der Universität Erlangen-Nürnberg. 1984

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Influencing factors on redox

two redox pairs / temperature

$$K = \frac{a(Fe^{3+})}{a(Fe^{2+}) \cdot (a_{O_2})^{1/4}}$$

$$Fe^{2+} + \frac{1}{4} O_2 \Leftrightarrow Fe^{3+} + \frac{1}{2} O^{2-}$$

$$K = \frac{a(As^{5+})}{a(As^{3+}) \cdot a(O_2)^{1/2}}$$

$$As^{3+} + \frac{1}{2} O_2 \Leftrightarrow As^{5+} + O^{2-}$$

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Influencing factors on redox

two redox pairs / temperature

$$K = \frac{a(Fe^{3+})}{a(Fe^{2+}) \cdot (a_{O_2})^{1/4}}$$

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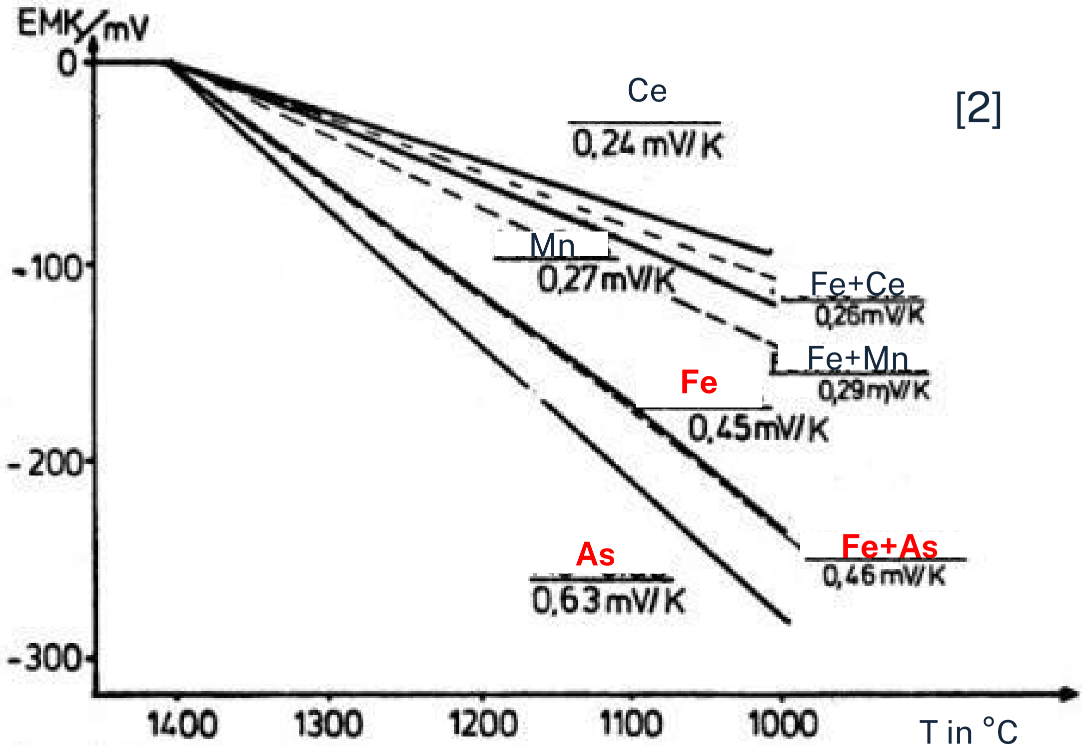

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Influencing factors on redox

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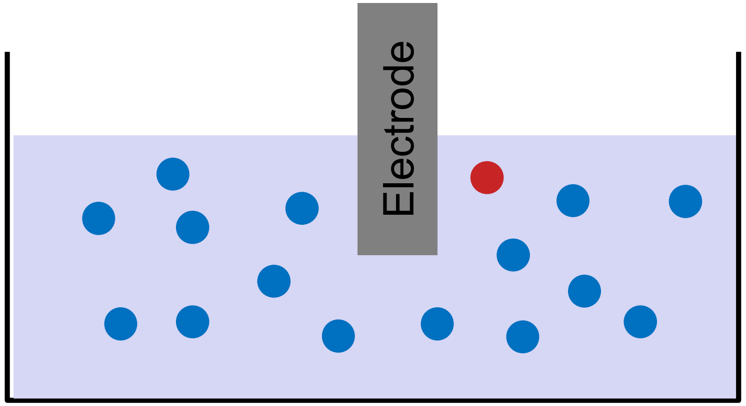
two redox pairs / temperature

$$K = \frac{a(As^{5+})}{a(As^{3+}) \cdot a(O_2)^{1/2}}$$



Who has a higher influence on the potential of the electrode low amount of Fe-Ion ● or high amount of As-Ion ● ?

Electrical potentials at electrodes are defined by redox pair ions, redox of the glass melt, **the concentration of redox pair ions and the electrode material.**

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Influencing factors on redox

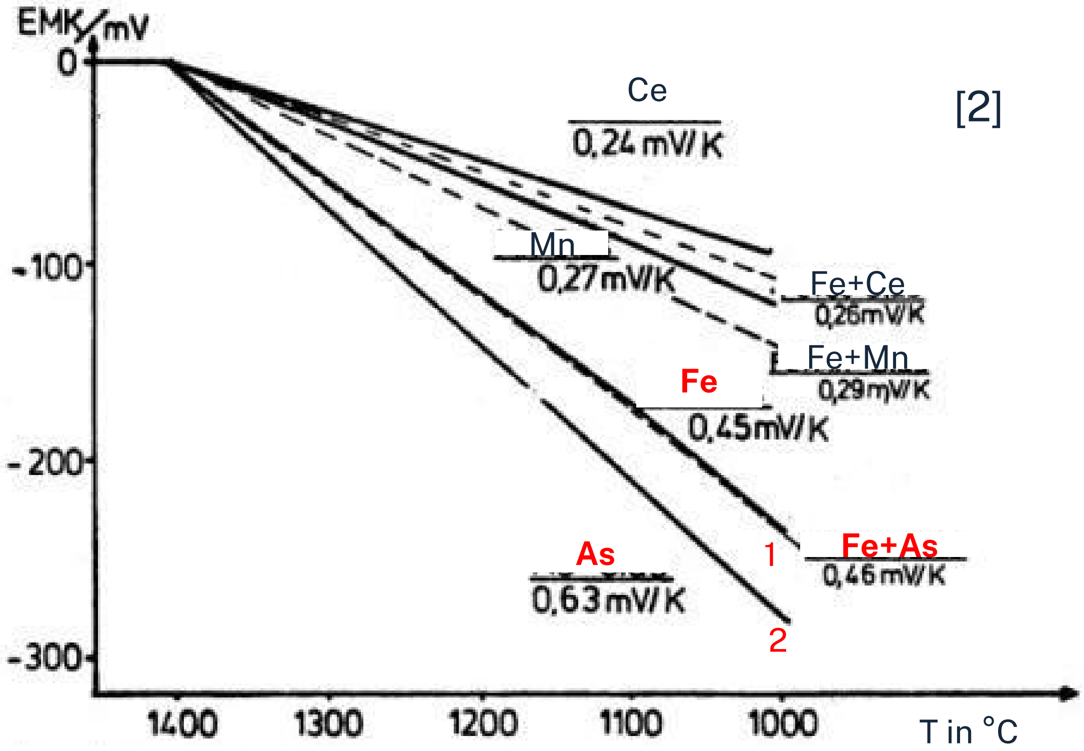
two redox pairs / temperature

$$K = \frac{a(Fe^{3+})}{a(Fe^{2+}) \cdot (a_{O_2})^{1/4}}$$

$$K = \frac{a(As^{5+})}{a(As^{3+}) \cdot a(O_2)^{1/2}}$$

$$E = E^0 + \frac{RT}{2F} \cdot ln \frac{a_{As5+}}{a_{As3+}}$$

$$(E_2 - E_1) \cdot \frac{2F}{RT} = ln\left(\frac{a_{AS5+}}{a_{AS3+}}\right)_2 - ln\left(\frac{a_{AS5+}}{a_{AS3+}}\right)_1$$



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Influencing factors on redox

two redox pairs / temperature

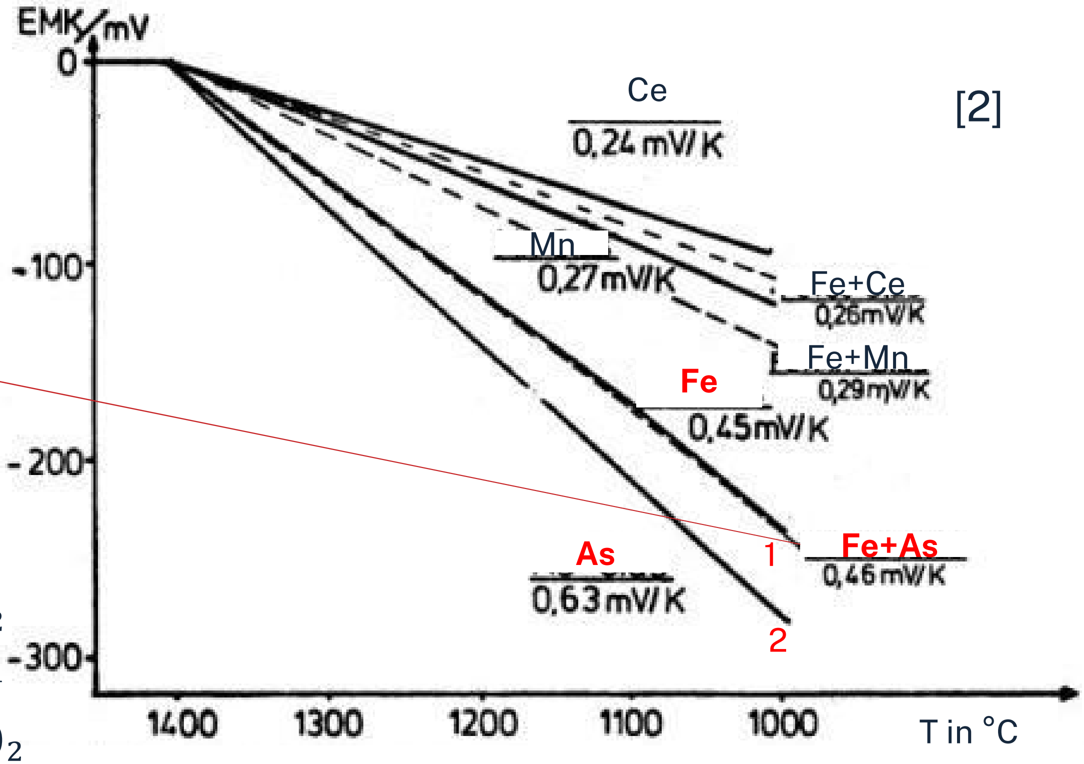
$$(E_2 - E_1) \cdot \frac{2F}{RT} = ln\left(\frac{a_{As5+}}{a_{As3+}}\right)_2 - ln\left(\frac{a_{As5+}}{a_{As3+}}\right)_1$$

$$-1.28 = ln\left(\frac{a_{As5+}}{a_{As3+}}\right)_2 - ln\left(\frac{a_{As5+}}{a_{As3+}}\right)_1$$ and $As_{total} = 1$

$$-1.28 = ln(1)_2 - ln(3.58)_1 \qquad (As^{5+} = 0.5)_2 \quad (As^{5+} = 0.78)_1$$

$$-1.28 = ln(3.000)_2 - ln(10.750)_1 \qquad (As^{5+} = 0.9997)_2 \quad (As^{5+} = 0.9999)_1$$

$$-1.28 = ln(10^{-3})_2 - ln(3.58 * 10^{-3})_1 \qquad (As^{5+} = 0.001)_2 \quad (As^{5+} = 0.0036)_1$$



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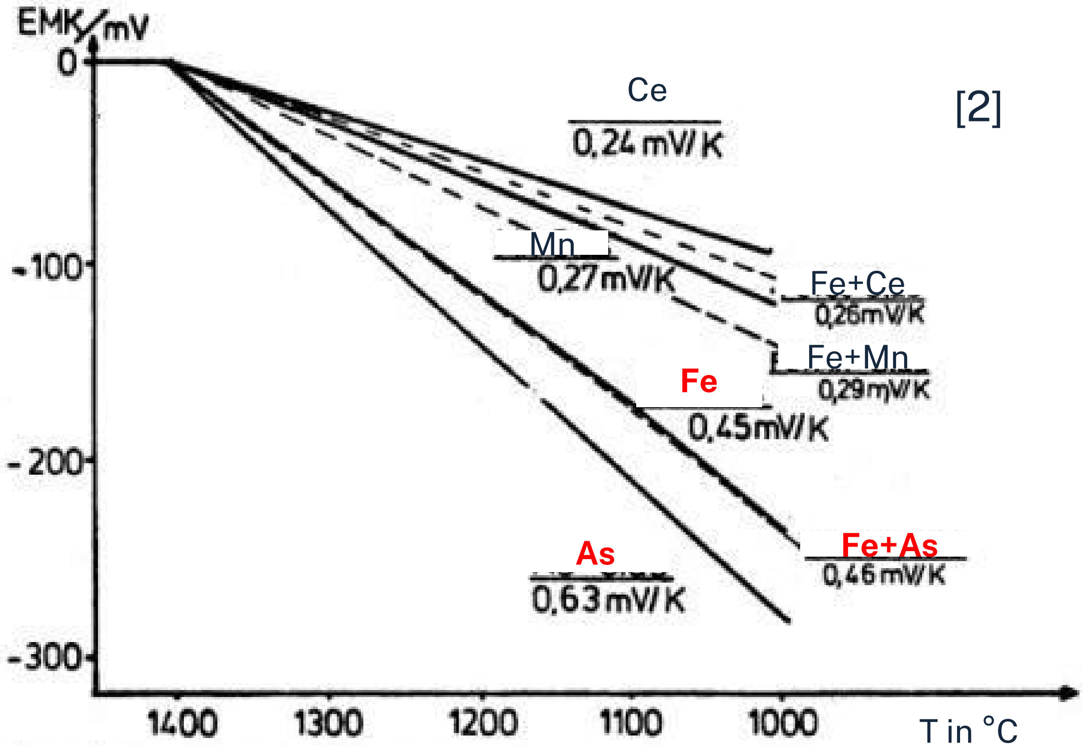
Influencing factors on redox

two redox pairs / temperature

Fining behaviour could be influenced by a second redox pair ion (if concentration is high enough)

Redox could be influenced by a second redox pair ion
- if concentration is high enough

Strong change of redox does not necessarily mean a strong change of the amount of each Ion.



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Influencing factors on redox

Square wave voltammetry – standard potentials

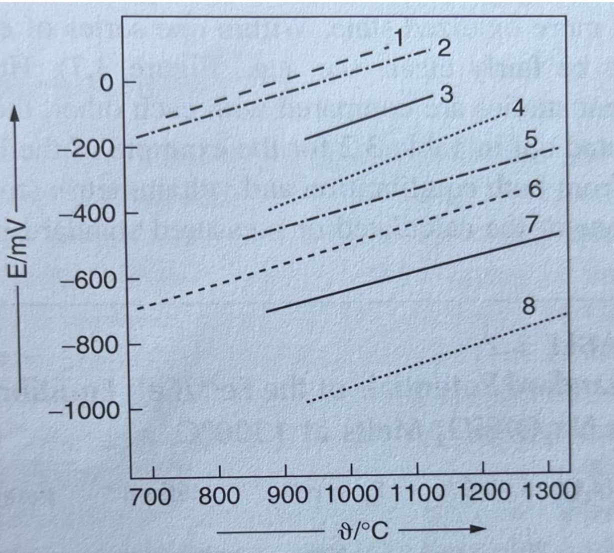

FIGURE 3.6 Voltammetrically determined standard potentials of various polyvalent elements recorded in a glass melt with the basic mol% composition of 74 SiO_2, 16 Na_2O, 10 CaO as a function of the temperature (illustrated by means of the regression lines). 1: Ce^{3+}/Ce^{4+}; 2: Cr^{3+}/Cr^{6+}; 3: Sn^{2+}/Sn^{4+}; 4: Sn^{0}/Sn^{2+}; 5: Bi^{0}/Bi^{3+}; 6: $U^{4+}/U^{5+}/U^{6+}$; 7: Co^{0}/Co^{2+}; 8: Cr^{2+}/Cr^{3+}.

Pye et al.:Properties of glass forming melts. Taylor & Francis. 2005. ISBN: 1574446622

→ Chapter of C. Rüssel concerning Electrochemistry of glass melts with data of the standard Potential $E_{1/2}$ as a function of the glass melt temperature

→ Evaluation of thermodynamic data could be used to calculate the behaviour as a function of temperature

Influencing factors on redox

Main parameters (?)

- → Atmosphere of the furnace
- → **Batch composition**
- → Temperature of the glass melt – Fining Process
- → **Other redox pairs**
- → Glass melt process (T(t))

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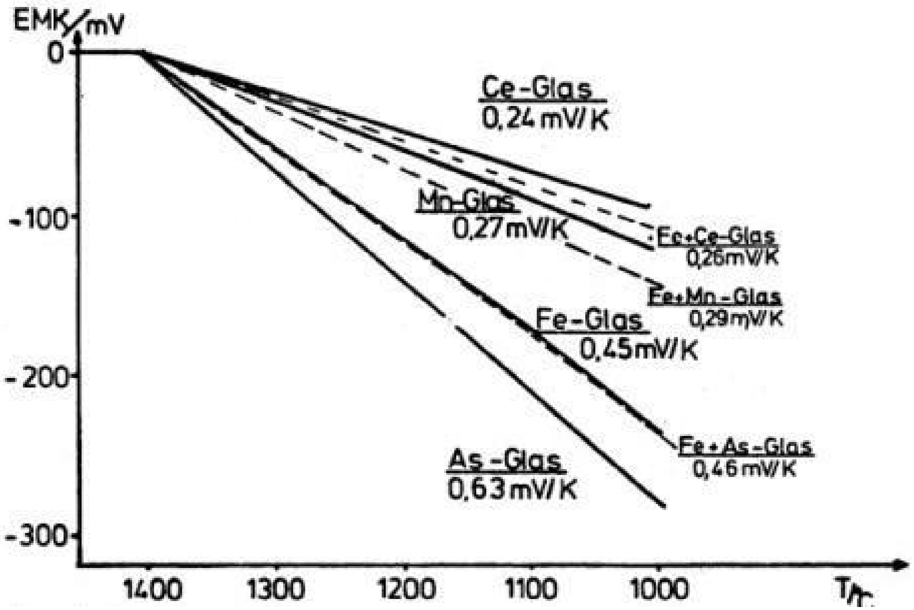
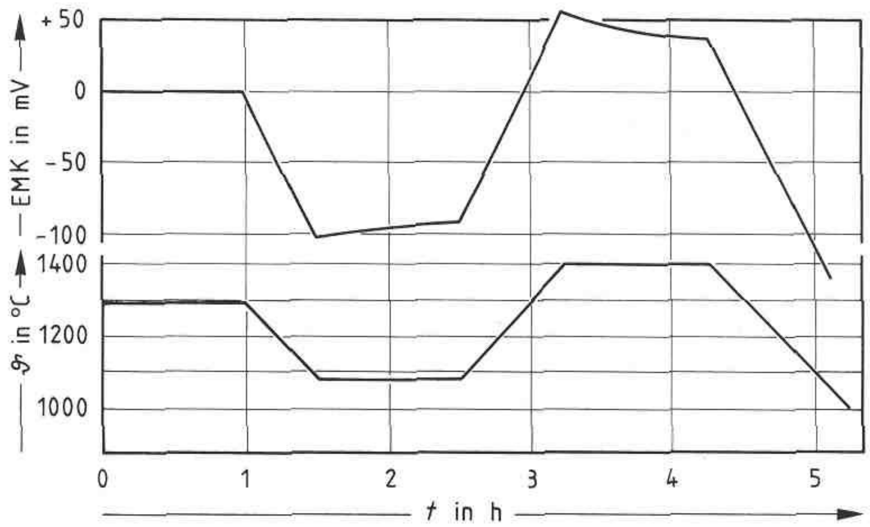
Influencing factors on redox

Glass melt process (T(t))





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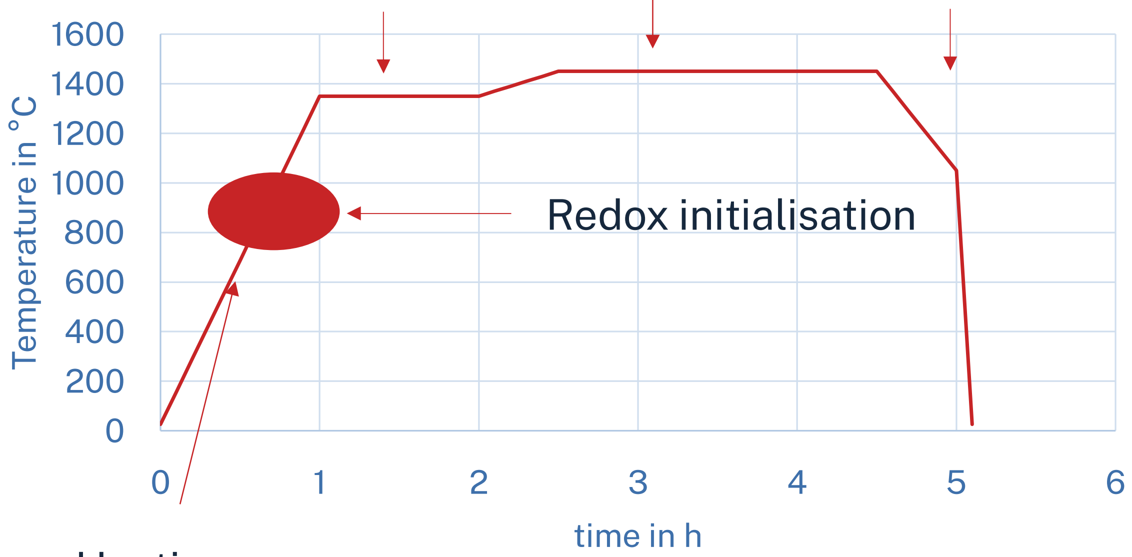
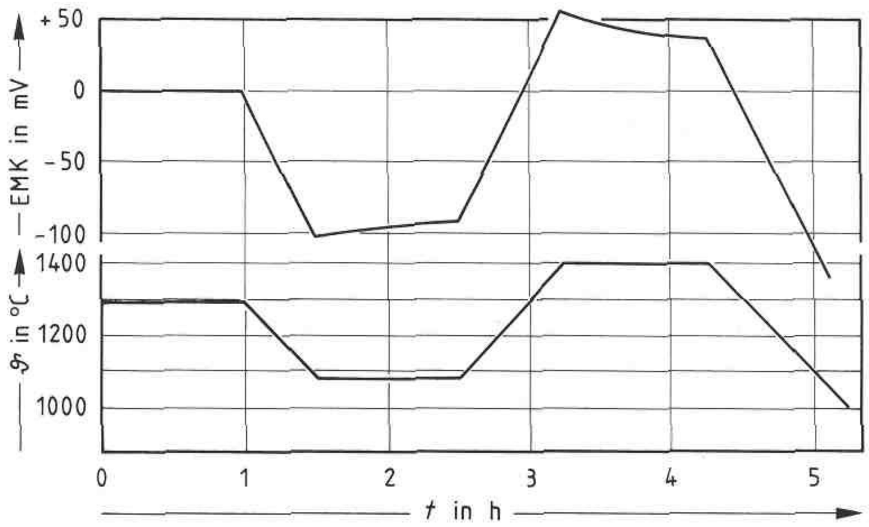
Influencing factors on redox

Glass melt process (T(t))

Final melting   Fining   Conditioning / forming



Heating +
Melting batch



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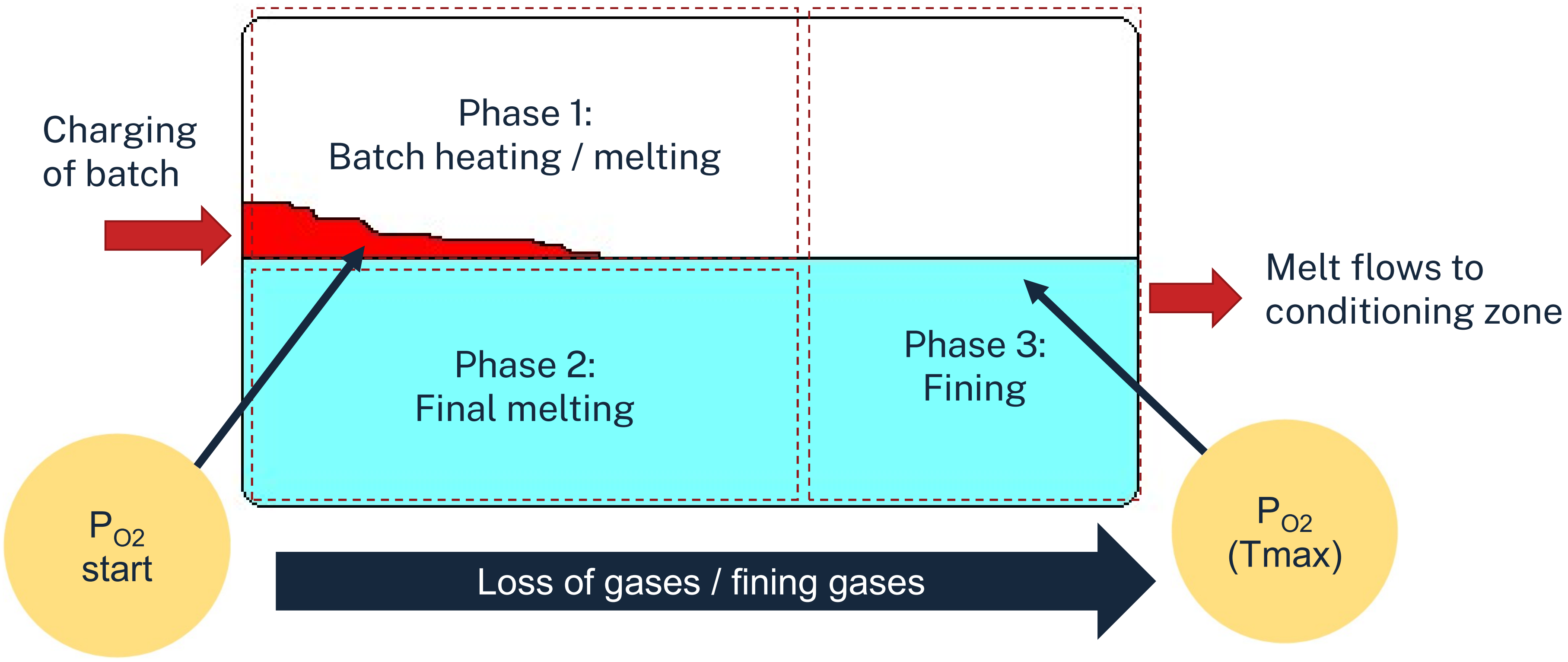
Influencing factors on redox

Glass melt process (T(t))



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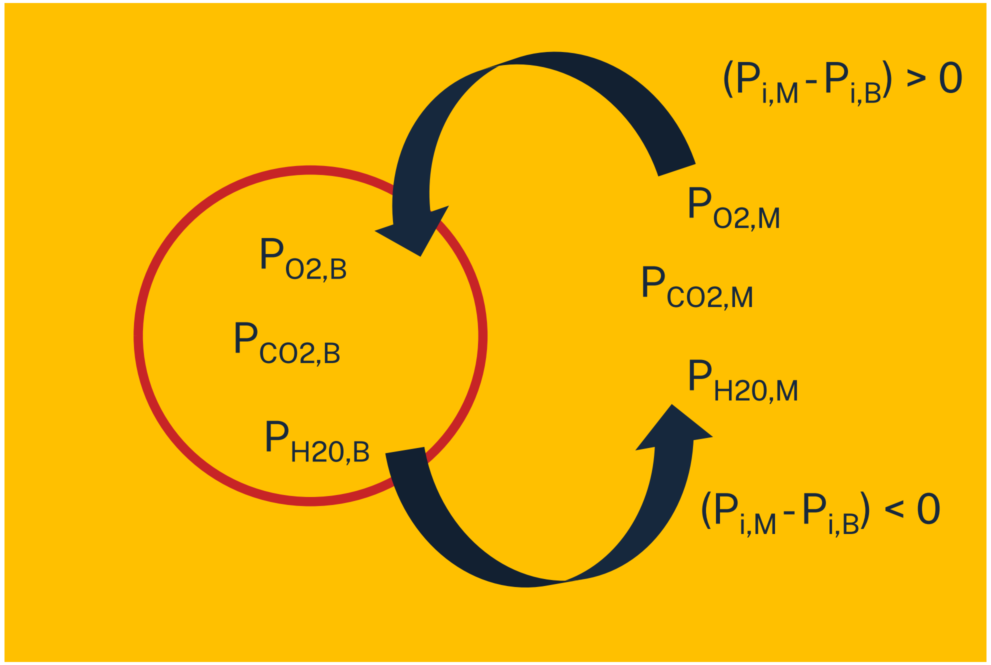
Influencing factors on redox

Glass melt process (T(t))

Basics of bubble growth



Partial pressure $P_{i,M}$ in melt changes due to:

- Temperature, redox situation and kind of fining agent

- If gases diffuse to the bubbles and bubbles ascend to the top of the melt

  → loss of gases (oxygen)
  → reduction of the glass melt due to bubble growth
  → Temperature and time T(t) influences reduction potential of glass melt process

Influencing factors on redox

Main parameters

→ Atmosphere of the furnace

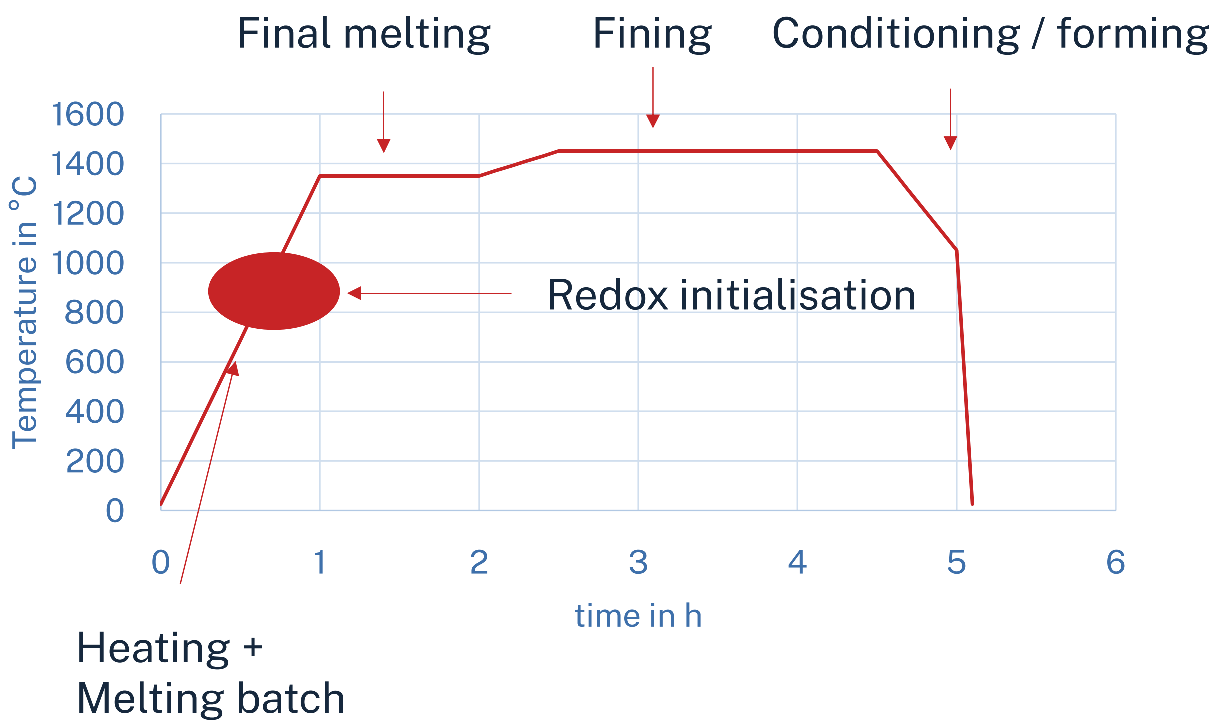
→ **Batch composition**

→ Temperature of the glass melt – Fining Process

→ **Other redox pairs**

→ Glass melt process (T(t)) (?)

Starting conditions



Volume change in a glass melt due to gas release after batch reactions

K. Al Hamdan (TU Freiberg, S. Wiltzsch (TH Nürnberg)

Comparative melting studies (w/o sulfate)

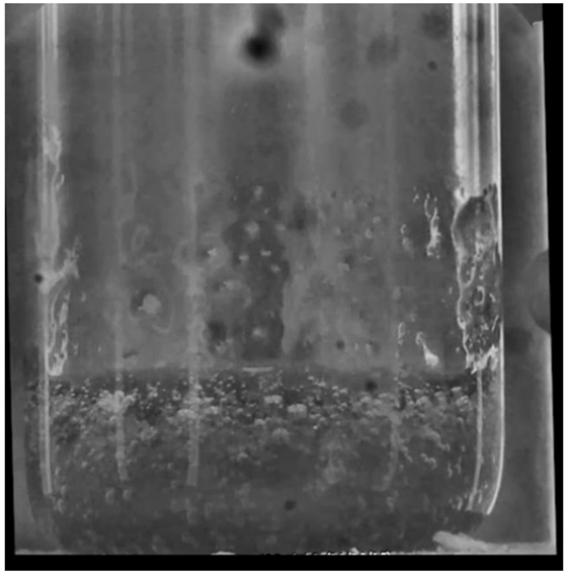
1) Standard ($CaCO_3$ / Na_2CO_3 as reference)
2) CaO instead of $CaCO_3$
3) NaOH instead of Na_2CO_3
4) CaO / NaOH instead of $CaCO_3$ / Na_2CO_3

Measurement: Dec. 2022 / TU-Freiberg,
Heating rate: 10 K/min

Starting conditions

Batch

Primary foaming



Glass melt

Starting conditions

Primary foaming

What defines the starting condition of the redox?

→ Gas composition of the primary bubbles (CO_2, H_2O, O_2, C, H_2)
Batch composition, kind of raw material (CaO instead of $CaCO_3$)

→ Amount of primary bubbles
a lot of small bubbles has a higher influences on reaction of gas with glass melt, than one big bubble

Grain size distribution of raw materials influences amount and size of primary bubbles.

→ Temperature of primary foaming (Equilibrium of gases f(T))
Heating rate, grain size of raw materials, kind of raw material, batch composition

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Redox number concept

→ Atmosphere of the furnace

→ **Batch composition**

→ Temperature of the glass melt

→ **Other redox pairs**

→ Glass melt process (T(t)) (?)

→ Starting conditions of Redox

Can you change atmosphere of the furnace easily?

Can you change redox pair ions easily?

Can you change raw materials ($CaCO_3$ to CaO) easily?

Can you change glass melt process easily?

Consider Minor reducing or oxidizing components of the batch composition.

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Redox number concept

Precondition

→ Production of the same glass composition

→ Main raw materials (Sand, Soda, limestone, dolomite e.g. $CaCO_3$ to CaO) does not change

→ Stable grain size distribution of raw materials

→ Stable water content of raw materials / batch

→ Constant cullet content

→ If there is a change, then you need to update the value of your redox number.

Redox number concept

Idea of the redox number concept

→ Neglect redox influence of main raw materials (constant charge)

→ Minor raw materials with strong reducing or oxidizing influence are considered.

→ Each minor raw material has a redox factor.

→ The sum of all minor raw materials gives a redox number.

minor raw material	redox factor
coal 100 % C	-6,7
coal 85 % C	-5,7
coal 65 % C	-4,36
FeS	-1,6
FeS2	-1,2
CaF2	-0,1
Calumite	-0,073
Fe2O3	0,25
NaNO3	0,32
BaSO4	0,4
CaSO4*2H2O	0,56
K2Cr2O7	0,65
Na2SO4	0,67
CaSO4	0,7
Na2Cr2O7	0,77
MnO2	1,09

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Redox number concept

How to calculate the redox number?

Example:
How much coal (100 % C) should be added to the batch (100 kg) in order to reach a redox number of –10?

Relevant parameter of the batch composition:

- 100 kg batch (no cullet) has **60.0 kg Sand**
- Oxidizing / reducing minor components

Fe_2O_3 0.50 kg, **Calumite 1.00 kg** und **FeS_2 0.10 kg**

minor raw material	redox factor
coal 100 % C	-6,7
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Redox number concept

How to calculate the redox number?

1. Calculate Sand factor S

S=(2000 kg)/(60 kg) = 33.33

Relevant parameter of the batch composition:

- 100 kg batch (no cullet) has **60.0 kg Sand**
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Fe_2O_3 0.50 kg, **Calumite 1.00 kg** und **FeS_2 0.10 kg**

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Redox number concept

How to calculate the redox number?

2. Calculate redox influence R_i of each minor material by using redox factor r_i and amount of minor component in original batch m_i

$R_i = S * r_i * m_i$

Fe_2O_3: $R_{Fe2O3} = 33.33 * +0.25 * 0.5 = +4.16625$

Calumite: $R_{Calumite} = 33.33 * -0.073 * 1.0 = -2.43309$

FeS_2: $R_{FeS2} = 33.33 * -1.2 * 0.1 = -3.9996$

Relevant parameter of the batch composition:

- 100 kg batch (no cullet) has **60.0 kg Sand**
- Oxidizing / reducing minor components

Fe_2O_3 0.50 kg, **Calumite 1.00 kg** und **FeS_2 0.10 kg**

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MnO2	1,09

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Redox number concept

How to calculate the redox number?

3. Calculate the sum of all redox influences R_i

$R_{Fe2O3} + R_{Calumite} + R_{FeS2} = +4.16625 - 2.43309 - 3.9996 = -2.26644$

-2.26644 is the redox number of the original batch.

However, we want a redox number of -10.

Thus, the difference of 2.26644 – 10 = -7.73356 should

be the influence of coal (100 % C).

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NaNO3	0,32
BaSO4	0,4
CaSO4*2H2O	0,56
K2Cr2O7	0,65
Na2SO4	0,67
CaSO4	0,7
Na2Cr207	0,77
MnO2	1,09

Redox number concept

How to calculate the redox number?

4. Calculate the required mass of coal (100% C) to reach -10.

$R_C = S^* r_C * m_C$

$m_C = R_C /(S^* r_C) = -7.73356/(33.33*-6.7) = 0.03463 \text{ kg} = 34.63 \text{ g}$

We need to add 34.63 g coal (100 % C) to the batch (100 kg)

to reach a redox number of -10.

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coal 100 % C	-6,7
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coal 65 % C	-4,36
FeS	-1,6
FeS2	-1,2
CaF2	-0,1
Calumite	-0,073
Fe2O3	0,25
NaNO3	0,32
BaSO4	0,4
CaSO4*2H2O	0,56
K2Cr2O7	0,65
Na2SO4	0,67
CaSO4	0,7
Na2Cr2O7	0,77
MnO2	1,09

ohm

Redox number concept

What needs to be done to assure quality / stable redox number?

→ Measurement of chemical oxygen demand of all raw materials.

reducing components could be considered as „coal“ for the redox number calculation

→ Cullet could be considered as Sand, if the amount of cullet is high.

→ Stable application of minor components (without negative effect on fining) and constant calculated redox number.

Redox number is the control value.

minor raw material	redox factor
coal 100 % C	-6,7
coal 85 % C	-5,7
coal 65 % C	-4,36
FeS	-1,6
FeS2	-1,2
CaF2	-0,1
Calumite	-0,073
Fe2O3	0,25
NaNO3	0,32
BaSO4	0,4
CaSO4*2H2O	0,56
K2Cr2O7	0,65
Na2SO4	0,67
CaSO4	0,7
Na2Cr207	0,77
MnO2	1,09

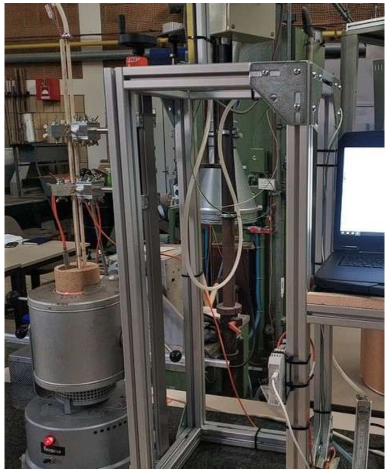
ohm

A view into the TH Nürnberg „High temperature electrochemistry laboratory“

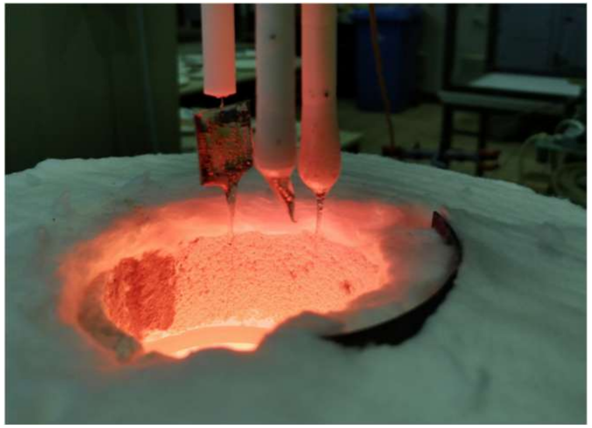
HTE1: 1200-1600 °C
DC-heating
Electrochemistry on
Pt and Mo-Electrode
Scientific and Industrial
Research

GreenGlass4.0

HTE5:
Tmax 1200 °C
AC-heating
Student training in
the field of HTE



GEFÖRDERT VOM
Bundesministerium
für Bildung
und Forschung

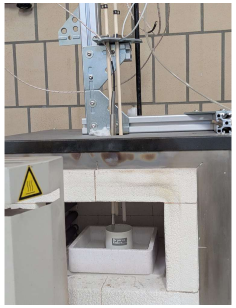


ohm

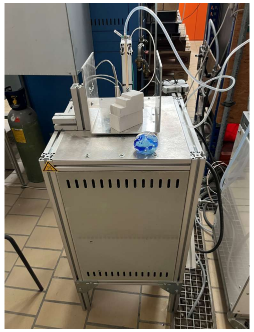
A view into the TH Nürnberg „High temperature electrochemistry laboratory“

HTE2: max. 1300 °C
DC or AC-heating
Electrochemistry
and Bubble nucleation
On Pt and Mo-Electrode
Scientific Research

HTE3: max. 1300 °C
AC-heating
Electrochemistry
on Pt-Electrode
Scientific Research

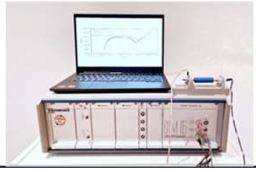


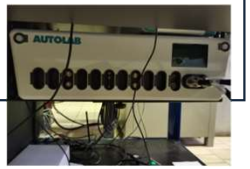
HTE4: 1100-1500 °C
AC-heating
Electrochemistry
on Mo-Electrode
Industrial Research



A view into the TH Nürnberg „High temperature electrochemistry laboratory“

Electrochemistry:
* 1 Zahner Potentiostat
* 2 Metrohm Potentiostats
* Prof. Dr. André Leonide
  (expert EIS)





Power sources:
- AC+DC source with frequency 5-1000 Hz
- DC source for compensation
- Different AC (50 Hz) sources

Measurement equipment:
- High resistance measurement tool
- Reference electrodes
- Voltage, current measurement
- Various ohmic resistance

Technische
Hochschule
Nürnberg

Thank you very much for your attention!