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In-line Oxygen Sensors for the Glass Industry, in Glass Melt, Atmosphere and Tin Bath

1

1

Activity & products

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Read-Ox & Consultancy BV established in 2001
In-line electrochemical sensors for glass melts, metal melts and molten salts

2

Product overview

for the glass industry

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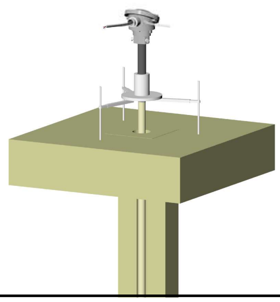
- **Glass melt** redox sensor
  (for the glass melt in the feeder channel, forehearth or canal)

- **Tin bath** oxygen sensors (in float glass production lines)
  - Tin melt oxygen sensor
  - Atmosphere oxygen sensor
  - Tin melt hydrogen sensor

- **Atmosphere** oxygen sensor for monitoring combustion process (T_{max} = 1650°C)
  - Crown
  - Flue gas channel / Regenerator



3

Contents

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- Importance of redox affecting glass melt /product properties
- In-line redox measuring system
  - Measuring principle
- Redox control (examples)
  - Heat transfer
  - Glass colour (container glass)
    - *Emerald green*
    - *Olive/Dead leaf*
    - *Antique green*
- Iron-ratio (cold glass) as sensor output
- Concluding remarks / New developments

4

4

Oxidation state of glass melt

Introduction

Oxidation state of the melt determines the valency state of the Multi-valent Ions (MI) :

$$MI^{x+} + {}^{n}/_{4}\, O_2 \leftrightarrow MI^{(x+n)+} + {}^{n}/_{2}\, O^{2-}$$

Reduced melt ←	→ Oxidised melt
Low valency	High valency

Iron		Fe^{2+} FeO	Fe^{3+} Fe_2O_3	
Sulfur	S^{2-} Na_2S	S^{4+} SO_2	S^{6+} Na_2SO_4	
Chromium	Cr^{2+} CrO	Cr^{3+} Cr_2O_3		Cr^{6+} CrO_3

→ *Redox → valency state multivalent ion → glass properties*

Effect of the redox state on properties

Overview

- **Gas production of the melt**
  - Fining behaviour $SO_4^{2-} + 2\,Fe^{2+} \rightarrow SO_2\,(g) + 2\,Fe^{3+} + 2\,O^{2-}$
  - Foaming behaviour $SO_4^{2-} \rightarrow SO_2\,(g) + {}^{1}/_{2}\,O_2\,(g) + O^{2-}$
- **Heat transfer** *Fe^{2+}: broad absorption band in near infrared*
  - Energy consumption
  - Temperature distribution / glass melt flow patterns in melting tank
  - Bottom temperatures (seed count and release of precipitates)
  - Crown temperatures (furnace lifetime)
- **Forming process via cooling rate**
  - Gob & (pre)form cooling rate in mould (*e.g.* surface cracks)
  - Fiber glass: cooling rate of fibers (Fiber breaks / hr)
- **Glass colour/optical properties**
  - Multivalent ions in solution Fe^{2+} Fe^{3+} Fe^{2+}/Fe^{3+} Cr^{2+} Cr^{3+} Cr^{6+} Fe^{3+}-S^{2-}
  - UV absorption (Fe^{3+}, Cr^{6+}, Ce^{4+})

→ *Every glass melt type has its optimal redox state*

→ *Redox variations destabilise the glass melting process*

Redox state & Fining

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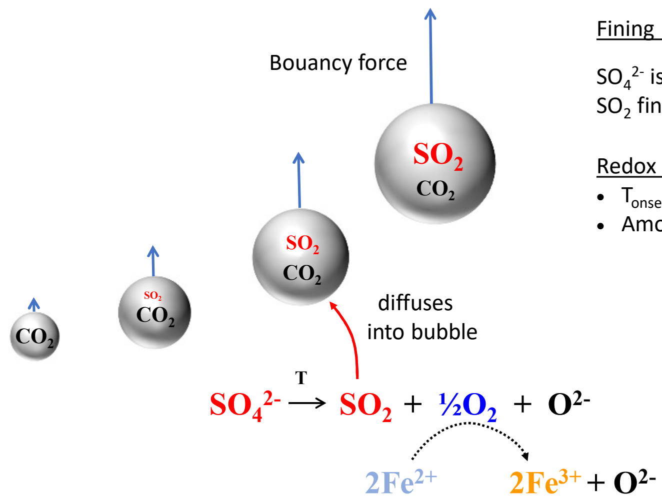

Fining by the sulfate–iron fining reaction:

SO_4^{2-} is reduced by Fe^{2+} (1100-1400°C) producing SO_2 fining gas inflating remaining CO_2 seeds

Redox controls:
- T_{onset} fining
- Amount of fining gas produced

7

Redox state & Foaming

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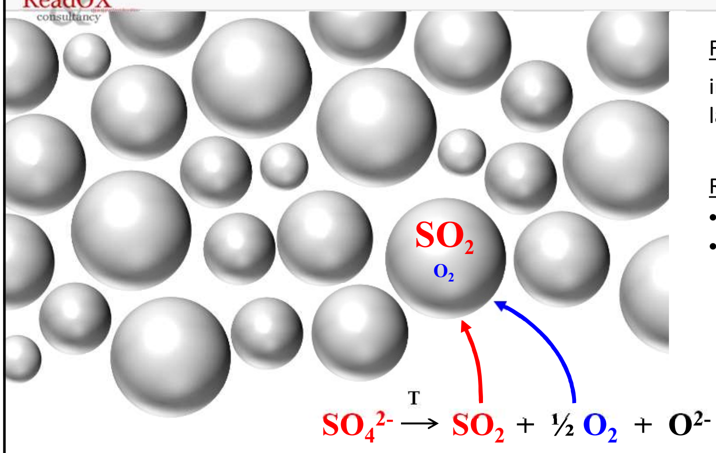

Foaming by thermal sulfate decomposition:

in oxidised glass melts (T > 1400 °C) producing large amounts of SO_2 and O_2 causing vigirous foaming

Redox controls:
- T_{onset} foaming
- Amount of foaming gas produced

8

Glass colour as a function of redox state

typical pO_2 ranges of various container glass colours

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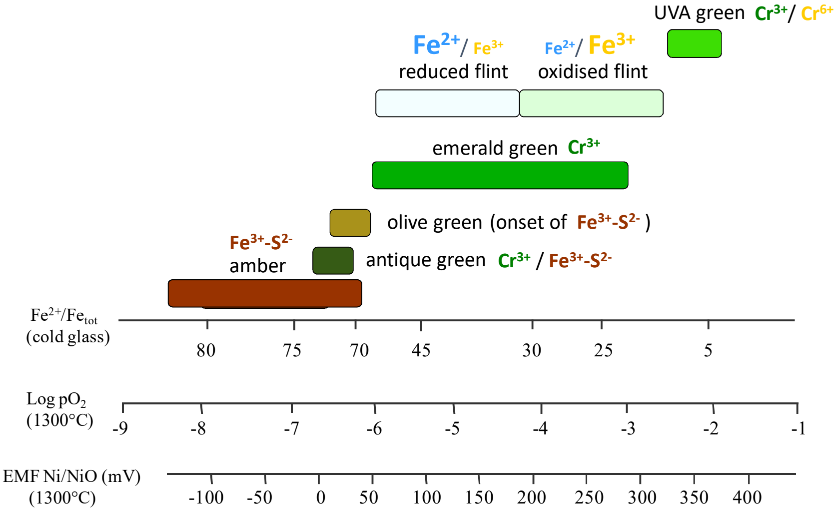

9

In-line glass melt redox measuring system

various components

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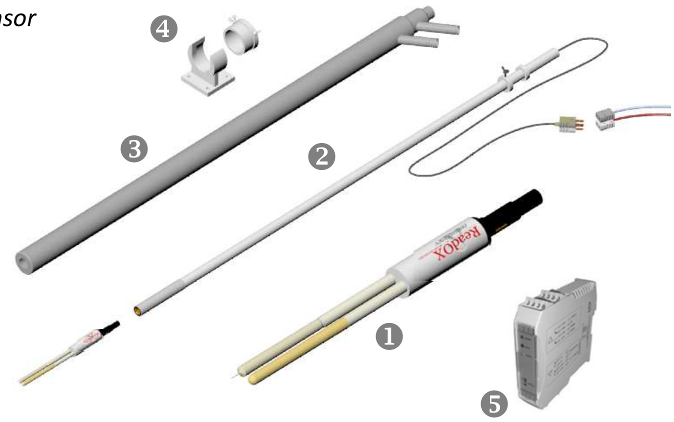
1. *Exchangeable redox sensor*
2. *Measuring lance*
3. *Water-cooled Jacket*
4. *Jacket holder unit*
5. *IOSI-01*



10

In-line glass melt redox measuring system

installed system

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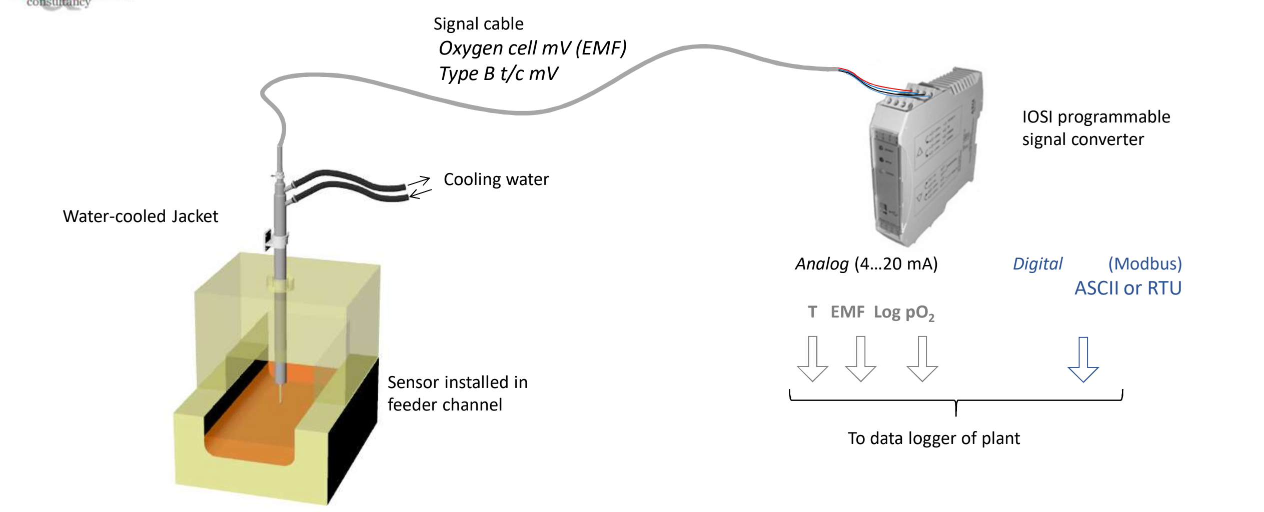

11

11

In-line glass melt redox measuring system

programmable IOSI converter and PC software

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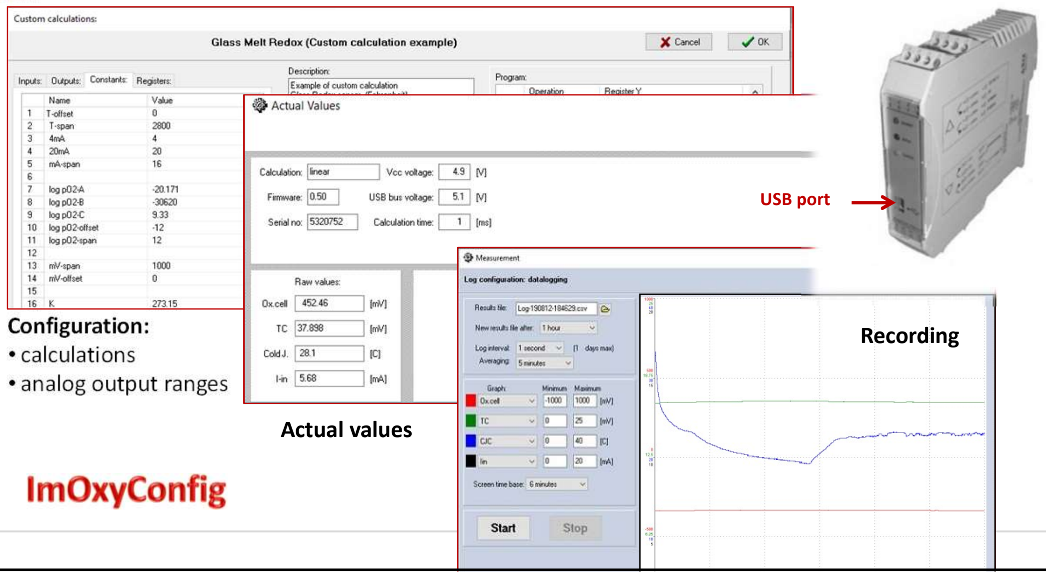

12

12

Redox sensor: measuring principle

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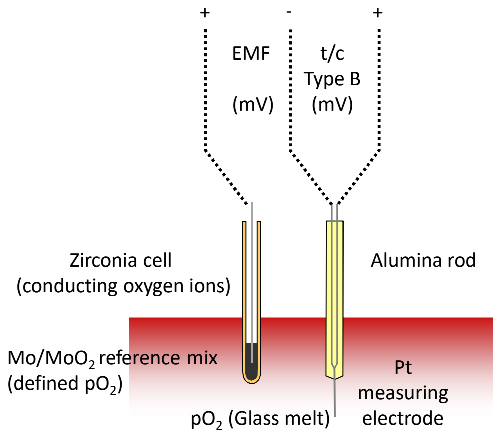
Oxygen sensor is an electrochemical cell: output Electro Motive Force (EMF)



13

Redox sensor: measuring principle

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Electrochemical cell

Pt / Mo-MoO$_2$ // ZrO$_2$ // pO$_2$ (glass) / Pt

- Mo–MoO$_2$ *reference material*
- ZrO$_2$ *solid electrolyte*
- pO$_2$ *oxygen activity in the glass melt*
- Pt *measuring electrode*

Nernst equation:

$$EMF = \frac{RT}{nF} \cdot \ln \frac{pO_2(glass)}{pO_2(ref. Mo/MoO_2)}$$

$$\log pO_2(Mo/MoO_2) = -\frac{30620}{(T+273)} + 9.33$$

$$\log pO_2(glass) = \frac{20.171 \cdot EMF - 30620}{T+273} + 9.33$$

EMF	(mV)
T	(°C)
pO$_2$	(bar)

Preprogrammed in the IOSI signal converter

14

In-line glass melt redox measuring system

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- Simple design, low-cost
- Flexible in location
- Exchangeable redox sensor (lifetime of about 6 weeks at 1150-1200°C)
- Easy sensor exchange (takes 10 to 15 minutes)
- No reference gas flushing due to solid reference (No gas bottles near furnace)
- Repair and part exchange can be done by personnel of the production facility

15

Redox measurements in industrial furnace

container glass

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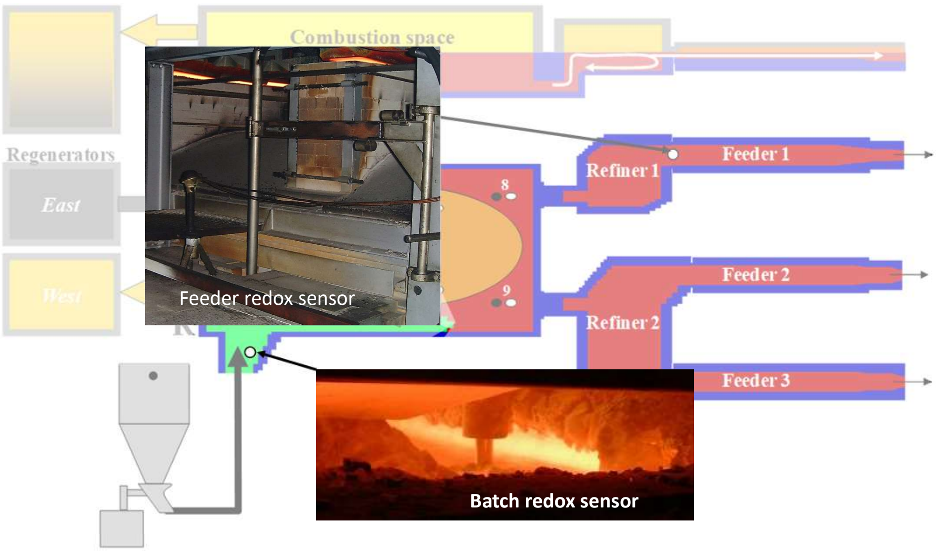

16

Redox measurements in industrial furnace

advantage of a continuous redox measurement

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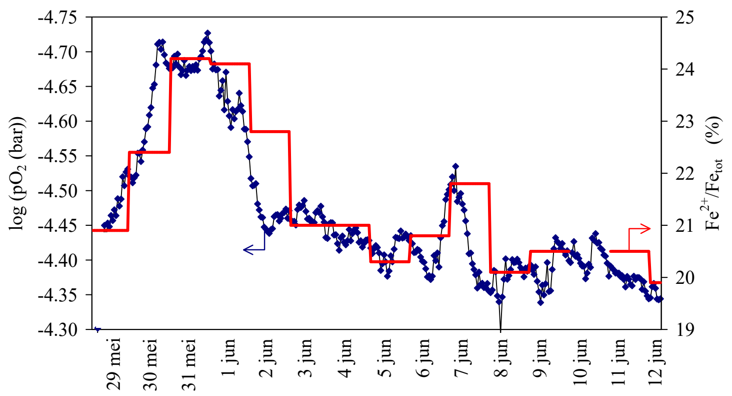
log pO_2 (feeder sensor) versus daily analysed Fe^{2+}/Fe_{tot} ratio:



Advantages in-line redox sensor:

- Time gain for control (max. ≈ 24 hr!)
- Redox state continuously available
  Level, direction and rate of change
  (also when laboratory is closed!)

➡ Operator is more confident and uses signal for batch redox number corrections

➡ Foreign cullet share could be increased by 5% (saving batch costs and energy costs!)

17

17

Redox control – Heat transfer

*Relation heat transfer - redox / **Emerald green container glass***

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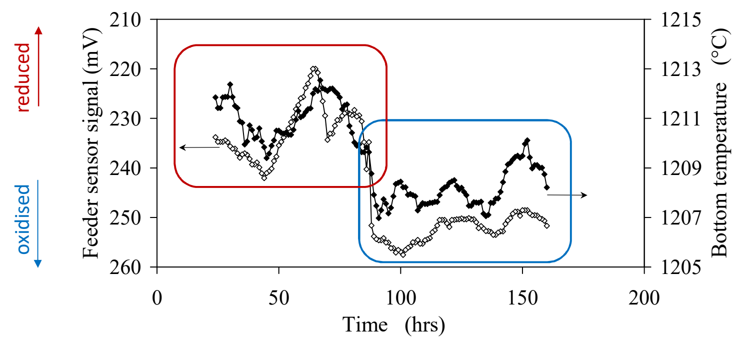
Use of in-line redox sensor revealed following relation*:



Oxidised melt → low bottom temperatures (bad heat transfer)

Reduced melt → high bottom temperatures (good heat transfer)

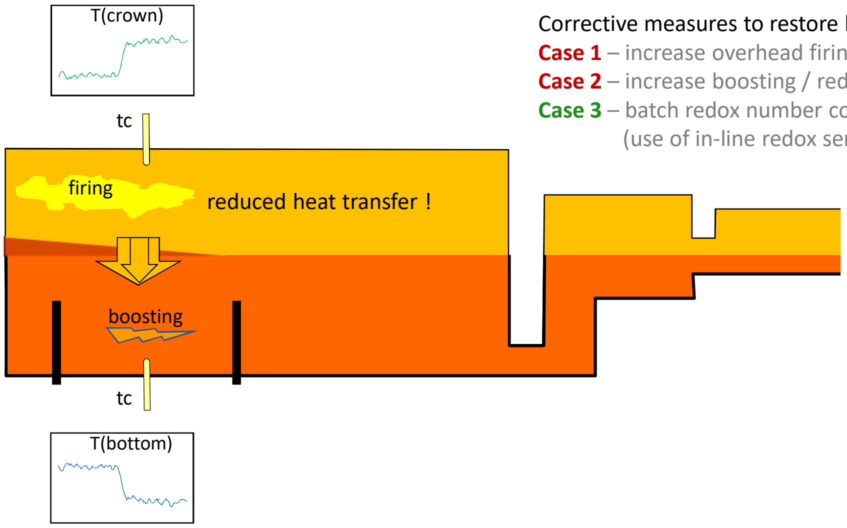
** in this particular emerald green container glass furnace (air fuel fired)*

18

18

Redox control – Heat transfer

Relation heat transfer - redox : better process control

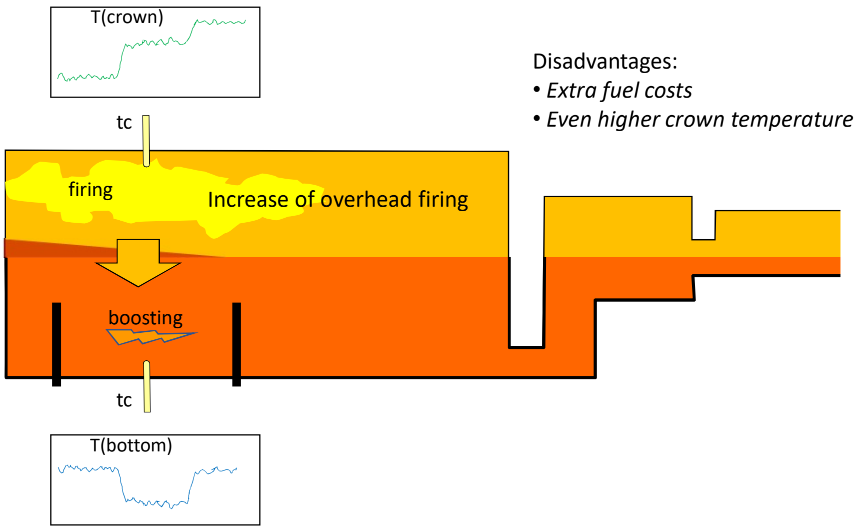


Corrective measures to restore bottom temperature:
Case 1 – increase overhead firing
Case 2 – increase boosting / reduce firing
Case 3 – batch redox number correction
(use of in-line redox sensor)

Case I

Redox control – Heat transfer

Relation heat transfer - redox : better process control



Disadvantages:
- *Extra fuel costs*
- *Even higher crown temperature*

Case II

Redox control – Heat transfer

Relation heat transfer - redox : better process control

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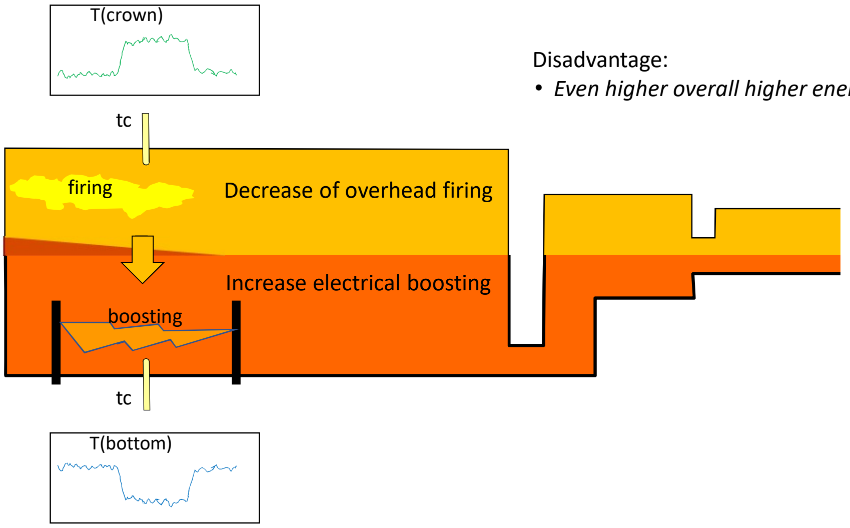
Disadvantage:
- *Even higher overall higher energy costs*



Case III

Redox control – Heat transfer

Relation heat transfer - redox : better process control

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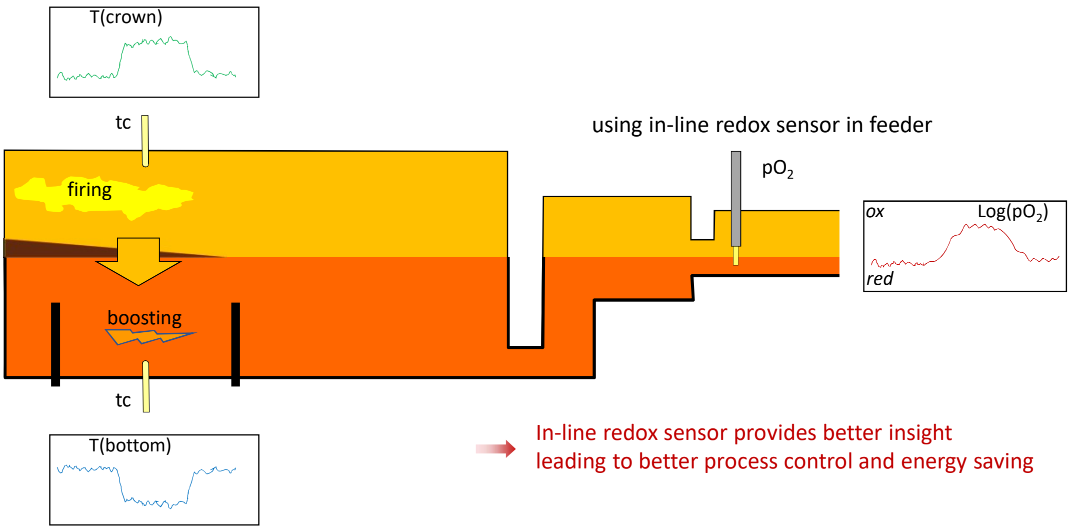
Reduce melt by lowering batch number



In-line redox sensor provides better insight leading to better process control and energy saving

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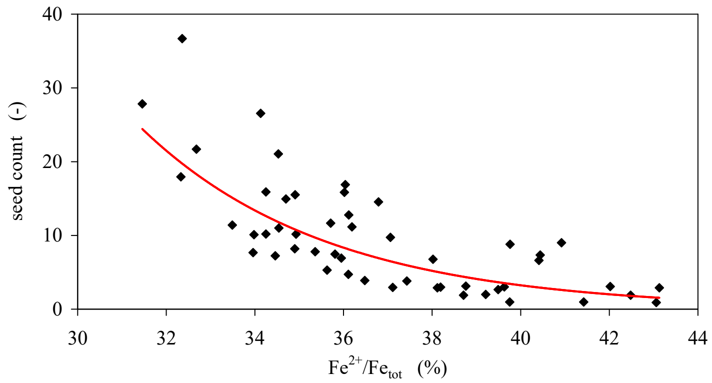
Redox control – Seed count

*Relation seed count – redox / **Emerald green container glass***

Emerald green : reduced melt – better heat transfer but also lower seed count *



** in this particular emerald green container glass furnace (air fuel fired)*

23

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Redox control in industrial furnace

*Relation redox - seed count - heat transfer / **Emerald green container glass***

Emerald green glass can be melted in a relatively large redox range:
Log pO_2 (1300°C) = -3 to –6 (Fe^{2+}/Fe_{tot} *(cold glass)* = 20 to 50%)

More reduced melt (Fe^{2+}/Fe_{tot} *(cold glass)* = 40 to 45%) :

→ *lower seed count*
→ *better heat transfer*

24

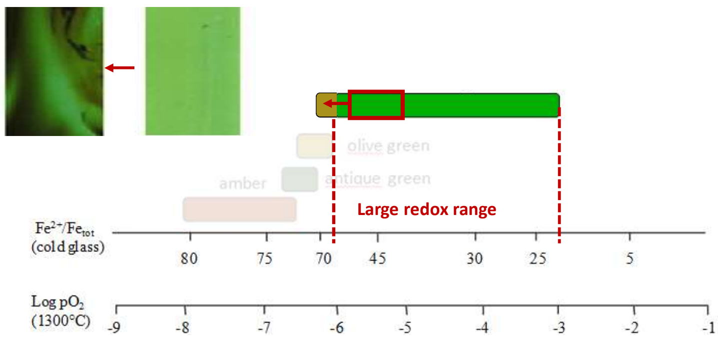
Redox control in industrial furnace

*Relation redox - seed count - heat transfer / **Emerald green container glass***

Emerald green glass can be melted in a relatively large redox range:
Log pO_2 (1300°C) = -3 to –6 (Fe^{2+}/Fe_{tot} *(cold glass)* = 20 to 50%)

Risk of melting more reduced :

melting foreign recycling cullet with incidentally high COD
→ amber cords and/or blisters may appear in the green glass



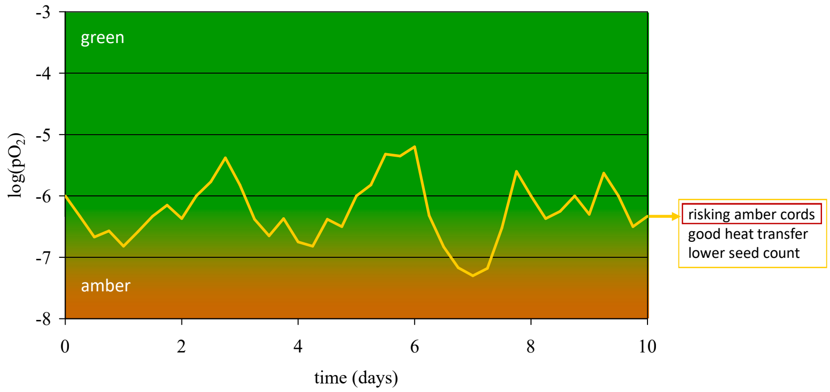
25

25

Redox control in industrial furnace

*Relation redox - seed count - heat transfer / **Emerald green container glass***

Melting emerald green under reduced conditions, with high levels of foreign recyling cullet:



→ Policy: melting oxidised (high batch sulfate) to avoid amber cords

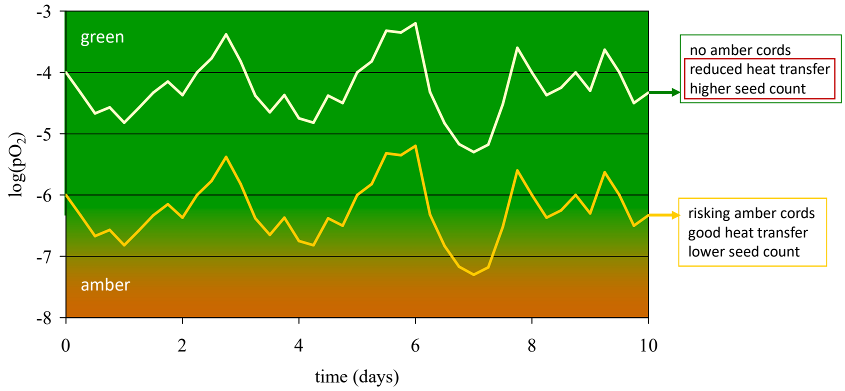
26

26

Redox control in industrial furnace

*Relation redox - seed count - heat transfer / **Emerald green container glass***

Melting emerald green under more oxidised conditions, to avoid amber cords

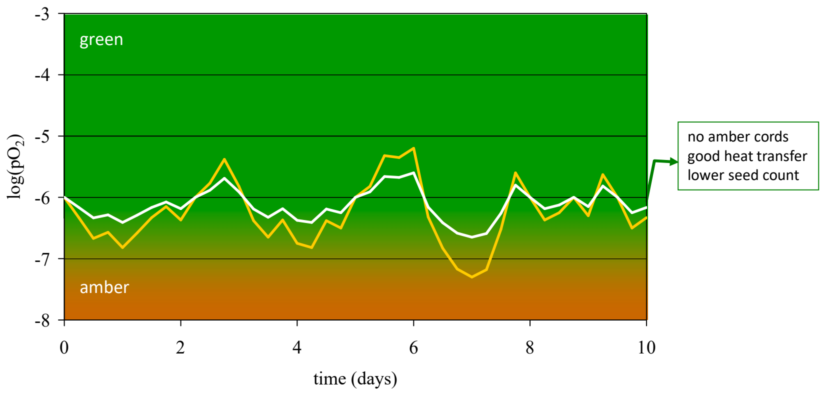


→ Policy: melting oxidised (high batch sulfate) to avoid amber cords

Redox control in industrial furnace

*Relation redox - seed count - heat transfer / **Emerald green container glass***

However, using an in-line redox sensor:



Variations can be reduced due to a better control by the continuously available redox value

→ The redox sensor may help to melt more reduced without risking amber cords!

Redox control in industrial furnace

Colour control of green glasses with an amber colour component

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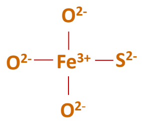
Antique green, olive green and dead leaf are very sensitive to redox variations

Mix of green and amber:

Cr^{3+}

Fe^{2+}/Fe^{3+}



Amber chromophore
Colour intensity ~ $[Fe^{3+}]\cdot[S^{2-}]$

Out of colour specification already as a result of small changes in :

- *firing condition (air/fuel ratio)*
- *weathering degree of recycling cullet*
- *batch humidity*
- *pull*

29

Redox control in industrial furnace

*Green glasses with an amber colour component : **Olive green***

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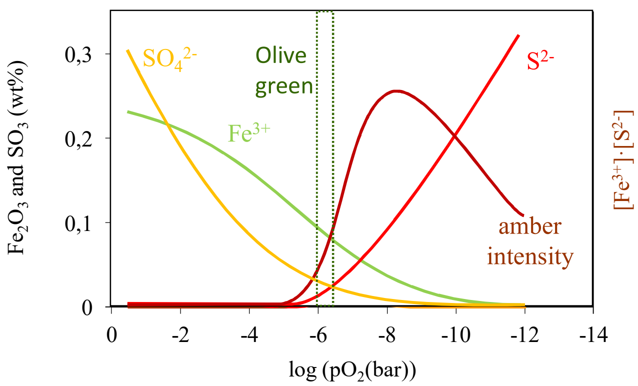

Amber chromophore
Colour intensity ~ $[Fe^{3+}]\cdot[S^{2-}]$

Olive green colour must be melted at the onset of the amber chromophore formation

→ Narrow redox operating window

30

Redox control in industrial furnace

*Green glasses with an amber colour component : **Olive green***

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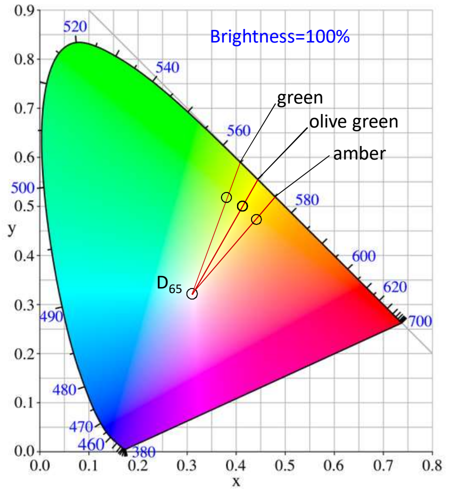
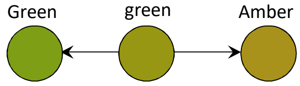


Brightness = 30% (~5 mm sample thickness)
Saturation = 75%



DWL (nm)	565	570	575
x y	0.38 0.53	0.42 0.50	0.44 0.47
T = 1250°C Sensor (mV) log(pO_2)	 **290** -6.93	 **280** -7.07	 **270** -7.20

Narrow color spec.range of only +/- 5mV
Sensor very helpful !

31

31

Redox control in industrial furnace

*Green glasses with an amber colour component : **Olive green***

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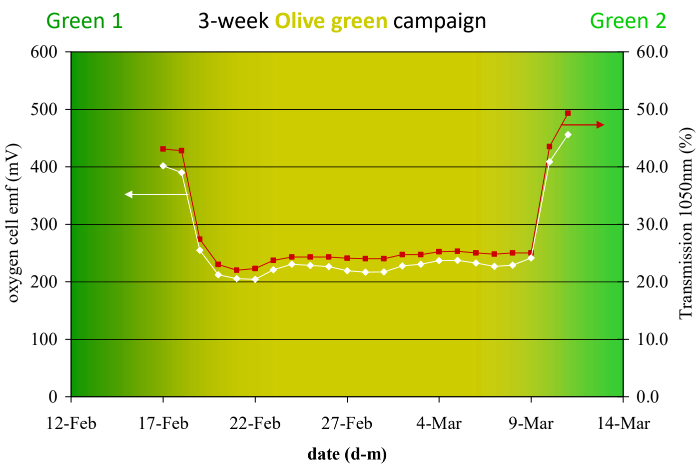

No sensor: daily 3 lab. values are needed

Sensor: one lab. value per day value suffices!

32

32

Redox control in industrial furnace

*Green glasses with an amber colour component : **Antique green***

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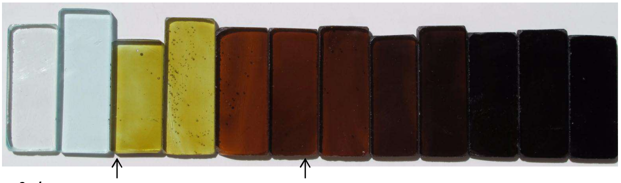
Antique green is also very sensitive to redox variations (problem: over-reduction!)

Amber in flint:

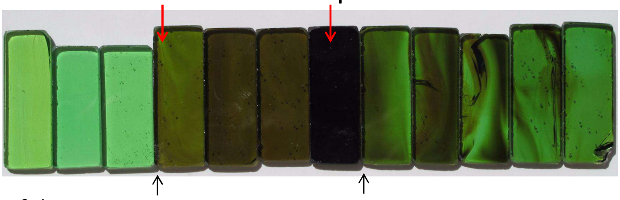


Fe^{2+}/Fe_{tot} 0.50 0.80

Antique:

Amber in chromium green :

Olive **Antique**



Fe^{2+}/Fe_{tot} 0.50 0.80

Data/Pictures by courtisy of Fehiman Akmaz, ŞİŞECAM

Redox control in industrial furnace

*Green glasses with an amber colour component : **Antique green***

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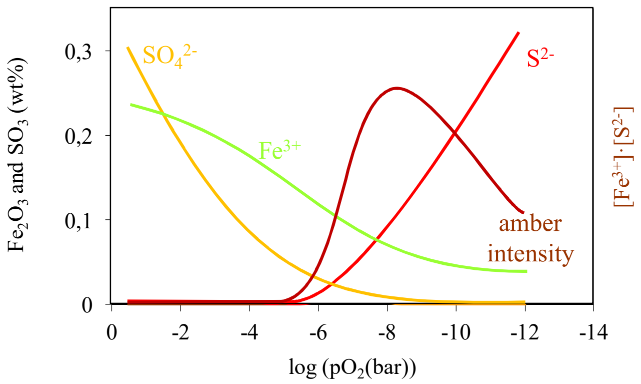
Antique green is sensitive to over-reduction

Amber in flint :

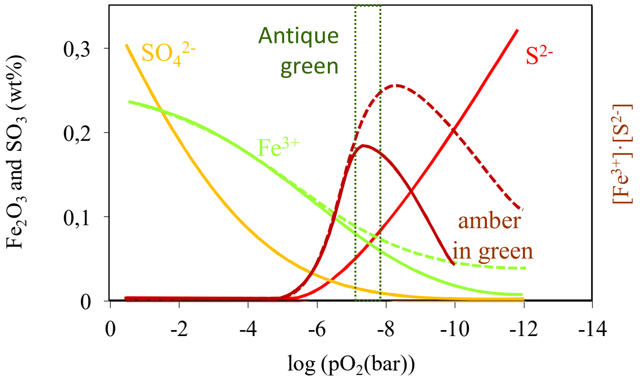


Redox control in industrial furnace

*Green glasses with an amber colour component : **Antique green***

Antique green is sensitive to over-reduction

Amber in chromium green:



Narrow redox operating window

Redox control in industrial furnace

*Green glasses with an amber colour component : **Antique green***

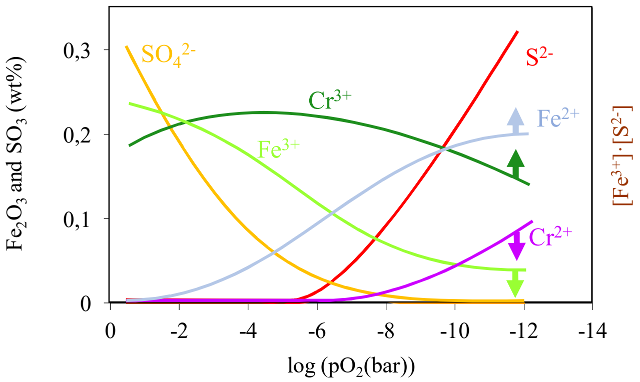
Antique green is sensitive to over-reduction

Amber in chromium green:

At melting temperature

On cooling down to T_g:

$Cr^{2+} + Fe^{3+} \rightarrow Cr^{3+} + Fe^{2+}$



Redox control in industrial furnace

*Green glasses with an amber colour component : **Antique green***

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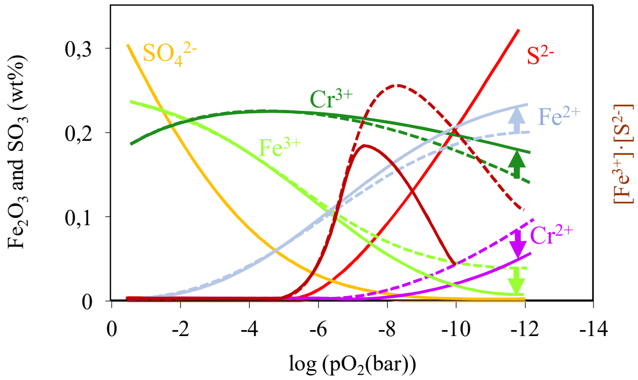
Antique green is sensitive to over-reduction

Amber in chromium green:

At Tg



Redox control in industrial furnace

*Green glasses with an amber colour component : **Antique green***

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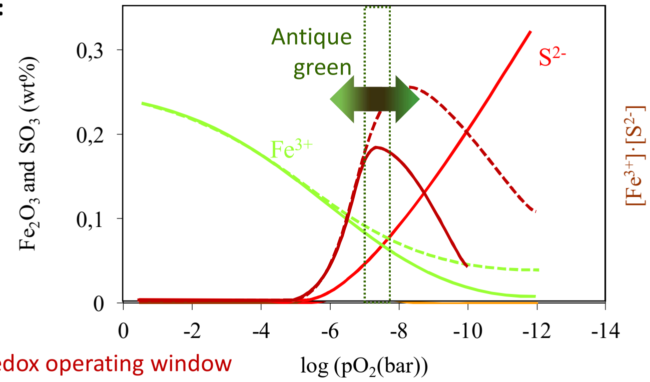
Antique green is sensitive to over-reduction

Amber in chromium green:



Narrow redox operating window

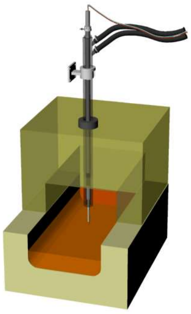
Antique green turns green (amber colour dissappears): glass can be too oxidised or too reduced !

In-line redox sensor very helpful for a fast correction in the right direction

Redox control : continuous iron ratio

Iron-ratio cold glass as continuous sensor output (with lab. calibration)

Present situation: redox sensor gives log pO_2 of the melt



$\log(pO_2)$?

Operator is used to work with daily lab analysis Fe^{2+}/Fe_{tot}

Semi-empirical relation

Fe^{2+}/Fe_{tot}(cold glass product) = f(EMF, T) →

"lab-analysis" continuous available !!

39

Redox control : continuous iron ratio

Iron-ratio cold glass as continuous sensor output (with lab. calibration)

Continuous iron-ratio is the sum of an iron-ratio calibration value (laboratory) and an (empirical) function of the EMF change and T change:

$$(Fe^{2+}/Fe_{tot})_t = \underbrace{(Fe^{2+}/Fe_{tot})_0}_{\text{laboratory}} + \underbrace{f(\Delta EMF, \Delta T)}_{\text{sensor}}$$

$(Fe^{2+}/Fe_{tot})_t$ = continuous iron-ratio of cold glass (sensor output)
$(Fe^{2+}/Fe_{tot})_0$ = iron-ratio calibration value (laboratory spectrometer)
ΔEMF = $EMF_t - EMF_0$
ΔT = $T_t - T_0$

t=0 : time at which the (later) analysed cold glass sample passed the sensor (EMF_0 and T_0) as a glass melt

Glass melt → Bottle → Lab result

t=0 : EMF_0 and T_0

At calibration procedure estimation of t=0

$\left(\frac{Fe^{2+}}{Fe_{tot}}\right)_0$

40

Redox control : continuous iron ratio

Iron-ratio cold glass as continuous sensor output (with lab. calibration)

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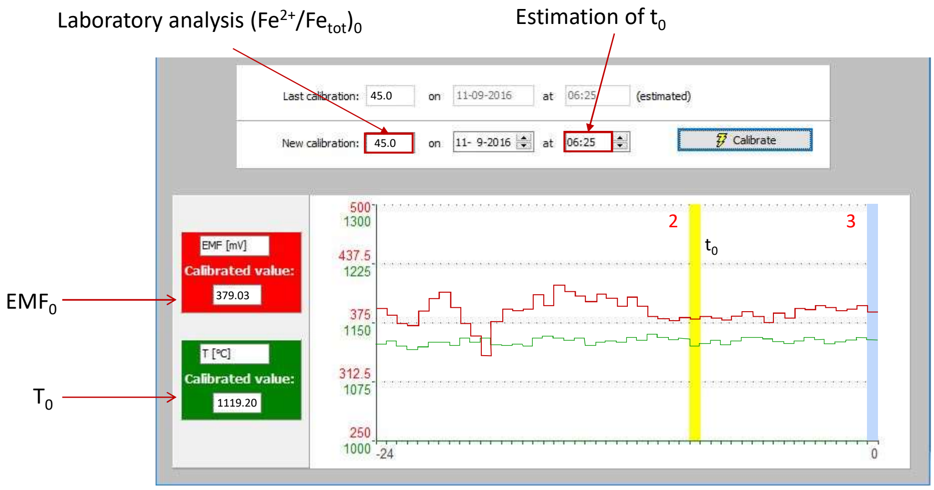

41

Redox control : continuous iron ratio

*Iron-ratio of cold glass as continuous sensor output (**Emerald green**)*

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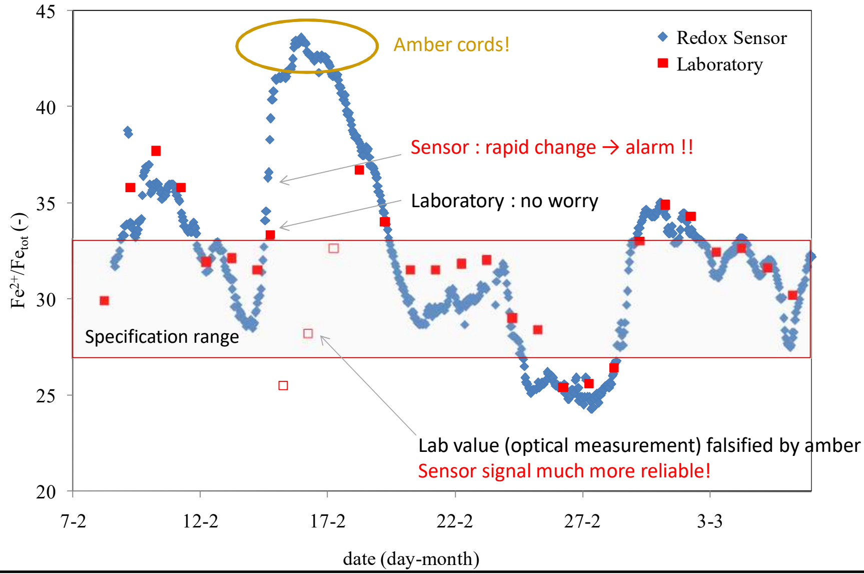

42

Redox control : continuous iron ratio

Iron-ratio cold glass as continuous sensor output (with lab. calibration)

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Continuous iron ratio of cold glass - Advantages:

- No miscommunication between lab and furnace operators
- Lab: single iron-ratio value once a day
  Sensor: continuous (level, direction and rate of change)

➡ In a few emerald green furnaces the continuous iron-ratio is running with great satisfaction

43

43

Concluding remarks

Advantages of using an in-line glass melt redox measuring system

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Continuous use:

- Always redox state available for monitoring and for fast correction
  - *Container glass with high levels of recycling cullet*
    (energy saving by optimal heat transfer, colour stability and low seed count)
  - *Glasses with narrow colour specifications (olive green, dead leaf, antique green)*

Occasional use:

- During a colour conversion (faster conversion without overshoot)
- During a campaign of a redox sensitive colour
- Batch recipe changes (new material supplier)
- Trouble shooting (is redox causing the process instability or product defect?)
- Research program: relation process/product parameters to glass melt redox (Big Data: PCA)

44

44

New developments

Advantages of an in-line glass melt redox measuring system

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New developments:

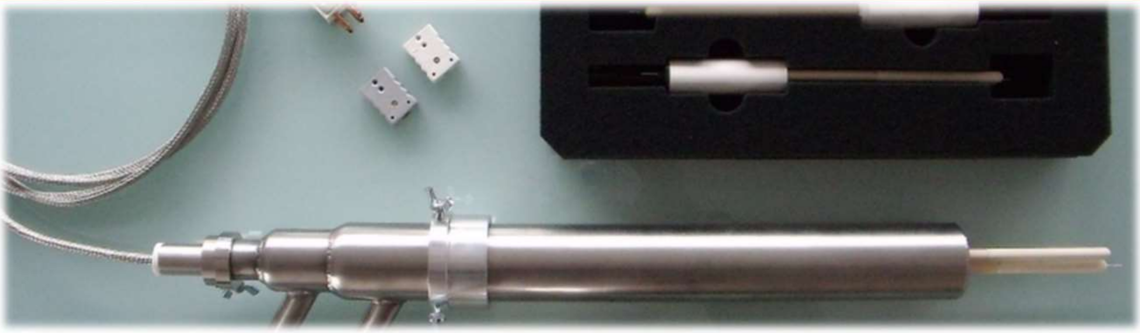
- For float glass lines: Nickel free stainless steel redox measuring system (water-cooled jacket, measuring lance)
- Glass melt redox sensor with high internal resistance (higher EMF stability in (ultra) clear glasses, with low levels of multivalent ions)

45

45

46

46



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Thank you for your attention !
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