

econox

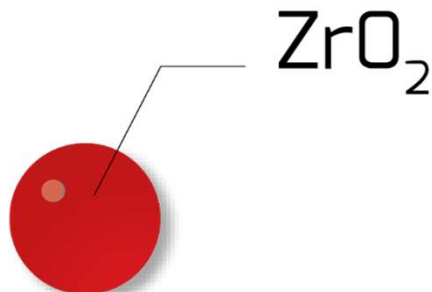
SWISS QUALITY SINCE 1984 

Measuring & control systems Carbon & Oxygen

- Swiss company
- Established in 1984
- Small family company
- Probe manufacturing for 40 years
- Was part of a bigger heat treatment company for 25 years
- Years of experience in the heat treatment industry
- Many partnerships with key suppliers

For the O₂ probes Econox is using 3 types of ZrO₂ sensor shapes

Exchangeable
ZrO₂ ball



ZrO₂ pellet
sealed to Al₂O₃ tube



Closed-end ZrO₂
tube



This presentation covers practical experiences of O₂ probe failures or deviations in heat treatment (%C) and the implemented corrective actions

We will not go into construction details or thermochemical considerations.

There are enough publications on this subject

Structure of the presentation :

The cases of malfunction are divided into various headings

- A : Possible causes of short lifetime of the probe
- B : Importance of the probe burnoff
- C : Possible causes of measured %C higher as real %C measured on foil test or on the parts.
- D : Possible causes of measured %C lower as real %C measured on foil test or on the parts
- E : Possible causes of low response time
- F : List of preventive maintenance controls

Observation:

- The lifetime of an oxygen probe can go from a few weeks to a few years depending on many variables like :
 - Working temperature
 - Process carbon potential (%C) value
 - Quench medium (chemical attack)
 - Lubricant or detergent residues (chemical attack)
 - Vibration or thermal shock
 - Soot deposit on the sensor
 - Low measurement-circuit input impedance ($<10\text{ k}\Omega$)

Cause 1 : Too low impedance of the measuring circuit

Explanation :

- A low impedance of the measurement circuit impacts the measured EMF (mV drop)
- Low impedance also impacts the lifetime of the sensor because the measurement current is too high, this causes a continuous mass transfer (O_2) through the cell.
- The thermodynamic equilibrium is never achieved.
- The electrolyte is gradually reduced

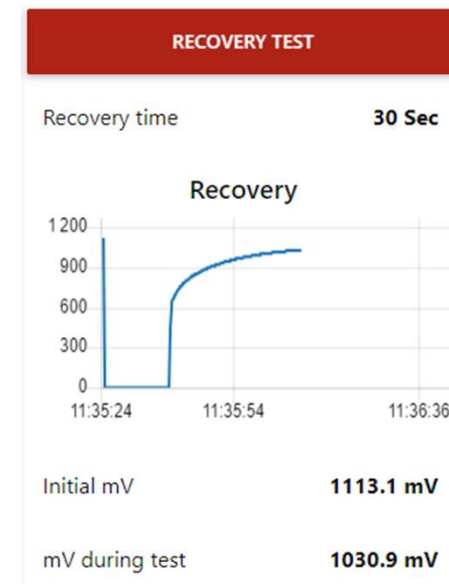
Solution :

- The inlet impedance should be at least 10 (or ideally 20) M Ω

Cause 2 : Chemical attacks

Observation on EMF reaction :

- After a few days, the probe's mV reacts very slowly to additional gas injection
- On our test furnace, we observed the following phenomenon after the recovery test :
 - 30 seconds after the short-circuit is lifted, a value of 1030 mV is reached, compared with an initial value of 1113 mV.
 - The probe is out of order



Explanation :

- After investigation, the customer informed us that he used **boron-based carburising stop-off paints**.
- Boric acid vapors formation results in **attacking** both the chromium oxide layer of the refractory material (vitrification) and the zirconia.



Solution:

Remove Boron protective stop-off paints and replace it with another one

Other example of chemical attacks

- Vapors from residual lubricants on badly washed parts.
- Vapors from quenching salts, in particular nitrite-nitrate mixtures entering the furnace during quenching or residual on fixtures.

Example of a ball (doped ZrO_2) and a seat tube (Al_2O_3) that have been subjected to chemical attack.

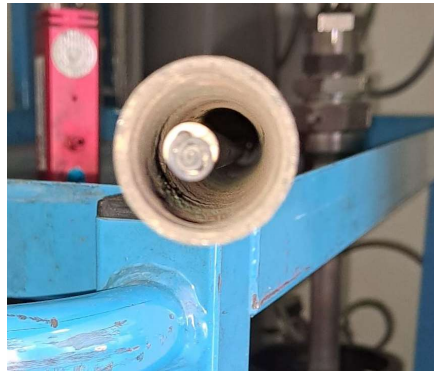


These are not carbon deposits, as the 2 parts were exposed to air at a temperature of 1000°C for 4 hours.

Case 3 : Corrosion of the outer tube

Observation :

- We received a probe back with the pellet at the end of the outer tube disintegrated.
- On the outer tube we can see white deposits.



Cause :

- The customer is using alkaline detergents.

Solution :

- Neutral detergents without salts should be used
- Carefully wash the parts and the loading material before heat-treatment

- A carbon sensor operates in a very harsh environment where carbon deposits (soot) often form on the sensor. As soot accumulates at the tip of the sensor, the sensing surface of the sensor is shielded from the furnace atmosphere.
- This leads to false, elevated mV reading, resulting in low carbon or decarburizing conditions.
- Additionally, the high nickel content in the protective sheath alloy, also acts as a catalyst, accelerating the deposit of carbon on the sheath.

CLEANING/ BURNOFF CYCLE HAS A DIRECT IMPACT ON THE LIFETIME OF THE ZrO_2 CELL AND THE OUTER TUBE

Critical points :

- During burnoff, fresh air is injected through the inside of the probe to remove soot accumulated on the ZrO₂ cell.

The higher the free oxygen content in the presence of soot, the more effective the cleaning.

- **Cleaning efficiency depends on:**
 - Injected air flow rate
 - Injection duration
 - Gas circulation around the probe, i.e. furnace type
 - **The more intense this circulation, the higher the air flow rate to obtain free oxygen**
 - Probe construction.
- For effective cleaning, **high air flow rates are often required**, resulting in :
 - A local rise in temperature due to an exothermic reaction with the process gas.
 - Interactions with the charge in the furnace (decarburization - oxidation), especially on low-volume furnaces.

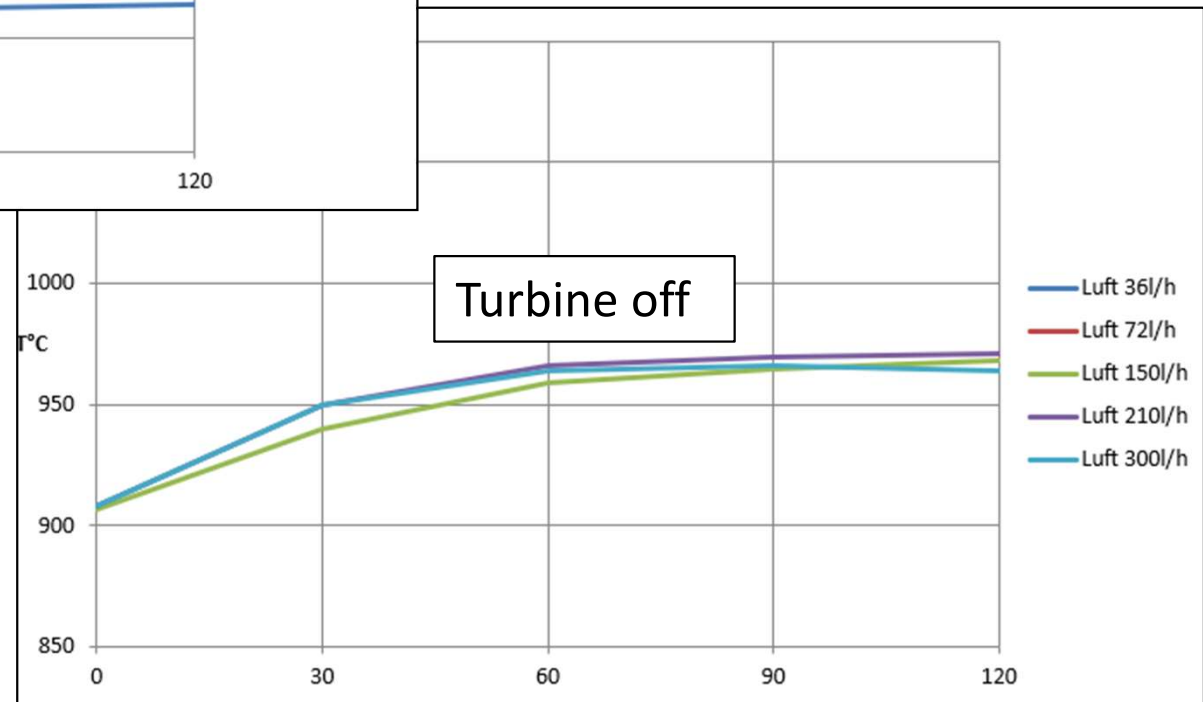
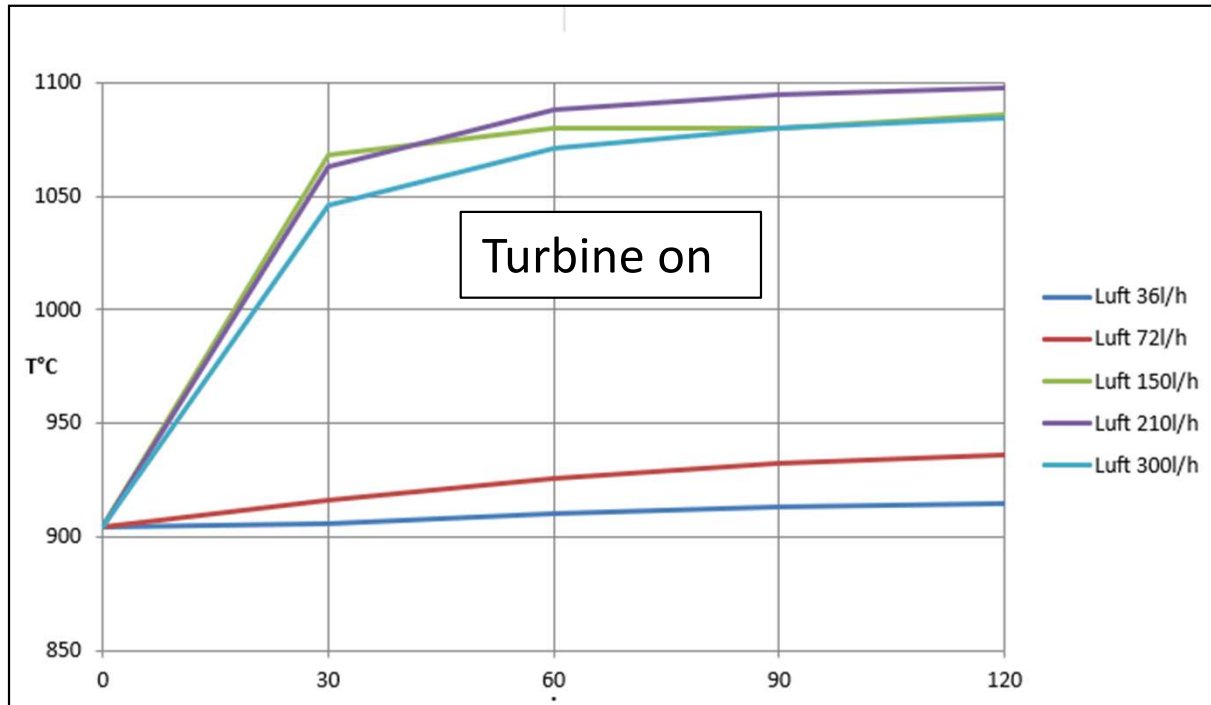
Furnace turbine influence on probe burnoff

- To avoid the often-random adjustment of purge air flow rates, the furnace turbine should be stopped for the duration of the burnoff.

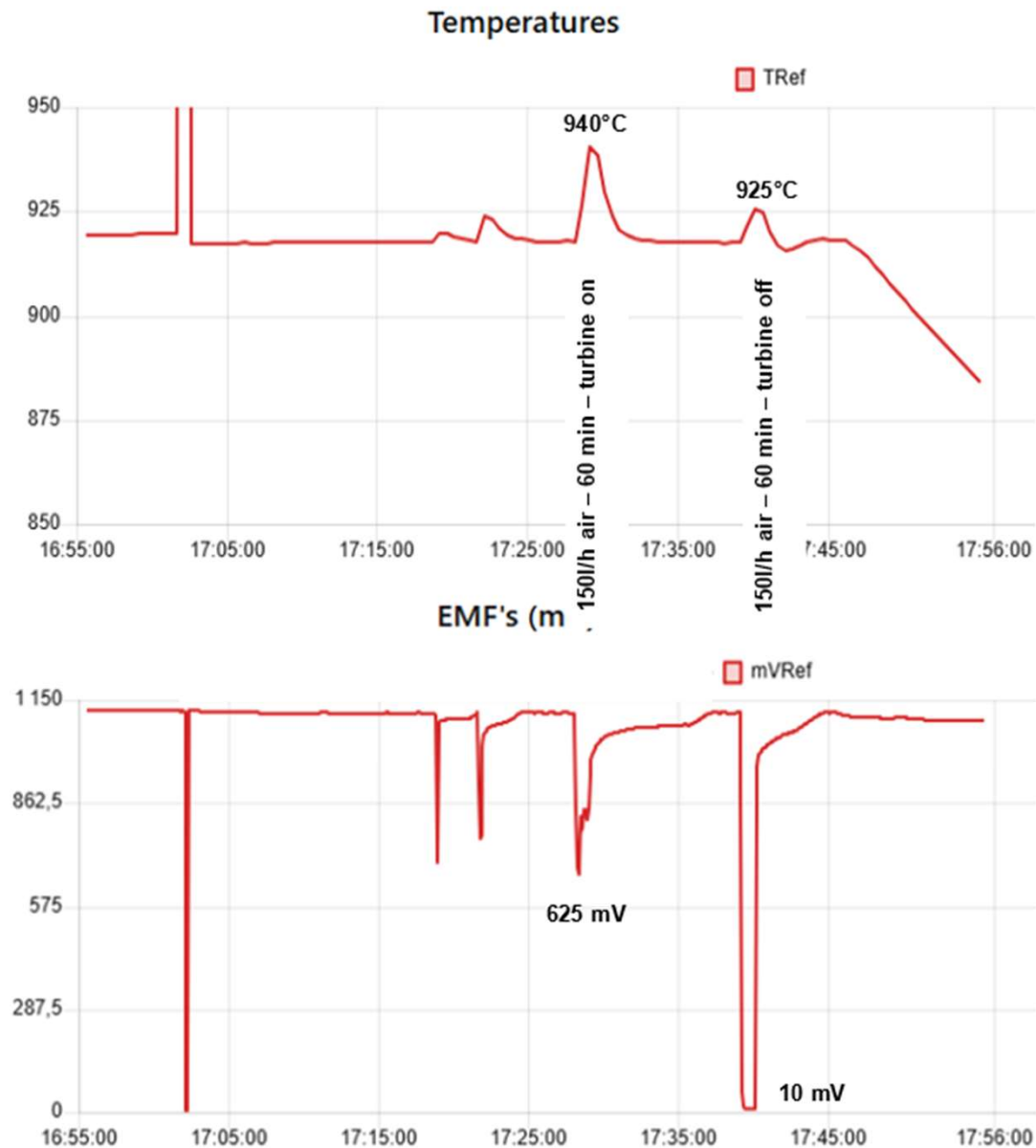
The following effects can be noted:

- A reduction in the exothermic effect of the reaction between the furnace atmosphere and the burnoff air
- An increase in the free oxygen value at the probe sensor, resulting in more efficient combustion of carbon deposits.
- In addition, by reducing the air flow rate, the carbon potential of the atmosphere is less disturbed.

T°C increasing on probe tip vs turbine on /off



Influence of the turbine on/off on EMF drop during burnoff



Possible cause - Case 1 :

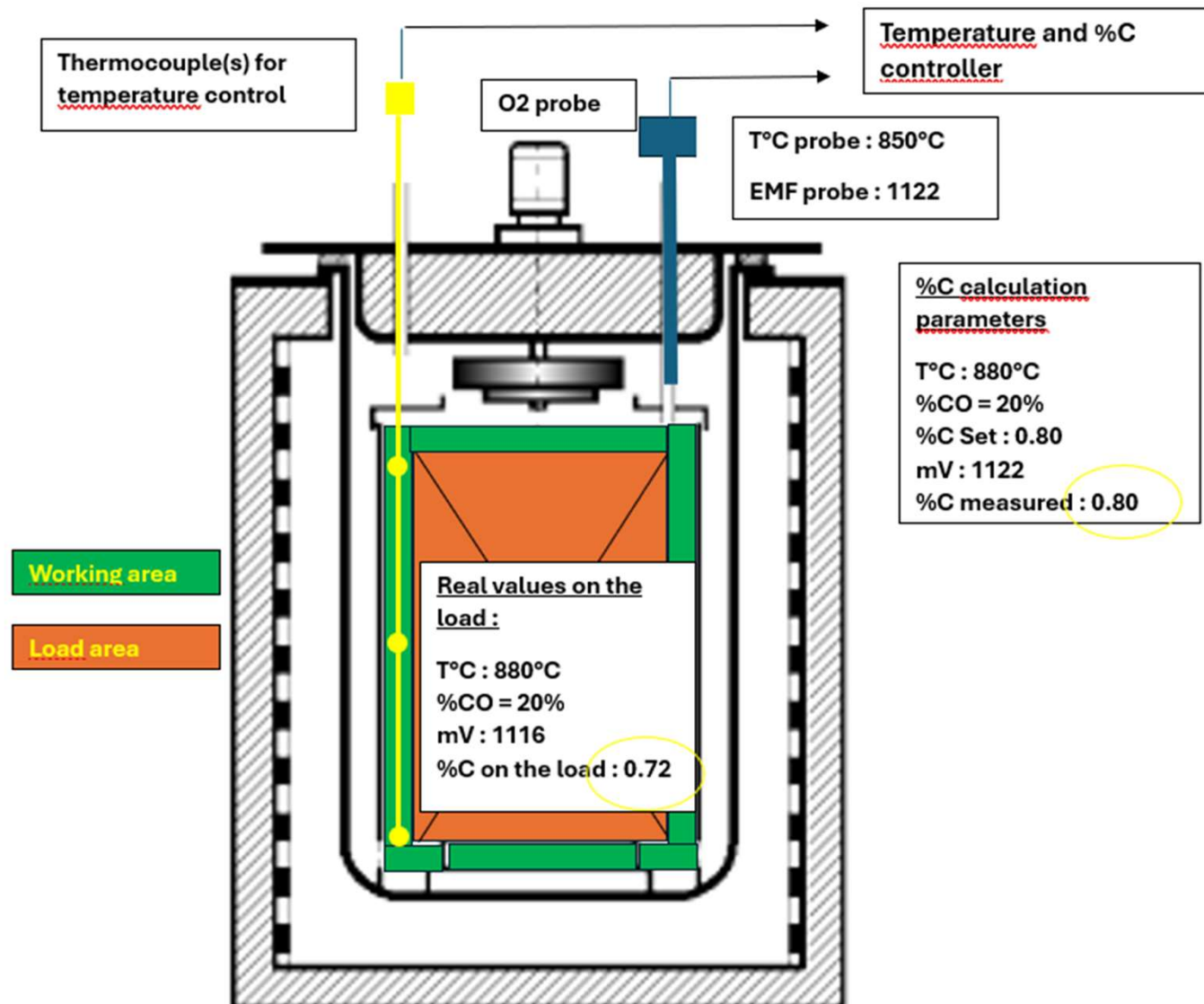
- Wrong location of the probe in the furnace

Explanation :

- The probe was not placed in the useful volume of the oven and was not fitted with a thermocouple.
- A difference of -30°C vs load temperature was measured.
- This results in a higher carbon reading than that in the load

C : MEASURED %C TOO HIGH VS REAL %C

Exemple : a difference of 30°C gives a deviation of 0.08%C



Possible cause - Case 2 :

- Wrong %CO value used for the carbon potential calculation

Explanation :

- Real %CO was lower as the %CO used for the carbon potential calculation
- A fixed %CO value was used in the controller
- The problem was due to **carrier gas flow deviations.**
=> Cause identified using a portable CO/CO₂ analyzer

Explanation :

- In some furnaces, the carrier gas is produced from a **methanol/nitrogen mixture**. In the event of flow drift (RDM, Rotameter or leaky valves), the actual %CO is different from the theoretical %CO used to calculate the carbon potential.
- %CO drift can also be caused by **excessive addition of additional carburising** gases (propane or methane).

The table below gives an overview of %C vs. %CO drift at constant temperature and mV.

Température (%C)	%CO	mV Probe	%C calculated	Δ %C
920	20	1147	1	0
920	19	1147	0.95	-0.05
920	18	1147	0.91	-0.09

Solution :

Online monitoring of %CO, %CO₂ and %CH₄
with help of an infrared gas analyzer.

Possible cause - Case 3 :

- Catalytic decomposition of the CH₄

Explanation :

- CH₄ values in excess of thermodynamic equilibrium are measured.
=> Cause identified using a portable CO/CO₂ analyzer
- The **probe's outer tube**, which is also used as an external electrode, acts on the decomposition of residual CH₄.
- In this case, the probe measures a local pO₂ lower than that of the atmosphere circulating in the furnace.
- The calculated carbon potential is higher than that of the atmosphere circulating around the charge.

Solution:

- Equip the probe with an outer tube made of a refractory alloy **with a low catalytic effect**

or

- Place an intermediate electrode between the zirconia and the outer tube.

Econox can supply the 2 above options

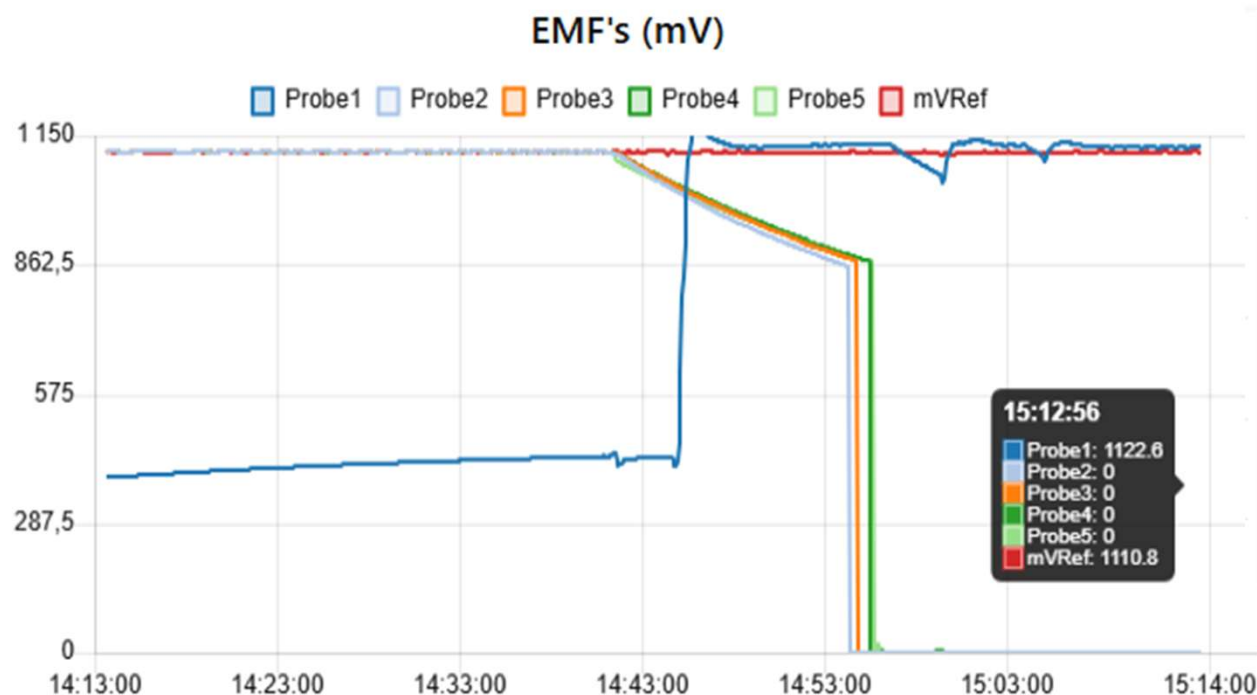
C: MEASURED %C TOO HIGH REAL %C

Possible cause : Case 4 :

- Soot deposit on the sensor

Observation:

-Over voltage on redundant Probe 5433 vs. reference probe



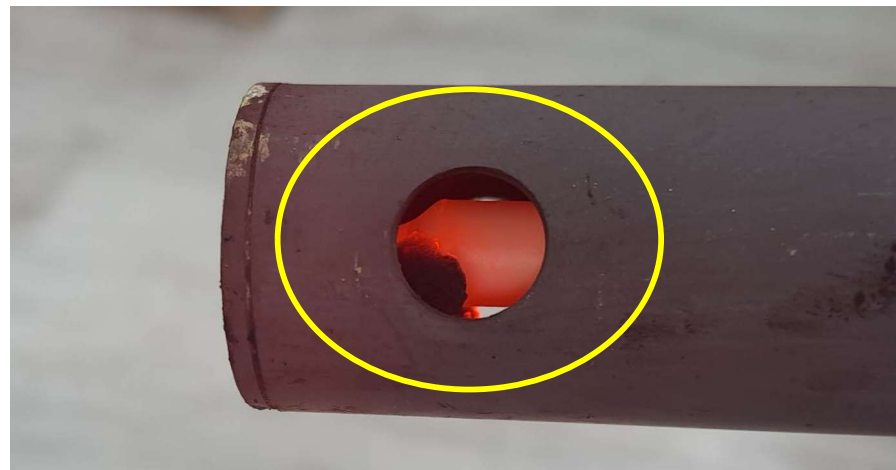
Table

Reference probe	Temp. Ref	917.8°C	EMF Ref	1111.7mV
Serial No1	5433	Temp. 1	916.2°C	EMF 1 1123.9mV
Serial No 2	0000	Temp. 2	1372°C	EMF 2 0mV
Serial No 3	0000	Temp. 3	1372°C	EMF 3 0mV
Serial No 4	0000	Temp. 4	1372°C	EMF 4 0mV
Serial No 5	0000	Temp. 5	1372°C	EMF 5 0mV

$$\Delta \text{ mV} = 12\text{mV}$$

Explanation :

- Carbon deposit on zirconia sensor
- Under certain conditions, **soot can form directly on the zirconia** (adherent soot) or form inside the tube at temperatures of 600-700°C.
- This soot can detach in chip form during thermal cycles and deposit on the zirconia (non-adhesive soot).



Solutions:

- For that case **air burnoff was not effective**
- Remove probe from furnace
- Let it cool down
- Clean it with compressed air **ONCE COLD!**

Results after manual cleaning

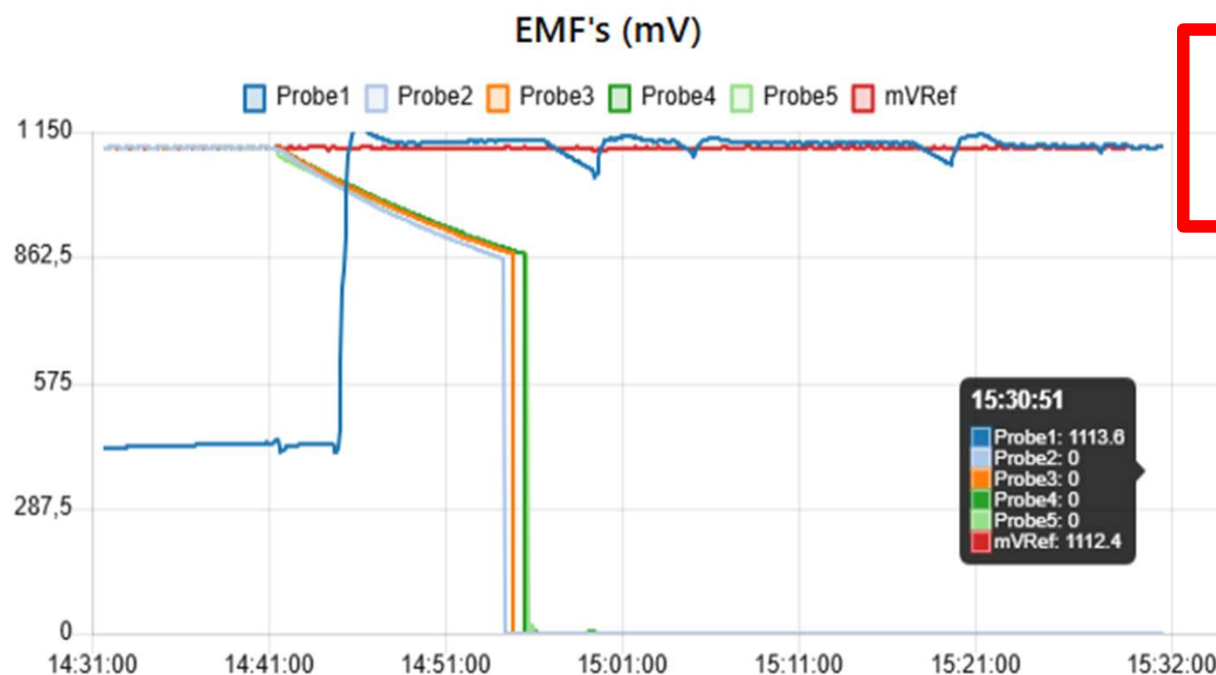


Table				
Reference probe	Temp. Ref	919.4°C	EMF Ref	1114.3mV
Serial No1	5433	Temp. 1	918°C	EMF 1 1115.7mV
Serial No 2	0000	Temp. 2	1372°C	EMF 2 0mV
Serial No 3	0000	Temp. 3	1372°C	EMF 3 0mV
Serial No 4	0000	Temp. 4	1372°C	EMF 4 0mV
Serial No 5	0000	Temp. 5	1372°C	EMF 5 0mV

$$\Delta \text{ mV} = 1\text{mV}$$

Possible cause - Case 1 :

- No reference gas flow

Observation:

- EMF too low

=> Cause identified using a portable CO/CO₂ analyzer and flowmeter control

Solution :

- See periodic probe monitoring under section F

Possible cause - Case 2 :

- Probe sensor not tight enough

Observation:

- EMF too low

=> Cause identified using a portable CO/CO₂ analyzer and tightness control

Solution :

-See periodic probe monitoring under section F

Possible cause - Case 3 :

- Leak on the purge air valve

Explanation :

- The purge air solenoid valve was **slightly leaking**, but the leak was not visible on the flowmeter.

**Therefore a little flow of fresh air is entering the furnace,
lowering the mV read by the ZrO_2 cell.**

- The air injected through the purge line caused the EMF to drop, but without giving inconsistent values.

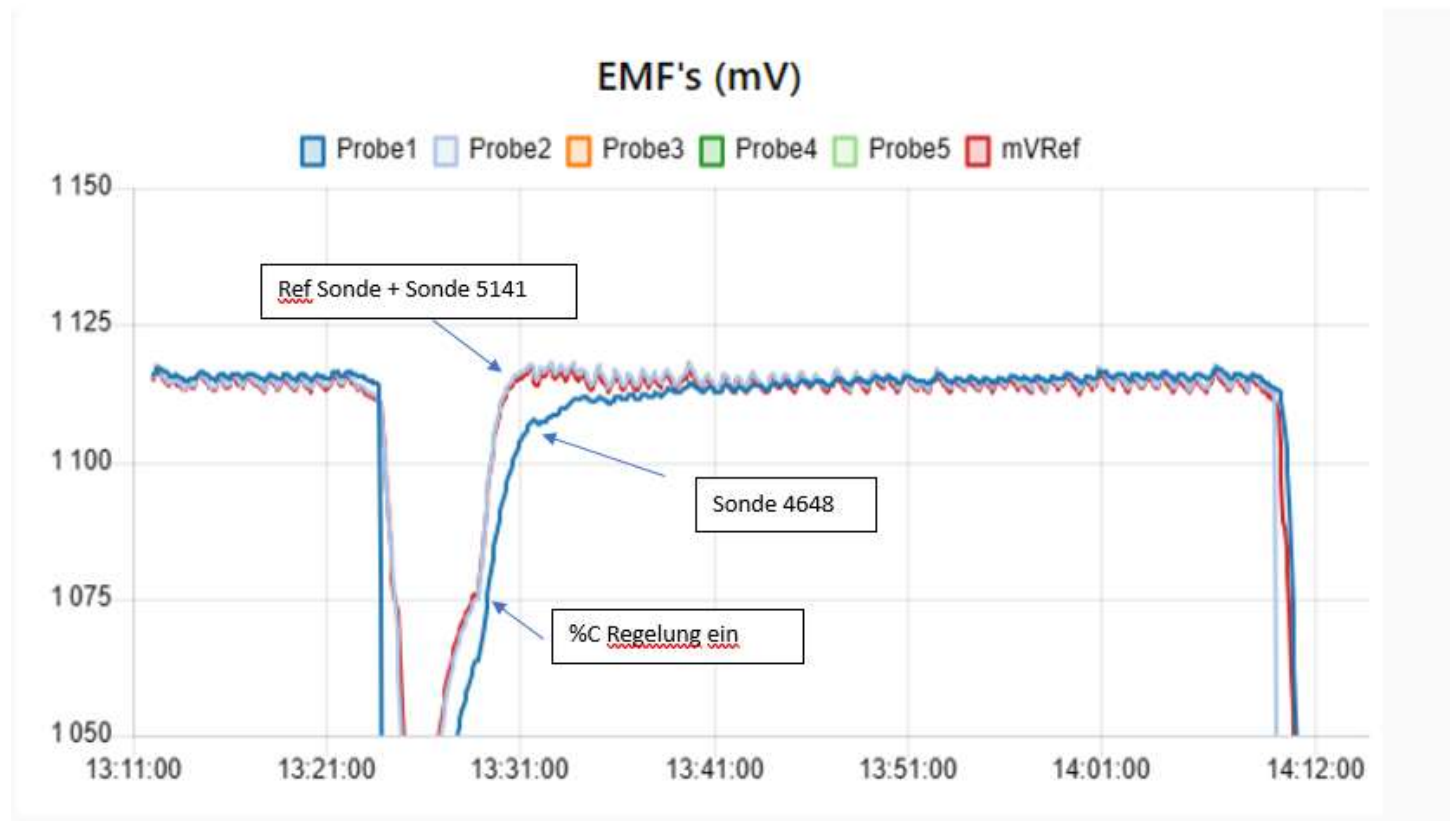
Solution :

- Replace valve or make sure it is gas-tight by inserting the purge air tube in a glass of water.
- When purge cycle is OFF. **No bubble should be seen**
- The tightness of the purge valve should be periodically checked according section F



Observation:

- Alteration of probe reactivity.
- Slow probe response



Cause

- When using sodium or potassium nitrite- and nitrate-based quenching salts, the vapors emitted in the furnace during quenching or during heating of **poorly washed charging material** cause **chemical reactions** with zirconia and the refractory metal outer electrode.
- Sodium or potassium vapors **destroy the protective chromium oxide layer**, leading to corrosion of iron and nickel, with the formation of oxide dust deposited on the electrolyte.



Solutions:

- Remove probe for furnace.
- Let it cool down
- Clean it with compressed air **ONCE COLD!**
- Take special care for washing the parts and the fixtures before entering the load in the furnace especially after salt quenching

HOW TO AVOID OR LIMIT THE IMPACT OF THESE ISSUES ON PRODUCTION

- Thermocouple line check (as for AMS or CQI-9 standards)
- mV probe line check (as for AMS or CQI-9)
- Thermocouple calibration, if any (as for AMS or CQI-9)
- Impedance check of mV measurement instrumentation
- Reference air flow control
- Check purge air flow rate
- Probe tightness check
- O₂ sensor impedance check
- Short-circuit recovery time check
- Control of recovery time after purge
- Foil test measurement test

**Contact us if you need more information or check
www.econox.ch**

Questions / Answers

THANK YOU