DO$_2$ MEASUREMENT TECHNOLOGY IN STEAM CYCLE WATER

ELECTROCHEMICAL VERSUS OPTICAL

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PRESENTATION OVERVIEW

• Dissolved Oxygen Measurement
• Electrochemical technology
• Optical technology
• Results
• Benefits
DISSOLVED OXYGEN MEASUREMENT

Wet Chemistry

• Winkler titration

• Colorimetric tests
  — Packaged kits

Instrumentation

• Electrochemical sensors
  — Standard for many years

• Optical (luminescent) sensors
  — ppm level
  — ppb level
ELECTROCHEMICAL (EC) SENSOR

Electrochemical reaction generated after O$_2$ passes through the membrane

Minimum sample flow required

O$_2$ is reduced below the membrane

Guard ring (Silver)

Anode (Silver)

Sample

Membrane

Electrolyte

Cathode (Gold)
EC SENSOR SIGNAL

- Reduction: \( 2 \text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^- \)
- Oxidation: \( 4\text{Ag} \rightarrow 4\text{Ag}^+ + 4\text{e}^- \)
- Overall: \( 2\text{H}_2\text{O} + 4\text{Ag} + \text{O}_2 \rightarrow 4\text{Ag}^+ + 4\text{OH}^- \)

\[ i = (\phi_{\text{temp}}) P_{\text{gas}} \]
- partial pressure \(\leftrightarrow\) concentration
- Henry’s Law \((c\text{O}_2 \propto p\text{O}_2)\)
BASIC OPTICAL PRINCIPLE

- A wave of blue light is emitted
- The active luminescent compound is excited
- The active compound emits red light
- The red light is detected
**SIGNAL - PHASE SHIFT TO DO₂**

O₂ partial pressure ⇔ phase shift

Stern-Volmer equation

\[ f_0 = \text{constant} \]
\[ K_{sv} = \text{sensitivity of active spot (known)} \]
\[ \Phi_0 = \text{phase in the absence of O}_2 \]

Partial pressure ⇔ concentration

Henry’s Law \( (cO_2 \propto pO_2) \)

\[ pO_2 = \frac{(\Phi_0 - \Phi)}{K_{sv} [\Phi - \Phi_0 (1 - f_0)]} \]

O₂ quenches the luminescence

Same with EC measurement

**SINGLE POINT CALIBRATION**
THEORY: EC VS. OPTICAL

EC – Electrochemical

- Smallest signal at zero

Cal in air
- 20% $O_2 \leftrightarrow 8$ ppm $dO_2$
- One point cal with fixed zero or zero adjustment to determine slope

Optical - Luminescence

- Largest signal at zero

Cal in $N_2$ gas
- Fixed slope ($K_{SV}$), hence one point cal at zero $O_2$
DO$_2$ RESULTS – IN THE LAB

Laboratory Results
RESULTS – FEEDWATER

Feedwater - AVT

O₂ leak test

dO 70 ppb peak
RESULTS EXPANDED EC VS. OPTICAL

Cracked fitting to produce O₂ leak
EC VS. OPTICAL

Repeatability K1100 ($r^{95}$) < 0.1 μg kg⁻¹

Difference K1100-EC < 0.4 μg kg⁻¹

AVT boiler FW sample
BWR IN HWC

Electrolyser stopped
No H₂ injection

Measurements below 0.6µg·kg⁻¹

Reactor water sample
FLOW SENSITIVITY

No effect of flow

Flow stopped

Flow started

OT FW
SPECIFICATIONS: EC VS. OPTICAL

**EC**
- Accuracy +/- 1 to 0.1 ppb
  - Detection limit 1 ppb to 0.1 ppb
  - Most are 1 ppb
- Consumes O₂
  - Minimum flow required
- ~ 6 month maintenance interval
  - Influenced by O₂ concentration and temperature

**OPTICAL**
- Accuracy +/- 1 ppb
  - Detection limit 1 ppb
- Does not consume O₂
  - No flow required
- 12 month maintenance interval
  - Not influenced by O₂ concentration or temperature
BENEFITS OF OPTICAL DO$_2$ TECHNOLOGY

• Optical performance comparable to EC

• Dry sensor with no membrane, no electrolyte and no chemical cleaning

• Not flow dependence

• Not influenced by the presence of magnetite on the sensor head

• Only 5 minute optical spot replacement and calibration every 12 months
THANK YOU FOR YOUR ATTENTION