

Non-Proprietary Version



BWRVIP-62 Rev. 1: Technical Basis for Inspection Relief for BWR Internal Components With Hydrogen Injection

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Topics

- Topic 1 Platinum Introduction, Transport, and Deposition
- Topic 2 Measurement of ECP
- Topic 3 Measurement of Dissolved Oxygen



Topic 1 — Platinum Introduction, Transport, and Deposition



Topic 1 — **Platinum Introduction, Transport, and Deposition**

- BWRVIP-62 refers to deposition of the platinum particles on the reactor vessel internal surfaces. What are the mechanism(s) of the deposition and adhesion? Discuss the basis for these conclusions.
- How does the platinum deposit effectively on the surfaces of the reactor vessel internal components under high flow-rate conditions? Discuss the basis for concluding that platinum is deposited as intended.
- What fraction of the injected platinum remains dispersed in the coolant 24 hours after being injected? After 1 week? After 1 month?
- If the platinum does not transport and deposit as expected, for example due to accumulation in the injection line, can the operators detect this and take corrective actions? What actions are taken and how long does it take to correct the problem? How do these conditions affect measurements such as dissolved oxygen and platinum concentration?



Mechanism(s) of Pt Deposition and Adhesion

- -Pt deposits by electroless deposition
- Electroless deposition involves the presence of a chemical reducing agent in solution to reduce metallic ions to the metal state
 - Deposit a coating or a particle without the passage of an electric current

Mechanism(s) of Pt Deposition and Adhesion

For reduction reaction

Na₂Pt(OH)₆ → 2Na⁺ + Pt(OH)₆⁻² Pt(OH)₆⁻² → Pt⁴⁺ + 6OH⁻ Pt⁴⁺ + 4e⁻ → Pt

For oxidation reaction

 $H_2O \rightarrow O_2 + 4H^+ + 4e^ H_2 \rightarrow 2H^+ + 2e^-$





 Normal operating flow and temperature (OLNC) promotes more uniform Pt particle deposition than NMCA min flow and lower temperature





 Pt deposition monitored in plants at the macro level with ECP

-In-vessel locations

- Recirc flange
- ECP-LPRM at bottom head and at core plate
- Bottom Head Drain Line (BHDL)



Pt deposition monitored at the macro level with ECP

- MMS allows access during operation
 - Replace ECP sensors
 - Remove deposition coupons (NMCA)



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- OLNC Injection Flow Path
 - Shroud ID and top guide are at the end of the flow path
 - Lowest deposition expected
 - Shroud ID samples had 0.01-0.04 μg/cm² after 2 OLNC applications



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Pt in Reactor Coolant After Injection is Terminated

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Pt Deposition in Injection Line

- Pt input for OLNC application is set by fuel area
 - Equivalent to 10 μ g/cm² on fuel surface
 - Typically 500-800 grams Pt input
- Pt injection rate has been varied when reactor water Pt is lower than usual (<10 ppt)
 - Application extensions from 10 days to 12 showed no notable effect
 - Doubled injection rate for one day showed no significant effect

Pt Deposition in Injection Line

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Topic 2 — Measurement of ECP



Topic 2 — Measurement of ECP Talking Points

- Describe the construction of the ECP probe(s) including the electrodes.
- Explain how ECP is measured and the effect of platinum electrodes such as those shown in Figure 2-13.
- Describe the variability in electrode type from plant to plant and among locations within a plant. For measured ECP values such as those in Figure 2-14, what exactly is being measured?
- Describe the methodology and guidelines for licensees to adequately demonstrate that the ECP measurements are not affected by platinum deposition on the ECP probe.

Introduction: Electrochemical Corrosion Potential (ECP)

- The potential **difference** between a metal and a reference arising from chemical interactions with the environment.
 - Oxidation of the metals in the alloy
 - Reduction of species in the environment
- Factors affecting ECP
 - Relative tendency of the metals to be oxidized
 - Nature and concentration of oxidizing agents at the metal surface
 - Nature and thickness of the passive oxide film
 - Temperature



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Introduction: Intergranular Stress Corrosion Cracking – Simplistic Description

- Crack advance along grain boundaries
 - Corrosive Environment
 - Oxidizing
 - Acid Forming Impurities: chloride, sulfate
 - Grain Boundaries Anodic
 - Chromium depletion by Cr-Carbide precipitation
 - Weld heat-affected zones particularly problematic
- Two-step process:
 - Crack Initiation: Long Time
 - Crack Propagation: Slip/Dissolution



Introduction: Relationship of ECP to IGSCC

- ECP \rightarrow Average Tendency of Surface to Oxidize
- IGSCC \rightarrow Very Localized Corrosion
 - Small fraction of surface
 - Minimal effect on ECP
- Elevated ECP leads to Localized Breakdown of Passive Film
 - Pitting, Grain Boundary Attack
 - Conditions favorable for Crack Initiation
- Elevated ECP leads to Corrosive Environment at Crack Tip
 - Oxidants in bulk water consumed by corrosion in crack
 - ECP inside crack decreases
 - Δ ECP (Surface-Inside) draws in Anions
 - pH Decreases, Dissolution Rate Increases
 - Crack Propagation Rate Increases



ECP and Crack Initiation

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ECP and Crack Propagation

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ECP Measurement

- The potential between the reference and the material is measured (volts)
 - High impedance electrometer
 - $o \Delta V = Reference Material$
- The potential between the reference and the standard hydrogen electrode (SHE) is calculated using the Nernst Equation for the reference half-cell reaction

o SHE is defined as 0







Construction of ECP Reference Probe/Electrodes

- Two types of reference electrodes (ECP probes) widely used in the BWR industry:
 - Pt ECP probe
 - Iron/Iron Oxide (Fe/Fe₃O₄) ECP probe
- Ag/AgCI electrode used in high temperature loop studies and at BWRs prior to HWC and in HWC mini-tests.
 - Under HWC, electrode functionality and reliability was affected due to the reduction of AgCl to Ag by the reaction, AgCl + $\frac{1}{2}$ H₂ \rightarrow Ag + HCl.
 - Still used at some international plants.
 - Not currently used by U.S. plants.
- Therefore, this presentation focuses on Pt and Fe/Fe $_3O_4$ probes.



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Reference Electrodes

- Requirements
 - Stable reference potential at operating temperature
 - Mechanical durability (pressure, temperature, flow)
- Iron/Iron Oxide: $Fe_3O_4 + 8 H^+ + 8e^- \rightarrow 3Fe + 4H_2O$
 - $E_{ref} = f(T,pH) = -787 \text{ mV}$ at 275°C, Neutral pH
- Platinum: $H^+ + e^- \rightarrow \frac{1}{2} H_2$
 - Requires Excess Hydrogen (Molar Ratio >2)
 - $E_{ref} = f(T,pH,H_2) = -404 54.4*log(ppbH_2)$ at 275 °C, Neutral pH



Construction of ECP Probe/Electrodes: Platinum Probe

- Ceramic insulator brazed Pt sensing cap.
- SS or Ni wire brazed to the underside of the Pt cap and passes through a drilled hole in the insulator, through the jacket and the SS transition piece, and is eventually joined to the central, insulated conductor of the MI (mineral insulated) coaxial cable.

•
$$H^+ + e \rightarrow \frac{1}{2} H_2$$



Pt electrode can be used as a reference only in the presence of excess hydrogen.

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Construction of ECP Probe/Electrodes: Iron/Iron Oxide

- The electrode consists of a Fe/Fe₃O₄ powder mix placed inside an yttriastabilized zirconia (YSZ) tube, which acts as the internal reference of the electrode.
- An iron wire embedded in the Fe/Fe₃O₄ powder mix acts as the sensing terminal of the electrode.
- The YSZ tube provides the necessary oxygen ion conduction to maintain equilibrium between the internal reference Fe/Fe₃O₄ mix and the external high temperature water phase.
- $Fe_3O_4 + 8 H^+ + 8e_- \rightarrow 3Fe + 4H_2O$



Fe/Fe₃O₄ electrode can be used as a reference under both NWC and HWC conditions.

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Iron/Iron Oxide and Platinum Electrodes



BWR ECP Monitoring Locations



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ECP Data Acquisition

Typical ECP Data Acquisition Set-up





NOTE : Junction boxes and Terminal Blocks are Not Shown

Need Common Ground Connection to Avoid Ground Loops

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ECP and Coolant Oxidant Concentration

- ECP Related to **Surface** Oxidant Concentration
 - − Very Low: ~0 ppb \rightarrow -550 mV(SHE)
 - − High (NWC): ~250 ppb DO \rightarrow +200 mV(SHE)
- Coolant Oxidant \rightarrow Mass Transport \rightarrow Surface Oxidant
- Mass Transfer Rate Increases with Flow Velocity
 - Important at Low (1 10 ppb DO) Coolant Oxidant
 - Not Significant at High or Very Low Concentrations
- IGSCC ECP Correlations Developed in Autoclaves
 - Low Velocity \rightarrow Lower ECP for Oxidant <10 ppb DO
 - EPRI Testing \rightarrow ECP Increase with velocity: **No Increase IGSCC**
- Plant ECP is measured at Higher Velocity
 - Higher ECP for Oxidant <10 ppb
 - Measured ECP \leq -230 mV(SHE) Conservative



In-Plant Locations for ECP: LPRM

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LPRM ECP Installation (re: Figure 2-13)

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ECP Mapping: BWR/3 HWC-M (Fig. 2-14)

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ECP Mapping: BWR/3 HWC-M (Fig. 2-14)

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ECP Mapping: BWR/3 HWC-M (Fig. 2-14)

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ECP Electrode Types and Locations (re: Figure 2-14)

- No specific or standard variability in electrode type from plant to plant or among locations within a plant.
- Same ECP values should be obtained with each type of electrode.
- Use of both Pt and Fe/Fe₃O₄ electrodes at the same location allows checks to confirm that the potential difference between the two reference electrodes is a constant.
 - Pt: Can only be used as a reference electrode in the presence of excess hydrogen (Molar Ratio >2).
 - Fe/Fe₃O₄: Provide ECP measurements over the range of plant chemistry from NWC to Moderate-HWC to NMCA/OLNC+HWC.



ECP Mapping: BWR/4 HWC-M

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ECP Mapping: BWR/4 Post-NMCA

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Effect of Noble Metal Deposition on Electrodes

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Topic 3 — Measurement of Dissolved Oxygen



Topic 3 — Measurement of Dissolved Oxygen: Talking Points

- Describe the construction of the oxygen probe(s), including the electrodes. Explain how oxygen is measured and the effect of platinum deposition on the sensor.
- Explain how the amount of oxygen in the coolant can be measured in the presence of excess hydrogen.
- How does the presence of H_2O_2 affect the oxygen measurement?
- Section 3.4 addresses measurements of dissolved oxygen in the reactor coolant system (RCS) water using an oxygen analyzer. Please address:
 - (a) typical shelf life and operational life of an oxygen analyzer;
 - (b) routine calibration frequency and maintenance requirements of an oxygen analyzer;
 - (c) typical problems associated with the oxygen measurements using an analyzer;
 - (d) variables that could potentially produce a false conservative measured oxygen value;
 - (e) how frequently the measurements can be made and, based on the feasibility, can continuous measurements be made;



Topic 3 — Measurement of Dissolved Oxygen

- (f) typical time required for obtaining a stable oxygen reading at any given location;
- (g) difficulties experienced with oxygen measurements in the reactor vessel or in an external location such as mitigation monitoring system.
- (h) For OLNC/NMCA plants, the oxygen measuring sample line could potentially be contaminated with platinum material. This in turn, will favor the recombination of oxygen with hydrogen before the sample is collected for measurement of oxygen of the RCS water (Section 5.1.5.2.2 of the report). Please describe whether this is an issue and how these potential biases can be avoided.

Topic 3 — Introduction: Purpose of Measurement of Dissolved Oxygen

- Reactor Water DO in Moderate HWC Plants
 - May be used as a secondary parameter to demonstrate effective implementation.
 - Correlation developed between measured ECP and DO during HWC ramp test.
 - Feedwater hydrogen concentration (or hydrogen injection rate and feedwater flow) and Main Steam Line Radiation Level also correlated.



Topic 3 — Introduction: Purpose of Measurement of Dissolved Oxygen

- Reactor Water DO in Noble Metal HWC Plants
 - May be used as a secondary parameter to demonstrate effective implementation.
 - DO along with dissolved hydrogen measurements also support the use of measured molar ratio as a secondary parameter.
 - Measured molar ratio ≥3 demonstrates sufficient hydrogen is injected to assure a molar ratio ≥2 in regions where IGSCC is mitigated.
 - HWC ramp test determines feedwater hydrogen concentration required to achieve a molar ratio ≥2 based on measured ECP ≤-230 mV(SHE) and/or measured molar ratio ≥2.





Topic 3 — Introduction: Purpose of Measurement of Dissolved Oxygen

- Reactor Water DO in Noble Metal HWC Plants (continued)
 - Ramp test results are correlated with the DO concentration and with chemistry predictions from a radiolysis model, such as BWRVIA.
 - Radiolysis model can then be used to determine molar ratios in other regions and at other times during plant operation.
 - Industry Guidelines
 - Sufficient hydrogen will be injected to provide a minimum molar ratio of 3 in the upper downcomer region (below the feedwater spargers).
 - Hydrogen injection rate is set based on ramp test predictions and from a radiolysis model that has been benchmarked against a ramp test.



Oxygen Probe Construction

- O₂ sensors have primarily used electrochemical (EC) technology:
 - Galvanic (natural potential between the electrode metals); old type, uses lead, no longer used.
 - Polarographic (applied potential between the electrodes).
- Optical (Luminescence) Sensors
 - Latest technology sensors for dissolved O₂
 - Some advantages over electrochemical sensors
 - Several are currently installed in a few BWR sites in the U.S.





Oxygen Probe Construction

- EC sensors have two electrodes:
 - Cathode (reduction of O_2)
 - Anode (corresponding oxidation)
 - Modern sensors are capable of measuring the DO concentration to <1 ppb.

Electrochemical Oxygen Probe Construction

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Polarographic EC Oxygen Sensor (also called Amperometric, Clark Cell)

- Center cathode and one counter electrode (anode) immersed in electrolyte solution
- Electrodes separated from the gaseous or liquid sample by a gas permeable membrane.
- An electronic circuit is linked to the anode and cathode.
- Through an applied voltage, current will flow between the anode and the cathode.
- Current produced by the cell is proportional to O2 partial pressure



- Gas penetrating through the semi-permeable membrane into the cell dissolves in the electrolyte.
- Reaction at the cathode, causing a measurable electric current to flow.
- Current is proportional to the amount of gas entering the cell, which is proportional to the partial pressure of gas in the sample outside the cell.
- Current is proportional to sample O₂ concentration.

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Polarographic EC Oxygen Sensor

- External potential polarizes electrodes.
- O₂ is <u>reduced</u> at the noble metal (Pt, Au, Pd) cathode.

 $- O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

- Anode (Ag) is <u>oxidized</u>:
 - 4Ag +4Cl⁻ \rightarrow 4AgCl + 4e⁻
- Overall reaction:

 $-4Ag + O_2 + 2H_2O + 4CI^- \rightarrow 4AgCI + 4OH^-$

- Anode/cathode pair causes current flow in direct proportion to the amount of O_2 entering the sensor.
- O₂ is consumed, creating a partial pressure gradient across the membrane, driving O₂ across the membrane into the electrolyte.





Polarographic EC Sensor Electronics

- Sensor electronics perform four functions:
 - Apply constant voltage to the anode
 - Measure the current flowing through the sensor
 - Compensate for temperature variation in the liquid sample
 - Convert the cell's electric current into an analog signal for sensor output

Optical (Luminescence) Sensors

- Method recognized by ASTM for O_2 measurement in water.
- Advantages over EC:
 - No oxygen consumption
 - Independence of sample flow/velocity
 - No electrolyte
 - Low maintenance



Optical (Luminescence) Sensor Construction

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Optical (Luminescence) Sensors

- Sensor coated with luminescent material (luminescent spot).
- Blue LED light excites luminescent material.
- Luminescent material emits red light as it relaxes.
- The more O₂ present, the shorter the time for red light to be emitted (O₂ quenching).
- By modulating blue light intensity, decay time is transformed into a phase-shift of modulated red light fluorescence signal, which is independent of intensity.
- Time from when blue light was sent to when red light was emitted is measured.
- The measured time is correlated to O₂ concentration.
- Between flashes of blue light, Red LED light is flashed on the sensor and used as an internal reference.



Optical sensing of oxygen is based on the measurement of the red fluorescence of a dye/indicator illuminated with a blue light.



- Two potential mechanisms by which Pt may interfere with the operation of O₂ these sensors:
 - Fouling the membrane
 - EC sensors susceptible; Optical much less susceptible since no O_2 is transported across the membrane.
 - Reacting oxygen with excess hydrogen on the membrane surface, reducing the rate of transport across the membrane.
- Neither mechanism will significantly affect the function of the sensor.

- Membrane fouling:
 - Membranes are subject to fouling from crud, reducing permeability for O₂, resulting in low readings which are detected by periodic calibration checks.
 - Maintenance (membrane replacement, sensor head cleaning) and calibration are performed to restore performance.
 - The concentration of noble metals in the coolant is negligible, even during application, compared to the crud concentration.
 - Therefore noble metals do not directly affect membrane fouling.



- Oxygen reduction with excess hydrogen:
 - If sufficient Pt were deposited on the membrane, O_2 reduction with excess H_2 could reduce the rate of O_2 diffusion through the membrane, resulting in a low measured DO concentration.
 - However, the sensor is located in an analyzer chamber which is at the end of a long, small-diameter sample line and downstream of sample coolers.
 - It is unlikely that significant quantities of Pt are delivered to the analyzer.
 - Plant experience: O_2 reacts with excess H_2 in sample lines upstream of both the O_2 sensor and the ECP manifold; any further reaction that may occur on the O_2 sensor membrane is a continuation of this process.

- No effects of Pt on sensors are observed.
- EC Sensor
 - Membrane replaced periodically as part of PMs
 - Temperature at sample is low; H_2/O_2 recombination on sensor would be small.
- Optical Sensor
 - Effect of ppt level of particles has no effect on luminescence; thus, no effect on O_2 detection.



Reactor Coolant O₂ Measurement with Excess H₂

- Polarographic EC O₂ sensors are negatively interfered with by H₂.
 - However, the interference is quite small and usually minimal, except for applications with very high H₂ and very low O₂; i.e., PWR RCS applications (<1 ppb O₂ and > 30 cc/kg or 2.5 ppm H₂).
 - In HWC application in BWRs, the level of H_2 has minimal effect the O_2 measurement.
- Optical O₂ sensors are not influenced by H₂.



Effect of H₂O₂ on O₂ Measurement

- At reactor water temperature above ~350 °F, H₂O₂ rapidly decomposes in the sample line and is not present in the sample.
 - $2H_2O_2 \rightarrow 2H_2O + O_2$
- EC Sensors:
 - Covered by a gas permeable membrane.
 - H₂O₂ does not permeate the membrane and would not directly interfere with an EC sensor.
 - $-H_2O_2$ only present in sample at low reactor temperature.
 - $-H_2O_2$ decomposes to O_2 at normal operating temperature.
- Optical sensors are not influenced by H_2O_2 .



Typical Shelf Life and Operational Life of an Oxygen Analyzer

- Electrodes of an operational EC sensor are immersed in electrolyte and sealed by a membrane.
 - This is not the ideal arrangement for storage, as evaporation / crystallization of electrolyte will eventually occur.
 - Therefore, EC sensors are stored dry (without electrolyte).
- Average operational life of an EC sensor: 5 to 10 years.
 - This operational life can be greatly influenced by operational conditions and maintenance frequency/proficiency.
 - Some EC sensors achieved operating life of more than 20 years.
- Optical sensors:
 - The shelf-life of the K1200 sensor spot is 2 years prior to first use.
 - The sensor spot needs to be replaced about once a year.



- EC O₂ Sensors: Manufacturer recommends maintenance intervals should be about 6 months.
 - If the sample temperature is below 25 °C, 1 year between maintenance is possible.
 - Condition Driven: Typically calibrate if drift >2 ppb.
 - Single point calibration with air is common; some require 2-point calibration.
 - Actual cal./maintenance checks typically weekly to monthly
- Optical O₂ Sensors: Manufacturer recommends maintenance frequency about 1 year at O₂ concentration < 2 ppb and temperature < 50 °C.
 - Condition Driven: Typically calibrate if drift >2 ppb.
 - Single zero-point calibration.
 - Replace sensor spot annually.



- EC O₂ Sensors: Normal Cleaning Procedure
 - Sensor recharge kit contains all required components
 - Remove protection cap
 - Remove old cartridge (with membrane)
 - Rinse sensor head
 - Remove and replace O-ring
 - Clean anode with supplied cleaning tool (bright silver appearance)
 - Rinse sensor head
 - Lower sensor head into recharge cartridge container with pre-mounted membrane and electrolyte
 - Screw sensor into the replacement cartridge until container is released
 - Rinse sensor
 - Install protection cap and protecting cap locking washer



- EC O₂ Sensors: Supplemental Nitric Acid Cleaning of the Cathode
 - Not to be used more than once every two years; should only be used if the cathode is obviously dirty and cannot be cleaned with water and a soft tissue
 - Additional steps within standard membrane replacement and sensor head cleaning procedure
 - Place cleaning tool on cathode
 - Add two drops nitric acid
 - Wait 30 seconds then drain acid
 - Rinse sensor
 - Remove cleaning tool
 - Rinse sensor head



- Optical O₂ Sensors: Cleaning Procedure
 - Requires a replacement sensor spot, O-ring and maintenance tool (delivered with sensor)
 - Push maintenance tool over sensor spot
 - Unscrew old sensor spot and remove
 - Discard old sensor spot
 - Replace O-ring if necessary
 - Push maintenance tool over new sensor spot
 - Place maintenance tool and sensor spot into the sensor
 - Screw in new sensor spot and remove the maintenance tool





Typical Problems Associated with Oxygen Measurements

- Problems typically related to maintenance issues:
 - Significantly higher than 25 °C sample temperature
 - Reactor water samples are cooled by roughing cooler followed by TCU (temperature control unit)
 - Sample temperature at the point of measurement is normally controlled to 25 ±3°C
 - Use of a membrane that is not suited for the application.
- Problem indications:
 - Spikes/erratic readings, results outside acceptance band during cross-checks/calibrations
 - Drifting upward is typical indication of need for calibration or failing sensor



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Potential for a False Conservative Measured Oxygen Value

- As an EC sensor approaches the need for maintenance the oxidation products build up causing resistance in the electrochemical circuit.
- This resistance drops the cell potential reducing the signal; could eventually drop to near zero and become unresponsive.
- Monitoring checks are defenses:
 - Calibrations
 - Cross-checks: Portable meter, wet method (ampoule, Rhodazine D method, low range 0 – 20 ppb, LLD 2 ppb)
 - Cross-checks are typically performed weekly to monthly, based on plant experience.
Frequency of Measurement and Recording: Reactor Water O₂

- Plants monitor reactor water dissolved O₂ continuously:
 - Required by BWR Water Chemistry Guidelines
 - Manual recording on daily/shiftly rounds/plant tours
 - Calibrations
 - Cross-checks
- Analyzers have capability to transmit digital data to an external data recording device (e.g., plant computer, laboratory information management system, data logger)
- Frequency of automatic digital recording of results can be set as needed; 1 – 5 minutes during transient conditions, may use longer intervals at steady state.





Time to Obtain Stable Oxygen Reading

- Response time for an EC sensor:
 - Common response times (90% signal) for trace level dissolved O₂ membranes vary from about 7 to 30 sec.
 - With a well maintained sensor ,sensitive membranes can go from air (~21%) levels to <10 ppb in less than 5 min.
 - For changes in dissolved O_2 in the normal ppb range, stabilization is attained in seconds to minutes.
 - Increases in O_2 are faster to stabilize than decreases.
 - The closer the decreasing signal is to zero the more asymptotic the approach.
- Optical O₂ sensor response is similar to EC sensor response.



Response: EC (A1100) and Optical (K1200) O₂ Sensors

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Reactor Water EC O₂ Sensor Response: HWC Ramp Test

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Reactor Water EC O₂ Sensor Response to H2 Injection Decrease and Increase

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Reactor Water EC O₂ Sensor Response HWC Trip and Return

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Reactor Water EC O₂ Sensor Response HWC Trip and Return

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Impact of Pt Deposition in Sample Line

- Catalyst usually affects reactor water and feedwater sample lines
 - Excess H2 (MR>2) results in zero or very low O2 measurement
 - Reactor water O2 is a secondary parameter for OLNC if ECP measurement is lost – shows catalyst working
 - Feedwater O2 estimated from condensate O2 measurement (upstream of OLNC injection point)



Effect of Low O2 in MMS

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Effect of Low O2 in MMS

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