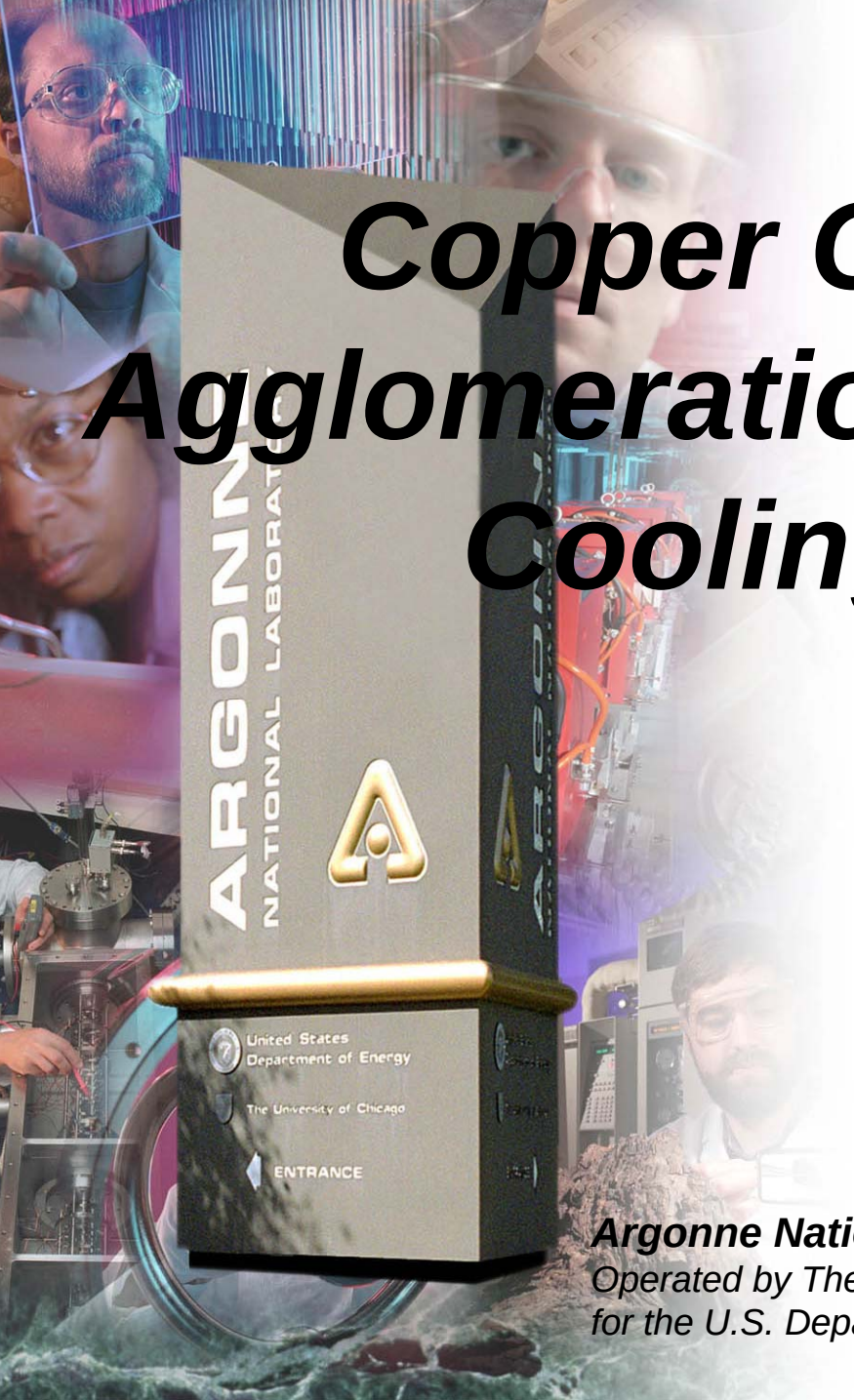

Copper Corrosion & Agglomeration in APS Water Cooling System

Bijaya Adak
Prof. Philip Nash
Dr. Sushil Sharma

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Argonne National Laboratory
Operated by The University of Chicago
for the U.S. Department of Energy

Office of Science
U.S. Department of Energy

Out Line

- **Pourbaix Diagram**
- **Literature Survey**
  - Description
  - Experimental Setup
  - ECP vs Dissolved Oxygen
  - ECP vs Particle Release Rate
  - Water Chemistry vs Phase Transformation
  - Discussion

Pourbaix diagram for Copper

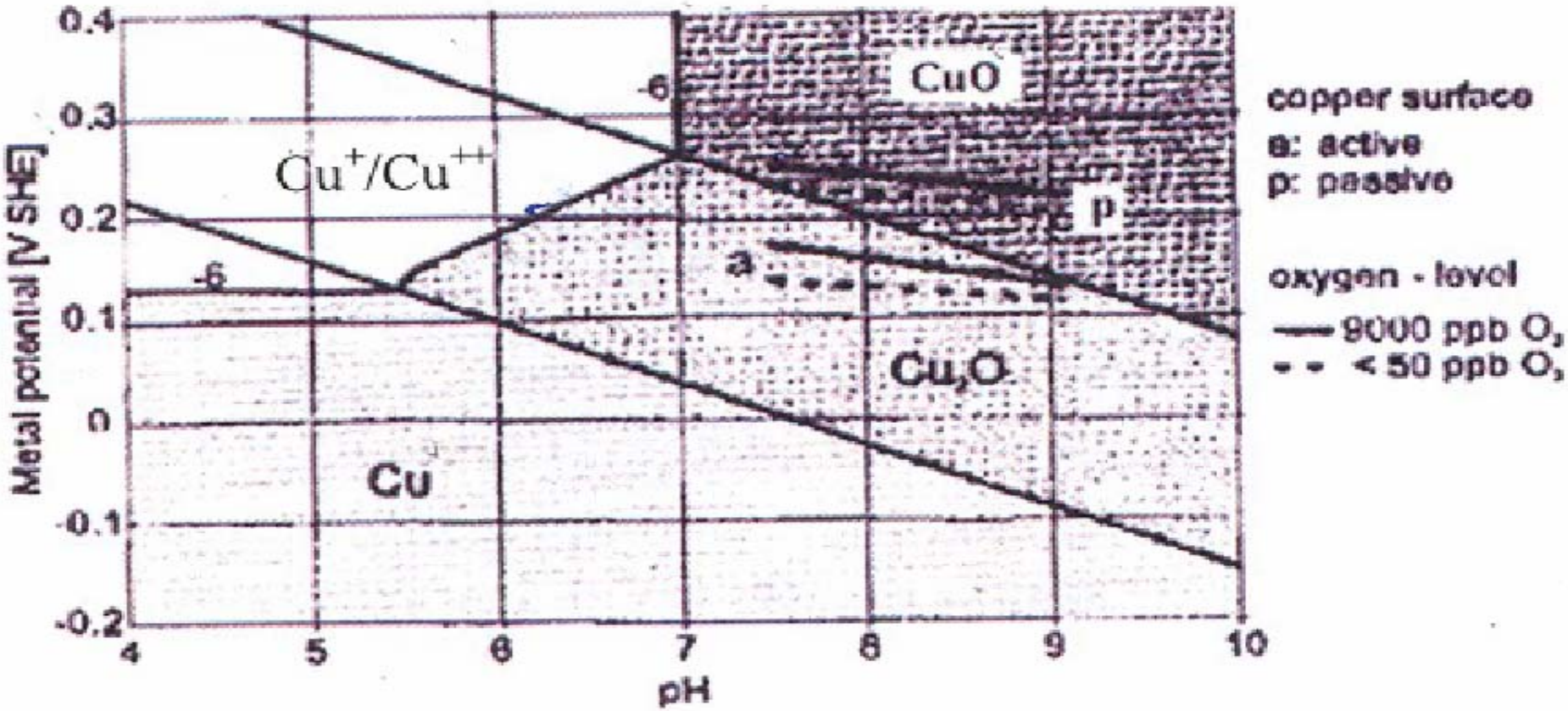


Figure 3: Pourbaix diagram for copper.

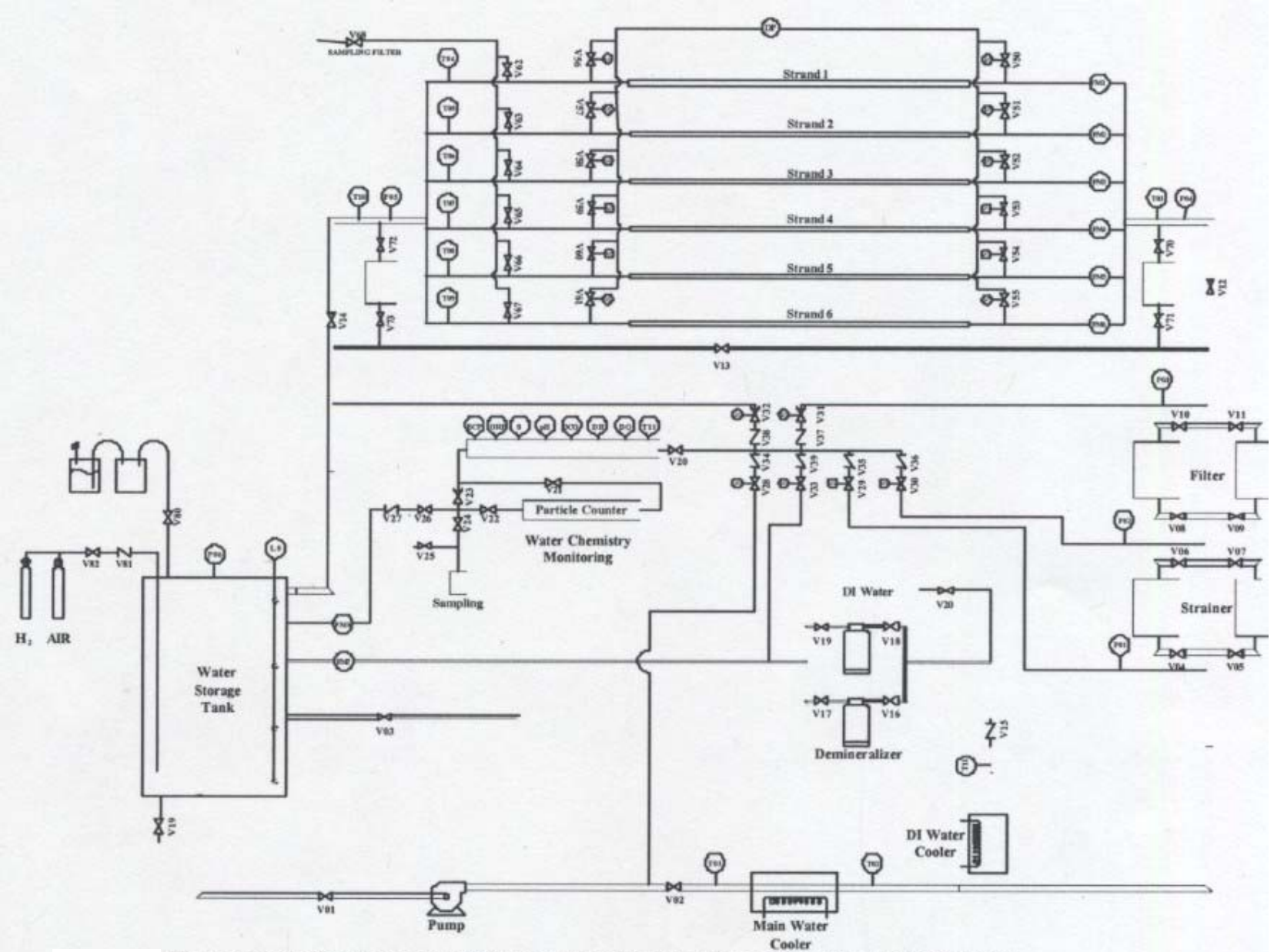
* E = E0 – (RT/ZF) ln (Activity of products / Activity of reactants)

Literature Survey

Description:

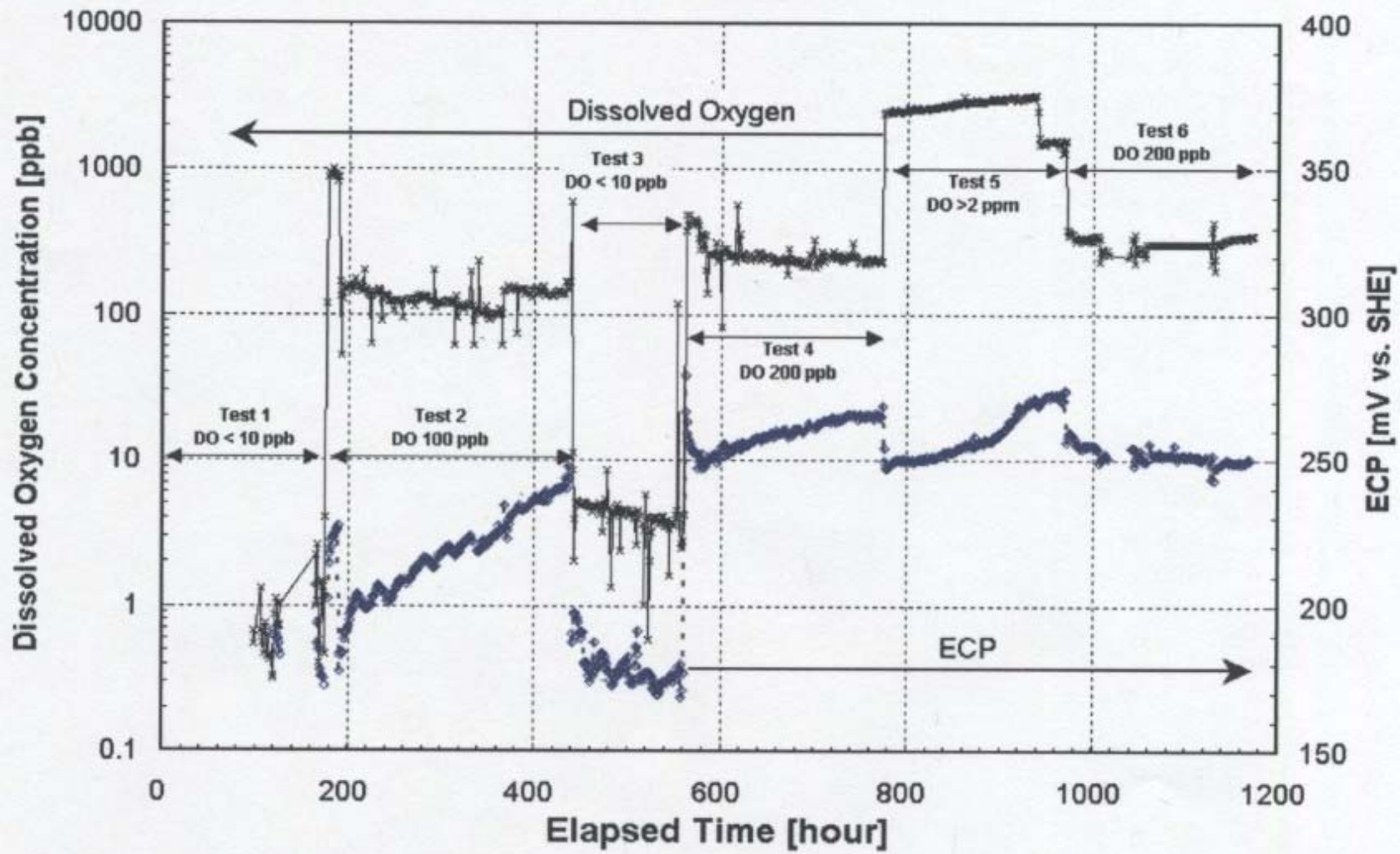
- Ref: Effect of Electrochemical Potential of Copper on Plugging of Generator Water-Cooling Circuit by *Byung Gi Park and Soon Hwang*
- Generator water cooling system (in nuclear & thermal power plants)
- Experimental Setup – A scale down replica of the original system
- Inlet temp 40 °C & outlet temp. 20 °C
- HOWC (High oxygen water chemistry) – greater than 2 ppm
- LOWC (LOW oxygen water chemistry) – less than 50 ppb

Experimental Setup



The schematic diagram of the SNU corrosion simulation loop (SCOSLO)

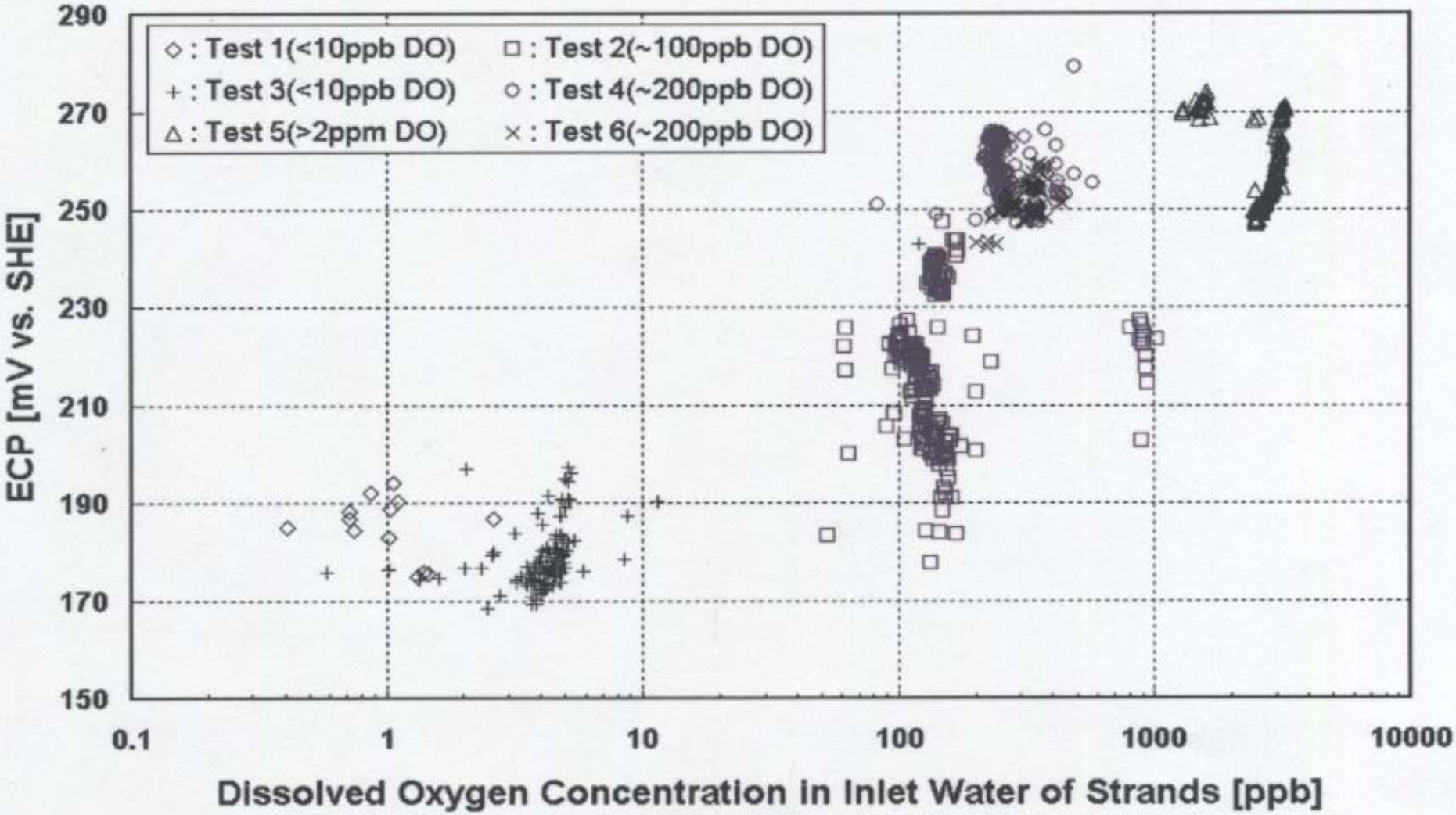
ECP vs Dissolved Oxygen



The ECP of copper in the inlet water of the specimens as a function of time

- **ECP increases along with dissolved oxygen**

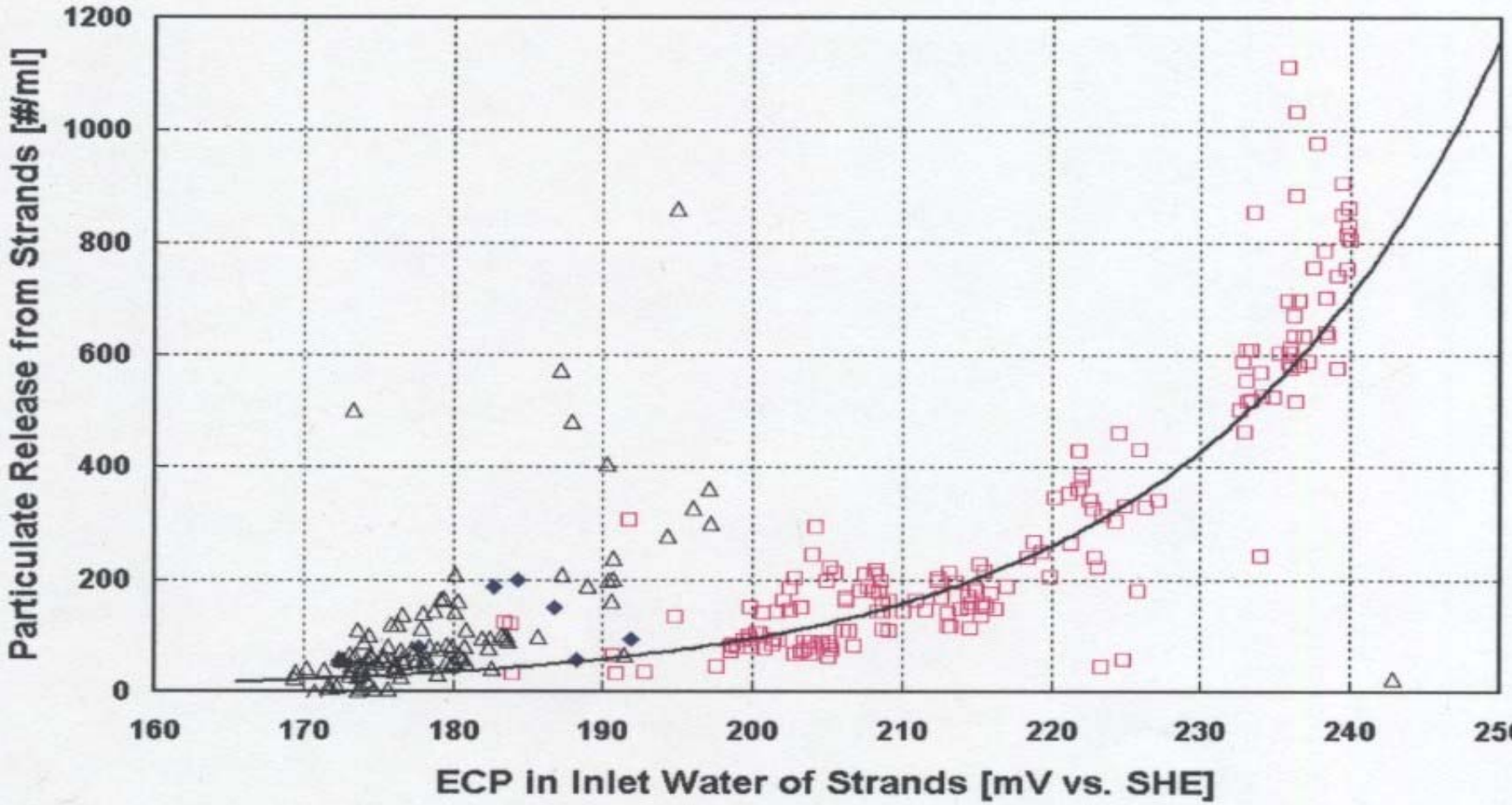
ECP vs Dissolved Oxygen



The ECP of copper in the inlet water of the specimens as a function of dissolved oxygen concentration

1. ECP at LOWC is around 180 mV (SHE) **2. ECP at HOWC is around 260 mV (SHE)**

ECP vs Particle Release Rate

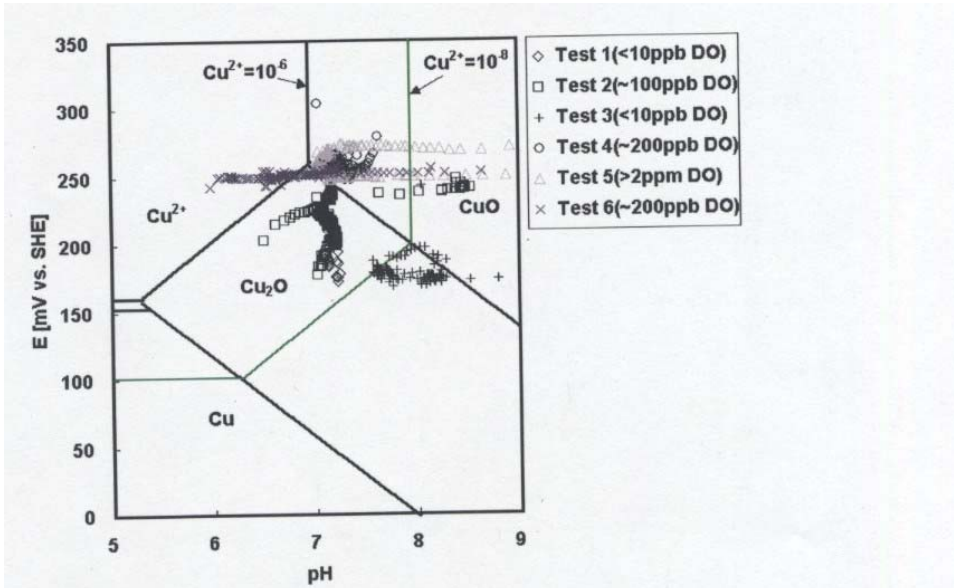


Net release of particulate corrosion products from copper surface as a function of the ECP of copper

- **Particulate release rate is exponentially proportional to ECP**
- **Around 240 mV (SHE) particulate release rate increases abruptly**

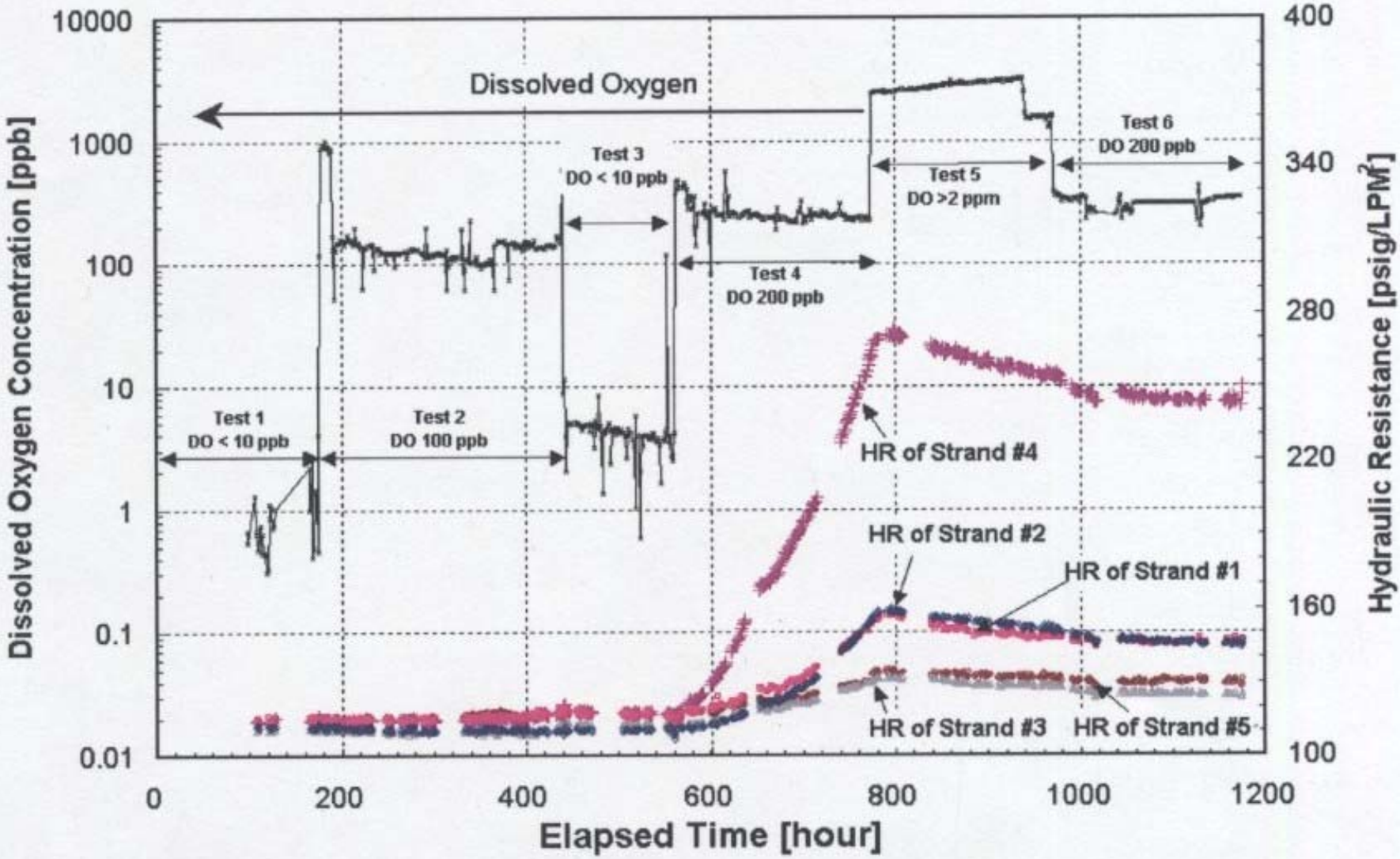
Water Chemistry vs Phase Transformation

- Water chemistry changes from LOWC to IOWC (250 mV) ⟶ Flower shaped cuprous oxide crystals grew on the copper surface with discernible change in hydraulic resistance
- Water chemistry changes from IOWC to LOWC ⟶ No release of cuprous oxide
- Water chemistry changes from IOWC to HOWC (260 mV) ⟶ Massive release of CU_2O and subsequent growth of blocky CuO.



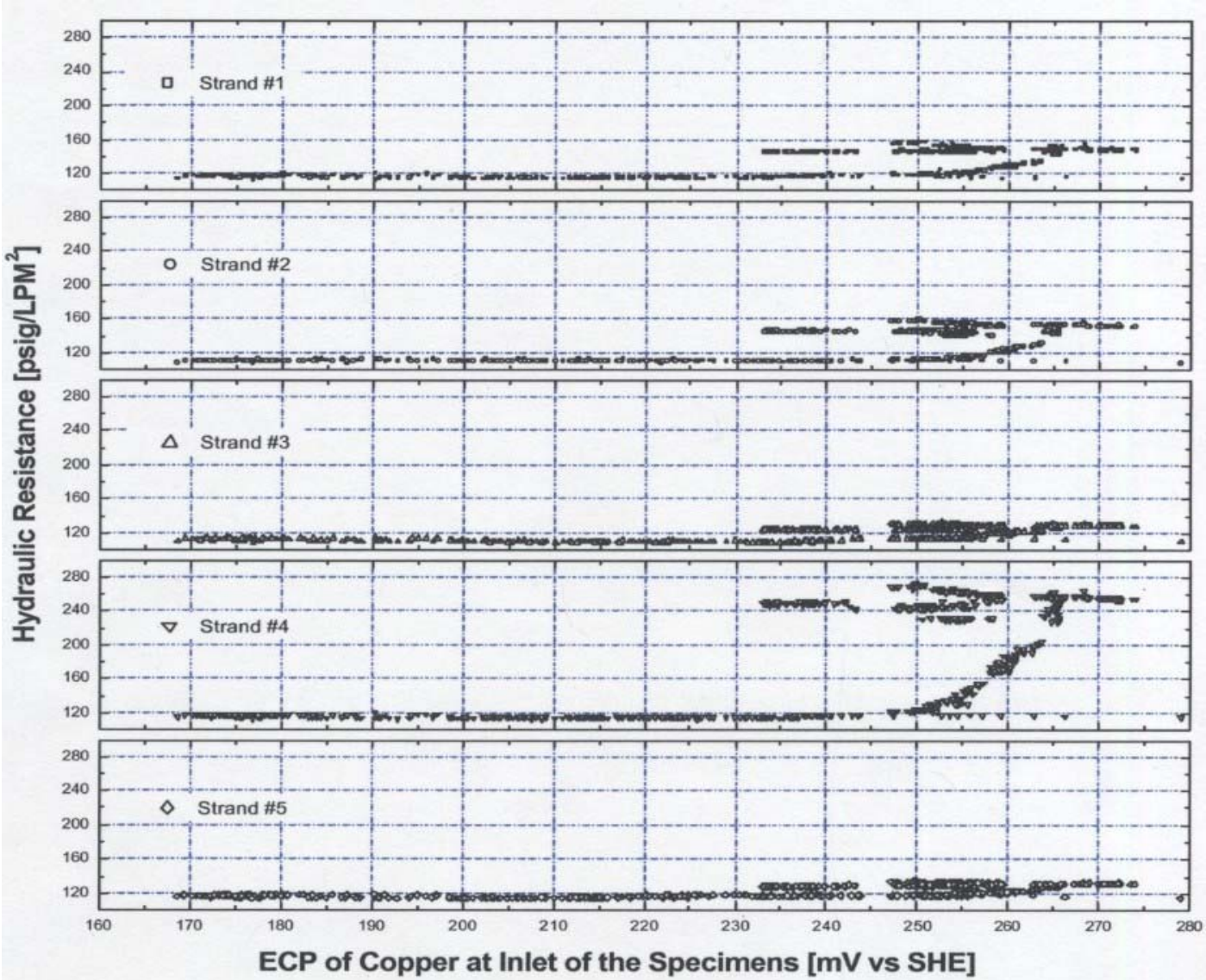
Experimental ECP and pH data superimposed on a potential-pH diagram of the copper-water system.

Samples and Flow rates



Effect of dissolved oxygen on the hydraulic resistance (HR) in hollow copper strands.

Hydraulic Resistance in various Samples



Dependence of the hydraulic resistance on the ECP of copper in hollow copper strands

Discussion

- Lattice Parameter of Cu_2O is 4.2696 Angstrom
- Lattice Parameter of CuO is:

  a = 4.6837 Angstrom

  b = 3.4226 Angstrom

  c = 5.1288 Angstrom

  ß = 99.54 degree
- Molar volume of Cu_2O is 23.9 cc/mol
- Molar volume of CuO is 12.4 cc/mol
- Transformation between these phases affect the stability of the oxide structure due to the difference in molar volume and lattice parameters. Instability of the oxides results in massive particulate release.

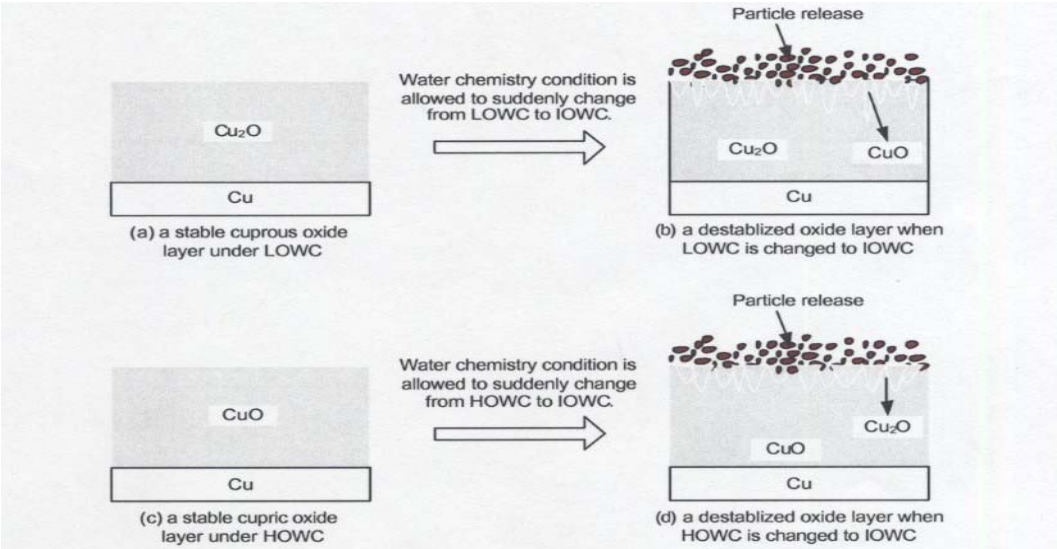


Figure 12. Mechanism of particle release caused by the change of water chemistry condition in generator water-cooling circuit

Discussion Contn....

- Oxide layer thickness was not influenced by the test conditions.
  - Uniform 1 µm thickness for all the test conditions
  - Therefore, it was concluded that oxide growth was not the cause for flow restriction.
- During the phase transformation particle can be released in two forms:
  - Particulates that affect ECP
  - Ionic species that affect conductivity
  - Change in conductivity was not as great as ECP. Hence, it was concluded that particulate release is predominant.