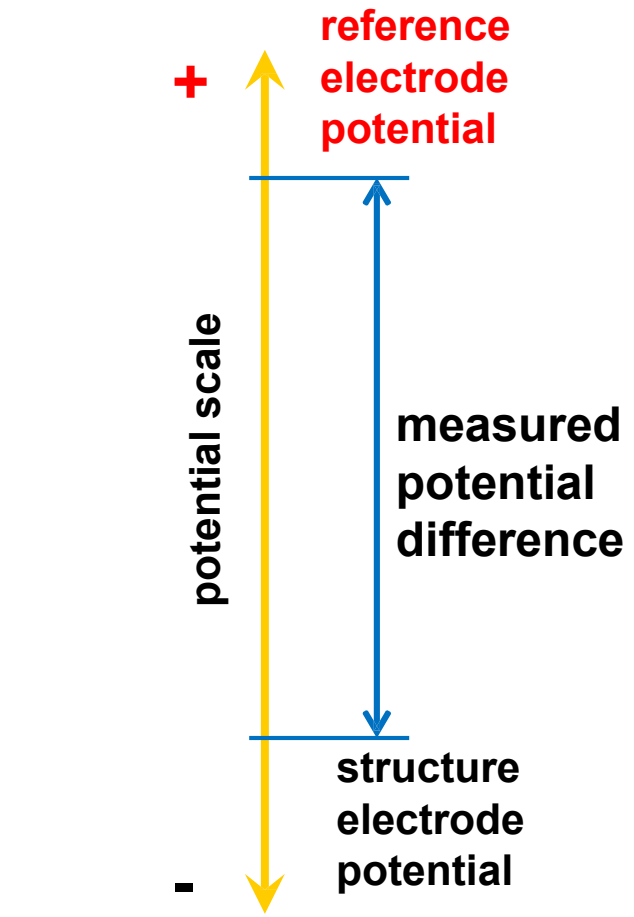
Understanding the Reference Electrode

Appalachian Underground Corrosion Short Course

Measuring Potentials



- When measuring potential, you are actually measuring the **difference** in potential between two electrodes.
- If the measured potential changes, it means that the potential of **one** of the two electrodes has changed.
- Which one changed?

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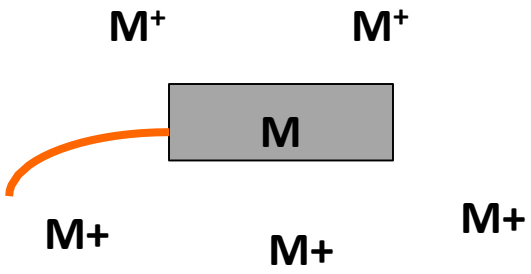
Simple Electrodes

- transfer electricity from a solid conductor to a liquid electrolyte
- make the transfer by means of a chemical reaction at the electrode surface
- establish an electrical potential unique to the electrode surface reaction
- In a reference electrode, the electrolyte, metal and reaction are precisely defined to produce a consistent potential

Two Types of Electrodes

1st type – Solid Junction

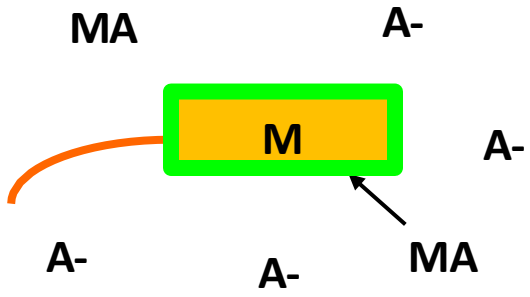
$$M^0 \leftrightarrow M^+ + e^-$$



$$E = E_0 + 2.3\frac{RT}{nF}\log(M^+)$$

2nd type – Liquid Junction

$$M^0 + A^- \leftrightarrow MA + e^-$$



$$E = E_0 + 2.3\frac{RT}{nF}\log(A^-)$$

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Electrolyte Forms

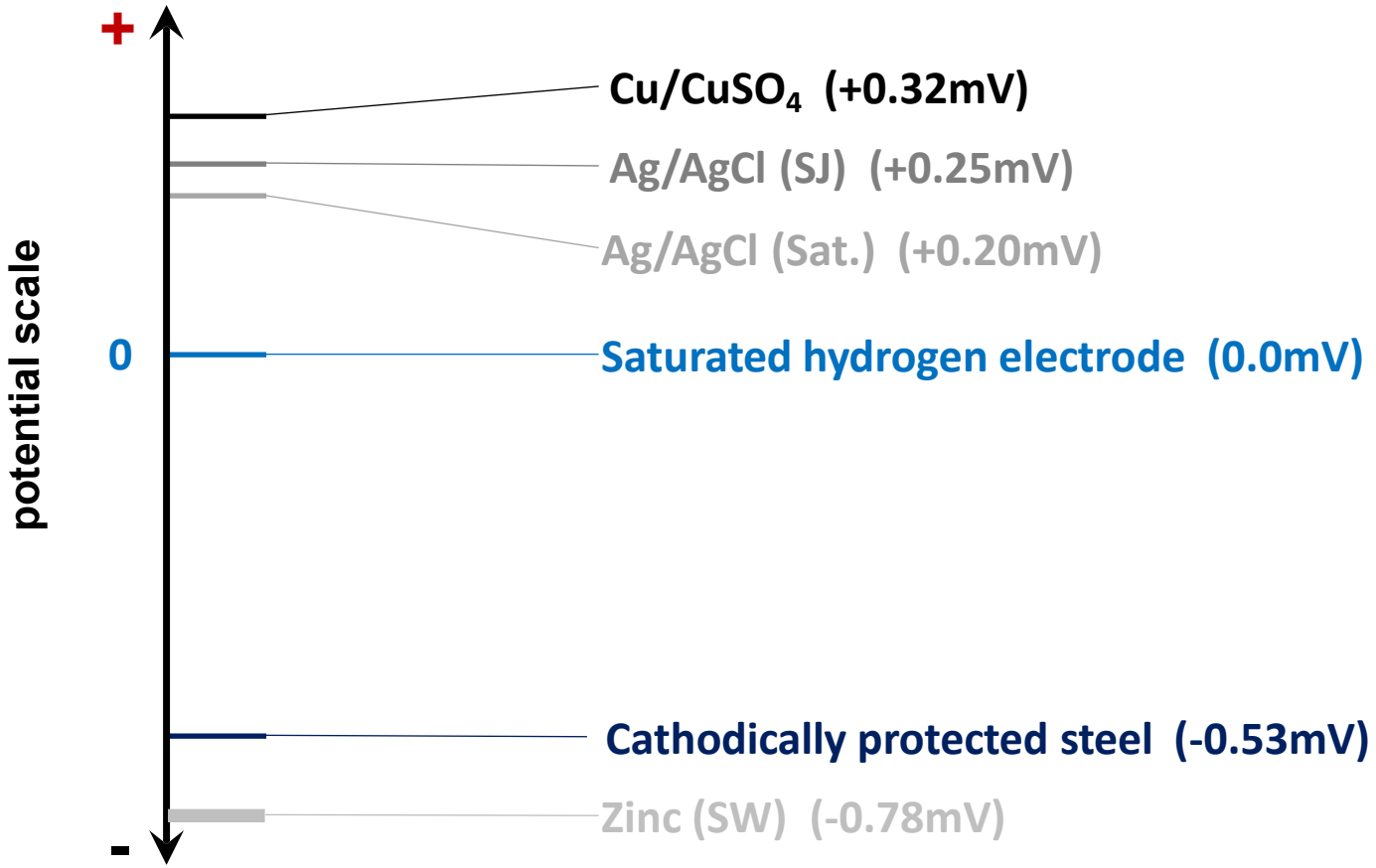
- Dry electrode (SJ) – Element in direct contact with the structure electrolyte
- Wet electrode (LJ) – Element immersed in a salt solution and separated from the environment by a porous plug
- Gelled electrode (LJ) – Element immersed in a gelled salt solution and separated from the environment by a conducting membrane

Commonly Used Reference Electrodes

- Copper/Copper Sulfate ($Cu/CuSO_4$) - LJ
  - Underground
  - Fresh water

- Silver/Silver chloride (Ag/AgCl) - LJ
  - Seawater
  - Saline mud
  - Concrete

Relative Potentials of Electrodes



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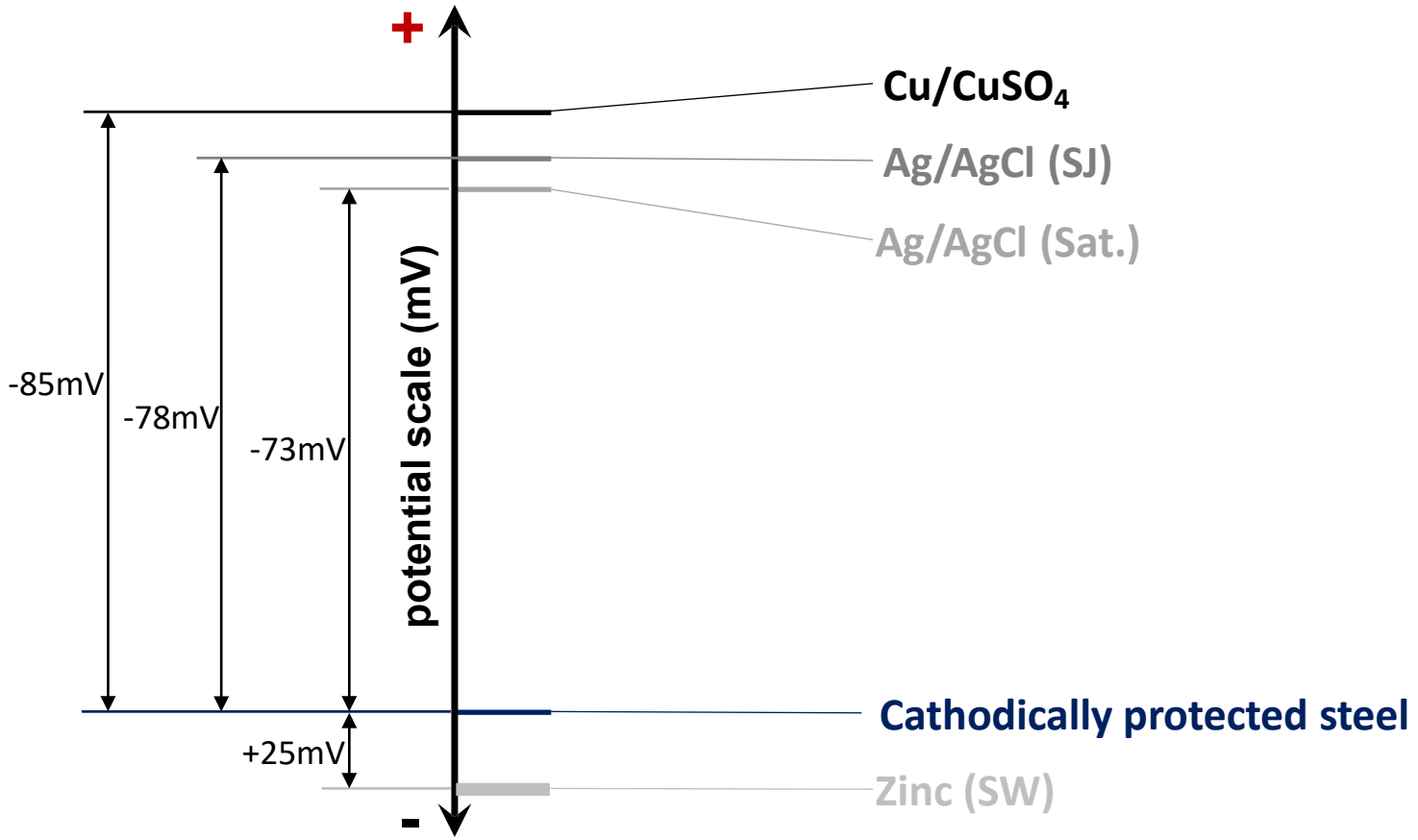
Relative Potentials of Cathodically Protected Steel

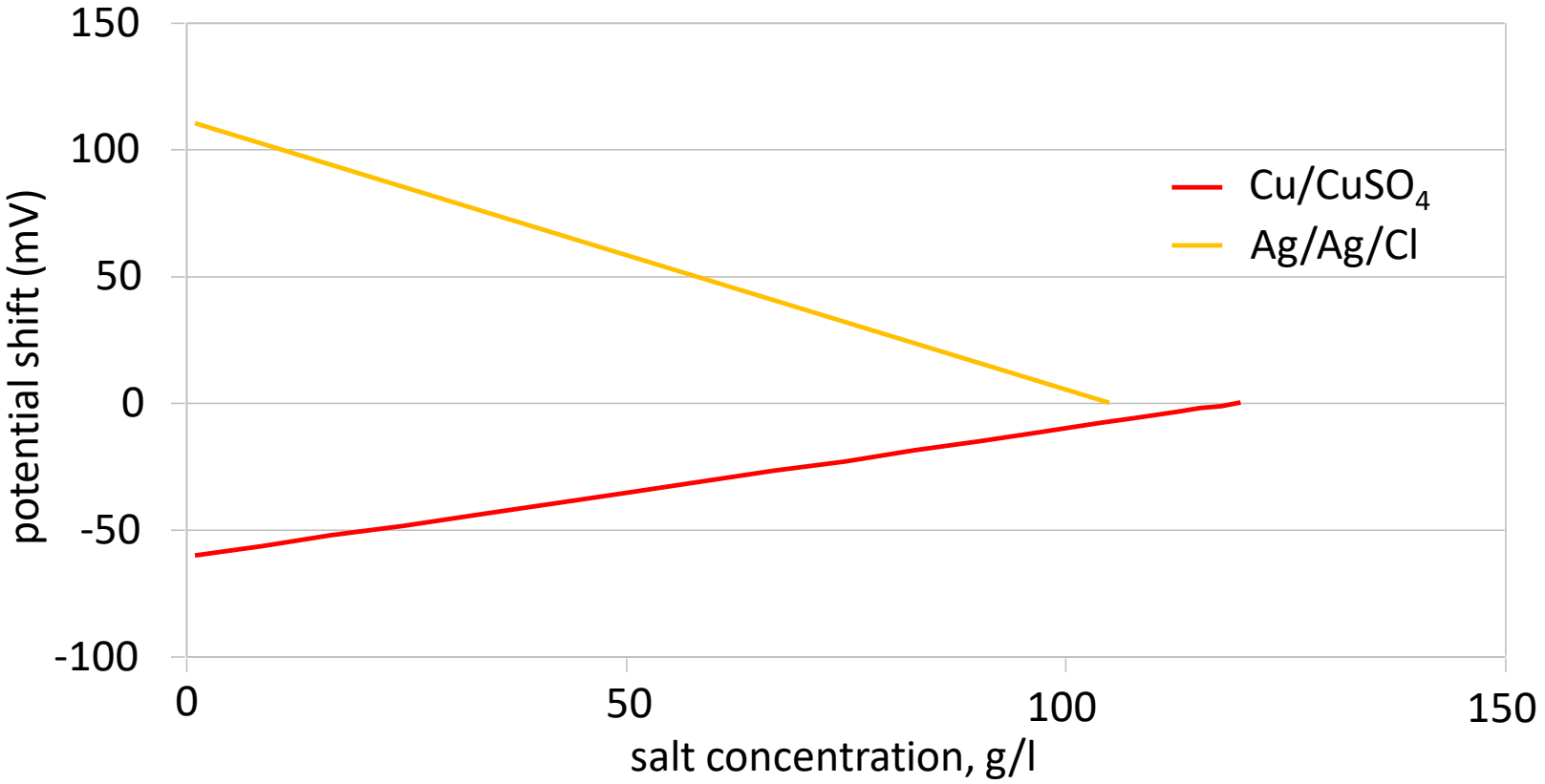


External Influences

- Reference potential (LJ) is influenced by:

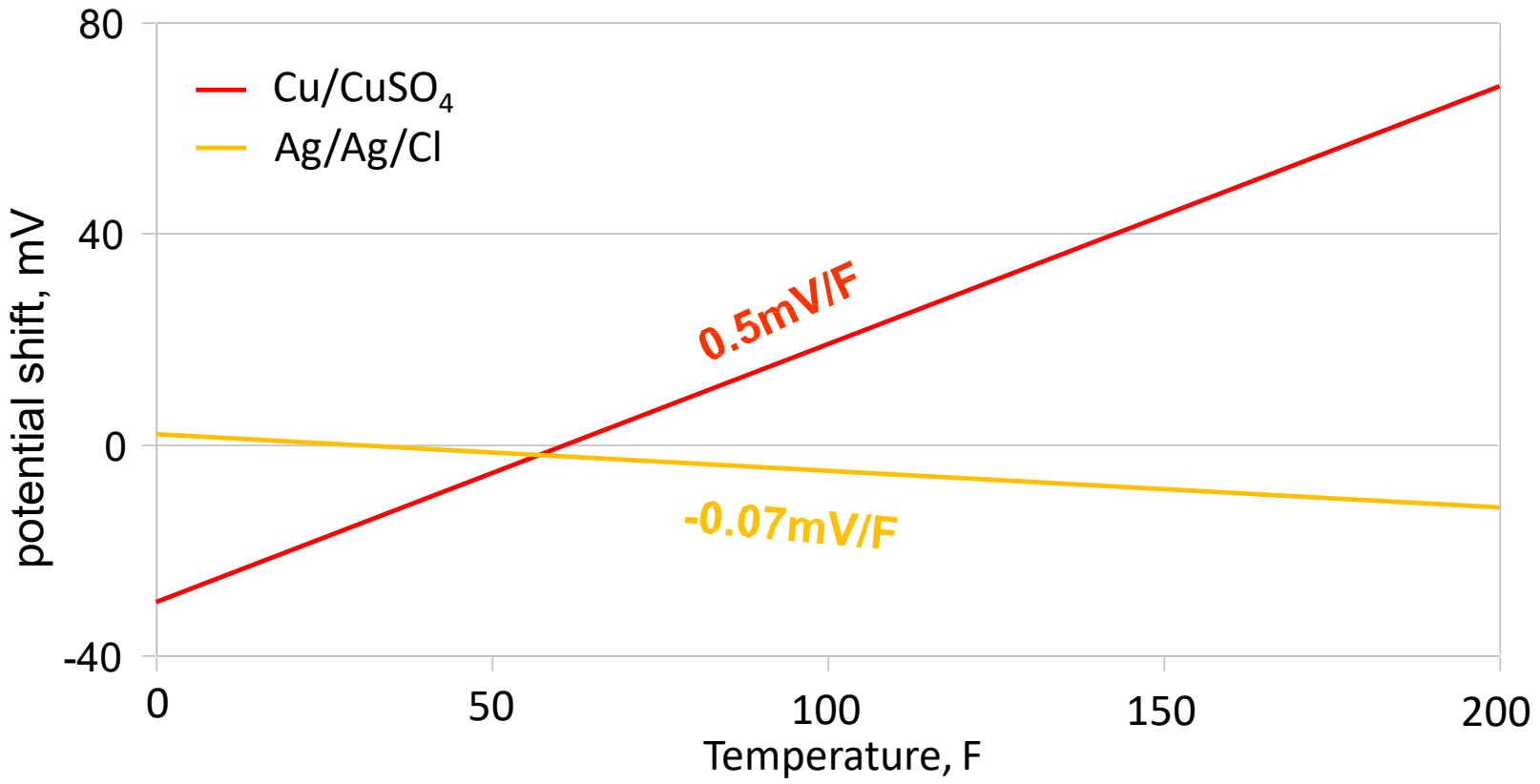
  a) Electrolyte Concentration
  b) Temperature
  c) Electrolyte Contamination
  d) Light (UV)

Electrolyte Concentration Affects Potential



- As the electrolyte salt concentration drops (less than sat.):
- $Cu/CuSO_4$ reference drifts in the negative direction
- Ag/AgCl reference drifts in the positive direction.

Temperature Affects Potential



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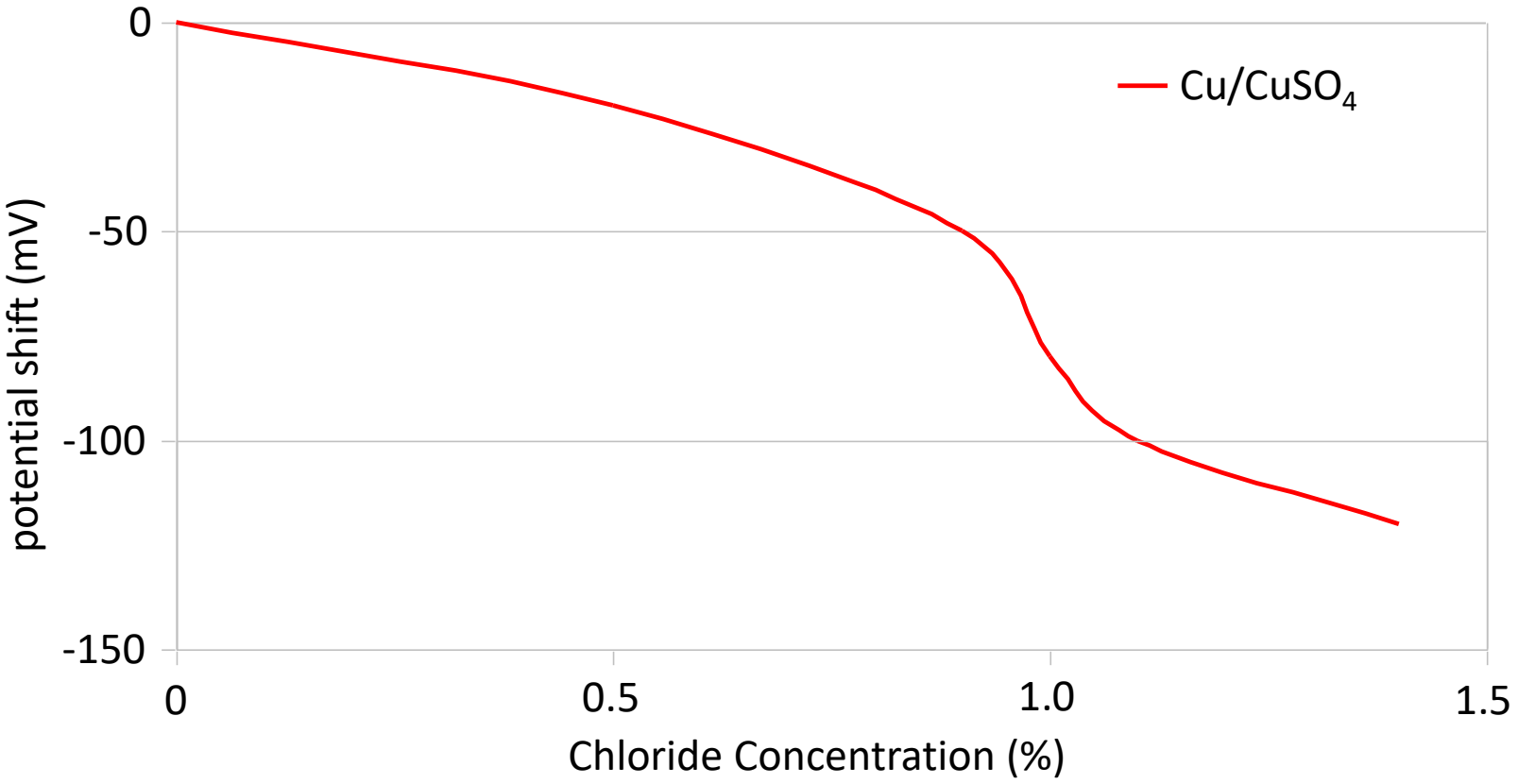
As the temperature increases:

- Cu/CuSO4 references drift in the positive direction
- Ag/AgCl references drift in the negative direction.

Contamination Affects Potential



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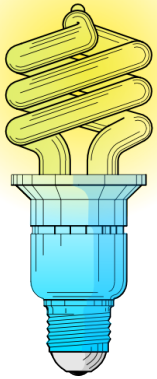
$Cu/CuSO_4$ references should not be used in chloride contaminated environments.

Light (UV) Affects Potential

Copper/Copper Sulfate ($Cu/CuSO_4$) Reference Electrodes are Sensitive to Light (UV)

Light Source Intensity	Change
High Noon – Direct Sunlight	-52mV
Open Shade – Indirect Sunlight	-10mV
Interior Fluorescent or CFL	-2mV



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Test Method

- AMPP (NACE) TM0113-2013
- Evaluating the Accuracy of Field-Grade Reference Electrodes

Permanently Installed Reference Electrodes

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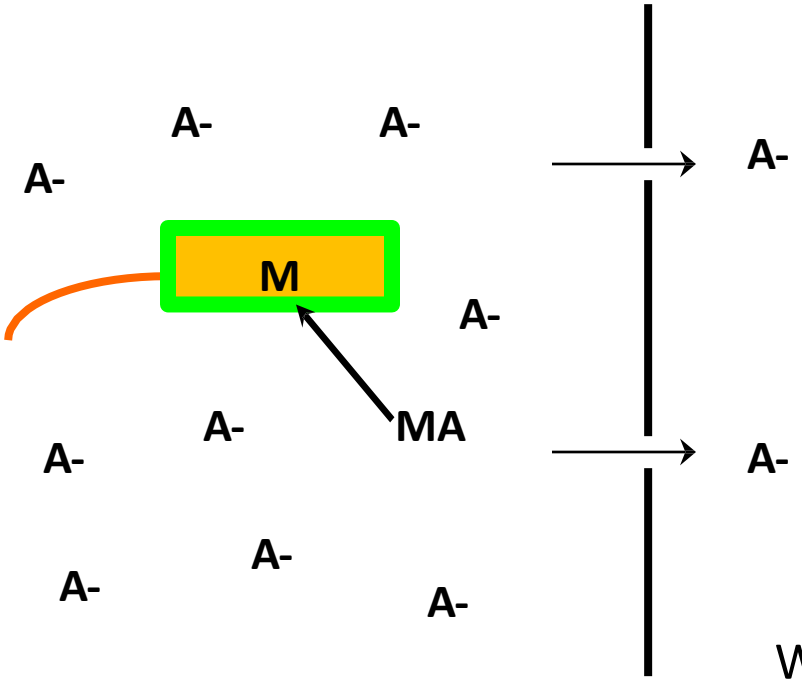
Service Life – Effect of Diffusion



Diffusion rate increases with:

- Temperature
- Membrane area
- Concentration difference

When the salt saturation or composition of electrolyte at the element changes, the reference potential will shift.

Service Life Factors

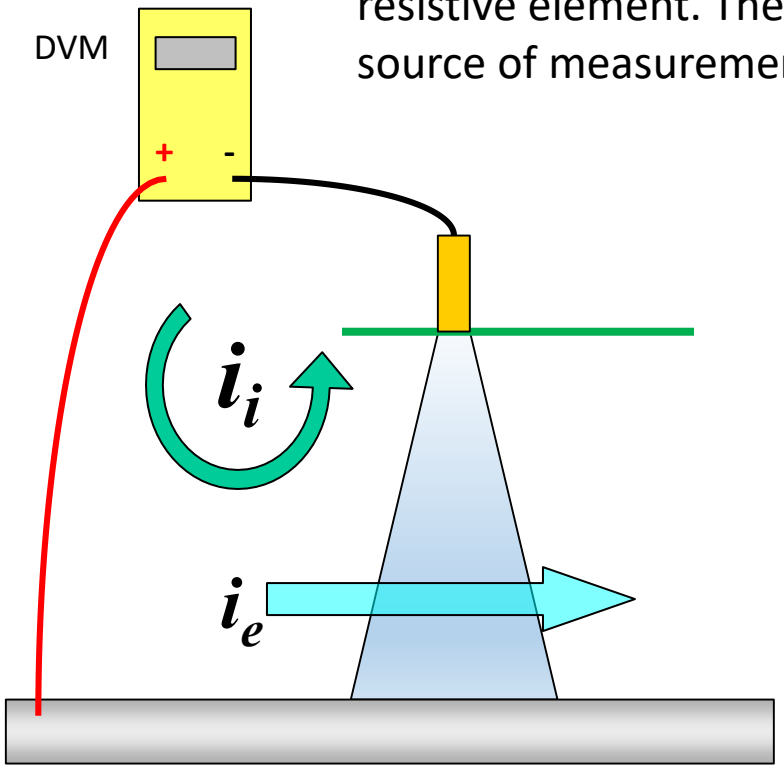
- Design
  - Electrolyte path length
  - Ion flow control
- Chemical
  - Gel binder composition
  - Salt loading
- Environmental
  - Electrolyte flow rate
  - Electrolyte contamination

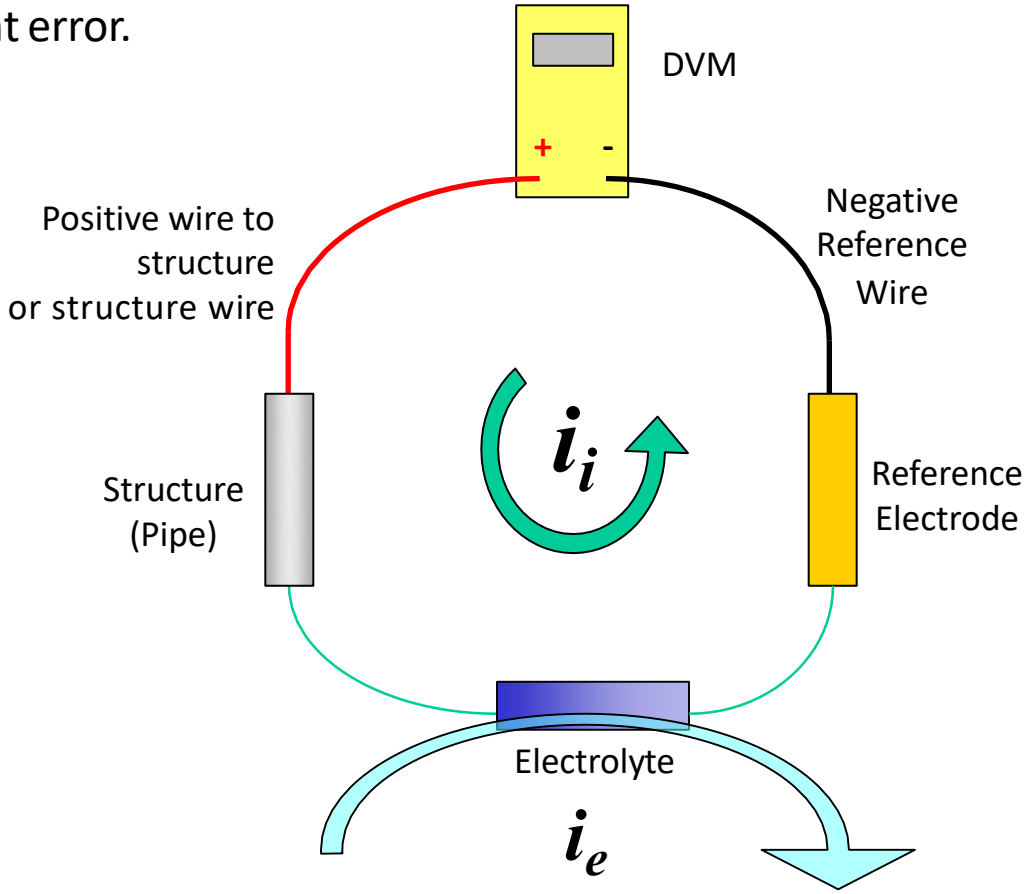
Failure Mechanisms

- Change of electrolyte ion concentration
- Electrolyte contamination
  - $Cu/CuSO_4$: chlorides & sulfides
  - Ag/AgCl: sulfides & other halides
- Loss of electrical circuit continuity
  - Wire failure
  - Electrolyte dry-out

Measurement Circuit

Current flowing through the measurement circuit will cause IR (voltage) drops across each resistive element. These voltage drops are a source of measurement error.





Measurement Errors
Internal IR Drop

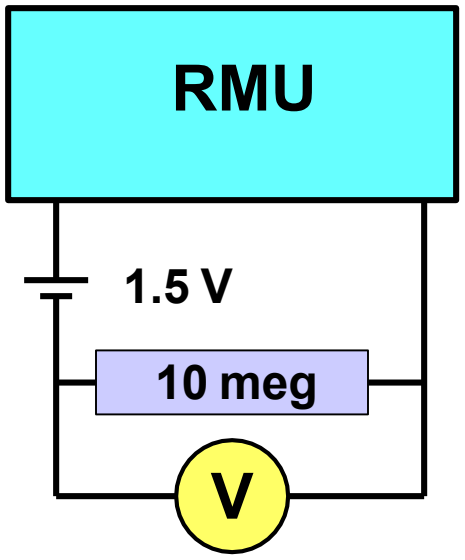
- Internal IR drop results from current flowing through the measurement circuit
- Reduce by using a higher input impedance meter or potentiometric voltmeter
  - 10 megohm (min.) for water and damp soil
  - 100 megohm (min) for semi-dry soil and concrete
- Measurements through asphalt should be avoided because asphalt is an insulator

Measurement Errors
Remote Monitoring Units

Input impedance on some RMUs drop when they are in stand-by or turned off.

Excessive current flowing through a reference electrode will shift the potential or destroy the cell.

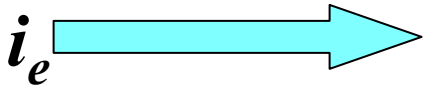
Input impedance must not drop below 10MΩ as unit is cycled through off, on-standby and on-measuring.



100 meg meter

Test circuit

Measurement Errors
External IR Drop



- External IR drop results from current flowing through the electrolyte, either from the CP system or stray currents from other sources
- Small reductions obtained by placing the reference close to the structure
- Larger reductions obtained by interrupting CP current or using CP coupons

Questions?

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  - Underground
  - Fresh water

- Silver/Silver chloride (Ag/AgCl)
  - Seawater
  - Saline mud
  - Concrete