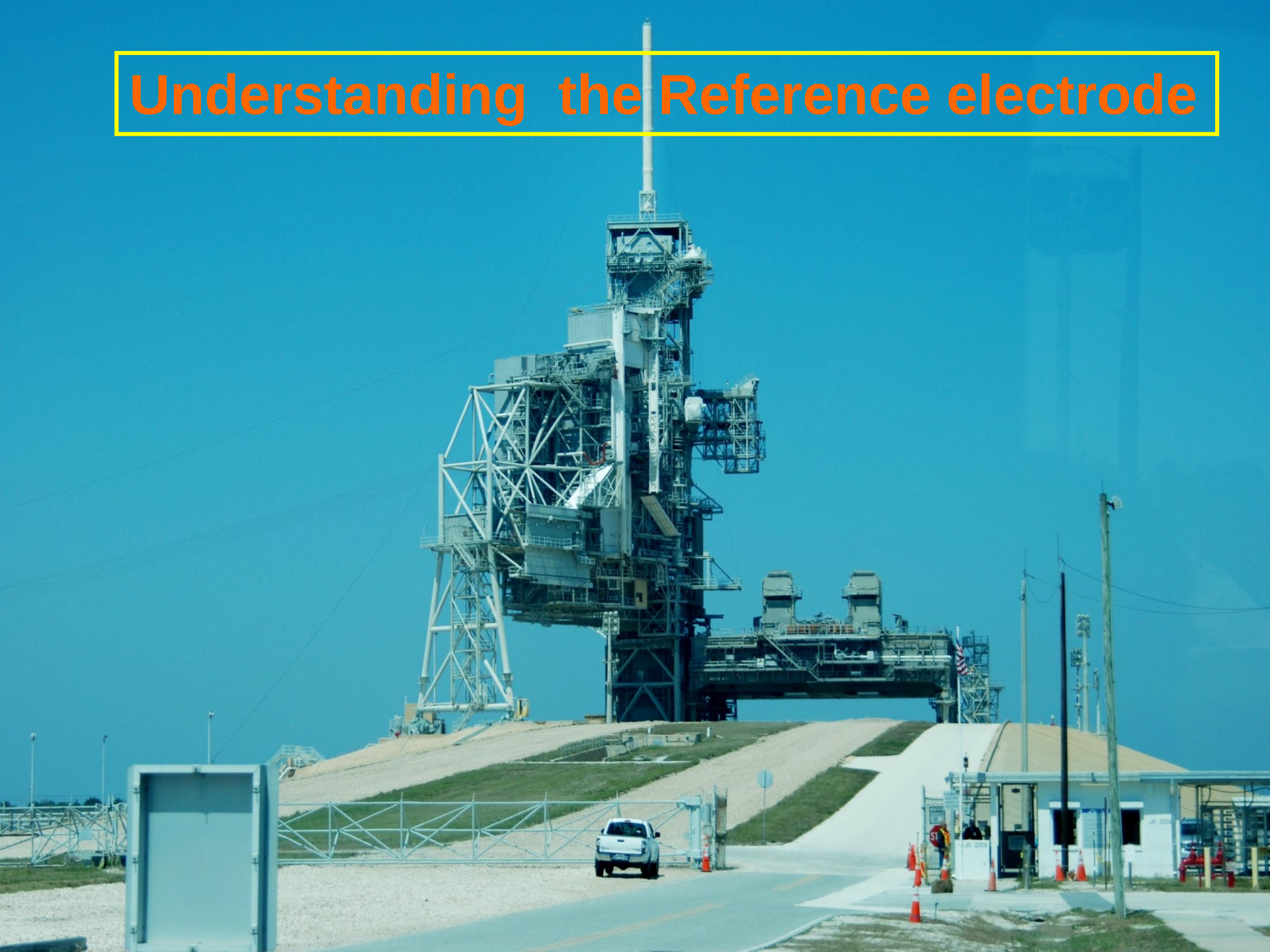
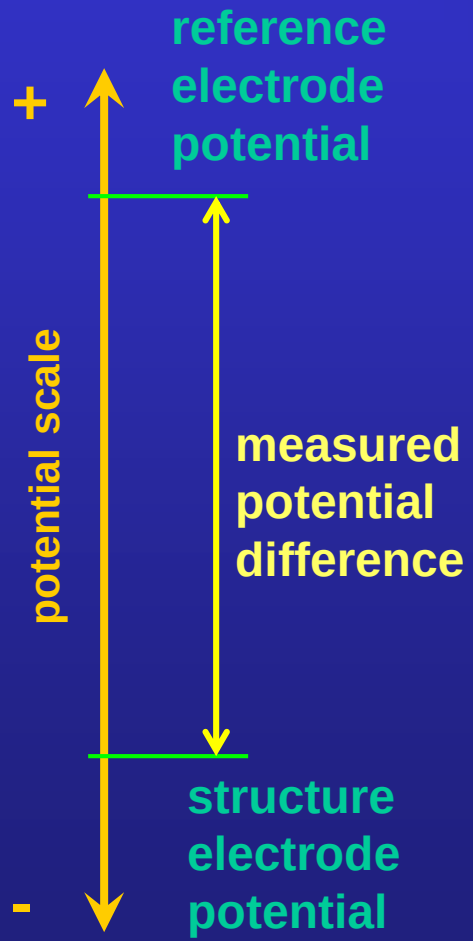
Understanding the Reference electrode



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?

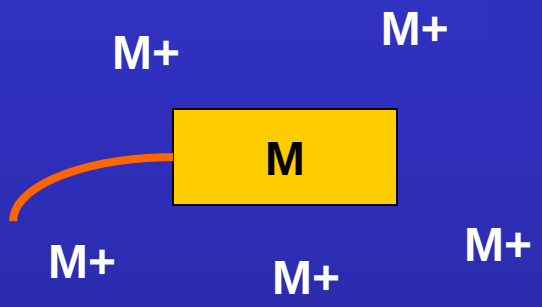
Simple Electrodes …

- 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 reaction
- In a reference electrode, the electrolyte, metal and reaction are precisely defined to produce a consistent potential

Two Kinds of Electrodes

1st kind

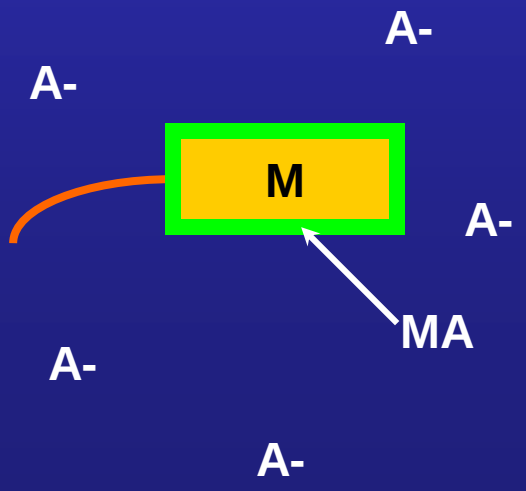
$M^0 \text{ <--> } M^+ + e^-$



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

2nd kind

$M^0 + A^- \text{ <--> } MA + e^-$



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

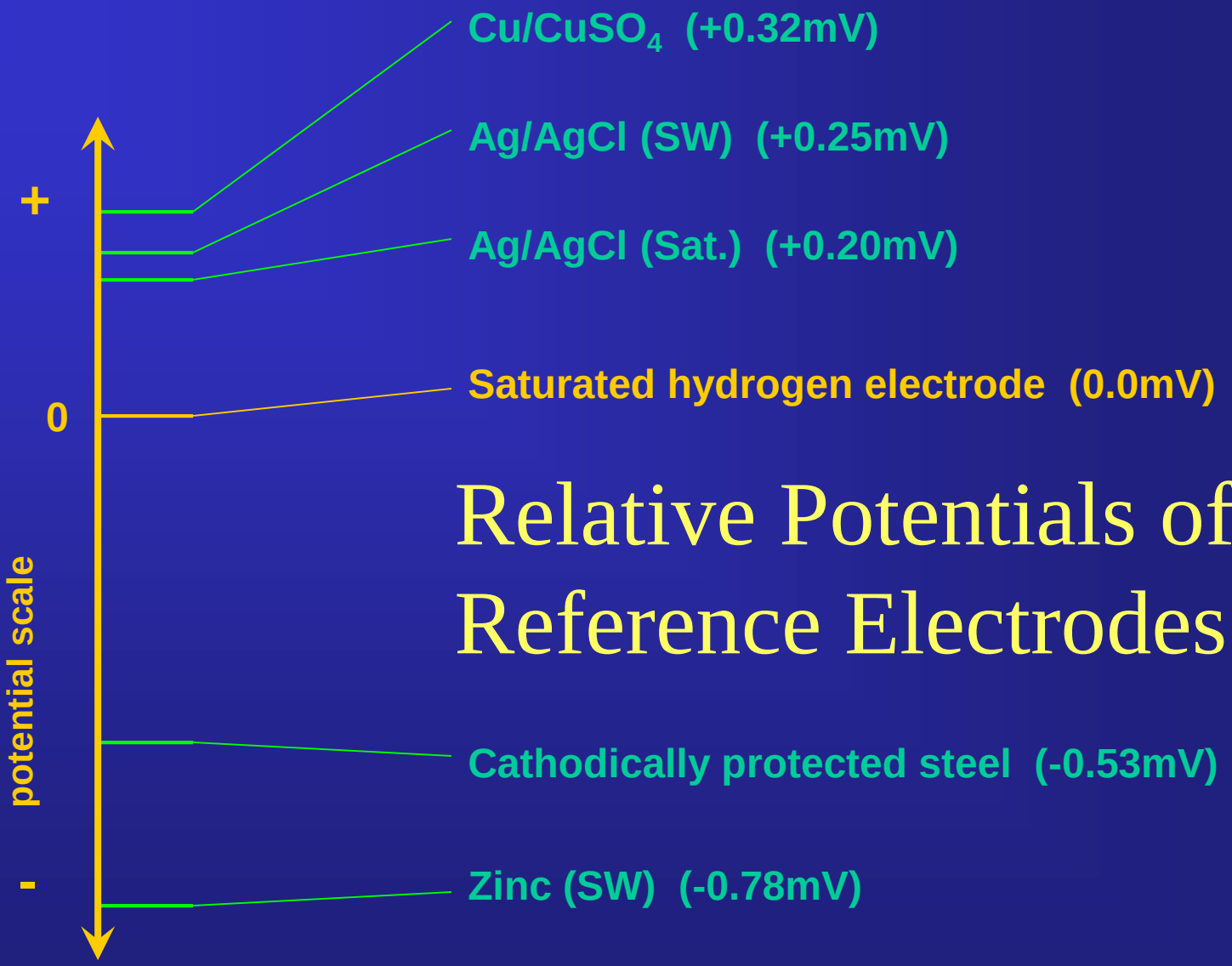
Electrolyte Forms

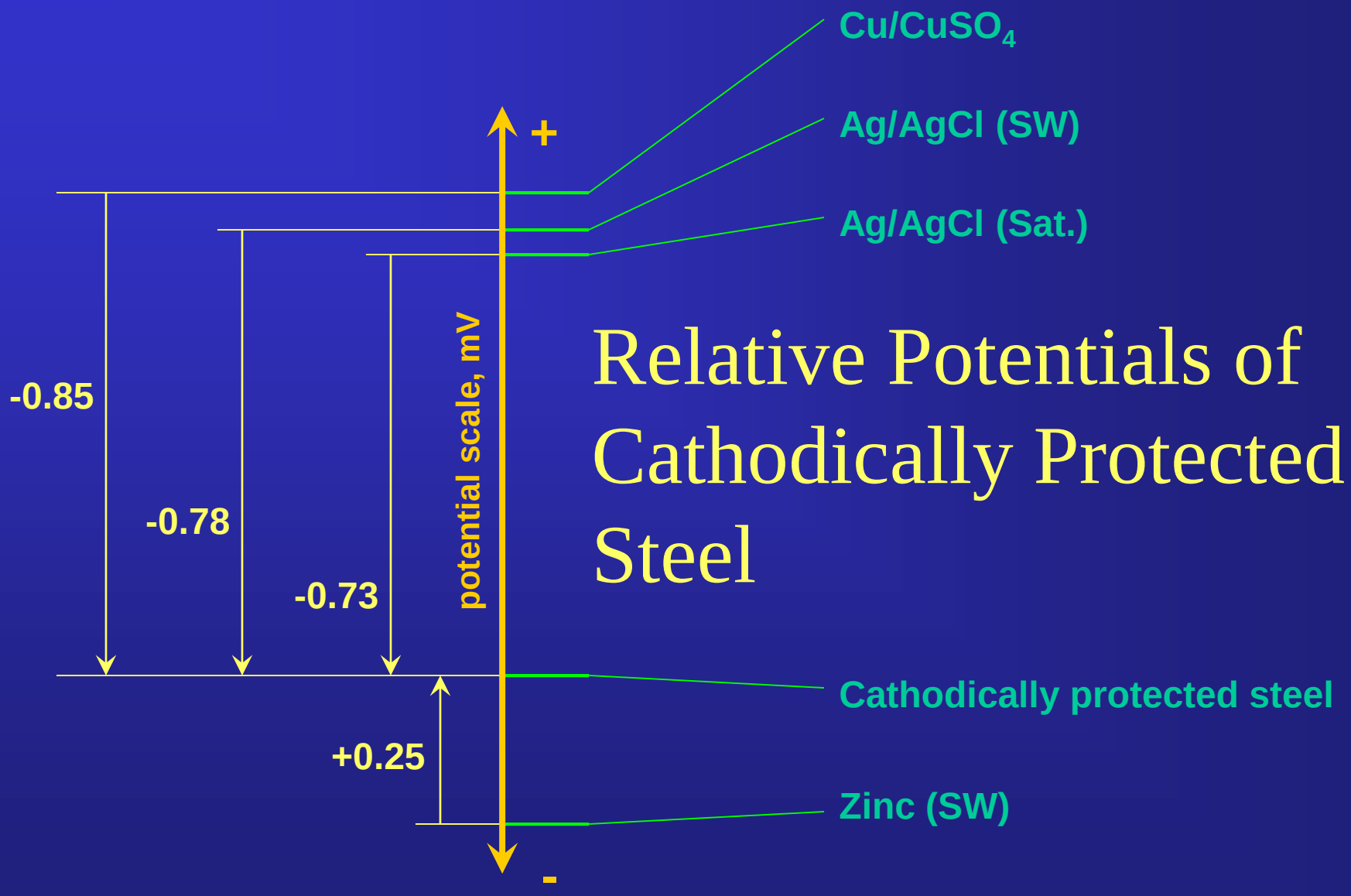
- Dry electrode – Element in direct contact with the structure electrolyte
- Wet electrode – Element immersed in a salt solution and separated from the environment by a porous plug
- Gelled electrode – Element immersed in a gelled salt solution and separated from the environment by a conducting membrane

Commonly Used Reference Electrodes

- Copper/copper sulfate ($Cu/CuSO_4$)
  - Underground
  - Fresh water
- Silver/silver chloride (Ag/AgCl)
  - Seawater
  - Saline mud
  - Concrete

Relative Potentials of Reference Electrodes





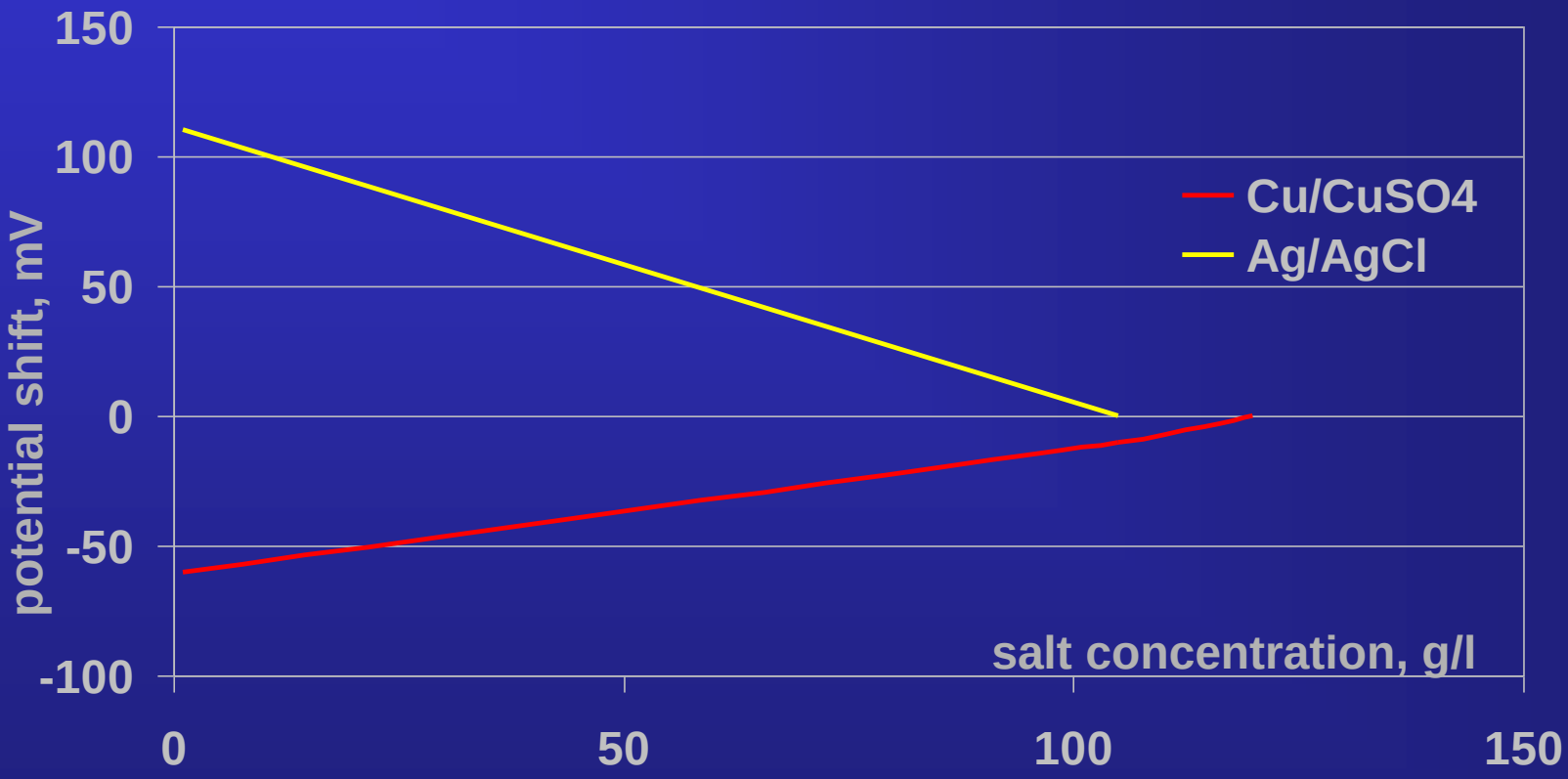
Relative Potentials of Cathodically Protected Steel

External Influences

Reference potential is influenced by

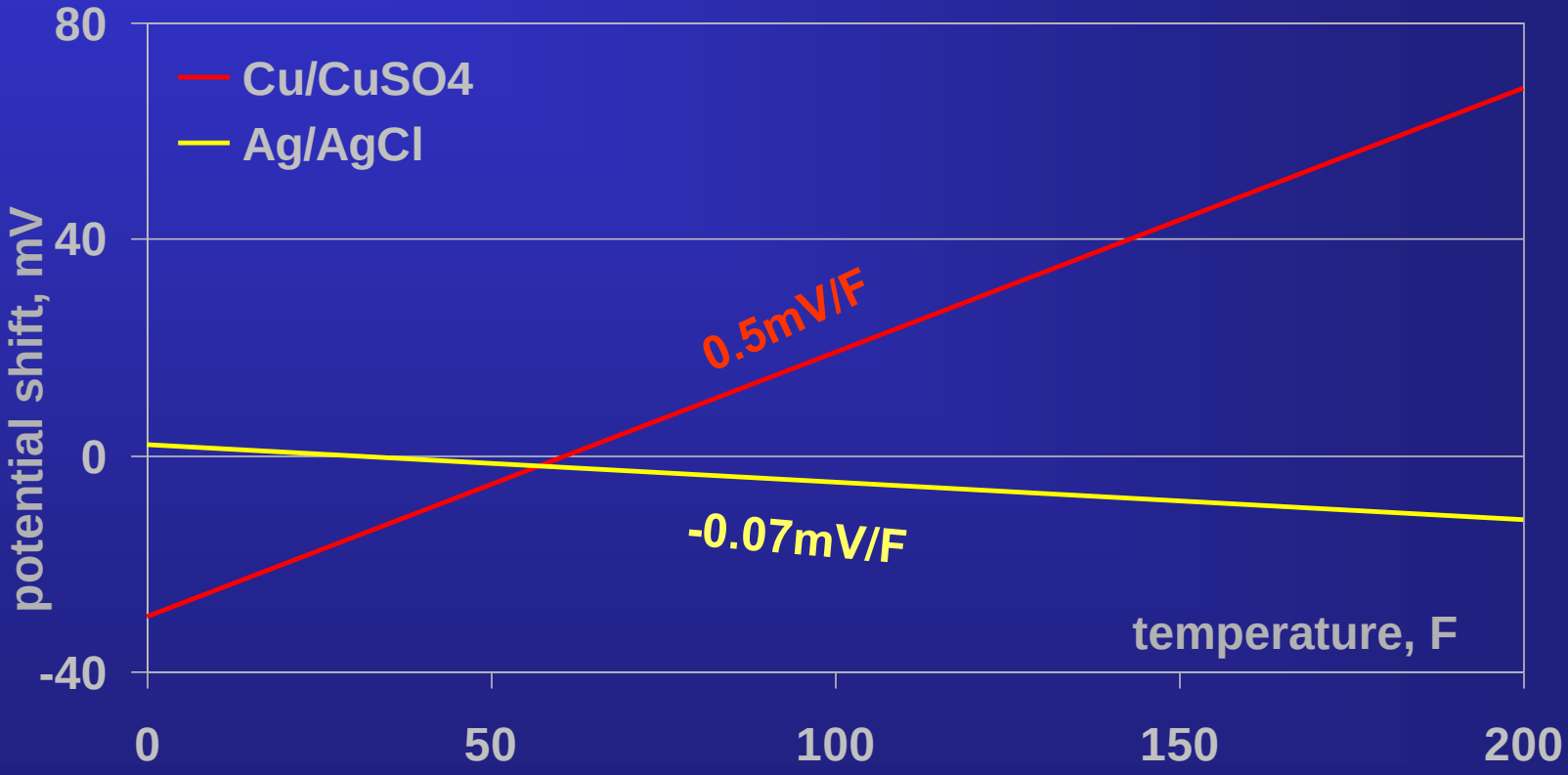
- Electrolyte Concentration
- Temperature
- Electrolyte Contamination
- Light

Electrolyte Concentration Affects Potential



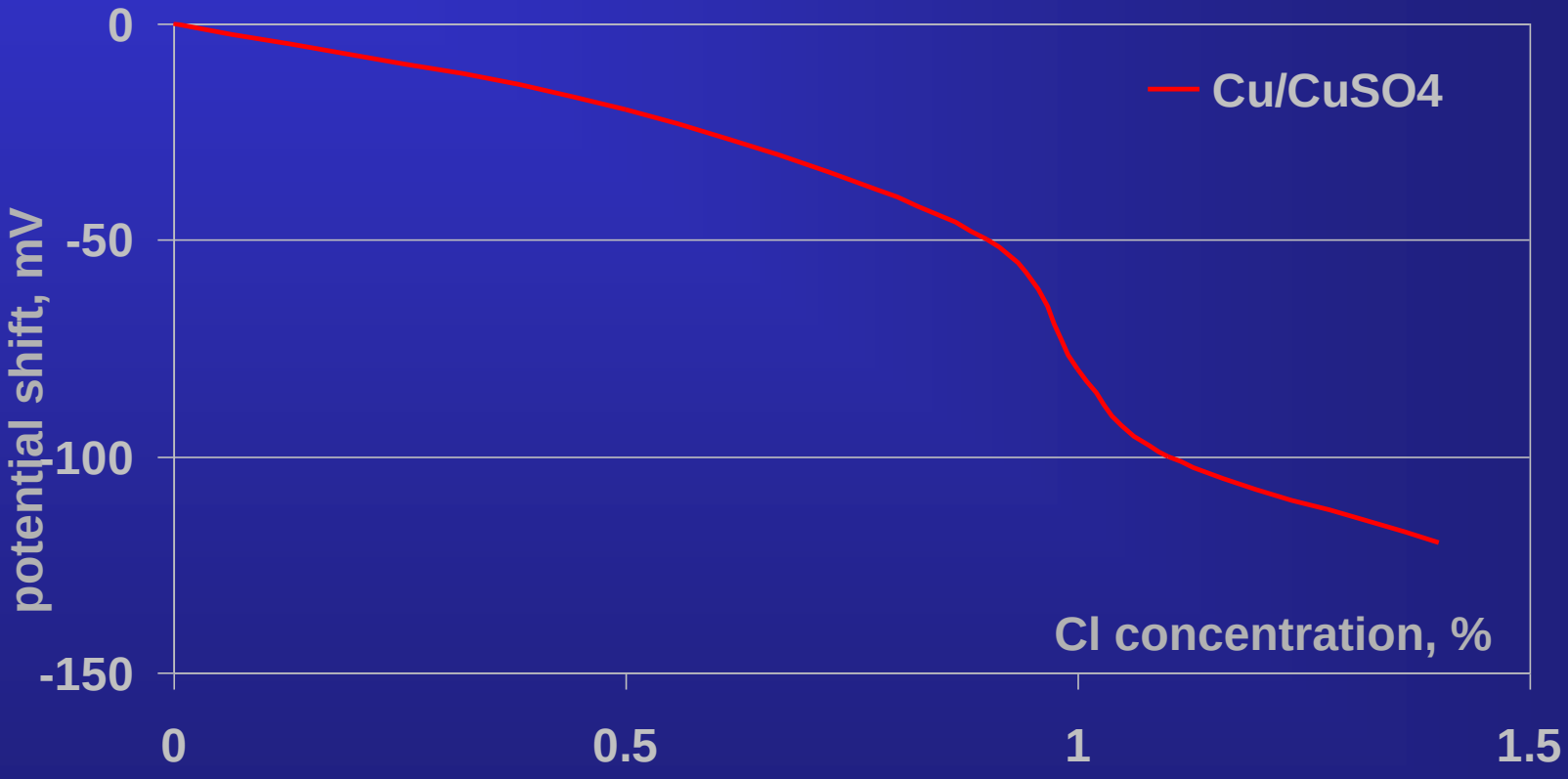
As the electrolyte salt concentration drops:
Cu/CuSO4 references drift in the negative direction,
Ag/AgCl references drift in the positive direction.

Reference Electrodes are Temperature Sensitive



As the temperature increases: Cu/CuSO4 references drift in the positive direction, Ag/AgCl references drift in the negative direction.

Contamination Affects Reference Potential



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

$Cu/CuSO_4$ Reference Electrodes are Light Sensitive

High Noon	-52mV
Open Shade	-10mV
Interior Fluorescent	-2mV

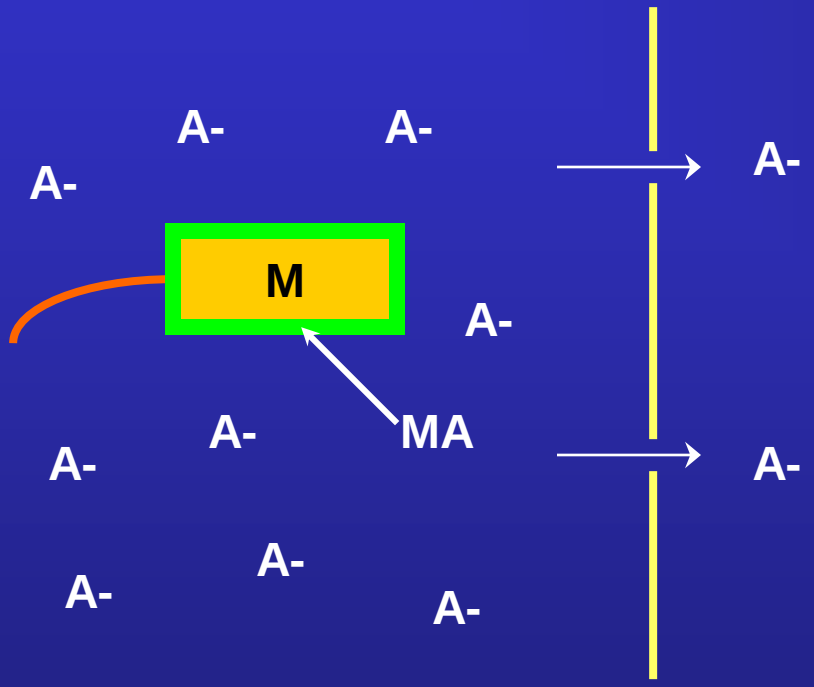
TEST METHOD

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

PERMANENTLY INSTALLED

REFERENCE ELECTRODES

Service Life – Effect of Diffusion



- Diffusion rate increases with
  - Temperature
  - Membrane area
  - Concentration difference

When the salt concentration or composition at the element changes, the reference potential will shift.

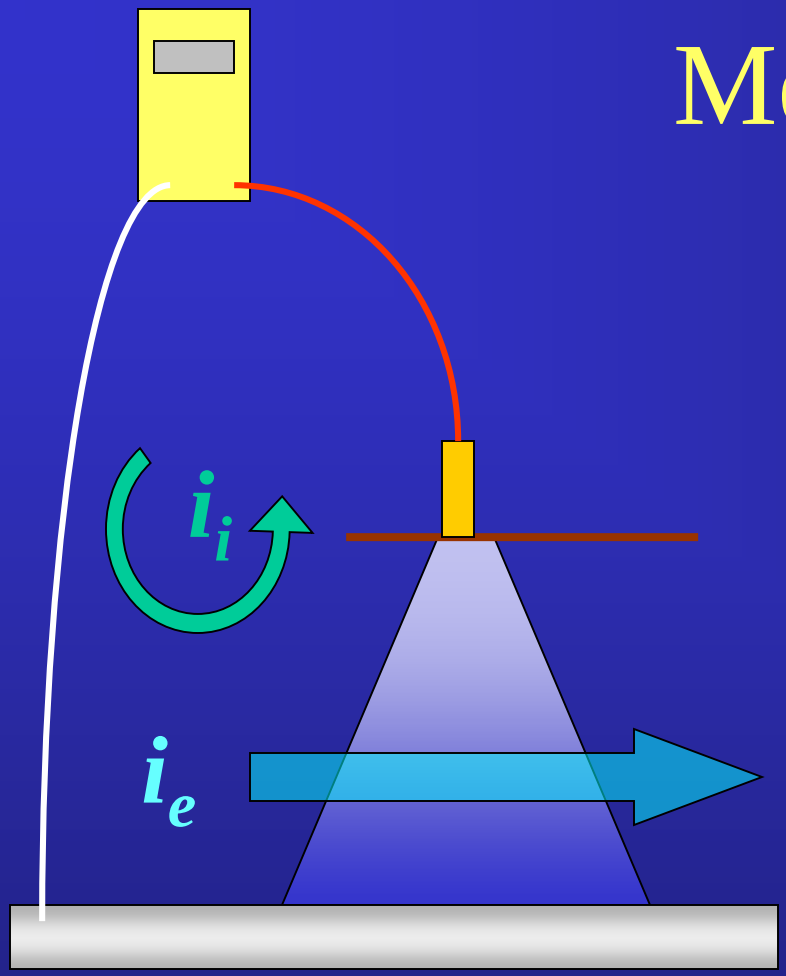
Service Life Factors

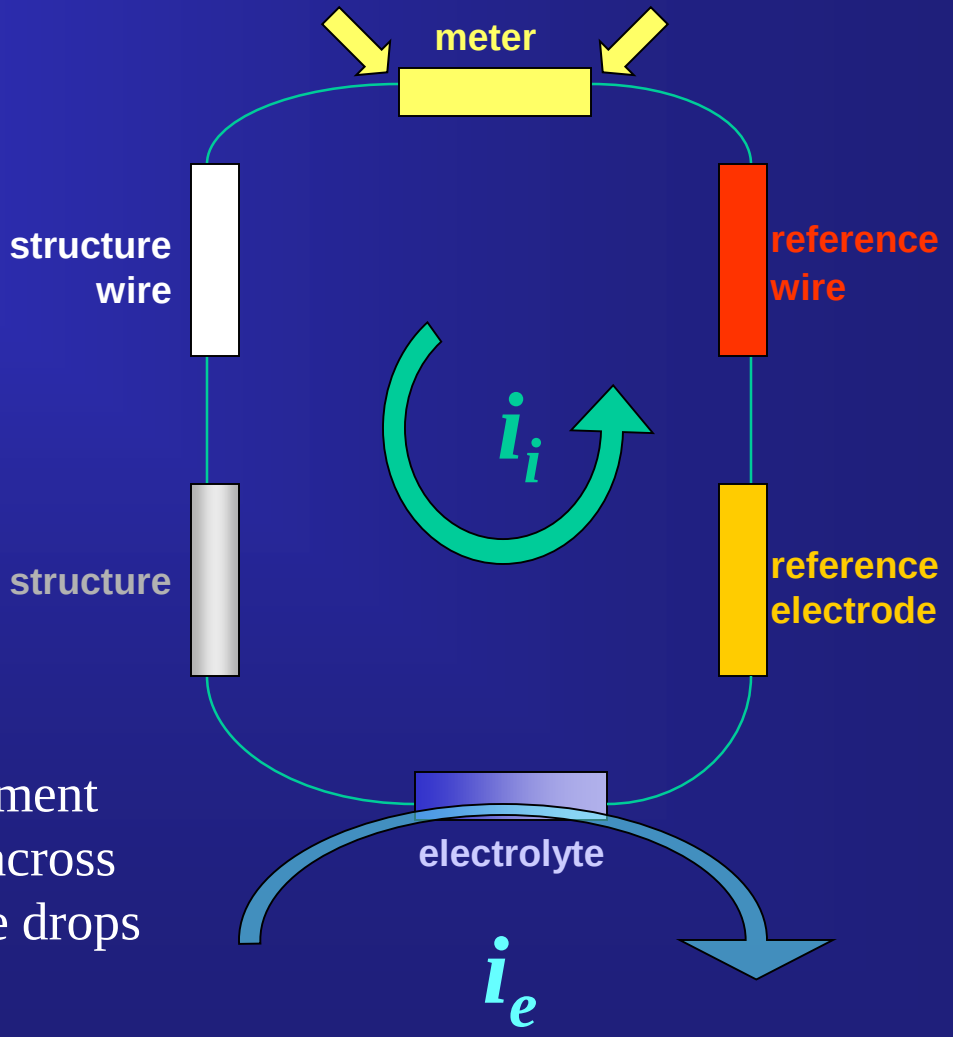
- Design
  - Electrolyte path length
  - Ion flow control
- Chemical
  - Gel binder composition
  - Salt loading
- Environmental
  - Electrolyte flow rate
  - Electrolyte contamination

Failure Mechanisms

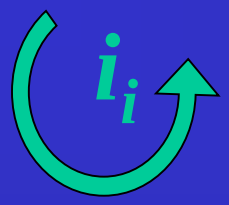
- Change of electrolyte ion concentration
- Electrolyte contamination
  - $Cu/CuSO_4$: chlorides & sulfides
  - Ag/AgCl: sulfides & other halides
- Loss of electrical circuit continuity
  - Wire failure
  - Electrolyte dry-out

Measurement Circuit



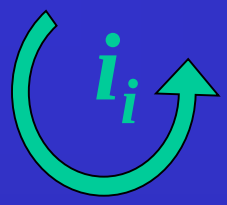


Current flowing through the measurement circuit will cause IR (voltage) drops across each resistive element. These voltage drops are a source of measurement error.



Measurement Errors
Internal IR Drop

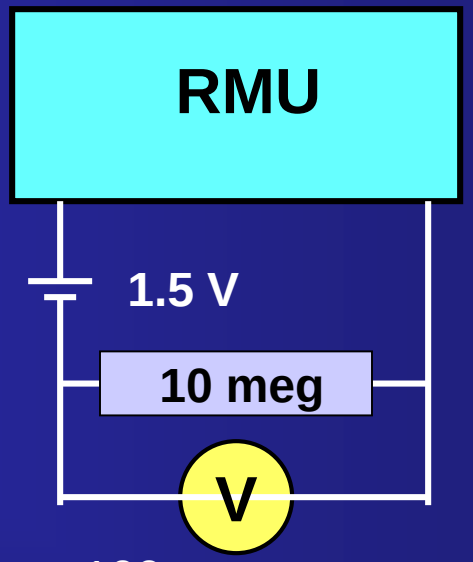
- Internal IR drop results from current flowing through the measurement circuit
- Reduce by using a higher input impedance meter or potentiometric voltmeter
  - 10 megohm (min.) for water and damp soil
  - 100 megohm (min) for semi-dry soil and concrete
- Measurements through asphalt should be avoided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



Test circuit

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

Measurement Errors External IR Drop

- External IR drop results from current flowing through 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