EC-013 - MODULE 6 OF 7

Reference Electrodes Types, Potentials, and Selection

Every potential you record is measured against something. This is that something - the measuring stick behind the number.

EXTERNAL CORROSION TRACK FOUNDATION ELECTROCHEMISTRY & THE GALVANIC SERIES ~30 MINUTES

BY THE END OF THIS MODULE

You'll be able to -

- Explain why a structure potential is always measured **against** a reference, and what "known and steady" buys you.
- Name the four field cells - copper sulfate, silver-silver chloride, saturated calomel, zinc - and the environment each one belongs in.
- Convert a reading from one cell to another, and carry the field shortcut: one offset straight back to copper.
- Recognize what quietly drifts a cell - temperature, light, contamination - and why none of it shows on the meter.
- Run the checks that keep a cell honest: the cell-to-cell comparison, the office master, and the everyday maintenance.

YOU INHERIT AN AREA, AND THE RECORDS DON'T LINE UP

Stations reading positive a quarter-volt - and history that says they're fine

A couple dozen test stations, handed over from a tech who retired. Most read the way you'd expect on a protected line. One cluster doesn't.

Your fresh readings

Most stations sit comfortable, around -0.900 to -1.050 V. Then a cluster reads up around **positive a quarter-volt** - on paper, like those stations aren't protected at all.

The audit file

The previous records for those same stations look fine, survey after survey - solid, protected numbers. Your readings and the history don't line up.

YOU CAN'T TELL A CELL BY ITS WIRING - SO YOU CHECK IT

A portable copper cell, held against the buried one, gives it away

Set your own portable copper-sulfate cell in the ground beside the station and read the permanent cell against it.

What the check shows

Two copper cells would agree within 25-50 mV. Instead they're off by about **1.1 volts** - the signature of a buried **zinc** reference cell.

Why the records were fine

Codes and the audit file are written to copper sulfate. Whoever logged those good numbers had been **converting** the zinc readings first. The new reader took them raw. The pipe was protected all along.

A reading is only as good as
the stick that took it.

A number with no cell written beside it
is half a measurement.

MODULE ROADMAP

Five sections, in order

01
The second point
Why every reading needs a reference.

02
The four cells
Copper sulfate, silver chloride, calomel, zinc.

03
The conversion
Same pipe, two rulers - carry it back to copper.

04
What drifts a cell
Temperature, light, contamination.

05
Trust, then verify
The checks that keep a cell honest.

SECTION 1 - WHAT A REFERENCE ELECTRODE IS

Voltage is a difference, so you always need two points

A METER NEVER READS ONE THING - IT READS A DIFFERENCE

The reference is the known, steady second point

A pipe-to-soil potential is the pipe measured against a fixed point planted in the electrolyte. That fixed point is the reference electrode.

> **"Known and steady" is the whole job.** If the second point wanders, every number you write down wanders with it - and nothing on the meter warns you.

Same tool, many names: **reference electrode**, **reference cell**, **half-cell**, or just the **survey stick**. Knowing all of them keeps you straight on a job where the last crew used different words.

A CONTROLLED CHEMISTRY, SEALED IN

A metal in a solution of its own salt, held at saturation

That sealed, saturated chemistry is what lets a cell hold a fixed potential for years - so long as it stays clean.

Kept clean

Solution saturated, tip clean, rod uncontaminated: the cell holds its number. It's a stable ruler you can trust survey to survey.

Let go

Dried out or contaminated, it starts reading wrong - quietly. This is the failure that costs the most, because the meter still shows a confident number.

WHERE THE CELL POTENTIALS ARE QUOTED FROM

Every cell's potential is measured from one shared zero: the SHE

The standard hydrogen electrode (SHE) is the agreed zero line on the yardstick. Nobody carries one - it's a laboratory construct.

> **All you need it for here:** every practical cell sits a fixed number of millivolts away from that shared zero. Those numbers are what make conversion between cells possible - the next section puts them to work.

SECTION 2 - THE TOOLKIT

The four cells worth knowing

THE DEFAULT FOR SOIL AND FRESH WATER

Copper-copper sulfate: the U.S. soil standard

A copper rod in saturated copper-sulfate solution. If a U.S. tech says "reference cell" without naming one, this is it.

Where it belongs

Buried structures and fresh water. Nearly every soil potential you'll ever take is CSE.

Why it matters

The entire -0.850 V world - the criteria, your records - is written against copper sulfate. Say "eight-fifty" and you mean vs. CSE.

THE CELL FOR CHLORIDE ENVIRONMENTS

Silver-silver chloride: seawater, brackish water, concrete

A silver wire coated in silver chloride, sitting in a chloride solution - built for environments where chloride is already present.

Where it belongs

Seawater and brackish water; the preferred choice in concrete. Its potential shifts a little with chloride concentration, so a seawater cell and a lab saturated-KCl cell read slightly different.

On concrete

Silver chloride is the preferred pick. Copper sulfate gets used there too and isn't wrong - it just drifts more easily, so it needs closer upkeep.

THE BENCH STANDARD

Saturated calomel: the stable cell you verify others against

A mercury-based laboratory cell. Accurate and stable on a bench - which is exactly where it stays.

Not a field cell

The mercury makes it a hazard and the glass makes it fragile, so it doesn't ride in the truck. Recognize the name and know it's a bench instrument.

What it's for

Its steadiness makes it a standard - the cell a shop checks a field or master cell **against**. The top of the chain your everyday cells trace back to.

RUGGED, CHEAP, HARD TO KILL

Zinc: the permanent cell that reads a protected pipe as a small positive number

A bar of zinc used as a reference - the usual choice for a permanent cell buried beside a structure or dropped in seawater, where a fragile cell wouldn't survive.

The trade

It gives up a little precision for toughness. Good where a cell has to sit in the ground for years and keep working.

The catch from the hook

Zinc reads a protected pipe as a small **positive** number, not the big negative one you're used to - which throws anyone who doesn't know it's in the ground.

STANDARD FIELD VALUES (TM0497 TABLE A1)

Potentials vs. the SHE zero

Reference cell	Electrolyte	V vs. SHE	Where it belongs
Copper-copper sulfate (CSE)	saturated $CuSO_4$	**+0.316**	soil, fresh water (U.S. default)
Silver-silver chloride	seawater (0.6 M NaCl)	**+0.256**	seawater, brackish, concrete
Saturated calomel (SCE)	saturated KCl	**+0.244**	laboratory / bench standard
Silver-silver chloride	saturated KCl	**+0.196**	brackish soils and water
Zinc	soil / saline	**-0.800**	rugged permanent installs

Copper sulfate sits about a third of a volt above the zero; zinc sits eight-tenths below. That ~1.1 V gap between them is the whole reason one pipe reads two very different numbers.

THE CHOICE THAT HAPPENS BEFORE ANY READING

Right cell, right ground

Copper sulfate in soil and fresh water. Silver-silver chloride in salt water and concrete. Calomel on the bench. Zinc where toughness beats precision.

> **The classic mistake:** a copper-sulfate cell in salt water. Chloride contaminates the copper-sulfate solution, the potential drifts, and every reading that day is off by an amount nothing on the meter reveals.

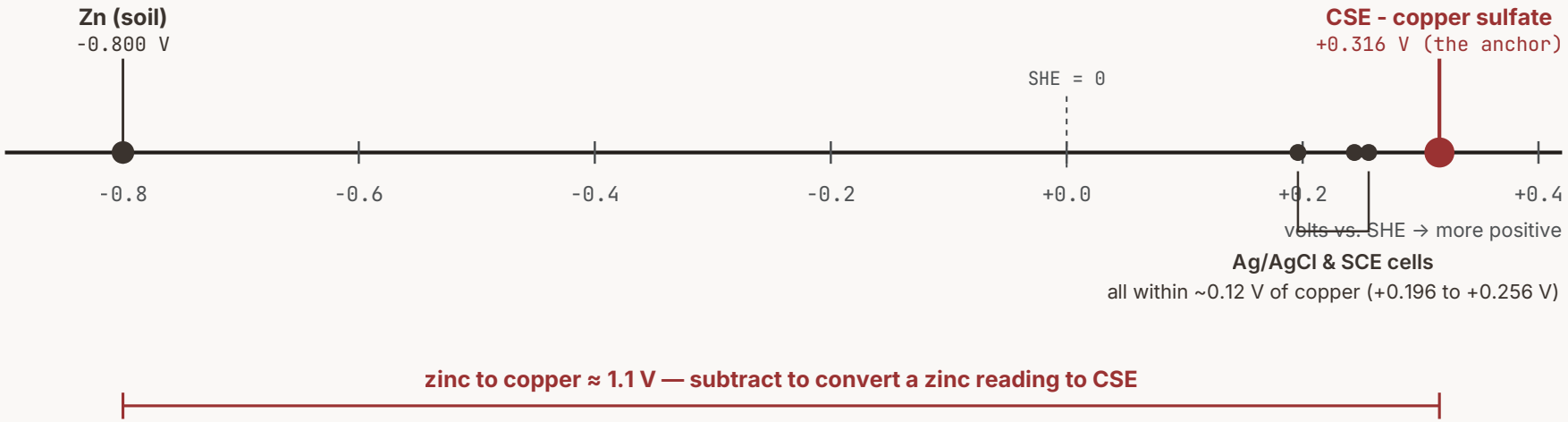
SECTION 3 - SAME PIPE, TWO RULERS

The conversion: carry a reading between cells

THE PIPE DOESN'T CHANGE - ONLY THE STARTING LINE DOES

Where the cells sit, and why the numbers differ

Reference cells on one scale — potential vs. the SHE zero



MOVE THE READING BY THE GAP BETWEEN THE TWO CELLS

One line, done in the truck

CONVERT A READING FROM ONE CELL TO ANOTHER

$$X = E(m)_1 + E(s)_1 - E(s)_2$$

- **X** - the reading you want, against the cell you care about
- **$E(m)_1$** - the reading you have, against the cell it was taken with
- **$E(s)_1$** - that first cell's potential vs. SHE (from the table)
- **$E(s)_2$** - the target cell's potential vs. SHE

In words: take the reading you have, add the standard potential of the cell it came from, subtract the standard potential of the cell you want.

ALMOST EVERY CONVERSION ENDS AT COPPER

The pocket version: one number straight back to copper

Codes and records speak copper sulfate, so techs skip the SHE step and carry one offset per cell. It's the same formula, done once and pocketed.

OFFSET TO CARRY A READING BACK TO CSE

```
From zinc … subtract about 1.1 V
From Ag/AgCl (sat KCl) … subtract about 0.12 V
From SCE … subtract about 0.07 V
From Ag/AgCl (seawater) … subtract about 0.06 V
```

Copper reads the most negative of the bunch, so every other cell's reading comes down to meet it. Meet a cell that isn't on the card, and the full formula builds the offset from scratch. **(This card is a printable download in the Listen step.)**

THE INHERITED ZINC STATION, BACK TO COPPER

+0.266 V on zinc is -0.850 V on copper

CONVERT +0.266 V (ZINC) TO CSE

```
X = ( +0.266 ) + ( -0.800 ) - ( +0.316 )
X = -0.850 V vs. CSE
```

That positive number was a protected pipe all along - a textbook -0.850, just read against a different cell.

Pocket check: +0.266 minus about 1.1 volts lands on the same -0.850. No lab electrode in sight.

THE OTHER DIRECTION - HANDING OFF TO A MARINE CREW

-0.850 V on copper is about -0.79 V on a seawater silver-chloride cell

CONVERT -0.850 V (CSE) TO AG/AGCL SEAWATER

```
X = ( -0.850 ) + ( +0.316 ) - ( +0.256 )
X = -0.790 V vs. Ag/AgCl (seawater)
```

Different cell, different decimals - the same protected steel.

> Marine practice sets its silver-chloride protection line right around **-0.80 V** for exactly this reason. Nobody's pipe changed; only the ruler did.

SECTION 4 - KEEPING A CELL HONEST

What quietly throws a cell off

NONE OF THEM SHOW ON THE METER - RECOGNIZE AND WORK AROUND

Temperature, light, contamination

TEMPERATURE

+0.5 mV per °F

A CSE drifts more positive as it warms - about 10 mV across a 20-degree morning-to-afternoon swing. Small, until you're right on a compliance threshold. Keep cells near room temp; record the temperature.

LIGHT

Tape the window

A CSE with a clear window drifts in direct sun — a photovoltaic effect the measurement standards name as a real error. The fix is simple: cover the window with electrical tape while you read.

CONTAMINATION

Keep it saturated

The solution has to stay clean and saturated. Chloride is the classic contaminant - the reason a CSE doesn't belong in salt water.

THE EVERYDAY CHECK - ABOUT THIRTY SECONDS

Check a cell against another, or against a clean master

Put one cell on the positive lead, one on the negative, set the meter to DC millivolts, and touch the two porous tips together.

The realistic spec

Cells that live in the dirt won't hold a millivolt. A typical field spec allows **5 to 10 mV** between cells - not a perfect zero.

The office master

Keep one clean cell that never goes in the ground and check every field cell against it. Many programs hold field cells within about 5 mV of that master.

THE UPKEEP, EVERY TIME

Four habits that keep a reading trustworthy

BEFORE USE

Wipe the tip

Caked mud on the porous tip adds resistance that shows up as error in your reading. Clean it first.

AFTER USE

Cap it

Cap the cell when you set it down so it stays saturated and doesn't leak out in the toolbox.

STORAGE

Out of the sun, topped up

Store out of direct sunlight; check the crystal and solution level before you head out.

THE ROD

Non-metallic sandpaper only

Clean a crusted copper rod with non-metallic sandpaper - metal grit embeds particles that throw the cell off worse.

WHY THE UPKEEP ISN'T BUSYWORK

A contaminated cell is worse than no cell

> No reading tells you to go look closer. A confident, wrong reading tells you everything is fine while the pipe corrodes.

False protection on paper is how a real problem hides in plain sight. Every survey we run, every compliance record our office signs, rides on cells chosen for the environment, checked against each other, and kept clean.

EVERYWHERE A POTENTIAL GETS MEASURED

The stick behind the whole survey

TEST STATIONS

Pipe-to-soil potentials

The everyday reading - a portable cell at grade over the line.

SURVEYS

Close-interval surveys

A portable cell walked along the line, reading after reading. The survey technique itself lives in later modules.

PERMANENT

Buried and stationary cells

Zinc or specialized cells left in the ground at crossings and deep pipe. Design details are Technician-tier.

CRITERIA

The -850 mV line

The protection criterion is defined against a copper-sulfate cell. Why that number means protected is EC-014's job - here it just names the stakes.

Record the cell next to the number.

A potential with no cell written beside it
is a length with no units -
and the conversion only saves you
if someone wrote down which stick was in the ground.

WHAT TO WALK AWAY WITH

The stick behind the number

- **A reading is always a difference** - the structure against a known, steady reference. Reference electrode, cell, half-cell, survey stick: all the same tool.
- **Four cells cover the work** - copper sulfate (soil, fresh water), silver-silver chloride (seawater, concrete), saturated calomel (bench standard), zinc (rugged permanent installs).
- **CSE is the U.S. soil default** - the whole -0.850 world is measured against copper sulfate; match the cell to the environment, and keep copper out of salt water.
- **Same pipe, two rulers** - convert with $X = E(m)_1 + E(s)_1 - E(s)_2$, or carry one pocket offset back to copper (a zinc reading, minus about 1.1 V, is the copper number).
- **Cells drift quietly** - temperature, sunlight, and contamination all move a reading with no warning on the meter.
- **Never trust one cell** - field cells agree within a company spec (often 5-10 mV, or against a clean office master), not a perfect zero. A contaminated cell is worse than none.

FURTHER READING + THE NEXT MODULE

Sources used + where this module hands off

- Peabody's Control of Pipeline Corrosion - reference-electrode types, potentials, and care
- Corrosion Basics: An Introduction - the electrochemistry behind reference potentials
- Field Notes from RCS - "Reference Cells - They're Pretty Cool" and "Portable and Stationary Reference Electrodes"
- NACE SP0169 - External Corrosion Control of Buried Piping (copper-sulfate basis for soil criteria)
- NACE TM0497 - Measurement Techniques for CP Criteria (tabulated reference-electrode potentials and temperature coefficients)

UP NEXT

EC-014 - Polarization

The set's closer: what a potential actually does while current is flowing - and why -0.850 V against a copper-sulfate cell is the number that means "protected."