Process Water Analysis

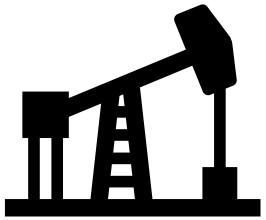
FELC 2024

Larry Tucker

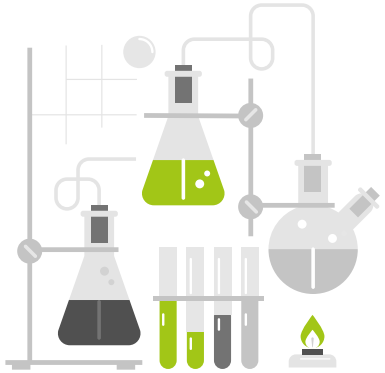
Metrohm USA

larry.tucker@metrohmusa.com

Water Usage



WATER



UTILITIES

SLURRY TANKS
AND LIQUIFICATION

FERMENTATION

Utility Water

At a minimum, boiler feedwater must be softened water for low pressure boilers and demineralized water for high pressure boilers. It must be free of oxygen and essentially free of hardness constituents and suspended solids.

Feedwater chemistry parameters to be controlled include dissolved solids, pH, dissolved oxygen, hardness, suspended solids, total organic carbon (TOC), oil, chlorides, sulfides, alkalinity, and acid- or base-forming tendencies.

Boiler Feedwater Guidance

Parameter	Concentration	Instrument
Cation Conductivity, µS/cm	<0.2	Conductivity
pH	9.0 - 9.6	pH
Dissolved Oxygen(O_2), µg/l	< 20	Oxygen Meter
Sodium (Na), µg/l	≤ 2	IC or ICP
Chloride (Cl), µg/l	≤ 3	IC
Silica (SiO_2), µg/l	< 10	Colorimetric
Iron (Fe) total, µg/l	< 2	Color/ICP
Copper (Cu) total, µg/l	<2	Color/IC/ICP
TOC, µg/l	<100	TOC
Alkalinity	100 - 400 P alk	Titration

Table 1
Recommended Feedwater Limits

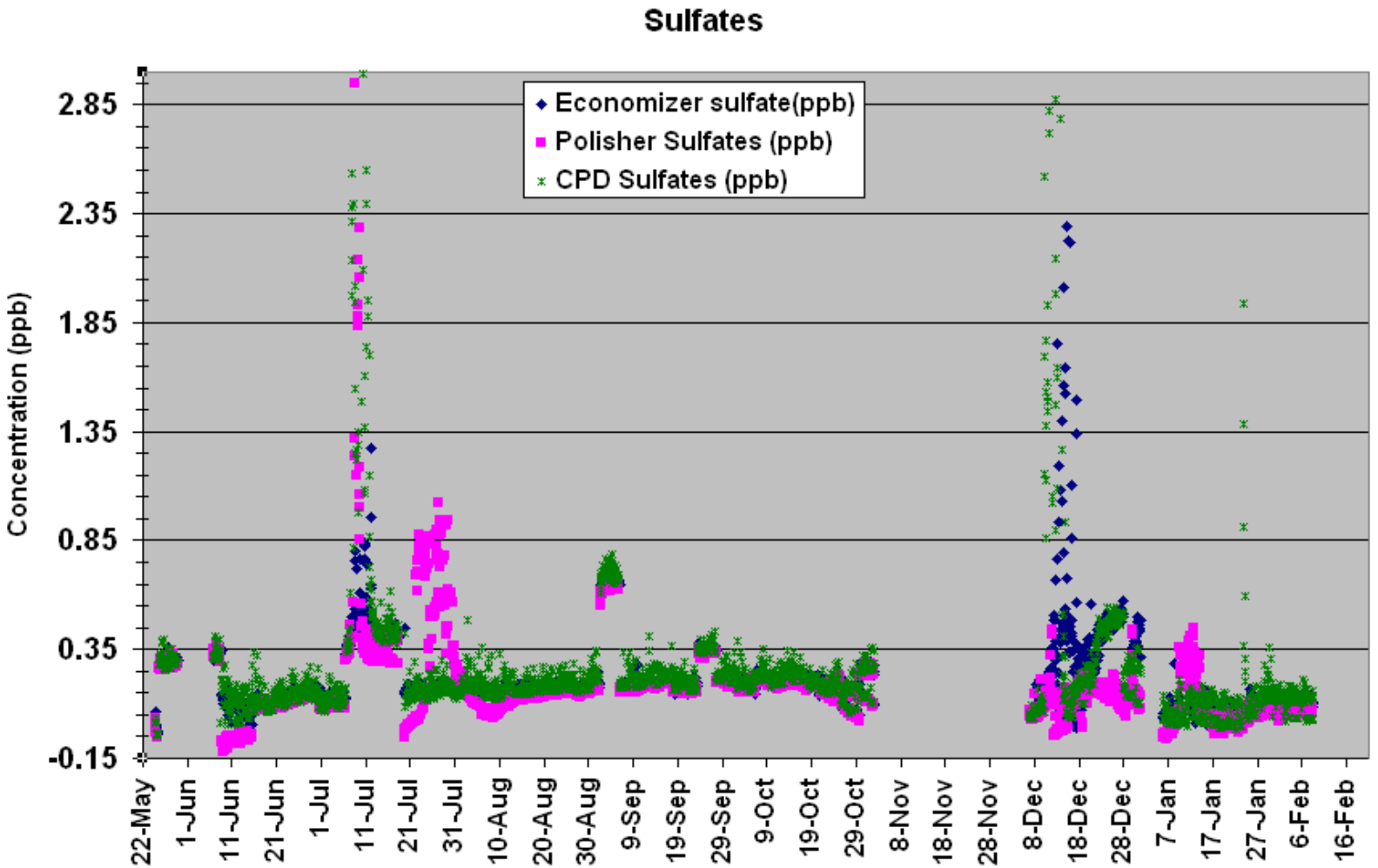
	Drum Boilers							Once-Through Boilers	
Pressure, psig (MPa)	15 to 300 (0.10 to 2.07)	301 to 600 (2.08 to 4.14)	601 to 900 (4.14 to 6.21)	901 to 1000 (6.21 to 6.90)	1001 to 1500 (6.90 to 10.34)	>1500 (>10.34)	with AVT[a] All	AVT All	Oxygen Treatment All
pH, all-ferrous heaters	9.3 to 10.0	9.3 to 10.0	9.3 to 10.0	9.3 to 9.6	9.3 to 9.6	9.3 to 9.6	9.3 to 9.6	9.3 to 9.6	8.0 to 8.5
pH, copper-bearing heaters	8.8 to 9.2	8.8 to 9.2	8.8 to 9.2	8.8 to 9.2	8.8 to 9.2	8.8 to 9.2	9.0 to 9.3[b]	8.8 to 9.2	N/A
Total hardness, as ppm $CaCO_3$ maximum	0.3	0.2	0.1	0.05	0.003	0.003	0.003	0.003	0.001
Oxygen, ppm maximum[c]	0.007	0.007	0.007	0.007	0.007	0.007	0.007[d]	0.007	0.030 to 0.150
Iron, ppm maximum	0.1	0.04	0.02	0.02	0.01	0.01	0.01	0.010	0.005
Copper, ppm maximum	0.05	0.02	0.01	0.01	0.005	0.002	0.005	0.002	0.001
Organic, ppm TOC max.	1.0	1.0	0.5	0.2	0.2	0.2	0.2	0.200	0.200
Cation conductivity, µS/cm max.	—	—	—	—	0.5	0.2	0.2	0.15	0.15

a All-volatile treatment.
b AVT not recommended for copper-bearing cycles and associated low feedwater pH where the drum pressure is less than 400 psig.
c By mechanical deaeration before chemical scavenging of residual.
d Dissolved oxygen for AVT(R); no oxygen scavenger used with AVT(O).

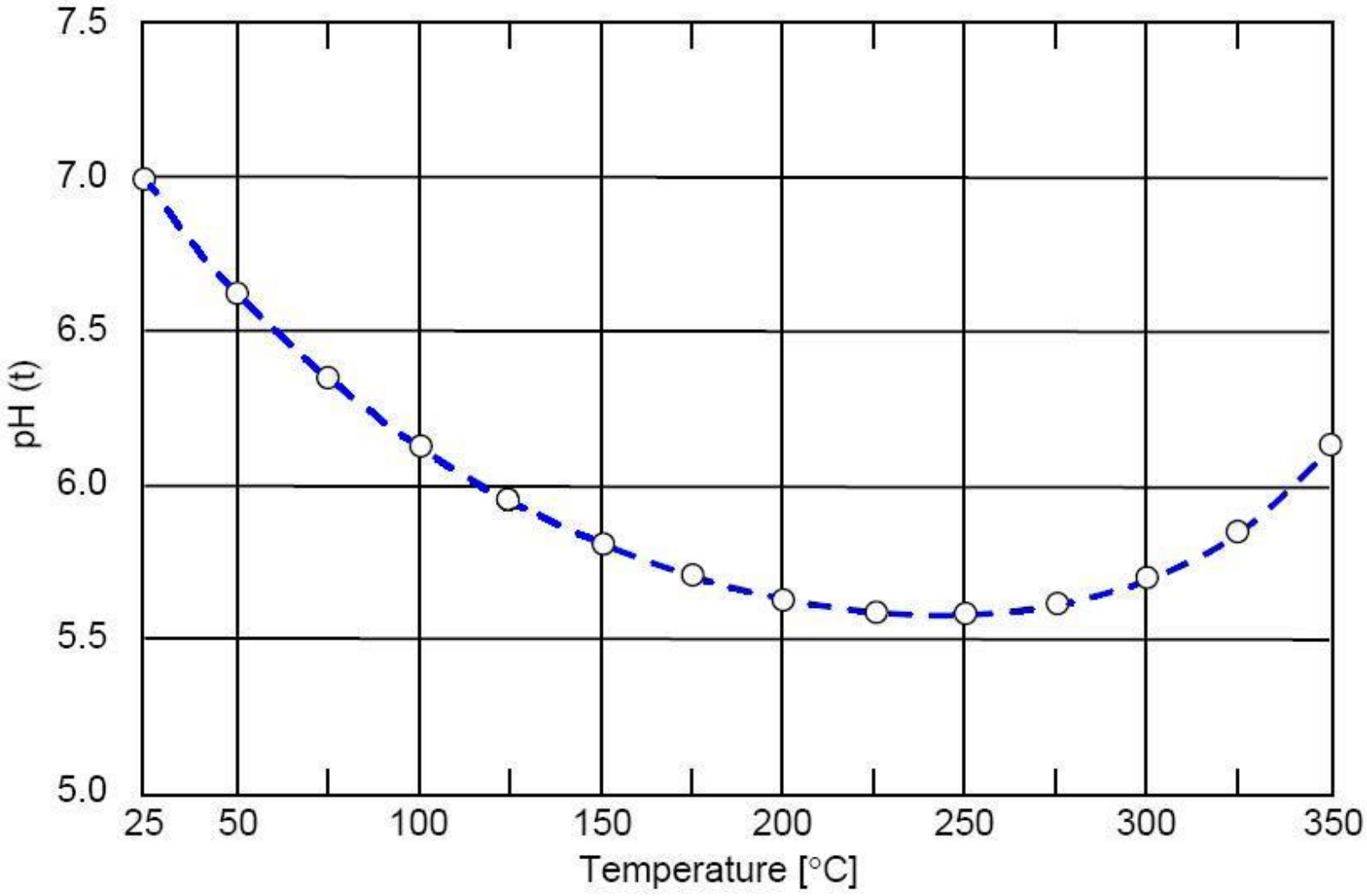
Note:
ppm = mg/kg

Metrohm

Trending for Predictive Maintenance



pH of Water At Temperature



pH Control

Ammonia

Alkalizing Amines

MONOETHANOLAMINE (MEA)

DIETHANOLAMINE (DEA)

TRIETHANOLAMINE (TEA)

ETC.

Wastewater plant

10 MG/L MEA, PH ~ 9.7 @ 25 °C

SHOCK LOAD TO BIO TREATMENT

Summary

Monitoring Plan

Efficient Operation

Control Corrosion

Run vs Repair

Economic Benefit

Resources

Analytical Methods for Water

ASTM COMMITTEE D19 WATER

STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER 24TH EDITION

THE B&W LEARNING CENTER HTTPS://WWW.BABCOCK.COM/HOME/ABOUT/RESOURCES/LEARNING-CENTER/THE-IMPORTANCE-OF-BOILER-WATER-AND-STEAM-CHEMISTRY#:~:TEXT=AT%20A%20MINIMUM%2C%20BOILER%20FEEDWATER,HARDNESS%20CONSTITUENTS%20AND%20SUSPENDED%20SOLIDS

Liquefaction & Fermentation

Regulating pH

Measuring pH

pH value: Temperature dependence

Nernst equation:

$$U = U_0 + \frac{2.303 \times R \times T}{z \times F} \times \log a_{H^+}$$

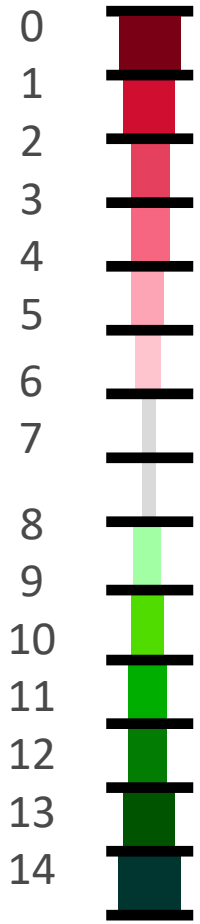
Correct measurement requires pH and temperature

e.g. pH 5.23 (24.5 °C)

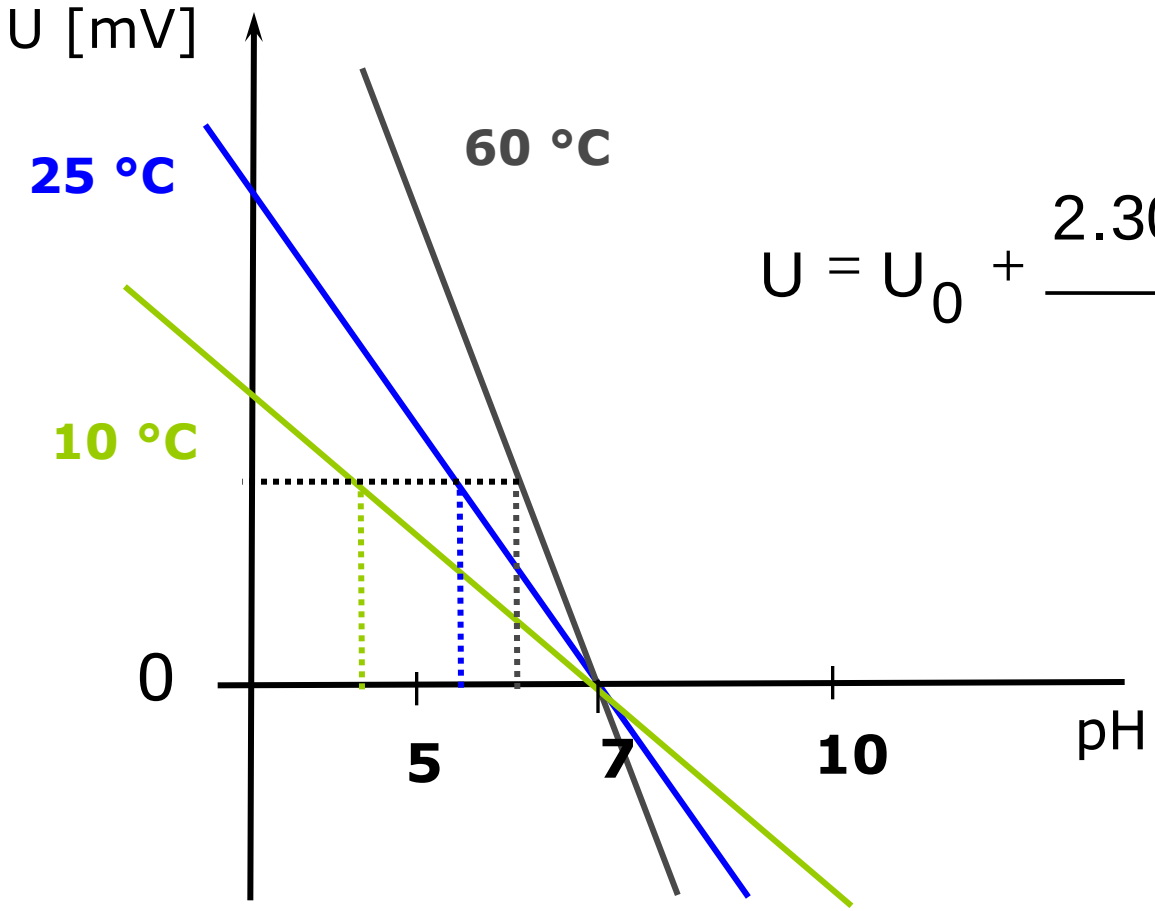
°C	pH
0	7.11
5	7.08
15	7.04
20	7.02
25	7.00
30	6.99
38	6.98
40	6.98
50	6.97
60	6.97
70	6.98
80	7.00
90	7.01

T [° C]	pH ±0.02
0	7.12
5	7.09
10	7.06
15	7.04
20	7.02
25	**7.00**
30	6.99
35	6.98
40	6.97
45	6.97
50	6.97

Temp. °C	pH	Temp. °C	pH
0	7,13	35	6,96
5	7,07	40	6,85
10	7,05	50	6,95
15	7,02	60	6,96
20	7,00	70	6,96
25	6,98	80	6,97
30	6,98	90	7,00



Calibration: Influence of the temperature



$$U = U_0 + \frac{2.303 \times R \times T}{z \times F} \times \log a_{H^+}$$

Temperature compensation

pH meter can only correct the temperature behaviour of the electrode and never of the sample

e.g. 0.001 M NaOH

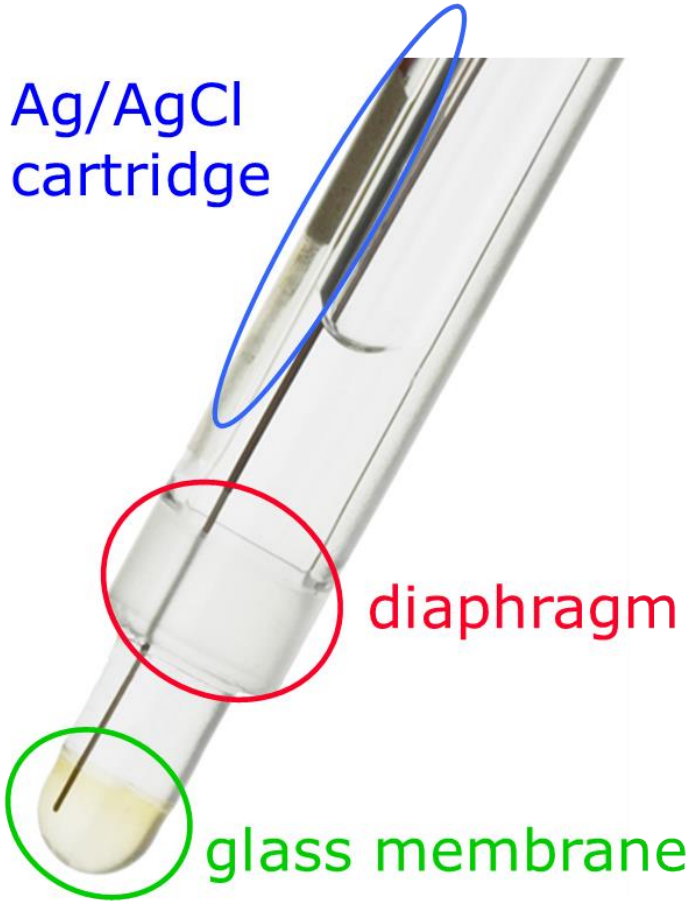
0 °C	25 °C	50 °C
11.94	11.00	10.26

Measurement uncertainty increases with temperature difference calibration to measurement

→ Recommendation: $T_{meas} = T_{cal}$

→ **always measure your samples at the same temperature if you want to compare their pH values**.

pH Regulation
Liquefaction & Fermentation



Electrode Maintenance

RINSE – DI WATER, ETHANOL, IPA

DO NOT WIPE OR RUB GLASS MEMBRANES

REFERENCE JUNCTION (DIAPHRAGM)

REFERENCE FILLED (KCL)

CALIBRATION

VIDEOS:
HTTPS://WWW.METROHM.COM/EN_US/SERVICE/PRODUCT-HELP-CENTER/ELECTRODES/MAINTENANCE-AND-CARE-OF-ELECTRODES.HTML

HTTPS://WWW.METROHM.COM/EN/DISCOVER/BLOG/2024/CALIBRATE-PH-METER.HTML#SLOPE-OFFSET

Thank You!

Larry Tucker

larry.tucker@metrohmusa.com