72.48 Applicability Analysis for Changes, Tests, Experiments

Description of Activity:

GE-MO License SNM-2500, Section 4.0, Paragraph 4.8.1 specifies basin water chemistry values for pH (4.5 to 9.0), $NaNo_3$ (<200 ppm), and Cl (<10 ppm). This 72.48 provides evaluation of a proposed change in water conductivity value to 1.35 (equivalent 5.5 to 8.0 pH) and eliminate $NaNo_3$ and Cl measurements.

(See discussion, justification and previous 72.48 attached)

Does this activity:

Yes	No	
☐	X	*Increase the probability of occurrence of an accident previously evaluated in the CSAR?*
☐	X	*Increase the consequences of an accident previously evaluated in the CSAR?*
☐	X	*Increase the probability of occurrence of a malfunction of equipment important to safety previously evaluated in the CSAR?*
☐	X	*Increase the consequences of a malfunction of equipment important to safety previously evaluated in the CSAR?*
☐	X	*Create the possibility of a different type of accident than any previously evaluated in the CSAR?*
☐	X	*Create the possibility of a different type of malfunction of equipment important to safety than any previously evaluated in the CSAR?*
☐	X	*Reduce the margin of safety as defined in the basis for any technical specification?*
☐	X	*Involve a significant increase in occupational exposure?*
☐	X	*Involve a significant unreviewed environmental impact?*

Prepared by: *E. W. Lecho* **Title:** Regulatory Compliance Mgr. **Date:** July 28, 2004

Safety Committee Approval (Required if any of the above questions are answered Yes.):

Manager, Morris Operation: _____ **Date:** _____

Operations & Maintenances Manager: _____ **Date:** _____

Regulatory Compliance Manager: _____ **Date:** _____

Radiation & Operations Safety Officer: _____ **Date:** _____

Specialist EHS, Facilities & Procurement: _____ **Date:** _____

72.48 Applicability Analysis for Changes, Tests, Experiments

As shown in GE-MO 72.48 prepared February 16, 1996, conductivity is a more accurate way to measure ultra pure water quality than pH and a conductivity value of 2.5 µmho/cm was established, corresponding to a pH of 4.5 to 9.0 in keeping with the reference license specification. This 72.48 lowers that value to 1.35 µmho/cm for the basin water, equivalent to a pH value of 5.5 to 8.0. This change is in keeping with the requirements in NUREG 1801, Chapter III, Table A5.1-e establishing a lower limit of 5.5 pH for water as non-aggressive to concrete. This value is also representative of the typical GE-MO basin water quality. Since March 1976 the average basin water conductivity has been 1.07 µmho/cm. There are no sources for $NaNo_3$ and Cl in the basin environment and values for these materials repeatedly are below detectable limit. During a recent test, basin water makeup, cooling and filtration were discontinued for a period of 50 days resulting in an actual conductivity increase to 1.22 µmho/cm. A conductivity value of 1.35 µmho/cm also provides a much lower tolerance for ionic impurities allowing the elimination of $NaNo_3$ and Cl measurements since values well below 5 ppm of either cause conductivity to significantly increase beyond 1.35 µmho/cm.

Spent fuel in the GE-MO basins are clad with either stainless steel or zircalloy. Per IAEA-TECDOC-1012, "Durability of Spent Nuclear Fuels and Facility Components in Wet Storage", the zirconium alloys represent a class of materials that is highly resistant to degradation in wet storage, including some experience in aggressive waters. The database for the zirconium alloys supports a judgment of satisfactory wet storage in the time frame of 50 to 100 years or more (IAEA 5). Stainless steel components in wet storage have an excellent history of performance, including service in aggressive waters. Specific examinations of LWR SS fuel claddings indicate no evidence of degradation after periods of wet storage. Satisfactory service of SS clad fuels and facility components can be expected for several decades if materials with favorable microstructure and low stress levels are involved (IAEA 5). This is based (IAEA 10.1) on the methods used to maintain water quality in storage pools including skimmers, periodic vacuuming and ion exchange filtration, (all of which are used in the GE-MO basins). When these water control methods are effectively and systematically applied, environmental conditions in the pools are in the benign range, e.g., conductivities near 1 µS/cm (equivalent to 1 µmho/cm), chloride concentrations <1 ppm, and pHs in the range of 4.5 to 8.0. Since March 1976 average GE-MO basin water conductivity has been 1.07 µmho/cm, (pH value of 5.60 minimum). Results of basin air and water sampling since the last fuel was received in January 1989 have been consistent, indicating the fuel cladding hasn't deteriorated. The quality of the GE-MO basin water and the more stringent values described here insure integrity of the fuel cladding and continue to demonstrate that no mechanism exists in the fuel storage environment to cause a release in quantities sufficient to result in exposures approaching the limits specified in 10 CFR 72.104.

Attachments:

> Letter "Justification for Updating Basin Chemistry Technical Specification", Prepared July 9, 2004, by C. A. Roche

> 72.48, "Justification for Assuming Equivalency Between Conductivity and pH", Prepared February 16, 1996, by L. D. Denio

Christopher A. Roche
Radiation & Operations Safety Officer

Morris Operation
General Electric Company
7555 East Collins Road
Morris, IL 60450
815/942-5590 Ext. 74

TO: Morris Operation Safety Committee
FROM: Christopher A. Roche
DATE: July 28, 2004
SUBJECT: **Justification for Updating Basin Chemistry Technical Specifications**

Purpose

This report will propose changes to the Technical Specifications in section 4.8.1 of
SNM-2500 and provide justification for the proposed parameters.
The proposed changes to section 4.8.1 Technical Specifications are:
1. Add a Conductivity specification of 1.35 μmho/cm max.
2. Remove the pH, Cl$^-$ and NaNO$_3$ Technical Specifications.

Background

The current Technical Specifications for basin water chemistry were implemented in the
early 1970s. At that time, basin water had a dissolved solid concentration of about 100
ppm, mainly as sodium nitrate with an average conductivity of 215 μmho/cm. With an
ionic content of this magnitude, the pH of water is an important parameter to ensure a
chemically inert environment. The pH analysis provides detection capability for an
addition of acidic or alkaline contaminates, since conductivity alone will not provide this
information.
The measurement of pH in high-ionic content water will yield accurate and consistent
results because of the good electrical contact between the sensitive areas on the
selective ion probe and the buffering capability of salts in solution.

In 1976, a campaign to improve the quality of the basin water was undertaken. This
resulted in the reduction of dissolved solids concentration to less than .1 ppm, and a
reduction of the basin water conductivity to around one μmho/cm. Since March 1976 the
average conductivity of the basin water has been 1.07 μmho/cm. At this conductivity,
the maximum range of pH is 5.60 to 8.63. The best measure of quality for low-ionic
content water is the conductivity of the water. The pH of low-ionic content water is
difficult to determine and can be influenced greatly by many factors including, sample
techniques, analysis equipment, atmospheric CO_2, and sample storage. By maintaining
low basin conductivity, we ensure the high quality of the basin water and an inert
environment for fuel storage.

Morris Operation Fuel Basin Chemistry Control

Chemistry is maintained in the fuel basin by using ultra pure makeup water, mechanical
and ionic filtering, and strict control of basin operations to prevent contamination of the
basin water.
The makeup water system is a closed loop ultra-pure water system that is continuously
monitored for resistivity. Normal resistivity of system water is over 18 megohms/cm

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(0.056 μmho/cm) and an alarm is actuated if water quality reaches 5 megohms/cm (.2 μmho/cm), this will prevent addition of impure makeup water to the fuel basin.
Fuel basin water is continuously purified using a mixed-bed ion exchange resin to maintain basin water quality.
Conductivity of basin water is measured continuously to detect problems, trends or the addition of contaminates, so that actions may be taken immediately to correct the problem.

The Morris fuel basin is open to air and is therefore susceptible to Carbon Dioxide (CO_2) absorption. Carbon Dioxide forms Carbonic acid in water, which is a weak acid that lowers the pH and raises the conductivity of demineralized water. Demineralized water saturated with CO2 could have a pH as low as 5.6. Ultra pure water equilibrated with CO2 will have a conductivity of 0.8 to 1.2 μmho/cm because of the ions present in the water from CO2 absorption.

Morris Fuel Basin Chemistry

pH vs. Conductivity 1976 - Present
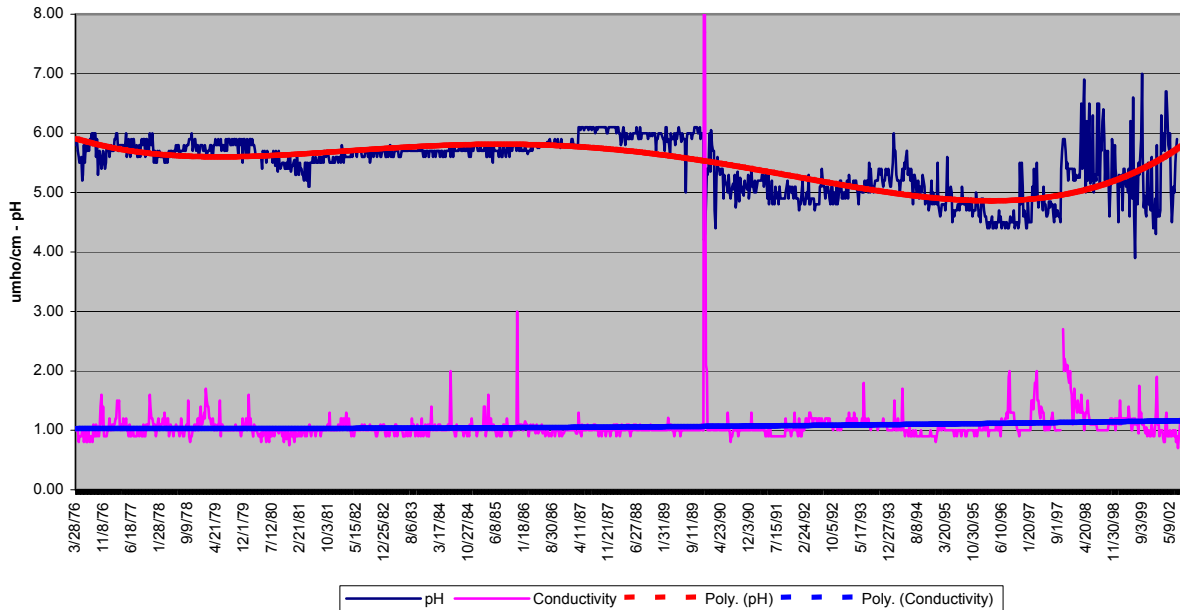
The above graph shows basin conductivity and pH since March 1976. Trend lines are imposed over the data to show data trends data over time. The conductivity has been very stable around 1.0 μmho/cm. Conductivity spikes are attributable to basin operations that would be expected to raise conductivity, and actions were taken to quickly bring the parameters back to normal values. The pH values during the same period do not correlate with the conductivity values as would be expected for the very low conductivity of the basin water. Many of the pH values are outside of the possible pH range for the measured conductivity of the water. If the basin water conductivity is

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maintained around 1 μmho/cm, a measured pH below 5.5 is outside of the theoretical pH range and is most likely erroneous.

Justification for Technical Specifications

A conductivity specification of 1.35 μmho/cm would provide a much lower tolerance for ionic impurities and allow the elimination of the Cl⁻ and $NaNO_3$ Technical Specifications. Conductivity measures the concentration of ions in solution; additions of ionic impurities would cause the conductivity to increase.
The conductivity of solutions can be calculated by multiplying the Equivalent Conductance by the number of Equivalents as shown in the following equation.
Conductivity = (ppm) / GFW x EC
Where:
      ppm   = Contaminate concentration in mg contaminate / kg solute.
      GFW = Gram Formula Weight of contaminate compound.
      EC   = Equivalent Conductance of contaminate compound.
   Note: the Infinite Dilution Equivalent Conductances are used for these calculations.

Examples:

A 5 ppm Chloride solution (assuming NaCl) would have the following conductivity:

   Conductivity = 5 ppm / 58 x 126.4 = **10.9 μmho/cm** at 25^0C

A 5 ppm Sodium Nitrate solution would have the following conductivity:

   Conductivity = 5 ppm / 85 x 121.5 = **7.1 μmho/cm** at 25^0C

As shown above, the concentrations required to exceed the 1.35 μmho/cm conductivity specification, are significantly below the current technical specifications for Chloride and Sodium Nitrate. Additional conservatism is built into the above calculations, as they do not take into account any other ions in solution such as hydrogen, hydroxyl, and carbonate ions from air exposure.

The following graph shows the permissible pH range for a given conductivity. A conductivity limit of 1.35 μmho/cm would maintain the pH of the basin water between 5.50 and 8.73. This is more restrictive than the current specification of 4.50 to 9.00. The average conductivity of the basin water since March 1976 is 1.07 μmho/cm. This conductivity has a pH range of 5.60 to 8.83.

GE Nuclear Energy

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**pH-Conductivity Permissible Domain
for NaCl System at 25 degC**
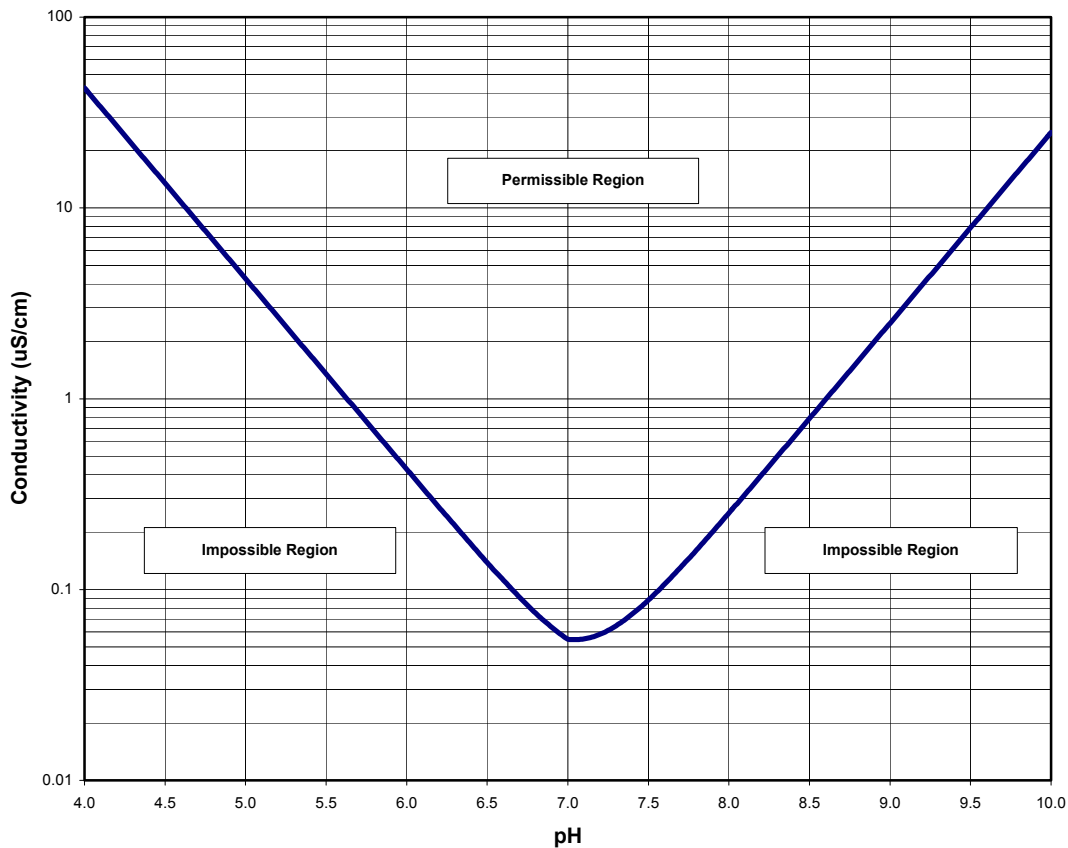
Conclusion

The current Technical Specifications are not consistent with the high quality water maintained in the Morris Fuel basins. The proposed Technical Specifications provide a stricter set of parameters for basin water chemistry control, and are best suited for maintaining an inert storage environment for the stored material and the basin components.

References

1. "Justification for Assuming Equivalency Between Conductivity and pH." *L. L. Denio* February 16, 1996.
2. Wu, Yung Chi and Berezansky, Paula A. Low Electrolytic Conductivity Standards." Journal of Research of the National Institute of Standards and Technology 100 (1995): 521-27
3. "Culligan Bulletin CI-9443, Deionized Water – Its Quality & pH." *Lee, Young P.E.* December 21, 1994.

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4. "Culligan Bulletin CI-9506, Deionized Water – Its Quality & pH: part II." *Lee, Young P.E.* February 15, 1995.
5. Moore, Walter J. *PHYSICAL CHEMISTRY*. 3rd ed. New Jersey: Prentice Hall, 1962.
6. Weast, Robert C. Ph.D. *CRC Handbook of Chemistry and Physics.* 54th ed. Cleveland, Ohio: CRC Press, 1973.
7. Sundberg, Lynn L. <lynn.sundberg@gene.GE.com> "pH Conductivity Domain." 29 Jun. 2004. Personal e-mail. (7 Jul. 2004).

Submitted by:

Christopher A. Roche
Radiation and Operations Safety Officer

February 16, 1996

To   : Morris Operation Safety Committee
From   : L.L. Denio

Subject: <u>Justification for Assuming Equivalency Between Conductivity and pH</u>

Ref: 1. Facility License SNM-2500, Section 4.8.1
        2. Letter from R.A. Morgan to Safety Committee dated February 8, 1996
        3. Culligan Bulletin, File CI-9443, "Deionized Water-It's Quality and PH"
        4. Culligan Bulletin, DI-111, "High Quality Water-PH and Specific Resistance"
        5. Ultrapure Water, July/August 1989
        6. "Instrumental Methods of Analysis", Willard, Merritt and Dean, May 1967

PURPOSE

The purpose of this report is to demonstrate equivalency between conductivity measurement and pH measurement as an assessment of excess acidity or alkalinity in the GEMO fuel storage basin water.

Background

SNM-2500 license condition 4.8.1 requires that pH of the fuel basin water must be maintained between 4.5 and 9.0. The basis is that basin water chemical characteristics are chosen to maintain a benign environment for stored fuel and equipment in basin water. This specification was written circa 1975 when the fuel storage basins contained about 100 ppm dissolved solids as sodium nitrate. This concentration of chemical ionic activity provided a suitable medium conducive to accurate measurement of pH. Circa 1976, GEMO conducted a massive campaign to improve the quality of the basin water. This was accomplished with basin filter resin changes each week. The sodium nitrate and eventually, sodium chloride concentrations were reduced by 1977 to less than 0.1 ppm effecting a conductivity of about one $\mu mho/cm$ - about the purity of thrice distilled water. About this time, GEMO witnessed a new phenomenon - the basin water pH evinced CO_2 equilibrium with a pH of about 5.5. Susequently, GEMO has been content with compliance with this pH since the required range was 4.5 to 9 which allowed adequate variance - usually. That is, since pH is a measurement of hydrogen ion activity, the error variance becomes a probability study since there are fewer hydrogen ions around to measure in very pure water. Therefore, the ± error bracket associated with pH estimates increased after about 1978 or 1979. Also, since basin water evaporative losses are compensated using demineralized water produced on site, pH was affected with each re-filling of the basin. On at least four occasions during the period from 1980 to 1990, the pH exceeded the lower limit of 4.5 ($\approx$ 4.3). This occurrence was traced to inadequate performance by the cation resin bed of the demineralizer system. Water introduced to the basin was found to contain trace cations such that the make-up water was slightly alkaline. This actually improved basin water pH since in CO_2 equilibrium it was slightly acidic. However, when the cations reached the basin filter, they were subsequently exchanged for H^+ ions which of course lowered the basin water pH as the basin filter and basin water came to equilibrium. The consequence was, on occasion, an offending pH. This situation was resolved by installing a resin polisher to compensate for any demineralizer unit deficiencies.

Recent Event

During the week February 12, 1996, the pH once again dipped to 4.3. The explanation this time relates to ion mobility as effected by temperature. Temperature tends to be inversely proportional to pH since the equivalent conductance of hydrogen ions is significantly greater than the anion counterparts (factor $\approx$ 4.5). Due to inclement cold weather and fear of freezing the basin coolers, the basin temperature was allowed to increase to about 40° C. The pH was observed to decrease proportionally.

Resolution

It can be demonstrated that a pH less than about 5.6 or greater than about 8.5 is impossible given a conductivity of 1 μmho/cm. For example, given that basin water is acidic and the associated anion is Cl^-, then we can calculate the pH of a basin water solution with a conductivity of one μmho/cm:

$$1/R = 1/(1000)(\Phi)[(C_H)(\Phi_H) + (C_{Cl})(\Phi_{Cl})]$$

where: $1/R$ = Conductivity
θ = Cell constant = 1.0/cm
C_H = Normal concentration of hydrogen ion

Φ_H = Equivalent conductance of hydrogen ion = 350

Φ_{Cl} = Equivalent conductance of chloride ion = 76

then, given $C_H = C_{Cl}$ and $1/R$ = one μmho/cm,

$$1 \times 10^{-3} = C_H(350+76)$$

$$C_H = 2.3 \times 10^{-6} \text{ normal or molar}$$

$$pH = -\log 2.3 \times 10^{-6}$$

$$= 5.6$$

Interestingly, pH 5.6 is close to CO_2 equilibrium.

Again, assuming the conductivity = one μmho/cm, then a pH = 4.3 is impossible.

The next step is to derive a conductivity range that will bracket the license required range of 4.5 to 9.0. The limiting condition is to assure the pH is not greater than 9.0 which is two units from neutrality of 7.0. Therefore, we must derive a conductivity that brackets the pH range of 5.0 to 9.0.

Then, $1000/R = [(1 \times 10^{-5})(350) + (1 \times 10^{-5})(76)]$

$\qquad 1/R = 4.3 \; \mu mho/cm \; (@ \; pH = 5.0)$

And $\quad 1000/R = [(1 \times 10^{-5})(50) + (1 \times 10^{-5})(198)]$

$\qquad 1/R = 2.5 \; \mu mho/cm \; (@ \; p_H = 9.0)$

Historical experience with basin water indicates that basin pH is acidic consistent with CO_2 equilibrium; however, accepting a conductivity limit of 2.5 $\mu mho/cm$ is conservative. Any conductivity less than 2.5$\mu mho/cm$ would indicate that the pH must be in the range of 4.5 to 9.0.

Evaluation of this proposed activity for compliance to license conditions and 10CFR72 requirements follows:

License Conditions

1.2.1 Quality Assurance

QA considerations include assuring that the accuracy of the conductivity measurement is consistent with acceptable analytical norms. Analytical Services supports a viable method control program.

1.2.2 Fuel Transfer Canal Closure

This license condition is not applicable to the proposed activity.

2.1.1 (a) and (b) Fuel Specifications

This condition specifically addresses spent fuel parameters and, therefore, is not relevant to the proposed activity.

2.1.1 (c) "Tools and equipment"

This condition is not applicable.

2.1.1 (d) "Specific tools and equipment"

This condition is not applicable.

2.2 Fuel Storage Provisions

The proposed activity does not effect fuel in storage nor shall any proposed activity be performed within close proximity of the fuel in storage.

2.3 Ventilation Exhaust Vacuum

This condition is not applicable.

3.1 Water Shield

The depth of water covering fuel in storage will be unaffected.

3.2 Criticality

Not applicable.

4.1 Effluent Air

Not applicable.

4.2 Holding Basins

This license condition will not be affected.

4.3 Sealed Sources

The proposed activity will not impact on how GEMO tests sealed sources.

4.4 Instrumentation

Instrumentation addressed by this condition includes the following:

- o Basin Leak Detection System
- o LAW Vault Leak Detection System
- o LAW Vault Intrusion System
- o Cladding Vault Leak Detection System
- o Area Radiation Monitors
- o Criticality Monitors

None of the above shall be affected by this change.

4.5 Coolers

Basin coolers are not applicable to the proposed activity.

4.6 Process Steam Bypass

This condition is not applicable.

4.7 Cask Coolant

The condition of cask coolant is not germane to the proposed activity.

4.8 Basin Water Chemical Characteristics

This license condition is directly applicable. Refer to initial discussion in this report.

4.9 Basin Water Radioactive Contaminants

No mechanism is known that would adversely effect basin water radiochemistry from conducting the proposed activity.

5.0 Design Features

These license conditions address fuel storage basin and associated equipment structure and capability to contain spent nuclear fuel. This section is not applicable to the proposed activity.

6.1 Administrative Responsibility

This license condition indicated that the Manager, Morris Operation maintains overall facility operation responsibility. Personnel not permanently assigned to the Morris Operation who perform duties associated with the proposed activity shall be subject to the Manager, Morris Operation for matters of employee and public safety, all license conditions and any other regulatory requirements such as, but not limited to, OSHA and EPA requirements.

6.2 Administrative Organization

For the purposes of compliance to these license conditions, no changes in organization are contemplated.

6.3 Plans and Procedures

For the purpose of administratively controlling the proposed activity, we recognize that at least an equal level of procedural control must be exercised in order to assure the proposed activity is performed in a safe manner well within the confines of current regulatory requirements. Procedures shall be written and approved at the appropriate level of authority prior to commencement with the proposed activity.

6.4 Review and Audit

The Plant Safety Committee shall continue to control activities at the Morris Operation, including proposed activities. Members of outside groups may be invited to present information to the Safety Committee membership.

6.5 Action Required for Specification Noncompliance

The proposed activity shall continue to be controlled as a license surveillance condition.

6.6 Logs, Records and Reports

Logs, records and reports shall continue to be maintained.

8.1 Environmental Monitoring Program

No changes to the GEMO environmental monitoring program are deemed necessary as a result of conducting the proposed activity.

Appendix C

Safeguards and Security shall not be compromised as a result of conducting the proposed activity. No increase in the number of personnel authorized to enter the Protected Area is anticipated.

10CFR72.30 Financial Assurance

No adverse impact on General Electric's commitment for decommissioning is recognized.

10CFR72.32 Emergency Plan

No new Emergency Plan accident scenario is identified. Proposed activities conducted after hours may require increased staffing and/or increased training in order to compensate for potential greater incidence and/or increased magnitude of accidents.

Conclusion

The change in methodology for measuring pH is well within the scope and spirit of requirements promulgated in 10CFR72.48.

TO: Safety Committee

FROM: R. A. Morgan

DATE: February 8, 1996

SUBJECT: pH and Conductivity Measurements of Fuel Basin Water

The apparent pH of the basin water has been declining in recent weeks to its present reading of 4.4, while the conductivity has remained around 1.0 μmhos/cm. L. L. Denio and I have done calculations to determine what the conductivity should be, based on pH, assuming the cation is hydrogen ion and the anion is either nitrate ion or carbonate ion. For water of pH 4.4, the conductivity should be 16.8 μmhos/cm, and if the pH is 4.5, the conductivity should be 13.2 μmhos/cm. If the water has a conductivity reading of 1.0 μmhos/cm as the basin does, the pH should be 5.6.

I talked to "Frank" at Yellow Springs Instrument Co., which manufactures conductivity equipment, and he said water at conductivity of 1.0 μmhos/cm was essentially pure water. Ultrapure water measures 18 megaohms resistance or 0.056 μmhos/cm in a closed system, but by the time you can measure the conductivity in an open system, the water will be about 1 μmhos/cm due to absorption of carbonate ion.

We have an ultrapure system, so I tested the theory. I took a sample of the ultrapure water with minimum air contact and measured the conductivity at 0.3 μmhos/cm. (The system was 0.056 μmhos/cm, internally.) After aerating the sample, the conductivity measured 0.9 μmhos/cm. The pH stabilized at 4.7, dropping from pH 6.5 during measurement.

Since it is nearly impossible to get an accurate pH measurement of ultrapure water such as the fuel basin, reason would dictate using conductivity as the determining factor for purity of the fuel basin water. The pH measurement can still be done, but conductivity should be the criteria for acceptance. A maximum measurement for conductivity could be established at something less than what water at pH 4.5 would exhibit (<13.2 μmhos/cm).

RAM:tlt

BECKMAN INSTRUMENTS

from time to time during the stirring process by tapping the container on the workbench. At saturation, the soil paste glistens as it reflects light, flows slightly when the container is tipped, and slides freely and cleanly off the spatula for all soils but those with a high clay content. After mixing, the sample should be allowed to stand for an hour or more, at which time the criteria for saturation should be rechecked. Free water should not collect on the soil surface nor should the paste stiffen markedly or lose its glistening appearance on standing. If the paste does stiffen or lose its glisten, remix with more water. If the paste is too wet, additional dry soil may be added.

Because soils puddle most readily when worked at moisture contents near field capacity, sufficient water should be added immediately to bring the sample nearly to saturation.

- Insert the electrodes into the paste and raise and lower repeatedly until a reproducible pH reading is obtained.

All three of the above methods give repeatable results but each method will give a slightly different value for the same sample. Because of this difference, the method used should be described when reporting soil pH values.

How to Measure pH in High Purity Water

There are many samples of high purity water in which it is extremely difficult to accurately measure the hydrogen ion activity. Examples are: acid rains, boiler feedwater, condensate streams, deionized water, etc. This is also true for other solutions having a conductivity of less than 20 micromhos. The cause of difficulty is low conductivity, reference liquid junction error, and actual pH drift resulting from CO_2 absorption. The following is a list of precautions that minimize this instability problem:

- Rinse the electrodes thoroughly before immersing in this unbuffered type of sample (high purity water).

- Avoid influence on measurement by absorption of CO_2 by taking a reading soon after placing the electrodes deep in the sample or blanket the sample solution with nitrogen purge or cover the container with a stopper (drill holes for electrodes).

- Use a reference electrode (calomel internal preferred) that provides minimal junction potential. If this type of sample is frequently measured, a diluted reference filling solution (0.1M KCl) may be used to provide greater stability and compatibility than the saturated filling solution. This is useful only with an electrode

dedicated for this measurement in samples at ambient temperature or by interposing a salt bridge between the reference and sample.

The sleeve junction reference is an electrode with a low resistance, fast-flowing junction which should provide minimal junction potential in this type of sample.

- Make measurements in a stainless steel beaker. The walls of the beaker provide a short path to ground for any stray charges. Connect the sample to the solution ground terminal. If you are measuring pH in a metal beaker, connect the conductive wire to the beaker rather than the sample.

How to Measure High or Low Temperature Samples

- The glass electrode has a high resistance at low temperatures. In fact, its resistance doubles for approximately every 7°C drop in temperature. Therefore, at low temperatures, a low resistance pH glass electrode (with a standard, ½ inch diameter body) is recommended to provide greater stability.

- For high temperature pH measurements, the silver-silver chloride reference electrode is preferred for its stability. (A calomel reference electrode breaks down at temperatures above 65°C.)

- For greatest accuracy, the temperature of the standard buffers should be the same as the sample measurement temperature.

- Remember, pH measurements made at one temperature cannot be extrapolated to other temperatures unless experiments are done to provide correlation data. See pH Measurement Technique Section.

Techniques for Measuring Nonaqueous Solvents, Mixed Solvents and Organic Acid Samples

Nonaqueous pH measurements and titrations are frequently desirable or required because of the increased sensitivity, improved selectivity, or greater solubility achieved with nonaqueous solvents. A far greater number of acids and bases can be determined in the nonaqueous solvents than in aqueous media because of the many organic acids and bases that require organic solvents.

Nonaqueous titrations are commonly used in well-established standard methods such as:

ASTM	TITLE
D664	Neutralization Number
D939	Saponification Number
D2896	Total Base Number of Petroleum Products

There are several problems measuring pH in mixed solvents. The following briefly explains the concept of pH in nonaqueous solvents and will provide procedures and techniques for simpler measurement.

16

Culligan.
BULLETIN

FILE NO.	CI-9443
DATE	December 21, 1994
SUBJECT	DEIONIZED WATER - ITS QUALITY & pH

"My customer is complaining about the pH of DI water. What's wrong with my DI unit?". Many of you called us recently with this question.

Chances are that nothing is wrong with your DI tank/system as long as the quality is within the expected range.

pH is the indication of degree of acidity or alkalinity of water. The pH value does not indicate the absolute quantity, but the intensity. The significance of pH value of high purity deionized water is questionable because of the following reasons:

- Hand–held pH meter commonly used for pH measurement gives an erroneous reading because the sample gets in contact with air and absorbs carbon dioxide. This results in a pH reading of substantially lower than the actual value. For example, 2 ppm of carbon dioxide in pure water will result in a pH of 5.4. The amount of carbon dioxide that dissolves in the sample depends on the contact time with the air.

- In-line pH meter prevents exposure of the sample to the air and eliminates the erroneous reading caused by carbon dioxide. However, it has its own source of error. The pH electrode is calibrated against a reference buffer and deionized water does not have many buffering ions. Therefore, the reading can be erroneous.

As a rule of thumb, the quality and pH of deionized water from various deionizer systems are as follows:

- Two-bed system with weak base anion unit: 30,000 - 100,000 ohm-cm; pH 5-8

- Two-bed system with strong base anion unit: 50,000 - 2,000,000 ohm-cm; pH 6-9

- Mixed bed system: 1 - 18 megohm-cm; pH 6.5-7.5

PAGE 2 FILE NO. CI-9443

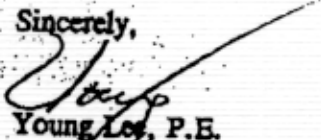**SUBJECT   DEIONIZED WATER - ITS QUALITY & pH**

The following quality and pH combinations cannot possibly be correct for deionized water:

- 10 megohm-cm & pH of less than 6 or greater than 8

- 1 megohm-cm & pH of less than 5 or greater than 9

- 100,000 ohm-cm & pH of less than 4 or greater than 10

If you run into the above conditions, please double check quality and the pH reading with a more accurate in-line meter. In general, the quality monitor is more accurate than a pH monitor.

Please let us know if we can be of further assistance to you on this subject or other DI applications.

Sincerely,

Young Lee, P.E.
Product Manager, Standard RO & DI
Commercial/Industrial Systems

YHL\lp

Culligan.
BULLETIN

FILE NO. CI- 9506

DATE February 15, 1995

SUBJECT DEIONIZED WATER - ITS QUALITY & pH: PART II

Thank you for your interest and feedback on the first bulletin on the subject (CI-9443 dated 12/21/94). For some of you who might have missed the first bulletin, its message was:

"The significance of pH value of high purity deionized water is questionable because...".

The Bulletin (CI-9443) also gave a range of quality and pH of deionized water from various deionizer systems. It also offered the quality and pH combinations that cannot possibly be correct for deionized water.

The purpose of this Bulletin is to answer some of your questions on the first Bulletin with more detailed information.

Q. As your Bulletin indicates, the pH of deionized water from a two-bed system with weak base anion unit runs higher than 7, sometimes as high as over 8 in the beginning of the cycle. How can this be?

A. Weak base anion resins are weakly ionized, and do not remove weak acids such as carbon dioxide(or bicarbonate) or silica. The weak base anion unit effluent, therefore, contains carbon dioxide, resulting in acidic pH (<7). However, most weak base anion resins contain 5-15% Type I strong base sites which remove carbon dioxide in the beginning of each service cycle, resulting in a basic pH (higher than 7). Duration of basic pH condition and actual pH level depend on many factors including the raw water chemistry, sodium leakage from the cation unit and the type of weak base anion resin. Resin manufacturers' testing data and field data from some of you indicate that this high pH (>7) condition may last up to 20% of the cycle.

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Q.   Are there ways to avoid a basic pH (higher than 7) condition with a weak base anion unit if my customer's process requires pH conditions below 7?

A.   Yes. The strong base sites on the weak base anion resin can be converted to chloride by feeding a small amount of brine. At the end of caustic regeneration, feed 5% brine solution diluted with decationized or soft water at a dosage of 0.5 - I lb. of NaCl for each ft.^{3} of weak base anion resin.

Q.   Does the amount of strong base sites on the weak base anion resin reflect the quality of the resin?

A.   Not necessarily. Strong base sites on the weak base anion resin are part of raw material. They even offer some advantages; less swelling, faster reaction and faster rinse.

Q.   If the pH of deionized water seems reasonable, can I assume that the quality is all right?

A.   No. The pH readings of deionized water should never be used as an indication of its quality because accurate measurement of pH in high quality water is very difficult. The reasons for this are discussed in the previous Bulletin (CI-9443). The pH data however, can be useful in troubleshooting the DI system because the possible causes can be narrowed down if both the quality and pH data are known. For example, in a two-bed DI system with strong base anion unit, a combination of poor quality and high pH (>9) condition is commonly caused by high cation leakage, poor rinse or caustic hideout.

Q.   Although it is difficult to accurately measure the pH of high quality water, some processes require pH monitoring. What type of instrument and precautions should be considered?

A.   As a minimum, continuous monitoring with an on-line pH monitor is recommended. A variety of continuous pH monitors is available. They all use a glass electrode and reference electrode with some form of temperature compensation, usually a temperature sensitive resistance element immersed in the water sample with the electrodes. Some important parameters to consider in selecting and using an on-line pH monitor include:
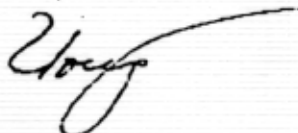
- Use of grounded conductive flow chambers to protect against noise pickup and static charges at the electrode.

- A low and constant sample flow rate (100 ml/min.)

- Discharging of samples to atmospheric pressure.

- Regular scheduled calibration

Q.   If my customer takes all these precautions to measure pH, is it reasonable to offer a guarantee on the pH level from my DI system?

A.   No. We do not recommend offering any guarantee on the pH level from a DI system because too many factors affect the pH of high quality water. The resistivity and pH ranges of deionized water discussed in the previous Bulletin should be used only as general guidelines.

Please call me at (708) 205-5707 if you need more information on this subject.

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YHL\lp

Then use your own judgement and knowledge of chemistry to estimate if any significant amount of the $KMnO_4$ was consumed by Fe'' and Mn''. Also, if tannins are reported, or if there is a clear yellow color with Fe, there may be organic iron consumed by the $KMnO_4$.

COD reported by other laboratories may be determined by an entirely different process, such as a hot dichromate titration. This procedure yields much different answers than the $KMnO_4$ method, but is also call COD.

TOTAL ORGANIC CARBON (TOC), will be reported on Culligan Water Analysis reports as soon as the new equipment can be made operational. This should be in the near future. The equipment determines total carbon from all sources. These sources include: carbon in non-ionized organic compounds like alcohol, ethylene glycol, acetone, etc.; carbon in ionized organic compounds like tannins, humic acid, acetic acid, etc.; and carbon from inorganic sources like carbonate, bicarbonate, carbonic acid, etc. Such a determination would be called T.C. for total carbon. Normally this test is not made because procedures are used that eliminate inorganic carbon. By acidifying the sample, the CO_3 and HCO_3 ions are converted to H_2CO_3 which is "swept" from the system (as CO_2) before carbon is measured. Thus only organic carbon is left and TOC is reported. The difference between TC and TOC would obviously be inorganic carbon. The TOC value can be quite different from COD because it measures all the organic carbon, not just those things which are oxidized by $KMnO_4$. It will be necessary to learn a new set of values to relate to the organic fouling of anion resins. As this is being written it is not known what these values will be.

pH by definition is the logarithm of the reciprocal of the H-ion concentration. It is also a number between 0 and 14 indicating the degree of acidity or alkalinity. The pH scale can be compared to the temperature scale because they both measure intensity, not quantity. Mid-point of the pH scale is 7 and a solution with this pH is neutral. Numbers below 7 denote acidity; those above denote alkalinity. Since pH is a logarithmic function, solutions having a pH of 6.0, 5.0, and 4.0 are 10, 100, and 1,000 times more acidic than one with a pH of 7.0. Mineral acids exist only at a pH of 4 and below. Hydroxide alkalinity exists only at a pH of 10 and above. Maximum limit for pH is 6.5 to 8.5 for potable water.

Some people assume that a constant relationship exists between the pH of any solution and the amount of reagent which must be added to change the pH to a specified target. This, however, IS NOT true. For example, 100 gallons of distilled water can be changed from pH 7 to pH 8 with only 3 drops of 10% NaOH solution. But if the water contains 1% sodium carbonate at pH 7, 3 quarts of the same caustic solution are needed.

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The measurement of pH of high purity water (in the multimegohm range) is very difficult at best and nearly impossible. The following quotation by Dr. Robert Kunin of Rohm & Haas was taken from Amber-Hi-Lites, No. 138, Jan. 1974.

"It is of importance to note that whereas the term pH is normally considered as a measure of the hydrogen ion concentration, its significance when applied to deionized water is most complicated. First, the measurement of the pH of very pure water is a most difficult measurement in view of the many problems with the electrode assembly in pure water. Second, it must be noted that the modern concept of the pH measurement, particularly as applied to unbuffered systems, makes it difficult to relate the measurement to the actual concentration of the hydrogen ions in the water. Third, although the term pH is related to hydrogen ion concentration by the equation

$$pH = -\log (H+)$$

the analytical measurement of pH can only be related to the hydrogen ion concentration by a most complicated system of calibrated reference electrodes and reference buffers, a system that decreases the significance of the interpretation of the measurement. As a result of these complications, the term pH loses much of its significance when applied to high quality deionized water. To distinguish, for example, between pH 6.8 and 7.3 of the high quality deionized effluent of a MONOBED system having a resistivity of 18 million ohm-cm is foolhardy. Any significance to the second decimal place or too much significance to the first decimal place of pH measurements of deionized water is without any basis."

In that same article there appeared Figure 2, a "tent like" graph which gives calculated limits of pH for HCl and NaOH versus specific resistance. It is a far better tool for predicting the pH of very high purity water. Any reported pH at a specific resistance that falls outside the "curves" cannot possibly be correct, and the pH measurement is usually suspect. For example, a reported pH of 5 at a specific resistance of 10,000,000 cannot possibly be correct.

Another way to get an indication of pH in multimegohm quality water is to add a "pinch" of
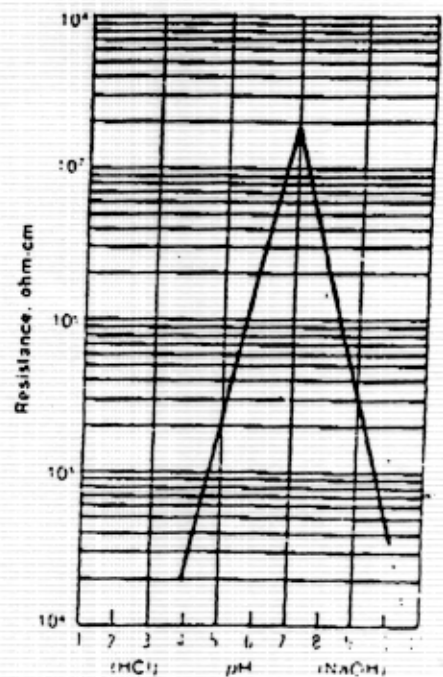
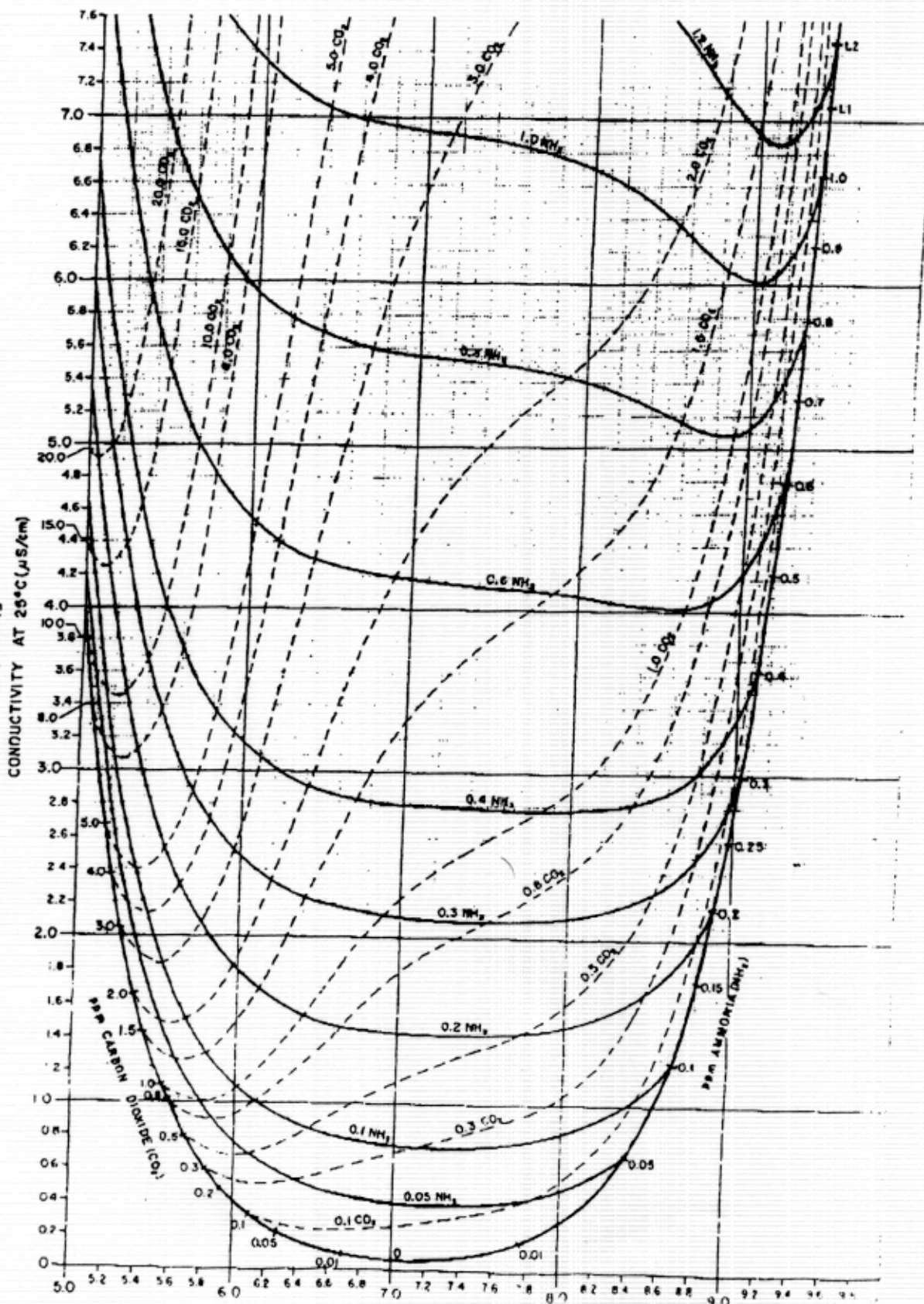Resistance of water due to traces of HCl and NaOH (25°C)

Figure 2

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VARIATION OF SOLUTION pH AND SPECIFIC
CONDUCTIVITY WITH TOTAL AMMONIA
CONCENTRATION AT 25°C IN THE
ABSENCE OF OTHER IONIC SPECIES

Figure 3-17

Source: NUS Corporation.

DATE _____ 1/76 _____

NUMBER _____ DI-111 _____

REFERENCE
INFORMATION _____ Water Quality _____

HIGH QUALITY WATER - pH AND SPECIFIC RESISTANCE

The past few years have seen a rapid growth in the use of extremely high quality water in various manufacturing processes. Culligan is a leader in the development of hardware and technology to meet this growing need. One of the problems encountered concerns our ability to comprehend just what "Ultra Pure" water is: how it behaves, how its quality can be measured (and how accurately).

First, let us briefly examine the preparation of water of various levels of purity. Table I lists several purification techniques and the typical water qualities obtained through these techniques.

Table I

Method of Production	Specific Resistance OHM-CM @ 25°C*
Theoretical Maximum	18,240,000
After 28 Distillations in Quartz	16,000,000
"Ultra-Pure" Water	12,000,000
Mixed-Bed Deionization	700,000 - 14,000,000
After 3 Distillations in Quartz	1,400,000
After 3 Distillations in Glass	700,000
Two-Bed Strong Base Deionization	17,500 - 350,000
Single Distillation in Glass	35,000 - 350,000
Tap Water (300 ppm TDS as $CaCO_3$)	1,200

*Formerly, the reference temperature used was 18°C. This resulted in a theoretical maximum of 26,000,000 ohms-cm. The accepted reference temperature is now 25°C.

Specific Resistance

Because it is extremely difficult to obtain accurate analytical (ppm or mg/l) values for electrolytes (dissolved solids) in high quality water, a more convenient method of expressing the quality of pure water is desirable.

The units of expressing electrical resistance ("ohm") and electrical conductance ("mho"*) are used. A mho, however, is a rather large unit, much akin to measuring the length of your arm in terms of miles, so a fraction of a mho, the "micromho" is used as the base measure for conductance. A micromho is one-millionth of a mho. Conversion of ohms to micromhos or micromhos to ohms, can be accomplished by the use of the following formulas:

$$\text{Micromhos} = \frac{1,000,000}{\text{Ohms}} \qquad\qquad \text{Ohms} = \frac{1,000,000}{\text{Micromhos}}$$

Specific resistance is most commonly used to express high water quality and is written as "ohms-cm", usually at 25°C, unless otherwise specified. This means that if we have 500,000 ohm water, the electrical resistance of the water between two electrodes spaced one centimeter apart is 500,000 ohms when the water is at a temperature of 25°C.

Effect of Temperature on Specific Resistance

The measurement of specific resistance, or conductance, depends on the ability of electrons to flow through a particular medium: in this case, water. The primary determining factor is, of course, the quantity of ionized material in the water. Graph I illustrates this, but for a given amount of dissovled solids in the water, a change in tempera- ture will result in a change in specific resistance. In other words, electrons move more easily in warm water (lower resistance, higher conductance) and with more difficulty in cold water (higher resistance, lower conductance). Table II illustrates this effect. Note how the specific resistance of absolutely pure water changes with temperatures. Remember that we normally express specific resistance at a standard temperature: 25°C (77°F).
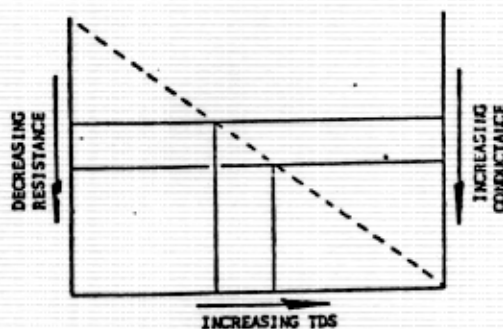
GRAPH I

*The units of resistance and conductance are reciprocals, or "opposites", therefore MHO (pronounced "moe") is simply ohm, spelled backwards. A relatively new term for conductance is gaining acceptance – siemens. This is the metric equivalent to "mhos".

Table II

Temperature °C	Specific Resistance ohm-cm @ 25°C
0	86,000,000
10	43,300,000
(18)	(26,000,000)
20	23,900,000
25	18,240,000
30	14,000,000
40	8,800,000
50	5,800,000
60	4,000,000
70	2,900,000
80	2,100,000
90	1,700,000
100	1,300,000

NOTE: The specific resistance of water is never infinite because water will dissociate into H^+ and OH^- ions under normal conditions.

All Culligan water quality instruments, except the Quality Indicator Lights, have circuits which automatically convert the actual specific resistance of the water to what it would be if the water were at a temperature of 25°C.

Effect of Different Electrolytes on Specific Resistance

In order for water to carry any significant amount of electric current, the substances dissolved in it must be able to break down, or dissociate, into ions. Sodium chloride (NaCl), for example, when dissolved in water dissociates into sodium and chloride ions (NA + and Cl-). At a specified concentration, and a specified temperature, sodium chloride in solution will conduct or resist the flow of electric current to a constant value. This holds true for all ionizable compounds. The only difference is that the value will be different for each compound. Graph II illustrates this fact.
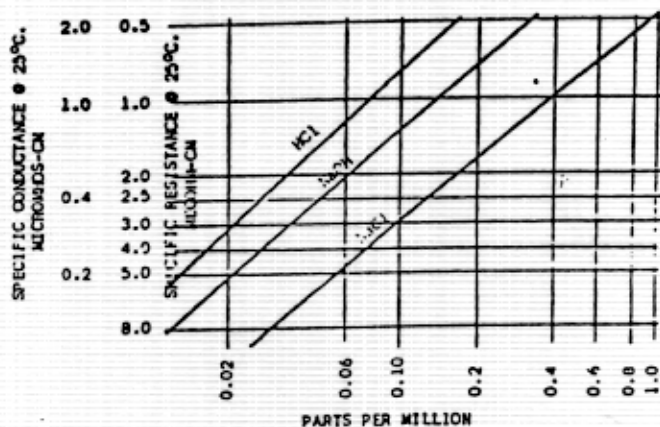
GRAPH II

High Quality Water and pH

pH is an expression of acidity or basicity (alkalinity) on a scale from 1 to 14, with 7 being neutral. The lower the pH, the more acidic the water is. Conversely, the higher the pH, the more basic the water is. Absolutely pure water has a pH of 7.

The pH of high quality water is determined by two factors:

1. The acidity or basicity of the contaminant, or dissolved ions, and...

2. The amount of contaminant present (tiny amounts can cause wide variations).

THEORETICAL LIMITING pH VALUES FOR
TRACES OF HCl AND NaOH IN PURE WATER

Graph III illlustrates the range of pH that can be encountered in high purity water based on these two factors.

With a few exceptions, an ionizable impurity in water has the ability to affect pH. Therefore, the greater the quantity of impurity, the greater effect it can have on pH.

It is generally considered the pH of the effluent from a mixedbed deionizer will be around 7.0. This normally is true, but from thé graph it can be seen that even 6 million ohm water can have a pH that ranges from pH 6.5 to 7.5. The actual pH within that range will depend, of course, upon what the impurity is.
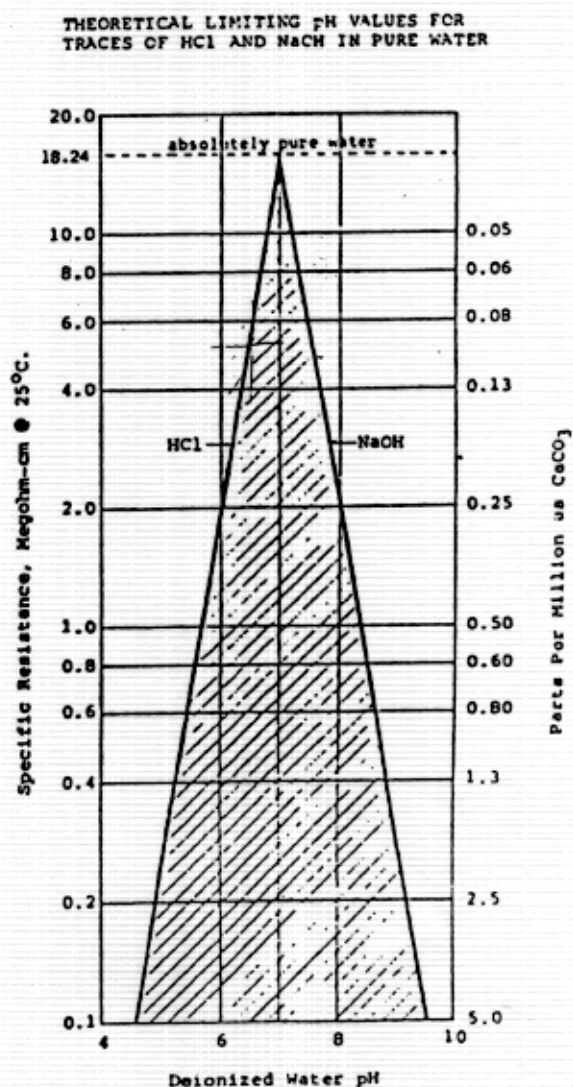
GRAPH III

Effect of Carbon Dioxide on Water Quality and pH

Water of the highest quality, if permitted to stand exposed to atmosphere,
will dissolve CO_2 from the air. Because CO_2 in solution forms weak
carbonic acid, it will affect both specific resistance (and conductance)
and pH.

If allowed to stand for a sufficient time, the specific resistance of
high purity water will eventually fall to around 500,000 ohms. This
assumes that no other airborne impurities are introduced. This is the
point at which the CO_2 dissolved in the water is in equilibrium with the
CO_2 in the air.

Simultaneously, the pH will decline because of the acidic nature of CO_2
in solution.

In two-bed strong base systems the carbonic acid generated in the cation
tank is removed by the anion tank. Sodium leakage from the cation tank
combines with hydroxide (OH) ion in the anion tank to form a weak caustic
solution. Thus, the deionized water pH from strong base systems will
have a pH greater than 7.

In the weak base systems carbonic acid in not removed and therefore is
present in the deionized water. Sodium leakage from the cation column
combines with chloride in the anion column to form a weak solution of
sodium chloride which has no affect on pH but will affect quality. As a
result, the carbonic acid (CO_2) in the deionized water gives the water a
pH less than 7. However, much of the CO_2 gasses off upon exposure to
atmosphere and the pH tends to elevate toward 7. In addition, as the
CO_2 leaves solution the specific resistance will increase.

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INSTRUMENTATION
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INSTRUMENTATION

CONTINUOUS pH MEASUREMENT IN HIGH PURITY WATER

Unsuccessful attempts at pH measurement in high purity water have left some with the sense that it cannot be done. The high resistivity of pure water, the vulnerability to contamination, the variability of reference electrodes, and additional temperature effects converge to make this a particularly difficult measurement. Overcoming these obstacles requires a thorough understanding of the problems and their systematic solution. Described here are practical developments in instrument and electrode design, installation, calibration, and operation that have proven successful. As a result, the confidence in pure water pH readings has been justifiably improved.

A reasonable question to ask at the onset is: Why measure pH of high purity water in the first place? A good case can be made that in pure water it is unnecessary to monitor pH since a conductivity or resistivity measurement is simpler and assures high purity. For example, if the conductivity is less than 0.06 microsiemens/cm (resistivity greater than 17 megohm-cm) then the pH must be between 6.9 and 7.2—the extremes possible with strong acid and base contaminants, respectively. This pH-versus-conductivity relationship has been documented in graphic form for strongly ionized acids and bases (1) and for weakly ionized carbon dioxide and ammonia typical of power plant samples (2).

If water treatment systems always produced pure water, there would be no need for pH measurement. However, conductivity and resistivity are nonspecific: They cannot distinguish among acids, bases, and salts. Thus when water becomes less than pure, the more specific nature of pH provides additional information useful in identifying sources of contamination. Applications that anticipate acidic or basic contaminants often require pH monitoring as a backup to the conductivity or resistivity measurement.

These applications include steam power plants and large industrial boilers that treat their water with traces of ammonia and/or amines. This treatment raises the pH to minimize corrosion at the high operating temperatures and pressures. Specifications for these expensive components require pH control within definite limits, referenced to 25° C. Pharmaceutical industry water specifications also require the pH of Purified Water and Water For Injection to be between 5 and 7 at 25° C. A further use of pH is in diagnosing deionization system problems.

Contamination and Sampling

One of the first difficulties in making a pure water measurement is preserving the integrity of the sample. Water has well earned its reputation as the universal solvent. It will dissolve traces of contaminants from sample lines, flow chambers, containers, and even the atmosphere. New or unused sample lines must be rinsed a surprisingly long period of time before representative measurements can be obtained.

A constant threat of contamination comes from carbon dioxide in the air. Although air contains only 0.03% CO_2, pure water in equilibrium (saturated) with air absorbs enough to yield a pH of approximately 5.6. Carbon dioxide ionizes in water to form a weak solution of carbonic acid. This can be seen in acid rain statistics where normal rain is considered to have a pH of 5.6, and pollu-

Figure 1. Portable high purity pH analyzer with electrode flow chamber.
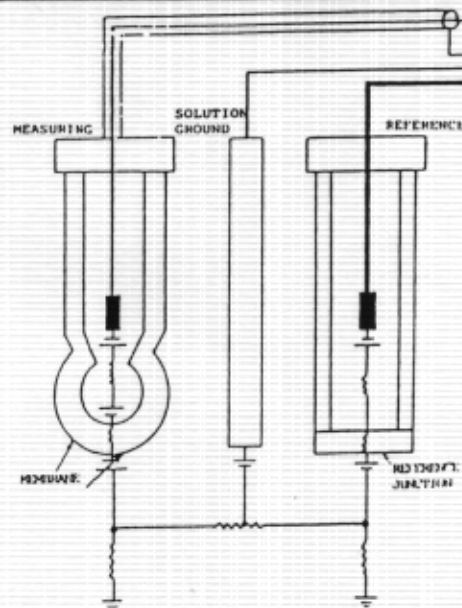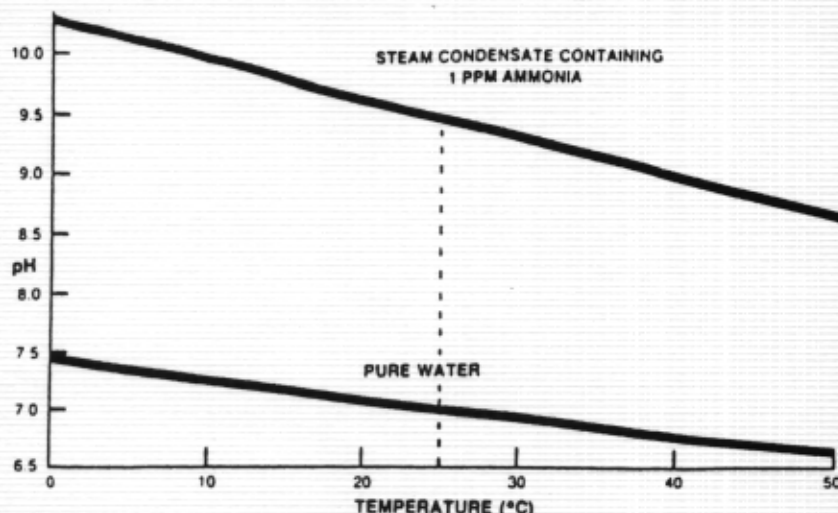

Figure 2. pH electrode schematic.

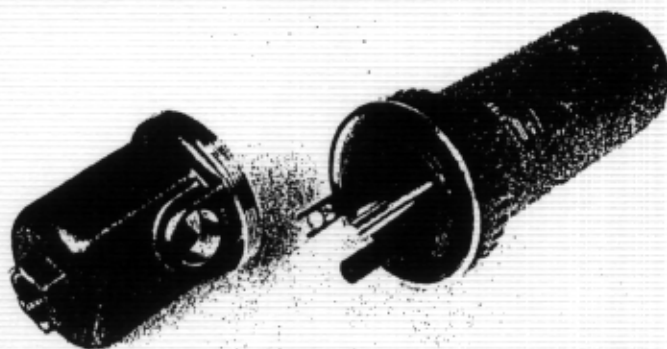Figure 3. pH versus temperature of high purity water.

Figure 4. Stainless steel electrode mounting showing concentric Meredian combination electrode. "401" solution ground and temperature sensor.
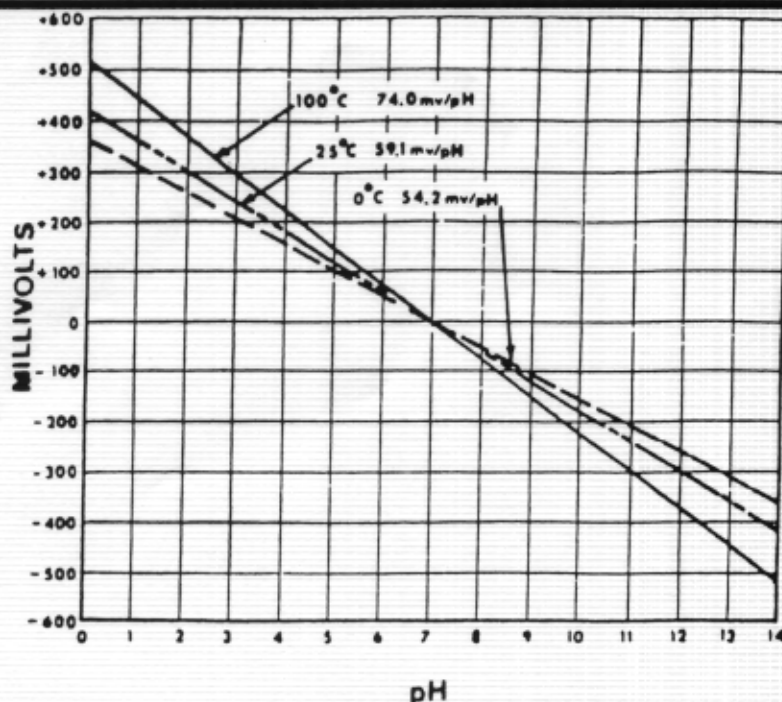

Figure 5. pH electrode signal and its temperature dependence.

tion by additional acids is measured as pH deviation below this value.

Thus a pure water sample cannot be held in a container with air without affecting the measurement. An appreciation for this can be gained by watching the pH of a freshly deionized water sample drop rapidly on exposure to air. If the observer then exhales over the sample, the increased carbon dioxide contamination will lower the pH still further.

For a measurement on deionized water to be meaningful, it should be made on a closed, flowing sample. When laboratory comparisons must be made, the best practice is to take the lab instrument and electrodes to the sample source. The sample line should go into a container to the bottom, letting the water overflow the top. The electrode should also be immersed deep in the container so that it is surrounded by fresh sample that has not had contact with the air. Portable instruments with flow chambers have been developed for this purpose, as shown in Figure 1.

With pH reference electrodes (even of the so-called solid-state, nonflowing, or immobilized type), traces of potassium chloride are invariably diffused into the sample. An evaluation of high purity pH equipment showed that losses of potassium chloride electrolyte into the sample were measurable by conductivity and were comparable for all the reference electrodes under test (3). Samples for pH measurement should therefore never be piped to a conductivity or resistivity measurement downstream and should not be returned directly to a pure water system. They should go to drain or to a reclaim system.

The flowrate of power plant samples should be high enough that any iron oxide particles or deionizer resin fines are swept through the sample lines and electrode flow chambers. This is especially true of boiling water reactor samples where particulates are common. The exchange of ionic species with accumulated particles in the electrode flow chamber can slow down response significantly. Low volume flow chambers and small sample line diameters enhance flow velocity and minimize this problem.

Ionization Temperature Effects—Solution Temperature Compensation. pH has been defined as $-\log_{10} [H^+]$, a measure of hydrogen ion concentration (or more precisely, activity). Water ionizes to a greater extent at higher tem-

perature. The widely accepted value of a pH of 7 for neutral water is valid only at 25 °C. Neutral water has a lower pH at higher temperatures (as shown in Figure 3) because it has increased hydrogen ion concentration (with a negative log function lower pH represents higher hydrogen ion concentration.) The water is still neutral because both the hydrogen and hydroxide ions increase equally in concentration. Since pH is the measurement of only the hydrogen ion, however, it appears to become more acidic at higher temperatures. Figure 3 also shows that a small amount of ammonia, as in power plant water treatment, actually increases the temperature influence slightly.

The temperature dependence of pH is ignored in most "dirty water" applications because it is negligible. The dissolved minerals in potable and waste waters typically have enough buffer capacity to make the pH/temperature curve almost horizontal, at least over the ambient temperature range. Thus there is no need for compensation for this effect in other applications and, in fact, most pH instrumentation has no provi-

"The confidence in pure water pH readings has been justifiably improved."

sion to compensate for this. (Conventional electrode temperature compensation adjusts only for the varying output of electrodes with temperature, which is described later.)

The need for solution temperature compensation in high purity water is reflected in the specifications for boilers, steam generators, turbines, and pure water systems, which specify pH at 25 °C. Instrumentation intended for high purity water measurement should have the capability for solution temperature compensation. It can then measure at other temperatures but provide display, alarm, and output signal of pH referenced to 25 °C. Modern power plant sampling systems sometimes employ chillers for sample temperature control to achieve the same goal. Instrumentation with solution temperature compensation can assure continued accurate operation even if the chiller system

should fail.

During calibration, solution temperature compensation is automatically disabled. Adjustment is made to the true pH (at temperature) of the standard buffer solution, which has a different temperature coefficient than that of high purity water. The buffer temperature/pH relationship is usually given in a table of values printed on its container.

pH Electrodes

pH is measured as a millivolt signal developed at the surface of a glass electrode membrane. This signal depends on the glass/solution ionic equilibrium in which it is immersed. It is represented by the variable voltage battery symbol at the tip of the measuring electrode in Figure 2. If this could be measured independently, none of the other components shown would be necessary. As for any voltage measurement, however, two connections must be made. For pH measurement, the connections have evolved into complete measuring and reference electrodes. Some electrode systems combine the measuring and reference functions into a single combi-

shown here to facilitate the explanation.

One connection is through the glass membrane itself, which may have a resistance on the order of 100 megohms. The inside of the measuring electrode is filled with a stable pH solution to give a constant potential at the inside surface of the glass. The filling solution also contains potassium chloride, which maintains a constant potential in contact with the inner element.

The high impedance signal is vulnerable to loss through any resistance path to ground. Dirty insulation in moist environments can shunt much of the pH electrode signal, causing significant errors. The signal is also vulnerable to electrical noise pickup, static electric charges, body capacitance, etc. Coaxial measuring electrode leadwire is used to minimize these problems. Also for these reasons, industrial installations usually employ a preamplifier near the electrodes to minimize the length of high impedance leadwire. Preamplifiers should be encapsulated to seal out moisture and enclosed in metal to provide electrical shielding.

The electrodes themselves are best shielded by a conductive (stainless steel) flow chamber that has been earth grounded. This not only protects from internally generated streaming potentials. Streaming potential is a phenomenon occurring in high purity water as it flows past insulating surfaces. It can develop a static charge along an in-line plastic electrode flow chamber, yielding an unstable flow-sensitive pH signal. Low flowrates in the 100 mL/minute range and a conductive flow chamber prevent this charge build-up.

A concentric combination measuring and reference electrode design can also reduce these effects (4). The symmetry and close proximity of the measuring and reference elements cancels most of the streaming potential the measuring circuit would otherwise pick up. Any potential gradient on one side between measuring and reference surfaces is canceled by an opposite potential gradient on the other side.

The pH circuit is completed through the process sample and reference electrode. The inside components of the reference and measuring electrodes are designed to be electrochemically similar, with matching inner element and potassium chloride filling electrolyte. A very critical part of the circuit is the reference junction where the filling salts have restricted contact with the process sample. The junction can take the form of porous ceramic or plastic, a narrow passage, or fibers. The purpose of the junction substance is to provide reliable electrical continuity without introducing a voltage contribution of its own.

The most reliable reference junctions are of the flowing type where a supply of potassium chloride electrolyte solution is allowed to slowly bleed through the junction, usually by gravity. These are common in the laboratory. Although used occasionally in industrial installations, flowing junctions do not lend themselves to convenient on-line installation, due to the need for a cumbersome reservoir to supply electrolyte 24 hours a day. Most industrial installations use unvented nonflowing type reference electrodes where the electrolyte and process sample diffuse together. These nonflowing reference junctions can develop problems in high purity water as electrolyte is rinsed out of the junction, leaving a high resistance. Resulting reference junction potentials can exhibit symptoms similar to streaming potentials: noisy, flow-sensitive response.

A measuring circuit with high input impedance capability for both the measuring and reference electrodes and using a solution ground, as in Figure 4, has a much greater tolerance for high

reference junction resistance. This patent-pending circuit can eliminate potentials caused by stray currents through the high resistance junction. It cannot eliminate all junction potentials, however. The flowing junction is superior for measuring both buffer solutions and high purity water. This is discussed further under the subject of calibration.

Conventional Electrode Temperature Compensation

The signal from all pH electrodes is temperature dependent. The gain in millivolts/pH is proportional to the absolute temperature of the membrane, as shown in Figure 5. The function of conventional electrode temperature compensation and calibration settings is to convert the temperature-dependent electrode millivolt signal into a pH value that can be displayed. This temperature dependence of the electrode response is routinely compensated by analog circuitry or microprocessor calculation to obtain the pH at the operating temperature.

If there are additional requirements that the pH be referenced to 25 °C, typical of high purity water specifications, the pH value must then be adjusted for ionization changes by solution temperature compensation. This is done with a microprocessor-based instrument especially designed to use the measured temperature for both types of compensation.

Earth Grounds

Figure 2 shows an earth ground connection through the solution. Process samples normally have some path to ground, especially when using the recommended conductive flow chamber for high purity water. The pH measuring circuit is tied to this earth ground through the electrodes and solution ground contact. The pH instrument circuitry itself is completely isolated from ground so that it can "float" to whatever ground potential may exist in the sample. The electrical power ground (green wire) connection to a pH instrument is strictly for shielding and safety purposes. It has no continuity with the actual measuring circuit. Similarly, pH preamplifier connections are not earth grounded.

It is absolutely necessary that the electrode/solution ground be the only ground in the entire instrument measuring circuit. If a nonisolated instrument output signal is connected to a grounded recorder, controller, computer, or data acquisition system, a second ground is introduced. The two grounds are invariably at different potentials and result in an unwanted current and voltage drop through the electrodes. The characteristic symptom is that pH measurement works fine in an isolated beaker of buffer solution or sample; but when electrodes are returned to the earth-grounded sample, an unpredictable offset or even off-scale reading results. Resolution of the problem is achieved by using an isolated output or isolation module between the pH instrument and the grounded device. Newer-generation instruments provide output signal isolation as a standard feature.

Calibration

The most reliable transfer of a pH standard from buffer solution to high purity water is done using a flowing-junction reference electrode—one which requires refilling with potassium chloride solution. It maintains more consistent junction conditions in both high ionic (buffer) and low ionic (high purity) samples. So-called low ionic strength buffer standards are not really low enough to approach pure water conditions. They must have substantial ionic strength to have useful buffer capacity.

Direct buffer calibration provides optimum accuracy when a flowing-junction

process reference electrode is used. Calibration may be accomplished in a buffer solution in the routine manner.

Comparison calibration is needed to obtain good accuracy when the more common nonflowing process reference electrode is used. The best practice is to take a portable pH meter and electrode flow chamber to the sampling site to avoid sample contamination. The portable reference electrode should be of the flowing-junction type to achieve the best transfer of standard accuracy. This is used to correct for the nonflowing reference electrode, which typically develops junction potential differences representing 0.2 to 0.3 pH between buffer solutions and high purity water.

The following comparison calibration procedure is recommended when a nonflowing reference electrode is used on-line:

- Disable solution temperature compensation for all calibration steps. This is usually done with an instrument HOLD function that also disables alarm action during calibration. (Electrode temperature compensation is always active.)

- Perform two-point calibration (standardize and slope) of both on-line and portable instruments with respective electrodes in quality buffer solutions. (This step is necessary at installation with on-line electrodes and at infrequent intervals thereafter, to establish the slope response.)

- Place the on-line and portable electrodes back in their flow chambers in parallel flowing samples. Allow rinsing until electrode temperatures reach equilibrium and readings are stable.

- Readjust the on-line instrument. Standardize to make its readout agree with the portable instrument with flowing-junction reference.

- Reactivate solution temperature compensation in the on-line instrument.

Recommendations

The following summary can be used as an equipment and operating checklist to avoid potential high purity measurement problems:

- A grounded, closed stainless steel electrode flow chamber protects against noise pickup, body capacitance, and streaming potential while preventing atmospheric CO_2 contamination.

- A low, constant sample flowrate near 100 mL/minute also minimizes streaming potentials and helps stabilize junction potential.

- A combination electrode design using concentric measuring and reference elements further minimizes streaming potential effects.

- Superior measuring circuitry using a solution ground is capable of handling high resistance reference junctions, and and greatly improves the stability of measurement. An alternative is to use a flowing-junction reference electrode on-line but located downstream of the measuring electrode to minimize KCl contamination.

- The measuring instrument should provide solution temperature compensation as well as conventional electrode compensation.

- The instrumentation should provide output signal isolation to prevent external ground-loop problems.

- Calibration should make use of a flowing-junction reference electrode, either in the process electrodes or by comparison calibration, for the crucial buffer-to-high-purity transfer of standard. ∎
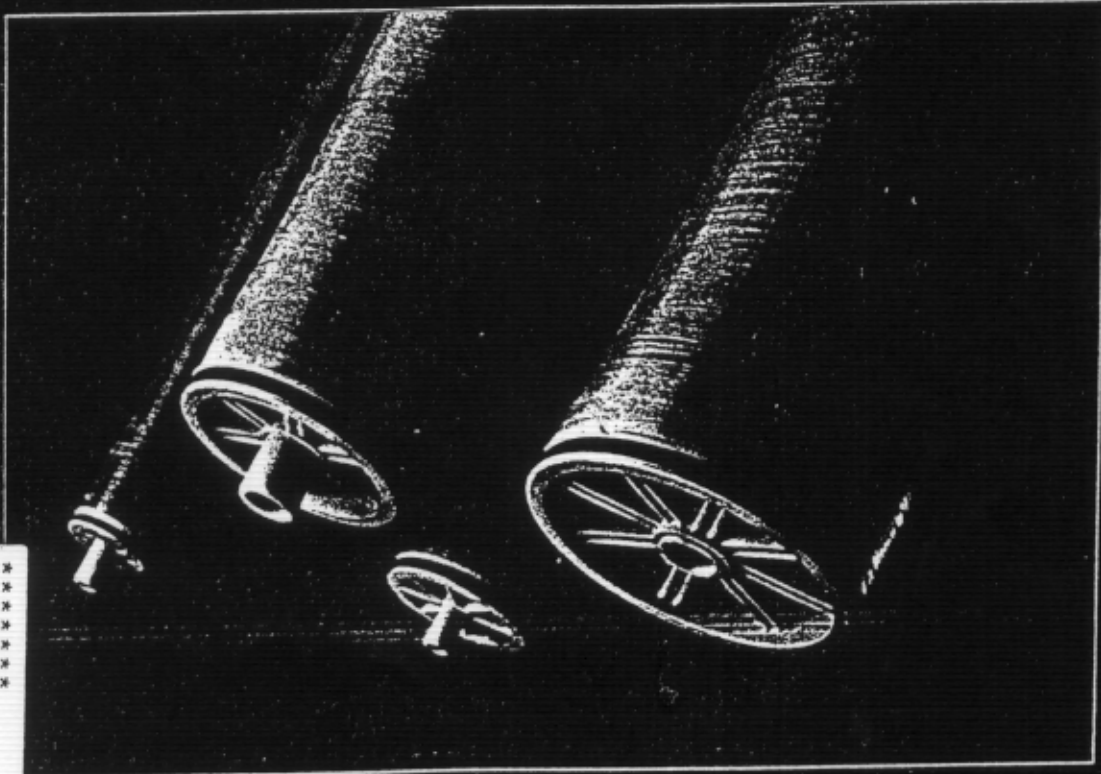
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BACK TO BASICS

MEASURING PH IN HIGH-PURITY WATER

An essential water quality measurement on all water samples is pH. Generally speaking, determining the pH of most waters is easy. Several methods are available that are both fast and accurate. High-purity waters, however, offer unique challenges to obtaining accurate pH readings. To find out why, let's go back to the basics.

Measuring pH

pH is the measurement of the hydrogen ion concentration. Water dissociates into hydrogen ions (H^+) and hydroxide ions (OH^-), as shown in Equation 1.

$$H_2O \longrightarrow H^+ + OH^- \qquad \text{Eq. 1}$$
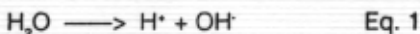
The concentration of the hydrogen ions (H^+) times the concentration of the hydroxide ions (OH^-) is a constant. This is called the dissociation constant, or K. At equilibrium, the dissociation constant is 10^{-14}, which is scientific notation for 0.00000000000001 (1 with 14 decimal places to the left). If the hydrogen ion concentration equals the hydroxide concentration, the H^+ is 10^{-7}, or 0.0000001.

It is inconvenient to routinely express the hydrogen ion concentration in decimal form or scientific notation. A short-hand method is used that expresses the H^+ as the opposite of the log of the hydrogen ion concentration, $-\log (H^+)$. This is expressed as pH. A hydrogen ion concentration of 10^{-7} becomes pH 7. A hydrogen ion concentration of 10^{-3} becomes pH 3, and so on.

Based on these conventions, the pH scale runs from 0 to 14. pH 7 is the midpoint, or neutral. pH levels of less than 7 (increasing hydrogen ion concentration) are acidic, and pH levels above 7 are basic.

Substances that dissolve in water often react to change the pH of the solution. The addition of an acid, for example, causes an increase in the hydrogen ion concentration and a corresponding decrease in pH. Bases have the opposite effect, causing the hydrogen ion concentration to decrease and the pH to increase.

The pH level can be determined by a number of methods. For most waters, accurate pH measurements can be performed with color indicators, pH paper, or pH meters. Color indicators are reagents that exhibit a characteristic color at a specific pH. Phenol red, a common indicator used to measure pH levels between 6.4 and 8.0, for example, is yellow at the low end of the pH range and red at the high end. Other indicators are available that change color within various pH ranges. pH paper is a variation on this same method. The paper is impregnated with the indicator, and changes color when dipped into the sample.

The most common method used to measure pH is the pH meter. A pH meter is actually a millivolt (mV) meter that measures the potential difference between a standard reference electrode and the pH electrode. These two half cells are known as the electrode pair.

Under ideal conditions, at 25 °C, the pH electrode would give a millivolt response as defined by Equation 2.

$$mV = -59.16(pH - 7.000) \qquad \text{Eq. 2}$$

At pH 7, the neutral point, the mV signal is zero (0).

Real electrode pairs, however, do not give ideal responses. As a result, all pH meters must be routinely calibrated to determine the correct slope and intercept for that meter and electrode pair.

Problems with High-Purity Water Measurements

Measuring the pH of most ordinary water samples presents few problems. If the pH meter is properly calibrated, an accurate pH measurement is just the push of a button away. Unfortunately, the same cannot be said of high-purity water samples (i.e. those having an ionic strength of less than 100 microsiemens per centimeter [μS/cm]).

The extreme purity of low conductivity samples makes accurate pH measurement difficult. Most waters contain dissolved solids that serve as a buffer against rapid changes in pH. Weak acids such as carbonic acid and its corresponding salts form chemical buffers that resist changes in pH despite the addition of small amounts of acid or base. High-purity samples lack this buffer system and are, therefore, susceptible to pH swings caused by contaminants that enter the sample prior to or during testing.

Many contaminants are known to cause a significant change in the pH of high-purity samples.

Carbon dioxide is present in the air in concentrations up to 300 ppm. When a high-purity sample, such as demineralized water or steam condensate, is collected, it is immediately exposed to the air. As little as 0.2 parts per million (ppm) of carbon dioxide can depress the pH of the sample by 1.11 pH units.

Sampling container contaminants can cause a significant change in sample pH. Trace amounts of acid or base will
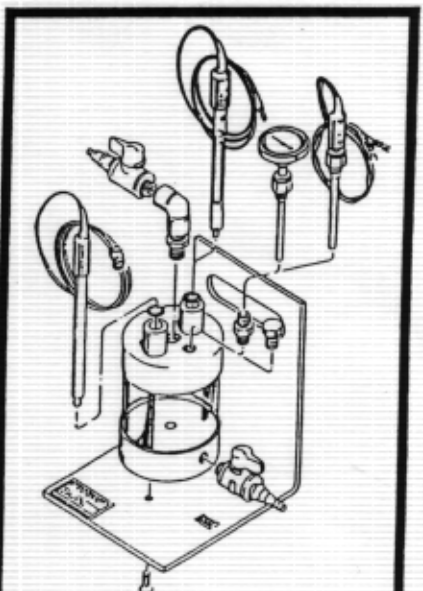

Figure 1. An exploded view of a high-purity water pH sensor.

Source: American Society for Testing & Materials, Proposed Test Methods for pH Measurement of Water at Low Conductivity, ASTM D 19 Proposal P 278 (1990) Figure 2 as published.

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change the pH by more than 1 pH unit. Studies performed on 0.1- µS/cm (10-megohm-cm) high-purity samples, for example, indicate that 1 ppm of sodium hydroxide or hydrochloric acid will shift the sample pH by 1.03 unit.

Loss of volatile components will change the pH of the sample. Steam condensate samples, for example, are frequently collected from lines or receivers that are under pressure. When exposed to atmospheric pressure, carbon dioxide gas and volatile amines are lost, causing a shift in sample pH.

Temperature of the sample impacts the pH reading. Most pH meters have automatic temperature compensation features that compensate for the standard Nernst equation temperature factor.

The solution temperature coefficient (STC) is the rate at which the pH changes with temperature. Unbuffered high-purity samples are particularly susceptible to STC effects. Even part-per-million levels of contaminants can cause the temperature coefficient to be -0.03 pH unit per °C.

pH meter and electrode types should be properly selected for high-purity water testing. The electrode pair should quickly equilibrate to each other and to the sample temperature. Many glass electrodes will degrade after prolonged exposure to high-purity water, causing sluggish readings or drift. Also, low-ionic-strength water can diffuse into the high-ionic-strength electrolyte of the reference electrode, causing unstable and inaccurate pH readings. A sealed reference half-cell electrode, which resists dilution of the electrolyte, is recommended to minimize these effects.

Calibration buffers are of much higher ionic strength than the high-purity water sample. Alternately immersing the electrode pair into the pH buffer and then into the sample will introduce pH errors. The electrode pair requires thorough rinsing after exposure to high-ionic-strength buffers to insure establishment of a stable liquid junction potential in the high-purity water sample.

How to Test High-Purity Water

Accurate pH readings are best obtained by in-line pH sensors. These devices minimize sample contamination from the air and sampling containers. A high-purity water pH sensor assembly is illustrated in Figure 1.

The pH electrode used in this assembly should be a low-impedance electrode to minimize the "streaming potentials" that develop in low-conductivity water streams. This is the static charge that is induced in flowing high-purity water across the glass pH electrode. These "streaming potentials" add to the millivolt signal and introduce error into the pH measurement. Also, as mentioned previously, to prevent diffusion of low-ionic-strength water into the electrolyte of the reference electrode, a sealed reference half cell should be used.

If it is not possible to measure the pH using an in-line pH sensor, then a grab sample can be obtained using a flow-through sample chamber. Such a sample chamber is depicted in Figure 2.

This sample chamber contains the pH electrodes and temperature probe in sealed fittings on the top of the unit. The water sample flows through the valve at the bottom of the container and out the top. The sample is collected by flushing the container for several minutes and then closing the bottom and top sample valves, effectively trapping the sample in the container and preventing its contamination by atmospheric gases. The sample is then transported to the laboratory for subsequent testing.

In addition to proper attention to detail during sample collection, the pH measurement must be made after proper calibration of the pH meter and by carefully following the test procedures established by the test equipment manufacturer. This includes flushing the sample manifold with 250 milliliters per minute of water for 3 to 4 hours, maintaining the sample pressure at 50 pounds per square inch gauge, and controlling the sample temperature at 25 °C. For more information on these procedures, refer to American Socity for Testing and Materials (ASTM) D-19 5128-90 entitled *Standard Test Method for On-Line pH Measurement of Water of Low Conductivity.*

Summary

pH measurement is an essential procedure for all water management programs. Obtaining accurate pH readings on unbuffered high-purity water samples is particularly difficult, however, because of the contaminants introduced from the air, sample containers, and test equipment. Fortunately, standard test methods have been developed that minimize these factors and produce an accurate pH determination.■

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Key words: HYDROGEN IONS, HYDROXIDE IONS, NEUTRAL POINT, pH

Figure 2 A sample pH chamber

S₁	SAMPLE INLET, 6.35 mm (1/4 in.) STAINLESS STEEL TUBE FITTING	PR₁	SECONDARY PRESSURE REGULATOR, 0 - 172.4 kPa (gage) (0 - 25 psig)
V₁	HIGH PRESSURE SAMPLE INLET SHUT-OFF VALVE	R₁	ROTAMETER, WITH CONTROL VALVE, 0 - 600 mL/min
P₁	SAMPLE INLET PRESSURE GAUGE, 0 - 689.4 kPa (gage) (0 - 100 psig)	P₂	FLOW-CELL PRESSURE GAUGE, 0 - 172.4 kPa (gage) (0 - 25 psig)
V₄	GRAB SAMPLE VALVE / ON-OFF	F₁	HIGH PURITY WATER pH SENSOR
V₃	TAMPER RESISTANT FLOW RATE VALVE, MAX 200 mL/min AT SPECIFIED SYSTEM PRESSURE	S₂	SAMPLE OUTLET, TO DRAIN, 6.35 mm (1/4 in.) STAINLESS STEEL TUBE FITTING
S₃	GRAB SAMPLE OUTLET	J₁	JUNCTION BOX WITH INTERFACE MODULE

Source: American Society for Testing & Materials, *Proposed Test Methods for pH Measurement of Water of Low Conductivity*, ASTM D-19 Proposal P228 (1990). Figure 4 in publication.