pH Measurement and Control Opportunities
– Greg is a retired Senior Fellow from Solutia/Monsanto and an ISA Fellow. Greg was an adjunct professor in the Washington University Saint Louis Chemical Engineering Department 2001-2004. Presently, Greg contracts as a consultant in DeltaV R&D via CDI Process & Industrial and is a part time employee of Experitec and MYNAH. Greg received the ISA “Kermit Fischer Environmental” Award for pH control in 1991, the Control Magazine “Engineer of the Year” Award for the Process Industry in 1994, was inducted into the Control “Process Automation Hall of Fame” in 2001, was honored by InTech Magazine in 2003 as one of the most influential innovators in automation, and received the ISA Life Achievement Award in 2010. Greg is the author of numerous books on process control, his most recent being *Advanced Temperature Measurement and Control*. Greg has been the monthly “Control Talk” columnist for *Control* magazine since 2002. Greg’s expertise is available on the web site: [http://www.modelingandcontrol.com/](http://www.modelingandcontrol.com/)
Top Ten Signs of a Rough pH Startup

1. Food is burning in the operators’ kitchen
2. The only loop mode configured is manual
3. An operator puts his fist through the screen
4. You trip over a pile of used pH electrodes
5. The technicians ask: “what is a positioner?”
6. The technicians stick electrodes up your nose
7. The environmental engineer is wearing a mask
8. The plant manager leaves the country
9. Lawyers pull the plugs on the consoles
10. The president is on the phone holding for you
## Extraordinary Sensitivity and Rangeability

<table>
<thead>
<tr>
<th>pH</th>
<th>Hydrogen Ion Concentration</th>
<th>Hydroxyl Ion Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
<td>0.000000000000001</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.000000000000001</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>0.0000000000001</td>
</tr>
<tr>
<td>3</td>
<td>0.001</td>
<td>0.000000001</td>
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<tr>
<td>4</td>
<td>0.0001</td>
<td>0.0000001</td>
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<td>5</td>
<td>0.00001</td>
<td>0.00001</td>
</tr>
<tr>
<td>6</td>
<td>0.000001</td>
<td>0.0001</td>
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<tr>
<td>7</td>
<td>0.0000001</td>
<td>0.01</td>
</tr>
<tr>
<td>8</td>
<td>0.00000001</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Hydrogen and Hydroxyl Ion Concentrations in a Water Solution at 25°C

\[
a_H = 10^{-\text{pH}}
\]

\[
\text{pH} = -\log (a_H)
\]

\[
a_H = \gamma \times c_H
\]

\[
c_H \times c_{OH} = 10^{-\text{pK}_w}
\]

\[
a_H = \text{hydrogen ion activity (gm-moles per liter)}
\]

\[
c_H = \text{hydrogen ion concentration (gm-moles per liter)}
\]

\[
c_{OH} = \text{hydroxyl ion concentration (gm-moles per liter)}
\]

\[
\gamma = \text{activity coefficient (1 for dilute solutions)}
\]

\[
\text{pH} = \text{negative base 10 power of hydrogen ion activity}
\]

\[
\text{pK}_w = \text{negative base 10 power of the water dissociation constant (14.0 at 25°C)}
\]
The water dissociation constant ($pK_w$) and solution pH decreases as temperature increases (e.g. -0.03 pH/°C)

A pH within spec but near the high constraint at an elevated temperature in the process can end up higher than pH limit as solution cools down in the effluent discharge. For example, a caustic and water solution at 9 pH and 60 °C will become 10 pH at 25 °C. The standard temperature compensation is for the effect of temperature on the potential developed by the glass electrode per the Nernst equation and does not correct for the change in the actual solution pH due to changes in the dissociation constants.
Effect of Water Dissociation (pK_w) on Solution pH
Hidden Assumptions in Nernst Equation

For the interior and exterior surface of the pH glass electrode:

\[ E_1 = K_{g1} + 0.1984(T + 273.16) \times [\log (a_1) - \log (a_{g1})] \]  \hspace{1cm} (4-1c)

\[ E_2 = K_{g2} + 0.1984(T + 273.16) \times [\log (a_2) - \log (a_{g2})] \]  \hspace{1cm} (4-1e)

If parameters are identical for inner and outer gel layers \((K_{g1} = K_{g2})\), then:

\[ E_1 - E_2 = 0.1984(T + 273.16) \times [\log (a_1) - \log (a_{g1}) + \log (a_{g2}) - \log (a_2)] \]  \hspace{1cm} (4-1f)

If activities are identical for inner and outer gel layers \((a_{g1} = a_{g2})\), then:

\[ E_1 - E_2 = 0.1984(T + 273.16) \times [\log (a_1) - \log (a_2)] \]  \hspace{1cm} (4-1g)

Since \(pH_1 = -\log(a_1)\) for external process and \(pH_2 = -\log(a_2)\) for internal electrolyte:

\[ E_1 - E_2 = 0.1984(T + 273.16) \times (pH_2 - pH_1) \]  \hspace{1cm} (4-1h)

We end up with equation seen if the internal buffer of the glass electrode is 7 pH:

\[ E_1 - E_2 = 0.1984(T + 273.16) \times (7 - pH_1) \]  \hspace{1cm} (4-1i)
Nonlinearity - Graphical Deception

Despite appearances there are no straight lines in a titration curve (zoom in reveals another curve if there are enough data points - a big “IF” in neutral region)

Yet titration curves are essential for every aspect of pH system design but you must get numerical values and avoid mistakes such as insufficient data points in the area around the set point.

For a strong acid and base the pKₐ are off-scale and the slope continually changes by a factor of ten for each pH unit deviation from neutrality (7 pH at 25 °C)

As the pH approaches the neutral point the response accelerates (looks like a runaway). Operators often ask what can be done to slow down the pH response around 7 pH.
Nonlinearity - Graphical Deception

Weak Acid and Strong Base
\[ p_{k_a} = 4 \]

Strong Acid and Weak Base
\[ p_{k_a} = 10 \]

Weak Acid and Weak Base
\[ p_{k_a} = 4 \]

Multiple Weak Acids and Weak Bases
\[ p_{k_a} = 3 \]
\[ p_{k_a} = 5 \]
\[ p_{k_a} = 9 \]

Slope moderated near each \( pK_a \)
\( pK_a \) and curve changes with temperature!
# Dissociation Constants (pK<sub>a</sub>) of Acids and Bases

<table>
<thead>
<tr>
<th>Acid or Base</th>
<th>pK&lt;sub&gt;a1&lt;/sub&gt;</th>
<th>pK&lt;sub&gt;a2&lt;/sub&gt;</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>4.76</td>
<td>---</td>
<td>60.05</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>4.26</td>
<td>---</td>
<td>72.06</td>
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<tr>
<td>Ammonium</td>
<td>9.24</td>
<td>---</td>
<td>18.04</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>12.80*</td>
<td>12.67</td>
<td>74.09</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>6.35</td>
<td>10.33</td>
<td>44.01</td>
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<tr>
<td>Formic acid</td>
<td>3.75</td>
<td>---</td>
<td>46.03</td>
</tr>
<tr>
<td>Fumaric acid</td>
<td>3.10</td>
<td>4.60</td>
<td>116.1</td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>3.77</td>
<td>6.08</td>
<td>132.12</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>-6.2</td>
<td>---</td>
<td>36.46</td>
</tr>
<tr>
<td>Hydrogen cyanate</td>
<td>3.46</td>
<td>---</td>
<td>43.03</td>
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<tr>
<td>Hydrogen cyanide</td>
<td>9.21</td>
<td>---</td>
<td>27.06</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>3.17</td>
<td>---</td>
<td>20.01</td>
</tr>
<tr>
<td>Hydrogen iodide</td>
<td>-8.26</td>
<td>---</td>
<td>127.92</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>11.64</td>
<td>---</td>
<td>34.02</td>
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<td>Hydrogen sulfide</td>
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<td>12.9*</td>
<td>34.08</td>
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<tr>
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<td>90.08</td>
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<tr>
<td>Magnesium hydroxide</td>
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<td>58.33</td>
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<tr>
<td>Maleic acid</td>
<td>1.91</td>
<td>6.33</td>
<td>116.1</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>-1.37</td>
<td>---</td>
<td>117.1</td>
</tr>
<tr>
<td>Phosphorous acid</td>
<td>2.00</td>
<td>6.40</td>
<td>82.00</td>
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<tr>
<td>Phthalic acid</td>
<td>2.95</td>
<td>5.41</td>
<td>166.1</td>
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<td>Sodium hydroxide</td>
<td>14.67</td>
<td>---</td>
<td>40.01</td>
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<td>Sorbic acid</td>
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<td>---</td>
<td>112.1</td>
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<tr>
<td>Sulfuric acid</td>
<td>-3.0</td>
<td>1.99</td>
<td>98.08</td>
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<tr>
<td>Uric acid</td>
<td>5.40</td>
<td>5.53</td>
<td>168.11</td>
</tr>
</tbody>
</table>

* - present value is disputed and should be adjusted for application per lab data
Common Problems with Titration Curves

- Insufficient number of data points were generated near the equivalence point
- Starting pH (influent pH) data were not plotted for all operating conditions
- Curve doesn’t cover the whole operating range and control system overshoot
- No separate curve that zooms in to show the curvature in the control region
- No separate curve for each different split ranged reagent
- Sequence of the different split ranged reagents was not analyzed
- Back mixing of different split ranged reagents was not considered
- Overshoot and oscillation at the split ranged point was not included
- Sample or reagent solids dissolution time effect was not quantified
- Sample or reagent gaseous dissolution time and escape was not quantified
- Sample volume was not specified
- Sample time was not specified
- Reagent concentration was not specified
- Sample temperature during titration was different than the process temperature
- Sample was contaminated by absorption of carbon dioxide from the air
- Sample was contaminated by absorption of ions from the glass beaker
- Sample composition was altered by evaporation, reaction, or dissolution
- Laboratory and field measurement electrodes had different types of electrodes
- Composite sample instead of individual samples was titrated
- Laboratory and field used different reagents

Representative titration curves with enough data points are essential for pH system design and analysis.
The Essential Uses of the Titration Curve

- The titration curve is the essential tool for every aspect of pH system design and analysis.
  - Model fidelity
  - Valve sizing and resolution requirements
  - Feedforward control
  - Reagent demand control
  - Controller Tuning
  - Performance analysis
  - Disturbance analysis

- The first step in the design of a pH system is to generate a titration curve at the process temperature with enough data points to cover the range of operation and show the curvature within the control band (absolute magnitude of the difference between the maximum and minimum allowable pH).

- For a set point on the steepest part of the titration curve, one stage of neutralization is needed for every two pH units away from set point. Advanced control and precise valves can eliminate one stage.
Effect of Sensor Drift on Reagent Calculations

The error in a pH feedforward calculation increases for a given sensor error as the slope of the curve decreases. This result combined with an increased likelihood of errors at low and high pH means feedforward could do more harm than good when going from the curve’s extremes to the neutral region.

Flow feedforward (ratio control of reagent to influent flow) works well for vessel pH control if there are reliable flow measurements with sufficient rangeability.

Feedforward control always requires pH feedback correction unless the set point is on the flat part of the curve, use Coriolis mass flow meters and have constant influent and reagent concentrations.
Double Junction Combination pH Electrode

Measurement becomes slow from a loss of active sites or a thin coating of outer gel.

Nernst Equation assumes inside and outside gel layers identical.

High acid or base concentrations can affect glass gel layer and reference junction potential. Increase in noise or decrease in span or efficiency is indicative of glass electrode problem. Shift or drift in pH measurement is normally associated with reference electrode problem.
Most calibration adjustments chase the short term errors shown below that arise from concentration gradients from imperfect mixing, ion migration into reference junction, temperature shifts, different glass surface conditions, and fluid streaming potentials. With just two electrodes, there are more questions than answers.
Middle Signal Selection

Advantages

- Inherently ignores single measurement failure of any type including the most insidious PV failure at set point
- Inherently ignores slowest electrode
- Reduces noise and spikes particularly for steep curves
- Offers online diagnostics on electrode problems
  - Slow response indicates coated measurement electrode
  - Decreased span (efficiency) indicates aged or dehydrated glass electrode
  - Drift or bias indicates coated, plugged, or contaminated reference electrode or high liquid junction potential
  - Noise indicates dehydrated measurement electrode, streaming potentials, velocity effects, ground potentials, or EMI
- Facilitates online calibration of a measurement

For more Information on Middle Signal Selection see Feb 5, 2010 post
Fouling and coating rate depend on velocity at glass surface and not glass geometry.
Shroud Designs

Shroud should protect glass from breakage but not contribute to fouling or coating.
Large Surface Area
Solid Reference Junction
Retractable Assembly with Flushing Chamber

Rear flushing connection [1]:
The rear flushing connection directs the cleaning medium or the steam tangentially to the immersion tube.

Front flushing connection [2]:
The front flushing connection directs the cleaning medium or the steam directly to the tip of the electrode. This ensures optimal cleaning.

Outlet flushing chamber [3]:
The outlet of the flushing chamber has a very small diameter. When installing the housing, it must be ensured that the outlet always faces downwards.

Temperature connection [4]:
The flushing chamber is equipped with an additional thread for a temperature probe. This temperature probe may only be used for checking the sterilization temperature.

Safety instruction
All valves must be closed during insertion and withdrawal of the immersion tube of the retractable housing as otherwise the contents of the reactor can escape via the flushing chamber.
Automated Maintenance System

- Smart pH Transmitter
- pH Control System
- Automated Maintenance System
- Automated Cleaning System

Flow Diagram:
- Smart pH Transmitter to Automated Maintenance System via Diagnostics
- pH Control System to Automated Cleaning System via Command to Clean
- Request to Clean from pH Control System to Automated Maintenance System
- Time Response and Calibration Test Results from Automated Cleaning System to Automated Maintenance System
Low Flow Assembly for Low Conductivity Streams

- 500 ml Electrolyte Reservoir
- Vent Tube
- Reservoir Filter
- Reference Tubing
- Combination Electrode
- Cal Cup Holder
- Mounting Plate 203.2 x 457.2 mm (8” x 18”)
- Reservoir Clip
- VP Connector
- Air Bleed Screw
- Sample OUT
- Diffuser (inside low flow cell)
- Low Flow Cell
- Sample IN
Life Depends Upon Process Conditions

High acid or base concentrations (operation at the extremes of the titration curve) decrease life for a given temperature. A deterioration in measurement accuracy (e.g. electrode efficiency) and response time often accompanies a reduction in life.
New High Temperature Glass Stays Fast

Glass electrodes get slow as they age. High temperatures cause premature aging.

![Graph showing mV vs minutes for New Glass and Other glass electrodes. The graph indicates that New Glass electrodes maintain a steady mV value over time, whereas Other electrodes show a decrease in mV.]
New Design Eliminates Drift after Sterilization

![pH Voltage Drift Graph](image)
High Temperature Glass with Removable Reference Junction
Online Diagnostics for Cracked Glass

- **Cracked Glass Fault**
  - pH Glass electrode normally has high impedance of 50-150 Meg-ohm
  - Glass can be cracked at the tip or further back inside the sensor
  - Recommended setting of 10 Megohm will detect even small cracks
Online Diagnostics for Coated Sensor

- **Coated Sensor Detection Can**
  - activate sensor removal and cleaning cycle
  - place output on hold while sensor is cleaned
AMS Configuration

pH Range and Compensation

Temperature Comp Parameters
Solution pH Temperature Correction
Isopotential Point Changeable for Special pH Electrodes
AMS Configuration
pH Diagnostics

- Impedance Diagnostics On/Off
- Reference Impedance Warning and Fault Levels
- Reference Zero Offset Calibration Error Limit
- Glass Electrode Impedance Warning and Fault Levels
- Glass Impedance Temp Comp (Prevents spurious errors due to impedance decrease with Temperature)
AMS Configuration
pH Calibration Setup

Live Measurements and Status

Calibration Constants from Last Calibrations

Buffer Calibration Type & Buffer Standard Used

Sensor Stabilization Criteria

Zero Offset Beyond this Limit will create a Calibration Error

If you want to know more about Buffer Calibration, hit this button...
AMS Configuration
Auxiliary Variables Dashboard
Horizontal Piping Arrangements

- Pressure drop for each branch must be equal to keep the velocities equal.

- Static mixer or pump.

- 20 pipe diameters.

- 5 to 9 fps to minimize coatings.
- 0.1 to 1 fps to minimize abrasion.

- 20 to 80 degrees.

- Series arrangement preferred to minimize differences in solids, velocity, concentration, and temperature at each electrode!
Vertical Piping Arrangements

Series arrangement preferred to minimize differences in solids, velocity, concentration, and temperature at each electrode!

Orientation of slot in shroud
- Coating: 5 to 9 fps
- Abrasion: 0.1 to 1 fps

Hole or slot
Options for Maximum Accuracy

- A spherical or hemi-spherical glass measurement and flowing junction reference offers maximum accuracy, but in practice maintenance prefers:
  - A refillable double junction reference to reduce the complexity of installation and the need to adjust reference electrolyte flow rate – This electrode is often the best compromise between accuracy and maintainability.
  - A solid reference to resist penetration and contamination by the process and eliminate the need to refill or replace reference particularly for high and nasty concentrations and pressure fluctuations – This electrode takes the longest time to equilibrate and is more prone to junction effects but could be right choice in applications where accuracy requirements are low and maintenance is high.

- Select best glass and reference electrolyte for process
- Use smart digital transmitters with built-in diagnostics
- Use middle signal selection of three pH measurements
  - Inherent auto protection against a failure, drift, coating, loss in efficiency, and noise (see February 5, 2010 entry on http://www.modelingandcontrol.com/)
- Allocate time for equilibration of the reference electrode
- Use “in place” standardization based on a sample with the same temperature and composition as the process. If this is not practical, the middle value of three measurements can be used as a reference. The fraction and frequency of the correction should be chosen to avoid chasing previous calibrations
- Insure a constant process fluid velocity at the highest practical value to help keep the electrodes clean and responsive
Symptoms and Causes

- **Slow measurement**
  - Coated glass, aged glass, dehydrated glass, thick glass, high temperature, low pH, low velocity

- **Noisy measurement**
  - Dehydrated glass, pure water, low water, low temperature, poor mixing, high velocity, EMI

- **pH decreases with temperature**
  - $pK_a$ or $pK_w$ decrease with temperature (missing solution temperature compensation)
  - Horizontal shift to right of Isopotential point due to measurement electrode type or problem

- **pH increases with temperature**
  - Nernst MV decrease with temperature (missing electrode temperature compensation)
  - Horizontal shift to left of Isopotential point electrode type or problem

- **pH increases with salt or solvent concentration**
  - Decrease in activity of hydrogen ion from increase in ionic strength or decrease in water content

- **Constant 7 pH measurement**
  - Broken glass, broken wires, protective caps still on electrodes

- **Decrease in measurement range (decrease in electrode efficiency)**
  - Dehydrated glass or aged glass

- **Daily drift in measurement (change in electrode offset)**
  - Coated reference junction

- **Hourly drift in measurement**
  - Slow equilibration of reference electrode

- **Off-scale pH measurement**
  - Poisoned reference electrode or high solvent concentration
Broadley-James Corporation
Wireless Bioreactor Setup

- Hyclone 100 liter Single Use Bioreactor (SUB)
- Rosemount WirelessHART gateway and transmitters for measurement and control of pH and temperature. (pressure monitored)
- BioNet lab optimized control system based on DeltaV
Wireless pH Transmitters
Eliminate Ground Spikes

Incredibly tight pH control via 0.001 pH wireless resolution setting still reduced the number of communications by 60%

Temperature compensated wireless pH controlling at 6.9 pH set point

Wired pH ground noise spike
Wireless Bioreactor
Adaptive pH Control
Calibration History in Probe

<table>
<thead>
<tr>
<th>Cal Method</th>
<th>1 - Latest</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5 - Oldest</th>
<th>Factory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run-Time</td>
<td>4.74</td>
<td>4.74</td>
<td>4.74</td>
<td>2.03</td>
<td>2.01</td>
<td>0 days</td>
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<tr>
<td>Slope</td>
<td>58.37</td>
<td>59.37</td>
<td>58.37</td>
<td>59.15</td>
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<td>Offset</td>
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<td>7.44</td>
<td>-4.50</td>
<td>6.23</td>
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<td>Temperature</td>
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<td>18.3</td>
<td>18.8</td>
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<td>Ref Impedance</td>
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<td>14 kOhm</td>
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</table>

Service Tools
- Service Tools
- Alerts
- Variables
- Trends
- Communications
- Maintenance
- Simulate

Overview
Configure
Service Tools
The Separations Research Program was established at the J.J. Pickle Research Campus in 1984.

This cooperative industry/university program performs fundamental research of interest to chemical, biotechnological, petroleum refining, gas processing, pharmaceutical, and food companies.

CO₂ removal from stack gas is a focus project for which WirelessHART transmitters are being installed.
Wireless Conductivity and pH Lab Setup

Wireless pH measurements offer

- Selecting the best sensor technology for a wide range of process conditions
- Eliminating measurement noise
- Predicting sensor demise
- Developing process temperature compensation
- Developing inferential measurements of process concentrations
- Finding the best sensor location considering velocity, mixing, delay, & bubbles
Wireless Inferential Measurement of Piperazine Solvent

Correlation of pH to CO₂ Weight % in Piperazine (PZ)

\[
PZ_{15\%} = (0.0776)(pH) - 0.2664 \\
R^2 = 0.9897
\]

\[
PZ_{12.5\%} = (0.118)(pH) - 0.7192 \\
R^2 = 0.9969
\]

\[
PZ_{10\%} = (0.1573)(pH) - 1.1783 \\
R^2 = 0.9407
\]

Graph showing the correlation between pH and CO₂ weight % in Piperazine (PZ) for different CO₂ concentrations.
Wireless Inferential Measurements for CO$_2$ Capture

- pH measures the activity of the hydrogen ion, which is the ion concentration multiplied by an activity coefficient. An increase in solvent concentration decreases the pH by a decrease in the activity coefficient and a decrease in the ion concentration from a decrease per the water dissociation constant.
- pH is also affected by CO$_2$ weight percent since pH changes with the concentration of carbonic acid.
- Wireless conductivity offers an inferential measurement of CO$_2$ weight percent to include effect on pH.
- In the UT lab that supports the pilot plant, solvent concentration and loading were varied and the conductivity and pH were wirelessly communicated to the DCS in the control room.
Axial Agitation Recommended for pH Control

The agitation in a vessel should be a vertical axial pattern without rotation and be intense enough to break the surface but not cause froth.
Radial Agitation Detrimental for pH Control

The stagnant zones introduce a large and variable dead time. The use of an external recirculation stream and an eductor ring can reduce stagnation.
Horizontal Tanks and Sumps are Bad News

Multiple recirculation streams can help but this type of geometry is best used for attenuation of oscillations upstream or downstream of a pH control system. The insertion of an inline pH control system in the recirculation line could make this a viable system by putting a fast system in series with a large volume.
Vessel Time Constant and Dead Time

For a vertical well mixed vessel:

\[ \tau_{dp} = \frac{\rho \cdot V}{F_i + F_r + F_c + F_a} \]  \hspace{1cm} (5-3a)

\[ F_a = \rho \cdot N_q \cdot N_s \cdot D_i^3 \]  \hspace{1cm} (5-3b)

\[ N_q = \frac{0.4}{(D_i / D_t)^{0.55}} \]  \hspace{1cm} (5-3c)

\[ \tau_{dp} = \left( \frac{L}{U} \right) \]  \hspace{1cm} (5-3d)

\[ \tau_p = \frac{\rho \cdot V}{F_i + F_r} \]  \hspace{1cm} (5-3e)

For a vessel with proper geometry, baffles, and axial patterns, the equipment dead time from mixing is approximately the turnover time.

For a vessel with proper geometry, baffles, and axial patterns, the continuous equipment time constant is the residence time minus the dead time.
Where:

\[ D_i = \text{impeller diameter (meter)} \]
\[ D_t = \text{tank inside diameter (meter)} \]
\[ F_i = \text{influent mass flow (kg per minute)} \]
\[ F_r = \text{reagent mass flow (kg per minute)} \]
\[ F_c = \text{recirculation mass flow (kg per minute)} \]
\[ F_a = \text{agitation mass flow (kg per minute)} \]
\[ L = \text{distance between inlet and outlet nozzles (meter)} \]
\[ N_q = \text{agitator discharge coefficient (0.4 to 1.4)} \]
\[ N_s = \text{agitator speed (revolutions per minute)} \]
\[ \rho = \text{average fluid density (kg per cubic meter)} \]
\[ \tau_{dp} = \text{process dead time from mixing (minutes)} \]
\[ \tau_p = \text{process time constant from mixing (minutes)} \]
\[ U = \text{average bulk velocity (meters per minute)} \]
\[ V = \text{vessel liquid volume (cubic meters)} \]
Reagent Injection Delay

For reagent dilution or after closing of a control valve to a dip tube or injection tube:

\[
\tau_{dp} = \frac{\rho \cdot V}{F_r}
\]

Where:

- \( F_r \) = reagent mass flow (kg per minute)
- \( \rho \) = average fluid density (kg per cubic meter)
- \( \tau_{dp} \) = process dead time from mixing (minutes)
- \( V \) = injection volume (cubic meters)

The delivery delay from an empty or back filled reagent pipe, injection tube, and dip tube is the largest source of dead time in a pH loop.

Use isolation valves close coupled to the injection point coordinated with the action of the control valve to reduce reagent holdup between process and reagent control valve.
Static Mixer - Good Radial but Poor Axial Mixing

Oscillations and noise will pass through a static mixer un-attenuated and the poor dead time to time constant ratio leads to more oscillations.

The extremely small residence time of a static mixer greatly reduces the magnitude of the dead time and the volume of off-spec material.

“The Future is Inline” due to a much lower cost, smaller footprint, and faster response if you can address oscillation and noise issues.
For a single vessel volume:

\[
A_o = A_i \times \frac{T_o}{2 \times \pi \times \tau_p}
\]

(5-3j)

Where:

- \(A_i\) = amplitude of input oscillation into volume (reagent to influent ratio)
- \(A_o\) = amplitude of output oscillation from volume (reagent to influent ratio)
- \(T_o\) = period of oscillation (minutes)
- \(\tau_p\) = process time constant from mixing (minutes)

Back mixed volumes attenuate oscillations in concentration that must be translated to pH via a titration curve to see the effect on the pH trend.

The average pH measurement upstream and downstream will differ due to the nonlinearity. The upstream pH fluctuations must be translated to concentration fluctuations (changes in reagent to influent ratio) and then attenuated per Equation 5-3j and translated back to pH via titration curve.
The effect of fluctuations in influent concentration or mixing uniformity on measurement error and the effect of pressure fluctuations and control valve resolution on the ratio of reagent to influent is less on flat portions of the titration curve but high acid or base concentrations at the curve extremes may attack glass and wetted materials of construction and increase reference junction potentials.
Control Valve
Rangeability and Resolution

$E_r = 100\% \times \frac{F_{imax}}{F_{rmax}}$

$F_{rmax} = A \times F_{imax}$

$E_r = \frac{B}{A}$

$S_s = 0.5 \times E_r$

Where:

$A$ = distance to center of reagent error band on abscissa from influent pH

$B$ = width of allowable reagent error band on abscissa for control band

$E_r$ = allowable reagent error (%)

$F_{rmax}$ = maximum reagent valve capacity (kg per minute)

$F_{imax}$ = maximum influent flow (kg per minute)

$S_s$ = allowable stick-slip (resolution limit) (%)
Everyday Mistakes in pH System Design

- Mistake 1: Missing, inaccurate, or erroneous titration curve
- Mistake 2: Absence of a plan to handle failures, startups, or shutdowns

Mistakes 3-12:
- Mistake 3 (single stage for set point at 7 pH)
- Mistake 4 (horizontal tank)
- Mistake 5 and 6 (backfilled dip tube & injection short circuit)
- Mistake 7 (gravity flow)
- Mistake 8 (valve too far away)
- Mistake 9 (ball valve with no positioner)
- Mistake 10 (electrode submerged in vessel)
- Mistake 11 (electrode in pump suction)
- Mistake 12 (electrode too far downstream)
Inline and Tank Control System Performance

The Inline system has the fastest recovery time and lowest cost but due to the lack of back mixing, the signal will wildly fluctuate for set points on the steep part of the titration curve. A signal filter (e.g. 12 sec) or reagent demand control attenuate the oscillations but an offset from the set point is seen downstream.

The tank responses shown above assumes a negligible reagent delivery delay and are thus faster than typical. In most systems the reagent injection delay is so large due to a dip tube, the period of oscillation is 10x slower than what is seen in an inline system.

The Inline system has the fastest recovery time and lowest cost but due to the lack of back mixing, the signal will wildly fluctuate for set points on the steep part of the titration curve. A signal filter (e.g. 12 sec) or reagent demand control attenuate the oscillations but an offset from the set point is seen downstream.
Methods to Reduce Capital and Operating Costs

- Use inline systems to replace vessels
- Use online models to provide inferential measurements of influent concentrations, 3rd voting pH measurement for tough applications, and online titration curves for reagent demand control and adaptive control
- Use high resolution valves and advanced process control to:
  - Reduce vessel size
  - Eliminate a stage of neutralization
  - Reduce reagent costs
  - Eliminate out-of-spec effluent
The period of oscillation (4 x process dead time) and filter time (process residence time) is proportional to volume. To prevent resonance of oscillations, different vessel volumes are used.

Small first tank provides a faster response and oscillation that is more effectively filtered by the larger tanks downstream.

Big footprint and high cost!
The period of oscillation (total loop dead time) must differ by more than factor of 5 to prevent resonance (amplification of oscillations).

Big footprint and high cost!

The large first tank offers more cross neutralization of influents.
Basic Neutralization System
Before

Can you spot the opportunities for process control improvement?
Basic Neutralization System

After

#1 - Isolation valve closes when control valve closes
Tight pH Control with Minimum Capital Investment

#1 – shuts to prevent back fill of reagent piping when control valve closes

#2 – shuts to stop effluent flow until tank pH is projected to be within control band
Methods of Reducing Reagent Delivery Delays

- Locate reagent throttle valve at the injection point
- Mount automatic on-off isolation valve at the injection point
- Reduce diameter and length (volume) of injector or dip tube
- Dilute the reagent upstream to increase reagent flow rate
- Inject reagent into vessel side just past baffles
- Inject reagent into recirculation line just before vessel entry
- Inject reagent into feed line just before vessel entry
- Reduce reagent control valve sticktion and deadband

The benefits of feedforward are realized only if the correction arrives at about the same time as the disturbance at the point of the pH measurement. Since the disturbance is usually in a high flow influent stream, any reagent delivery delays severely diminish the effectiveness of feedforward besides feedback control because the disturbance hits the pH measurement before the correction.
High Uniformity Reagent Dilution Control

Big old tank acts an effective filter of reagent concentration fluctuations
Cascade pH Control to Reduce Downstream Offset

- **FT 1-1**: Coriolis Mass Flow Meter
- **Static Mixer**: Feed
- **AT 1-1**: Filter
- **Sum**: Flow Feedforward
- **AC 1-1**: Linear Reagent Demand Controller
- **RSP**: Trim of Inline Set Point
- **PV signal Characterizer**: 10 to 20 pipe diameters
- **SP signal characterizer**: Linear Reagent Demand Controller
- **Any Old Tank**
- **Integral Only Controller**: AC 1-2
- **AT 1-2**: Integral Only Controller
Section 3-5 in *New Directions in Bioprocess Modeling and Control* shows how this strategy is used as a head start for a PID controller.
Reduces injection and mixing delays and enables some cross neutralization of swings between acidic and basic influent. It is suitable for continuous control as well as fed-batch operation.
Linear Reagent Demand Control
(PV is X axis of Titration Curve)

- **Signal characterizer converts PV and SP from pH to % Reagent Demand**
  - PV is abscissa of the titration curve scaled 0 to 100% reagent demand
  - Piecewise segment fit normally used to go from ordinate to abscissa of curve
  - Fieldbus block offers 21 custom space X,Y pairs (X is pH and Y is % demand)
  - Closer spacing of X,Y pairs in control region provides most needed compensation
  - If neural network or polynomial fit used, beware of bumps and wild extrapolation

- **Special configuration is needed to provide operations with interface to:**
  - See loop PV in pH and signal to final element
  - Enter loop SP in pH
  - Change mode to manual and change manual output

- **Set point on steep part of curve shows biggest improvements from:**
  - Reduction in limit cycle amplitude seen from pH nonlinearity
  - Decrease in limit cycle frequency from final element resolution (e.g. stick-slip)
  - Decrease in crossing of split range point
  - Reduced reaction to measurement noise
  - Shorter startup time (loop sees real distance to set point and is not detuned)
  - Simplified tuning (process gain no longer depends upon titration curve slope)
  - Restored process time constant (slower pH excursion from disturbance)
Pulse Width and Amplitude Modulated Reagent

Pulse width modulation is linear. The addition of pulse amplitude modulation introduces a severe nonlinearity but greatly increases the sensitivity and rangeability of reagent addition.
Key Insights

- pH electrodes offer by far the greatest sensitivity and rangeability of any measurement. To make the most of this capability requires an incredible precision of mixing, reagent manipulation, and nonlinear control. pH measurement and control can be an extreme sport.

- Solution pH changes despite a constant hydrogen ion concentration because of changes in water dissociation constant (pK\textsubscript{w}) with temperature, and activity coefficients with ionic strength and water content.

- Solution pH changes despite a constant acid or base concentration because of changes in the acid or base dissociation constants (pK\textsubscript{a}) with temperature.

- Titration curves have no straight lines. A zoom in on any supposed line should reveal another curve if there are sufficient data points.

- Slope of titration curve at the set point has the greatest effect on the tightness of pH control as seen in control valve resolution requirement. The next most important effect is the distance between the influent pH and the set point that determines the control valve rangeability requirement.

- Titration curves are essential for every aspect of pH system design and analysis.

- First step in the design of a pH system is to generate a titration curve at the process temperature with enough data points to cover the range of operation and show the curvature within the control band (absolute magnitude of the difference between the maximum and minimum allowable pH).
The time that glass electrodes are left dry or exposed to high and low pH solutions must be minimized to maximize the life of the hydrated gel layer.

Most accuracy statements and tests are for short term exposure before changes in the glass gel layer or reference junction potential are significant.

The pH measurement error may look smaller on the flatter portion of a titration curve but the associated reagent delivery error is larger.

The cost of pH measurement maintenance can be reduced by a factor of ten by more realistic expectations and calibration policies.

The onset of a coating of the glass measurement electrode shows up as a large increase in its time constant and response time.

The onset of a non conductive coating of the reference electrode shows up as a large increase in its electrical resistance.

Non-aqueous and pure water streams require extra attention to shielding and process path length and velocity to minimize pH measurement noise.

Slow references may be more stable for short term fluctuations from imperfect mixing and short exposure times from automated retraction.

The fastest and most accurate reference has a flowing junction but it requires regulated pressurization to maintain a small positive electrolyte flow.

The best choice might not be the best technical match to the application but the electrode with the best support by maintenance and operations and vendor.

For pH < 1 or > 12 consider conductivity or Coriolis measurements.
Key Insights

- For non-abrasive solids, installation in a recirculation line with a velocity of 5 to 9 fps downstream of a strainer and pump may delay onset of coatings.
- For abrasive solids and viscous fluids, a thick flat glass electrode can minimize coatings, stagnant areas, and glass breakage.
- For high process temperatures, high ion concentrations, and severe fouling, consider automatic retractable assemblies to reduce process exposure.
- When the fluid velocity is insufficient to sweep electrodes clean, use an integral jet washer or a cleaning cycle in a retractable assembly.
- The control system should schedule automated maintenance based on the severity of the problem and production and process requirements.
- pH measurements can fail anywhere on or off the pH scale but middle signal selection will inherently ride out a single electrode failure of any type.
- Equipment and piping should have the connections for three probes but a plant should not go to the expense of installing three measurements until the life expectancy has been proven to be acceptable for the process conditions.
- The more an electrode is manually handled, the more it will need to be removed.
- A series installation of multiple probes insures the electrodes will see the same velocity and mixture that is important for consistent performance.
- Wireless pH measurements can be used to find optimum sensor technology and sensor location and eliminate spikes from electrical noise.
Key Insights

- Use properly sized sliding stem (globe) reagent valves with diaphragm actuators, tuned digital positioners, and properly tightened low friction packing.
- The extremely small reagent valves used in pH control are prone to improper sizing, irregular flow characteristics, greater stick-slip, and plugging.
- The extremely small reagent valves used in pH control may be operating in laminar flow where the flow is proportional to pressure drop or even worse in the transition region where the flow response is erratic.
- To prevent plugging and a transition to laminar flow for pH control on a well mixed volume, use pulse width modulation.
- Most statements in the literature as to valve rangeability are erroneous because they ignore the installed valve gain and stick-slip.
- The reagent flow required for neutralization is usually so small that the installed valve characteristic is the inherent trim characteristic.
- A small plug flow volume may have a smaller integrated error than a large back mixed volume because the dead time magnitude is smaller.
- For large volumes, maximize back mixing and minimize plug flow to minimize the error from load upsets and the effects of the pH nonlinearity.
- For a vessel with proper geometry, baffles, and axial patterns, the equipment dead time from mixing is approximately the turnover time.
- The actual equipment dead time is often larger than the turnover time because of non ideal mixing patterns and fluid entry and exit locations.
A system considered to be well mixed may be poorly mixed for pH control.

To be “well mixed” for pH control, the deviation in the reagent to influent flow from non ideal mixing multiplied by the process gain must be well within the control band.

Back mixing (axial mixing) creates a beneficial process time constant and plug flow or radial mixing creates a detrimental process dead time for pH control.

The agitation in a vessel should be vertical axial pattern without rotation and be intense enough to break the surface but not cause froth.

The actual equipment dead time is often larger than the turnover time because of non ideal mixing patterns and fluid entry and exit locations.

Horizontal tanks are notorious for short circuiting, stagnation, and plug flow that cause excessive dead time and an erratic pH response.

The dead time from back filled reagent dip tubes or injection piping is huge.

To provide isolation, use a separate on-off valve and avoid the specification of tight shutoff and high performance valves for throttling reagent.

Set points on the steep portion of a titration curve necessitate a reagent control valve precision that goes well beyond the norm and offers the best test to determine a valve’s actual stick-slip in installed conditions.

Reagent valve stick-slip may determine the number of stages of neutralization required, which has a huge impact on a project’s capital cost.
For a vessel with proper geometry, baffles, and axial patterns, the continuous equipment time constant is the residence time minus the dead time.

For batch operations without acid-base reactions, there is no steady state and the concentration ramp is described by an integrator gain rather than a time constant.

Horizontal tanks are notorious for short circuiting, stagnation, and plug flow that cause excessive dead time and an erratic pH response.

Back mixed volumes attenuate oscillations in concentration that must be translated to pH via a titration curve to see the effect on the pH trend.

An un-agitated vessel with a pH control loop can be turned from a terrible loser into a big time winner by moving the loop upstream or downstream.

Use volumes upstream to reduce reagent use and smooth out disturbances and volumes downstream to reduce pH constraint violations.

Oscillations and noise will pass through a static mixer un-attenuated and the poor dead time to time constant ratio leads to more oscillations but the extremely small residence time of a static mixer greatly reduces the magnitude of the dead time and the volume of off-spec material. pH measurements or online estimators on a downstream volume can reveal that a static mixer loop is doing a great job.

pH control loops should not be installed on sumps, ponds, and lagoons but on a static mixer or vertical well mixed vessel upstream or downstream.
A split range gap adds dead time and a split range overlap increases the severity of a limit cycle from slip stick and increases reagent use.

- Use a split range gap that is about twice the stick-slip or the potential error in the positioner calibration, whichever is largest.
- Split ranging and signal reversing is better implemented in a Fieldbus function block than via a special calibration of an I/P or positioner.
- Gaseous and solid reagents often have huge hidden costs from additional reagent consumption, emission, solids disposal, and maintenance costs.
- The delivery delay from an empty or back filled reagent pipe, injection tube, and dip tube is the largest source of dead time in a pH loop.
- The best method of reducing reagent delivery delay and mixing dead time is to inject the reagent into a high feed or recirculation flow.
- While the shape of the titration curve doesn’t change much by dilution, dilution can dramatically decrease reagent delivery delays, improve reagent addition reproducibility by eliminating transitions to laminar flow, increase valve reliability by reducing plugging, and enhance mixing by increasing the reagent injection velocity and reducing the differences in viscosity and density between the reagent and the influent, which is a normally a dilute water stream.
More so than for any other loop, it is important to reduce dead time for pH control because it reduces the effect of the nonlinearity.

The effectiveness of feedforward control greatly depends upon the ability to eliminate reagent delivery delays.

If there is a reproducible influent flow measurement use flow feedforward, otherwise use a head start or full throttle logic for startup.

The reliability and error of a pH feedforward is unacceptable if the influent pH measurement is on the extremities of the titration curve.

Except for fast inline systems, use cascade control of pH to reagent flow to compensate for pressure upsets and enable flow feedforward.

Use adaptation of the charge balance model pH or online identification of the titration curve to compensate for a distortion of the curve.

Linear reagent demand can restore the time constant and capture the investment in well mixed vessels, provide a unity gain for the process variable, simply and improve controller tuning, suppress oscillations and noise on the steep part of the curve, and speed up startup and recovery from the flat part of the curve.