# pH IN THE BLEACH PLANT
# WHY IT'S IMPORTANT AND WHAT TO DO ABOUT IT
# PART 1 – $ClO_2$ STAGES

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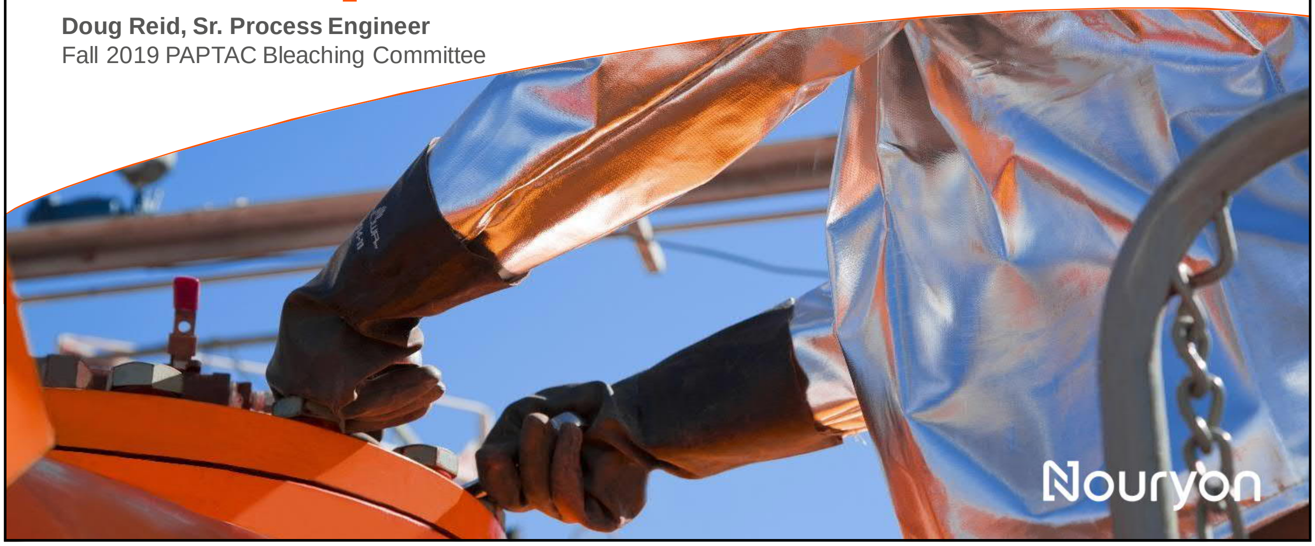
Fall 2019 PAPTAC Bleaching Committee




## Introduction

- pH is critically important in D stages
- pH must be well-controlled if advanced controls are to perform to their full capability
- Goals of this paper:
  - Review reasons why pH is important
  - Provide an overview of current industry performance
  - Summarize tips for obtaining accurate pH measurements

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# Contents

- Why is pH important in D stages?
  - **Optimum pH curves**
  - $ClO_2$ bleaching chemistry
- Industry performance
- How is pH measured?
  - pH meter design
  - Common problems and troubleshooting
  - Maintenance & calibration
  - Comparing online and lab measurements
  - Installation
- Control strategies

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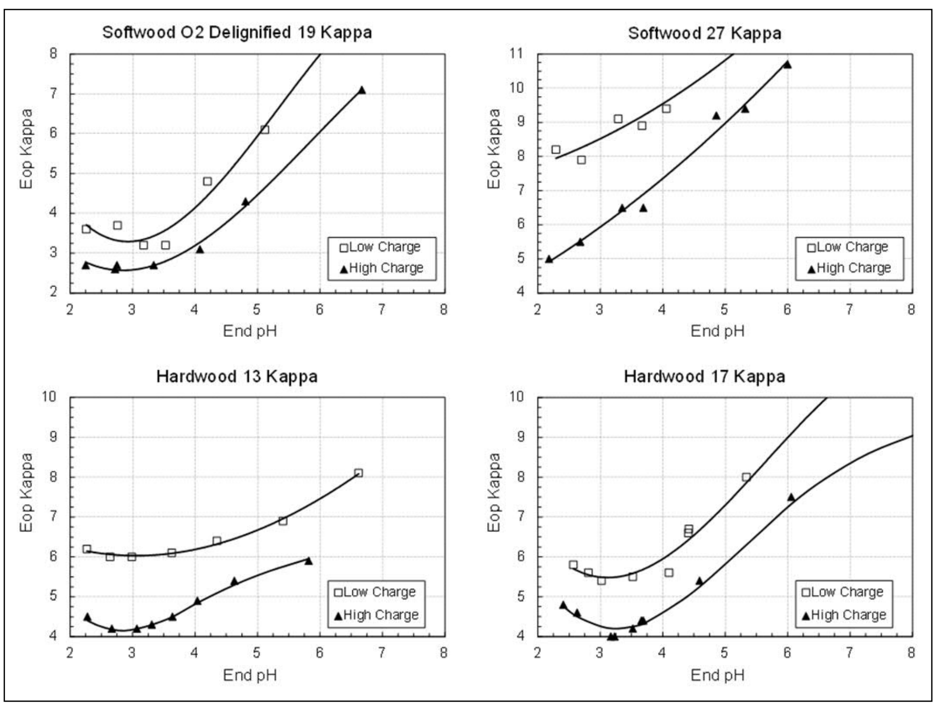
# Optimum pH in D0

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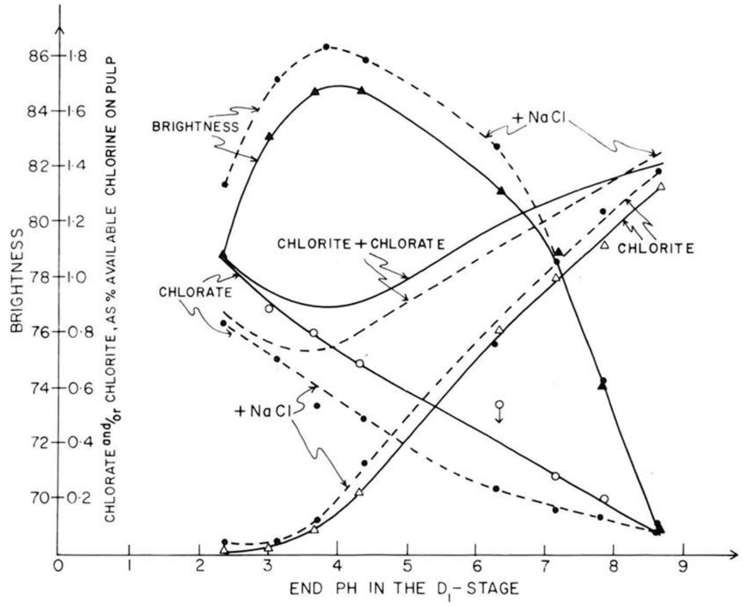
## Optimum pH in D1

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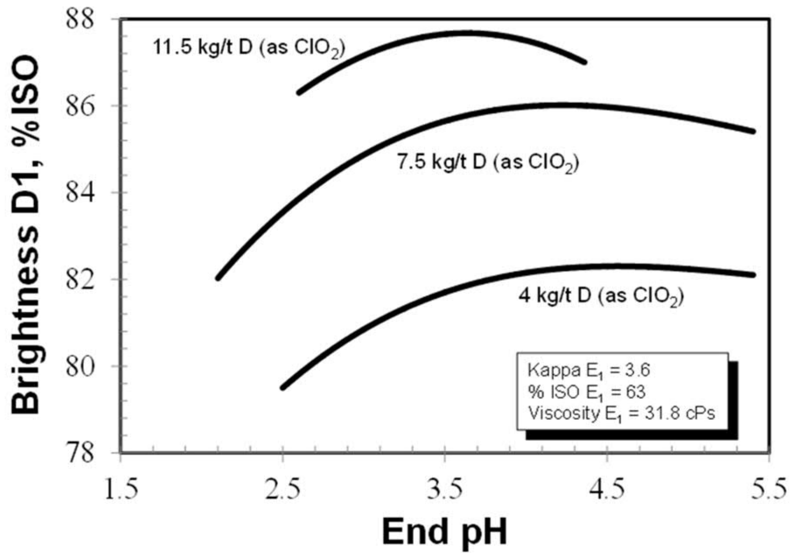
## Optimum pH in D1

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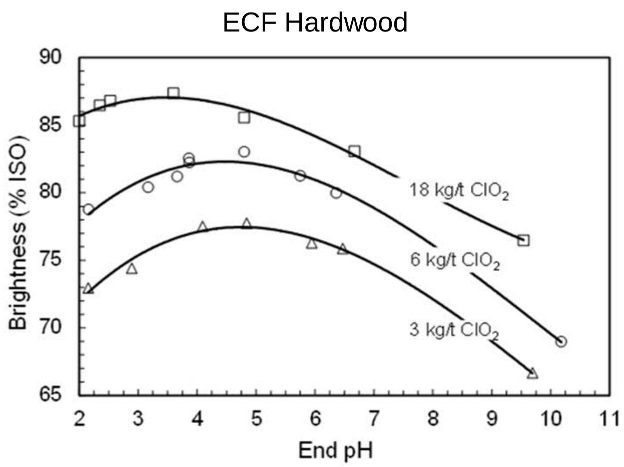
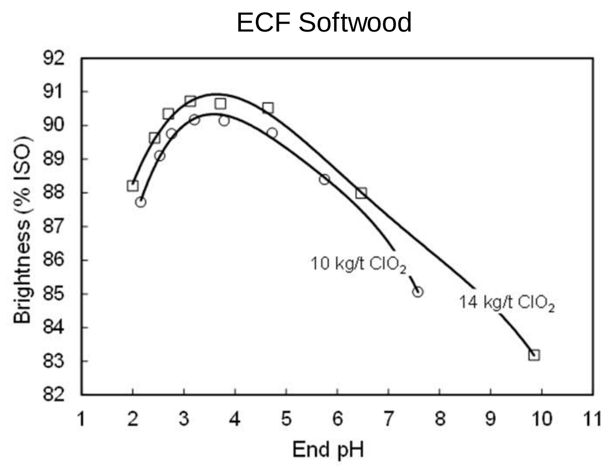
# Optimum pH in D1

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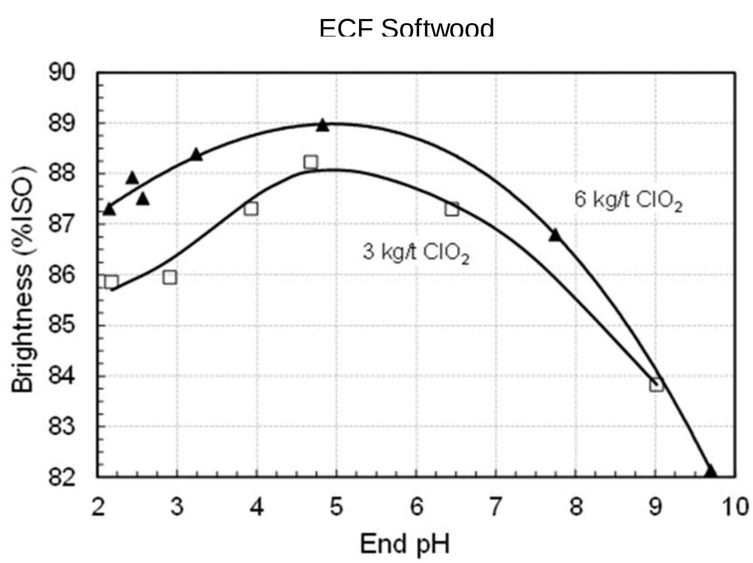
# Optimum pH in D2

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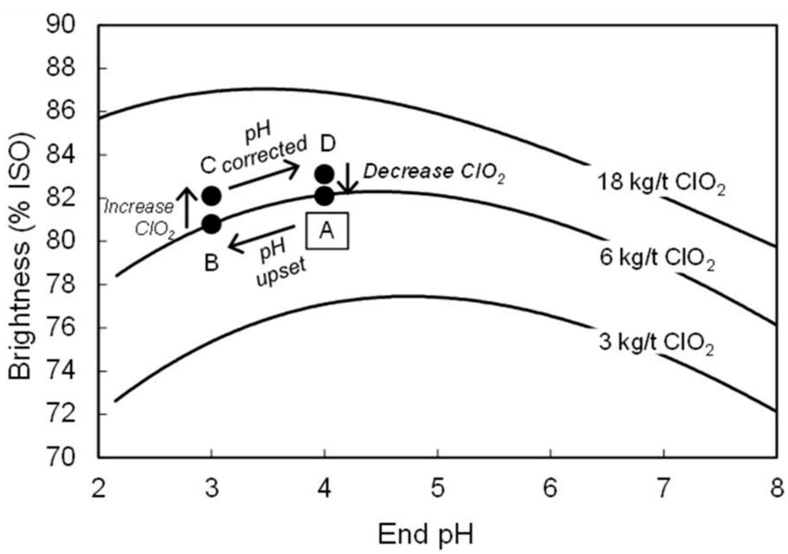
## Example – pH Upset in D1




Net result:

- Brightness varies by 2.3% ISO
- $ClO_2$ increases by 2.5 kg/t

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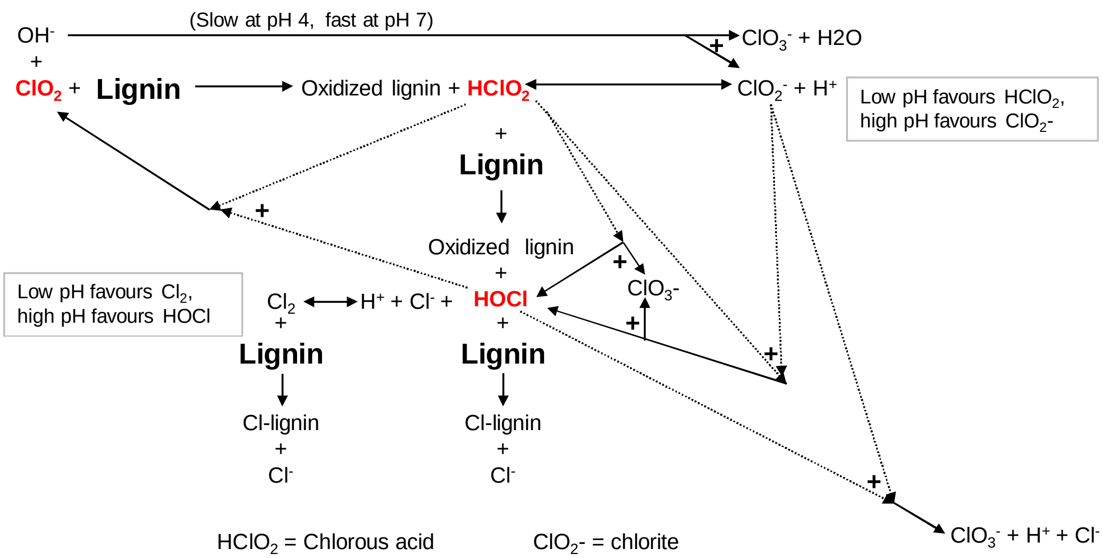
## Simplified $ClO_2$ Bleaching Chemistry




$HClO_2$ = Chlorous acid

HOCl = Hypochlorous acid

$ClO_2^-$ = chlorite

$ClO_3^-$ = chlorate

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## Industry Performance

**Standard Deviation of Terminal pH (Filtered Data)**

| Stage | Typical Standard Deviation | Best Mills Standard Deviation |
|---|---|---|
| D0 | 0.30 | 0.20 |
| D1 | 0.45 | 0.25 |
| D2 | 0.40 | 0.25 |

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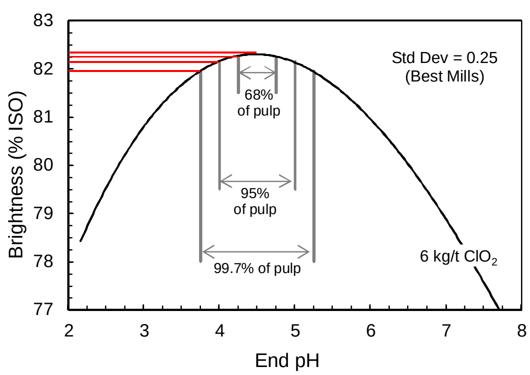
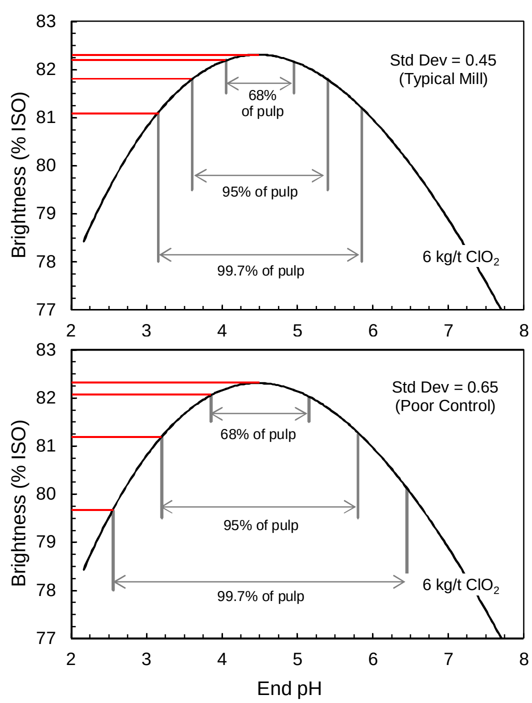
## Industry Performance

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## pH Meter Design

- Invented in 1934
- pH probe = very weak battery whose voltage changes with pH (and temperature)
  - One half-cell = glass measurement electrode
  - Other half-cell = reference electrode
- Circuit completed at one end by process solution
- Circuit completed at other end by a voltmeter (the pH meter)

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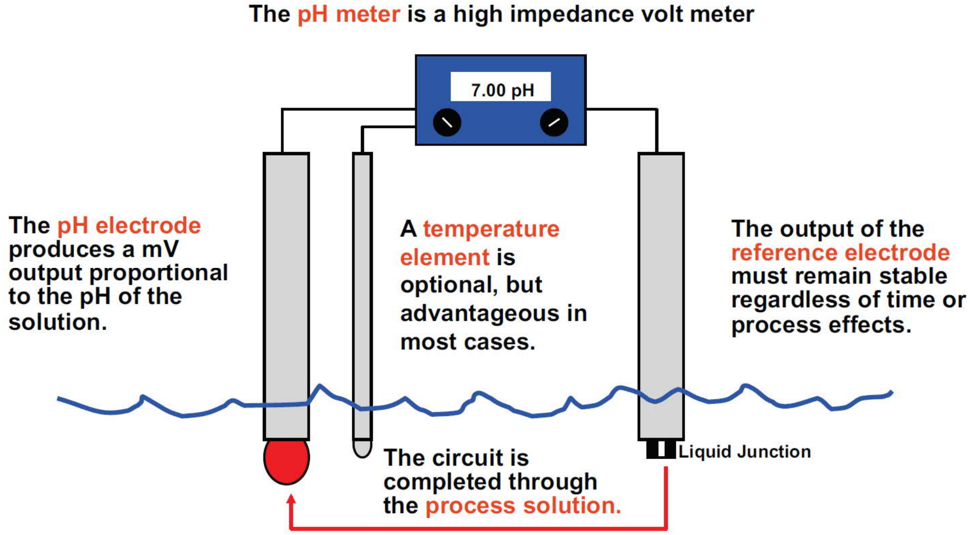
## pH Meter

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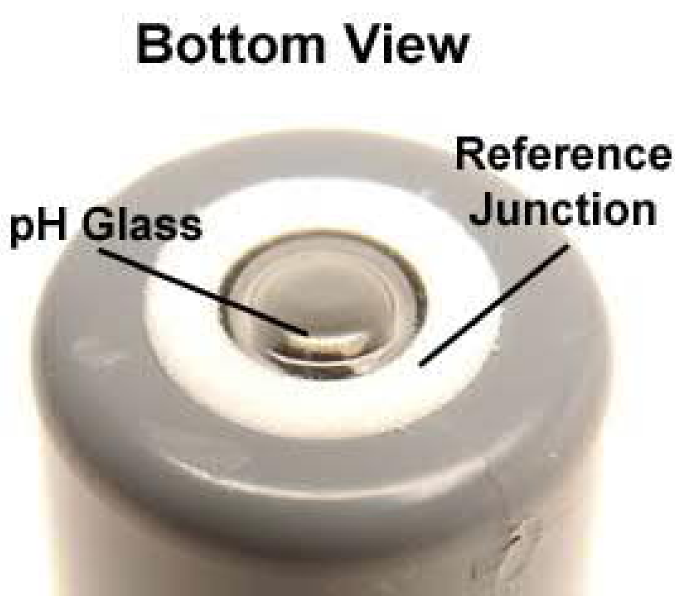
## pH Probe

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## Problems and Troubleshooting

- All pH meters must receive regular attention to operate correctly
- Can be difficult to tell when a probe needs to be serviced or replaced
  - Usually still respond and may even be accurate in part of its range
  - May need to perform diagnostics or compare to a brand new probe
- Most failures are related to the reference electrode
  - Plugged/coated reference junction affects accuracy or stops measurement altogether
    - Indicator = high reference impedance (>20 kohm)
  - Poisoned reference electrode (process solution replaces or reacts with electrolyte) affects accuracy
    - Indicator: Offset > ± 30 mV
    - In theory, buffer 7 @25°C should read 0 mV

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## Problems and Troubleshooting

- Measuring electrode problems include:
  - Cracked glass
    - Indicator: low glass impedance (<10 Mohm)
  - Glass tip deteriorated due to age or improper cleaning
    - Indicator: Slope < 49 mV/pH
    - Theoretical slope @ 25°C = 59.16 mV/pH
  - Glass tip coated with scale, pitch, etc.
    - Clean with weak acid (5% HCl), weak caustic (<4% NaOH), or compatible detergent/organic solvent. Do not use brushes or abrasive powders.
  - Glass tip dried out
  - Installed with tip facing up

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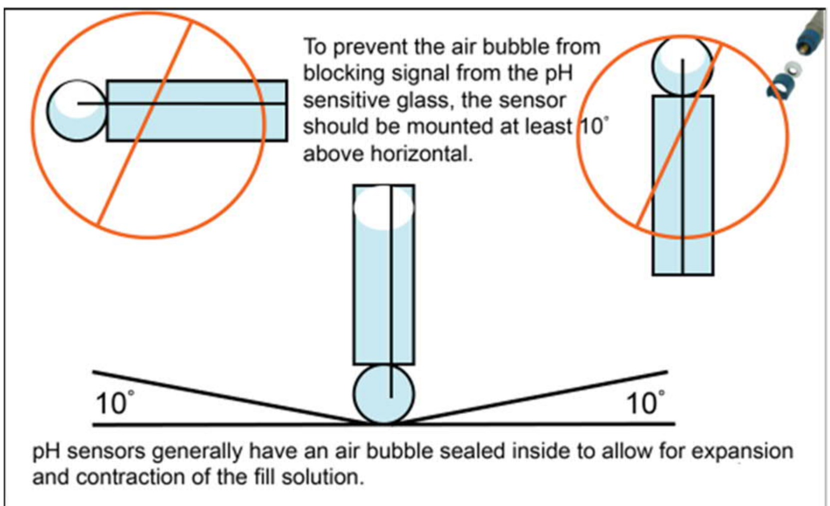
## Problems and Troubleshooting




[From Rosemount/Emerson]

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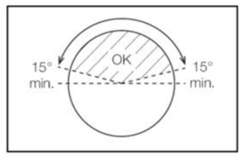
## Problems and Troubleshooting

**pH/Redox (ORP) Sensors for Process Monitoring**
TB(X)5 Series

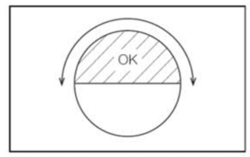
**1 Installation**

Install sensors:

- in full pipelines to prevent the sensor from drying out
- with the electrode pointing downwards
- as shown below (flat glass electrodes)
- as shown below (hemispherical glass)




*Mounting Range for Flat Glass Electrodes in Horizontal Piping*




*Mounting Range for Hemispherical Glass Electrodes in Horizontal Piping*

*[From ABB manual]*

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## Problems and Troubleshooting

- Incorrect installation
  - Always follow manufacturer’s recommendations
  - Tip should be facing down (horizontal is ok for some probes)
  - Some probes should be installed 90° to flow, others pointing slightly into it
  - Insert probe to correct depth (past laminar flow layer at edge of pipe, but not so far that it will break)
- Incorrect probe specified
  - Literally hundreds of different possible combinations
  - Double check with distributor/manufacturer and online materials

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## Problems and Troubleshooting

- Faulty temperature indicator or manual temp adjustment not used
- Ground loops cause erratic and/or inaccurate readings
  - Test by removing sensor from process and placing it in a sample in a glass or plastic container, then ground sample to the process with a wire
  - Usually caused by high current motors and improper or different grounds somewhere in the system

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## Maintenance and Calibration

- Routine PM schedule
- If calibrating with buffers, follow manufacturer's procedure
  - Use fresh buffers
  - Remember that buffer pH changes with temperature
- Online probes may get better results from calibrating to a known process sample
  - Reference junction becomes acclimated to process
  - Buffer is much cleaner → Equilibrium is disrupted → Junction potentials

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## Comparing Online and Lab Measurements

- Do not assume the lab measurement is always correct
  - Lab probe may be fouled, damaged, or worn out
    - Check offset and slope or simply replace lab probe on a regular schedule
    - Store lab probe in buffer 7 (not water) between tests
  - Use built-in temperature compensation
  - Use one pH meter for low pH's and one for high pH's
- Ensure that sample is representative of online probe
- Actual pH changes with temperature (but not as much as with extraction stage filtrates)

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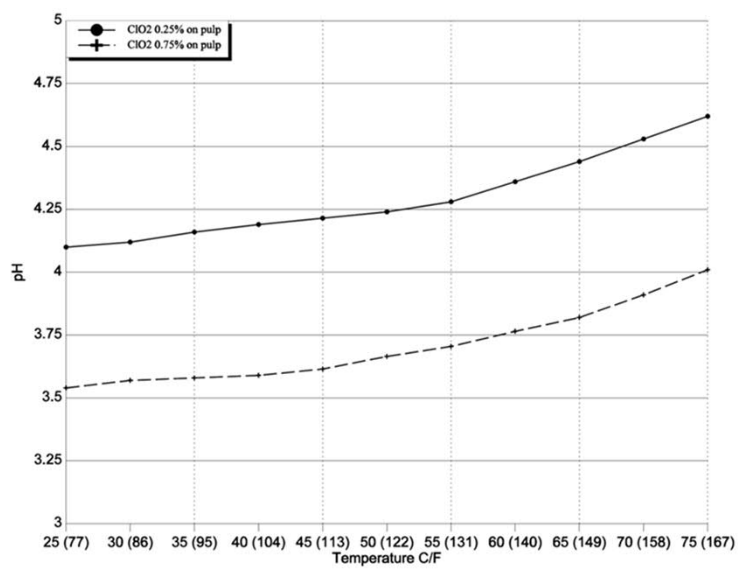
## Impact of Temperature on D Stage Filtrate pH

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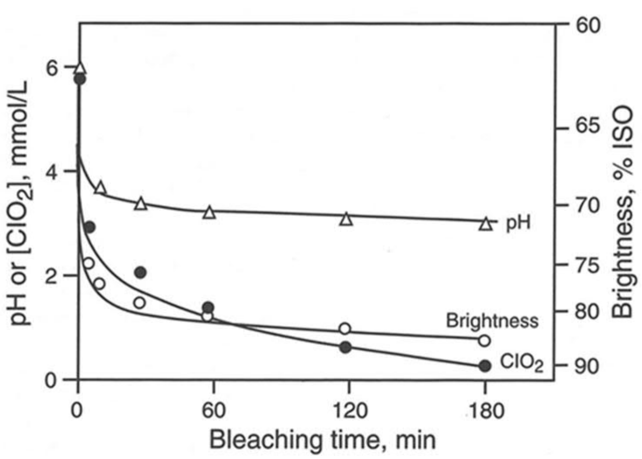
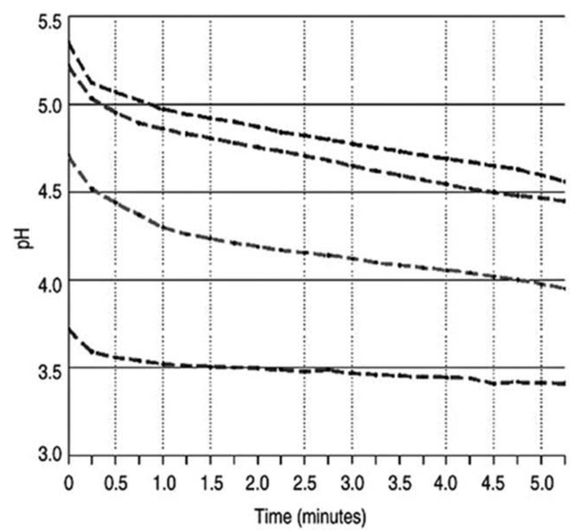
# Fast pH Drop at Beginning of Reaction

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## Inline Probe vs. Filtrate Extractor

- Both can work well
- Inline probe issue:
  - Can be difficult to remove and reinstall for routine maintenance
    - Specialized valve assemblies, safety clamps, etc.
- Filtrate extractor issues:
  - Sometimes plug or provide an erratic sample
    - Newer extractors seem to be much better than twenty or thirty years ago
  - Sample cools, making full temperature compensation more important than it is for an inline probe

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## Control Strategies

- Ultimate target is terminal pH
- pH meter at beginning of stage
- Simple PID control
- Some mills that cannot maintain a reliable inlet pH measurement ratio the NaOH or $H_2SO_4$ to $ClO_2$

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## Conclusions

- pH has a large effect on $ClO_2$ bleaching
- pH meters are very common in industry but are also relatively complex. A number of issues must be considered:
  - Design
  - Installation requirements
  - Calibration
  - Process conditions & maintenance
  - Troubleshooting & diagnostics
  - Replacement frequency
- There is a wide range of pH control performance across the industry

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# Questions ??

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