Tips and Tools for the 21st Century W/WW Process Monitor

Maryland Center for Environmental Training
301-934-7500
info@mcet.org
www.mcet.org

Tips and Tools for 21st Century Water/Wastewater Process Monitoring

7 contact hours
9 CC10 hours

To maintain the water/wastewater treatment process at peak operational performance, operators can effectively utilize simplified on-site monitoring tools and techniques. This interactive course examines reduction/oxidation (redox) and simple alkalinity monitoring as tools that enable the operator to assess current operational conditions, identify problem areas, and make operational changes. This course also covers simplified monitoring methods for nutrient measurements and residuals measurement such as fluoride, pH, and dissolved oxygen.

1. Describe reduction/oxidation and simple alkalinity monitoring in detail;
2. Identify other simplified monitoring methods for nutrient measurements;
3. Demonstrate monitoring method for residuals such as fluoride, pH, and dissolved oxygen.

A) Workshop objectives (45 Minutes)

1) Simply monitoring of water/wastewater process
2) Resource conservation
3) Better process operations

B) Simplified techniques

1) Oxidation Reduction Potential (ORP) (60 Minutes)
2) Alkalinity monitoring
3) Simplified DO
4) Simplified Nutrient monitoring
5) Other simplified tests

C) Oxidation Reduction Potential ORP (120 Minutes

1) Definitions
2) Demonstrations
3) Reference
4) Applications in Water/wastewater processes
5) Verifications
6) Case histories

D) Alkalinity Monitoring (120 Minutes)

1) Definition
2) Measurement demonstrations
3) Reference
4) Applications in Water/Wastewater Processes
5) Verifications
6) Case Histories

E) Other simplified process monitoring tools (60 Minutes)

1) DO measurements
2) Simplified Nutrient measurements
3) Simplified Fluoride measurements

F) Conclusions, Q & A (15 Minutes)

Tips & Tools for the 21st Century Water/Wastewater Process Monitor

Simple Operations Monitoring Tools

Mike Harrington

ORP

Contact Info, Mike Harrington

- cmhco@verizon.net
- 410-739-2331, Cell
- 410-928-3591, Office

Objectives

- Simplify – Simplify - Simplify
- Avoid a potential catastrophic event
- Save some time
- The KISS principle really does apply here!
- Manual control or manual over-ride is still a valid control option.
- We don't necessarily need "Rocket-Science" to manage our processes…all the time

Questions to consider????

- In your opinion, what's the most important simple process control measurement an operator can run?
- What's the second?
- What's the third?
- T or F, My chemical supplier always delivers the same consistent product….upon every delivery?
- T or F, I always VERIFY every chemical delivered to my facility?

Questions to consider???

- Name a compound that expands when heated and when frozen?
- At what temperature is that compound most dense?
- How many of you operators like math?
- In an Activated Sludge facility, what percent (%) of your bugs capacity to do work is lost if the wastewater temperature drops 10ºC

Applications

- Water
- Wastewater
- Industrial Wastewater

What Kind of Tools?

- Redox Monitoring
- Alkalinity Monitoring
- Simplified Nutrient Monitoring
- Fluoride Monitoring

REDOX

Redox?

- What is Redox?
- Redox measurements?
  - Apparatus?
- Verification?
- Applications?

Why Redox?

- Reduce process monitoring
- Simplify monitoring
- Chemical test reagent cost
- Reagent disposal costs
- Time-saver

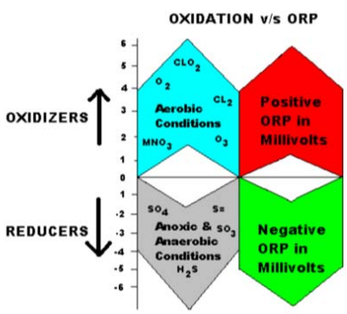
Transfers of Electrons Thru

- Microrganism destruction
- Enzyme destruction
- Nutrient removal
- Sludge digestion

What is REDOX(ORP)

- Oxidation Reduction Potential is…………
- *A measurement of a waters capacity to oxidize and reduce*

Redox v/s Oxidation



Chlorination/Dissolved Oxygen

- Steal electrons from
  - Organics
  - Microrganisms
- Seek to balance chemistry

Down to Earth Examples

- In the stock market, someone purchases a share of stock, someone else must sell that share
- Rust - Iron is oxidized, Oxygen is reduced
- Fire - Carbon & Hydrogen oxidized, Oxygen reduced

Redox Measurement

- Colorimetric
  - Subject to errors
- Electrometric
  - Metal v/s chemical
  - Generates millivolts

Redox Electrode

Seven Deadly Sins of Probe and Meter Measurements

- Probe /meter selection
- Proper filling solutions
- Probe storage errors
- Limiting ions and demand in dilution waters
- Infrequent calibrations
- Forgetting temperature compensation
- Reused standards/buffers

Portable Redox Meter

Generates Millivolts

- Reaction w/ probe metal
- Compared to reference voltage
- changing oxidized state from one another
- Electron transfer
- Form of battery

KEY ORP POINTS

- All measurements are taken on-site
- All measurements in Millivolts (mV)
- ORP probes not typically temperature compensated.
- May take longer time window to get stabilized readings
- Expect more probe maintenance than w/ typical pH probes.

Field Redox Measures

Field Redox Measures

- Probe should be suspended about 2' deep in Anoxic Zone

Field Redox Measures

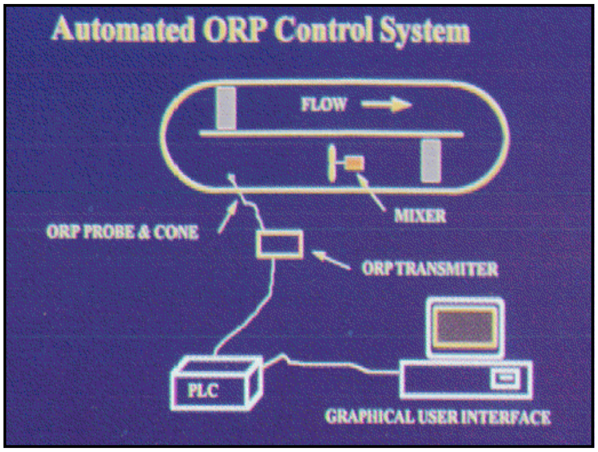
Probe 2' deep

Process REDOX

- Continuous monitoring
- Insitu installation
- Computer interface
- Process Control

Process Applications

- Collection system monitoring
- Nitrification/Denitrification
- Phosphorus removal
- Toxicity screening
- Chlorination/Dechlorination
- Sludge digestion



Process Instruments

Verification/Reference

- Light's Solution
  - 453 mV @ 20 deg C
- pH buffers w/ (4&7)
  - Quinhydrone
  - 96mV @ 20C (7)
  - 170-185 mV about 7 buffer (4)

Maintenance

- Electrode cleaning
  - Chemical
  - Polishing
- Reference checks
- Meter

Wastewtr. Applic.

Disinfection

Biological Nutrient Removal (BNR)

Sludge Digestion

- Aerobic
- Anaerobic

Wastewtr Applic.

- General W/W Applications
- Odor control
- Organic Carbon Reduction
- Industrial Wastewater

Chlorination

- Process/Portable
- Indirect residual measure
- 380 - 750 mV potent.
- Demand-based (Poise)

Process Disinfection REDOX

- High purity Platinum sensor
- Probe contamination
- Reference junction
- Self-cleaning probes

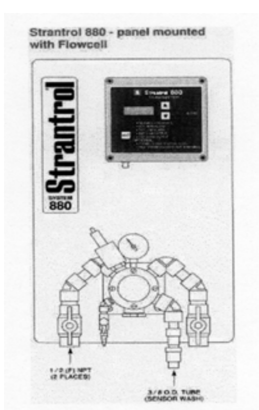
Dechlorination

- Low mV control
- Slight overdose Sulfite
- Separate sensor/controller
- Chemical conservation

Process Disinfection REDOX

- High purity Platinum sensor
- Probe contamination
- Reference junction
- Self-cleaning probes

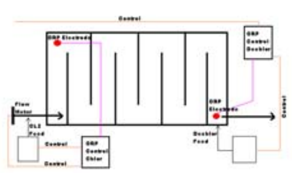
HHR REDOX Controller

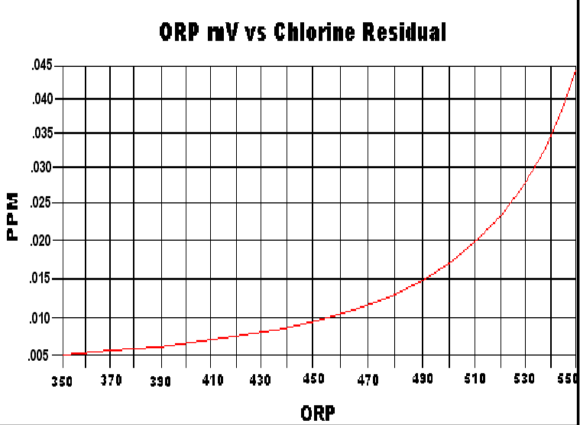


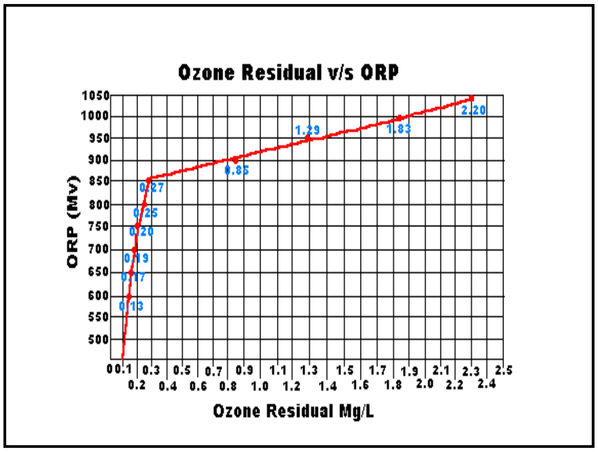
Case History, Lancaster, PA

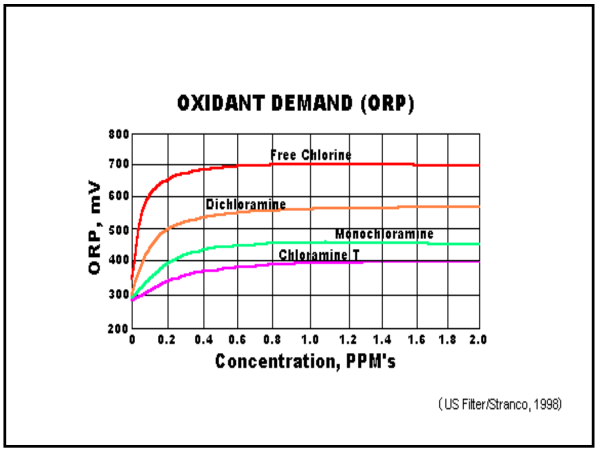
- Model 890 Stranco Unit
- Chlorination setting: 400mV
  - 2nd monitor 10 min downstream
- Dechlorination(Poise): 190mV

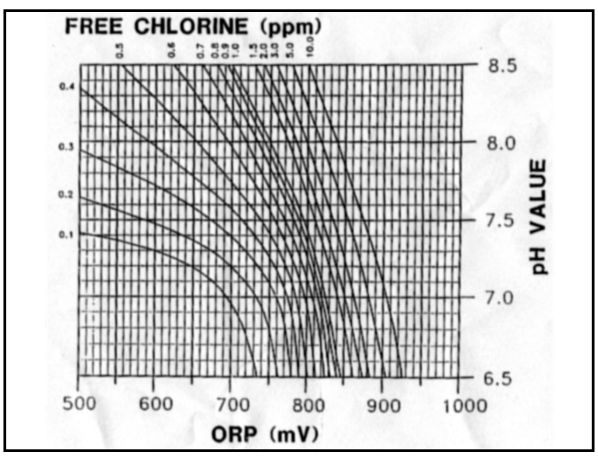
Typical Wastewater REDOX Chlor/Dechlor Configuration






Ozone Residual v/s ORP
ORP (Mv)
1050
1000
950
900
850
800
750
700
650
600
550
500
0.13
0.17
0.19
0.20
0.25
0.27
0.85
1.29
1.83
2.20
0 0.1 0.3 0.5 0.7 0.9 1.1 1.3 1.5 1.7 1.9 2.1 2.3 2.5
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4
Ozone Residual Mg/L

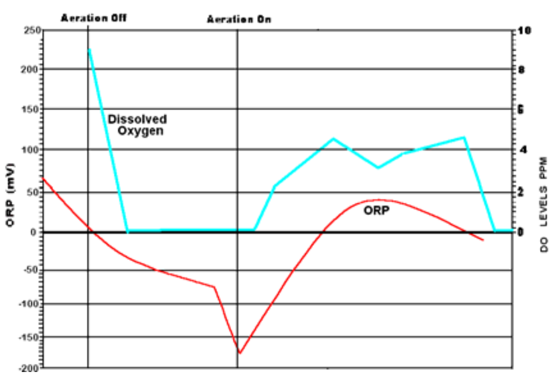

OXIDANT DEMAND (ORP)
ORP, mV
800
700
600
500
400
300
200
Free Chlorine
Dichloramine
Monochloramine
Chloramine T
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
Concentration, PPM's
(US Filter/Stranco, 1998)


FREE CHLORINE (ppm)
0.4
0.3
0.2
0.1
8.5
8.0
7.5
7.0
6.5
pH VALUE
500 600 700 800 900 1000
ORP (mV)

Phosphorus Removal

- Aerobic and Anaerobic process
  - Anerobic zone releases phosphorus (bacteria)
  - Aerobic zone absorbs (bacteria)
- Target REDOX:
  - Anaerobic Zone: -200 to -300 mV
  - Aerobic Zone: > +100 mV

Phosphorus Removal Oxidation Ditch



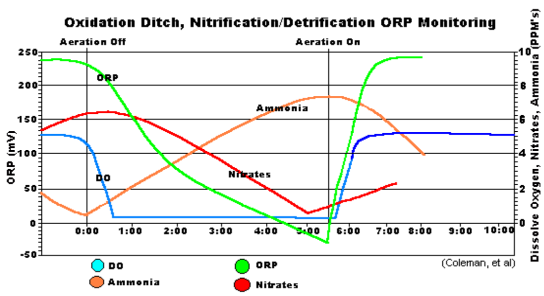
Biological Nutrient Removal

- Nitrification
  - Monitor Ammonia to Nitrate conversion
  - Oxic zone

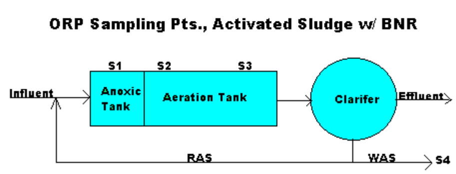
Biological Nutrient Removal

- Denitrification
  - Monitor Nitrate to Nitrogen gas conversion
  - Anoxic zone
  - Microprocessor control

BNR Applications

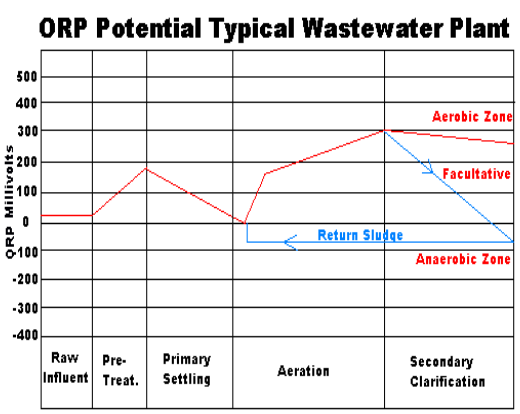


BNR REDOX Sampling

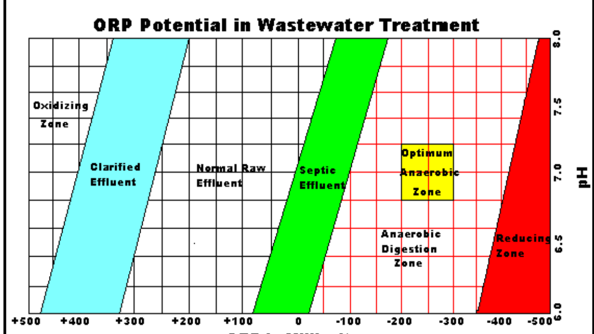


General Monitoring

- Influent monitoring(Sulfates)
- Clarifier effluent
- Aeration basin
- Trickling filter eff
- Anaerobic digestion



REDOX/pH Comparison



Toxicity Screening

- ID Ilicit Inflows
- Trace Unk. Inflows
- REDOX Varies w/ Waste Stream

Odor Control

- Oxidizers
- Control
  - Sulfides formation
  - Other odor causes
  - +250 to +500 mV potential

Anaerobic Sludge Digestion

- Negative REDOX values
- Acid formation (Volatile)
  - -50 to -250 mV potential
- Methane formation
  - -175 to -350 mV potential

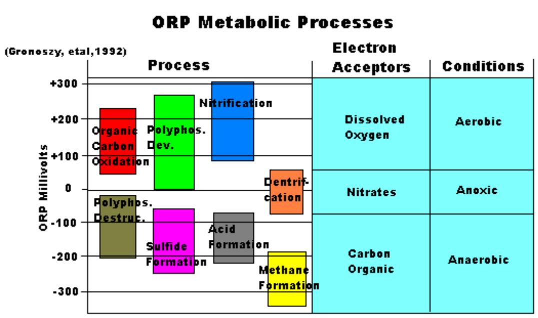
Aerobic Digestion

- Oxidize organics
- Oxygen presence
  - +50 - +250 mV potential
- Restart O2 after decant cycle

Organic Carbon Reduction

- Oxidation
- Approx. +50 - +225 mV potential

Typical REDOX Potential



Industrial Wastewater

- Metal finishing wastes
  - Cyanide destruction
    - Excess Chlorine
    - High pH
    - +300 to +600 mV potential

Industrial Wastewater

- Chromate reduction
  - Excess Sulfite
  - Low pH
  - -50 to -300 mV potential

Case Histories

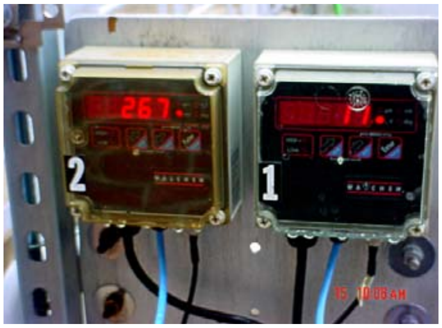
- South Berwick, ME
  - 250,000 GPD
  - SBR process
  - Process REDOX
  - +250mV range
  - Aerobic oxidation monitoring

So. Berwick, ME

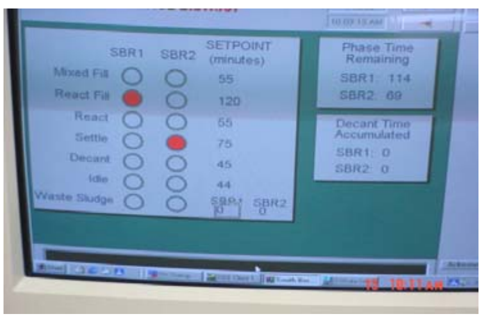
So. Berwick, ME

So. Berwick, ME

So. Berwick, ME



So. Berwick, ME



St. Clairsville, OH

- 0.1 MGD Extended air plant
- 28,000 equalization added
- Filamentous Problem
- Some redesign consideration

Page 66

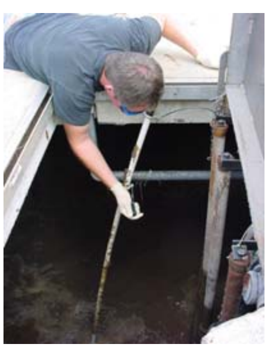
St. Clairsville, OH

Problem Resolution

- Microscopic filament Identification
- Dominant organism.. (S. Natans likes low DO)
- ORP measurements in equalization
- RAS redirected to equalization

Page 67

St. Clairsville, OH



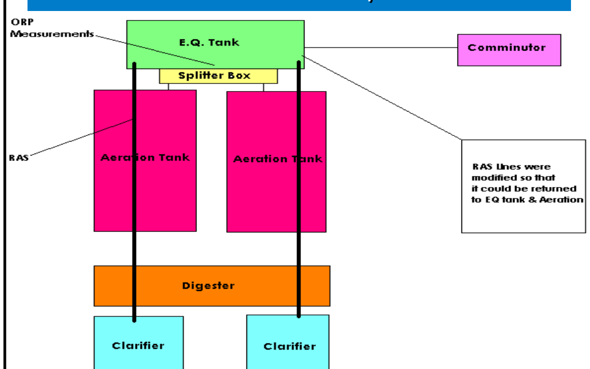
Filament Control Considerations

- ORP maintenance
- Range -50 to -100 Mv
- Controls filament growth
- Blower control to add DO

Page 68

St. Clairsville, OH

St. Clairsville, OH



Page 69

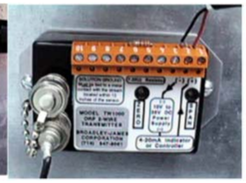
Town Of Zillah, WA

- Oxidation Ditch
- BNR Process REDOX
  - -50 - +50mV, Anoxic
  - +250 to +300mV, Oxic

BNR Control - Off

DO/REDOX

Indication & Control



BNR Control - On

ALKALINITY

Alkalinity - Definition

- Ability of water to resist change in pH
- Buffering capacity
- Results as CaCo3

Benefits?

- Immediate results
- Better process control
- Potential to save on electrical costs
- Predictability

Types of Alkalinity

- Total Alkalinity
  - Carbonate
  - Bicarbonate
  - Hydroxide
  - Other minor forms,(Borate, Phosphates)

Why Monitor Alkalinity?

- Direct/Immediate Indicator
- Predictable
- Real time, right now results

Monitoring Methods

- Onsite
- Portable/insitu
- On-line process
  - Monitor
  - Control

Alkalinity

- Key parameter in both:
  - Water
  - Wastewater
  - Simple monitoring test

Water

- Treatment processes need Alk
  - Lime-Softening
- Certain treatment chemicals use up Alk
  - Alum
  - Ferric Chloride

Lead/Copper Rules

- Alkalinity
  - Key water quality parameter
  - Required measurement
  - Minimize leeching

Corrosion Control

- Major element of corrosion Indexes
  - Langelier
  - Aggressive
  - Driving Force, etc
- Depositing waters

Potable Waters (well, Surface)

- Low raw Alkalinity
- Low pH's common

Water Treatment

- Raise pH & Alkalinity
  - Caustic
  - Soda Ash
  - Lime
  - Calcite

Alkalinity Chemicals

pH adjustment chemical	Typical feed rate	1 mg/L adds ___mg/L alkalinity[a]	Equipment required
Lime, as $Ca(OH)_2$	1–20 mg/L (8–170 lb/MG)	1.35	Quicklime-slaker, hydrated lime-solution tank, and feed pump with erosion-resistant lining as eductor
Caustic soda, NaOH (50% solution)	1–29 mg/L (8–170 lb/MG)	1.25	Proportioning pump or rotameter
Soda ash, Na_2CO_3	1–40 mg/L (8–350 lb/MG)	0.94	Solution tank, proportioning pump, or rotameter
Sodium bicarbonate, $NaHCO_3$	5–30 mg/L (40–250 lb/MG)	0.59	Solution tank, proportioning pump, or rotameter

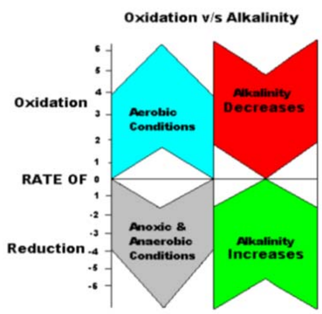
[a]Caustic soda and lime add only hydroxide alkalinity. Soda ash and sodium bicarbonate add carbonate or bicarbonate alkalinity, depending on pH.

Wastewater

Rate of change in Alkalinity corresponds to the biological reaction

- Aerobic reactions
  - Alkalinity decrease
- Anoxic & Anaerobic reactions
  - Alkalinity Increase

Oxidation v/s Alkalinity



Wastewater

- Measuring Alk changes
  - Indicates rate of biological reactions
- Biological reactions change Alkalinity
  - @ a predictable rate

DO v/s Alkalinity

- DO measure of residual
- Oxygen demand met
- Excess DO provides no additonal Info

Alkalinity v/s DO

- Indicates rate of oxidation
- Independent of other factors
- Direct relationship(Nitrification)

Ball Park Parameters

- Calculate Ammonia v/s Alkalinity Demand
- Effluent - > 50 -70 ppm
- Raw infu - 200 ppm

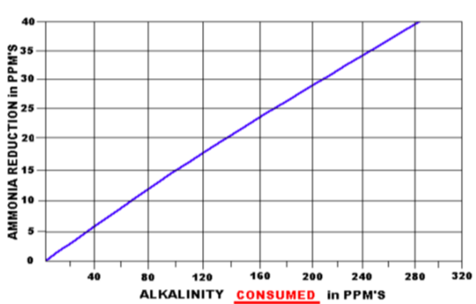
Alkalinity measurements

- Essentially Bicarbonate
- Real time
- Predictable

Bio. Nutr. Remov.(BNR)

- Nitrification(Aerobic)
  - For every ppm of Ammonia
  - Uses 2 Bicarb for every Ammonia converted
  - Uses 7.1 ppm Alk.

Nitrifications v/s Alkalinity



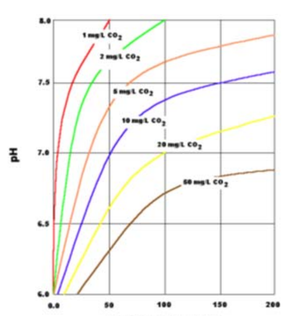
Bio. Nutr. Remov.(BNR)

- Denitrification(Anoxic)
  - 1 bicarb produced for every Nitrate converted
  - For every PPM of Nitrates
  - Adds 3.6ppm Alk.

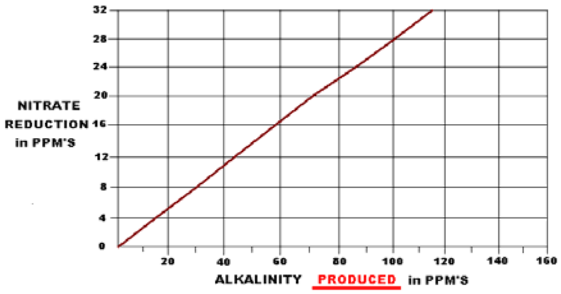
ALK V/S CO2

- Buildup thru bacterial actions
- Change pH
- O2 drives off CO2
- Raises pH

CO2 Concent. @ pH/ALK



Denitrification v/s Alkalinity



Sulfate Reduction(Anaerobic)

- 5 Bicarbs produced for Ammonia produced
- For every PPM of Ammonia
- Adds 17.86 PPM of Alkalinity

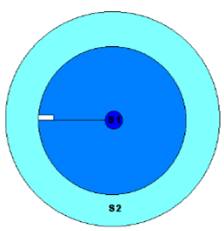
Predictability

- Rate of Alkalinity loss predicts Nitrification rate
- Rate of Alkalinity gain predicts Anoxic/Anaerobic rate
- Alkalinity rate gain difference
  - Distinquish between anaerobic/septic conditions

Typical Sampling Points

- Primary Clarifier
  - Influent
  - Effluent

Sampling Pts



Sampling Points Cont'd

- Aeration Basin
  - Mix basin
  - #1 Effluent
  - #2 Effluent

Sampling Points, Cont'd

- Secondary Clarifier
  - Influent
  - Effluent

Sampling Points, Cont'd

- Digesters
  - #1
  - #2
  - #3

Alkalinity & Predictability

- Select sampling points
- Run Alkalinity test
- Record results
- Gather historic data

Primary/Secondary Clarifiers

- Influent v/s effluent testing
- About the same at both pts
- Increase in Alk
  - Potential Anaerobic/Anoxic
  - Reduce solid retention time

Aeration Basin

- Compare Alk @ all Pts
- If Alk is < expected
  - Nitrification insufficient
  - Increase air
  - Adjust
    - MLSS
    - Inhibitors
    - RAS/WAS

Aeration Basin

- If Alk > than expected
  - Too rapid Nitrification
  - Low buffering
  - Low pH
  - "Pinfloc"

Aerobic Digestion(On)

- Excess DO
  - Limits buffering
  - Lowers pH

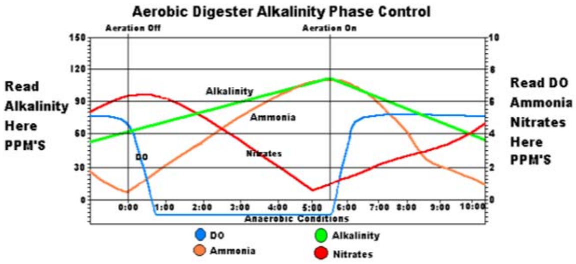
Aerobic Digestion(Off)

- Uses up Residual DO
- Reduces Nitrates
- Adds Alkalinity
- Watch septicity

Aerobic/Anoxic Phasing

- Controls air on/off cycles
- Sets control points for Alkalinity
- Precise control
  - Decant cycle
  - Bio activity

Aerobic Digester Control



Alkalinity Measurements

- Color Endpt. Titration
- Mtr. Endpt Titration
- Direct Measure via pH Mtr.

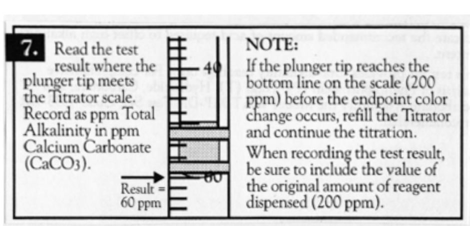
LaMotte

- Color endpt. titration
- Simple field kit
- Quick/Inexpensive
- Accurate results

Measurement

Measurement

Results Reading



7. Read the test result where the plunger tip meets the Titrator scale. Record as ppm Total Alkalinity in ppm Calcium Carbonate ($CaCO_3$).

NOTE:

If the plunger tip reaches the bottom line on the scale (200 ppm) before the endpoint color change occurs, refill the Titrator and continue the titration.

When recording the test result, be sure to include the value of the original amount of reagent dispensed (200 ppm).

pH Mtr. Titration

- Cal. pH mtr.
- Titrate Sample w/ acid
- Endpoint Titration
- Ideal for wastewaters

pH Mtr. Titration

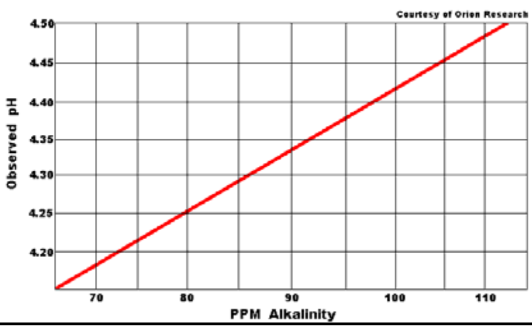
- "P" Alkalinity pH 8.3
  - Hydroxide & 1/2 Carbonate
- "M" Alkalinity pH 4.5
  - Remaining Carbonate/Total

Orion

- 2 -step Total Alk./pH
- Solids - no problem
- Quick/inexpensive

Direct Measurements

pH to Alkalinity



Process Alk Measures

- Timed auto sampling
- Reagent Injection
- Colormetric Analysis
- Digital Interface/Computer control

Process Alk Analyzer

Results Verification

- Standards
- Standard addition
- Titrant Standardization

Two Rivers WWTP, (WI)

Case History

Two Rivers WWTP (WI)

- Raw influent Alk. - 220 PPM
- Ferric Chloride addition
  - 25 - 30 PPM Alk Demand

Two Rivers WWTP (WI)

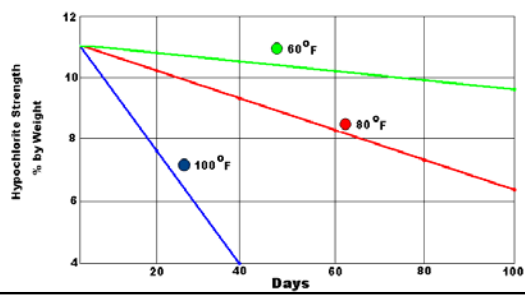
- Average Raw Ammonia
  - 20 PPM
  - requires 145 PPM Alkalinity
- Residual of 40 - 50 PPM
  - Maintains Effluent pH

Simplified, Low-cost, On-site Monitoring

Simplified On-site Tests

- DO
- pH
- Ammonia
- Nitrate
- Nitrites
- Phosphorus
- Specific Gravity
- Hypochlorite
- Bleach
- Caustic
- Acid
- Peroxide
- Permanganate
- Leak Detection

Chemical Decay Rate Chart



Chemical Strength - How?

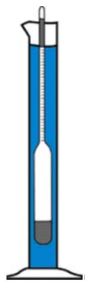
Refractometer

Hydrometer

Chemical

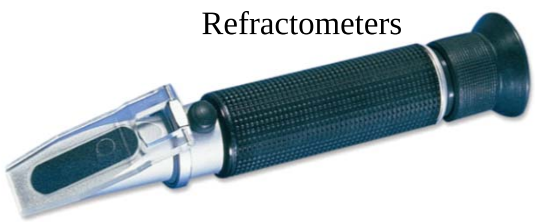
Chemical Strength

Hydrometers

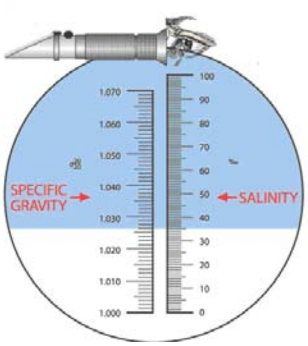


Specific Gravity Measurements

Refractometers



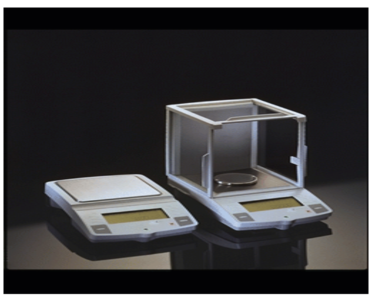
Reading A Refractometer



Specific Gravity by Weight

- 10 mL sample in a weighing bottle
- Analytical weight measurement to 4 decimals places
- Divide the measured weight by 10
- Result represents Specific Gravity
- Convert to % available Chlorine
- ***<u>Note: This method can used to measure SG of any liquid chemical</u>***

Balances



Specific Gravity Limitations

- Other components of hypochlorite “add” to SG
  - – Sodium chloride concentration
  - – Caustic concentration- excess present
  - – Amount of Sodium Chlorate present
  - – Amount of available chlorine
  - – Temperature compensation of the measuring apparatus.
    - Most measurement taken at 20°C

Conversions

TABLE II

SODIUM HYPOCHLORITE CONCENTRATIONS vs. SPECIFIC GRAVITY*

Trade %	gpl	wt. % NaOCl	SP.GR @ 20° C
1.0	10.0	1.03	1.020
1.5	15.0	1.53	1.027
2.0	20.0	2.03	1.034
2.5	25.0	2.52	1.041
3.0	30.0	3.01	1.048
3.5	35.0	3.48	1.055
4.0	40.0	3.95	1.062
4.5	45.0	4.42	1.069
5.0	50.0	4.88	1.076
5.5	55.0	5.33	1.083
6.0	60.0	5.78	1.089

Chemical Tests

Chemical Tests Methods

- Hypochlorite/Bleach
- Hydrogen Peroxide
- Potassium Permanganate
- Acids
- Caustics

Monitoring for

- Nutrients
- Corrosion Control
- Fluoride residual
- Aeration process control
- Leak detection
- Hypochlorite strength

Nutrient Monitoring Objectives

- Biological Nutrient Removal (BNR) process.
- Optimize peak performance of the three distinct biological processes.
- Response to changing conditions
- Results are for monitoring ONLY!

Background, (Review)

- Nitrification - conversion. Ammonia to Nitrites
- Denitrification - Conversion of Nitrates under anoxic conditions (not Septic) to Nitrogen gas via temperature sensitive bacteria using organic matter as food source, (or other carbon source)

Reduction Byproducts

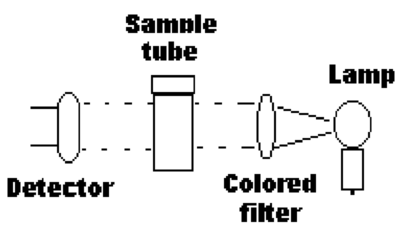
- Nitrification/Denitrification process will effect some key water quality parameters:
  - pH
    - Alkalinity
    - Ammonia
    - Nitrites
    - Nitrates

Simplified Testing Protocol

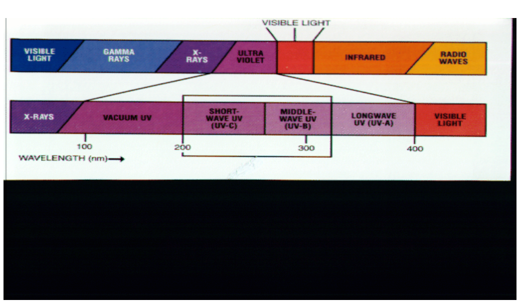
- pH - meter & probe
- Alkalinity - Titration
- Ammonia - Colorimetric
- Nitrates - Colorimetric
- Nitrites - Colorimetric

Colorimeters

Colorimeter Design



Light Spectrum



Ammonia Testing, Typical

Nitrates Testing, Typical

Seven Deadly Sins of Colorimetric Testing

- Glassware errors
- Battery replacement
- Reagent systems shelf-life
- Colorimeter chamber issues
- Standards (primary versus secondary)
- Chlorine Demand Free Dilution Waters
- Blanking (sample versus reagent)

Glassware Issues(10)

- Reagent System Staining
- Cleanliness
- Scratches
- Variability between different pieces of glassware
- Glassware variability in a single cuvette

Residuals Testing(10)

- Inspect glassware for scratches and cleanliness routinely.
- Clean glassware regularly
- Replace glassware
- Watch for variability
- Use matched pairs where available.

pH Measurements, Current

- Glass sensitive probe
- Wet Storage
- Freq Calibrations
- Analog
- Reading drift
- 1000's probe choices

Next Generation pH Meter

- Compact
- Micro-chip Tech.
- Dry storage
- Water-proof
- Liquid/solids meas.
- Low-cost

Compact pH

Digital pH

Simple Dissolved Oxygen Monitoring

Common Meter Technology

- Warmups
- Membrane replac.
- Air Sat. Cal.
- Variables comp.
  - Salinity
  - Temp
  - Altitude
  - Barometric Press.
- Expensive

21st Century Technology

- Polarographic DO
  - Waterproof housings
  - No warmup time
  - Auto air cal.
  - Cartridge membranes
  - Long battery life
  - Weighted probe
  - Auto variables compensa
  - Low-cost
- No Membrane Electrode
- Luminescence Technology
  - Hach LDO

YSI 550 Series Membrane Polarographic Meter

Luminescent Technology

- The Hach LDO™ sensor is coated with a luminescent material. Blue light from an LED is transmitted to the sensor surface where it excites the luminescent material. When the luminescent material relaxes it emits red light. This red luminescence of the sensor is proportional to the dissolved oxygen present. A red LED is incorporated into the sensor as an internal reference.

LDO Probe & Sensor

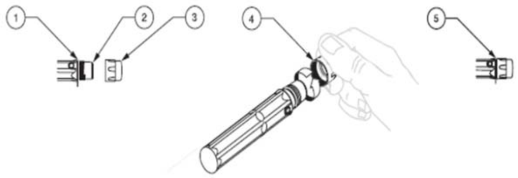
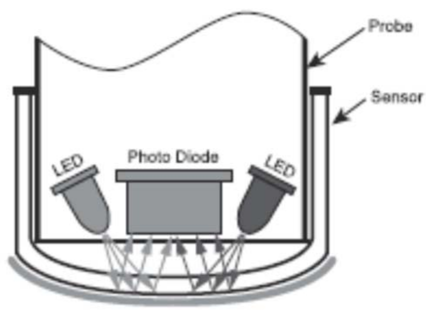


Figure 2 Installing the Sensor Cap

1 Cap Seal; Place the narrow shoulder towards probe tip.	3 Sensor cap	5 Narrow shoulder is inside the cap.
2 O-ring in place on probe tip	4 Screw sensor cap onto probe tip.	

LDO Probe Design



LDO Type Meters

Leak Detection

- Simplified Field Fluoride measurements
- Simplified Chlorine Residual measurements

Current Methods

- SPADNS colorimetric method
  - Hi-temp sample pretreatment
  - Expensive Colorimeter
  - Reagent Disposal issues

Current Methods

- Ion Specific Electrodes
  - Short-life Specific Electrode
  - Frequent calibration
  - Sample pretreatment

Simple Field Method

- No sample pretreatment
- Quick-to-run
- Visual comparative test
- Inexpensive
- Monitoring results only

Simple Fluoride Method