NEUTRALIZATION

Prepared By
Michigan Department of Environmental Quality
Operator Training and Certification Unit

NEUTRALIZATION

Addition of an acid or alkali (base) to a liquid to cause the pH of the liquid to move towards a neutral pH of 7.0.

ACID

Adds Hydrogen Ions

H^+

Hydrochloric Acid

$$HCl \rightarrow H^+ + Cl^-$$

BASE

Adds Hydroxyl Ions

OH^-

Sodium Hydroxide

$$NaOH \rightarrow Na^+ + OH^-$$

Acid + Base = ?

$H^+ + OH^- \rightarrow H_2O$

$HCl + NaOH \rightarrow H_2O + NaCl$ + energy

acid + base → water + salt + heat

NEUTRAL

How to Measure Strength of Acid

Concentration of H^+

mg / L

or

moles / L

Typical Value

0.000001 moles/L

1×10^{-6} moles/L

pH

$$pH = -\log [H^+]$$

$$pH = -\log (1 \times 10^{-6})$$

$$pH = -(\log 1 + \log 10^{-6})$$

$$pH = -(0 + (-6))$$

$$pH = -(-6)$$

$$pH = 6$$

Concentration of H^+

moles / L

Typical Value

0.000001 moles/L

1×10^{-6} moles/L

pH = 6.0

Liquid Water Separates Slightly into Ions

$$H_2O \rightarrow H^+ + OH^-$$

H^+ conc. = 0.0000001008 grams/Liter

0.0000001008 grams/Liter X 1 mole/1.008 gram =

0.0000001 mole/Liter

1×10^{-7} molar

$pH = -\log [H^+]$

$= -\log [1 \times 10^{-7}]$

pH = 7

$$H_2O \rightarrow H^+ + OH^-$$

$$[H^+] = [OH^-]$$

Neutral

$$pH = 7.0$$

$$[H^+] \times [OH^-] = \text{constant} = 10^{-14}$$

$$pH + pOH = 14$$

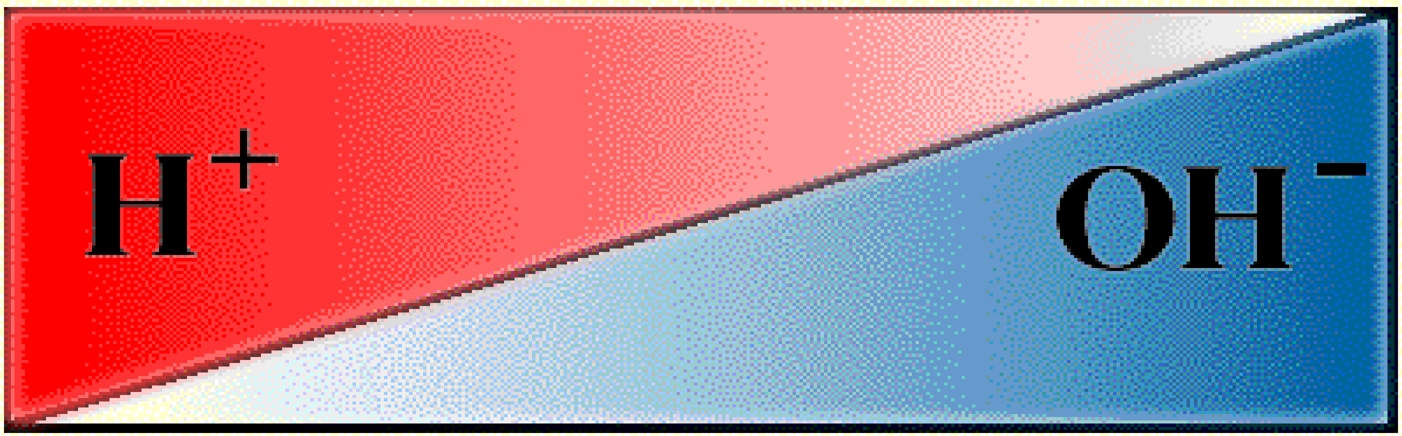
Entire pH range from 0 to 14

pH Scale

Increasing Acidity ← NEUTRAL → Increasing Basicity

pH = 0 4 7 10 14

$[H^+]$ = 10^{0} 10^{-4} 10^{-7} 10^{-10} 10^{-14}



$[OH^-]$= 10^{-14} 10^{-10} 10^{-7} 10^{-4} 10^{0}

5% Sulfuric Acid

Lemon juice

Orange juice

milk
water
Body fluids
Egg white

Milk of magnesia

Milk of lime

4% caustic soda

Increasing Acidity

Neutral

Increasing Alkalinity

pH	H^+	OH^-
0	1×10^{0}	1×10^{-14}
1	1×10^{-1}	1×10^{-13}
2	1×10^{-2}	1×10^{-12}
3	1×10^{-3}	1×10^{-11}
4	1×10^{-4}	1×10^{-10}
5	1×10^{-5}	1×10^{-9}
6	1×10^{-6}	1×10^{-8}
7	1×10^{-7}	1×10^{-7}
8	1×10^{-8}	1×10^{-6}
9	1×10^{-9}	1×10^{-5}
10	1×10^{-10}	1 X
11	1×10^{-11}	1×10^{-3}
12	1×10^{-12}	1 X
13	1×10^{-13}	1 X
14	1×10^{-14}	1 X

pH Scale

Logarithmic Scale

Each unit Change is a
10 Times
Change in Concentration

Two Unit Change is a 10 X10 Change
or 100 Times Change

Three Unit Change is a 10 X 10 X10 Change
or 1000 Times Change

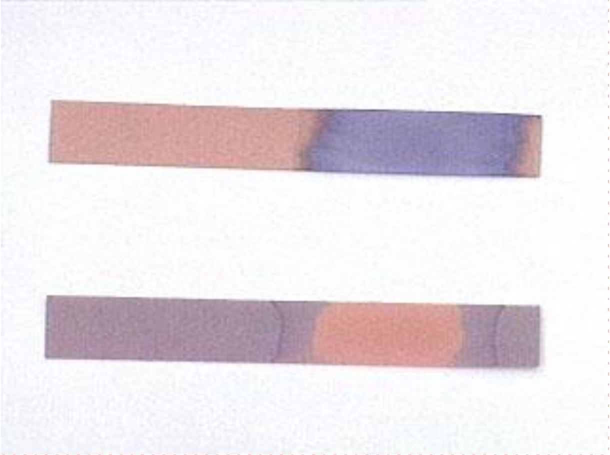
Importance Of pH

1. Lab Analyses
2. Corrosion Control
3. Cyanide Treatment
4. Precipitation Processes
5. Biological Systems
   a. WWTP's
   b. Streams

MEASUREMENT OF pH

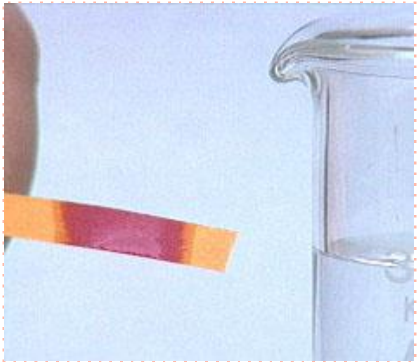
Rough Checks

~~Taste~~



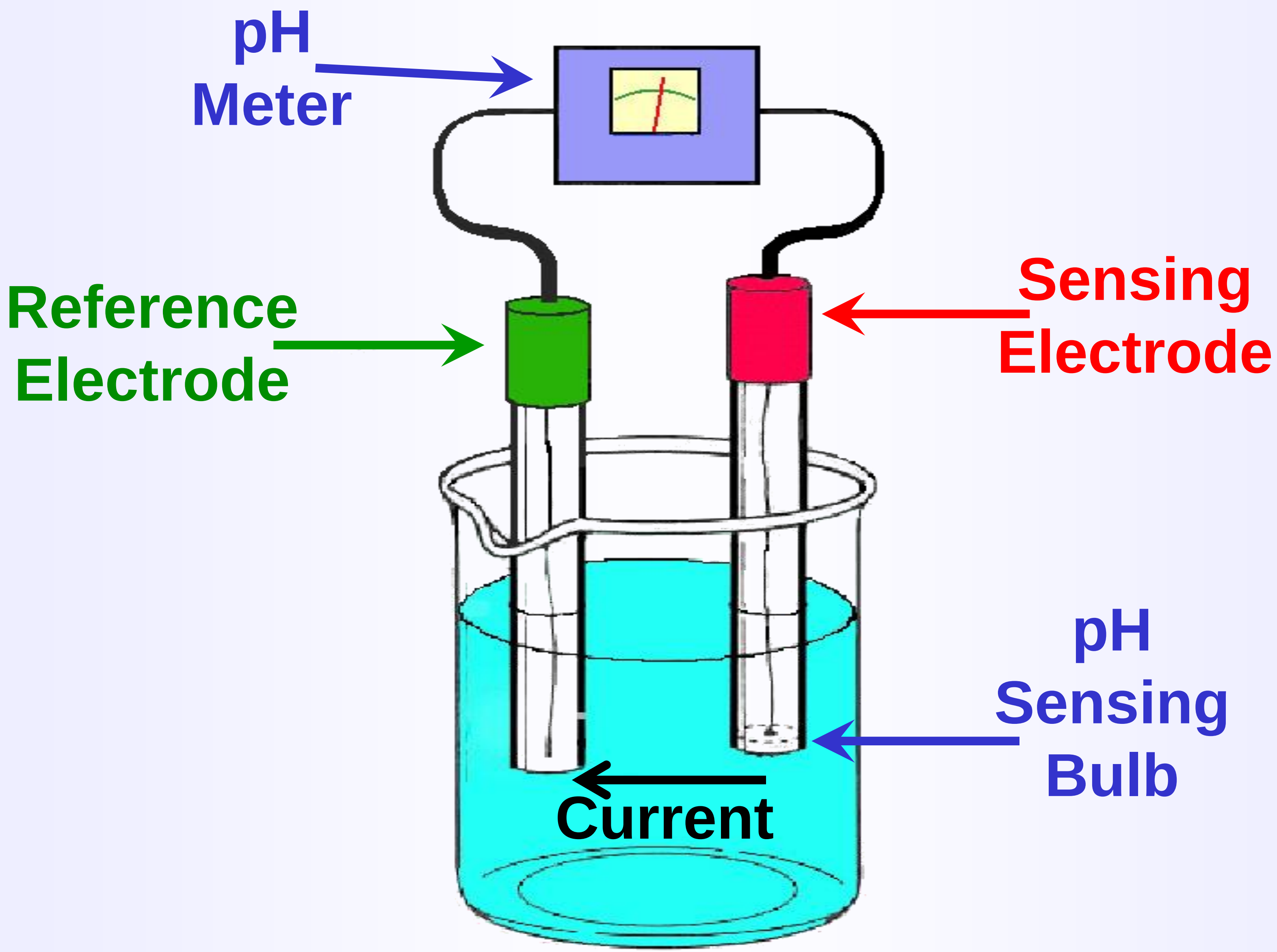
L er

Co ors



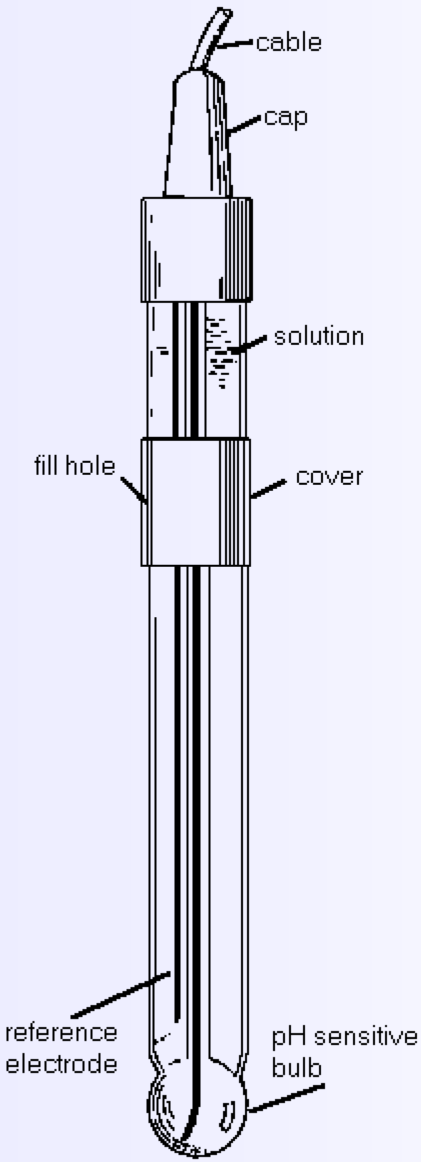
Not f rting

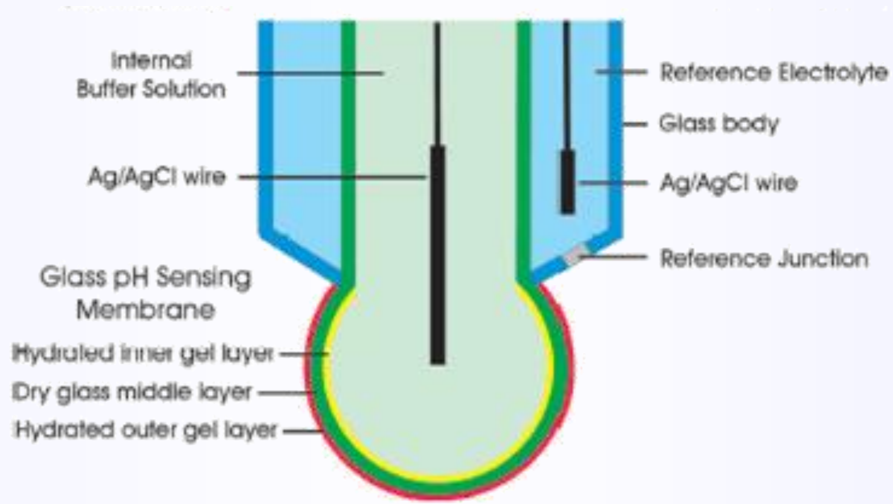
Electrometric or Potentiometric Method



Electrometric or Potentiometric Method

Combination Electrode





Electrometric or Potentiometric Method

MEASUREMENT OF pH

Procedure

Standard Methods "In each case follow manufacturer's instructions for pH meter and for storage and preparation of electrodes for use."

Meter Calibration

- two pt. Calibration
- order of calibration important for analog meters
- stirring required

Measurement of pH

PROCEDURE

1. Adjust or Compensate for Temperature.
2. Rinse Electrode(s).
3. Calibrate in Buffer at pH 7.0.
   (gentle mixing for all readings)
4. Rinse Electrode(s).
5. Immerse Electrode(s) in Second Buffer.
   A. 3 pH Units Different from First.
   B. Bracket Expected Sample pH.
6. Adjust Meter to Proper Reading
   using “Slope” Control.
7. Rinse Electrode(s) and Read Sample.
8. Properly Store Electrode(s).

MEASUREMENT OF pH

Sample Measurement

- use auto temp compensation if available
- bring samples close to room temp.
- stirring required

Electrode Maintenance ---

Probably the largest source of errors in determining pH.

MEASUREMENT OF pH

Some Things to Watch For:

- Physical condition of electrodes
- KCl precipitation in reference elec.
- KCl liquid level too low
- Fill hole of reference electrode should not be covered while making measurement
- Ability to calibrate with 2 standards
- Slope of electrode too low
  should change 59 mV per pH unit

Need to check slope often to assure proper operation of electrodes.

Checking <u>Slope</u> of pH Electrodes

The <u>Slope</u> of an Electrode
is the <u>millivolt Change</u> that is seen
for a <u>Ten Times</u> Change
in Concentration.

Checking Slope of pH Electrodes

1. Set meter to read millivolts (mv).
2. Rinse electrode(s) and immerse in fresh pH 7.0 buffer.
3. Record mv reading.
4. Rinse electrode(s) and immerse in either pH 4.0 or pH 10.0 buffer.
5. Record new mv reading.
6. Subtract the lower mv reading from the higher mv reading.

EXAMPLES:

180	170	- 5
(-) 5	(-) - 5	(-) -180
175	175	175

7. Divide the difference in mv readings by the difference in pH readings.

EXAMPLES:

	pH 10	pH 7
	(-) <u>pH 7</u>	(-) <u>pH 4</u>
	3	3

175 / 3 = 58.3 = <u>SLOPE</u>

8. The theoretical slope is 59.16. A slope greater than <u>53</u> is acceptable.

(Note: When required to enter the slope in a digital meter, be sure to assign it a negative value).

NEUTRALIZATION

Addition of an **acid** or alkali **(base)** to a liquid to cause the **pH** of the liquid to move towards a neutral pH of 7.0.

Secondary Problems Associated with Neutralization

Does Not Remove Other Contaminants (metals)

May Change Solids Removal Efficiency (precipitate)

Will Increase Dissolved Solids (salts)

May Create a Safety Hazard (cyanide)

Chemicals Used for Neutralization

Other Wastewater Flows ?

- Most Economical
- May Increase Secondary Problems
- May Complicate Further Treatment
  - Cr Reduction
  - CN Removal
  - Oil and Grease
  - Chelating Compounds

Chemicals Used for Neutralization

To REDUCE pH:

add Acid (H^+)

1. **Sulfuric Acid (H_2SO_4)**
2. **Hydrochloric Acid (HCl)**
3. **Carbon Dioxide (CO_2)**
4. **Sulfur Dioxide (SO_2)**
5. **Flue Gases**

Chemicals Used for Neutralization

To INCREASE pH:

add Base (OH^-)

1. Potassium Hydroxide (KOH)
2. Trisodium Phosphate (Na_3PO_4)
3. Sodium Carbonate - "soda ash" (Na_2CO_3)
4. Calcium Carbonate - "limestone" ($CaCO_3$)
5. Calcium Magnesium Carbonate - "dolomite" ($(Ca\text{-}Mg)CO_3$)
6. Sodium Hydroxide - "caustic soda" ($NaOH$)
7. Calcium Hydroxide - "hydrated lime" ($Ca(OH)_2$)
8. Ammonium Hydroxide (NH_4OH)
9. Magnesium Hydroxide ($Mg(OH)_2$)
10. Calcium Oxide - "quicklime" (CaO)
11. Magnesium Oxide (MgO)
12. Sodium Sulfide (Na_2S)
13. Potassium Permanganate ($KMnO_4$)

Chemicals Used for Neutralization

Commonly Used Bases:

1. Calcium Oxide - CaO
   (lime)
2. Calcium Hydroxide - $Ca(OH)_2$
   (hydrated lime)
3. Magnesium Oxide - MgO
4. Magnesium Hydroxide - $Mg(OH)_2$
5. Sodium Hydroxide - $NaOH$
   (caustic soda)

How Much Chemical To Add ?

Calculation

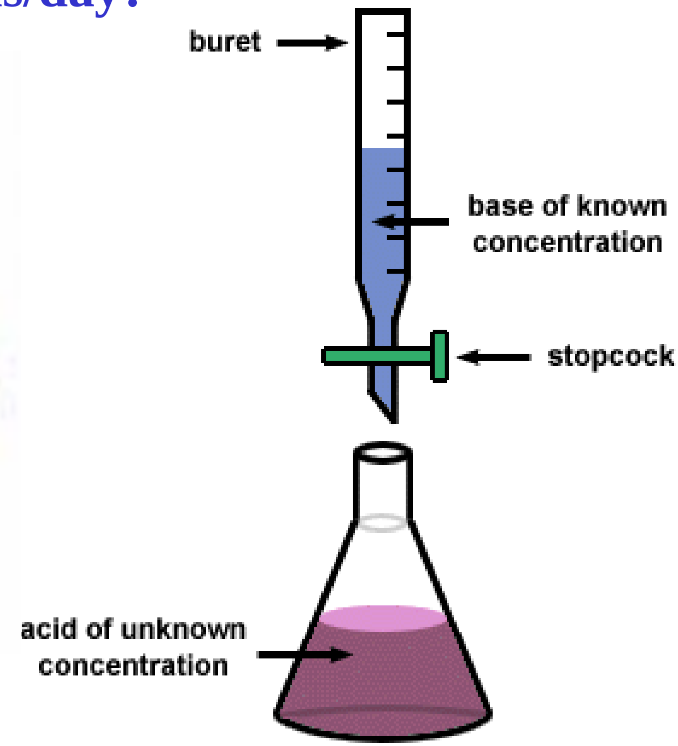
- **Difficult (logarithms)**
- **Competing Reactions (buffers)**

Titration

- **Cost Comparison**
- **Start-up**

Example Calculation

A 100 mL portion of wastewater was titrated with the chemical that will be used to neutralize the wastewater. 3.6 mL of the chemical were used. What rate should a chemical feed pump be set at in gallons/minute to neutralize the wastewater at a flow of 45,000 gallons/day?



Example Calculation

A 100 mL portion of wastewater was titrated with the chemical that will be used to neutralize the wastewater. 3.6 mL of the chemical were used. What rate should a chemical feed pump be set at in gallons/minute to neutralize the wastewater at a flow of 45,000 gallons/day?

$$\frac{\text{3.6 mL chemical}}{\text{100 mL wastewater}} \times \frac{\cancel{\text{Conversion Factor mL to Gallons}}}{\cancel{\text{Same Conversion Factor}}}$$

Example Calculation

A 100 mL portion of wastewater was titrated with the chemical that will be used to neutralize the wastewater. 3.6 mL of the chemical were used. What rate should a chemical feed pump be set at in gallons/minute to neutralize the wastewater at a flow of 45,000 gallons/day?

$$\frac{3.6 \text{ mL chemical}}{100 \text{ mL wastewater}} = \frac{3.6 \text{ gallons chemical}}{100 \text{ gallons wastewater}} = \frac{0.036 \text{ gal chemical}}{1 \text{ gallon wastewater}}$$

$$\frac{45{,}000 \text{ gal wastewater}}{\text{day}} \times \frac{0.036 \text{ gal chemical}}{\text{gal wastewater}} = \frac{1620 \text{ gal chemical}}{\text{day}}$$

$$\frac{1620 \text{ gal}}{\text{day}} \times \frac{1 \text{ day}}{1440 \text{ min}} = 1.125 \text{ gal/min}$$

Practice Problem

A 500 mL portion of wastewater was titrated with the chemical that will be used to neutralize the wastewater. 5.8 mL of the chemical were used. What rate should a chemical feed pump be set at in gallons/minute to neutralize the wastewater at a flow of 15,000 gallons/day?

Work Calculation on Separate Paper
Answers Given on Next Slide

Practice Problem

A 500 mL portion of wastewater was titrated with the chemical that will be used to neutralize the wastewater. 5.8 mL of the chemical were used. What rate should a chemical feed pump be set at in gallons/minute to neutralize the wastewater at a flow of 15,000 gallons/day?

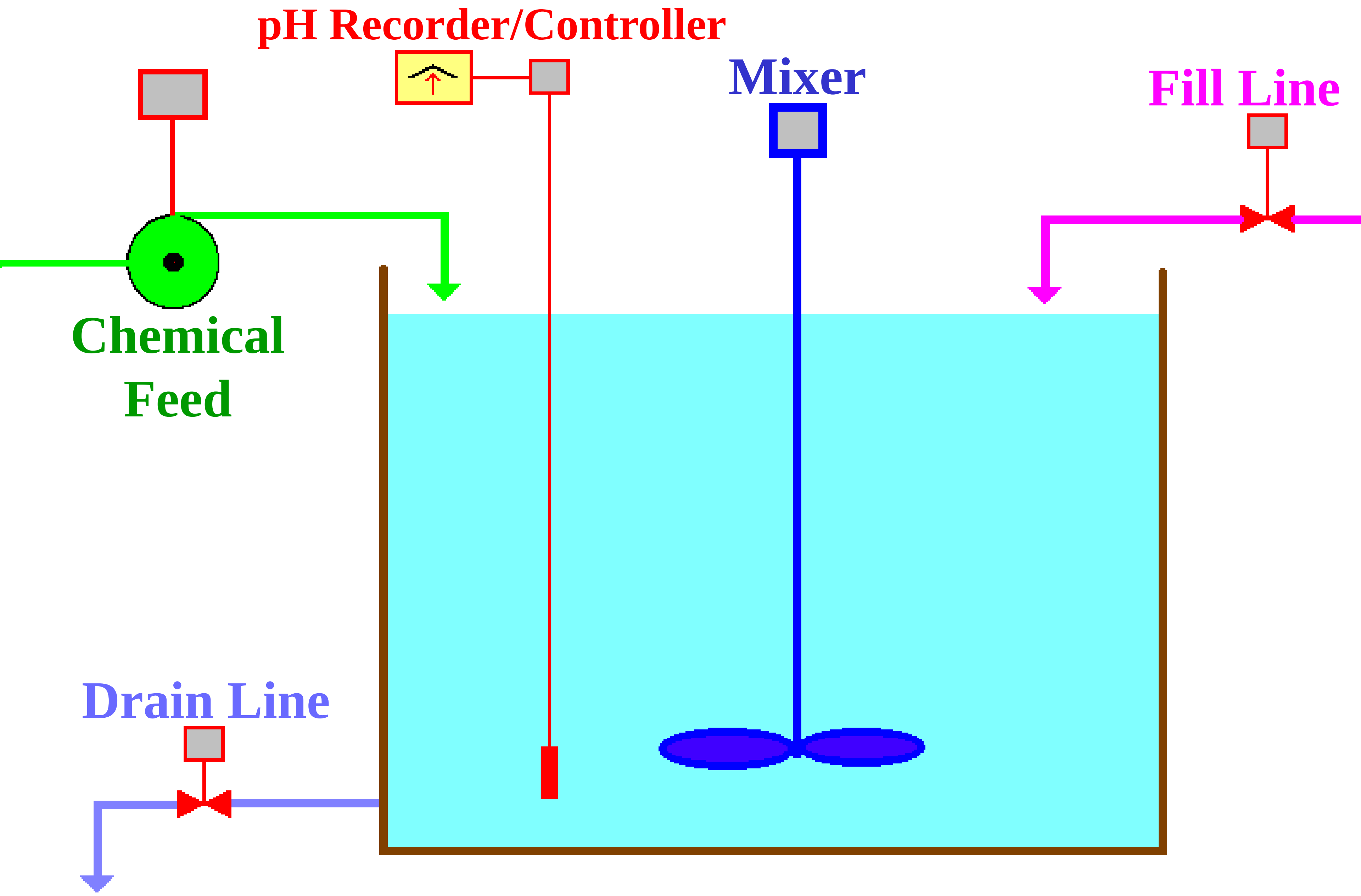
$$\frac{5.8 \text{ mL chemical}}{500 \text{ mL wastewater}} = \frac{5.8 \text{ gallons chemical}}{500 \text{ gallons wastewater}} = \frac{0.0116 \text{ gal chemical}}{1 \text{ gallon wastewater}}$$

$$\frac{15{,}000 \text{ gal wastewater}}{\text{day}} \times \frac{0.0116 \text{ gal chemical}}{\text{gal wastewater}} = \frac{174 \text{ gal chemical}}{\text{day}}$$

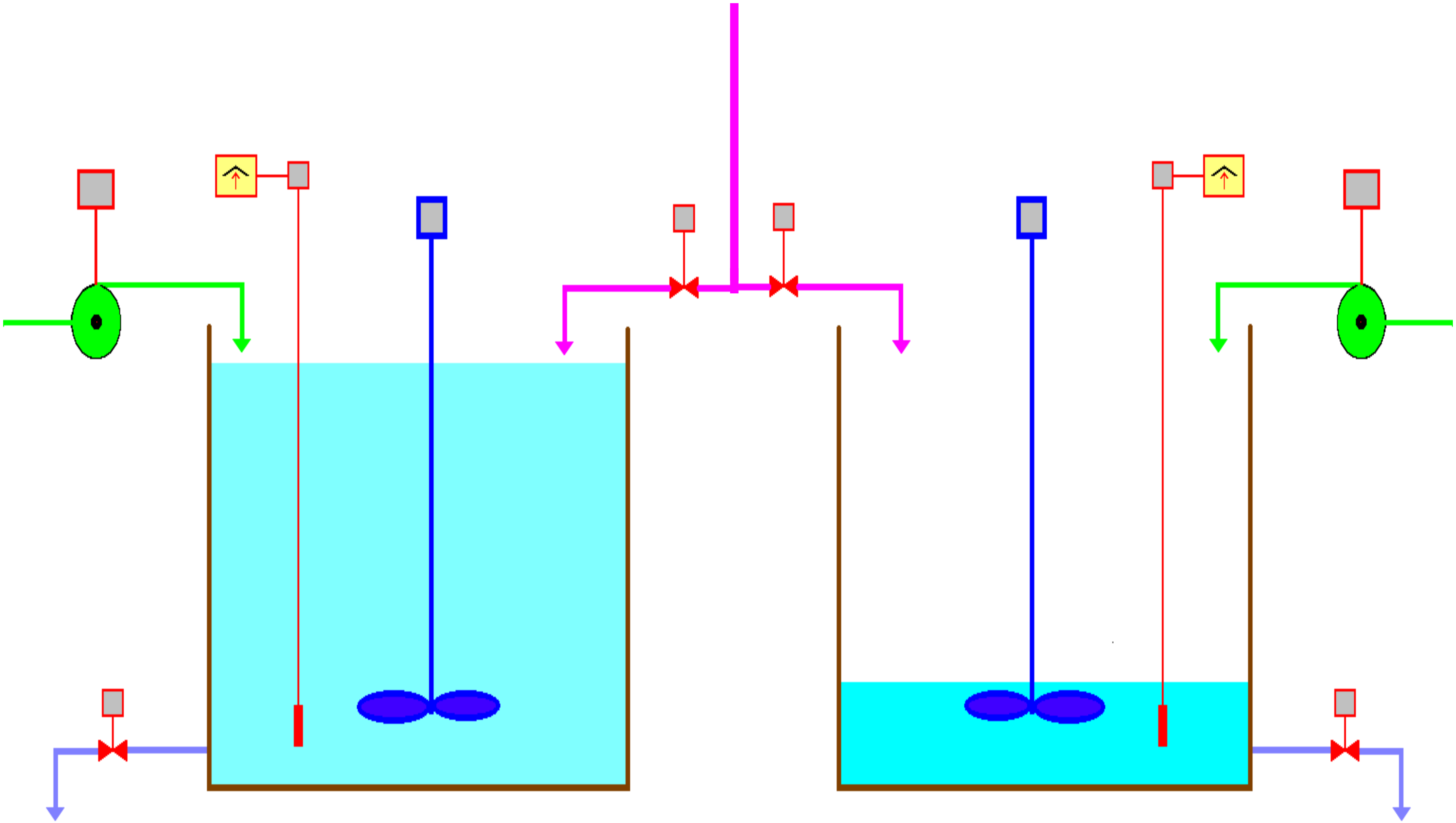
$$\frac{174 \text{ gal}}{\text{day}} \times \frac{1 \text{ day}}{1440 \text{ min}} = 0.12 \text{ gal/min}$$

$$0.12 \text{ gal/min} \times \frac{3785 \text{ mL}}{1 \text{ gal}} = 454 \text{ mL/min}$$

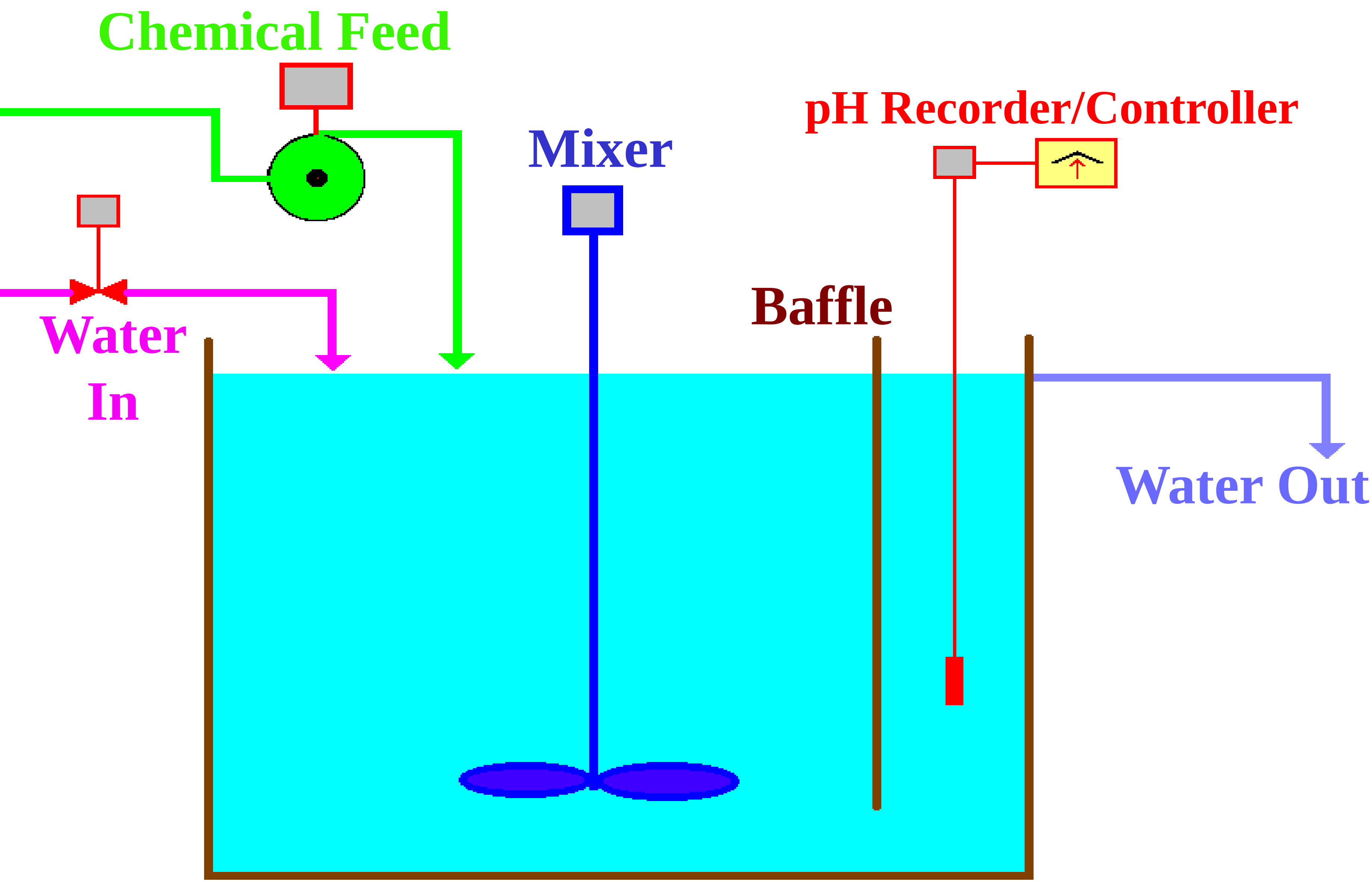
Batch Neutralization System



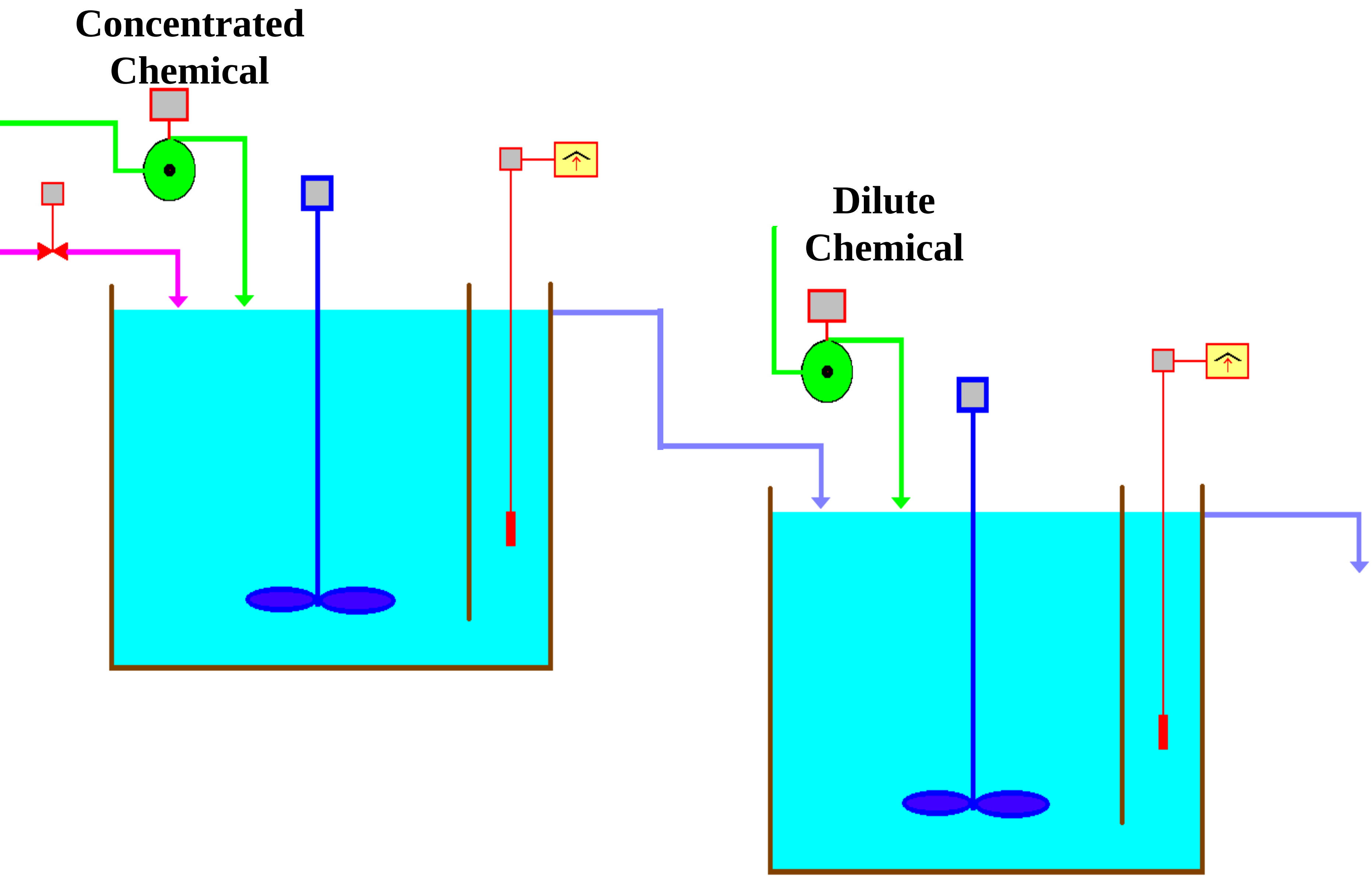
Two Tank - Batch Treatment System



Continuous Neutralization System



Continuous Neutralization System



Maintenance of Neutralization System

1. Primary sensors
   - level probes
   - pH probes
2. Chemical feed pumps
   - bearings
   - seals
3. Chemical feed controllers
4. Automatic valves
5. Mixers

Preventive Maintenance Program

Safety Concerns

Dilution

Always add Concentrated acids or bases to water, never the reverse!

Chemical Handling

storage

pumping

Hazardous Atmosphere

vapors

reactions

Emergency Procedures

splash

personal protection

spill clean-up

NEUTRALIZATION

Prepared By
Michigan Department of Environmental Quality
Operator Training and Certification Unit