# Nitrification and Denitrification

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

### Nitrogen



# Environmental And Public Health Concerns









#### Forms of Nitrogen in Wastewater



Ammonia – NH

**Oxygen Demand** 





Nitrate – NO<sub>3</sub><sup>-</sup>
Health Concern



All Are
Nutrients
(fertilizer)



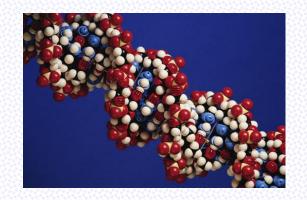


#### Forms of Nitrogen in Wastewater

#### **Organic Nitrogen**

Complex Compounds
Protein (plant & animal)
Amino Acids

etc.



Oxygen Demand Nutrient Source

### N

#### Forms of Nitrogen in Wastewater

#### Total Kjeldahl Nitrogen - "TKN"

Sum of Organic N + Ammonia

Total Inorganic Nitrogen - "TIN"

Sum of Ammonia + Nitrite + Nitrate

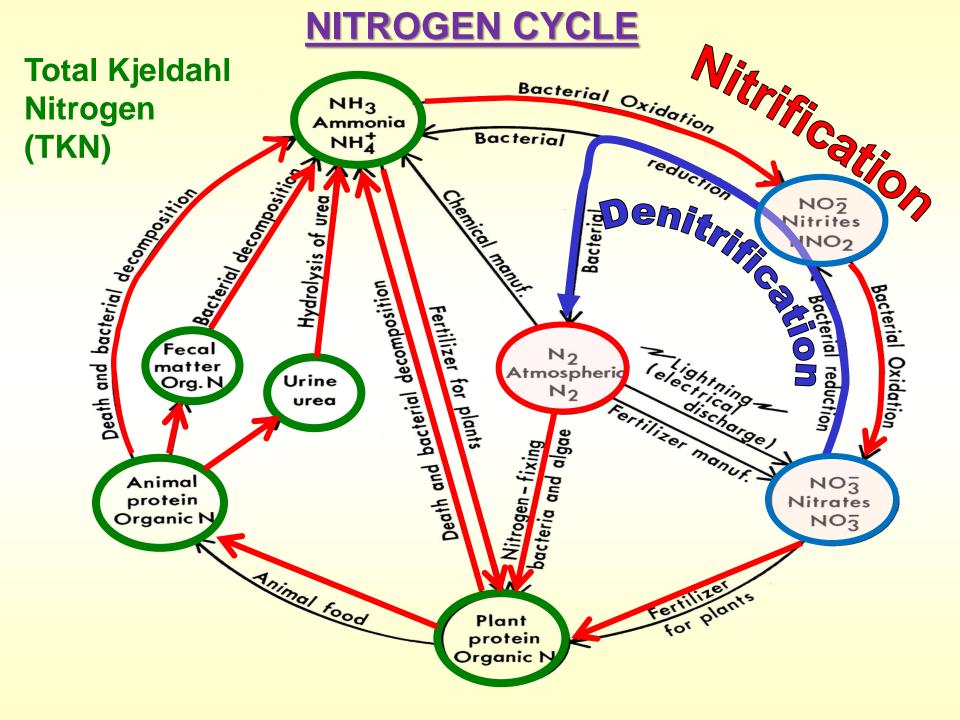


#### Forms of Nitrogen in Wastewater

Ammonia –  $NH_3$ Nitrite –  $NO_2^-$ Nitrate –  $NO_3^-$ Organic

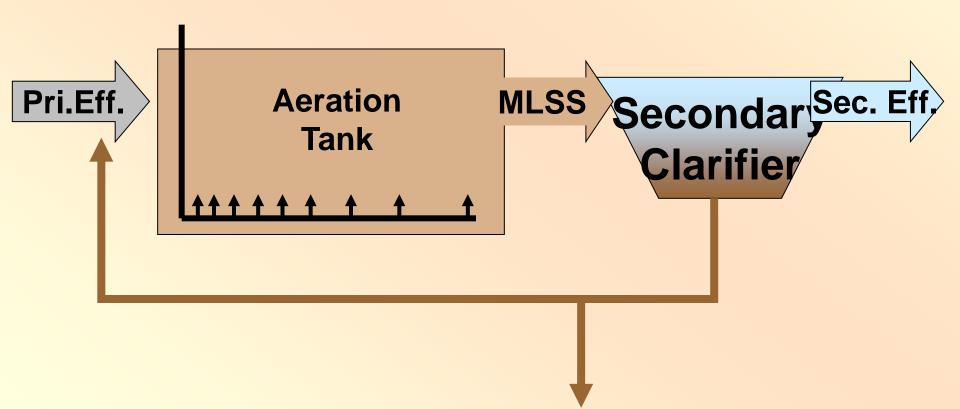
> TKN TIN

"Transform"
In Environment
And
Treatment Plants



### N

# WASTEWATER "TREATMENT" Of Nitrogen





"Raw" Sewage

Organic Nitrogen & Ammonia
No Nitrite or Nitrate



#### **Primary Clarification**

Some Organic Nitrogen Removed (settled solids)

No Ammonia Removed

May Increase

(Solids Handling)



**Primary Effluent** 

(Secondary Influent)

**Organic Nitrogen (Less)** 

**Ammonia** 



### Secondary "Treatment" (Biological)



### N

## Some Nitrogen Will be Removed By the Biomass (assimilation)

Heterotrophic Bacteria Breakdown Organics (Proteins, etc.)

To Ammonia

**Bacteria Also Take Up Ammonia** 

100:5:1

C: N: P



### Some Nitrogen Will be Removed By the Biomass (assimilation)

To Meet an Ammonia Limit or a Total Inorganic Nitrogen (TIN) Limit the Process Must be Capable of <a href="Nitrification">Nitrification</a>

Biological Oxidation of Ammonia to Nitrite to Nitrate

$$NH_3 \longrightarrow NO_2 \longrightarrow NO_3$$

#### **Nitrification**

\*Heterotrophic Bacteria Break Down Organics Generate NH<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>O

\*Autotrophic Bacteria Utilize Inorganic Compounds (and CO<sub>2</sub> as a Carbon Source)

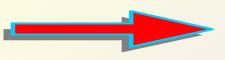
#### **Nitrification**

#### Nitrification of Ammonia Occurs in Two Steps

\*Autotrophic Bacteria-Utiliz Imorganic Compounds Ammonia N CO<sub>2</sub> as a Carbon Source)

#### **Nitrosomonas**

NO<sub>2</sub>-N Nitrite N



NO<sub>3</sub>-N Nitrate N

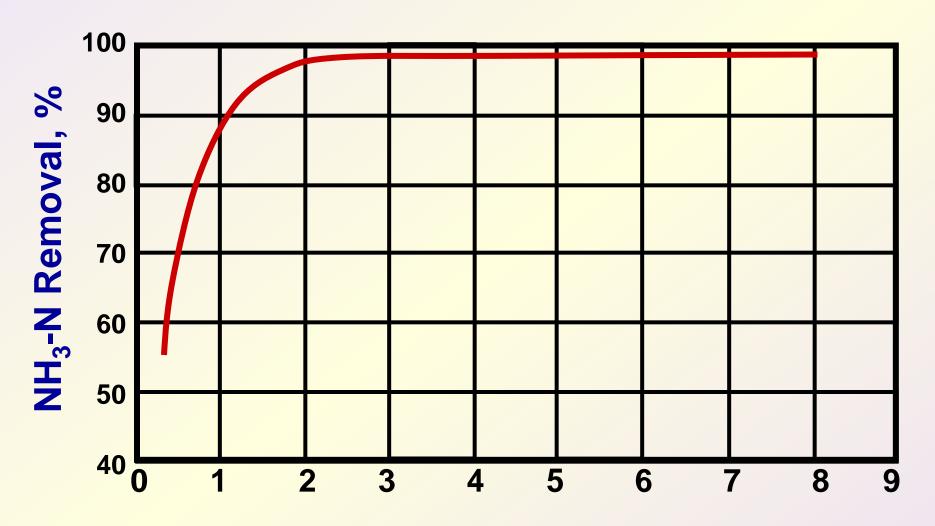
**Nitrobacter** 

#### **Operational Controls for Nitrification**

Air Requirements
1.5 lbs O<sub>2</sub> / lb BOD
4.6 lbs O<sub>2</sub> / lb TKN

Increase D.O. in Aeration Tank to 3 - 5 mg/L

#### Nitrification VS D.O.



Dissolved Oxygen, mg/L

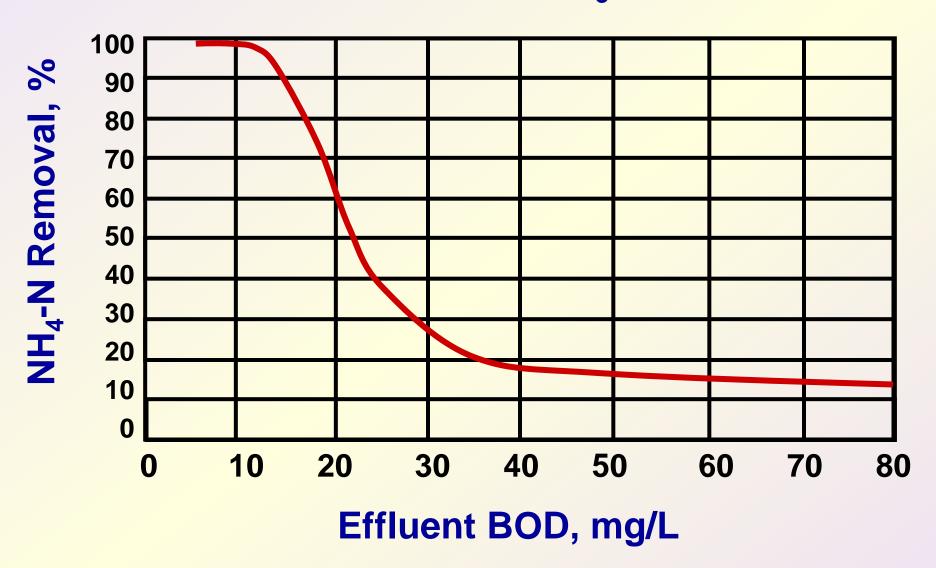
#### **Operational Controls for Nitrification**

Aerobic React Time Must Be Long Enough (> 5 hrs.)

(BOD Removal Must Occur First)

F:M Ratio Must Be Low Enough (< 0.25)

#### Effluent BOD Vs % NH<sub>3</sub>-N Removal



#### **Operational Controls for Nitrification**

#### **Control Solids Handling**

**In-plant Return Flows**High in BOD and Ammonia

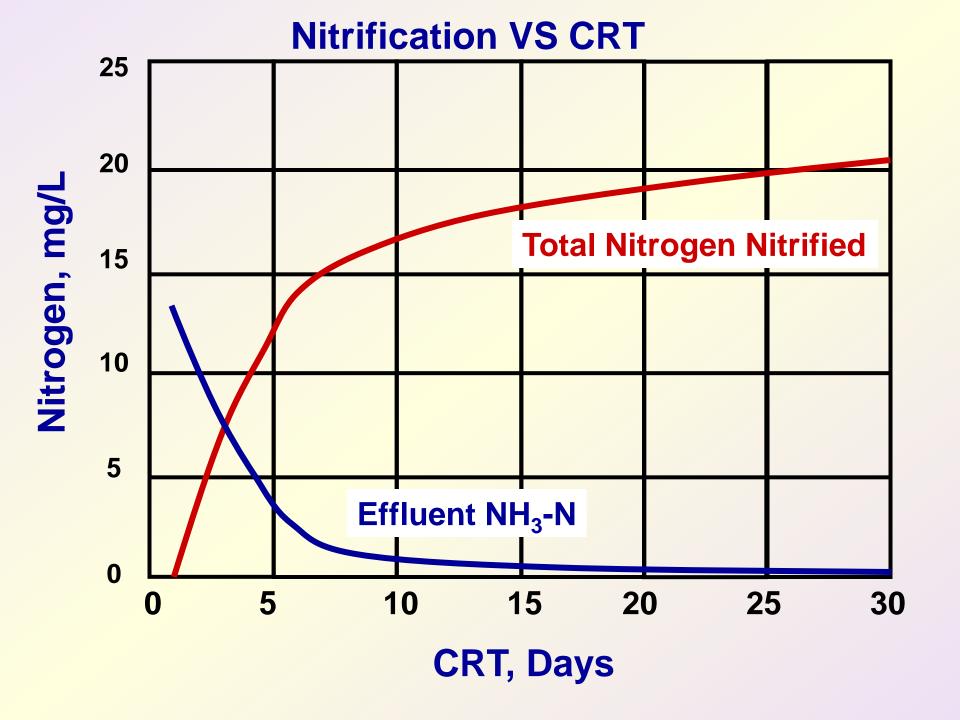
Return Slowly
Low Quantities
At Low Loading Times

#### **Operational Controls for Nitrification**

#### **Nitrifiers Grow Slowly**

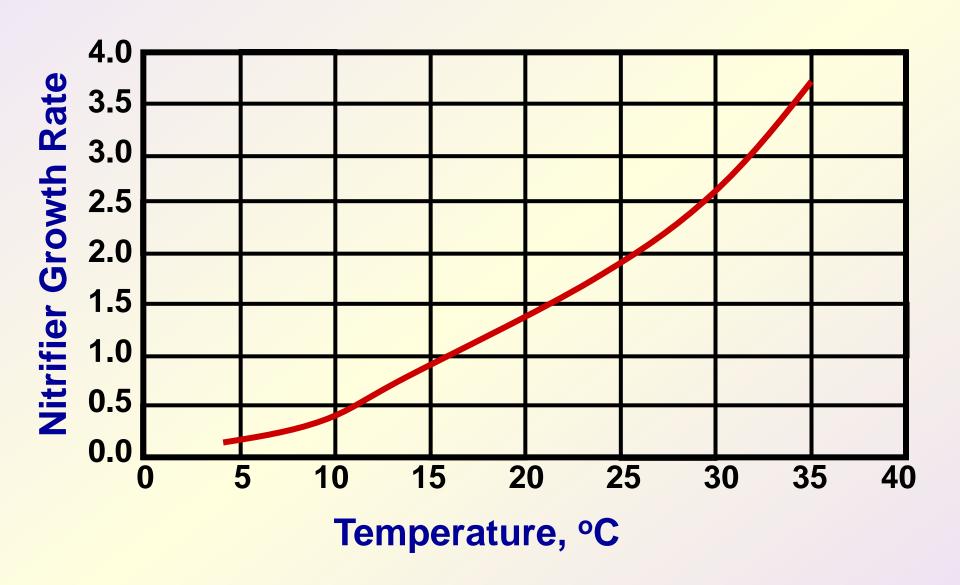
**CRT Must Be Long Enough** 

> 5 Days (minimum)
Best > 8 Days



Lower Temperatures Cause Slower Nitrifier Growth Rate





Lower Temperatures Cause Slower Nitrifier Growth Rate

Minimum of 59 Degrees F. (15 °C) for 90 % Nitrification

Below 50 Degrees F. (10 °C)

Expect Maximum of 50 % Nitrification



Lower Temperatures Cause Slower Nitrifier Growth Rate

Higher MLSS Concentration

May Compensate for Lower Temperature

**Limited By:** 

Oxygen Transfer
Maximum MLSS Controllable
High CRT Problems

$$NH_4HCO_3 + O_2 \longrightarrow HNO_3 + H_2O + CO_2$$

#### 7 mg Alkalinity Destroyed Per mg NH<sub>3</sub>-N Oxidized

Chemicals Added For Phosphorus Removal Also Destroy Alkalinity

5.3 - 13.5 lbs Alkalinity per lb Fe Added

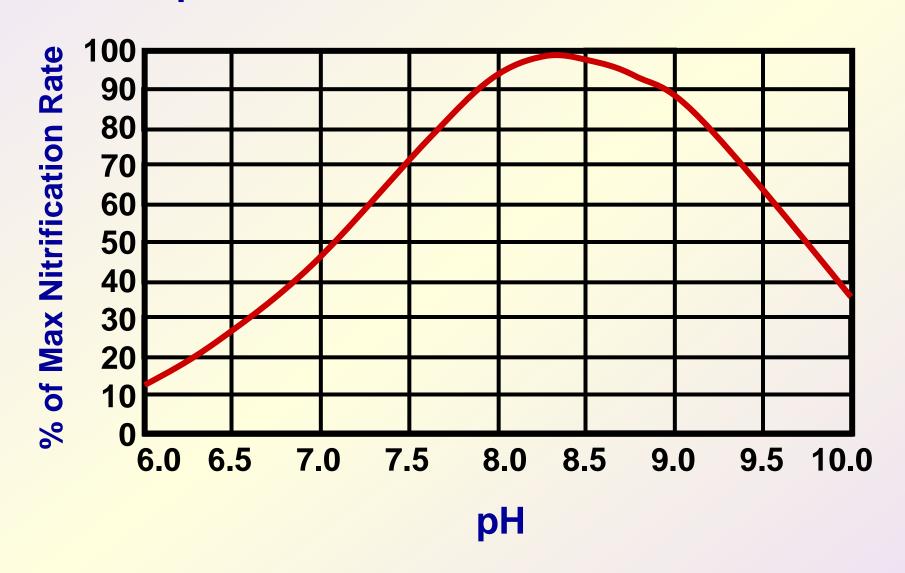
6.0 - 9.0 lbs Alkalinity per lb Al Added

pH May Become Depressed If Not Enough Alkalinity is Present

Nitrifiers are pH Sensitive Most Efficient at pH 8.0 - 8.5



#### pH VS Nitrification Rate at 68 °F



$$NH_4HCO_3 + O_2 \longrightarrow HNO_3 + H_2O + CO_2$$

7 mg Alkalinity Destroyed Per mg NH<sub>3</sub>-N Oxidized

Assure Adequate Alkalinity
Effluent Above 50 mg/L
Influent Above 150 mg/L

 $NH_4HCO_3 + O_2 \longrightarrow HNO_3 + H_2O + CO_2$ 

#### 7 mg Alkalinity Destroyed Per mg NH<sub>3</sub>-N Oxidized



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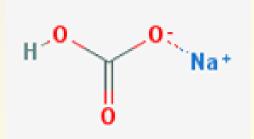




$$NH_4HCO_3 + O_2 \longrightarrow HNO_3 + H_2O + CO_2$$

#### 7 mg Alkalinity Destroyed Per mg NH<sub>3</sub>-N Oxidized

Assure Adequate Alkalinity
Effluent Above 50 mg/L
Influent Above 150 mg/L



#### **Sodium Bicarbonate**





#### **Nitrification Problems**

$$NH_3 \longrightarrow NO_2 \longrightarrow NO_3$$

**Dissolved Oxygen** 

CRT, F/M

**Temperature** 

**Alkalinity** 

**Return Flows From Solids Handling** 

pH Swings

**\*Toxics in Influent** 

#### DENITRIFICATION

$$NO_3 \longrightarrow NO_2 \longrightarrow N_2$$

Why Denitrify ???

Groundwater Discharge Permits Limit
Total Inorganic Nitrogen

 $(5 \text{ mg/L} \text{ NO}_3 - \text{N} + \text{NO}_2 - \text{N} + \text{NH}_3 - \text{N})$ 

Biological Phosphorus Removal Depends on Removal of Nitrate



#### **Definitions**

Aerobic – Dissolved (Free) Oxygen Present – O<sub>2</sub>

Oxic – Dissolved (Free) Oxygen Present – O<sub>2</sub>

**Anoxic** – No Free Oxygen

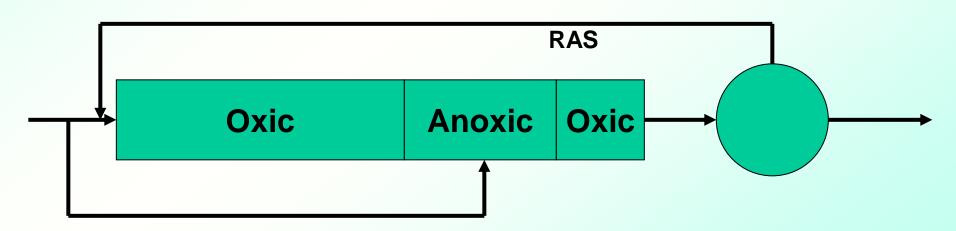
(Combined Oxygen –Nitrates NO<sub>2</sub> and Nitrites NO<sub>3</sub>)

**Anaerobic** – Oxygen Absent

#### **DENITRIFICATION**



In an anoxic environment, heterotrophic bacteria will use the oxygen from nitrates as they assimilate BOD, producing nitrogen gas.



# **DENITRIFICATION**

#### **Added Benefits**

- Minimizes Rising Sludge
- Helps Recover Oxygen
- May Help Control Filamentous Bacteria
- Recovers Alkalinity

Nitrite is a Chlorine "Sponge"



**Chlorine reacts with Nitrite**Instead of Disinfecting

Can't Meet Fecal Coliform Limits Even With Increased Chlorine Dosage

$$CI_2 + H_20 \longrightarrow HCI + HOCI$$
 $HOCI \longrightarrow H^+ + OCI^ OCI^- + NO_2^- \longrightarrow NO_3^- + CI^-$ 

Amount of Cl<sub>2</sub> Consumed: 5 mg Cl / mg NO<sub>2</sub>



## **Nitrification**

Above 63 °F (17 °C) First step is slowest

$$NH_3 \longrightarrow NO_2 \longrightarrow NO_3$$
Slow Fast

(results in  $< 1 - 2 \text{ mg/L NO}_2$ )

#### **Nitrification**

Cold Water NO<sub>2</sub> Problem
At 54 to 57 °F (12 to 14 °C)

Second step becomes slowest

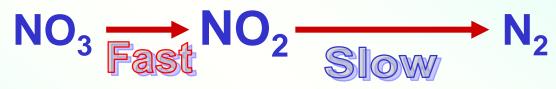
$$NH_3 \rightarrow NO_2 \rightarrow NO_3$$
Slow Slow

NO<sub>2</sub> can reach 15 mg/L

Disinfection with Chlorine Becomes Very Difficult

Warm Water NO<sub>2</sub> Problem

<u>Denitrification</u>

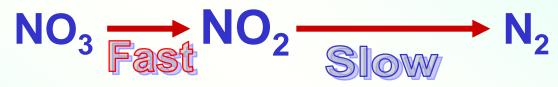


Second step is slower

Worst when carbon (BOD) is limited

Warm Water NO<sub>2</sub> Problem

<u>Denitrification</u>



Second step is slower

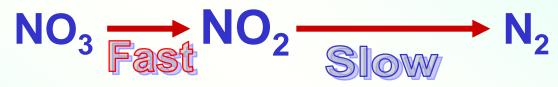
**Denitrification Not Needed** 

**Keep System Aerobic** 



Warm Water NO<sub>2</sub> Problem

<u>Denitrification</u>



Second step is slower

**To Intentionally Denitrify** 

Make Sure BOD is Available During Denitrification



## **Toxicity**



Nitrifiers are more affected than other bacteria

Some toxins affect the Nitrobacter more than the Nitrosomonas

Results in a build-up of NO<sub>2</sub>

#### **Effect of Ammonia**

If ammonia is not present, Free CI reacts quickly with NO<sub>2</sub>

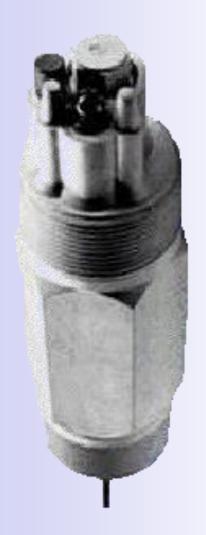
If enough NH<sub>3</sub> is present, CI reacts to form Chloramines.

NH<sub>3</sub> + Cl — Chloramines

Chloramines disinfect, but don't react quickly with NO<sub>2</sub>

# ORP

# **Oxidation-Reduction Potential**



The electrical potential (mv) required to transfer electrons from one compound to another.

Used as a qualitative measure of the state of oxidation.

# <u>ORP</u>

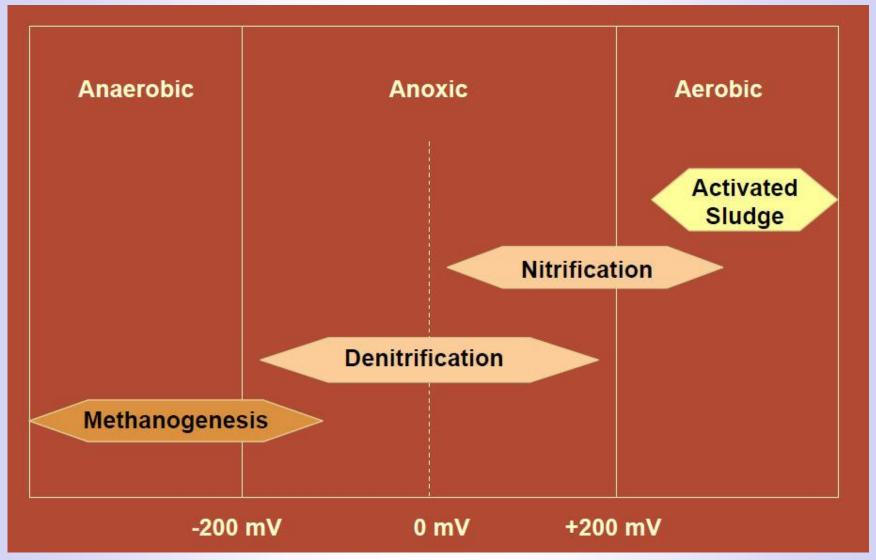
## **Oxidation-Reduction Potential**





Raw (influent)	~ -200 mV (dependent on strength of ww)
Primary effluent	~ -150 mV (change due to loss of settleable solids)
Secondary effluent	~ +100 mV (dependent on strength of ww)
Final effluent	~ +150 mV (dependent on strength of ww)





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