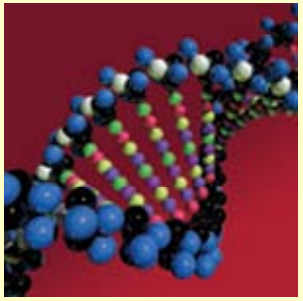
Upgrade of the Marathon Louisiana Refining Division's Wastewater Treatment Plant to a State-of-the-Art Nitrification-Denitrification Facility


Presented to

Air & Waste Management Association

Louisiana Section

November 19, 2008

by

Carl E. Adams, Jr., PhD, P.E.

ENVIRON International Corporation

Presentation Outline

- Background and Pre-Upgrade Facilities
- Upgrade Design and Implementation
- Performance
- Recent Developments

Background and Pre-Upgrade Facilities

- Refinery and wastewater treatment plant (WWTP) began operation in 1976
  - Originally two treatment trains
  - Third activated sludge train added in 1983
  - Conventional systems with External Secondary Clarifiers
- Past and planned expansions raised concern for capacity of existing WWTP and desire for cost-effective application of state-of-the-art technology
- Regulatory concern regarding potential future nitrogen discharge limits
- 250,000 bbls/day rated crude capacity in 2000

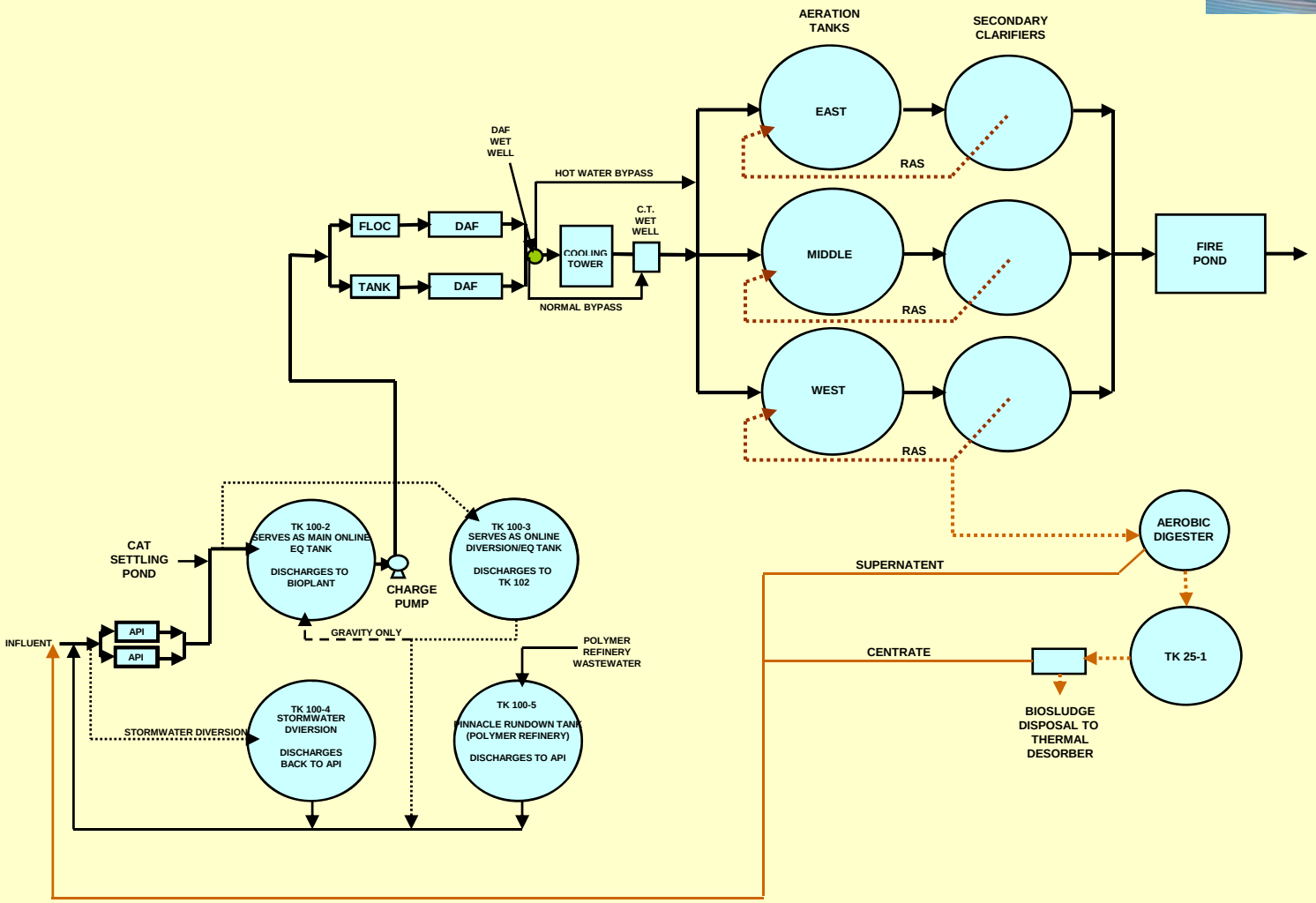
Background and Pre-Upgrade Facilities

- ENVIRON retained by Marathon in 2000 to review WWTP operations and assist in developing a wastewater Master Plan, including planning for VOC emissions and sludge residues
- 2001 Flows and Loads
  - 2,100 gpm design average dry-weather flow
  - 700 mg/L design average COD (17,900 lbs/day)
  - 40 mg/L design average TKN (1,025 lbs/day)
- Projected Flows and Loads
  - 2,310 gpm design average flow
  - 21,640 lbs/day COD
  - 1,250 lbs/day TKN

Background and Pre-Upgrade Facilities

- Pre-Upgrade Wastewater Facilities
  - API
  - Equalization
  - Stormwater diversion
  - Dissolved air flotation (DAF)
    - Two treatment trains
  - Cooling Tower
  - Conventional Activated Sludge, i.e., external clarifier
    - Three treatment trains (East / Middle / West)
  - Effluent (Firewater) Pond
  - Sludge Handling (aerobic digestion, centrifugation)

Background and Pre-upgrade Facilities



Background and Pre-Upgrade Facilities

- Pre-Upgrade Performance
  - Hydraulic capacity
    - Limited to 2,700 gpm maximum throughput
    - Projected future max flow of up to 3,500 gpm
  - Marginal DAF performance
    - Hydraulic limited
  - Marginal activated sludge performance
    - Organic overload
    - Limited aeration capacity – no standby facilities
    - High operating temperatures

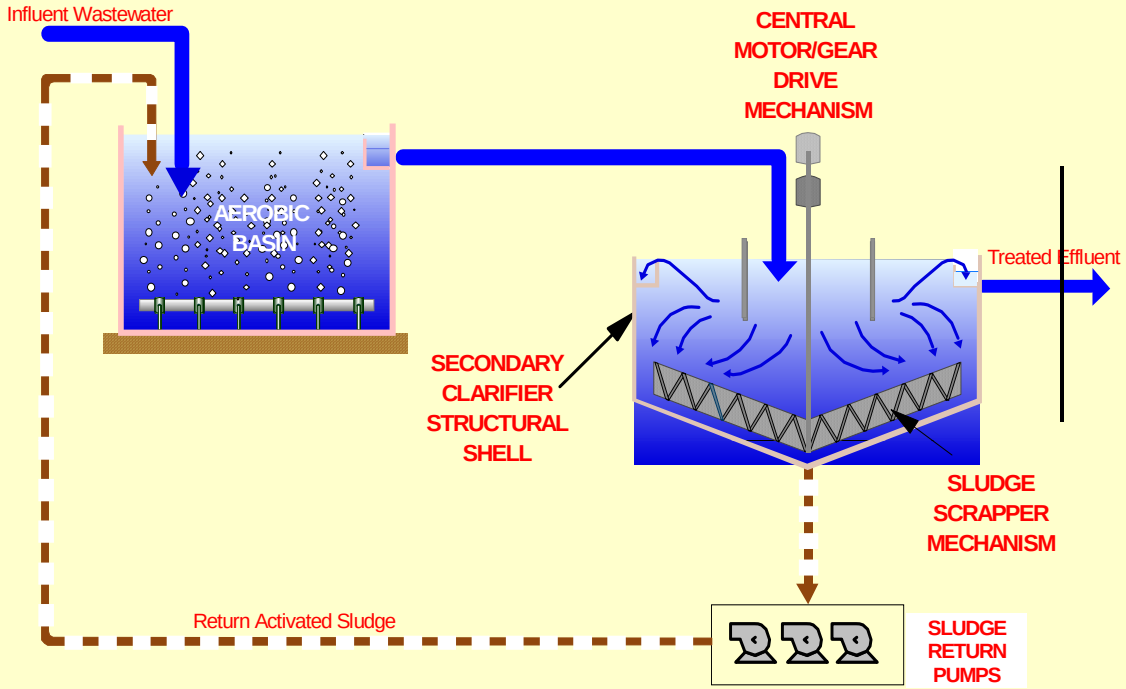
Background and Pre-Upgrade Facilities

- ENVIRON recommendations (2001)
  - Provide additional flotation train
  - Activated sludge system (near term)
    - Increase MLSS/MLVSS (i.e., lower F/M)
    - Add standby aeration capacity
    - Decrease aeration basin temperatures
  - Activated sludge system (long term)
    - Add additional bioreactor aeration and clarifier capacity
    - Design for nitrogen removal (nitrification-denitrification)
    - Limited footprint – consider state-of-the-art integral clarifier system

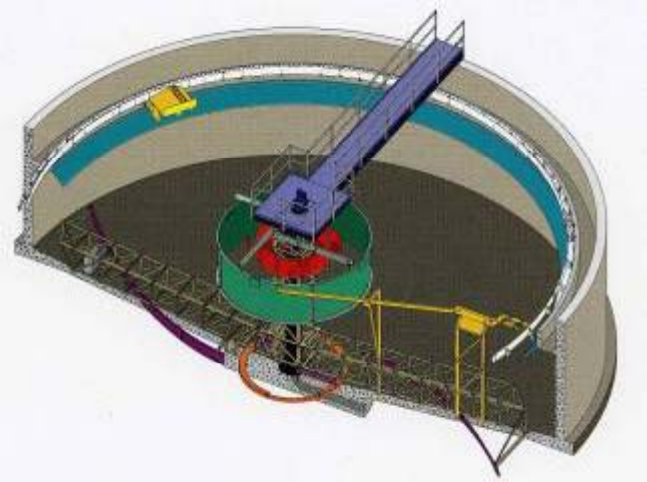
Upgrade Design and Implementation

- 2002 ENVIRON Feasibility Study
  - Feasibility level design and cost estimates for new fourth treatment train
  - New fourth train to include
    - Induced Gas Flotation
    - Closed Circuit Cooling Tower
    - Activated sludge with nitrification-denitrification
  - ADVENT Integral System (AIS) technology

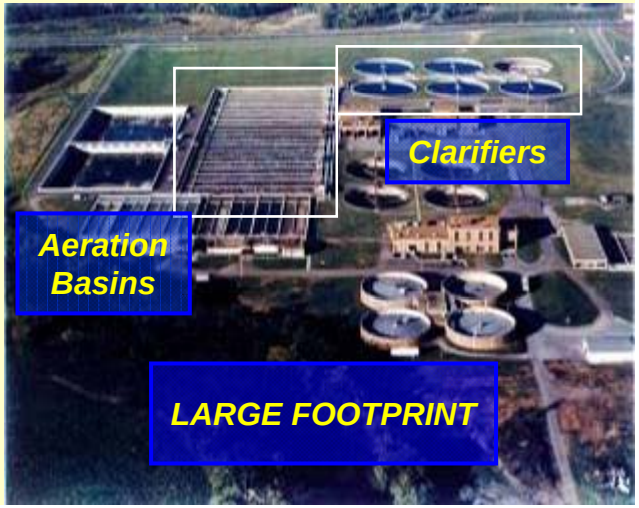
Conventional System Aspects



Conventional clarifier has capital and operating constraints...

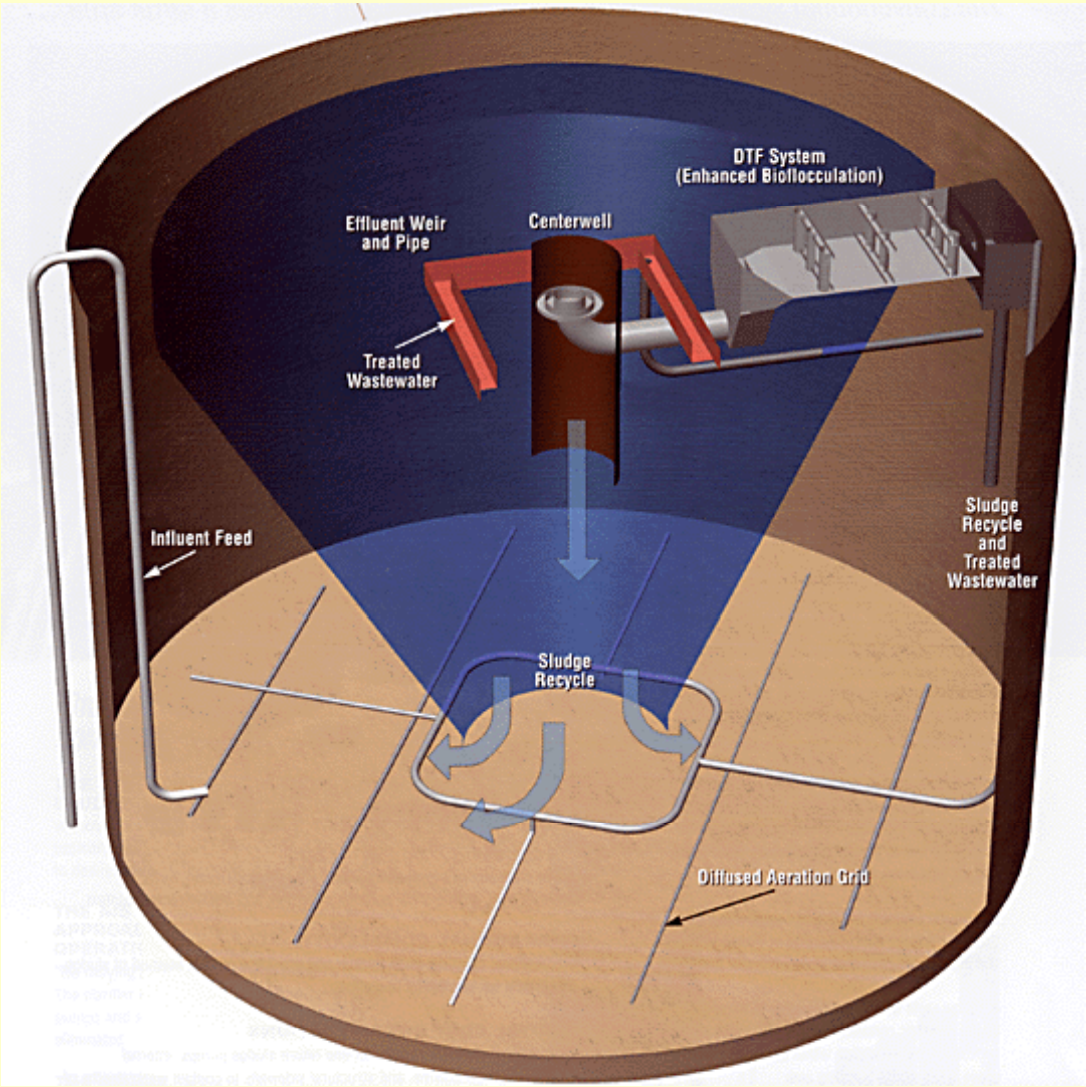


- Concrete or steel structural shell to hold 3-5 m of water.
- Internal sludge raking mechanism.
- Sludge return pumps and piping.



What is The ADVENT Integral System (AIS)?

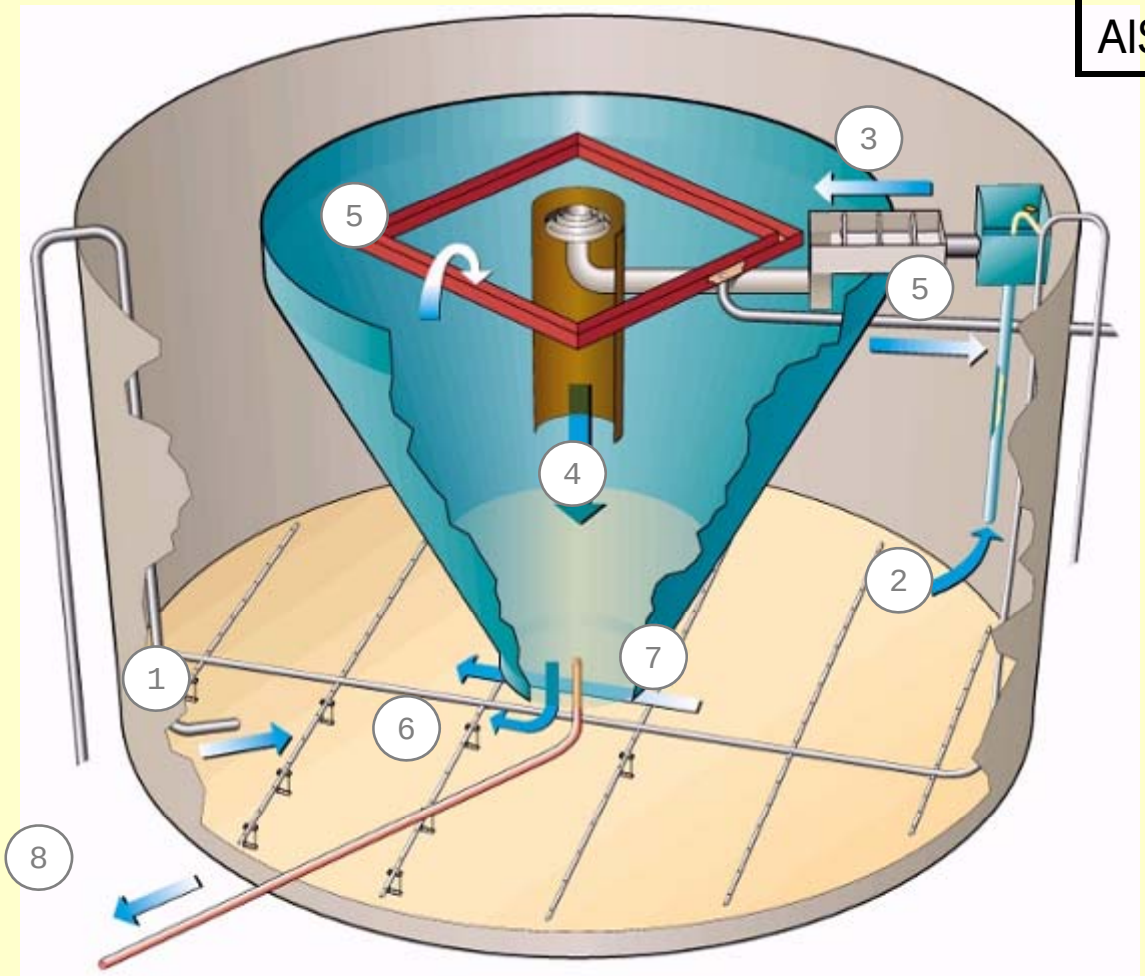
Basically,
a Cost-Efficient Reconfiguration of the Conventional Activated Sludge Process



AIS Components

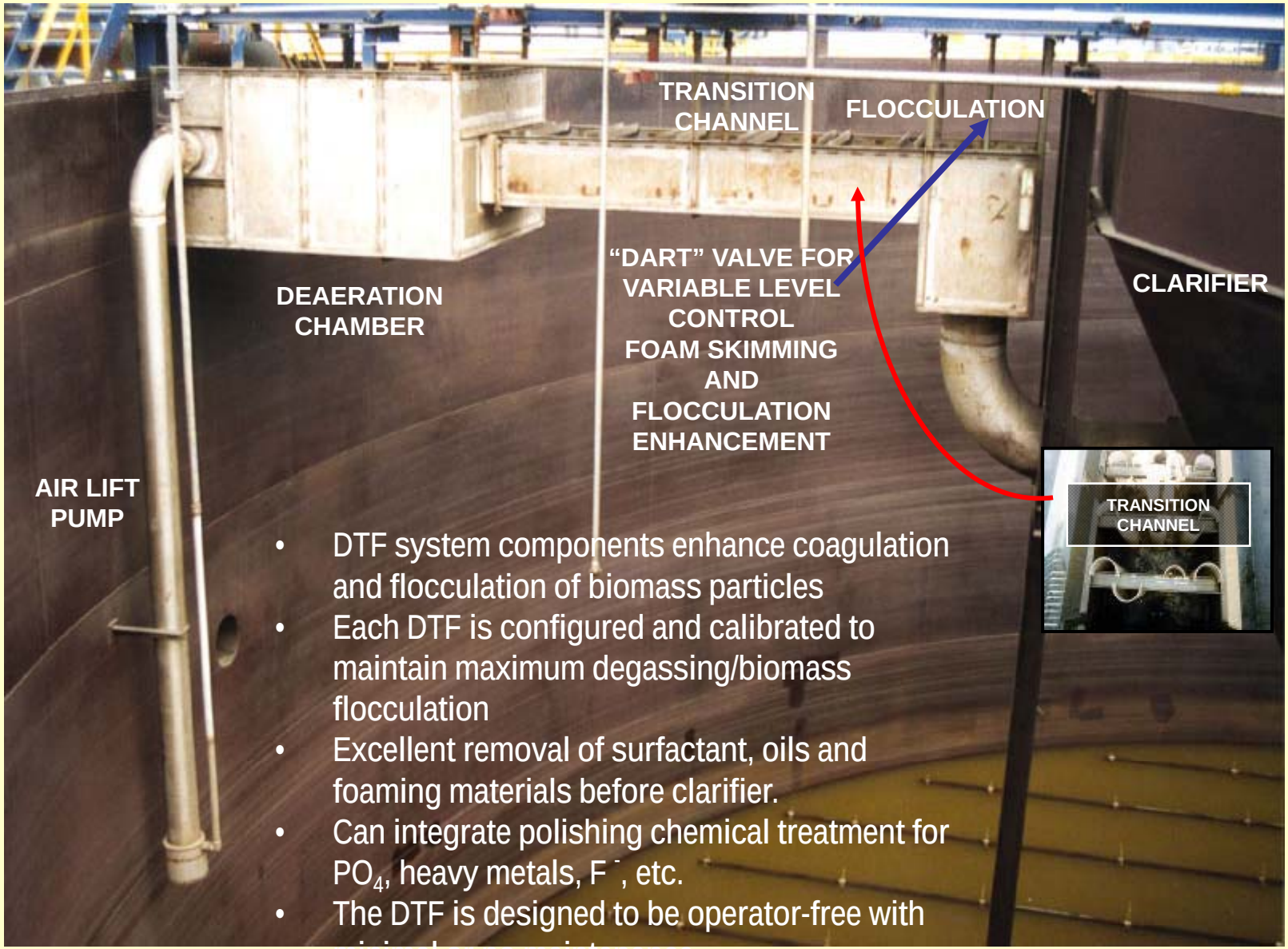
Patented Induced Downward Velocity allows higher concentrations of MLSS.

System	MLSS, mg/L
Conventional Activated Sludge	2,000 to 4,000
AIS	6,000 to 8,000



1. **Influent**
2. **Mixed Liquor Inlet to Airlift Pump**
3. **Deaeration / Transition / Flocculation Effluent (DTF) to Clarifier**
4. **Center Well Discharge**
5. **Effluent over Weir & to Final Discharge**
6. **Thickened MLSS Return to Aeration Basin**
7. **Aeration Current to Remove MLSS from Clarifier**
8. **Waste Excess Biomass**

DTF Components



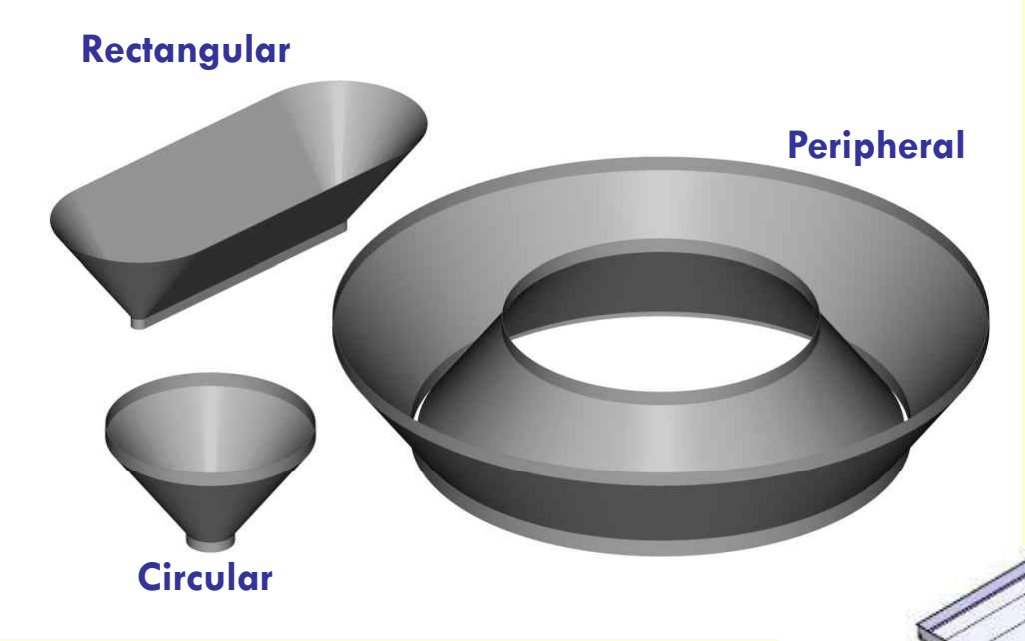
- DTF system components enhance coagulation and flocculation of biomass particles
- Each DTF is configured and calibrated to maintain maximum degassing/biomass flocculation
- Excellent removal of surfactant, oils and foaming materials before clarifier.
- Can integrate polishing chemical treatment for PO_4, heavy metals, F^-, etc.
- The DTF is designed to be operator-free with minimal or no maintenance.

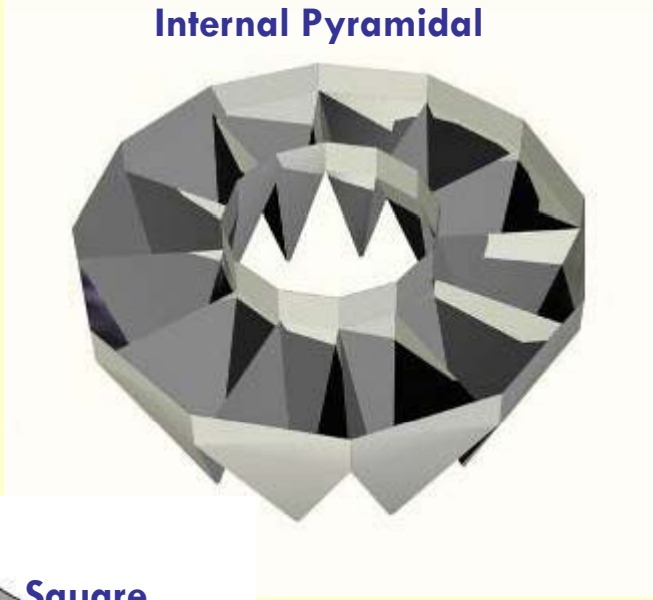
The First AIS System (1993)-
CIRCULAR Configuration...

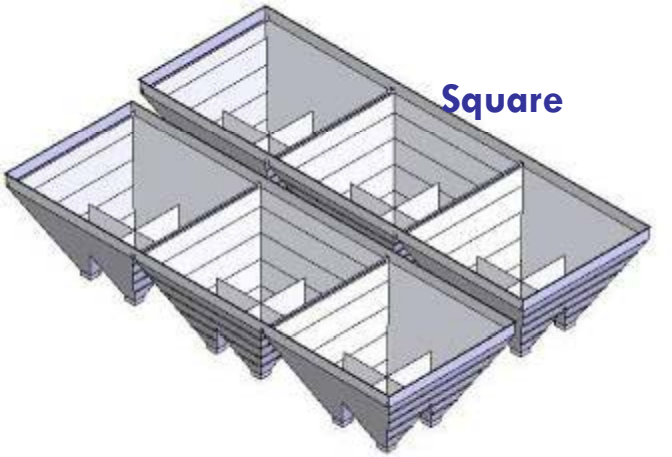
GE Plastics
Grangemouth, Scotland

The AIS System -
System Configurations

The five most common configurations are . . .







Upgrade Design and Implementation
Biological Treatment Chemistry

- **Organic Removal** – Biological Oxidation of Organics (e.g., Hydrocarbons, Phenols) to Carbon Dioxide and Water:

  $C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O$ + new bacteria

- **Nitrification** – Biological Oxidation of Ammonia to Nitrate:

  $NH_4^+ + 2O_2 + 2HCO_3^- \rightarrow NO_3^- + H_20 + 2H_2CO_3$ + new bacteria

- **Denitrification** – Biological Oxidation of Organics *and* Conversion of Nitrate to Nitrogen Gas:

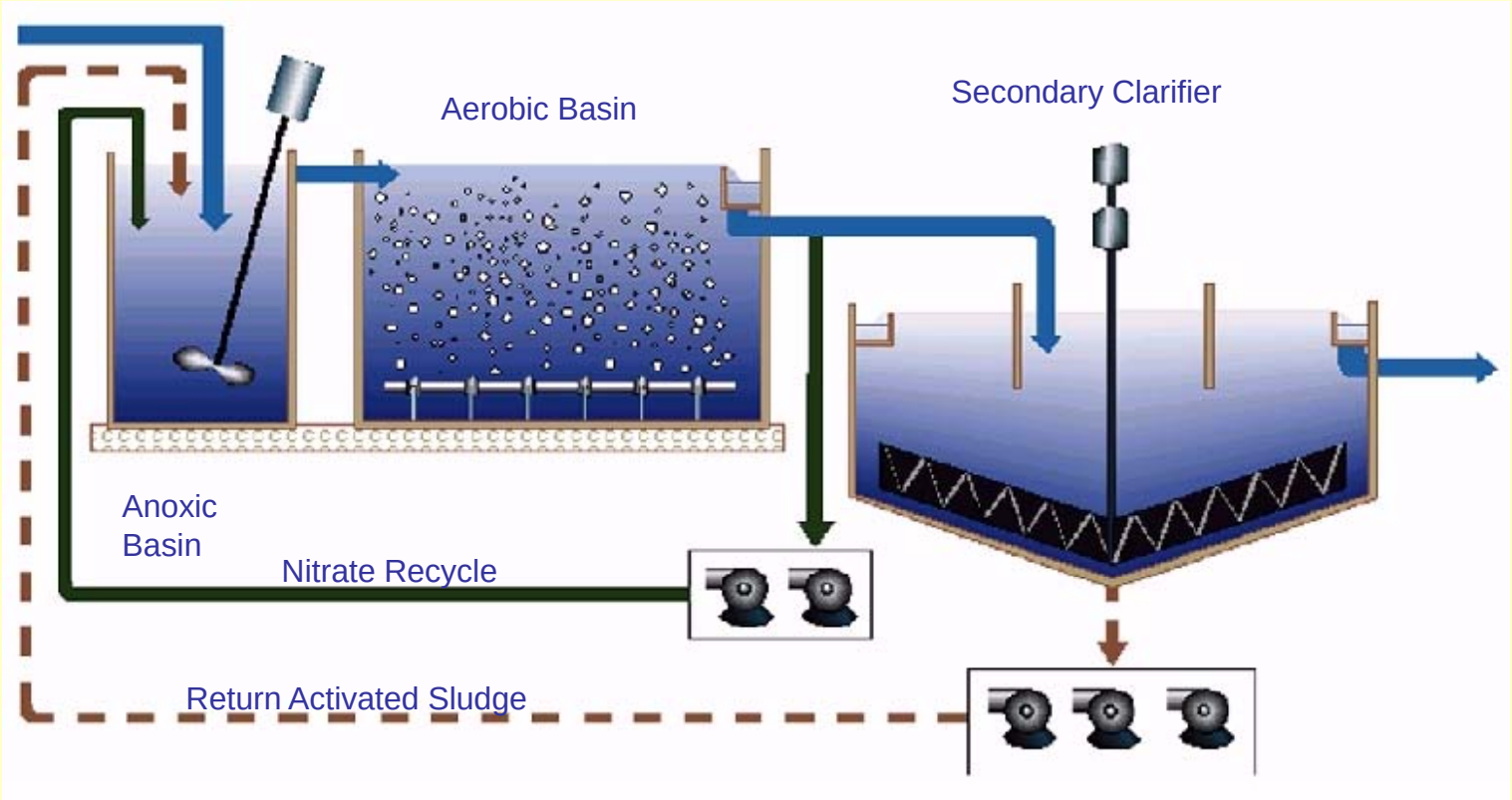
  $NO_3^- + 0.83CH_3OH + 0.17H_2CO_3 \rightarrow 0.5N_2 + 1.33H_20 + HCO_3^-$ + new bacteria

AUTOTROPHS
Strict aerobes, must have D.O.

HETEROTROPHS
Aerobic w/D.O.
Anoxic w/no D.O. but NO_3

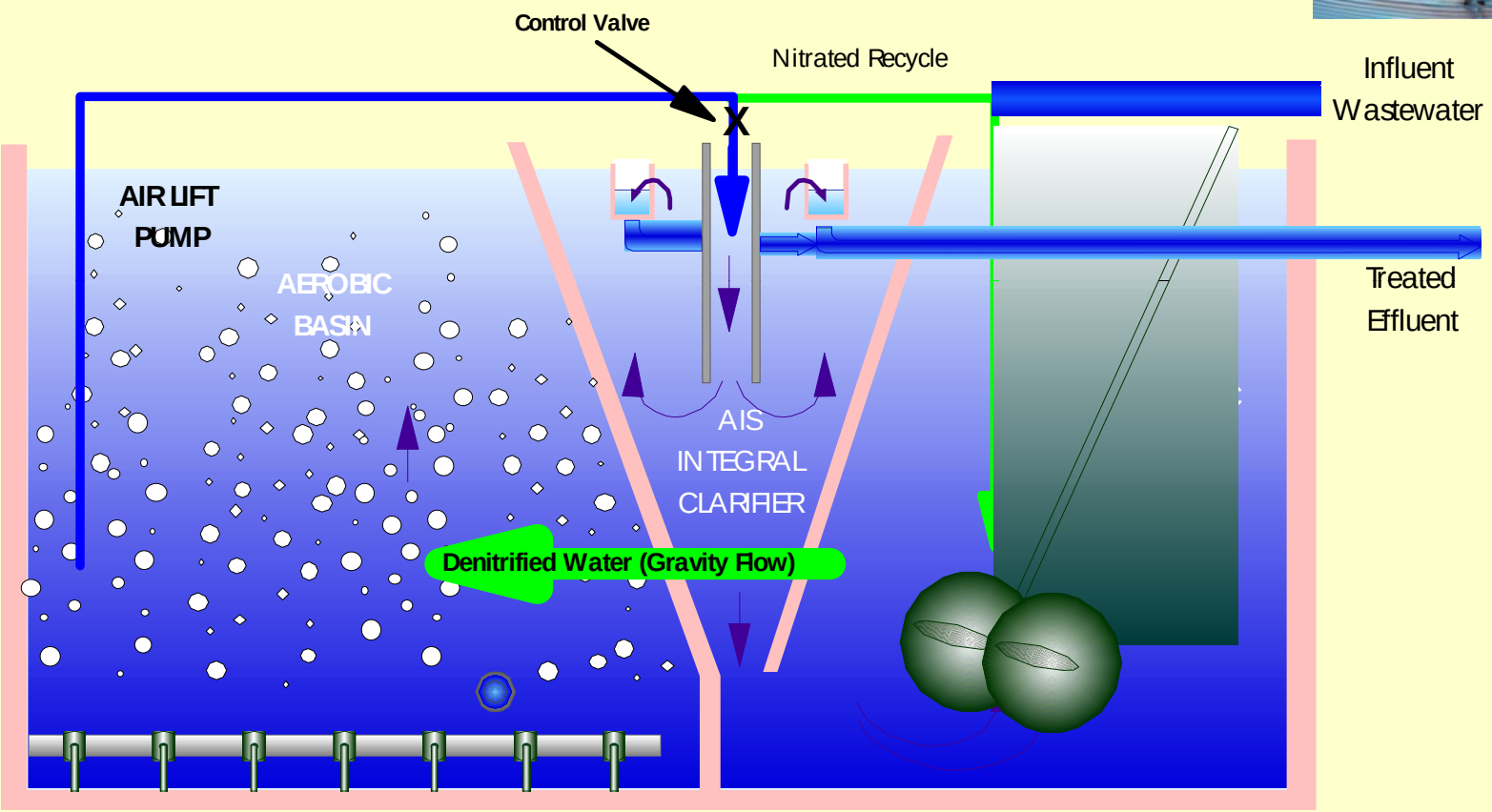
Upgrade Design and Implementation
Conventional Nitrification-Denitrification

A Typical Nitrifying-Denitrifying Activated Sludge System...



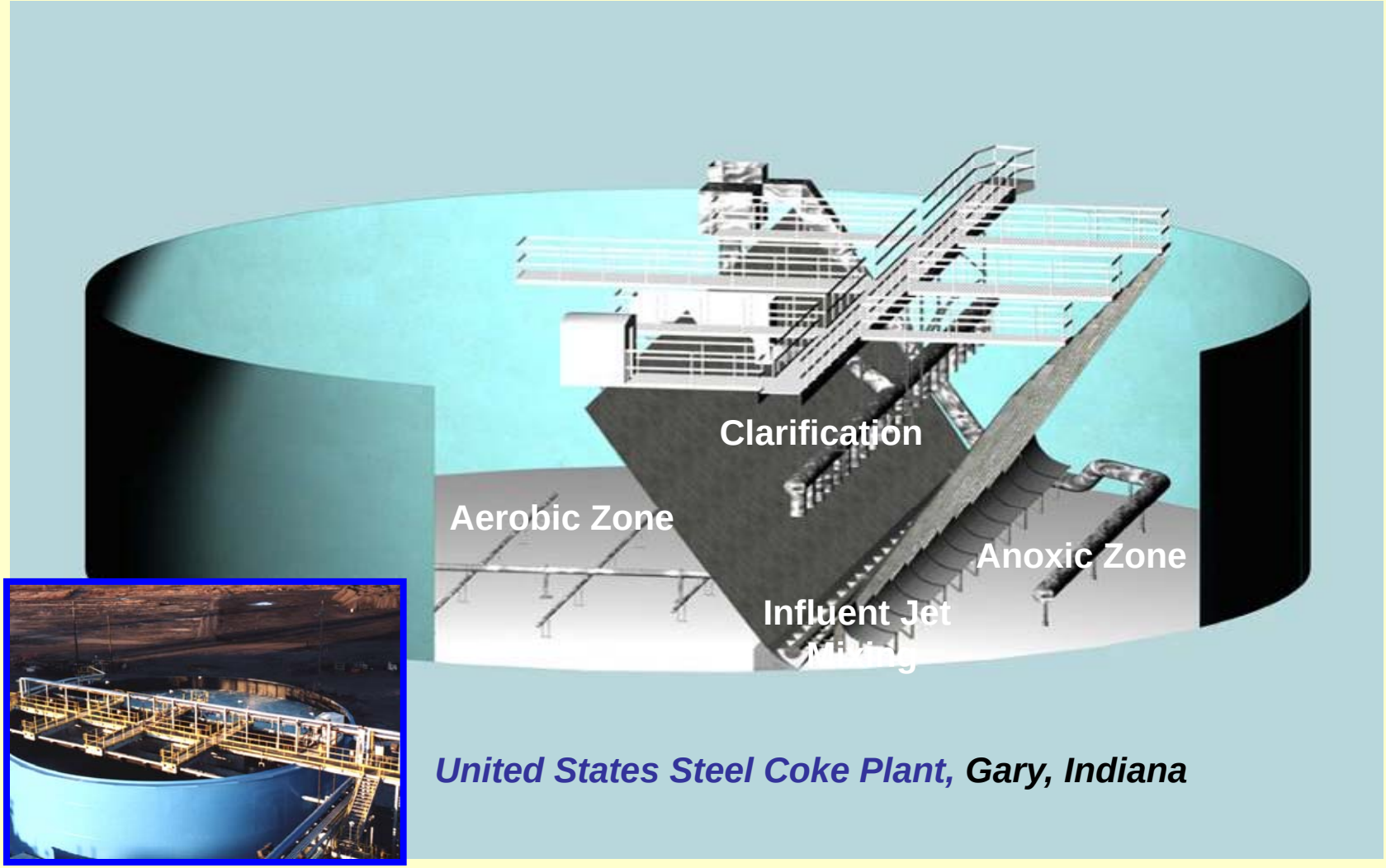
Upgrade Design and Implementation

AIS Nitrification-Denitrification



First Major AIS Nitrification-Denitrification System

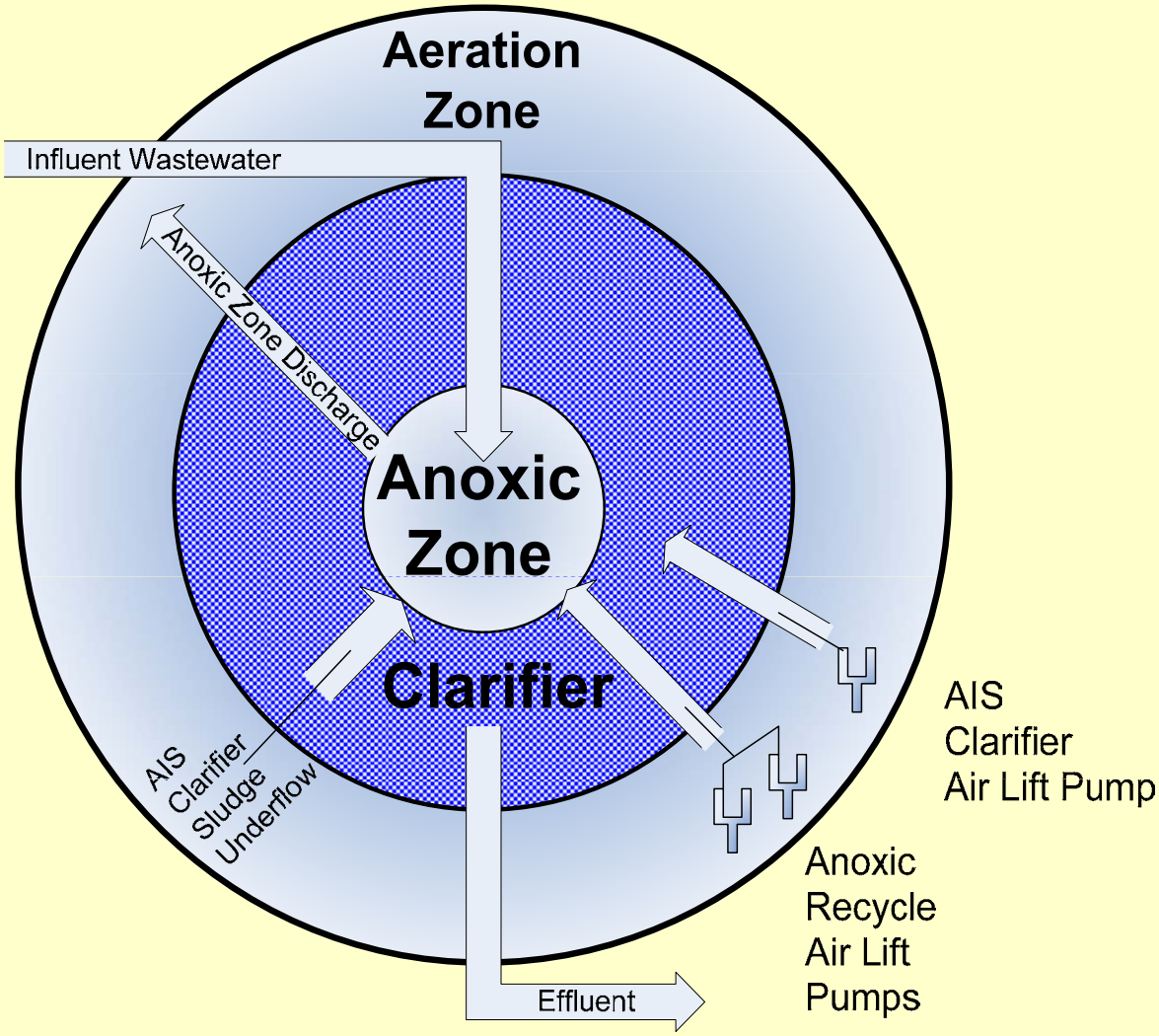
NH_4-N = 4,000 mg/L



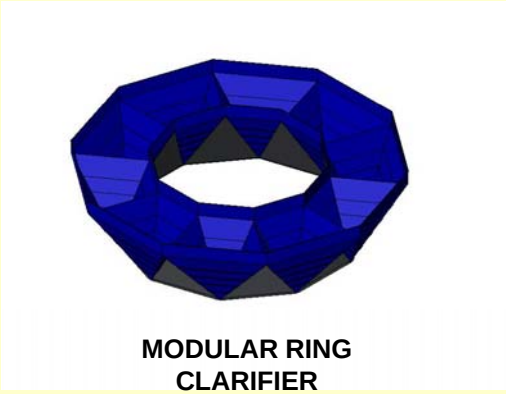
United States Steel Coke Plant, Gary, Indiana

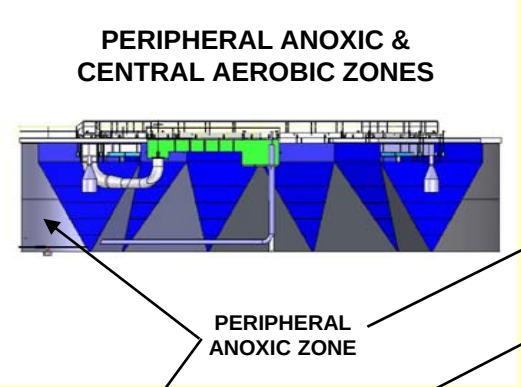
Upgrade Design and Implementation

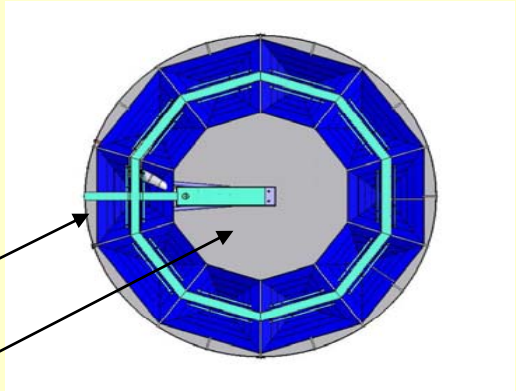
AIS Flow Path



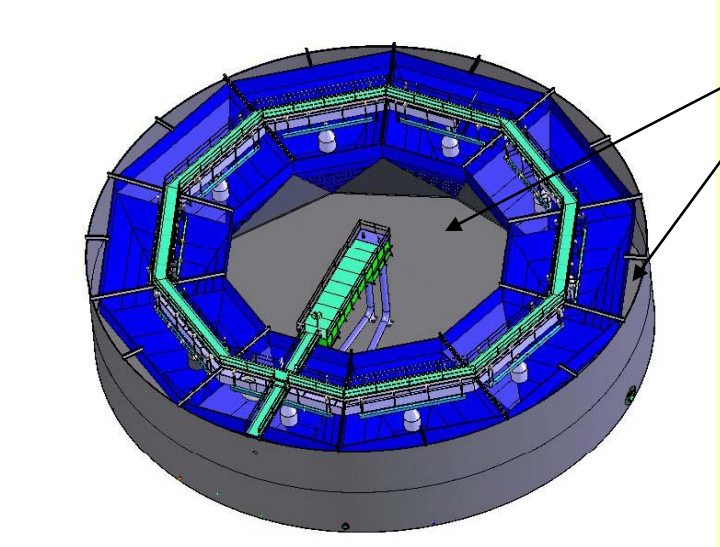
Modular Ring Configuration

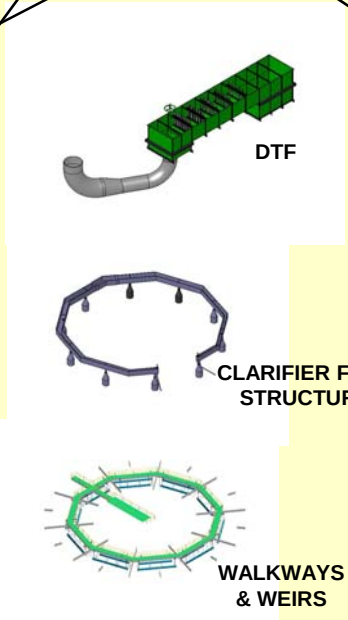


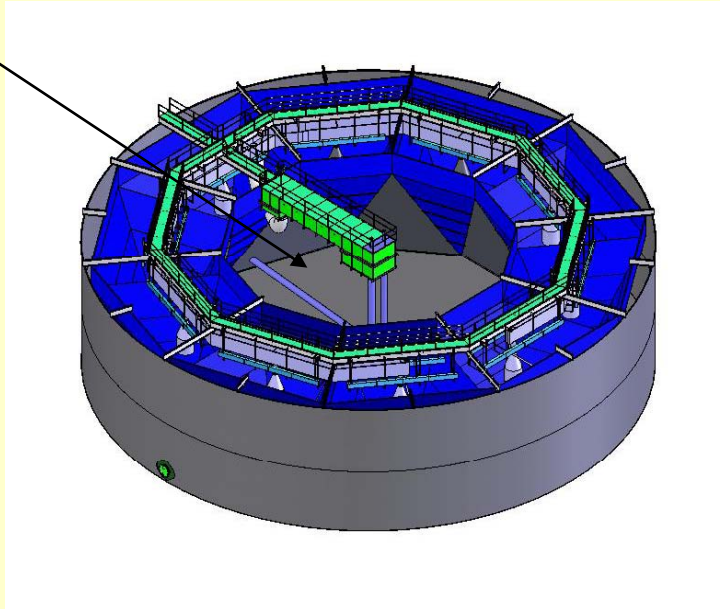


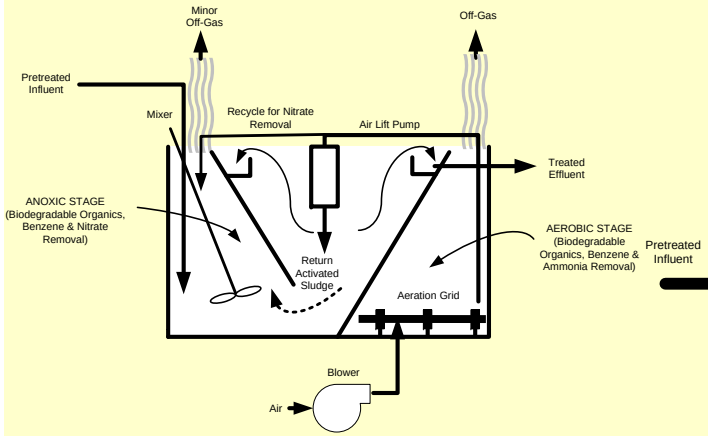


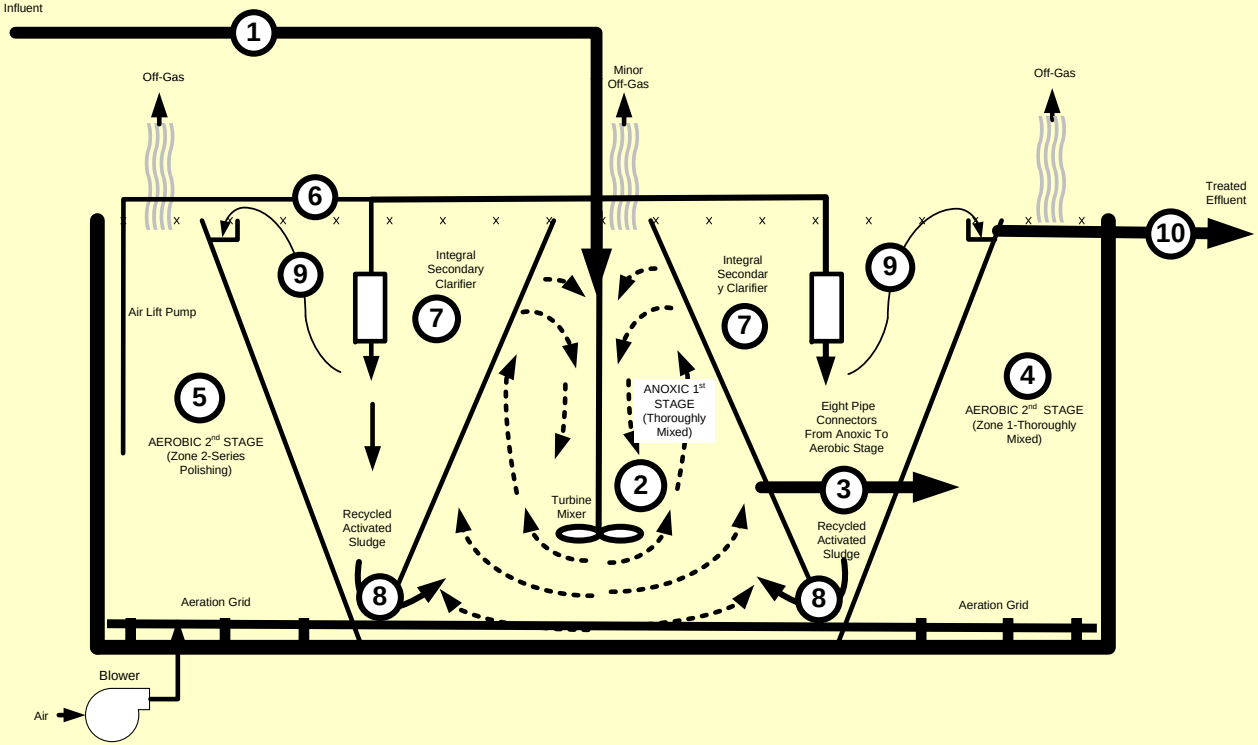
CENTRAL
AEROBIC ZONE











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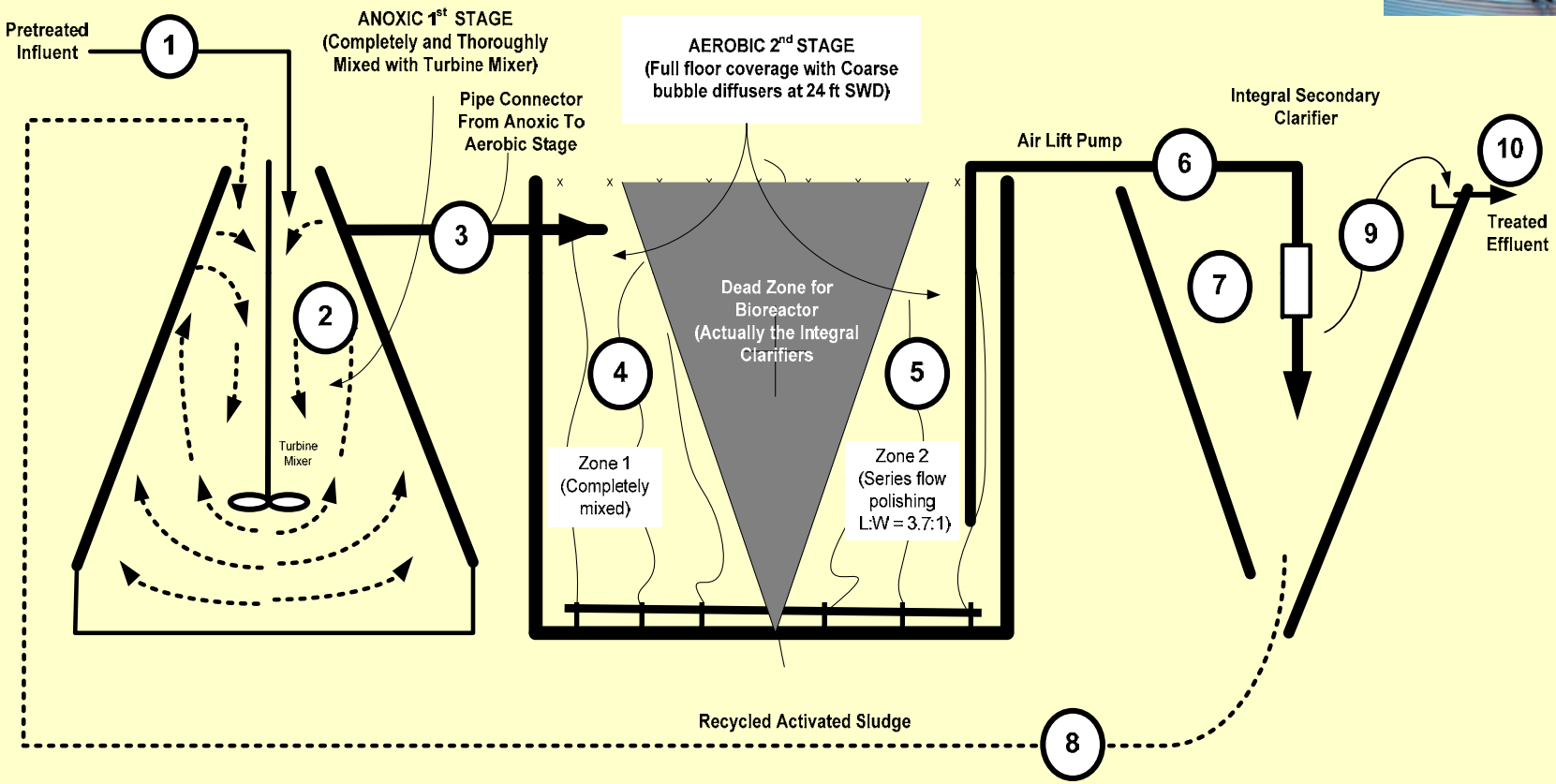
Louisiana Refining Division

Marathon Petroleum Company LLC



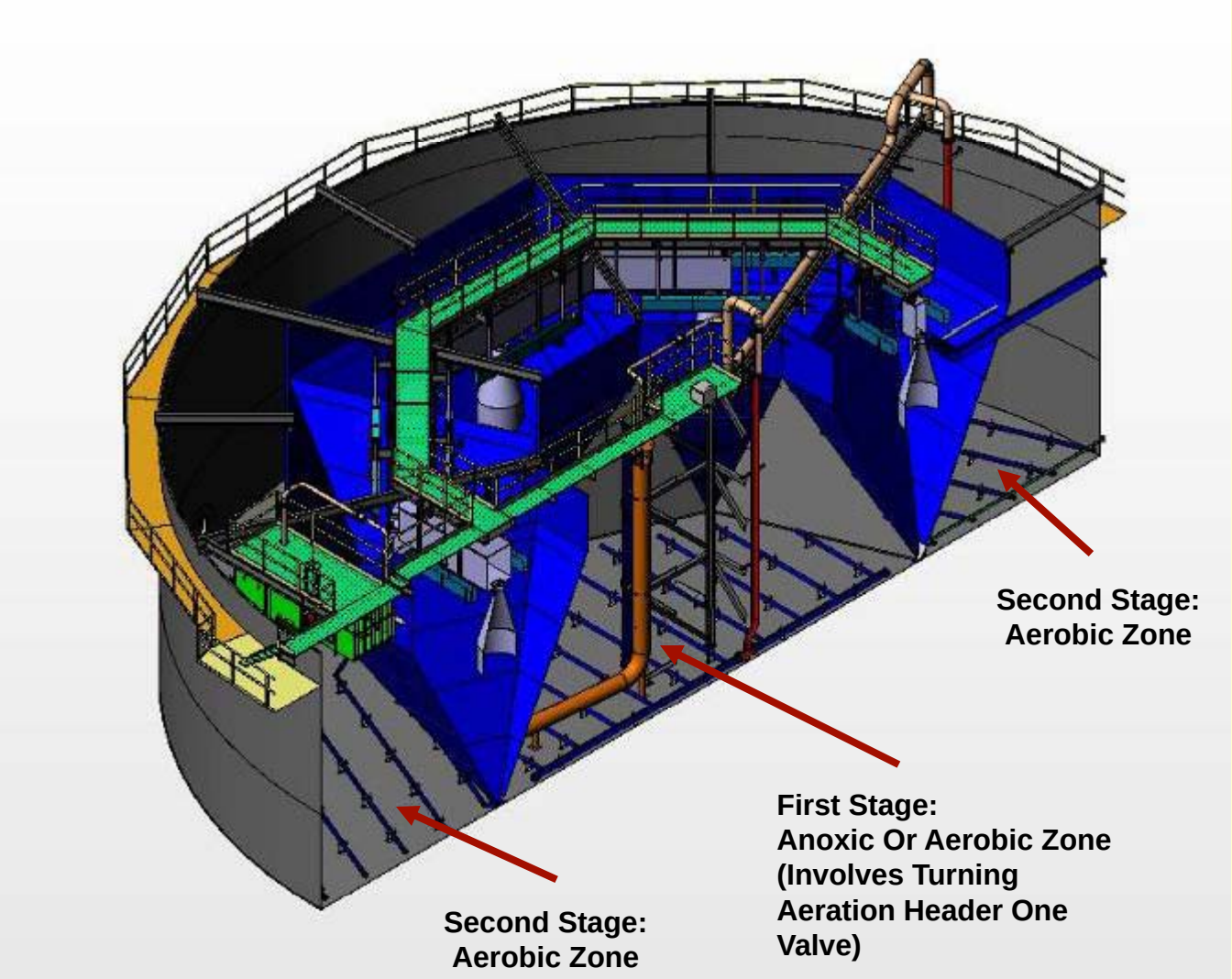
ENVIRON

Louisiana Refining Division

Marathon Petroleum Company LLC

Upgrade Design and Implementation

AIS Flow Path



Marathon Oil Co.
Louisiana
Refining Division
Garyville, LA

<u>Influent Design</u>

Flow	=	900 gpm (design)
	=	1,400 gpm (max)
COD	=	6,000 lbs/day
TKN	=	485 lbs/day

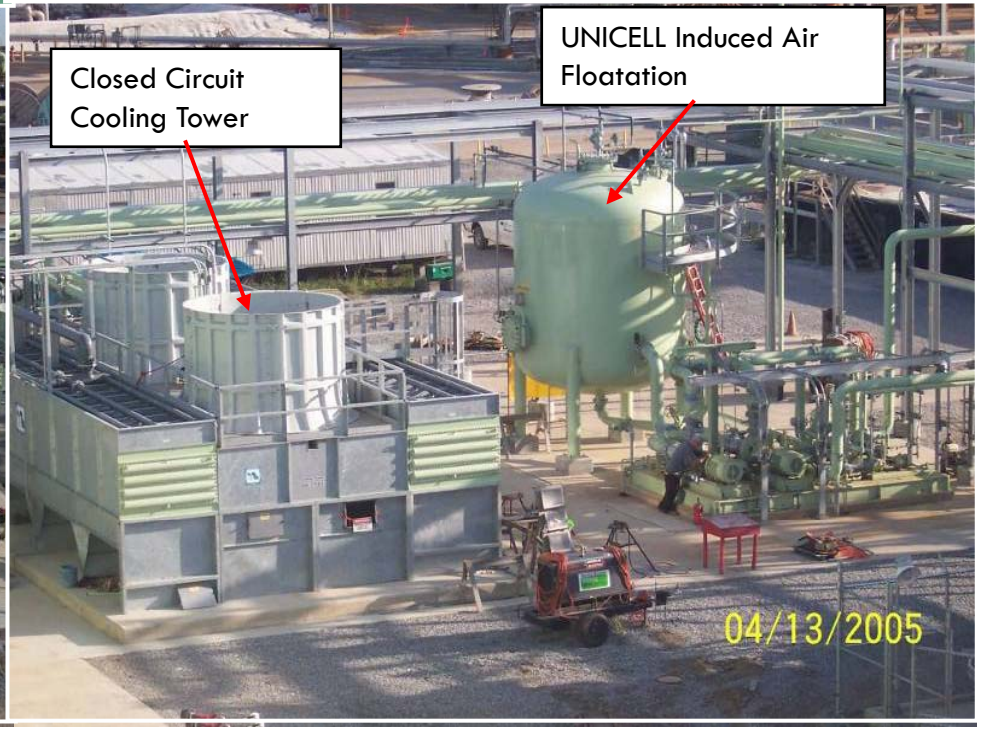
<u>Effluent Design</u>

BOD_5(s)	< 15 mg/L
NH_3-N	< 5 mg/L
NO_3-N	< 6 mg/L
TSS	< 30 mg/L

Upgrade Design and Implementation

- Front End Engineering Design (FEED) in 2003
- AIS Contract Awarded April 2004
  - Technology, Design and Startup by The ADVENT Group, Inc. (now ENVIRON)
  - Reactor Fabrication and Construction by Matrix Service, Inc.
- AIS Commissioned in April 2005
- Performance Test Completed July 2005

Fourth Train Construction



Performance

2007 AIS Nitrogen Balance: Short Term

- Nitrates Are Annually Reported on Marathon's Toxic Release Inventory (TRI)
- Marathon and ENVIRON Executed a One Week Sampling and Analysis Effort in July 2007 to Develop a Nitrogen Balance for AIS Train One

Performance

2007 AIS Nitrogen Balance: Short Term

AIS Influent Characteristics

PARAMETER	UNITS	MONDAY	TUEDAY	WEDNESDAY	THURSDAY	FRIDAY	AVERAGE
FLOW	gpm	1,100	1,100	1,100	1,033	1,025	1,072
COD	mg/L	372	260	354	307	300	318
TKN	mg/L	21	18	20	18	16	19
NH_3-N	mg/L	15	16	16	16	15	16
NO_3-N	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
TSS	mg/L	34	44	95	77	50	60

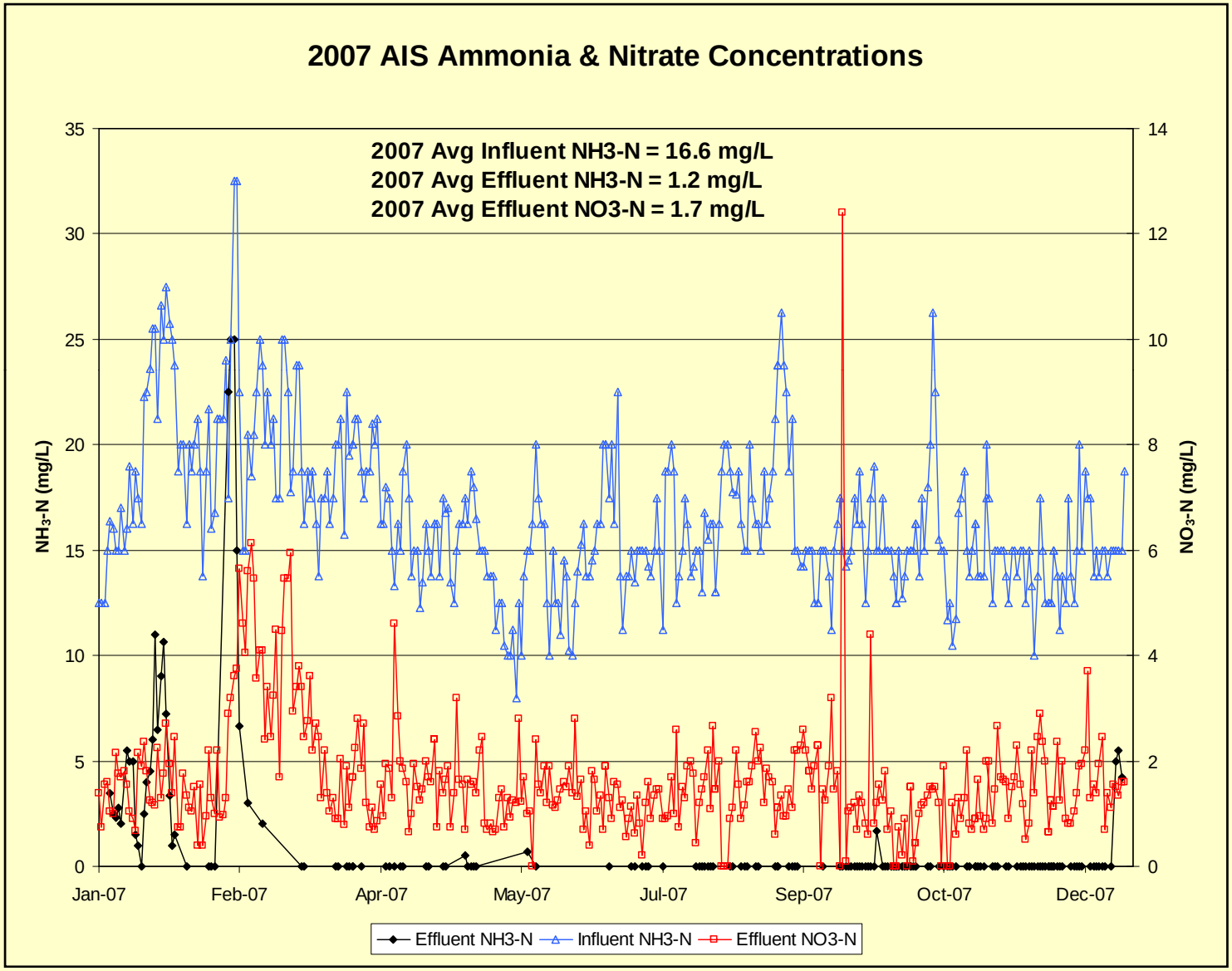
AIS Effluent Characteristics

PARAMETER	UNITS	MONDAY	TUEDAY	WEDNESDAY	THURSDAY	FRIDAY	AVERAGE
FLOW	gpm	1,088	1,096	1,085	977	1,017	1,052
COD (s)	mg/L	40	38	43	55	43	44
TKN (s)	mg/L	1.3	2.3	1.3	2.3	1.8	1.8
NH_3-N (s)	mg/L	1.3	1.0	1.0	1.8	1.2	1.3
NO_3-N (s)	mg/L	1.5	0.1	0.2	0.1	0.1	0.4
TSS	mg/L	19	19	18	23	17	19

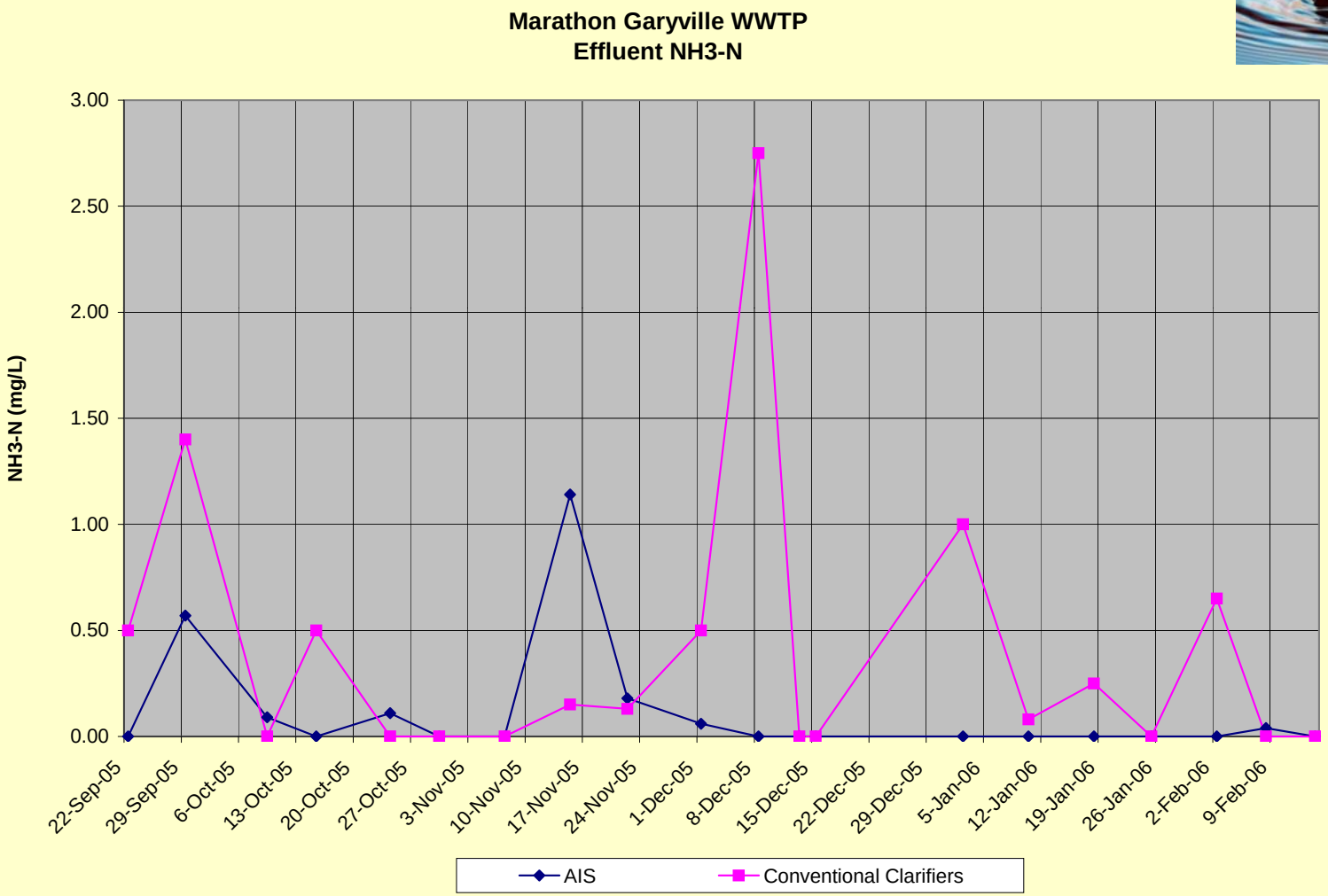
Performance
2007 AIS Nitrogen Balance: Short Term

- Conclusions of the Study
  - Average Total Nitrogen Removal Efficiency During the Study was ~ 89%
  - Denitrification in the AIS was Confirmed
  - Presents an Opportunity for TRI Reduction
    - Without Denitrification ~ 87 tons/yr NO_3 (AIS Only, Assumes 10 mg/L Effluent NO_3-N)
    - With Denitrification ~ 15 tons/yr NO_3 (AIS Only, Based on 2007 Average Effluent NO_3-N of 1.7 mg/L)

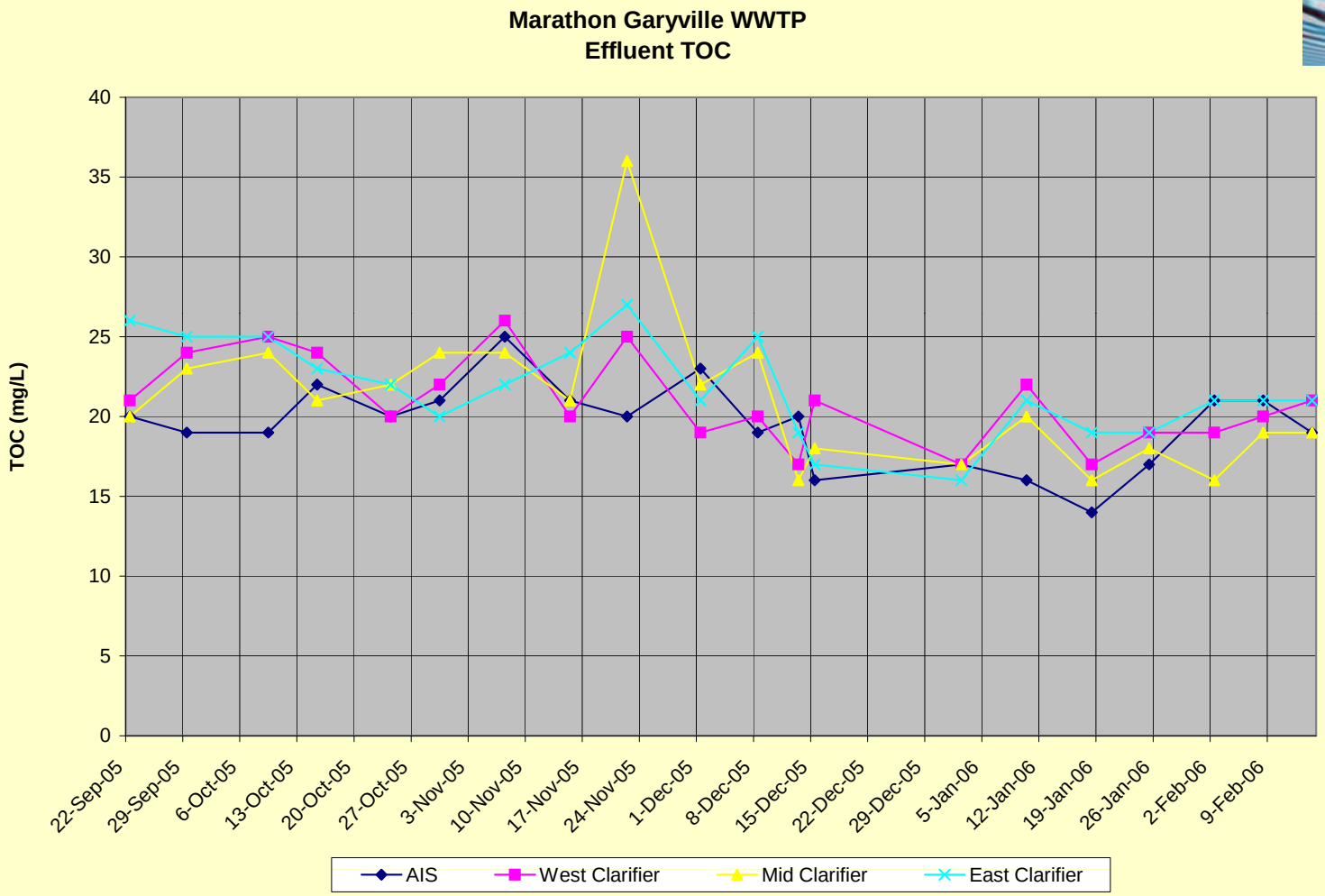
Performance: Long Term



Performance: Long Term

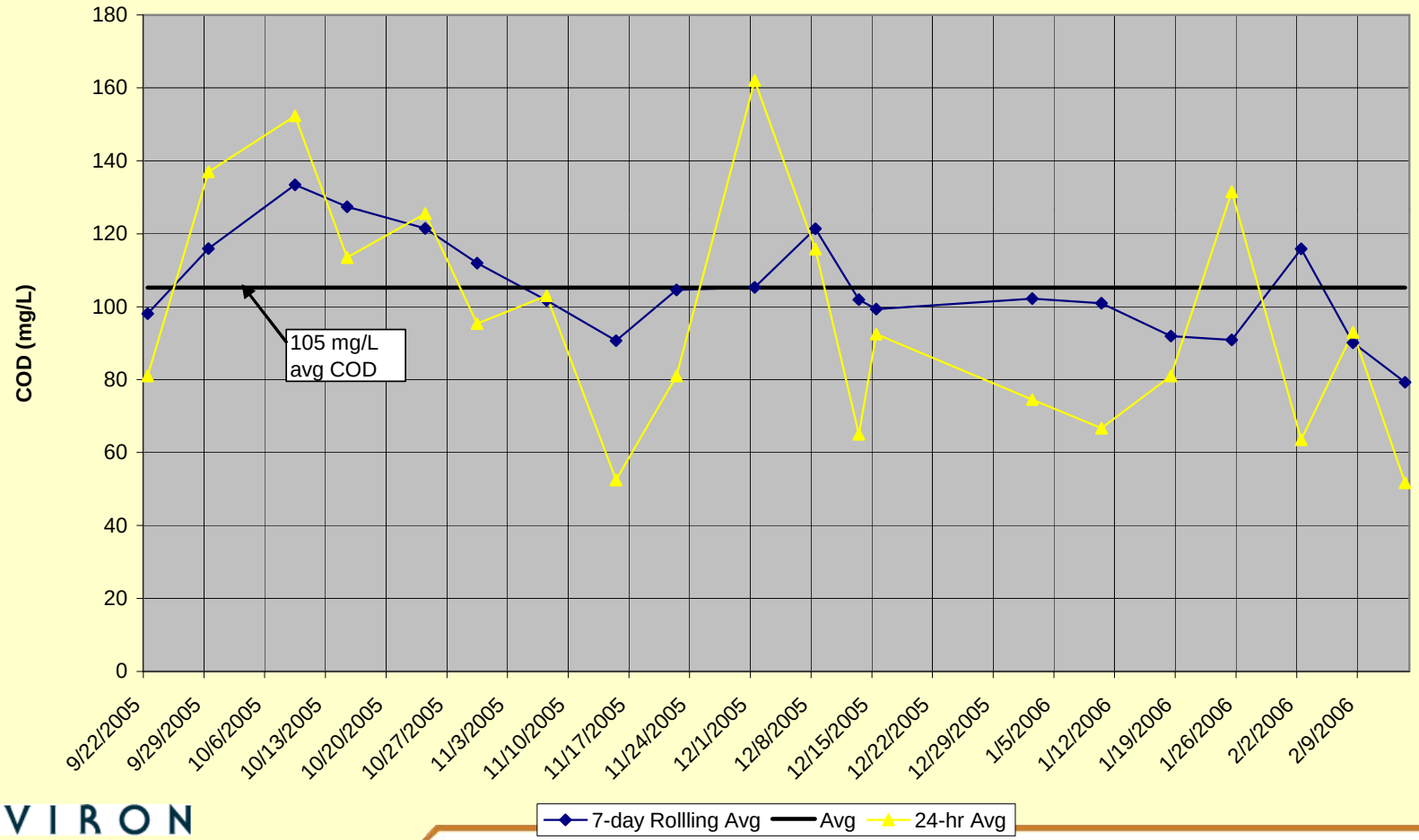


Performance: Long Term

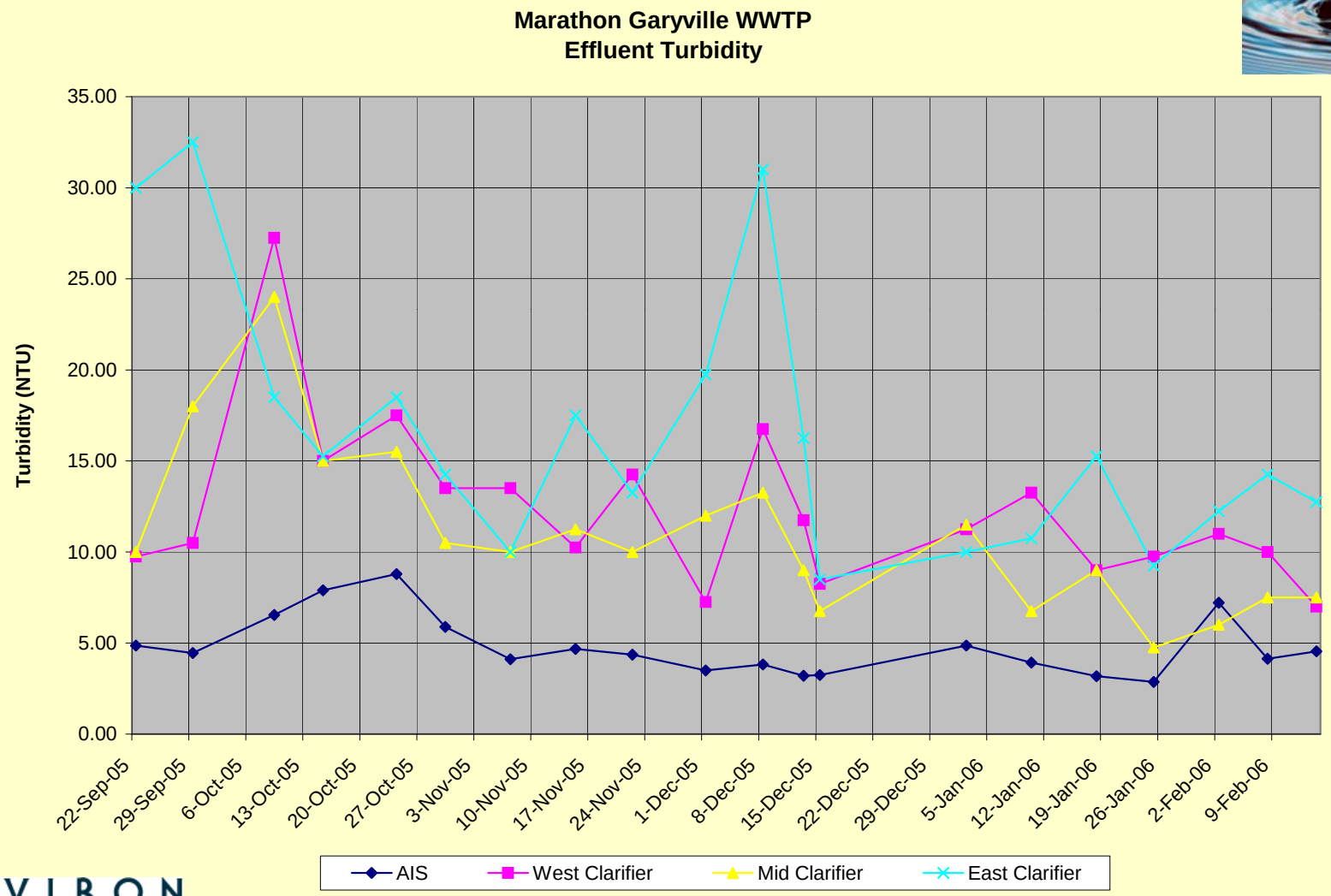


Performance: Long Term

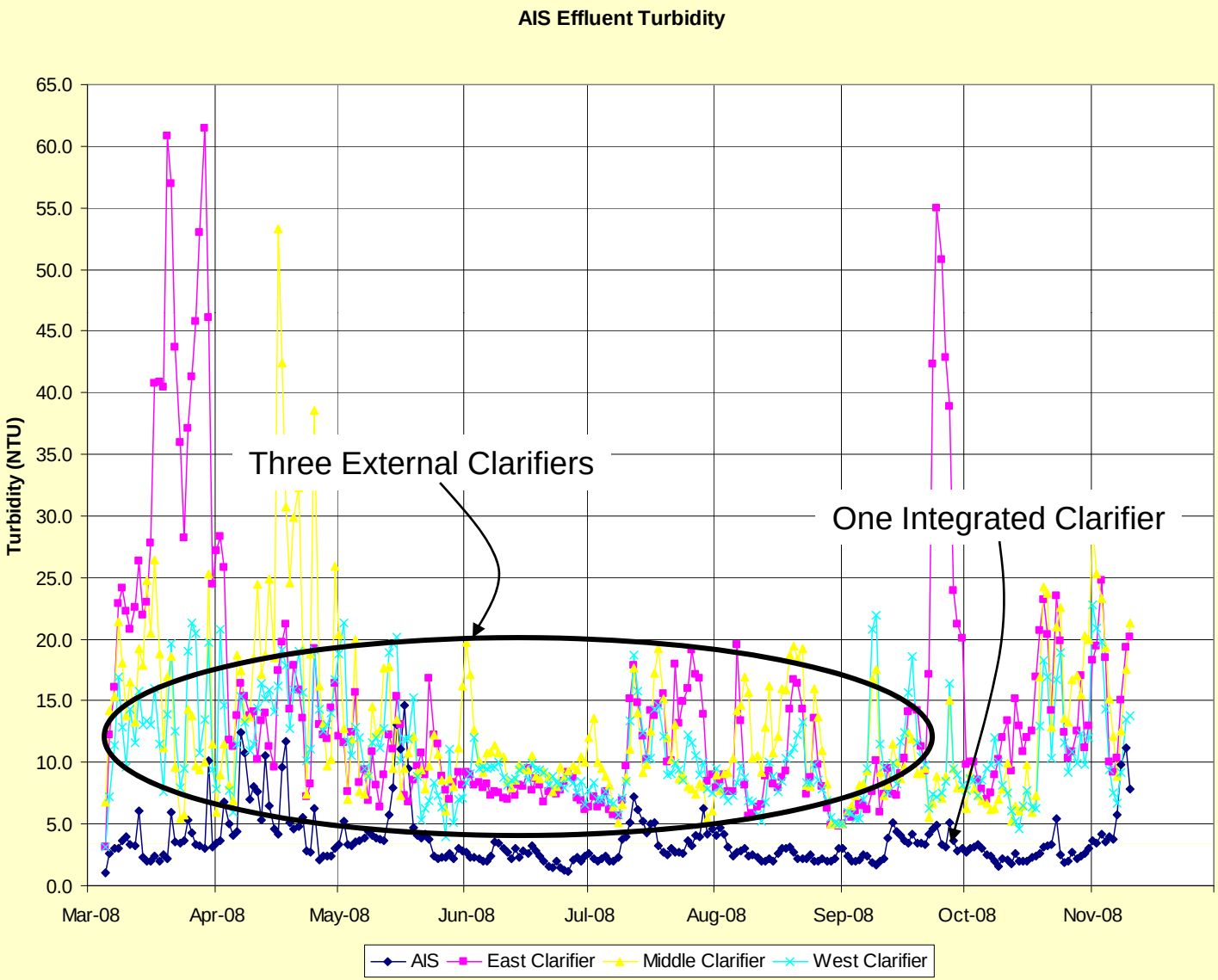
Marathon Garyville WWTP
Clarifier Composite Effluent COD



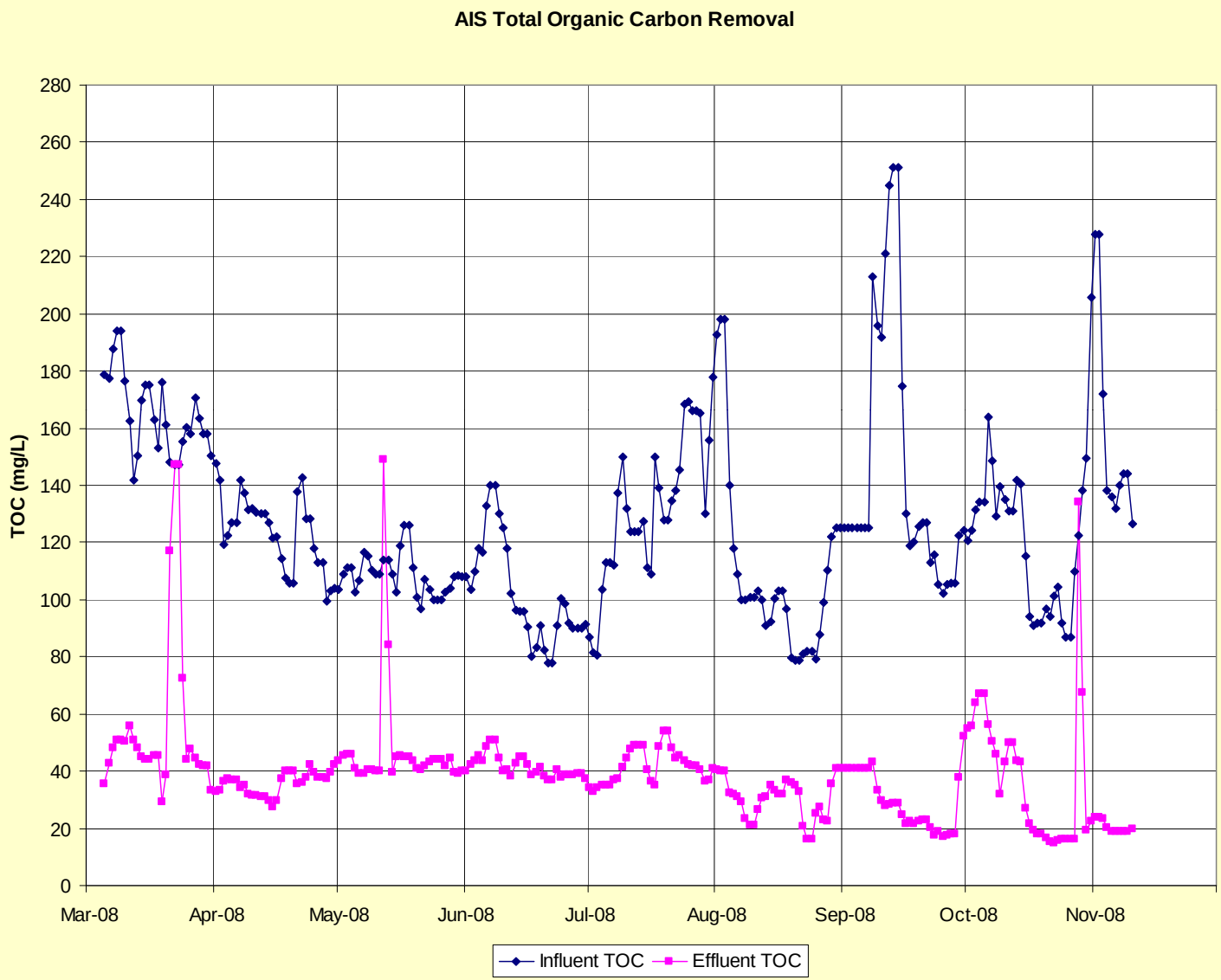
Performance: Long Term



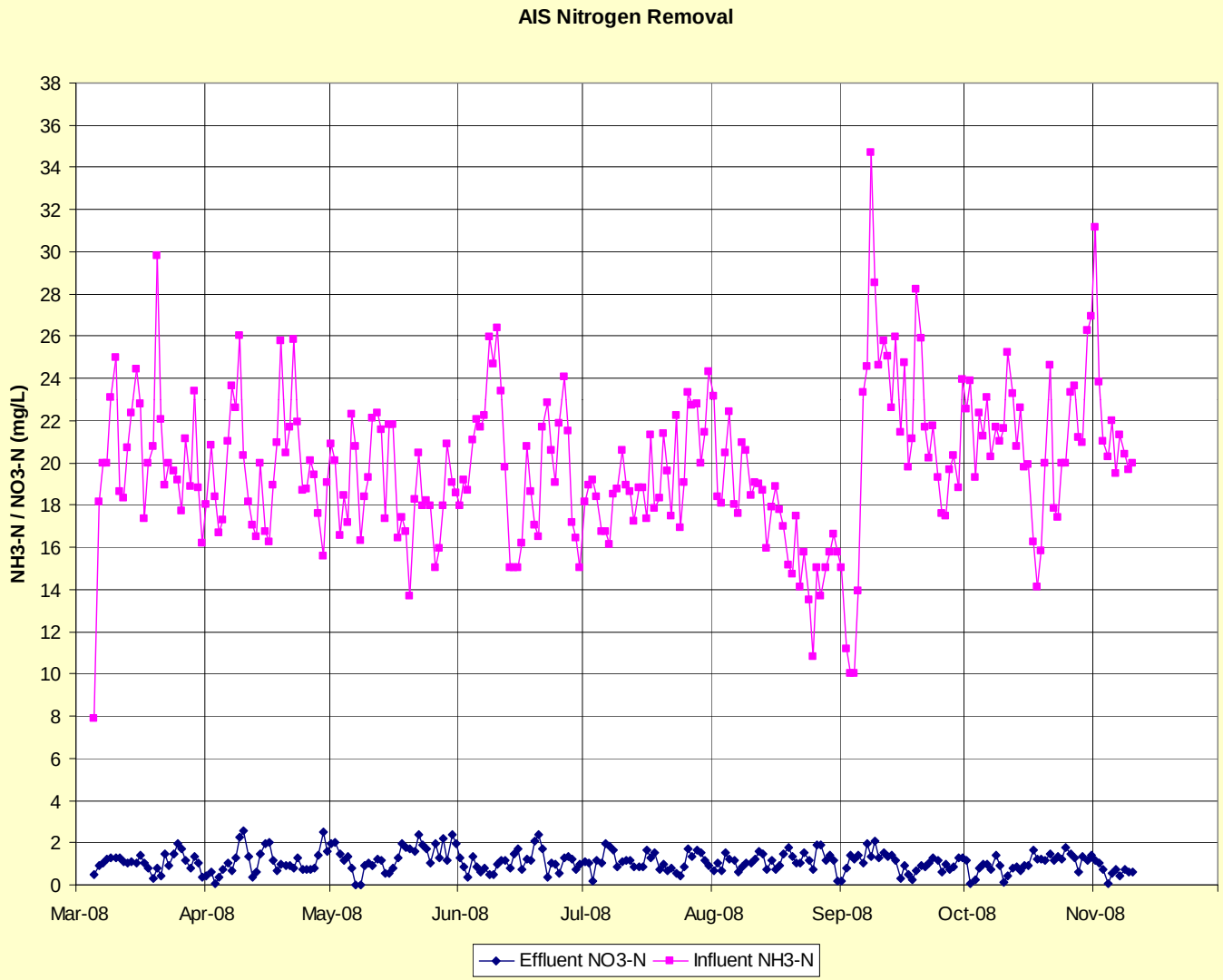
2008 Comparative Effluent Turbidity



2008 AIS TOC Performance



2008 AIS Effluent NO_3-N

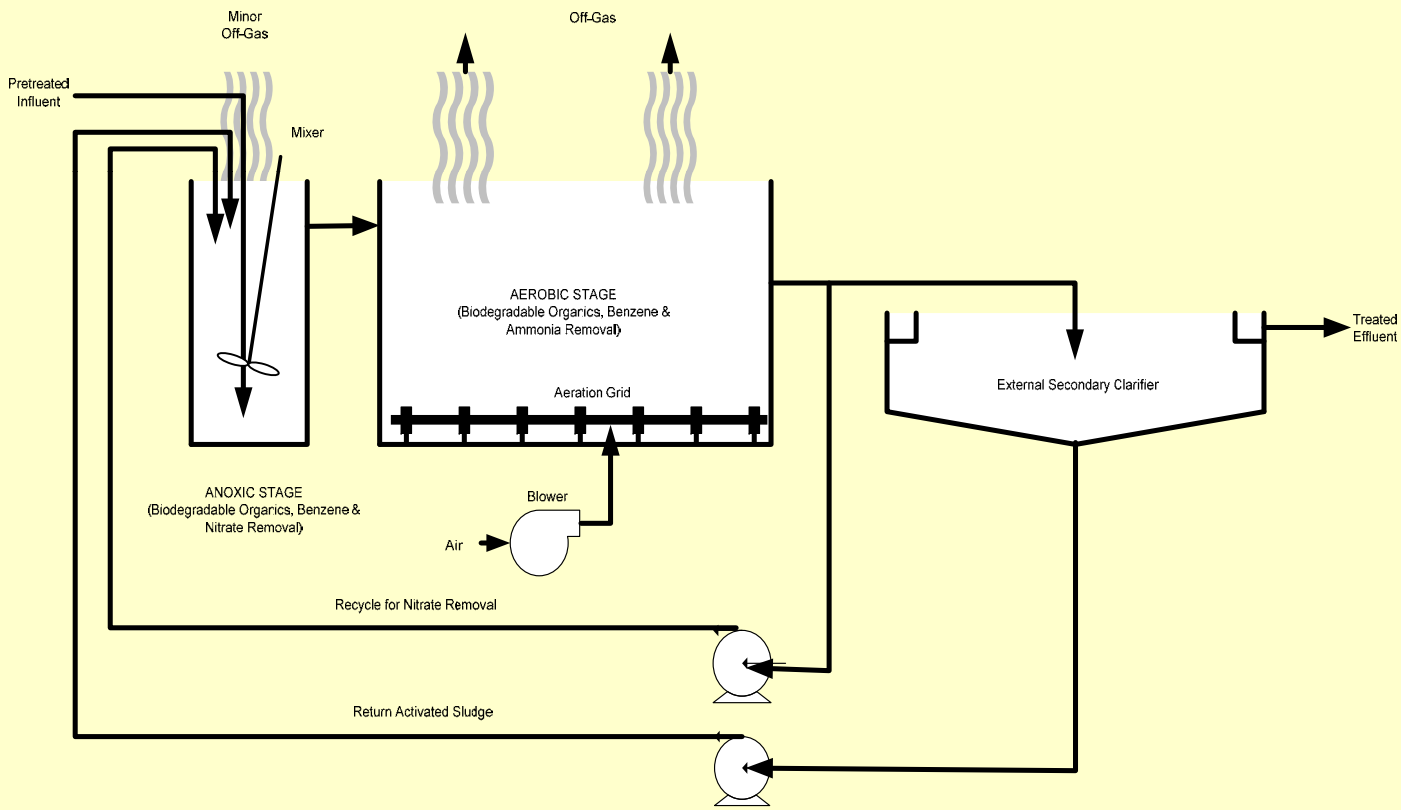


Recent Developments

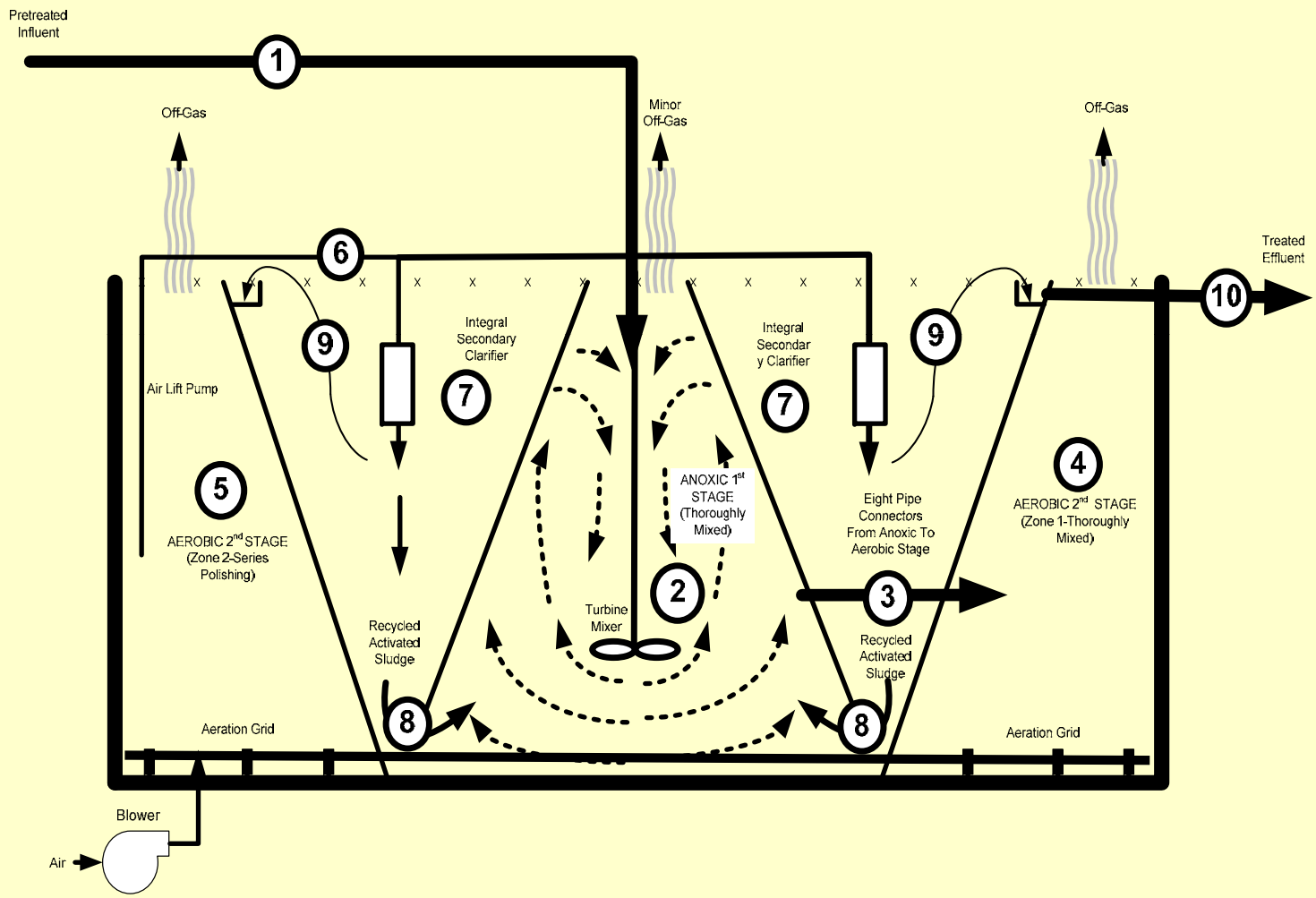
- Garyville Major Expansion Project
  - 180,000 bbls/day capacity expansion at LRD
  - New 5th Train (AIS Train Two) under construction at WWTP
- Potential to treat API/DGF and other WWTP VOC emissions with AIS
- VOC emissions are vented through aeration blowers into coarse or fine bubble diffusers along with normal air for biotreatment
- Low surface area for AIS is optimum for VOC emissions modeling

VOC Off-Gas Potential From Conventional Activated with External Clarifier (High Surface Area)

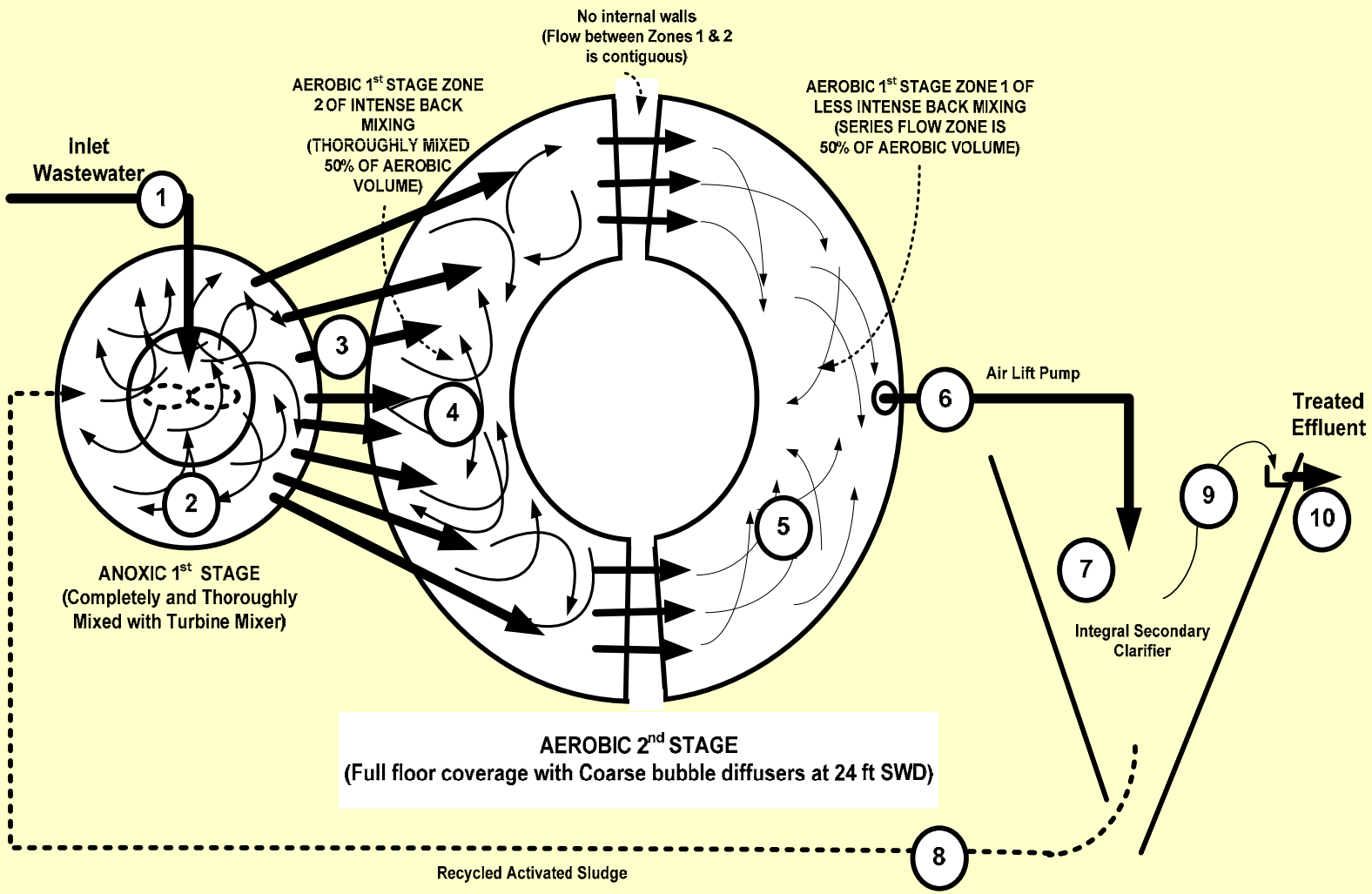
FIGURE 10. CONVENTIONAL ACTIVATED SLUDGE WITH EXTERNAL SECONDARY CLARIFIER
(Aerobic and Anoxic Stages for Organics Removal. Nitrification and Denitrification)



VOC Off-Gas Potential From Conventional Activated with Integrated Clarifier (Low Surface Area)



Optimum Configuration for VOC Off-Gas Modeling



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