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

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Air & Waste Management Association
Louisiana Section
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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

- ENVI RON 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

• 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

- **ENVIROMON 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)?

AIS Components

Patented Induced Downward Velocity allows higher concentrations of MLSS.

<table>
<thead>
<tr>
<th>System</th>
<th>MLSS, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Activated Sludge</td>
<td>2,000 to 4,000</td>
</tr>
<tr>
<td>AIS</td>
<td>6,000 to 8,000</td>
</tr>
</tbody>
</table>

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 . . .

- Rectangular
- Peripheral
- Circular
- Square
- Internal Pyramidal
Upgrade Design and Implementation
Biological Treatment Chemistry

- **Organic Removal** – Biological Oxidation of Organics (e.g., Hydrocarbons, Phenols) to Carbon Dioxide and Water:
  \[ C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O + \text{new bacteria} \]

- **Nitrification** – Biological Oxidation of Ammonia to Nitrate:
  \[ NH_4^+ + 2O_2 + 2HCO_3^- \rightarrow NO_3^- + H_2O + 2H_2CO_3^- + \text{new bacteria} \]

- **Denitrification** – Biological Oxidation of Organics and Conversion of Nitrate to Nitrogen Gas:
  \[ NO_3^- + 0.83CH_3OH + 0.17H_2CO_3^- \rightarrow 0.5N_2 + 1.33H_2O + HCO_3^- + \text{new bacteria} \]

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

**AUTOTROPHS**
Strict aerobes, must have D.O.
Upgrade Design and Implementation
Conventional Nitrification-Denitrification

A Typical Nitrifying-Denitrifying Activated Sludge System...

Influent

- Aerobic Basin
- Secondary Clarifier
- Anoxic Basin
- Nitrate Recycle
- Treated Effluent
- Return Activated Sludge
Upgrade Design and Implementation
AIS Nitrification-Denitrification

- Influent Wastewater
- Nitrate Recycle
- Control Valve
- AERIAL FLIGHT PUMP
- AEROBIC BASIN
- AIS INTEGRAL CLARIFIER
- Treated Effluent
- Denitrified Water (Gravity Flow)
First Major AIS Nitrification-Denitrification System
NH₄-N = 4,000 mg/L

United States Steel Coke Plant, Gary, Indiana
Upgrade Design and Implementation
AIS Flow Path

E N V I R O N

Louisiana Refining Division
Modular Ring Configuration

- Modular Ring Clarifier
- Peripheral Anoxic & Central Aerobic Zones
- Central Aerobic Zone
- Central Aerobic Zone
- DTF
- Clarifier Feed Structure
- Walkways & Weirs
Upgrade Design and Implementation
AIS Flow Path

Marathon Oil Co.
Louisiana
Refining Division
Garyville, LA

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

Effluent Design
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
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

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>UNITS</th>
<th>MONDAY</th>
<th>TUESDAY</th>
<th>WEDNESDAY</th>
<th>THURSDAY</th>
<th>FRIDAY</th>
<th>AVERAGE</th>
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<td>1,100</td>
<td>1,100</td>
<td>1,033</td>
<td>1,025</td>
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<td>COD</td>
<td>mg/L</td>
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<td>260</td>
<td>354</td>
<td>307</td>
<td>300</td>
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<td>TKN</td>
<td>mg/L</td>
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<td>18</td>
<td>20</td>
<td>18</td>
<td>16</td>
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<tr>
<td>NH₃-N</td>
<td>mg/L</td>
<td>15</td>
<td>16</td>
<td>16</td>
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<td>16</td>
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<tr>
<td>NO₃-N</td>
<td>mg/L</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
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<td>TSS</td>
<td>mg/L</td>
<td>34</td>
<td>44</td>
<td>95</td>
<td>77</td>
<td>50</td>
<td>60</td>
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### AIS Effluent Characteristics

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>UNITS</th>
<th>MONDAY</th>
<th>TUESDAY</th>
<th>WEDNESDAY</th>
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<th>FRIDAY</th>
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<tr>
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<td>1,096</td>
<td>1,085</td>
<td>977</td>
<td>1,017</td>
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<td>COD (s)</td>
<td>mg/L</td>
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<td>38</td>
<td>43</td>
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<td>TKN (s)</td>
<td>mg/L</td>
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<td>NH₃-N (s)</td>
<td>mg/L</td>
<td>1.3</td>
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<td>NO₃-N (s)</td>
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<td>mg/L</td>
<td>19</td>
<td>19</td>
<td>18</td>
<td>23</td>
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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 NO₃ (AIS Only, Assumes 10 mg/L Effluent NO₃-N)
    - With Denitrification ~ 15 tons/yr NO₃ (AIS Only, Based on 2007 Average Effluent NO₃-N of 1.7 mg/L)
Performance: Long Term

2007 AIS Ammonia & Nitrate Concentrations

- 2007 Avg Influent NH3-N = 16.6 mg/L
- 2007 Avg Effluent NH3-N = 1.2 mg/L
- 2007 Avg Effluent NO3-N = 1.7 mg/L
Performance: Long Term

Marathon Garyville WWTP
Effluent NH3-N

<table>
<thead>
<tr>
<th>Date</th>
<th>NH3-N (mg/L)</th>
<th>AIS</th>
<th>Conventional Clarifiers</th>
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<td>29-Sep-05</td>
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<tr>
<td>6-Oct-05</td>
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<td>13-Oct-05</td>
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<td>20-Oct-05</td>
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<tr>
<td>27-Oct-05</td>
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<td></td>
</tr>
<tr>
<td>3-Nov-05</td>
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<td>8-Dec-05</td>
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<td>22-Dec-05</td>
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<td>26-Jan-06</td>
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<td>2-Feb-06</td>
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<tr>
<td>9-Feb-06</td>
<td>0.00</td>
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Performance: Long Term

Marathon Garyville WWTP
Effluent TOC

TOC (mg/L)

22-Sep-05
29-Sep-05
6-Oct-05
13-Oct-05
20-Oct-05
27-Oct-05
3-Nov-05
10-Nov-05
17-Nov-05
24-Nov-05
1-Dec-05
8-Dec-05
15-Dec-05
22-Dec-05
29-Dec-05
5-Jan-06
12-Jan-06
19-Jan-06
26-Jan-06
2-Feb-06
9-Feb-06

AIS
West Clarifier
Mid Clarifier
East Clarifier
Performance: Long Term

Marathon Garyville WWTP
Clarifier Composite Effluent COD

COD (mg/L)

105 mg/L avg COD

7-day Rolling Avg  Avg  24-hr Avg
Performance: Long Term

Marathon Garyville WWTP
Effluent Turbidity

Turbidity (NTU)

AIS West Clarifier Mid Clarifier East Clarifier
2008 Comparative Effluent Turbidity

AIS Effluent Turbidity

Turbidity (NTU)

Three External Clarifiers

One Integrated Clarifier

Mar-08 Apr-08 May-08 Jun-08 Jul-08 Aug-08 Sep-08 Oct-08 Nov-08
2008 AIS TOC Performance

AIS Total Organic Carbon Removal

TOC (mg/L)

Mar-08 Apr-08 May-08 Jun-08 Jul-08 Aug-08 Sep-08 Oct-08 Nov-08

Influent TOC  Effluent TOC

ENVI RON

Louisiana Refining Division
2008 AIS Effluent NO$_3$-N

AIS Nitrogen Removal

Mar-08  Apr-08  May-08  Jun-08  Jul-08  Aug-08  Sep-08  Oct-08  Nov-08

Effluent NO$_3$-N  Influent NH$_3$-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)
VOC Off-Gas Potential From Conventional Activated with Integrated Clarifier (Low Surface Area)
Optimum Configuration for VOC Off-Gas Modeling

AERobic 1st Stage Zone 1 of Less Intense Back Mixing (Series Flow Zone is 50% of Aerobic Volume)

No internal walls (Flow between Zones 1 & 2 is contiguous)

AERobic 2nd Stage
(Full floor coverage with Coarse bubble diffusers at 24 ft SWD)

Recycled Activated Sludge

Treated Effluent

Integral Secondary Clarifier

Air Lift Pump

Environ

Louisiana Refining Division
Authors

- Dr. Carl E. Adams, Jr., Global Practice Leader, Integrated Industrial Wastewater Management
  ENVRON International Corporation
cadams@environcorp.com

- Mr. Wally E. Dows, III; ES&S Manager
  Marathon Oil Company, Louisiana Refining Division
wedows@marathonoil.com

- Mr. John Driver, Project Manager
  ENVRON International Corporation
jdriver@environcorp.com

- Mr. Chad Louque; Operations Supervisor
  Marathon Oil Company, Louisiana Refining Division
cplouque@marathonoil.com