

***PHYSICAL / CHEMICAL
TREATMENT FOR REFINERY
WASTEWATER***

***William Conner
Mohammed Al Hajri
John Liu***

Problem

- 💧 ***New Environmental Requirements***
- 💧 ***Low Energy Costs - High Maintenance Sensitivity***
- 💧 ***Highly Abnormal Refinery Wastewater***
 - ***High Temp (> 50 C) – Bio Difficult***
 - ***High TDS (ave. 18,000 mg/L)***
 - ***High Ammonia (80 mg/L)***
 - ***High Phenol (>60 mg/L)***
 - ***V. High Variability (TDS From 8 – 35,000 mg/L)***
 - ***Frequent Flow interruptions***
- 💧 ***High Removal Efficiencies Required***
 - ***Phenol -> 0.1 mg/L (99.8% Removal)***
 - ***Ammonia -> 1 mg/L (98.7% Removal)***

Problem

Upstream Process Modifications

Unfeasible

Treat Wastewater As Is

Treatment Options

💧 *Oil/Water Separation & Biological*

- *Traditional Treatment Method*
- *Low Cost*

--- HOWEVER ---

- *High Removal Efficiencies Required*
- *Operational Considerations*
 - *Biosystem Sensitivities*
 - *Solids Settling Requirements*
- *Challenging Operating Conditions*
 - *Feed Modification Very Expensive*
- *Unpopular Technology*

Treatment Options

Traditional Treatment

--- DECISION ---

Alternative

Physical/Chemical Treatment

Treatment Options

Physical / Chemical Treatment

- ▶ **Non Traditional - Unproven**
- ▶ **Higher Cost**
- ▶ **More Treatment Steps**

--- HOWEVER ---

- ▶ **Adaptable to Varying Operating Conditions**
- ▶ **High Removal Efficiencies Possible**
- ▶ **Better Start-up / Shut-down**
- ▶ **Easier to Operate**

Design Development Physical/Chemical

Engaged USFilter/Siemens

- ▶ *Treatment Needs Evaluation*
- ▶ *Literature Search*
- ▶ *Bench Scale Testing*
- ▶ *Field Pilot Plant*
- ▶ *Equipment Design – Economic Evaluation*
 - *Biological*
 - *Physical/Chemical*

Treatment Needs Evaluation

💧 **BOD/COD/TOC**

➔ 150 mg/L BOD -> Less Than 25 mg/L

💧 **Ammonia**

➔ 80 mg/L -> Less Than 1 mg/L

💧 **Phenol**

➔ 60+ mg/L -> Less Than 0.1 mg/L

Indicator Parameters

Ammonia & Phenol

Literature Search

💧 *Treatment Options Identified:*

➤ **Phenol & BOD/COD/TOC**

- **Steam Stripping**
- **Polymeric Resins**
- **Carbon Adsorption**

➤ **Ammonia**

- **Steam Stripping**
- **Clinoptilolite Clay**
- **Ion Exchange Resin**
- **Air Stripping**
- **Breakpoint Chlorination**

Bench Scale Testing

💧 *Ammonia*

- *Ion Exchange – Low Exchange Capacity*
- *Air Stripper - > 97% Removal*

💧 *Phenol*

- *Polymeric Resins – 1 - 2 mg/L*
 - *Steam Regeneration Possible*
 - *Pre Treatment Only*
- *Carbon Adsorption - < 0.1 mg/L*
 - *Steam Regeneration Not Indicated*

Polishing Only

Field Plant Testing - Goals

--- Confirm ---

💧 **Resin Column**

- **Bulk Removal of Phenol**
- **Regeneration Capability – Long Term**

💧 **GAC Column**

- **Polishing Capability**

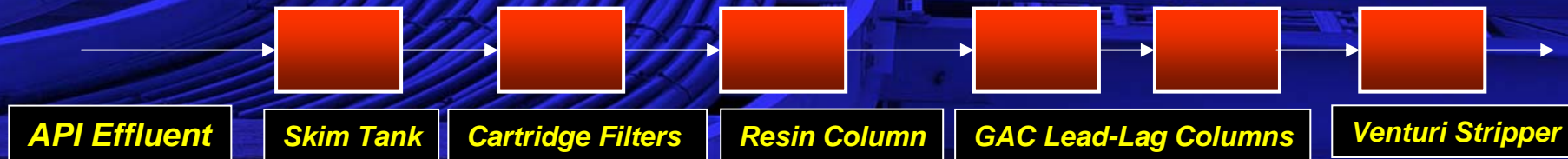
💧 **Venturi Air Stripper**

- **Bulk Removal of Ammonia**

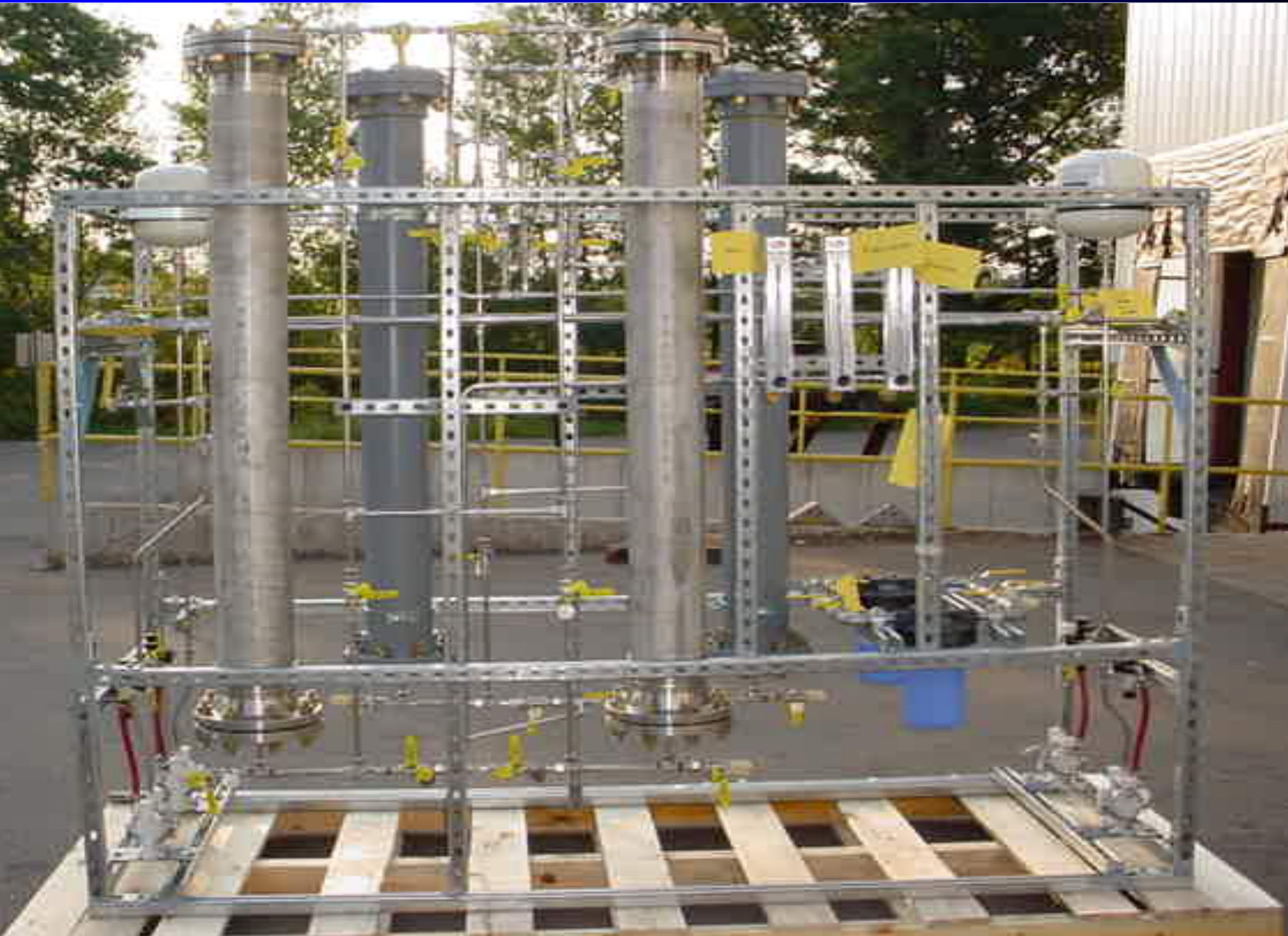
💧 **Design Specifications**

Field Pilot Setup

- 💧 *API Separator Effluent*
- 💧 *Skim / Equalization Tank*
- 💧 *50 micron Cartridge Filter*
- 💧 *Single Resin Column*
- 💧 *2 GAC Columns – Series*
- 💧 *Venturi Air Stripper*

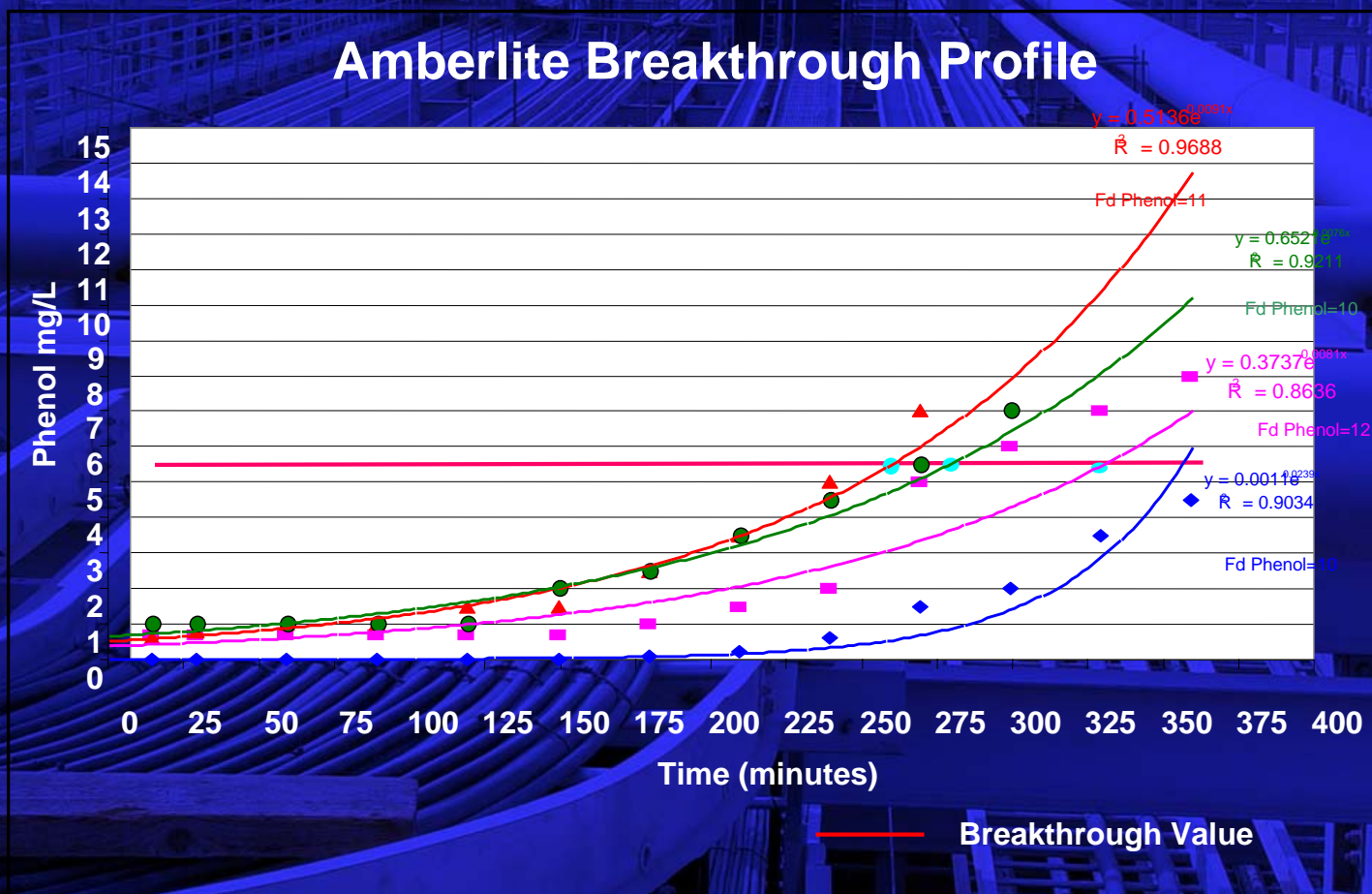


Field Pilot Plant



Resin Pilot Plant Testing – Results

- Resin Column – 1st Goal Confirm:
 - Bulk Removal of Phenol (@17+ BV/Hr Feed)

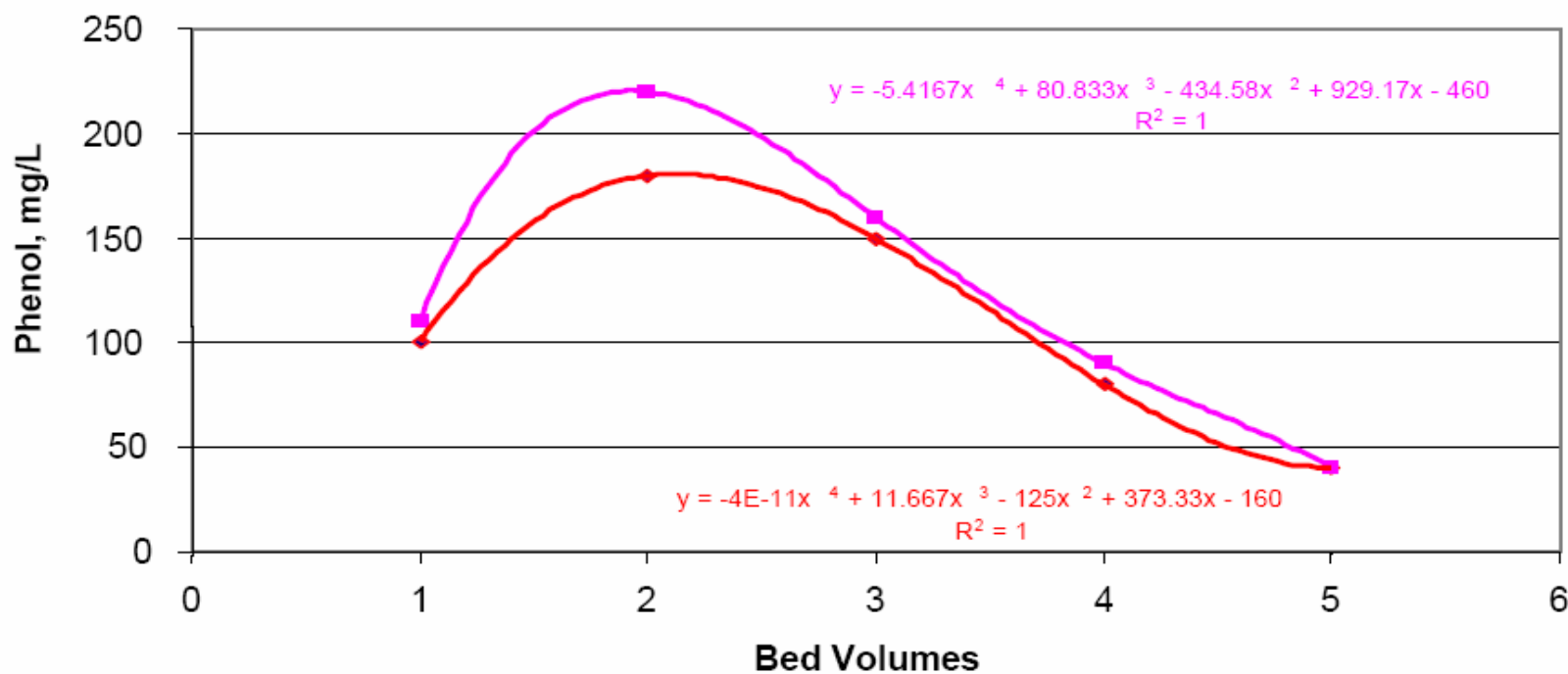


Resin Pilot Plant Testing – Results

💧 **Resin Column – 2nd Goal:**

➔ **Steam Regeneration**

Steam Regenerant Phenol Concentration



◆ 11/30/2003 ■ 12/1/2003 — Best Fit (12/1/2003) — Best Fit (11/30/2003)

Resin Pilot Plant Testing – Results

💧 *Resin Column*

➤ *Regeneration Results:*

- *60% Removal w/ 4 Bed Volumes*
- *Post Regeneration [Phenol] <1.0 mg/L*
- *No Change in Removal Capacity With Time*

– Steady State Indicated

➤ *Data Indicated Fewer Steam BVs Possible (3)*

- *Insulation Important*
- *Higher Temperature*
- *Cost Benefit Analysis*

Resin Pilot Plant Testing – Conclusions

💧 *Resin Column Test Goals*

- *Bulk Removal of Phenol - Confirmed*
- *Regeneration Capability - Confirmed*
- *12 Hr Run Time w/ 7 BV/Hr Loading*

--- Additionally ---

- *Robust System*
 - *Accommodates Process / Operator Problems*

GAC Pilot Plant Testing - Results

💧 GAC Polishing – Confirm Polishing

➤ Field Setup

- Feed to GAC From Resin Column
- Lead / Lag Column Arrangement
 - Switch 1st Column @ Breakthrough of 2nd
(0.1 mg/L)

GAC Pilot Plant Testing - Conclusions

💧 GAC Polishing

- **GAC Polishing Capability – Confirmed**
- **Design:**
 - **1 BV/Hr = 30 Days Useful Bed Life**
 - **Economics = Multiple Columns in Series**

NH3 Pilot Plant Testing

- ***Ammonia – Confirm Bulk Removal***
 - ▶ ***Field Setup – Venturi Stripper***
 - ***API Separator Effluent in Batch Mode***
 - ***Removal Coefficients***
 - ***Used Removal Coefficients to Simulate Stages***
 - ***98% Removal***
 - ***Cost Analysis Performed***

Pilot Venturi Stripper



NH₃ Pilot Plant Testing - Conclusions

💧 *Ammonia Removal*

➤ **NH₃ Removal – Confirmed**

➤ **Design**

- **Multiple Stages Required for 99.9% Removal**
- **Polishing Potentially Required**

Decision

Design Confirmed

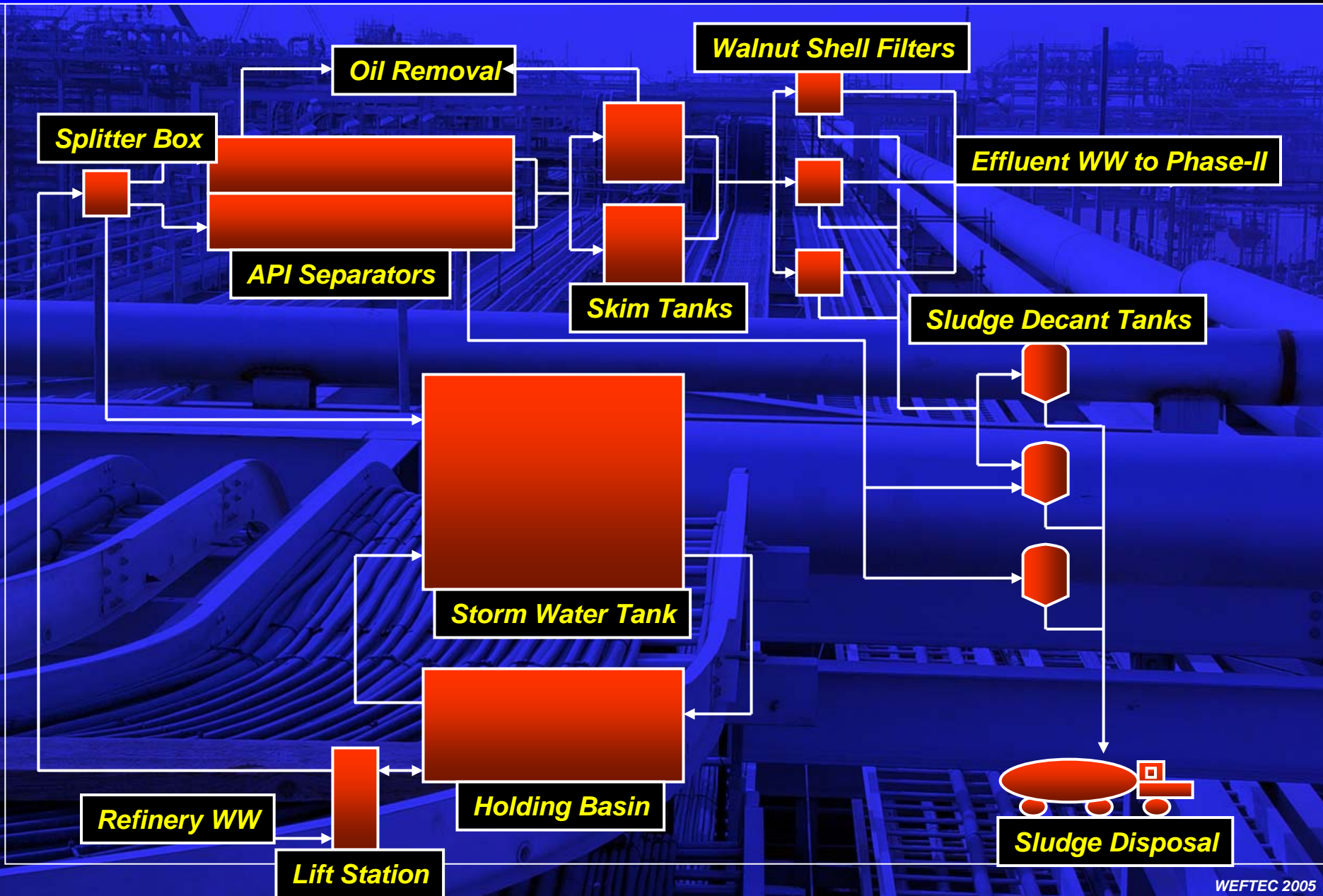
Scale-up For Refinery

Cost Analysis

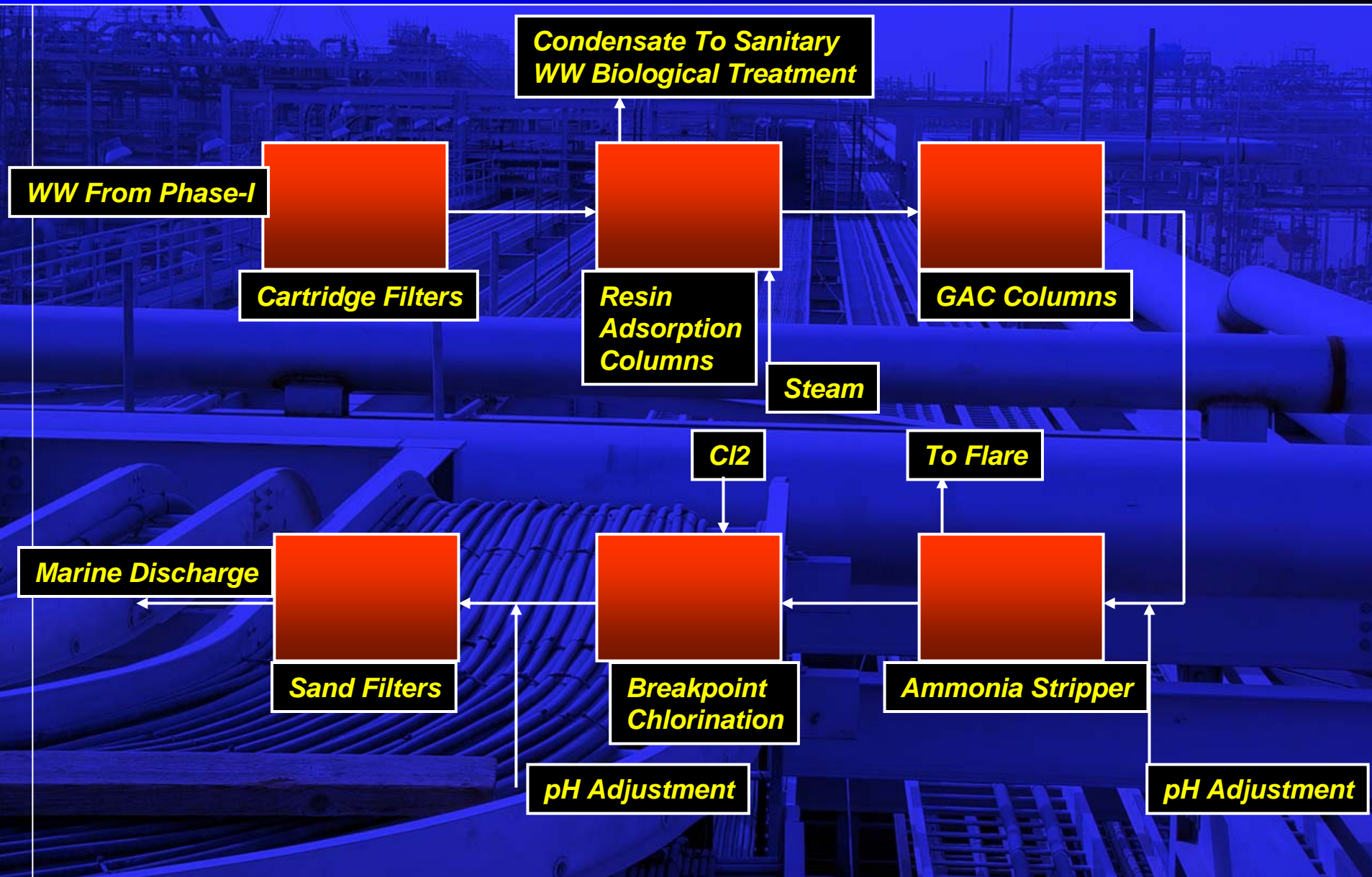
Physical & Biological

Operational Advantages

Primary Treatment Process Design



Physical/Chemical Process Design



Conclusions

💧 *Identified & Demonstrated Feasibility of Physical / Chemical Treatment for:*

- **Organic Removal**
- **Ammonia Removal**

💧 *Evaluated Project Life Cycle Costs*

- **Physical/Chemical**
 - **Slightly Lower Cost**
 - **More Reliable & Easier To Operate**



Thank You