PHYSICAL / CHEMICAL TREATMENT FOR REFINERY WASTEWATER

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**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
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

物理/化学处理

- 非传统 - 未经证实
- 高成本
- 更多处理步骤

然而

- 适应性较好，适应各种运行条件
- 高去除效率可能
- 更好的启动/关闭
- 更容易操作
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
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
Resin Pilot Plant Testing – Results

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

Amberlite Breakthrough Profile

- $y = 0.5136e^{0.0091x}$, $R^2 = 0.9688$
- $y = 0.6521e^{0.0076x}$, $R^2 = 0.9211$
- $y = 0.3737e^{0.0081x}$, $R^2 = 0.8636$
- $y = 0.0011e^{0.0239x}$, $R^2 = 0.9034$
Resin Pilot Plant Testing – Results

Resin Column – 2nd Goal:
- Steam Regeneration

Steam Regenerant Phenol Concentration

\[ y = -5.4167x^4 + 80.833x^3 - 434.56x^2 + 929.17x - 460 \]
\[ R^2 = 1 \]

\[ y = -4E-11x^4 + 11.667x^3 - 125x^2 + 373.33x - 150 \]
\[ R^2 = 1 \]
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
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

- Splitter Box
- API Separators
- Storm Water Tank
- Holding Basin
- Lift Station
- Oil Removal
- Skim Tanks
- Walnut Shell Filters
- Sludge Decant Tanks
- Effluent WW to Phase-II
- Refinery WW
- Sludge Disposal
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