Siemens Industry, Inc.
Rothschild, Wisconsin, USA

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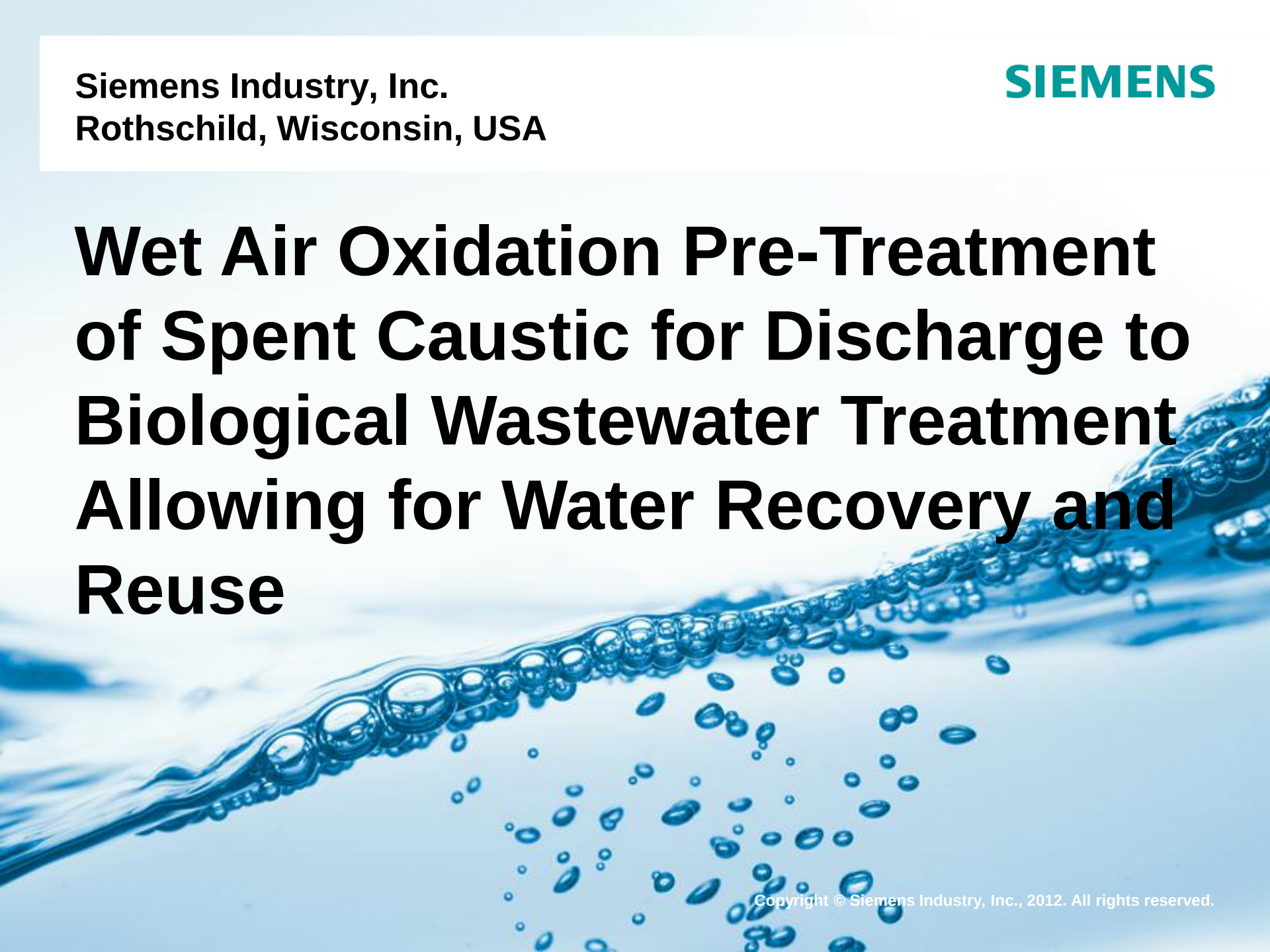
Wet Air Oxidation Pre-Treatment of Spent Caustic for Discharge to Biological Wastewater Treatment Allowing for Water Recovery and Reuse



Refinery Spent Caustic Treatment Using Wet Air Oxidation

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Zimpro® wet air oxidation (WAO) is used to treat refinery spent caustic, resulting in an oxidized effluent that can be safely and easily polished using standard biological waste water treatment allowing for water recovery and re-use

The following presentation will discuss:

- Typical characteristics of refinery spent caustic
- Issues related to the treatment of refinery spent caustic
- Overview of the Zimpro® wet air oxidation (WAO) Process
- Test methods for evaluating spent caustic treatment effectiveness
- Case studies of three existing refinery WAO treatment systems
- A novel process currently in R&D for recovering fresh NaOH

Classification of Spent Caustics

Type	Source	Principle Contaminants
Sulfidic	Ethylene or LPG	Sulfides and/or mercaptans
Cresylic	FCC Gasoline	Phenolic compounds and reduced sulfur
Naphthenic	Kerosene, Diesel, and Jet Fuel	Naphthenic compounds and reduced sulfur

Refinery Spent Caustic
Typical Characteristics

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Inorganic Sulfides as S %	0 to 4
Mercaptides %	0 to 4
Salts of Cresylic Acids %	0 to 20
Salts of Napthenic Acids %	0 to 10
NaOH %	1 to 15
COD mg/l	50,000 to 400,000
pH	13 to 14

Refinery Spent Caustic Disposal Concerns

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Typical Concerns with on-site disposal of spent caustic:

- **Naphthenic** spent caustics
  - High COD (50,000 to 150,000 mg/l)
  - Cause of serious foaming issues when agitated or aerated
  - Limited biodegradability
- **Cresylic** spent caustic
  - Extremely high COD (> 100,000 mg/l)
  - Cresylic compounds are derivatives of phenol
    - Limited biodegradability
    - Can cause operational issues with WWTP (primarily related to sludge settling)

- **Sulfidic** spent caustic
  - Release of potentially dangerous H_2S and Mercaptans
  - Extremely odorous
  - Can cause operational issues with WWTP (pH swings)

Zimpro® Wet Air Oxidation – Typical Process Flow Diagram

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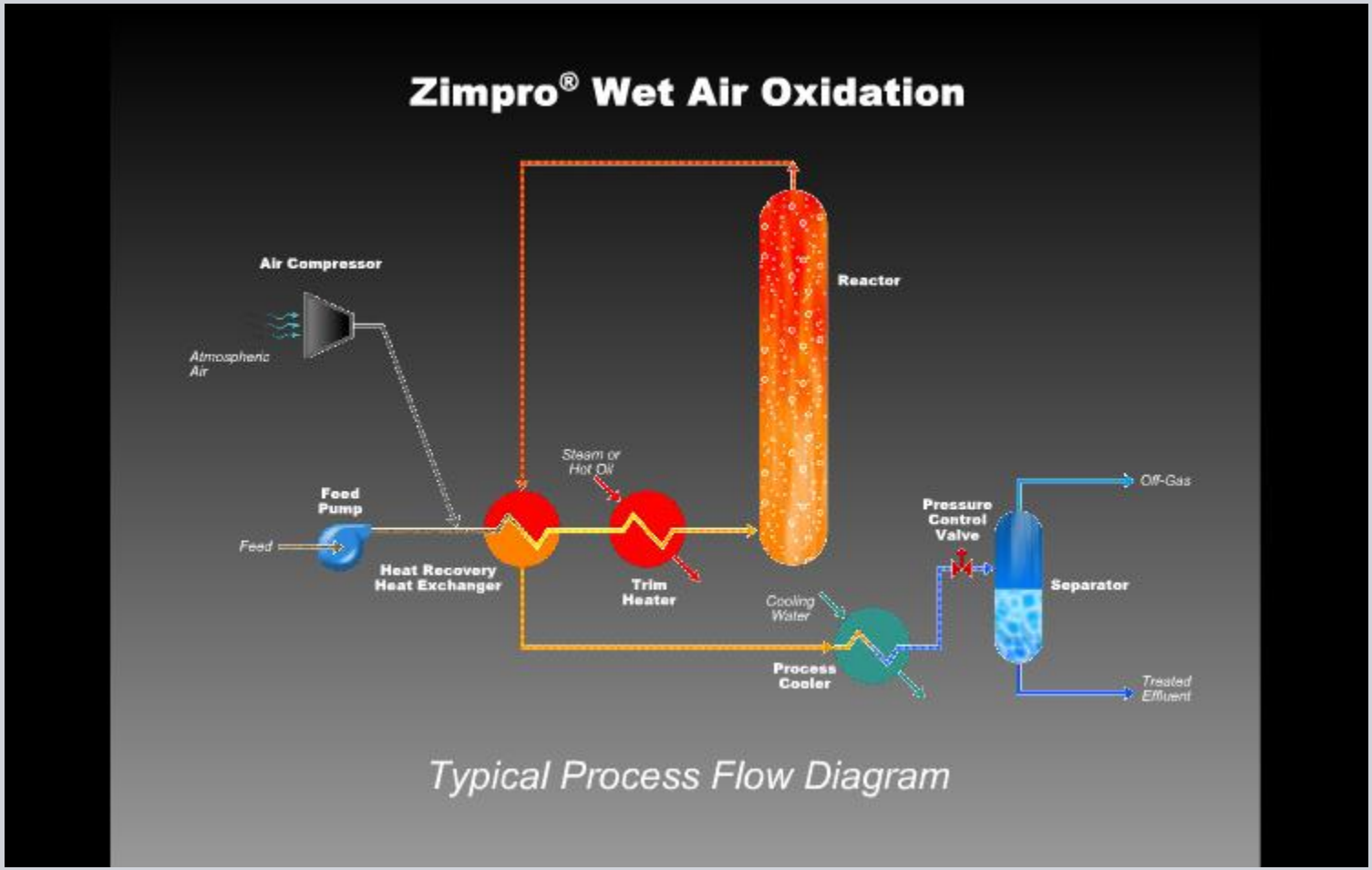

Refinery Spent Caustic – Zimpro® WAO Spent Caustic Treatment Systems

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Treatment objectives for Siemens WAO spent caustic treatment systems:

- Pre-treat the spent caustic and make it suitable for polishing by the facilities WWTP.
- Destroy sulfides and mercaptans
- Make refractory or toxic organics biodegradable
- Destroy foaming characteristics

Refinery Spent Caustic
Methods for Testing Biodegradability

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Measuring the biodegradability of a high COD / high TDS wastewater

Standard BOD_5 Test

- Samples are small
- High dilutions are typically required – often leading to exaggerated error and the potential remove toxicity concerns
- Test is a batch system – single data point at end of test

Continuous Flow Bench Scale Testing

- Requires large sample amounts
- Requires significant resources
- Requires long operating schedule

Refinery Spent Caustic – Respirometery Testing Method

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Siemens uses closed cell respirometery to measure a high TDS samples ability to be degraded biologically.

Respirometery is based on the rate at which the biomass consumes dissolved oxygen. This rate is measured by monitoring the changes in gaseous oxygen concentration using volumetric techniques.

Siemens respirometery method is based on EPA Method OPPTS 835.3110

Refinery Spent Caustic – Respirometery Testing Method

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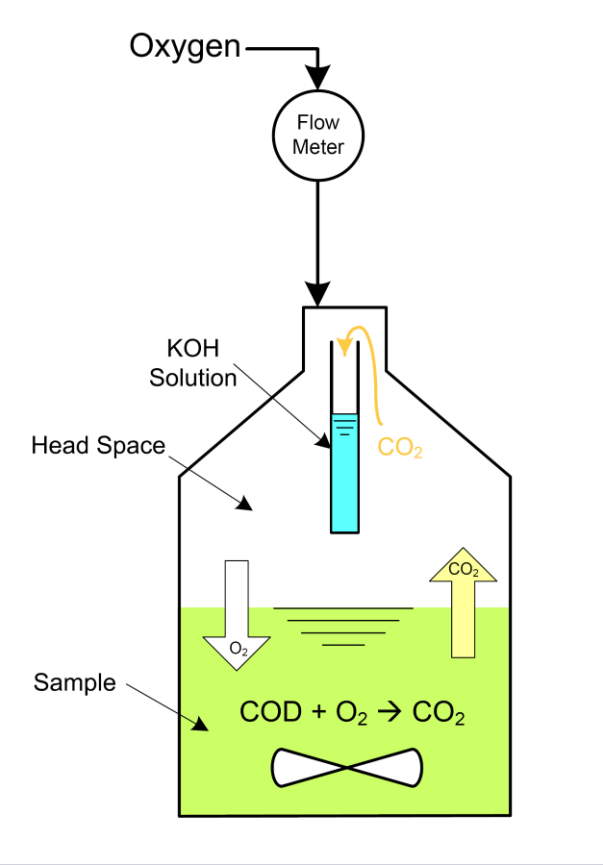
Respirometery uses closed cell metabolic rate monitoring to evaluate biological activity.



Respirometery allows:

- Testing of multiple samples simultaneously
- Testing of control samples to assure proper operation
- Monitoring of biological activity over time

Refinery Spent Caustic – Respirometery Testing Method

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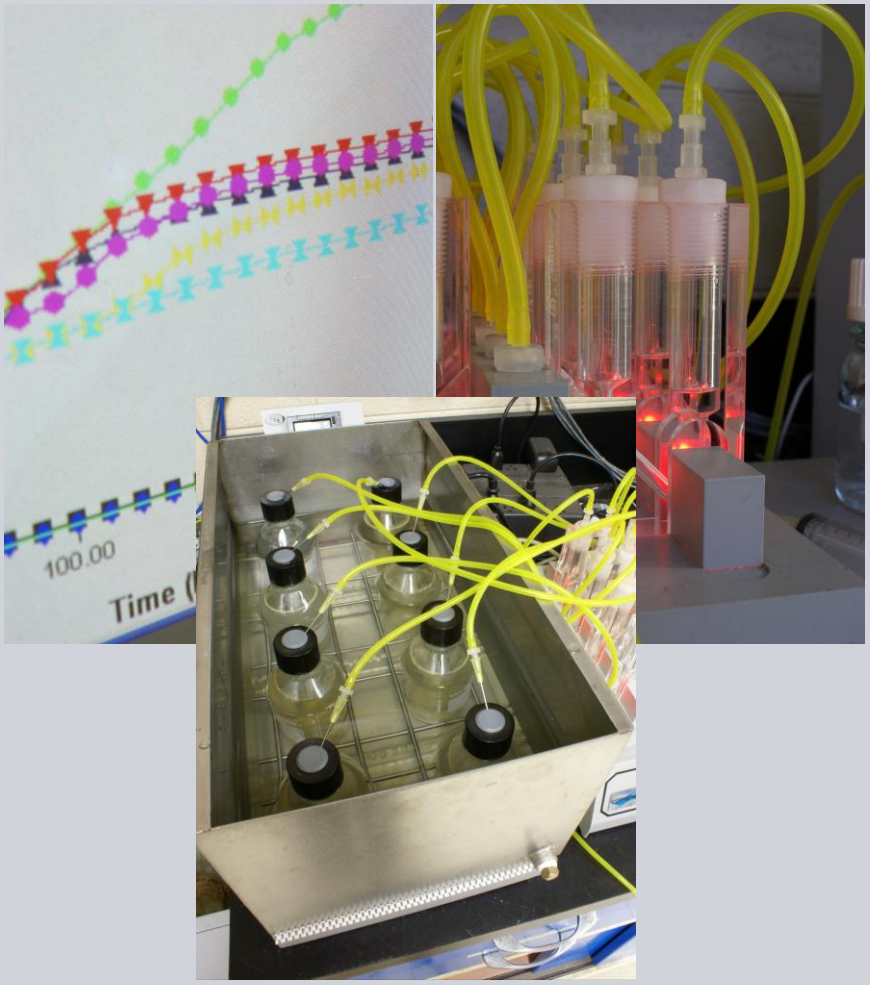
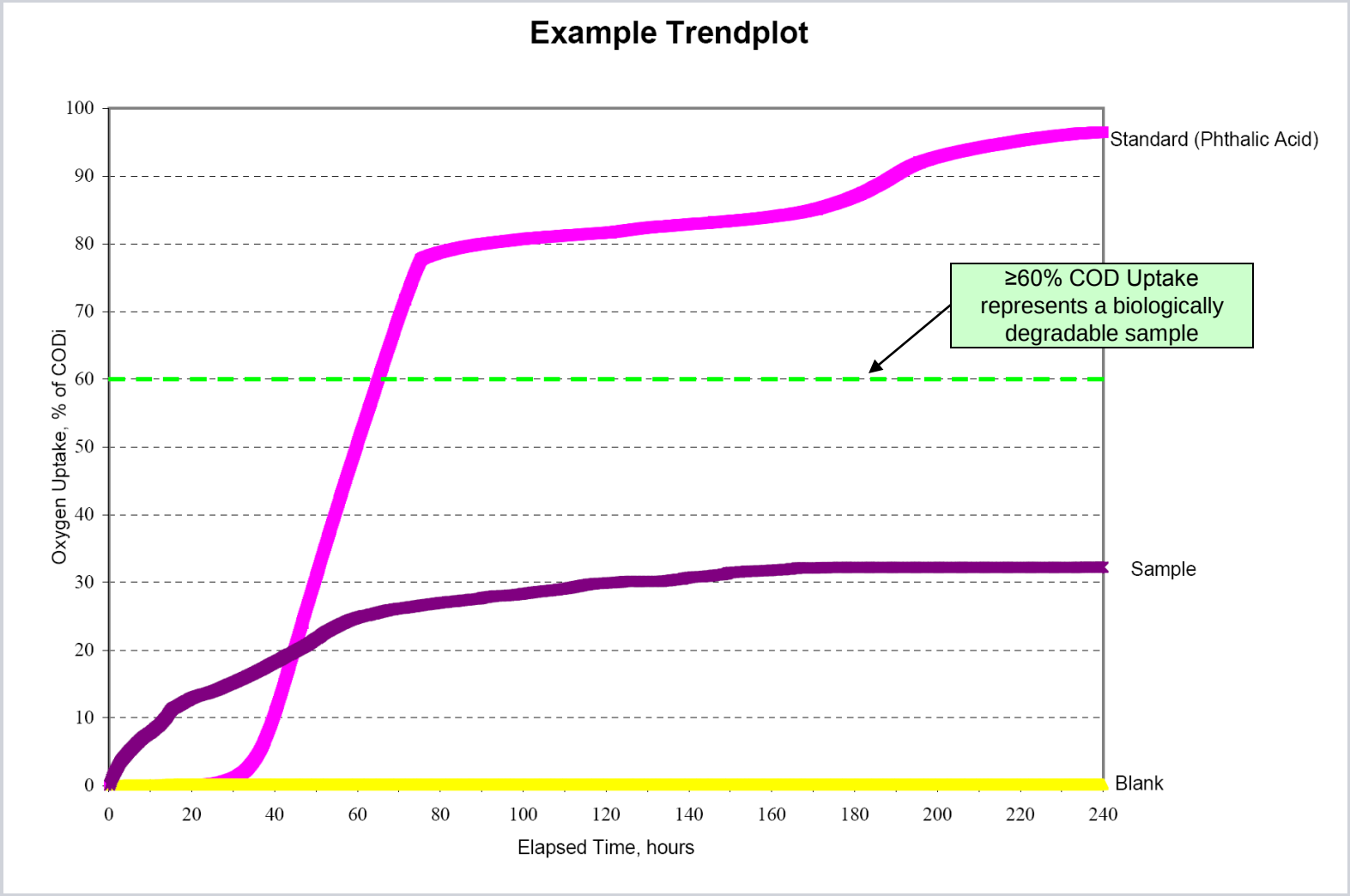
For high TDS spent caustic samples Siemens uses:

- Challenge Technology AER-208 FlowCell Respirometer
- Controlled temperature bath
- Biological seed acclimated for high TDS wastewaters
- 10 day run period



Respirometery COD Consumption Trend Plot



Refinery Spent Caustic – Zimpro® WAO Case Studies

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The following slides present data collected from three refineries using Zimpro® WAO technology to pre-treat their spent caustic

- Refinery Case A – Spain
- Refinery Case B – China
- Refinery Case C – India

Refinery Spent Caustic – Case A
Respirometery COD Consumption Trend Plot

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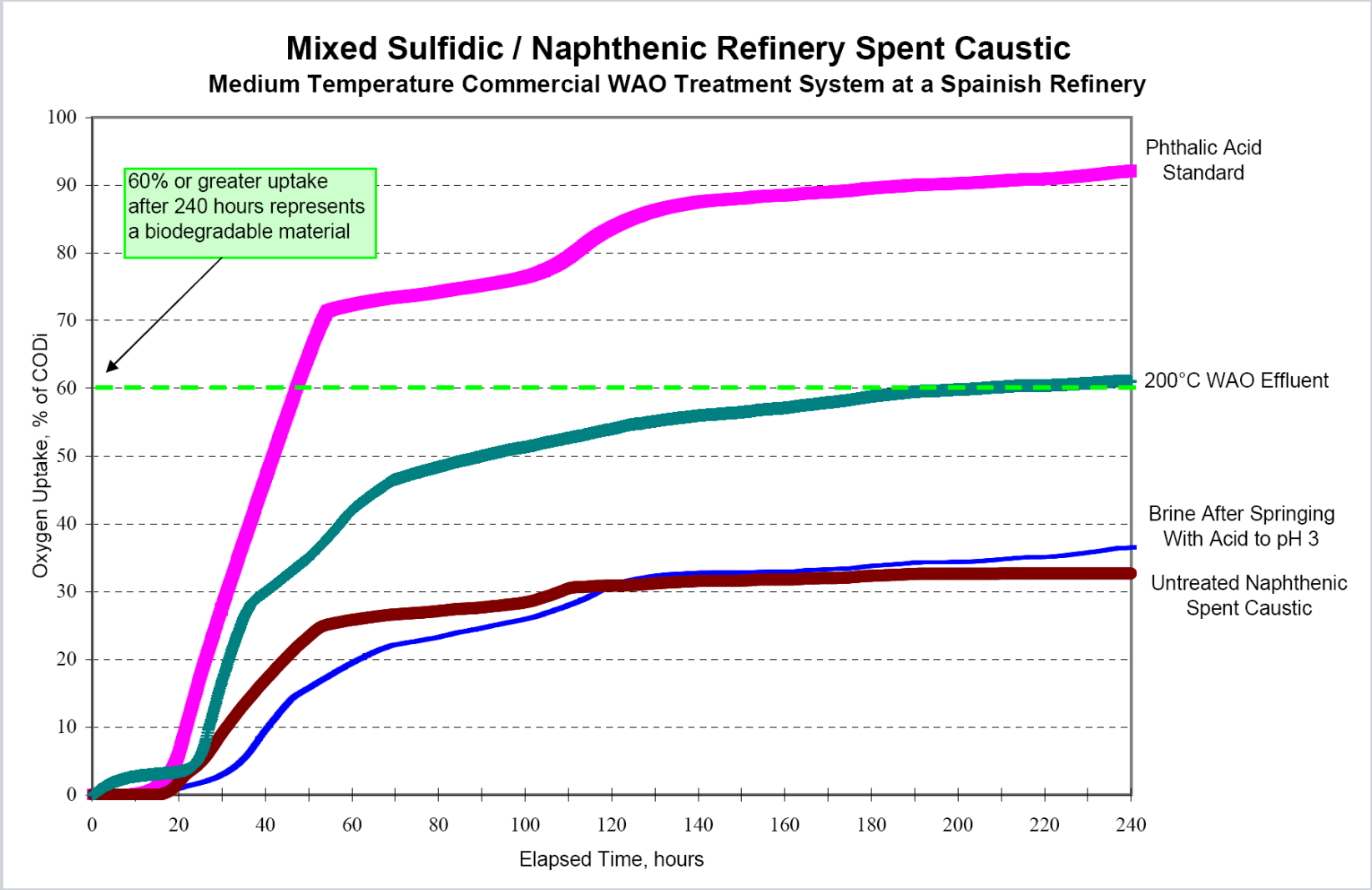

Refinery Spent Caustic – Case B
Respirometery COD Consumption Trend Plot

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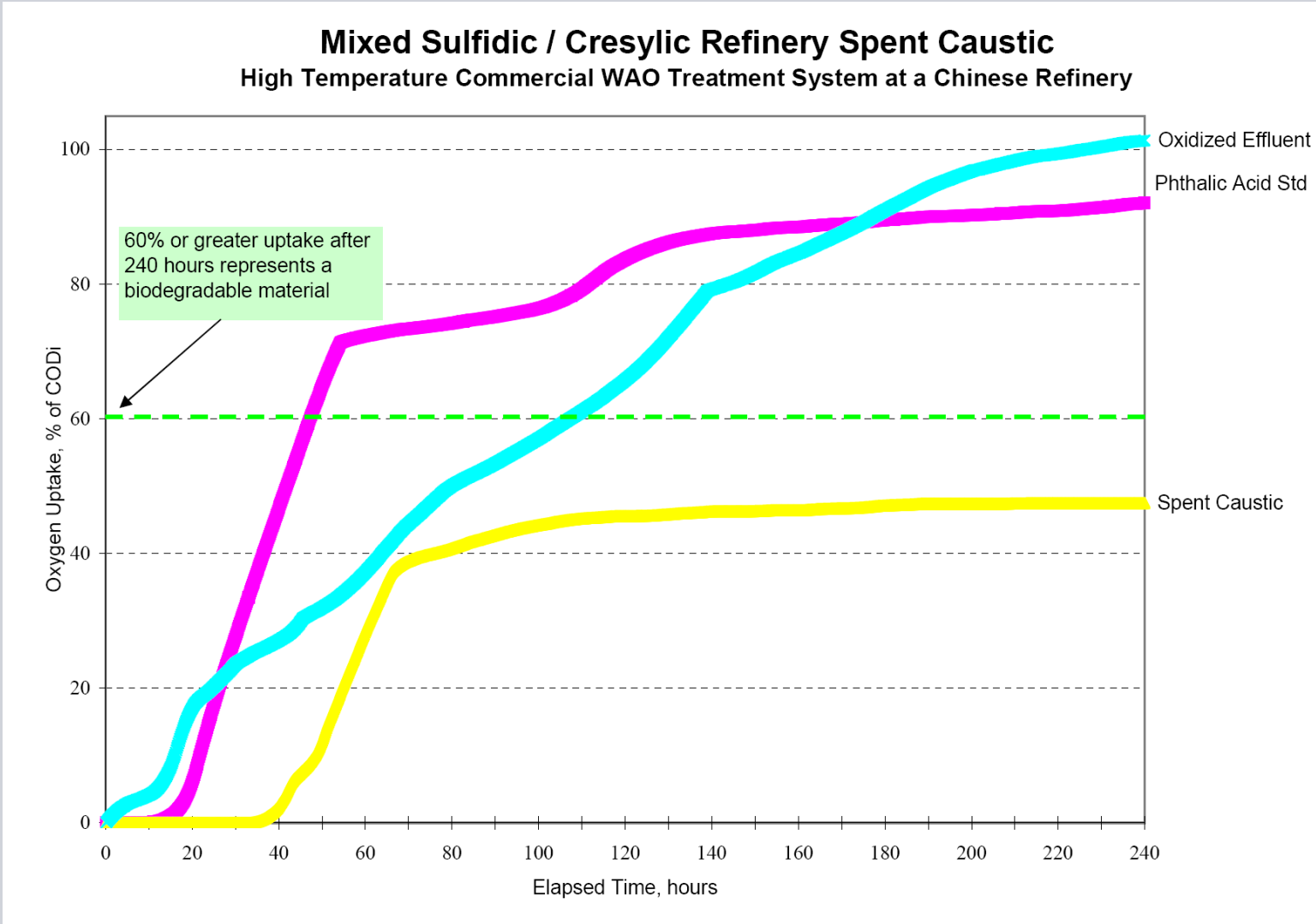

Refinery Spent Caustic – Case C
Respirometery COD Consumption Trend Plot

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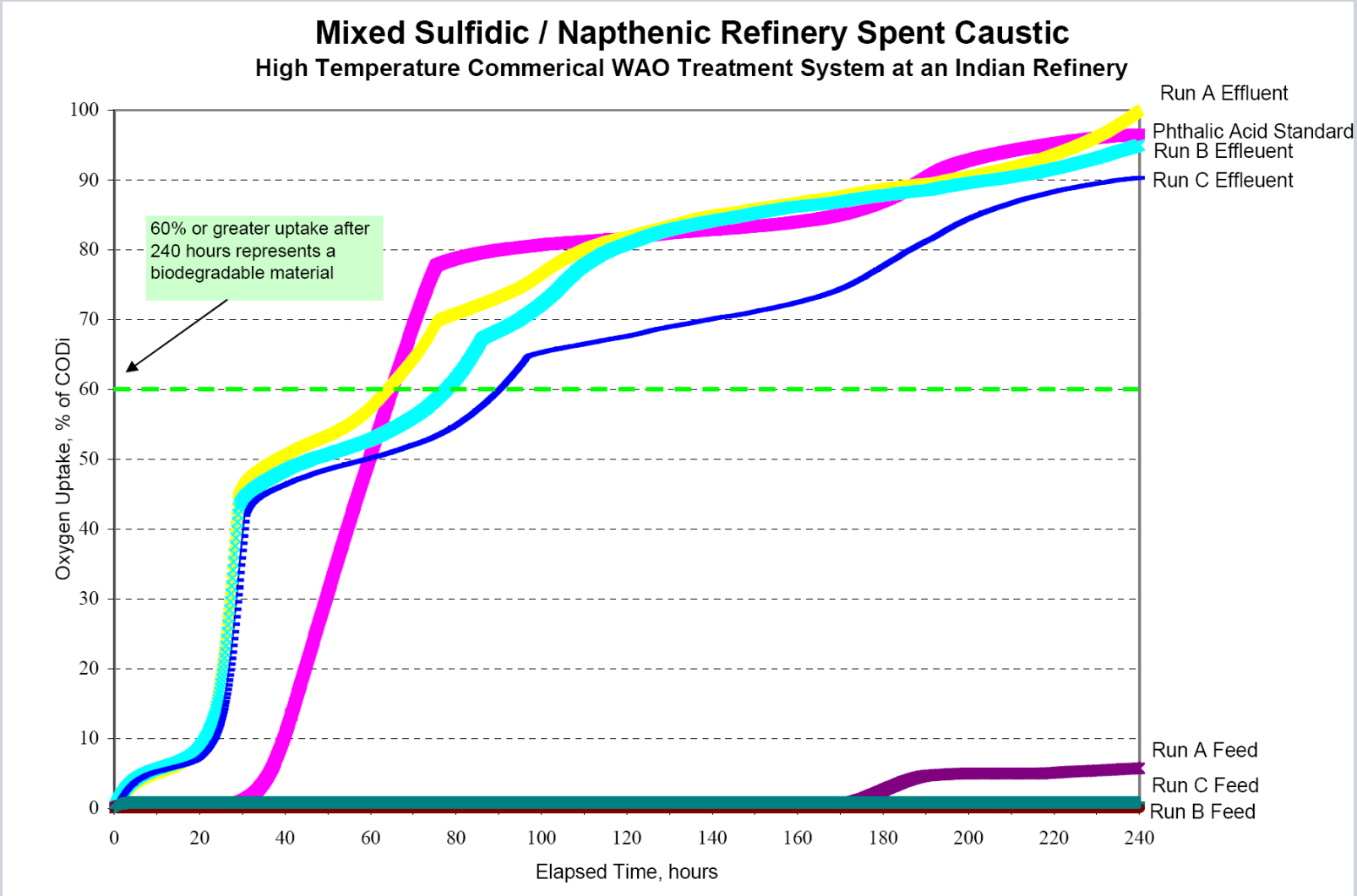

WAO Treatment of Refinery Spent Caustic – In Summary

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Zimpro® wet air oxidation of refinery spent caustic will:

- Destroy Sulfides and Mercaptans
- Eliminate Noxious Odors and H_2S Emissions
- Destroy Toxic Constituents
- Destroy Refractory Organics
- Destroy Foaming Characteristics
- Break Apart Large Organic Constituents

Zimpro® wet air oxidation produces a biodegradable effluent suitable for polishing in typical activated sludge treatment systems.

Recovery of NaOH using ED
Purpose and Objective

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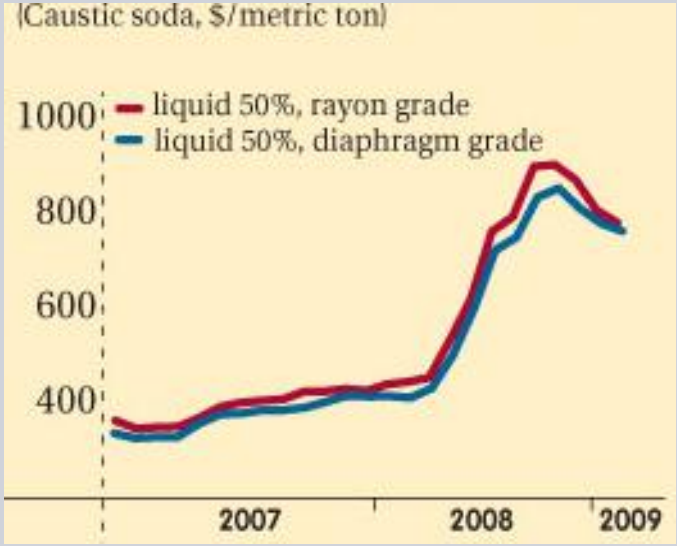
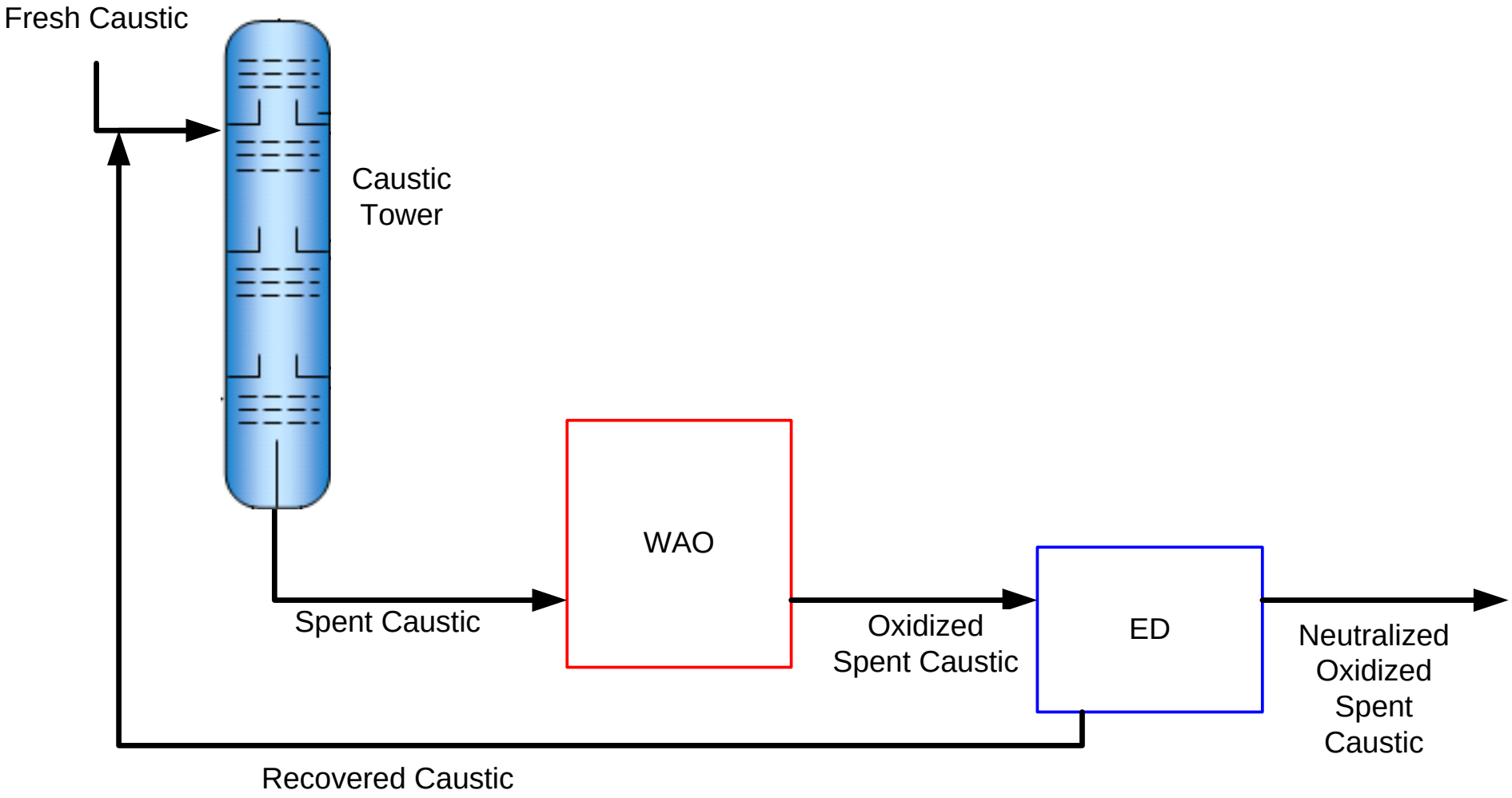
- Recover NaOH from waste oxidized spent caustic
  - Re-use in caustic tower
  - Useful strength – target 10 wt%
- Cost effective
  - Product should cost less than commodity purchase price
- Eliminate acid neutralization
  - Use the ED process to pH neutralize the oxidized spent caustic
  - Eliminate acid costs
- Reduce TDS to downstream biological treatment



Source: www.purchasingdata.com

Integrated ED System in an Ethylene Refinery



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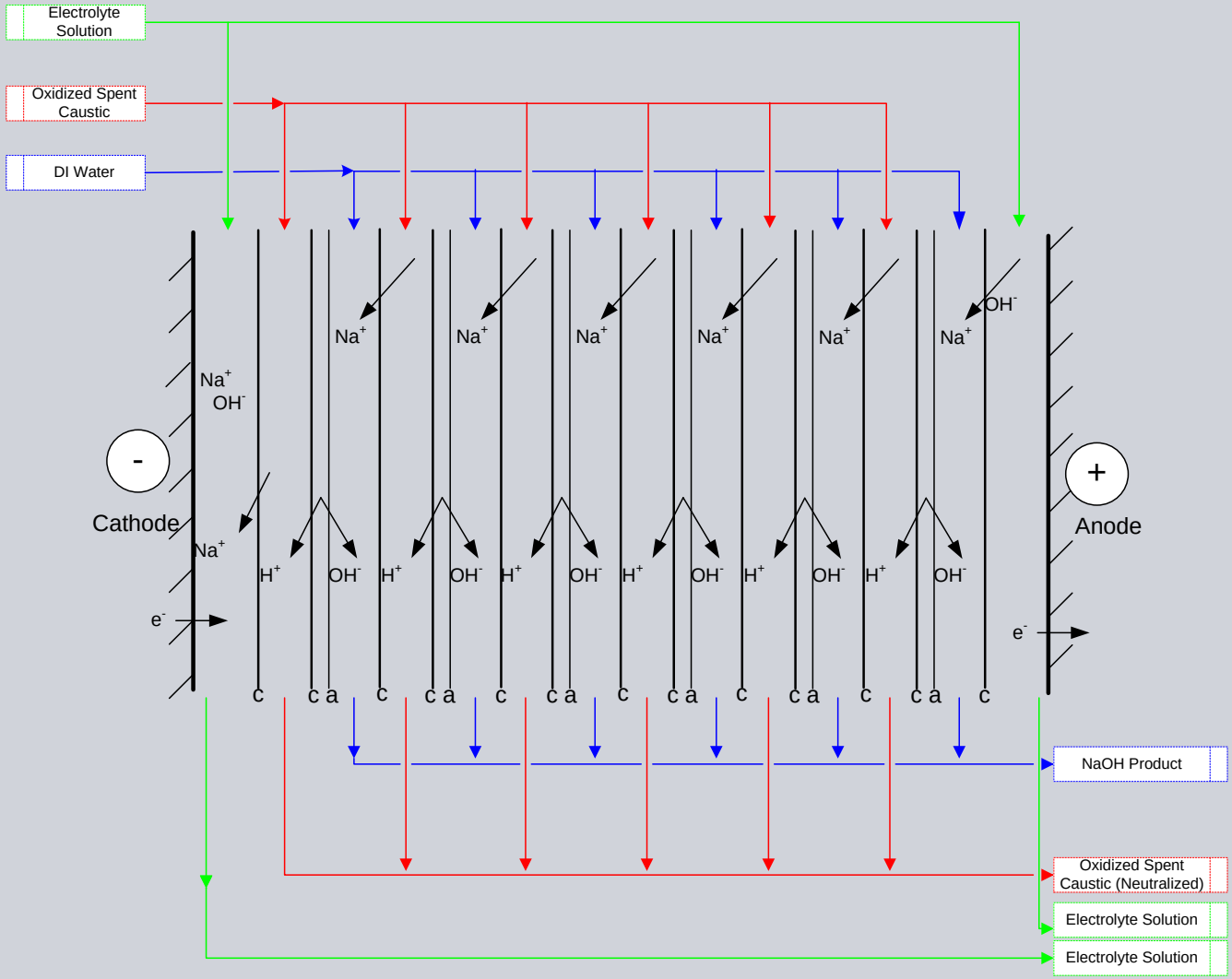
Laboratory Test Work



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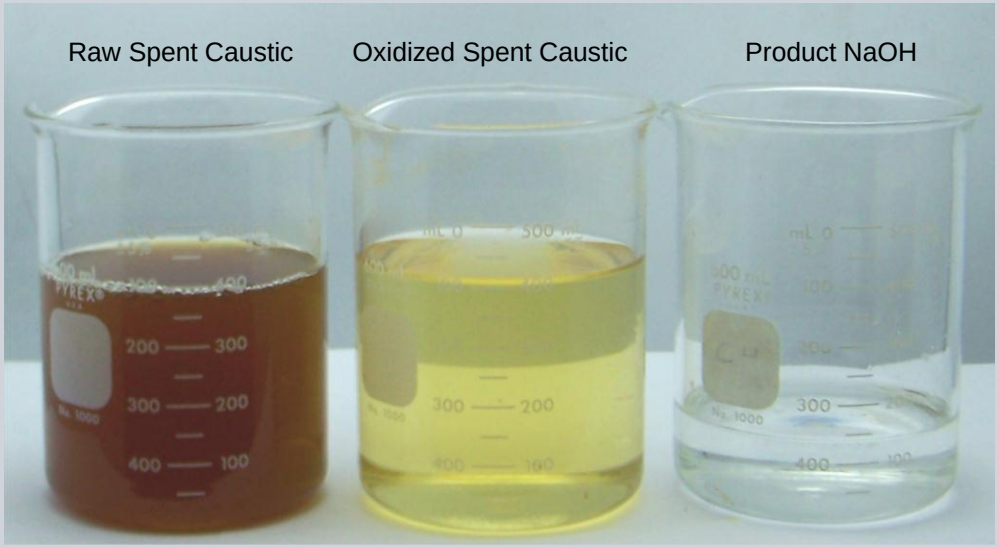
Other Key Laboratory ED Results

- Product acceptable for caustic tower
- Up to 20 wt% NaOH produced
- Power consumption less than chlor-alkali process
- No major obstacles encountered
- No apparent performance or efficiency decline after 320 hours of testing
- No fouling



WAO Treatment of Refinery Spent Caustic –

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