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Wet Air Oxidation Treatment of Spent Caustic in Ethylene Plants and Petroleum Refineries

SAWEA

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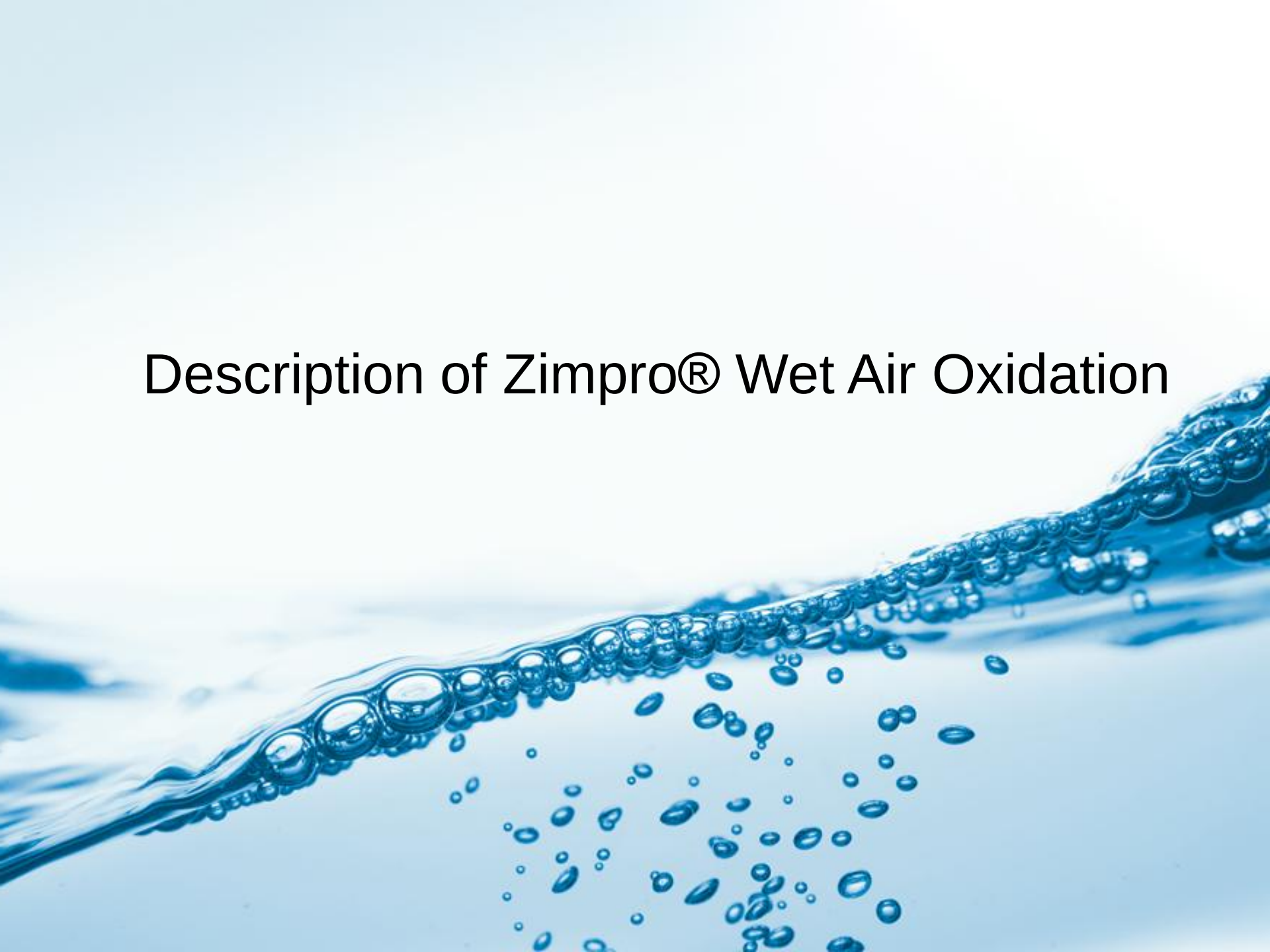
Overview

- Description of the Zimpro® WAO process
- Spent Caustic Chemistry
- Autoclave and Full Scale Data
  - Ethylene Spent Caustic
  - Refinery Spent Caustic
- Conclusions

Description of Zimpro® Wet Air Oxidation



What is Wet Air Oxidation?

- Oxidation of Soluble or Suspended Components in an Aqueous Matrix
- Oxygen (Air) is the Oxidizing Species
- Oxidation Reactions Occur at Elevated Temperatures and Pressures

BASF, Port Arthur, Texas

Wet Air Oxidation For High Strength Industrial Wastewaters

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Repsol, Tarragona, Spain

Common Uses

- Destruction of Specific Constituents
- Pretreatment for Biological Polishing
- Gross Reduction in COD Loading

Wet Air Oxidation For High Strength Industrial Wastewaters

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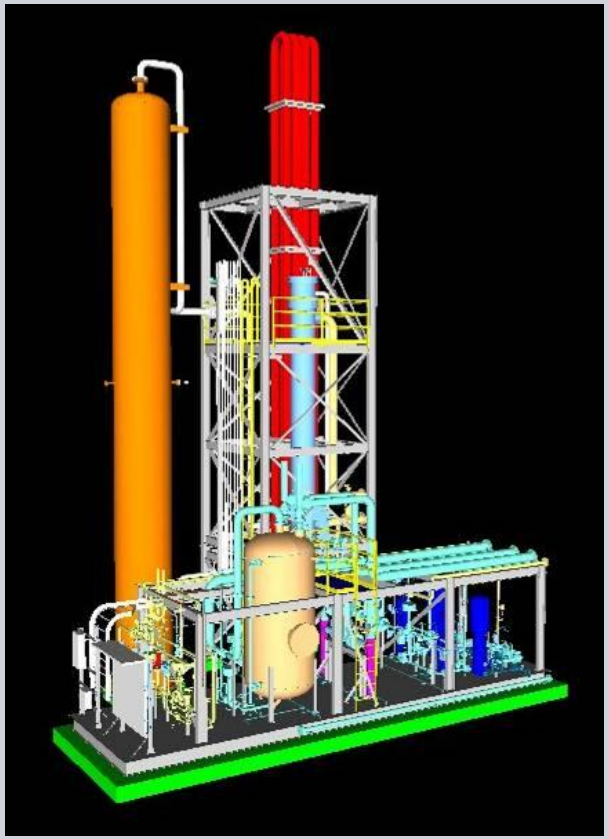
Typical Industrial Wet Air Oxidation Feed Characteristics

Flow Range:	1 to 50 m^3/h
COD Range:	10,000 to 100,000 mg/L
Temperature Range:	150 to 320°C
Pressure Range:	5 to 225 barg



Wet Air Oxidation –Typical Process Flow Diagram

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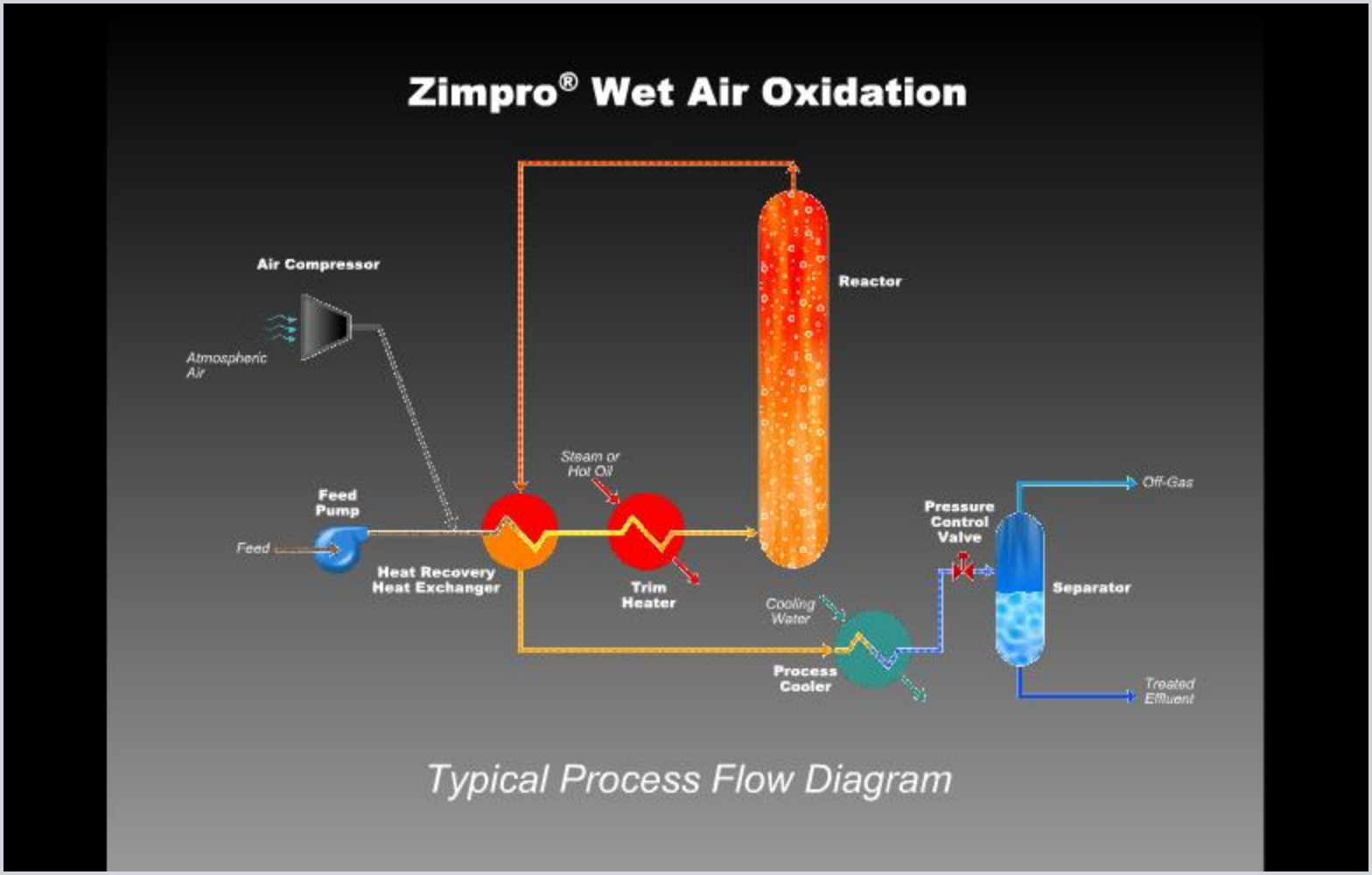

Wet Air Oxidation

Process Variables

- Oxidation Temperature and Pressure
- Hydraulic Detention Time
- Oxidant – Typically Air or Oxygen
- Flow Configuration
- Oxidation Enhancer

Atofina, Rho Italy

Spent Caustic Chemistry

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Classification of Spent Caustics

Type	Principle COD Source	Source	Operating Conditions
Sulfidic	Sulfides and/or mercaptans	Ethylene or LPG	130°C / 7 barg to 200°C / 27.5 barg
Cresylic	Phenolic compounds and reduced sulfur	FCC Gasoline Washes	200°C / 27.5 barg to 260°C / 86 barg
Naphthenic	Naphthenic compounds and reduced sulfur	Kerosene, Diesel, and Jet Fuel	240°C / 55 barg to 260°C / 86 barg

Issues With Spent Caustic Produced in the Petrochemical Industry

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Spent Caustic
Before and After
WAO Treatment

- Odors caused by sulfides, mercaptans and volatile organics
- Potential inhibitory or toxic effects in biological treatment
- Hazards associated with toxicity
- High chemical oxygen demand
- Tendency to foam
- Corrosive

Sulfidic Reactions During WAO of Spent Caustics

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Sulfide - NaHS

$$NaHS + O_2 + NaOH \rightarrow Na_2SO_4 + H_2O$$

$$NaHS + O_2 \rightarrow \tfrac{1}{2}\, Na_2S_2O_3 + \tfrac{1}{2}\, H_2O$$

Thiosulfate - $Na_2S_2O_3$

$$Na_2S_2O_3 + O_2 + NaOH \rightarrow Na_2SO_4 + H_2O$$

Mercaptan - NaSR

$$NaSR + O_2 \rightarrow RSO_3\text{-}Na$$

Organic Reactions During WAO of Spent Caustics

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Cresylic Acids - C_6H_5O-Na

- $C_6H_5O\text{-}Na + O_2 + NaOH \rightarrow Na_2CO_3 + H_2O$
- $C_6H_5O\text{-}Na + O_2 + NaOH \rightarrow Na_2CO_3 + CH_3COO\text{-}Na + H_2O$

Naphthenic Acids - Na-$C_{12}H_{22}O_2$

- $Na\text{-}C_{12}H_{22}O_2 + O_2 + NaOH \rightarrow Na_2CO_3 + H_2O$
- $Na\text{-}C_{12}H_{22}O_2 + O_2 + NaOH \rightarrow Na_2CO_3 + CH_3COO\text{-}Na + H_2O$

Autoclave and Full Scale Results

Wet Air Oxidation of Various Spent Caustic Types

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Autoclave and Full Scale Results

- Oxidation of Sulfidic Components
- Biotreatability of WAO Effluent
- Overall COD Destruction

Ethylene Spent Caustic

Wet Air Oxidation
Ethylene Spent Caustic – Sulfidic Components

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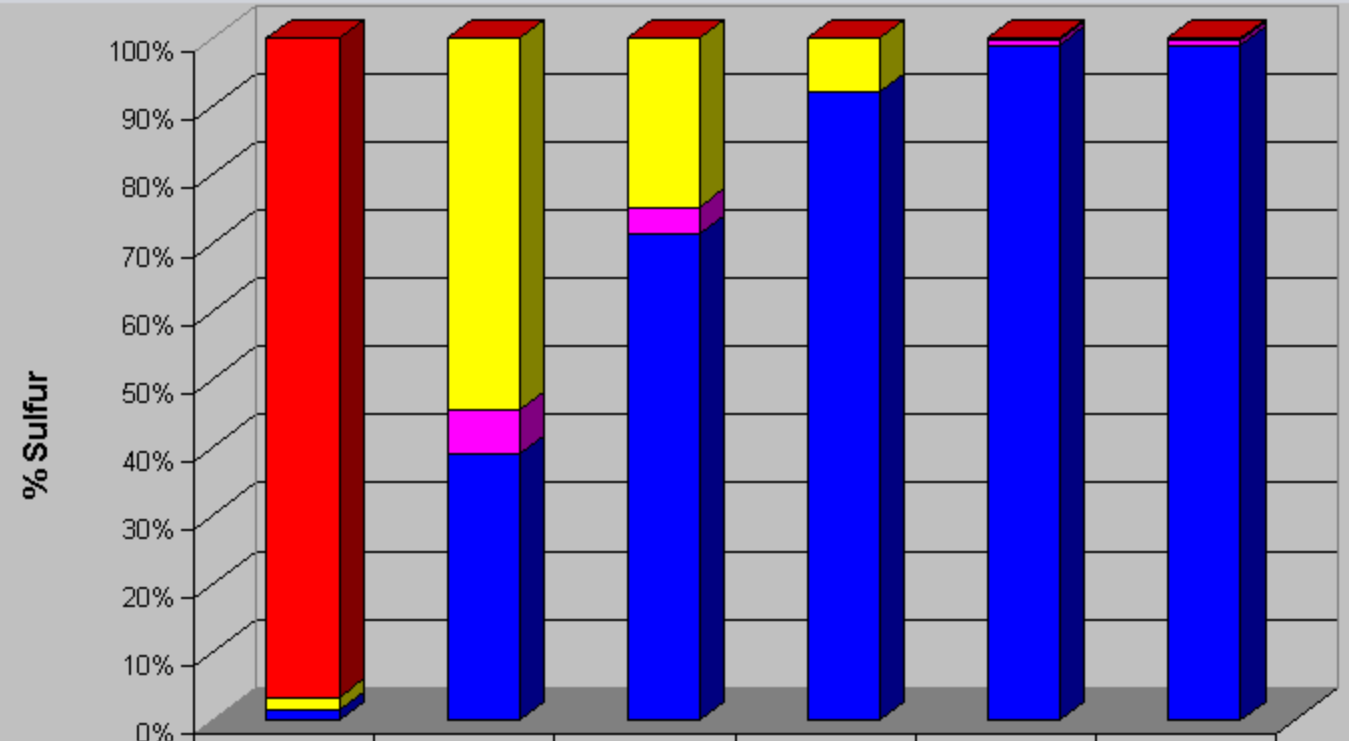

Oxidation Temperature, °C	Feed	110	125	150	200	240
Sulfide (NaHS/Na2S as S)	13900	<10	<10	<10	<1	<1
Thiosulfate (Na2S2O3 as S)	275	5,503	2,686	949	40	31
Sulfite (NaSO3 as S)	5	643	435	4	81	85
Sulfate (Na2SO4 as S)	200	3,940	7,740	11,200	12,500	11,100

Wet Air Oxidation
Ethylene Spent Caustic – Sulfidic / Organic COD

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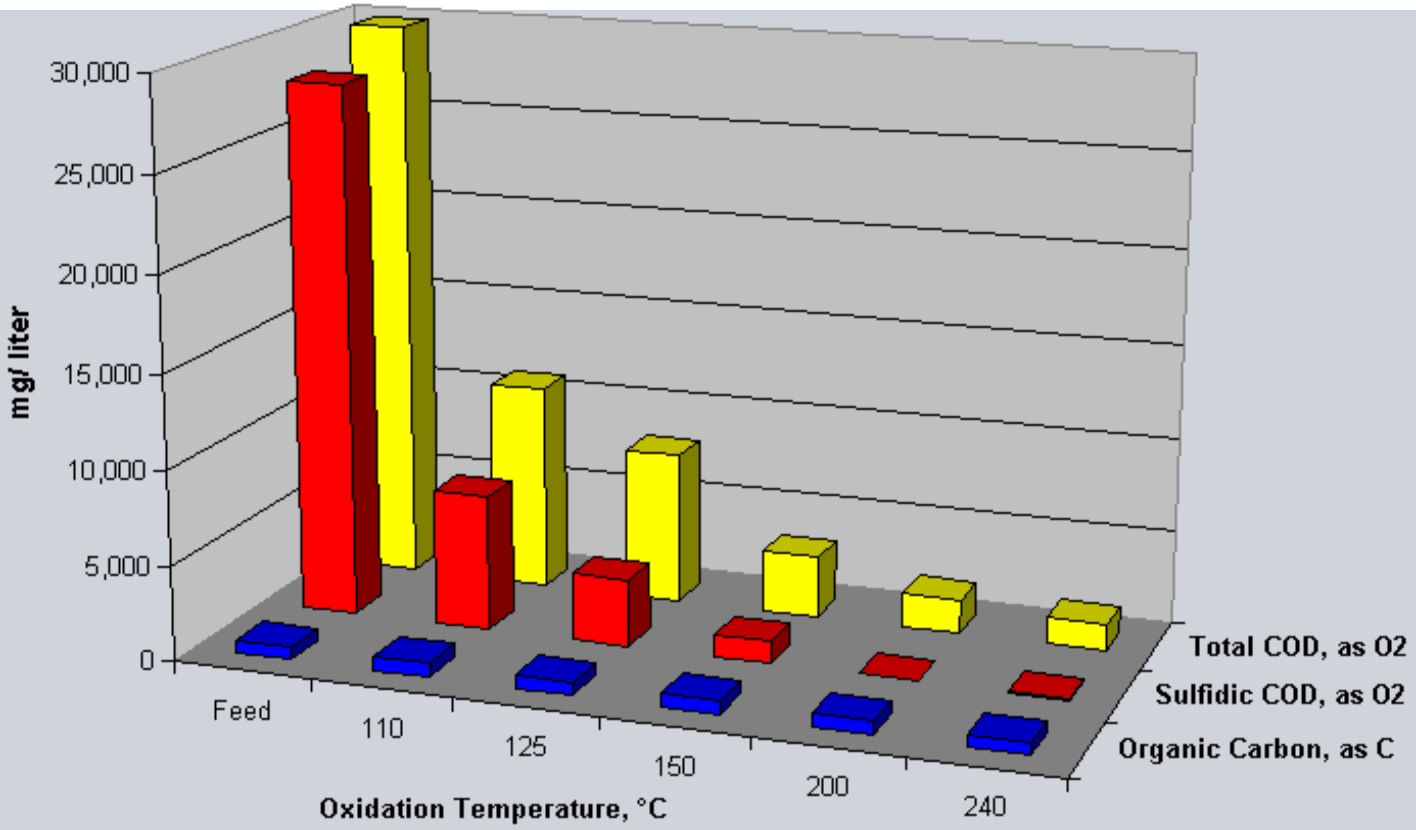

	Feed	110	125	150	200	240
Organic Carbon, as C	648	747	708	710	641	537
Sulfidic COD, as O2	28,085	7,184	3,567	1,185	90	80
Total COD, as O2	29,800	10,900	8,040	3,260	1,830	1,410

Full Scale WAO Case Studies
Ethylene Spent Caustic

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		ConocoPhillips, Texas		BASF, Texas	
		Feed	Effluent	Feed	Effluent
Temperature, °C			135		200
Residence Time, minutes			60		60
Analysis	**Units**				
COD	**mg/L**	**10,500**	**2,300**	**11,700**	**2,870**
Sulfide-S	**mg/L**	**4,031**	**<1**	**4,990**	**<1**
Thiosulfate-S	**mg/L**	**<224**	**959**	**49**	**<16**
Sulfite-S	**mg/L**	**<64**	**204**	**28**	**10**
Sulfate-S	**mg/L**	**<55**	**2,940**	**507**	**5,190**
Mercaptan-CH3SH	mg/L	---	---	298	---
Methyl Mercaptan	mg/L	---	---	---	<0.4
Ethyl Mercaptan	mg/L	--	---	---	<0.4
Calculated Sulfidic COD	mg/L	8,060	1,300	10,500	<50
% Sulfidic COD Destruction	**%**	**---**	84	**---**	>99.5

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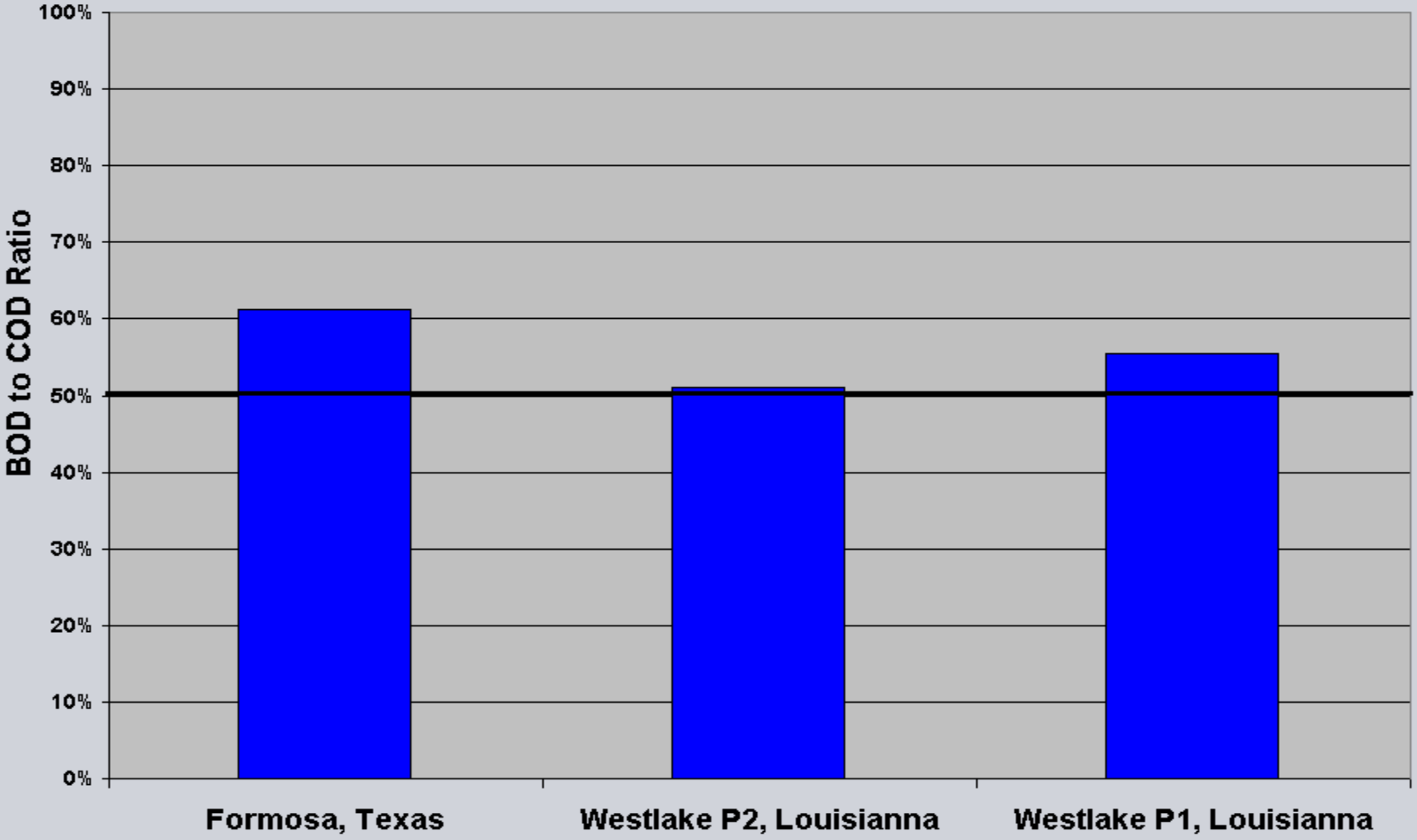
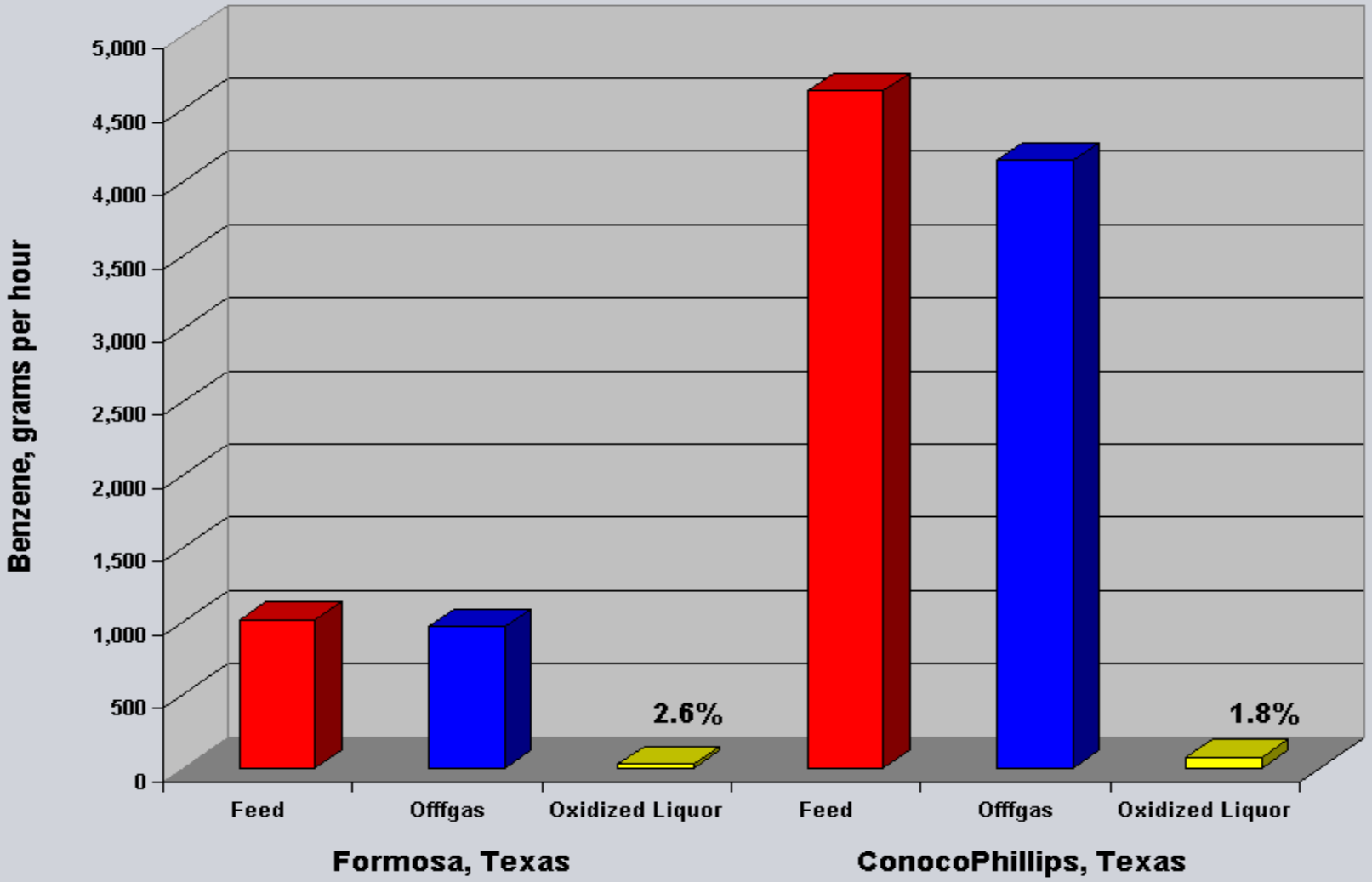
WAO Ethylene Spent Caustic Biodegradability



Benzene Stripping



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WAO Ethylene Spent Caustic

- **Operation at 200°C**
  - **Sulfide < 1 mg/l as S**
  - **Mercaptan < 1 mg/l as Methyl / Ethyl**
  - **Thiosulfate < 100 mg/l as S**
- **Remaining Organic COD is Biodegradable**
  - **BOD to COD Ratio > 0.5**

Refinery Spent Caustic

Wet Air Oxidation
Refinery Spent Caustic

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- Operating Conditions Dependent on Mixture Composition
- Assure Biological Treatability

- Sulfidic (LPG, etc) - 200°C / 27.5 barg
  - **Higher Mercaptan Content**

- Cresylic – 200°C / 27.5 barg to 260°C / 86 barg
  - **COD Reduction**

- Napthenic – 240°C / 55 barg to 260°C / 85 barg
  - **Prevent Foaming**

Wet Air Oxidation
Organic Refinery Spent Caustic – 260°C

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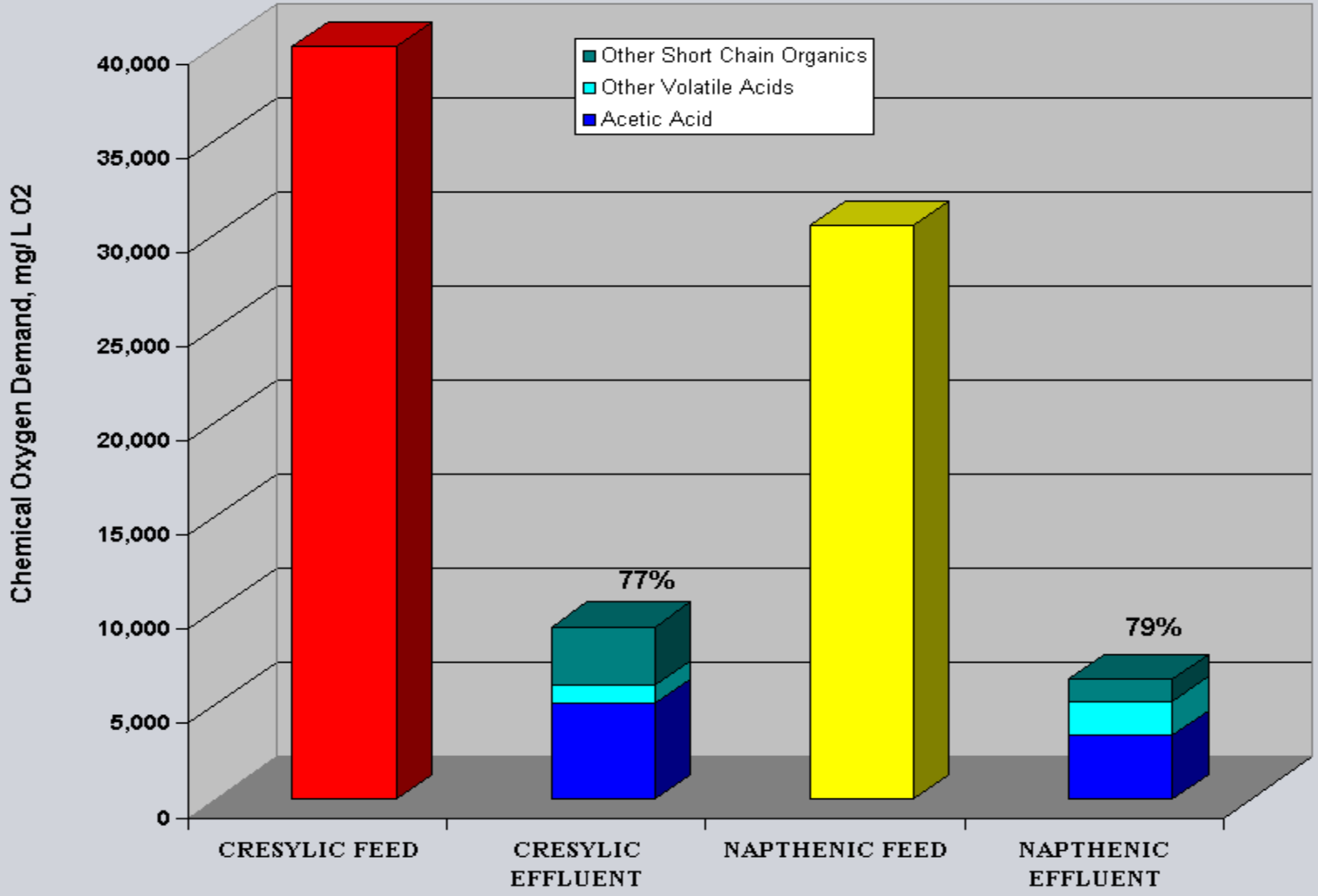

WAO of Napthenic Spent Caustic – Respirometer Trendplot

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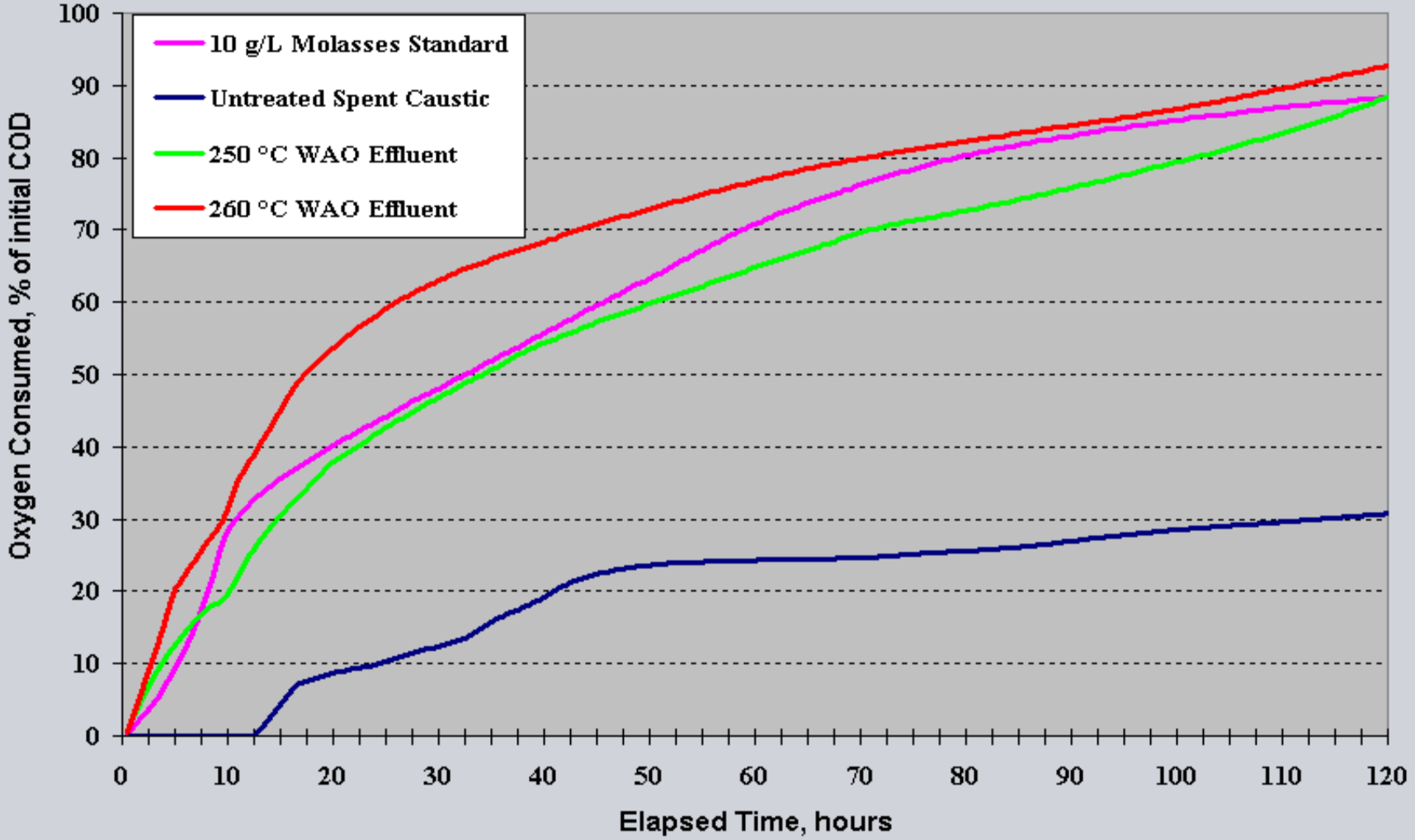

Full Scale WAO Study – Refinery Spent Caustic Mixture

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Repsol-YPF, La Pampilla, Peru

Repsol YPF Refinery
Spent Caustic Composition

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	Sulfidic spent caustics	Naphthenic spent caustics	Cresylic spent caustics
COD as g/l	7 - 110	50 – 100	165 - 230
TOC, g/l as C	0.02 – 4	11 – 25	23 - 60
DIC, g/l as C	0.15 – 5	0 – 0.16	0.33 – 0.35
Sulfide, g/l as $S^{=}$	2 – 53	< 0.001	0 - 64
Mercaptans, g/l as $S^{=}$	0 – 28	< 0.03	0 – 5.4
Thiosulfate, g/l as $S^{=}$	0 – 3.7	0.07 – 0.13	10 - 12
Total Phenols, g/l	0.003 – 002	2 – 10	14 - 20

Repsol YPF Refinery
Zimpro® WAO Performance

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	Destruction	Feed	Effluent (measured, after dilution)
COD, mg/l as O_2	85%	73,000	6,300
TOC, mg/l as C	73%	15,000	2,400
Sodium, mg/l as Na	-	41,000	24,000
pH	-	13.2	8.9
Sulfide, mg/l as $S^{=}$	> 99.9	8,500	< 1
Sulfite, mg/l as $S^{=}$	> 99.9	100	< 2
Mercaptans, mg/l as CH_3SH	> 98.8	1,500	< 30
Thiosulfate, mg/l as S_2O_3	> 98.8	1,500	< 30
Total phenols, mg/l as C_6H_6O	> 99.6	6,500	36
Flow rate, m^3/h		0.67	1.14

Repsol YPF Refinery
Zimpro® WAO Performance

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- Biological Treatability
  - Effluent BOD/COD Ratio : 0.58
  - Volatile Acid COD: 4,150 mg/L
    - 66% of Effluent COD
  - Sulfidic Components Non-Detectable
    - Including Mercaptans

Conclusions

- **Reasons For Treatment**
  - **Biotreatable Effluent**
  - **No Sulfide Odors**
  - **No H_2S emissions**
  - **Minimize Downstream Corrosion**
  - **Eliminate Foaming Problems**

Conclusions

- **Ethylene Spent Caustic (Sulfidic)**
  - **Sulfide <1 mg/l as S**
  - **Mercaptans <1 mg/l**
  - **Thiosulfate <100 mg/l as S**

Conclusions

- **Refinery Spent Caustic (Higher Temperature for Organics)**
  - **Elimination of Sulfides and Mercaptans**
  - **High Conversion of Complex Organics to Short Chain Compounds**
  - **Both Sulfidic and Organic COD Reduction**

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Thank You!

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