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Zimpro® Wet Air Oxidation

EnviroArabia 2007

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Introduction / Contents

Overview

- Description of the Zimpro® WAO process
- Description of spent caustic samples
- Test Procedures
- Results
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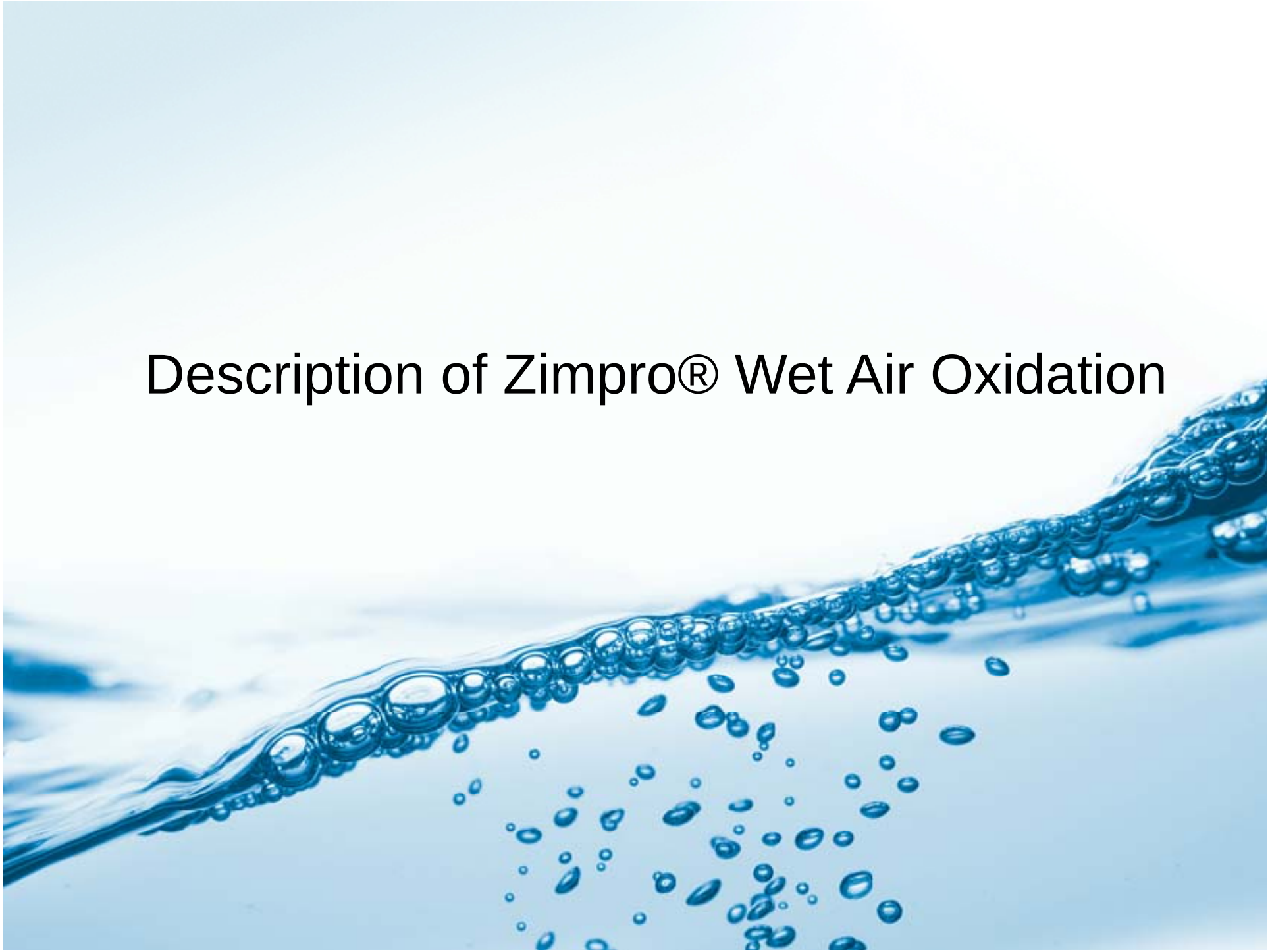
- Conclusions

Description of Zimpro® Wet Air Oxidation



Wet Air Oxidation –Typical Process Flow Diagram

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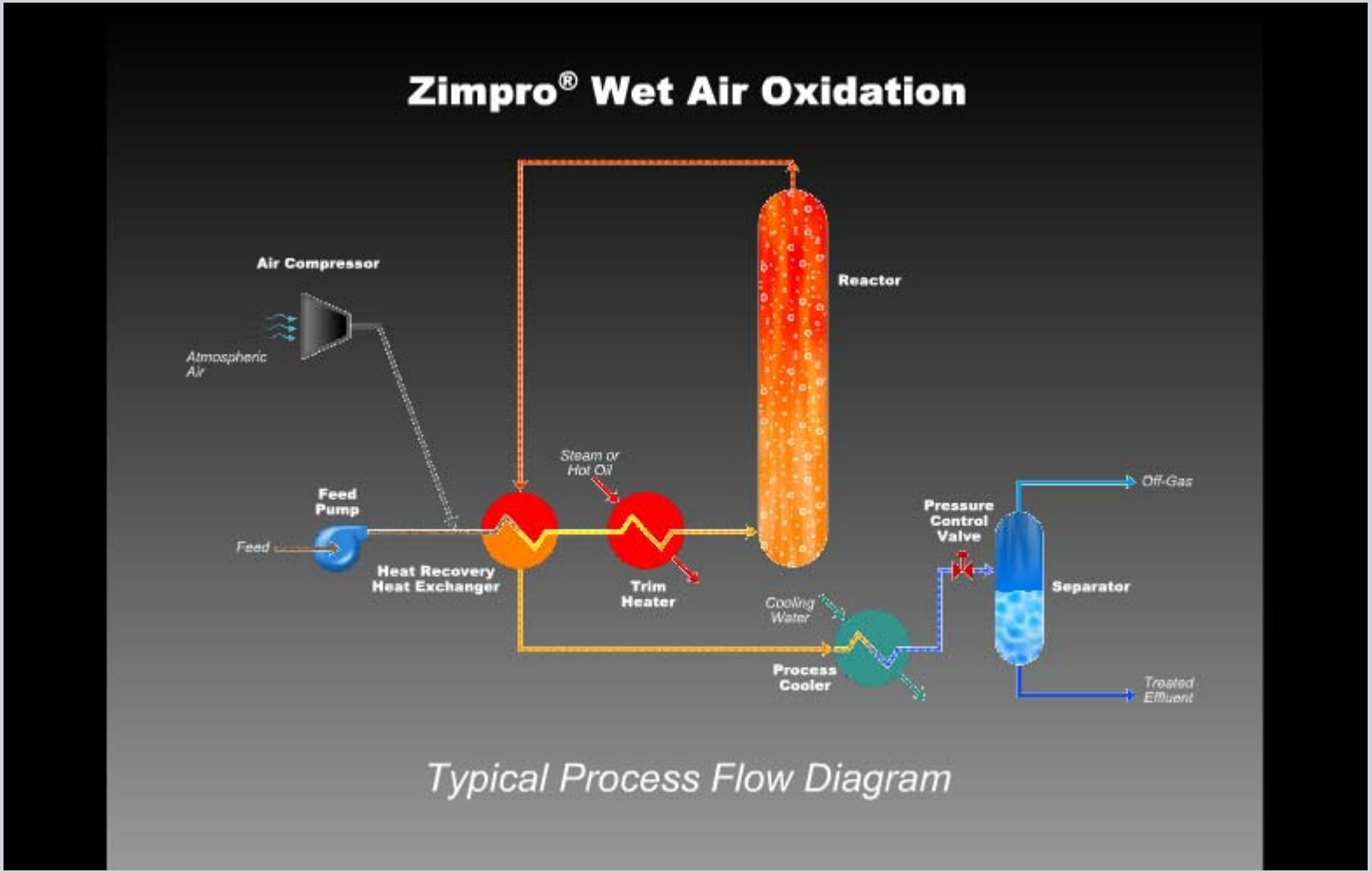

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Wet Air Oxidation

Process Variables

- Oxidation temperature and pressure
- Hydraulic detention time
- Oxidant – typically air or oxygen
- Flow configuration
- Catalyst

Wet Air Oxidation For High Strength Industrial Wastewaters

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Repsol POSM, Tarragona, Spain

- Destruction of specific constituents
- Pretreatment for biological polishing
- Gross reduction in COD loading

Wet Air Oxidation –
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 mg/l to 100,000 mg/l
Temperature Range:	150 to 320°C
Pressure range:	5 to 225 barg

Description of Spent Caustic Streams

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Classification of Spent Caustics

Type	Principle COD Source	Source
Sulfidic	Sulfides and/or mercaptans	Ethylene or LPG Scrubbers
Cresylic	Phenolic compounds and reduced sulfur	Scrubbing or FCC gasoline washes
Naphthenic	Naphthenic compounds and reduced sulfur	Scrubbing kerosene, diesel, and jet fuel

Issues With Spent Caustic Produced in the Petrochemical Industry

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

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Reactions During WAO of Spent Caustics

Sulfide

$NaHS + 2\ O_2 + NaOH \Rightarrow Na_2SO_4 + H_2O$

Mercaptan

$NaSR + {}^{3}/_{2}\ O_2 \Rightarrow RSO_3\text{-}Na$

Cresylic

- $C_6H_5O\text{-}Na + 7\ O_2 + 11\ NaOH \Rightarrow 6\ Na_2CO_3 + 8\ H_2O$
- $C_6H_5O\text{-}Na + 5{}^{1}/_{2}\ O_2 + 8{}^{3}/_{4}\ NaOH \Rightarrow 4{}^{1}/_{2}\ Na_2CO_3 + {}^{3}/_{4}\ CH_3COO\text{-}Na + 5{}^{3}/_{4}\ H_2O$

Naphthenic

- $Na\text{-}C_{12}H_{22}O_2 + 16{}^{3}/_{4}\ O_2 + 23\ NaOH \Rightarrow 12\ Na_2CO_3 + 22{}^{1}/_{2}\ H_2O$
- $Na\text{-}C_{12}H_{22}O_2 + 13{}^{1}/_{4}\ O_2 + 17{}^{3}/_{4}\ NaOH \Rightarrow 8{}^{1}/_{2}\ Na_2CO_3 + 1{}^{3}/_{4}\ CH_3COO\text{-}Na + 17{}^{1}/_{4}\ H_2O$

Laboratory Testing Objectives and Procedures

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Study Objectives

1. To investigate the effect of temperature on the destruction of chemical oxygen demand in different types of spent caustic streams.

2. To investigate the biodegradability of effluent from wet air oxidation of spent caustic at various WAO oxidation conditions.

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Test Apparatus

- Laboratory WAO testing was performed in autoclaves constructed from nickel 200 or Inconel 600
- The volume of the autoclaves ranged between 500 ml to 750 ml

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Test Apparatus

The autoclave reactor is loaded into a shaking heater assembly for mixing and temperature control

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Determination of Biodegradability

Biodegradability was monitored in two ways

1. BOD to COD Ratio (BOD/COD > 0.4 is considered readily biodegradable)

2. An analytical investigation of the types of organics present in the oxidized effluent samples.

Laboratory Test Results

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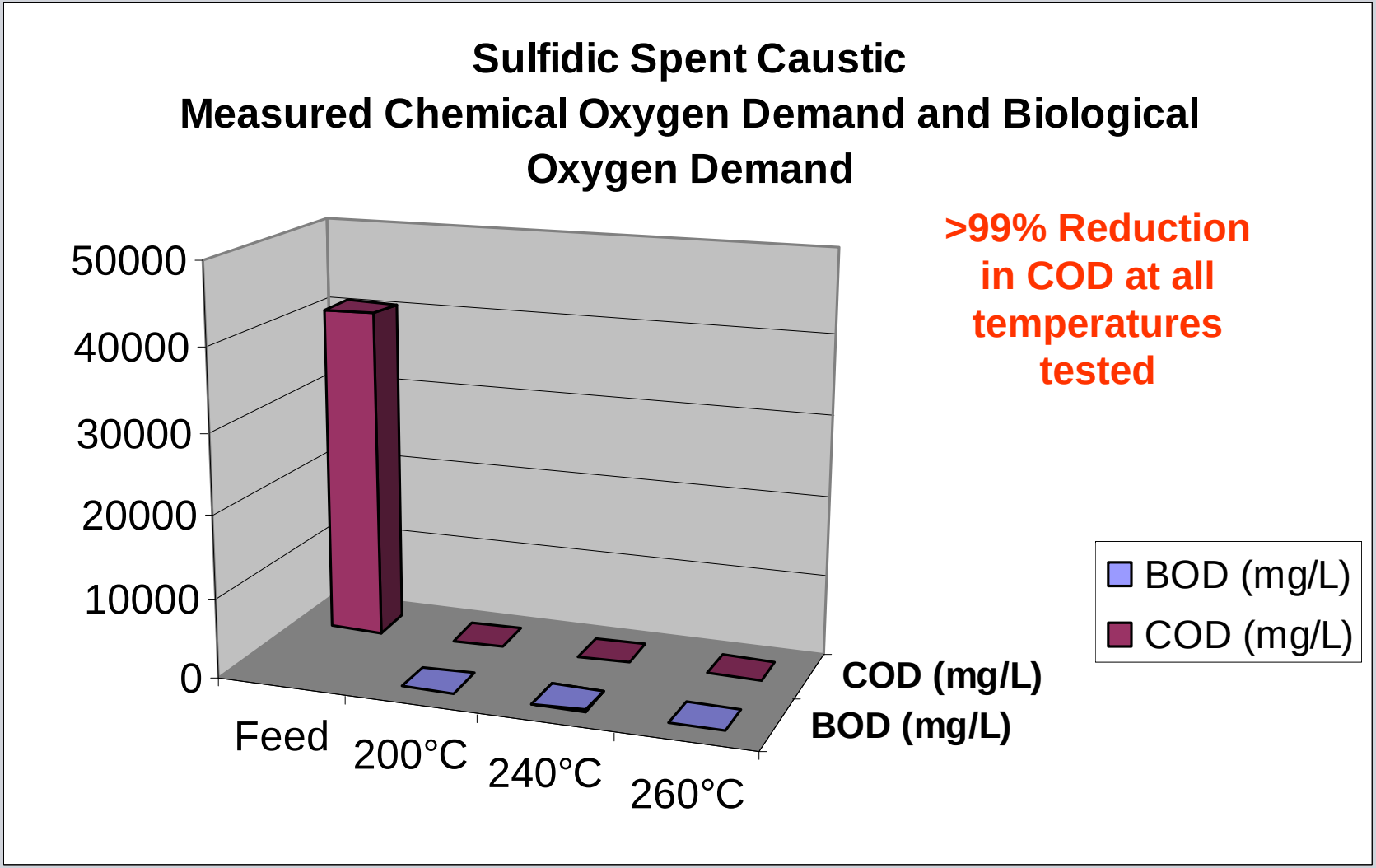
Results – Sulfidic Spent Caustic



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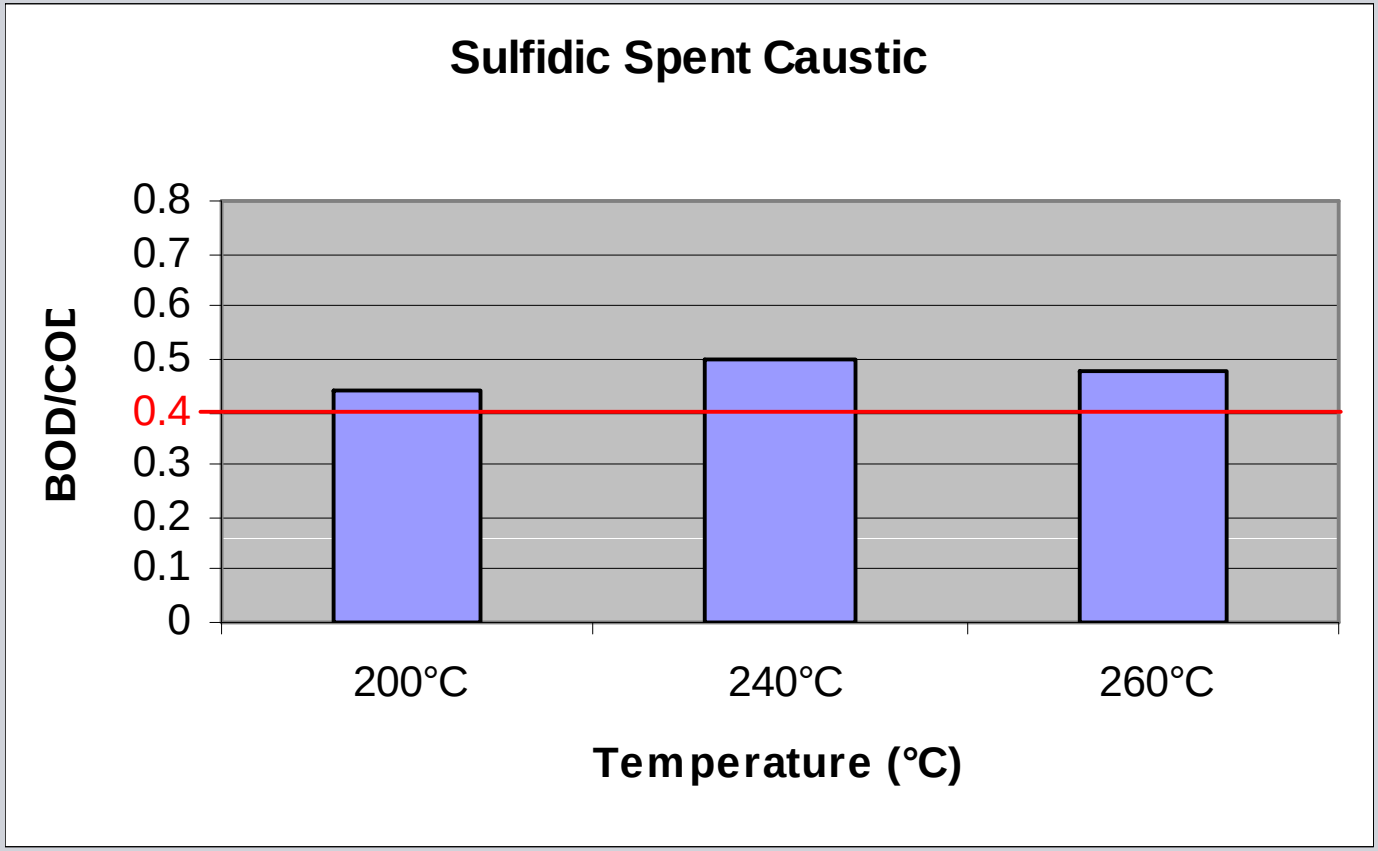
Results – Sulfidic Spent Caustic



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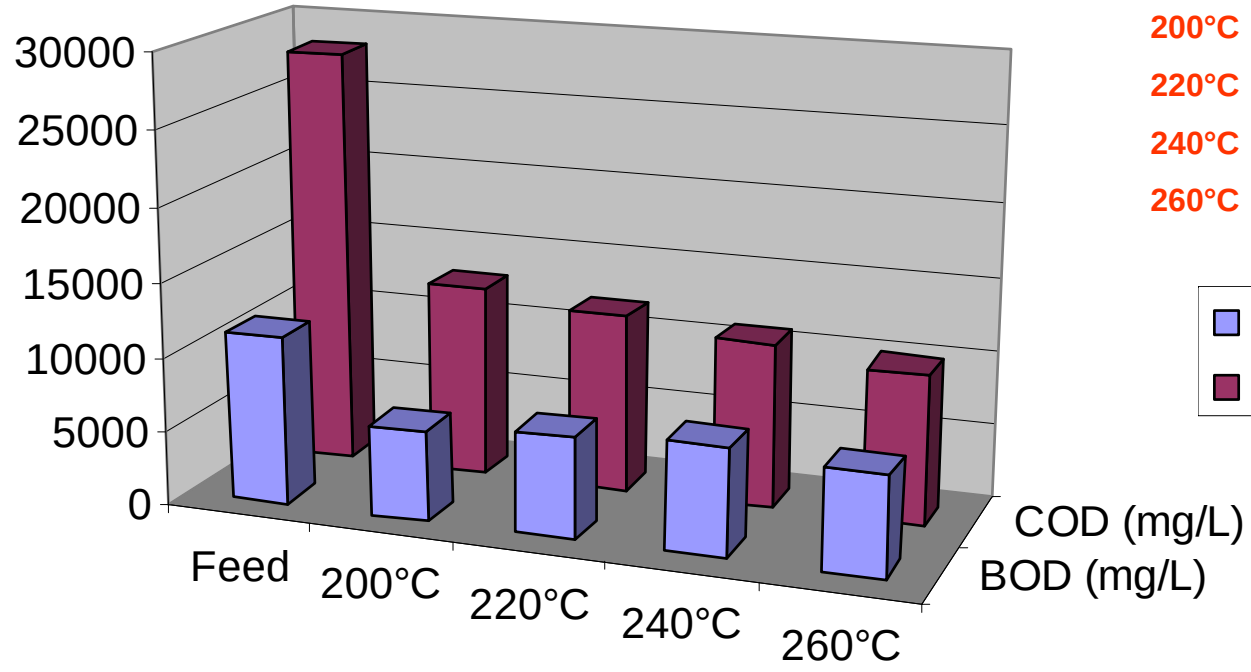
Results – Cresylic Spent Caustic

Cresylic Spent Caustic
Measured Chemical Oxygen Demand and Biological Oxygen Demand



%COD Reduction	
200°C	54%
220°C	57%
240°C	60%
260°C	64%

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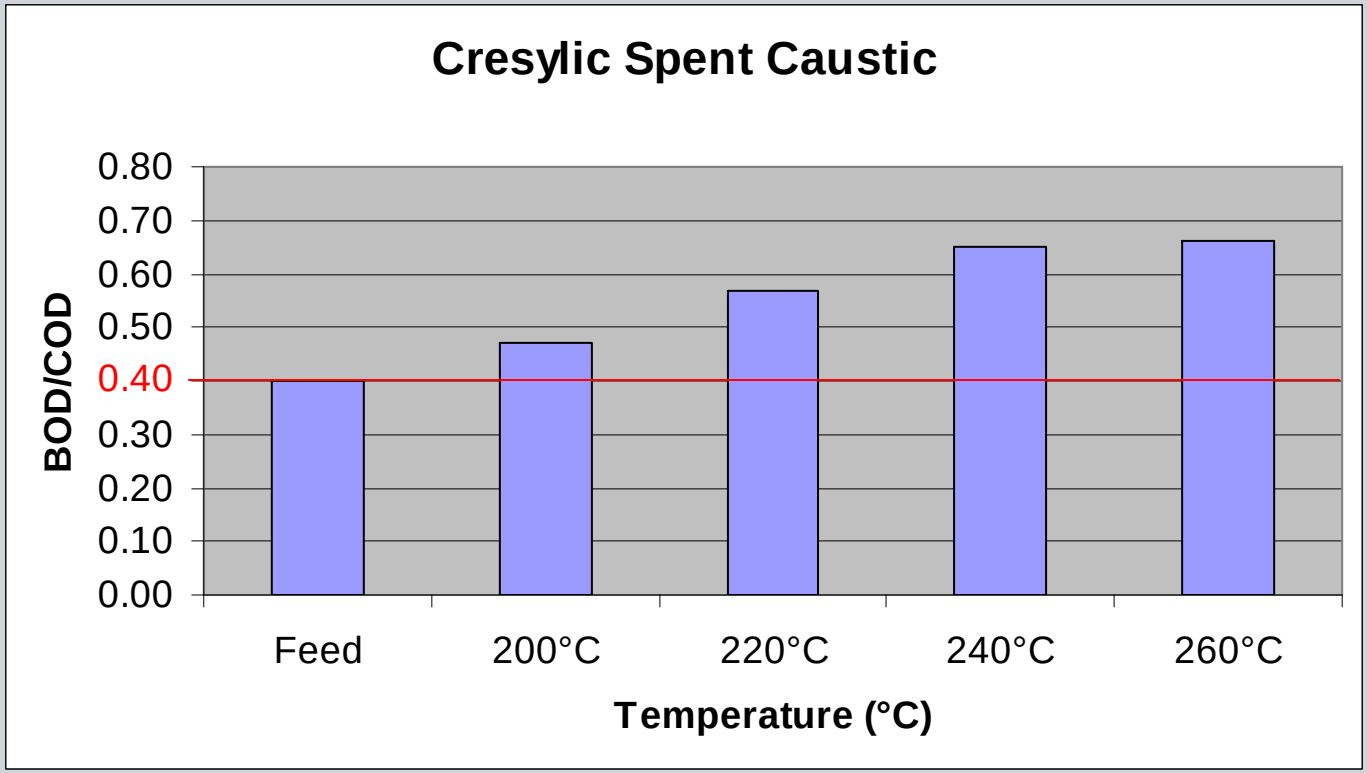
Results – Cresylic Spent Caustic



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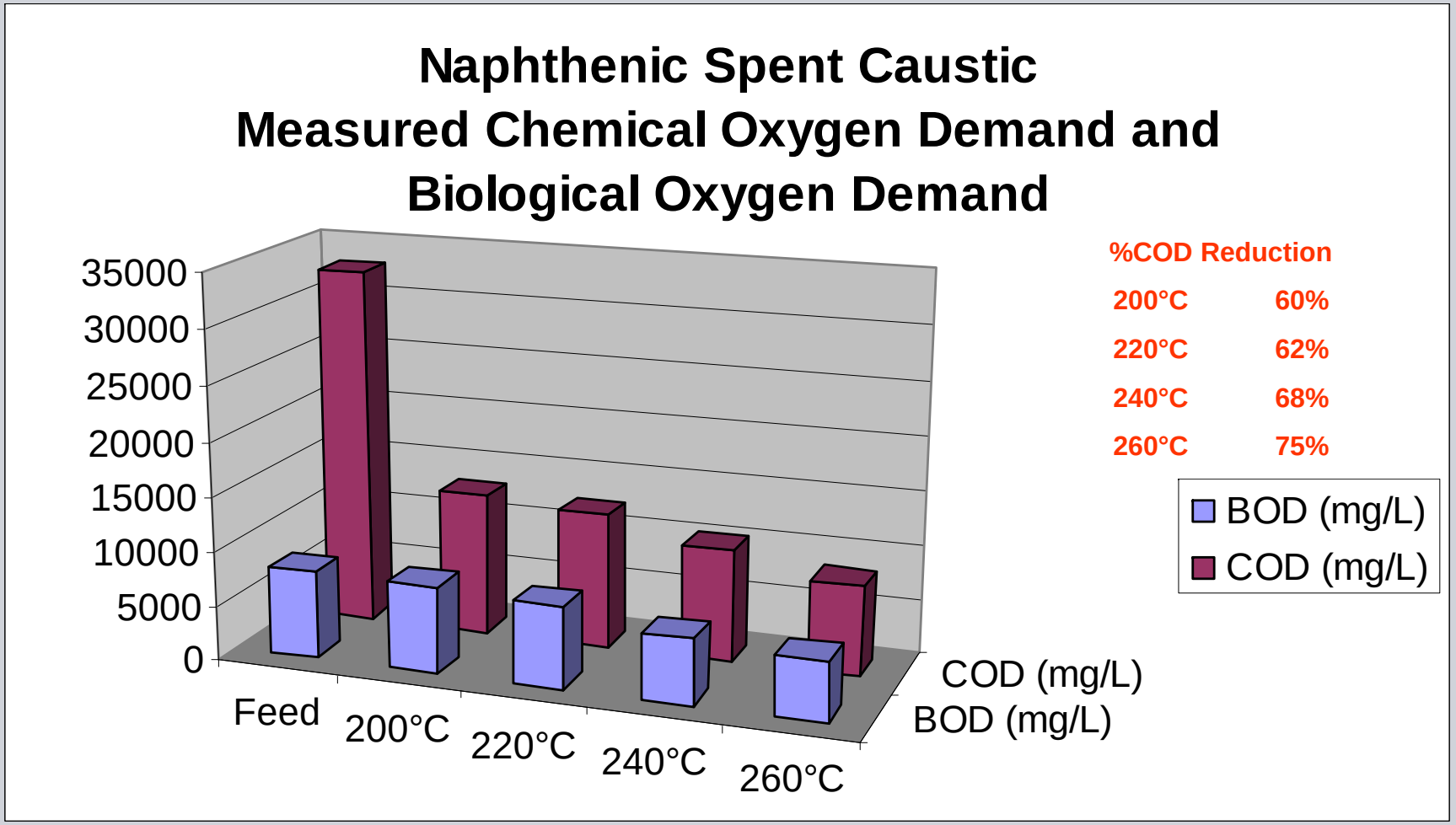
Results – Naphthenic Spent Caustic



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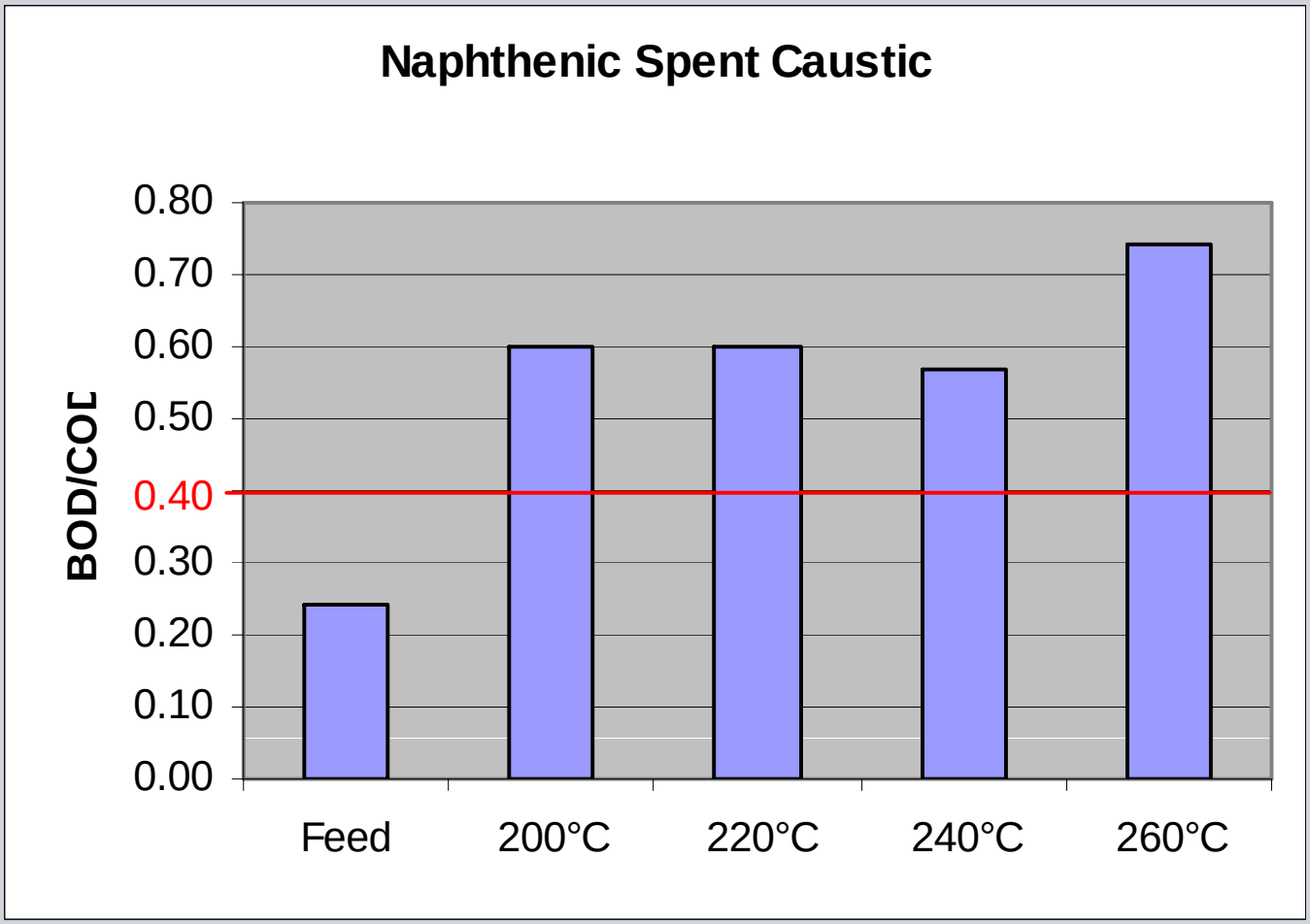
Results – Naphthenic Spent Caustic



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TOC - Investigation

			Sulfidic	Cresylic	Naphthenic
	Reported As	Units			
Oxidation Temperature		°C	200	240	260
Retention Time		min	60	60	60
TOC	C	mg/L	3370	2420	2770
Acetic Acid	CH_3COOH	mg/L	5650	1720	3190
Formic Acid	HCOOH	mg/L	760	1910	2820
Fumaric Acid	HOOCCH=CHCOOH	mg/L	11	9	<1
Propionic Acid	CH_3CH_2COOH	mg/L	620	<250	<100
Succinic Acid	$HOOCCH_2CH_2COOH$	mg/L	940	360	599
Oxalic Acid	HOOCCOOH	mg/L	560	1610	1560
Acetone	CH_3COCH_3	mg/L	---	---	202
% Recovery of TOC		%	97.8	73.0	101

Full Scale WAO Case Studies

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Full Scale WAO Case Study - Sulfidic

Data From A Full Scale WAO Unit Treating Sulfidic Spent Caustic			
Temperature - 200°C Retention Time - 60 minutes			
		Feed	Effluent
Analysis	Units		
COD	mg/L	10880	2410
TOC	mg/L	1060	930
Sulfide-S	mg/L	3380	<1
Thiosulfate-S	mg/L	1790	34
COD Destruction	%	---	77.8
TOC Destruction	%	---	12.3

There are currently >30 full scale WAO systems treating sulfidic spent caustic.
There have been no reported issues with biodegradability of the oxidized effluent.

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Full Scale WAO Case Study - Cresylic

Data From A Full Scale WAO Unit Treating Cresylic Spent Caustic			
Temperature - 260°C Retention Time - 60 minutes			
		Feed	Effluent
Analysis	Units		
COD	mg/L	71200	15400
TOC	mg/L	20800	5790
Sulfide-S	mg/L	2870	<1
Thiosulfate-S	mg/L	520	<30
BOD	mg/L	---	7900
BOD/COD	---	---	0.51
COD Destruction	%	---	78.4
TOC Destruction	%	---	72.2

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Full Scale WAO Case Study - Naphthenic

Data From A Full Scale WAO Unit Treating Naphthenic Spent Caustic			
Temperature - 250°C Retention Time - 90 minutes			
		Feed	Effluent
Analysis	Units		
COD	mg/L	62600	9750
TOC	mg/L	12000	3250
Sulfide-S	mg/L	6820	<1
Thiosulfate-S	mg/L	1610	<40
BOD	mg/L	---	5710
BOD/COD	---	---	0.59
COD Destruction	%	---	84.4
TOC Destruction	%	---	73.0

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Conclusions

1. COD destruction increased with oxidation temperature
2. WAO was effective at eliminating compounds responsible for causing odor issues such as sulfide and mercaptans.
3. WAO increased the BOD/COD ratio
4. Majority of the TOC present in oxidized spent caustic samples was small chain organic acids.

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Thank you!