Ozonation of Produced Water from Oil Production Wells

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Abstract

In the process of pumping oil from wells, the oil industry generates "produced water," which is usually seawater contaminated with various organic substances. Before produced water is returned to the environment, it needs to be treated for organics. One method to eliminate organic substances from produced water is oxidation, using ozone. Several experiments have been conducted in this study to investigate the effectiveness of ozone in oxidizing organic substances in real produced water from two oil companies. In these experiments, ozone was produced by a corona-discharge ozone generator and flushed through a large batch reactor containing a stir bar. Produced water was then injected in the reactor. Gas and water samples were taken at varying intervals from 0 to approximately 1600 minutes. Samples were analyzed for concentration of CO_2, extractable organics, ozone, and organic acids. Results show that organic compounds can be successfully removed from produced water with the use of ozone. Heating the produced water improved the rate of removal. This information was used for preliminary design and cost estimation.

Objectives

- Decrease the amount of extractable organics from produced water
  - Investigate the use of ozone for the oxidation of organics
- Investigate ozonation at room temperature (23°C) and at 80°C

Setup

- 4-L batch reactor containing ozone and produced water
- Sealed with Teflon-lined stoppers for injections and sampling
- Mixing provided by a stir bar

Methods

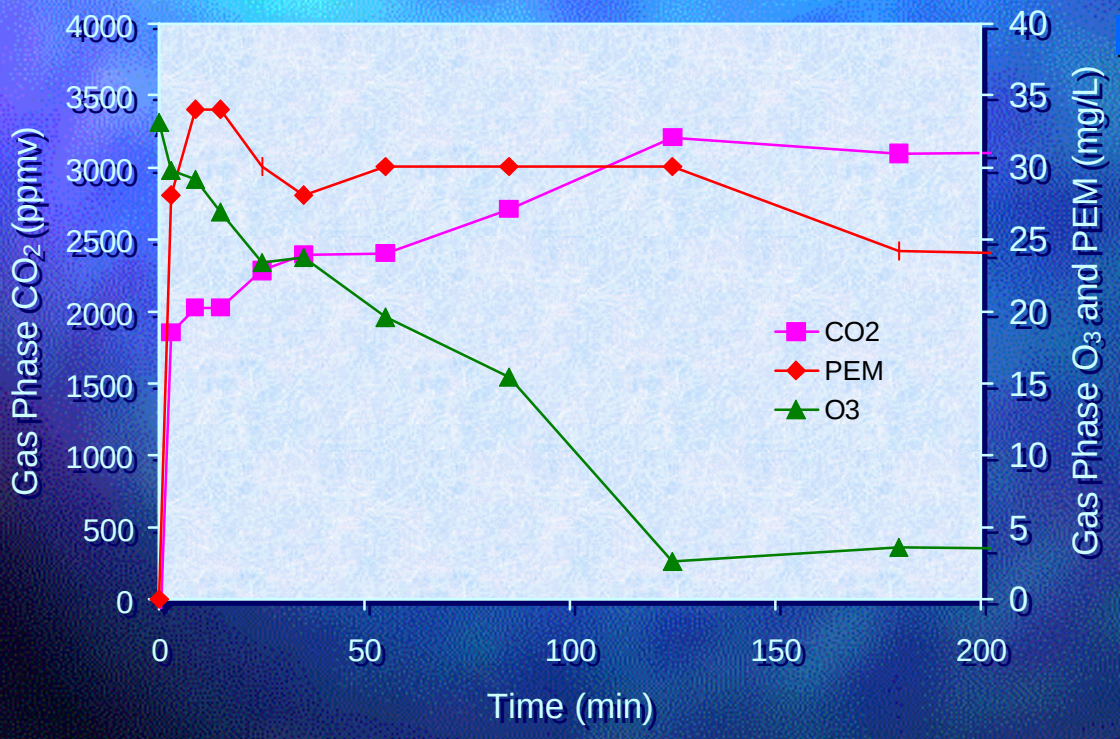
- **Ozone Analysis**: Wet chemistry test based on oxidation of indigo blue
- **Acids Analysis**: Ion Chromatography
- **CO_2 Analysis**: Gas Chromatograph
- **Water Soluble Organics**: Extraction with PCE and infrared absorption spectroscopy

Procedure

- Flush ozone through reactor containing stir bar for approximately one hour prior to experiment
- Add 200mL produced water and 10mL 4N HCL
- Sample water phase and gas phase
- Take samples from 0 to approximately 1600 min at various intervals depending upon disappearance of ozone
- Analyze for ozone and CO_2 at time of sampling
- Extract liquid samples with PCE; allow to sit overnight; and measure IR absorbency

Results

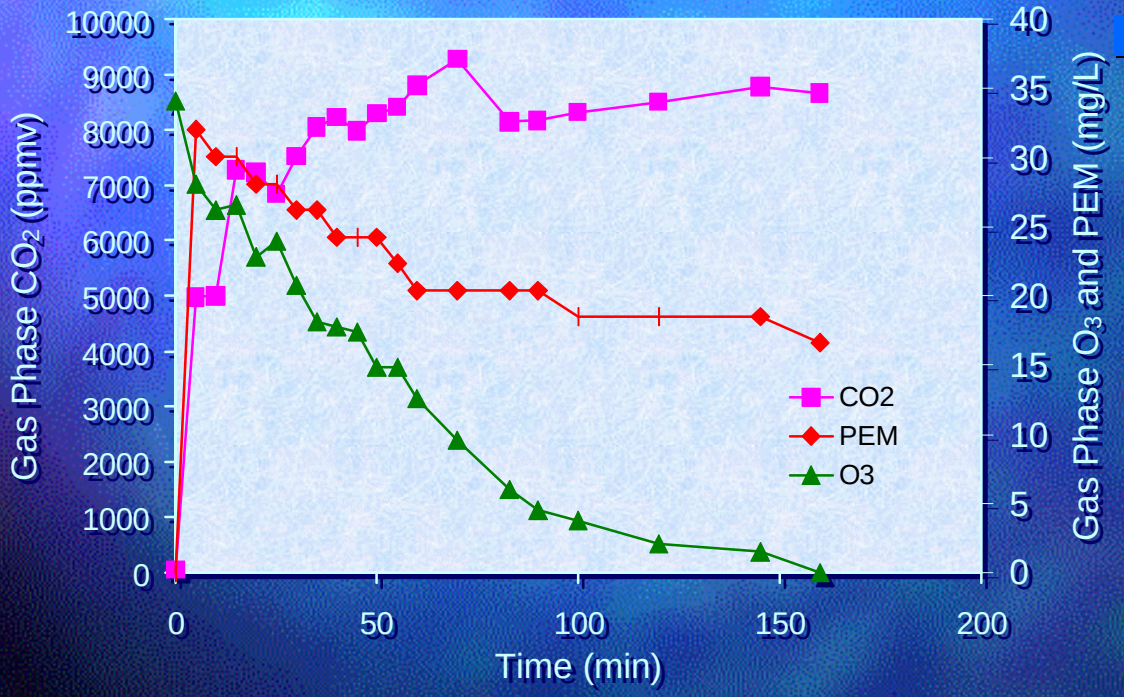
Ozonation of Produced Water



- Summary results from large-scale batch experiments conducted with Company A-supplied produced water at 23°C.

Results

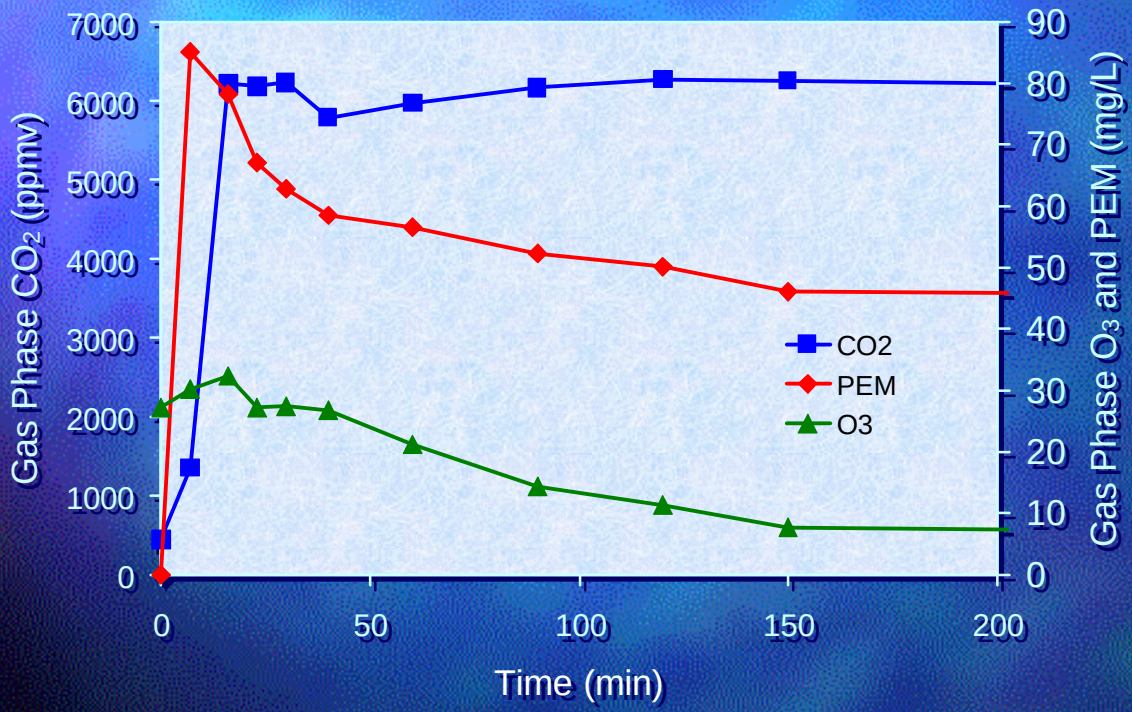
Ozonation of Produced Water



- Summary results from large-scale batch experiments conducted with Company A-supplied produced water at 80°C.

Results

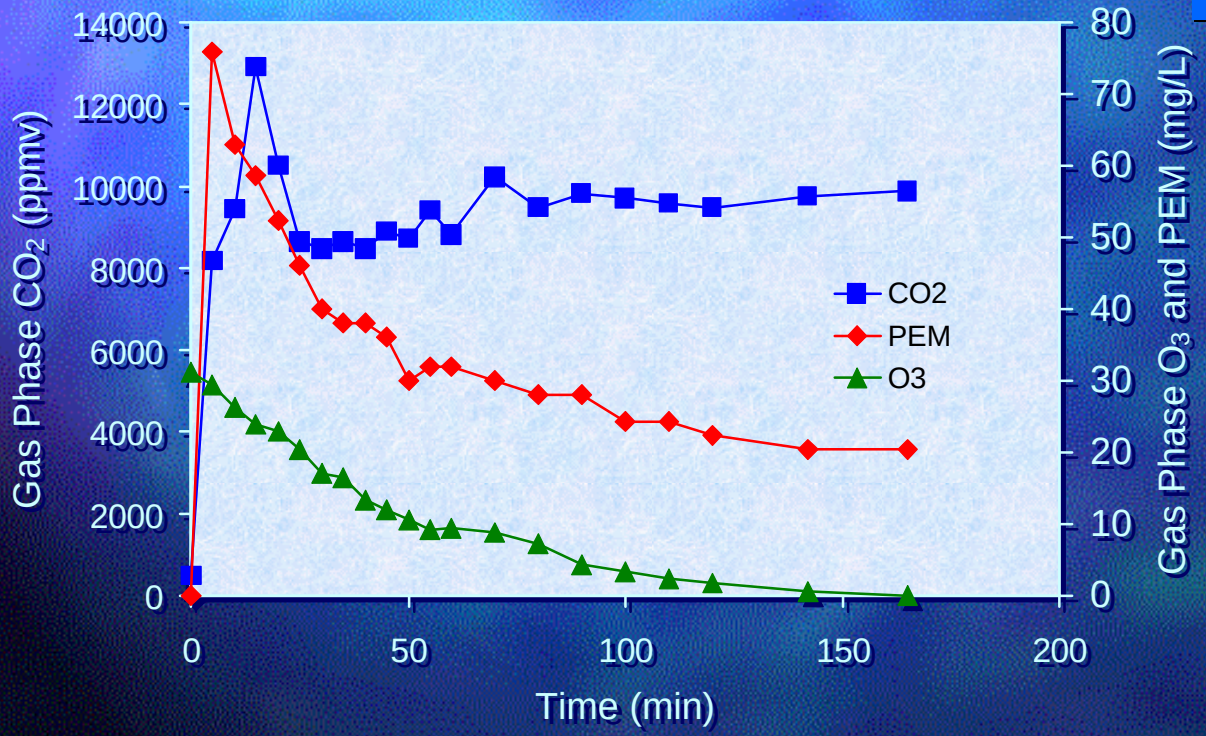
Ozonation of Produced Water



- Summary results from large-scale batch experiments conducted with Company B-supplied produced water at 23°C.

Results

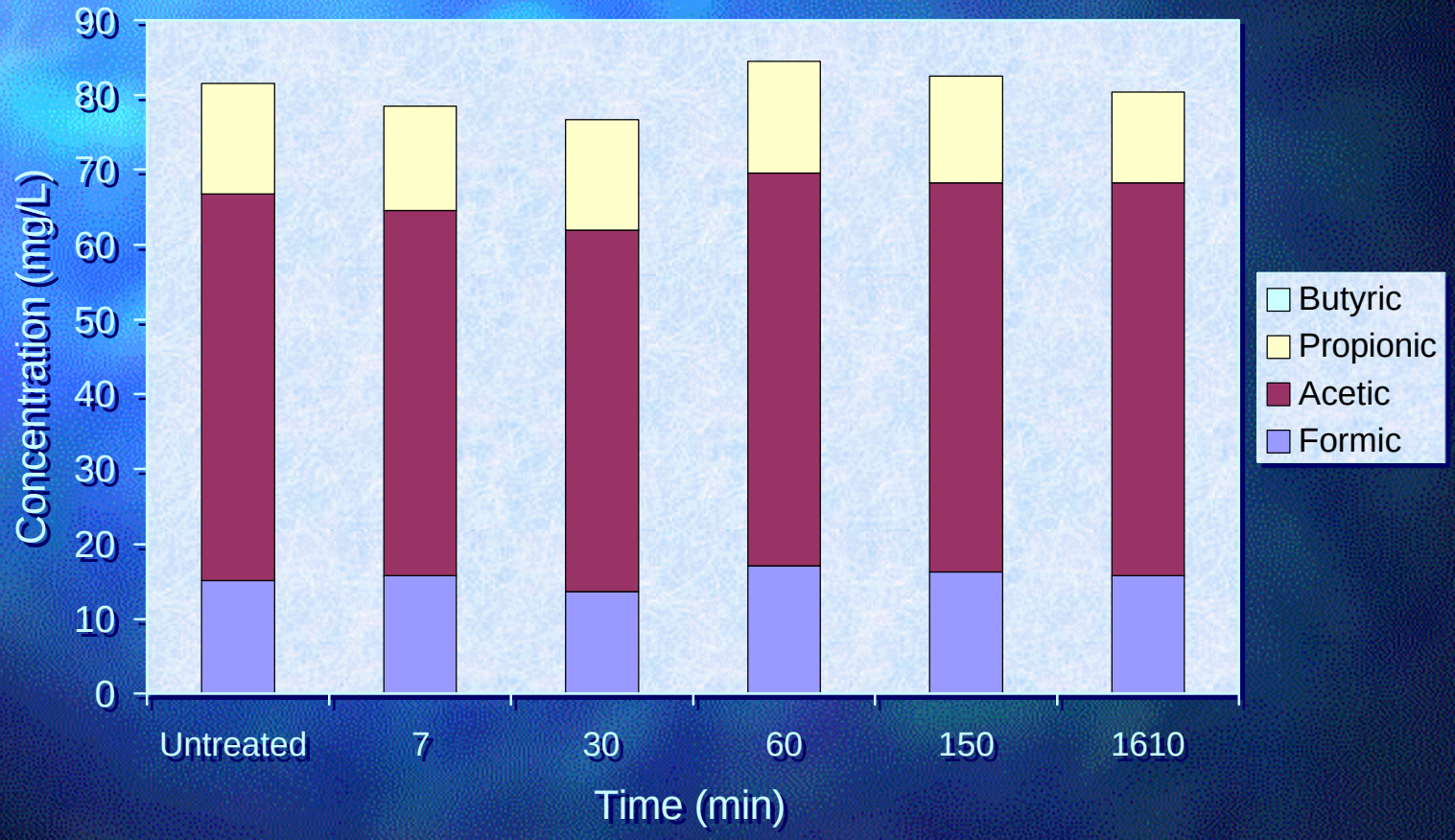
Ozonation of Produced Water



- Summary results from large-scale batch experiments conducted with Company B-supplied produced water at 80°C.

Results

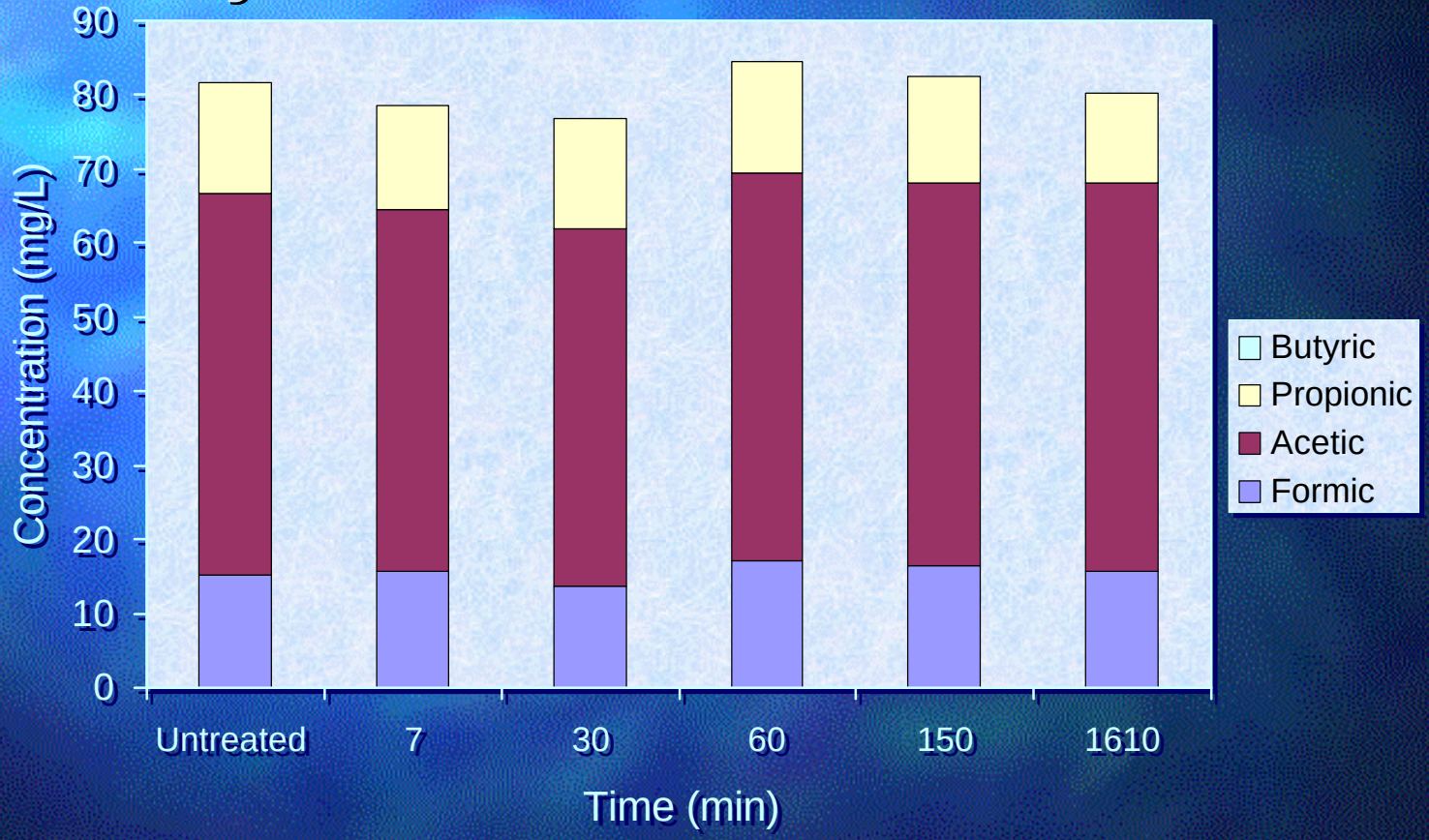
Acid Analysis



Amount of acid versus prolonged treatment with ozone in Company A produced water.

Results

Acid Analysis



Amount of acid versus prolonged treatment with ozone in Company B produced water.

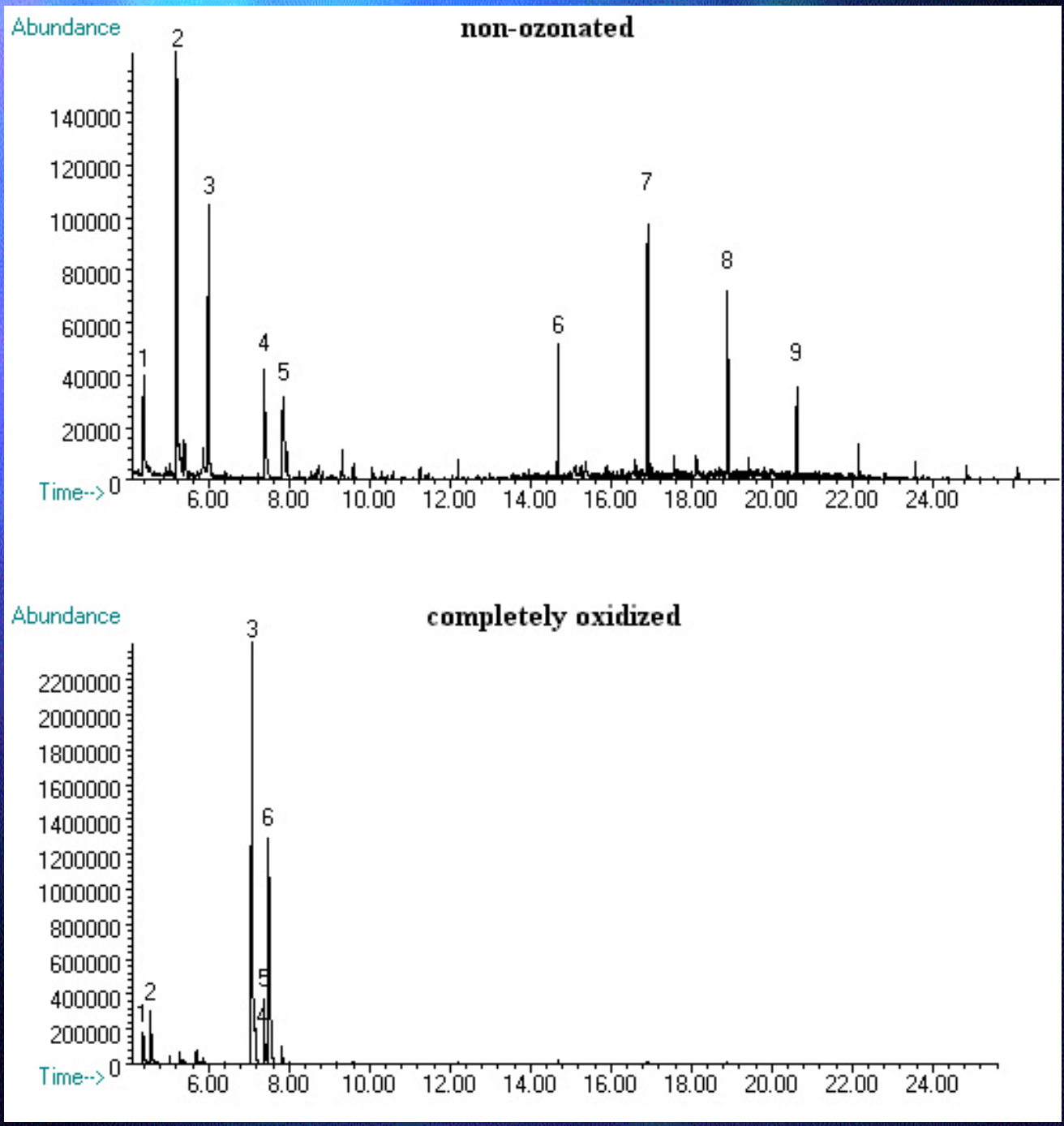
Results

Rate of Disappearance of Extractable Materials

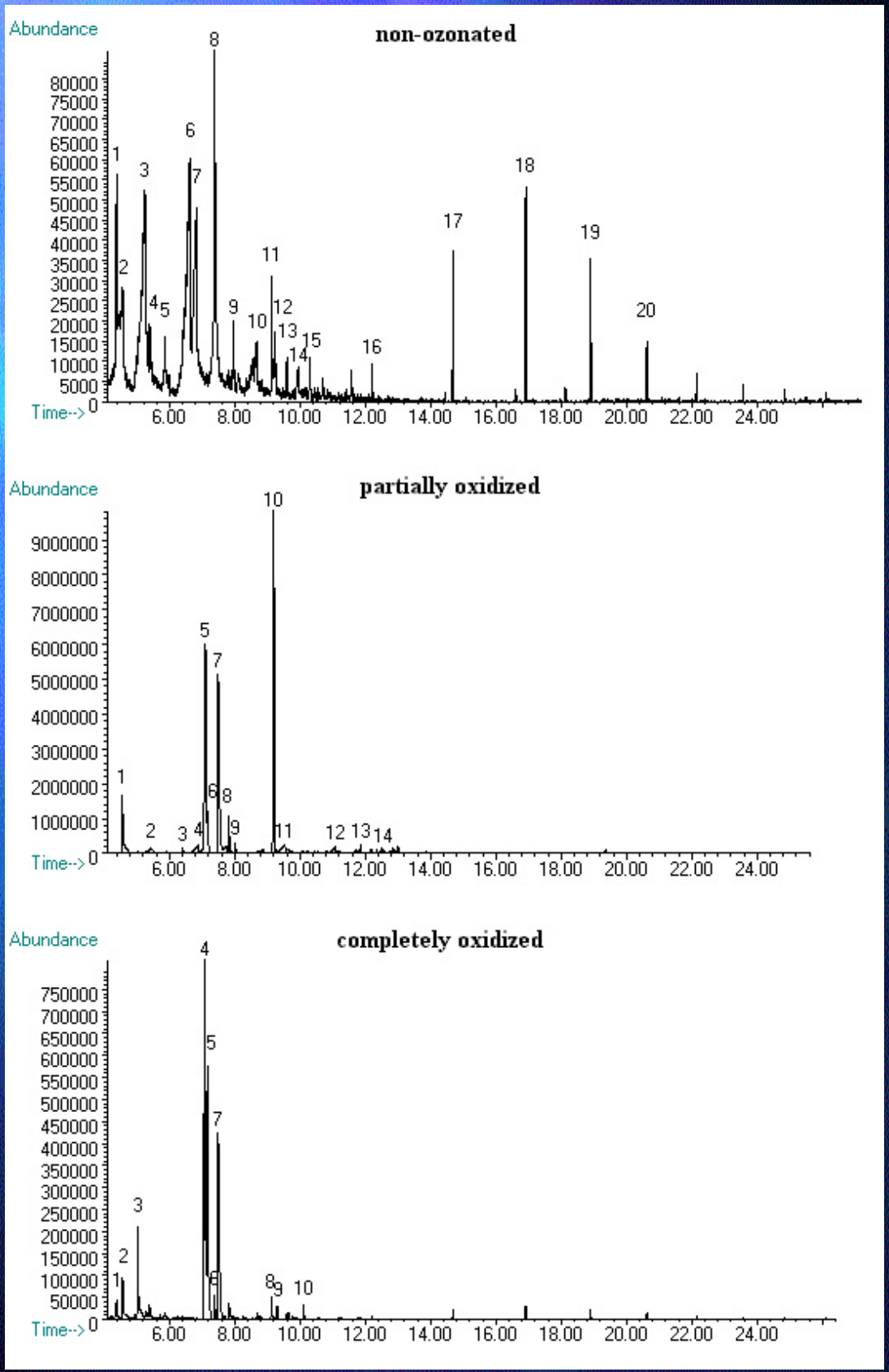
Source Of Produced Water	k- Value with 95% Confidence [L/(mg·min)]	
	22ºC	80ºC
Synthetic		0.000120-0.000138
Company A	0.0000505-0.0000880	0.000297-0.000396
(duplicate experiment)	0.0000506-0.000115	
Company B	0.000231-0.000400	0.000867-0.00104

Identification of Dichloromethane Extractables

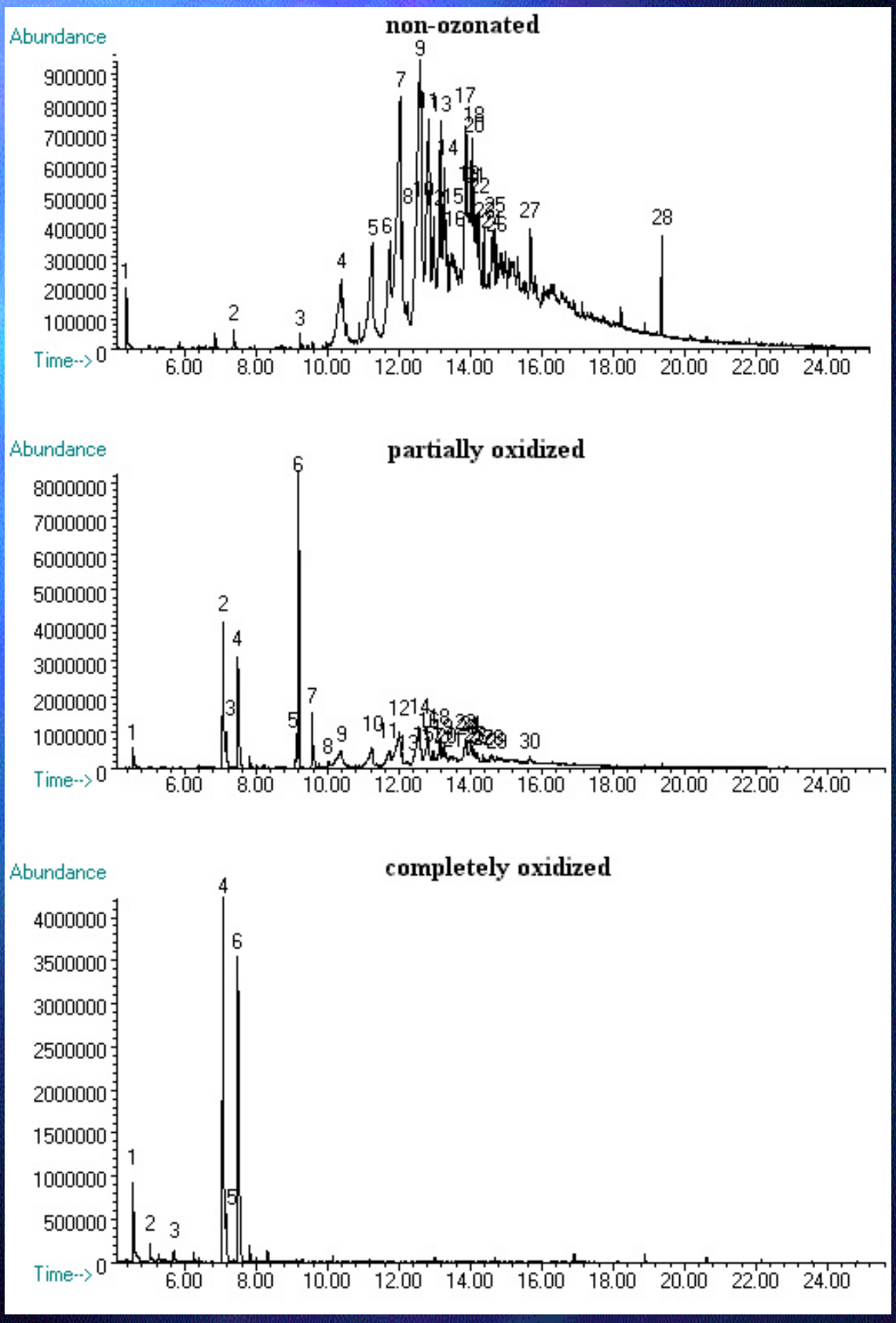
Synthetic



Company A


non-ozonated
Abundance
Time-->
partially oxidized
Abundance
Time-->
completely oxidized
Abundance
Time-->

Company B


non-ozonated
Abundance
Time-->
partially oxidized
Abundance
Time-->
completely oxidized
Abundance
Time-->

Economic Analysis

Capital Cost Estimate for Installed Ozonation System for Produced Water Treatment
(no provisions for emulsified oil removal, 100% of ozone provided from air)

Input Variables	400	Chemical Engineering Cost Index
	1100	Marshall and Swift Cost Index
	10000	Produced water production rate (bbl/day)
	75	Hexane-extractable materials removed (HEM) (mg/L)
	30	Residence time in ozonation contact vessel (min)
	10.0	Ozone requirement (mg ozone/mg HEM)

Output Values	262.85	HEM input (lb/day)
	2628.49	Ozone demand (lb/day)
	$2,524,167	Cost of ozonation system (installed)[1] (excluding piping, pump, ozone contact vessel, and buildings)
	17500	Volume of ozone contact vessel (100% excess) (gal)
	2339	Volume of ozone contact vessel (100% excess) (cu ft)
	9.0	Diameter of ozone contact vessel (H/D = 4) (ft)
	36.2	Height of ozone contact vessel (H/D = 4) (ft)
	2	Low Pressure and Carbon Steel Cost Factor, F_c
	$225,032	Cost of plastic-lined ozone contact vessel (uninstalled)
	$225,032	Installation cost of plastic-lined ozone contact vessel (100% of cost)
	11	Pump Size Power Requirement (kW)
	$16,410	Cost of carbon steel centrifugal pump (uninstalled)
	$29,538	Installation cost of carbon steel centrifugal pump (180% of cost)
	$80,400	Cost of piping for ozone contact vessel (uninstalled)
	$80,400	Installation cost of piping for ozone contact vessel (100% of cost)
	$3,180,978	Total cost of complete ozone system (excluding protective buildings)
	$3,857,626	Fixed Capital Investment (including protective buildings)

Conclusions

- Organic Acids are not attacked or destroyed by the ozone.
- The rate of disappearance of the extractables is of first order.
- The degradation rates and ozone demands of the extractable organics were slightly better at higher operating temperatures.
- The products contained halogenated compounds.
- An economic evaluation indicated that a system for 75% conversion of extractable organics would have a fixed capital cost in the range of $3.2 million, with an annual operating cost of $1.1 million (or $7.31/1000 gal). The estimation was based on a produced water flow rate of 10,000 bbl/day (17,500 gal/hr), an initial content of 100 ppm of hexane-extractable organics, a liquid residence time of 30 minutes, and an ozone consumption of 10 g ozone/g PEM.

Acknowledgments

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