Ozone Treatment of Soluble Organics in Produced Water (FEAC307)

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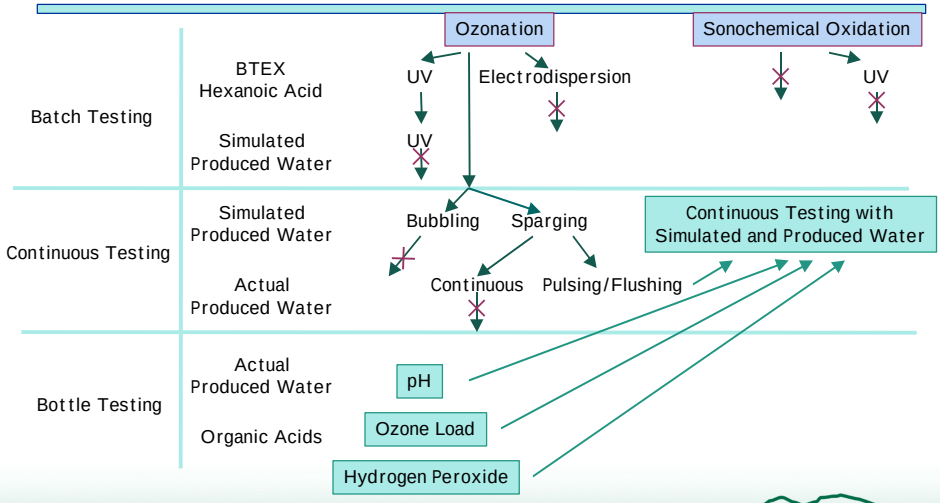
Sponsored by FE NPTO Office, Tulsa, OK

Objective

- Develop oxidation treatment systems for water-soluble organics in produced water generated during deep-water offshore operations
- The project investigates:
  - oxidant production by methods suitable for offshore operations
    - ozonation
    - sonochemical oxidation
  - increasing the mass transfer rate in the reactor by forming micro bubbles during ozone injection
    - electrodispersion
    - diffusers
  - using ultraviolet irradiation to enhance the reaction if needed

Project Description

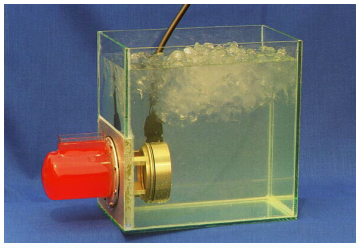


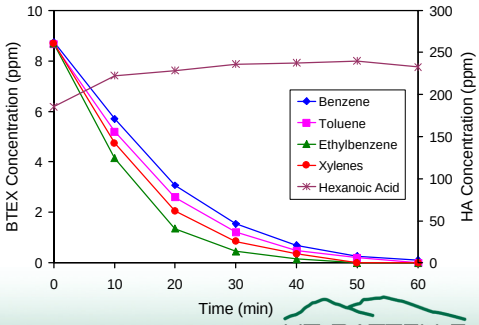
Status of Deliverables

- Experimental Plan - Nov. '98
- Batch Testing - May '99
- Continuous Testing - Moved from Dec. '99 to Dec. '00 by request from partners
- Site Selection - Moved from Oct. '99 to Mar. '01
- Prototype Testing - Mar. '02
- Move Prototype - Apr. '02
- Field Testing - Sept. '02

Accomplishments
Batch Testing: Sonochemical Oxidation

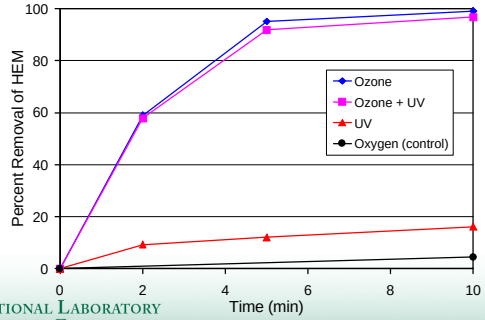
- First-order reactions for BTEX
- Hexanoic acid recalcitrant
- Linear relationship to power input
- Testing discontinued due to power requirements, slow kinetics





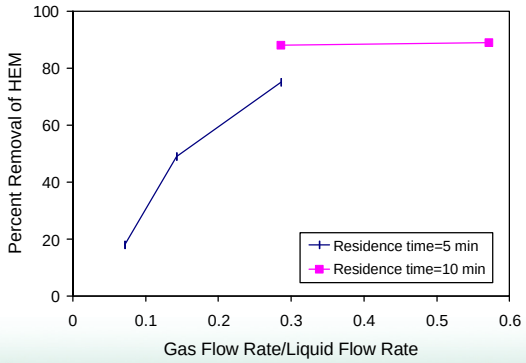
Accomplishments
Batch Testing: Ozonation

- Simulated produced water from downhole separator project
- Excellent destruction efficiency of hexane extractable materials (HEM)
- Continued testing of UV eliminated



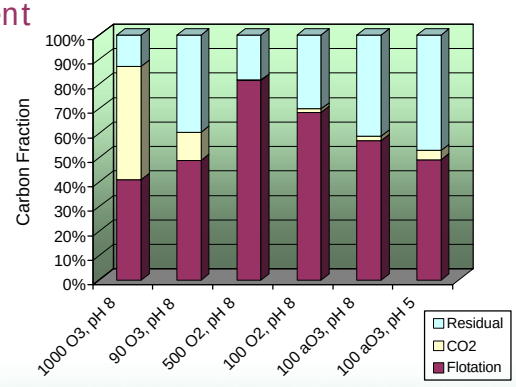
Accomplishments
Continuous Testing: Ozonation

- Simulated produced water from downhole separator project
- High removal HEM efficiency (~90%) achievable



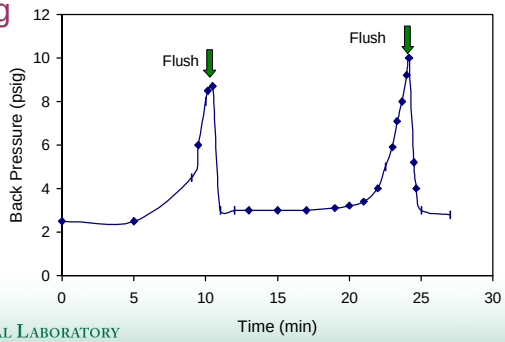
Accomplishments
Continuous Testing: C Balance in Ozonation

- Simulated produced water (oil dispersed in water)
- Flotation removes the majority of droplets suggesting two-stage treatment
- Ozone loading important for complete oxidation



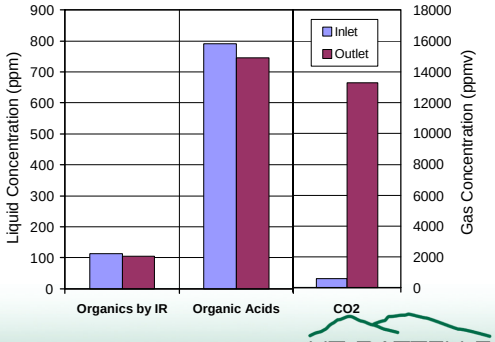
Accomplishments
Continuous Testing: Ozonation Sparging

- Simulated sea water with iron
- Clogging mainly due to evaporation, not precipitation
  - dependent on gas flux
- Sparging problem solved with flushing or pulsing



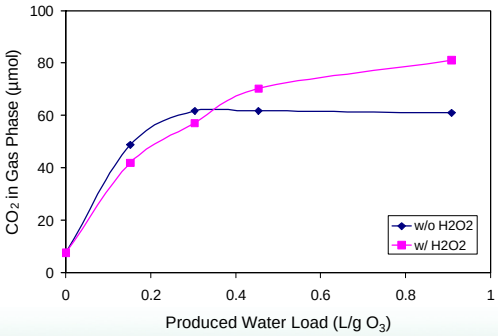
Accomplishments
Continuous Testing: Actual Samples

- Produced water from an industrial participant
- Lots of iron and free oil phase in samples
- Complete oxidation noted of some compounds; CO_2 data indicate that more compounds have been destroyed



Accomplishments
Bottle Testing: Complete Oxidation Potential

- Produced water from an industrial participant
- Hydrogen peroxide lowers overall ozone effectiveness, but may improve destruction of target compounds



Utility of Results

- Ozone has already been recognized and preliminary evaluated by one private participant
  - these results were made available to the rest of the PERF group
  - results from our studies can be compared with past study
  - data will allow for preliminary estimation of costs
- Contributes to scientific knowledge
  - Walker, A. B., C. Tsouris, D. W. DePaoli, and K. T. Klasson, "Ozonation of Soluble Organics in Aqueous Solutions Using Microbubbles," accepted in *Ozone Science and Engineering*, May 2000
  - Walker, A. B., C. Tsouris, D. W. DePaoli, and K. T. Klasson, "Removal of Organics from High-Ionic-Strength Aqueous Solutions," presented at 11th *Symposium on Separation Science and Technology for Energy Applications*, Gatlinburg, TN, October 17-20, 1999

Benefits and Value
Collected Data will be Used for Comparisons

	Previous Study	This Study
Organics concentration	35-40 ppm (soluble O&G)	25 ppm (HEM)
pH	6.9	7.5
Operating temp (^{o}F)	95	70-75
Ozone dose (mg/L treated)	290	40
Residence time (min)	45	10
Removal efficiency	46%	88%
Capital cost (10,000 bbls/day)	$1,400,000	$570,000
Operating (ozone) cost	$73,000	$7,300

Problems

- Definition of soluble organics (in produced water)
  - suspended oil versus no suspension
  - changing analytical procedure (hexane versus freon)
  - organic acids
- Selection of a suitable surrogate composition difficult
  - oil suspended in salt water
  - salt water from oil/water separator
  - salt water with organics
- Only small volumes of produced water samples available

Conclusions

- Very good feedback from industrial participants
  - Chevron, Shell, Phillips, BP, Statoil, and Marathon
- Promising results from surrogate studies indicating cost savings
- More work on actual samples needed to increase destruction efficiency
  - close the mass balance