Ozone Treatment of Soluble Organics in Produced Water (FEAC307)

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Sponsored by FE NPTO Office, Tulsa, OK

Solubles Review Meeting
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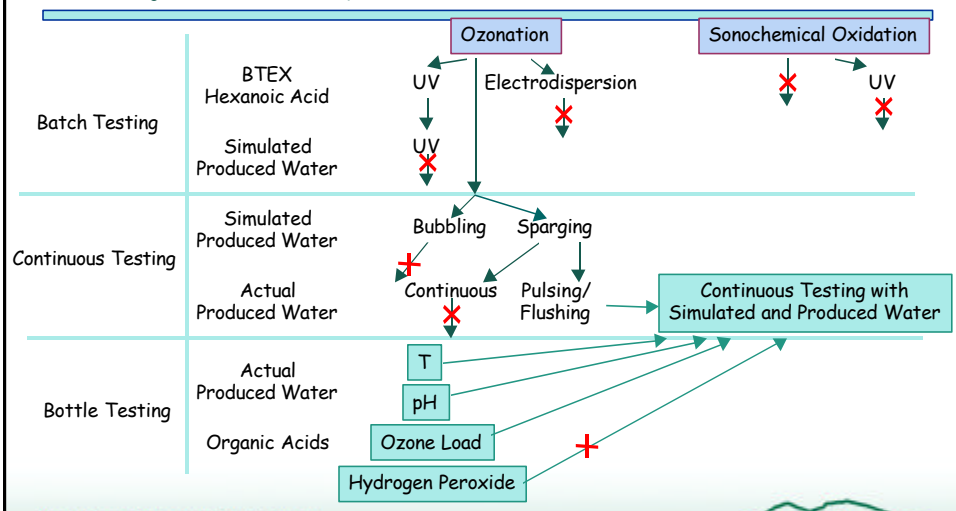
Objective

- 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
  - kinetics and products of oxidation

Project Description

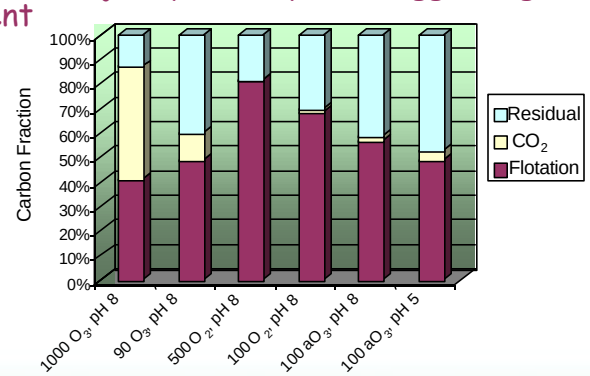


Project Schedules

• Complete planned laboratory tests	Dec. '00
• Decision Point - Develop path forward for additional studies or field demo	Mar. '01
• Demo Site Selection	Mar. '01
• Prototype Testing	Mar. '02
• Move Prototype	Apr. '02
• Field Testing	Sept. '02

Accomplishments
Continuous Testing: C Balance in Ozonation

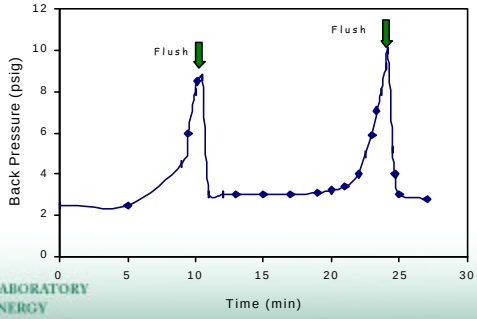
- Simulated produced water (oil dispersed in water)
- Flotation removes the majority of droplets, suggesting two-stage treatment
- Ozone loading important for complete oxidation



Conditions:
20 mL/min liquid flow rate
10 min liquid residence time
O3 rate given in mL/min

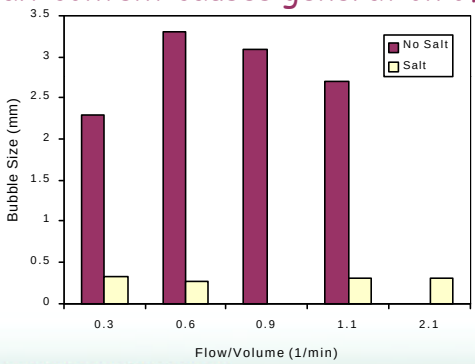
Accomplishments
Continuous Testing: Ozonation Sparging

- Simulated sea water with iron
- Clogging mainly due to evaporation
  - dependent on gas flux
- Sparging problem solved by periodic flushing or pulsing of frit using sea water



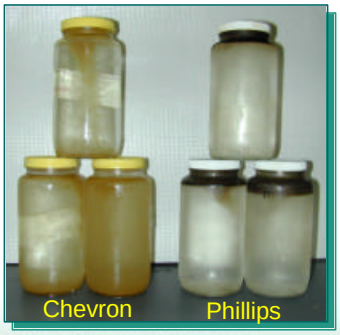
Accomplishments
Continuous Testing: Ozonation Sparging

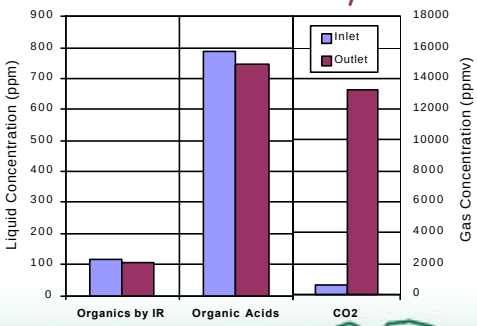
- Simulated sea water in larger-scale system
- Sparging problem solved using flushing with sea water
- Salt content causes generation of small bubbles



Accomplishments
Continuous Testing: Actual Samples

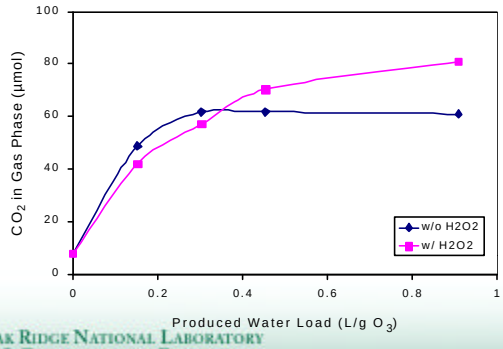
- Produced water from Phillips
- Lots of iron and free oil phase in samples, little orgaincs
- Complete oxidation of some compounds; CO_2 data indicate that more compounds have been destroyed





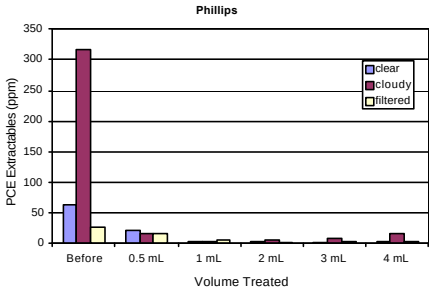
Accomplishments
Bottle Testing: Complete Oxidation Potential

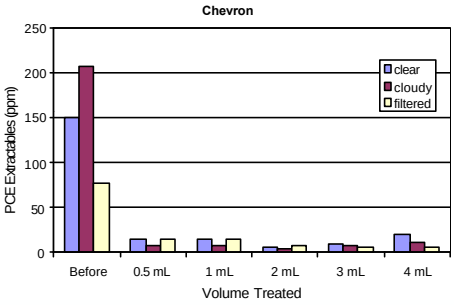
- Produced water from Phillips and Chevron
- Hydrogen peroxide does not increase overall ozone effectiveness, but may improve destruction of target compounds



Accomplishments, Bottle Testing: Complete Oxidation of Extractables

- Produced water from Phillips and Chevron
- Ozone destroys most extractable compounds in different fractions of the produced water

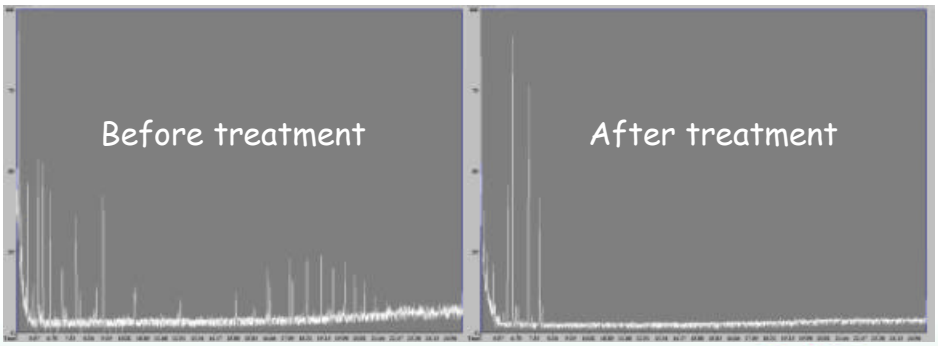




Each sample treated with 160 mL of 40 mg/L O_3 in O_2

Accomplishments, Bottle Testing: Complete Oxidation of Extractables

- Cloudy produced water from Phillips
- Ozone destroys most hydrocarbons, as determined by GC/MS



Benefits and Value Economics

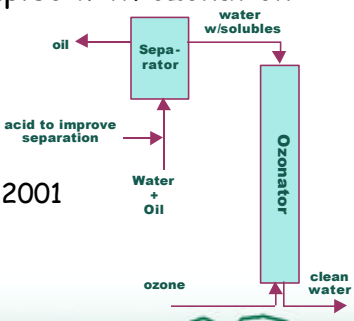
- From batch studies, it appears that ozonation could feasibly meet treatment standards
- Process economics are needed to evalutate this option
- Preliminary economics are currently being developed based on bottle testing and continuous flow experiments
  - Professor R.M. Counce of the University of Tennessee is taking the lead.
  - Industrial experience
  - Experienced in mass-transfer in gas/liquid contactors
  - Experienced in system design and economic analysis

Issues

- **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**
  - bottle testing
- **Mass (carbon) balances**

Summary

- Ozone appears to be a viable option for destruction of soluble organics by oxidation.
  - Significant destruction of hydrocarbons (PCE extractables)
  - Low consumption of ozone by organic acids; conversely, low destruction of these acids
- Items still needing to be resolved
  - Products and kinetics of oxidation
    - Target of current bottle tests
  - Removal of organic droplets
    - Large source of O&G, consumes ozone
  - Economic evaluation
  - Process demonstration
  - Data comparisons with other PERF 98-04 tasks

Proposed Path Forward

- Complete investigation of ozonation kinetics and product identification
  - By August 30, 2001
- Test centrifugal separator for the removal of organic droplets from produced water, coupled with ozonation test
  - Allows continuous testing with large volumes of simulated produced water at ORNL
  - Investigate soluble vs suspended oil
  - Complete continuous testing of bench-scale coupled system by December 31, 2001
- Economic Evaluation
- Site Demonstration