

Electrolytic Oxidation – Providing an Alternative to the Disposal of Produced Water

The definition of Produced Water includes all water sources associated with the production of petroleum oil, natural gas, and bio-diesel. In the United States, the greatest source of Produced Water is land-based. Historically, because of the cost of removing the soluble hydrocarbons, and chlorides, the vast majority of this water has either be re-injected or disposed of as a hazardous waste. In areas traditionally with little fresh water sources or long periods of drought, this has resulted in vast sections of land as being both unusable and uninhabitable (central states – Nevada, Wyoming, Utah, New Mexico, Arizona, and Texas).

Based on trials conducted using both petroleum-based Produced Water and condensate from Natural Gas pumping from the North Sea, electrolytic oxidation like our patented EOH₂O® process provide an alternative to disposal of brackish and freshwater-based Produced Water containing hydrocarbon pollutants.

Summary of Scottish Trials:

Starting in 2004, Aquatic Technologies began looking at using electrolytic oxidation to increase the level of reductions of hydrocarbons, including Aromatic and Aliphatic compounds in Produced waters generated from petroleum and natural gas production in the North Sea, as ell as refined diesel products (diesel and kerosene). Produced water sources included polyglot wastewaters of oil and natural gas condensate; washout water from heavy crude transport barges; drilling mud; and natural gas condensate both pre and post glycol recapture.

The following will highlight the results received from 2005 to 2007 in Aberdeen, Scotland. The rest of this presentation will discuss application of the technology to reduce or eliminate the need to dispose of otherwise good water as a hazardous waste, where it could be used for irrigation, municipal, or commercial use.

2005-2007 Results:

All tests performed without the use of skimmers or other filtration of solids or free oil.

First Test Results:

Source: Heavy crude barge washout water. Seawater with conductivity exceeding 50uS used to washout the barges. No filtration or oil skimming performed. 250gallon tote recirculated at 200gpm through 3-gallon electrode chamber (COP = 9:1). Washout water contains some surfactants/cleaning solutions used in washing out the barges.

Sample Water	Time	pH	Suspended Solids (mg/l)	COD (mg/l)	Total (mg/l) Hydrocarbons	Aromatic(mg/l) Hydrocarbons
Untreated		7.19	2282	9680	10,041.00	1,094.00
Mixed Fluid	10hrs	7.96	71	1430	5.07	1.32
Supernatant	6hrs	7.57	48	1680	4.87	0.83

Conclusion:

- a. Free and soluble oil super-coagulated within first 30-minutes. To prevent continued breakdown of crude/oil – skimming or scraping of oil from surface needs to occur;
- b. COD can not be reduced within a reasonable time frame where skimming/scraping does not occur;
- c. Electrolytic oxidation alone (no surfactants) breaks hydrophilic (water loving) aspect of soluble oil.
- d. Reduction of THC and Aromatics occurs in the supernatant, even where coagulated oil is not readily removed.

Reduction of BTEX and MEG in NG Condensate to allow Direct-to-Ocean Discharge

NG condensate was also tested, as the then current pricing for disposal of condensate off-site exceeded \$3.08USD (2006). All Natural Gas from North Sea is received at the Bacton Natural Gas Plant. Condensate is comprised of seawater and glycols and must be hauled to hazardous waste treatment site. Condensate volume ranges from a low of 10m³ (2,640 gallons) to 100m³/day (26,400 gallons).

Test was to determine ability to treat the condensate on-site in batch mode to allow direct discharge to the Thames River (freshwater river). Expected Regulation in 2009 was BTEX of 5mg/l and MEG of 10mg/l for direct discharge.

First Natural Gas Condensate Test:

Source: Natural Gas Condensate – North Sea (provided by Petrofac Corp.). Post Free Glycol Recapture

Sample Water	Time	pH	Suspended Solids (mg/l)	COD (mg/l)	Total (mg/l) Hydrocarbons	Aromatic (mg/l) Hydrocarbons
Untreated		6.00	44	824	27	17
1hr treatment		6.51	84	827	13	5
2hr treatment		6.48	82	755	8	2
3hr treatment		6.58	80	785	<1	<1
4hr treatment		6.59	58	734	6	<1

Note: Petrofac denoted that surfactant contaminants and failure of the glycol recapture system in the condensate water were primary sources of COD.



Petrofac NGL Condensate **Right:** Untreated

Left: Post Treatment (No filtration)
(Oxidized iron and other metals in sludge)

Second Natural Gas Condensate Test Results:

Source: Petrofac (Bacton Natural Gas Plant) – 250 gallon tote

Determination of Batch Treatment for Reduction of BTEX and MEG in Natural Gas Condensate (post-MEG Removal)

Sample	pH	Concentration - mg/l						Components	
		Benzene	Toluene	Ethyl-benzene	Xylene	2-butoxy-ethanol	Aliphatic	Aromatic	
Untreated	4.11	37.57	9.54	0.23	1.16	4168	2.75	50.34	
50min	4.21	18.68	4.13	<0.1	0.64	4210	2.41	25.01	
90min	4.23	15.93	3.39	<0.1	0.59	3386	2.67	21.17	
150min	4.26	13.19	2.66	<0.1	0.5	3414	1.48	17.78	
240min	4.32	6.48	1.3	<0.1	0.33	1984	1.48	9.76	
300min	4.35	5	0.91	<0.1	0.34	2586	0.94	7.87	
365min	4.39	2.98	0.6	<0.1	0.29	3943	1.1	5.21	

Both NG Condensate results denote a >50% reduction of THC, Aromatic and BTEX within first hour. Results achieved without use of coagulants or mechanical filtration. MEG reduction occurs, but not quickly enough to discontinue the use of MEG recapture system. However, at levels 100mg/l or less, a standard 8-hour day would be sufficient to remove the MEG to meet expected 2009 Direct-to-Ocean/River Discharge regulation.

Additional trials were conducted, with the above results being representative of the additional tests. Conclusion was filtration is needed to meet TSS and surface skimmers will remove coagulated free and soluble oil better than oil-water separators or coalescer can provide.

Additional Oily Wastewater Tests

The question arose following completion of the Scotland trials of whether the EOH₂O® electrolytic oxidation process could coagulate synthetic oils – like those used as cooling and cutting lubricants in metal machining/parts manufacturing. Additionally, could this be done where the wastewater would contain very high levels of surfactants and other cleaning products.

The trials in Scotland denoted that surfactants did not interfere with coagulation of free and soluble unprocessed petroleum oils – even though the surfactants themselves were reduced only marginally.

Wastewater from a mower engine manufacturing plant in St. Louis was obtained. This wastewater contains high levels of soluble synthetic cutting/cooling oils, mop water, and various other cleaning solutions with high levels of oil and soluble metals (copper, nickel, chrome, zinc, iron, silver, cadmium, etc.)

The picture below denotes the results of applying the electrolytic oxidation process to the wastewater.

Left to Right:

Bottle #1: Synthetic Oily wastewater following pretreatment through BOSS oil-water separator.

Bottle #2: Mixed liquor following 15-minutes of batch treatment.

Bottle #3: Mixed liquor at 30-minutes.

Bottle #4: Mixed liquor of 30-minutes filtered through 3-micron filter and treated another 15-minutes.

Bottle #5: Supernatant following additional 30-minute treatment.



Conclusion:

- a. Supercoagulation of the oil will occur even with high levels of surfactants and soaps present.
- b. Skimming of the oil will greatly reduce the treatment period.

Geothermal and CBM Water:

Geothermal (Southern Idaho) – Water Temperature at Extraction – 152 degrees F. (Batch treatment with Air injection using venturi)

Water Sample	Phosphate	Sulfate	Fluoride	pH	Iron	Magnesium
	(All measurements in mg/l)					
Untreated	4400	6100	6000	1.7	78	3000
30-minutes	3300	2700	2700	1.8	51	1800
60-minutes	1700	1300	1200	1.9	20	820

No filtration utilized.

(Photo on next page denotes precipitated solids)



CBM Water (Denver, Colorado) –Static Chamber Test

Test #1

Water Sample	Initial Alkalinity (As Carbonate/Bicarbonate)	(Reductions in “Red”)
Untreated	2250 mg/l	
15-minute	2180 mg/l	(70)
30-minute	2120 mg/l	(60)

Test #2 – CBM Water in Batch Treatment mode with 92% oxygen gas injection via injector (steel electrode)

	Initial Alkalinity	Bicarbonate	Carbonate	pH	Conductivity
Untreated	1920 mg/l	1650 mg/l	540 mg/l	8.89	667.8uS
15-minutes	1770 mg/l	1360 mg/l	480 mg/l	8.21	442.5uS

Carbon and Titanium electrodes:

Untreated	1700 mg/l	1610 mg/l	180 mg/l
15-minutes	1670 mg/l	1520 mg/l	300 mg/l
30-minutes	1590 mg/l	1350 mg/l	480 mg/l
45-minutes	1520 mg/l	1160 mg/l	720 mg/l
Total	(180)	(450)	+540

NOTE: (Carbon and titanium electrodes had comparable results. This disputes claims that electrode material type determines reduction rate and/or ability)

Utilizing Produced Water as a Fresh Water Source for Rural Economic Development in the South Western United States

**Tests results on Produced Water from Texas and New Mexico –Barnett Shale, Frac water, and small oil production wells
(information to be provided at January 2009 Produced Water Association following December 2008 field tests)**

End.