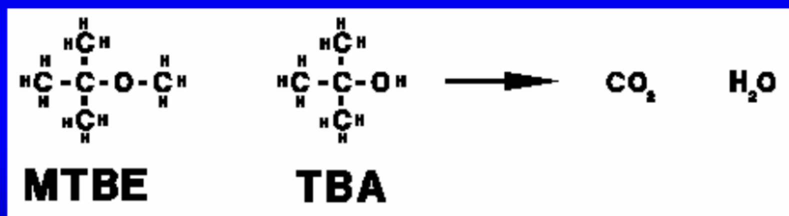
Bioreactor Treatment of Ethers and Alcohols such as MTBE & TBA



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Fluidized Bed Bioreactor

- **Microorganisms attached to particles degrade contaminants in a water stream**
- **Ex-situ treatment applicable to GW pump-and-treat operations**
- **Particles are distributed in the bioreactor by an upflow of the water being treated**
- **Used in a variety of other applications including wastewater treatment and industrial waste treatment**

Oxygen Demand

O_2 is required for biodegradation

Ratio O_2:Contaminants = 3:1

O_2 solubility in water = 9 ppm (eq. with air)

6 ppm O_2 usable - so –

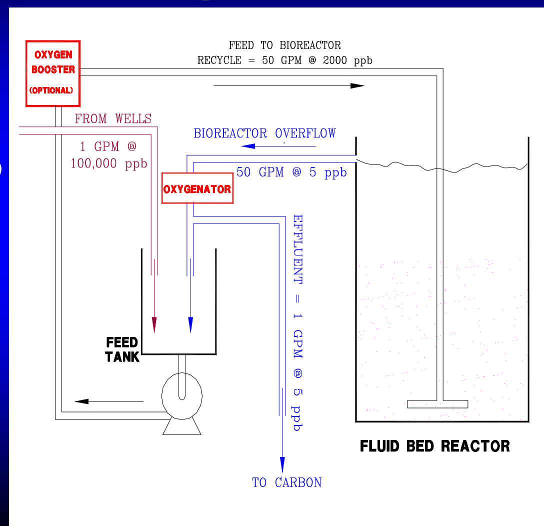
Contaminant bio. limited to 2 ppm in FBR tank unless O_2 is added

HISTORY

- Microbes at JWPCP – Carson, CA - 1997
- Scow Laboratories- UCD isolate PM-1 - 1998
  - CA native
  - Very long doubling time
- UCD – Civil Eng. Pilots 4-inch Trickling Bed Filter - 1998
- ERI installs eight 16-inch TBFs at Healdsburg – using cultures from Davis - 1999
- ERI pilots fluidized bed reactors using cultures from Davis and Healdsburg-1999
  - Six months to populate
- First full-scale fluidized bed - in Palo Alto – 2000
- ~30 other full-scale FBRs to date

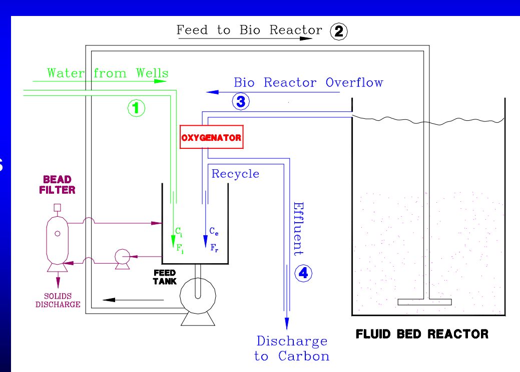
Fluidized Bed Operation

- Re-oxygenation by air or O_2 in packed tower
- Recycle dilutes feed
- Recycle rate is fixed @ 50 or 10 gpm to fluidize the bed
- HRT ~ 15 minutes
- Feed – 100,000 ppb-gpm, or 1.3 pounds/day



Bead Filter Operation

- Bead filter handles the solids (Fe, Mn, hardness precipitates)
- Separate recycle loop
- Upflow until solids accumulate
- Isolate bead filter to backwash
- Beat the cake off the beads
- Allow beads to rise
- Filter cake will sink
- Take cake out as slurry
- Put filter back on line
- 1 drum/6 months typical
  - Non-hazardous

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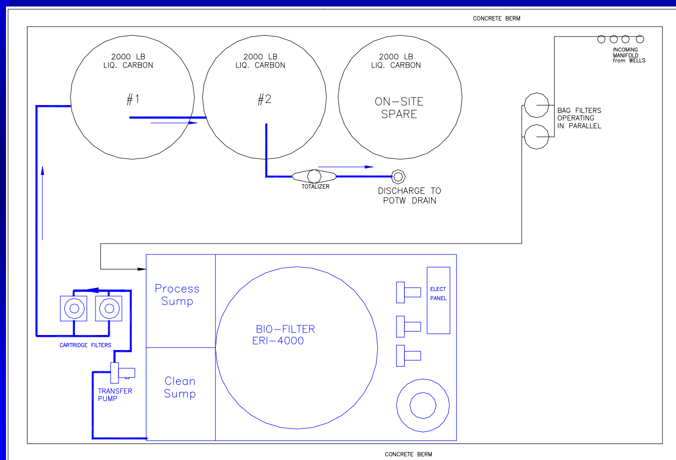
534D-

FBR Placement in Treatment Train

- **Upstream**
  - **Control sources**
  - **Remove gross free product**
  - **Remove high BTEX (e.g., by air stripping or GAC)**
  - **Particulate filter**
- **Downstream**
  - **Particulate filter to remove bugs**
  - **GAC**
    - **Polishing, and to handle upsets**
    - **Very infrequent carbon changeouts**

Palo Alto System Layout



NOTES

1) Flow controlled at wells
2) Bag filters on well water
3) Well water fed directly to process water sump
4) Discharge taken directly from clean sump
5) Cartridge filters used on BioReactor discharge
6) Three carbon canisters on site. But only two in use at any one time.

APPROXIMATE SCALE

0 1FT 2FT 5FT

IN FEET

Palo Alto Fluidized Bed

Date	Flow	MTBE in	MTBE out	TBA in	TBA out	Method
	gpm	ppb	ppb	ppb	ppb	
8/9/00	10	6,200	ND<2.5			
8/11/00	10	7,420	ND<0.5	ND<284	ND<20	(8260)
8/29/00	10	8,000	2,330	Nutrients Needed (N, P, K)		
9/19/00	10	7,600	ND<2.5			
9/22/00	12	13,700	30.6	Reactor Capacity Exceeded		
				O_2 Booster added		
9/28/00	12	11,100	ND<1	ND<984	ND<3.9	(8260)
10/12/00	14	8,400	3.5			
10/26/00	17	9,670	6.1	ND<980	ND<3.9	
11/9/00	17	12,000	ND<0.5	300	ND<5	Kiff
11/21/00	17	5,300	1.2	120	ND<5	Kiff

Palo Alto Fluidized Bed

Date	Flow	MTBE in	MTBE out	TBA in	TBA out	Method
	gpm	ppb	ppb	ppb	ppb	
11/9/00	17	12,000	ND<0.5	300	ND<5	(8260)
12/20/00	19.5	3,800	0.72	260	ND<5	(8260)
2/14/01	19	7,600	300	O_2 Booster Re-installed		
8/9/01	19	3,500	ND<2			
10/4/01	15	1,300	ND<2	740	ND<5	(8260B)
11/6/01	14	1,400	ND<2	530	ND<5	(8260B)
12/6/01	17	1,100	ND<2	1100	ND<5	(8260B)
5/8/02	17	710	6	2100	15	(8260B)
9/4/02	17	3,600	1.1	1500	ND<20	
11/6/02	17	900	1	2000	ND<5	
1/03		Found and fixed leaks (holes in vapor recovery system)				

Palo Alto Fluidized Bed

Date	Flow gpm	MTBE in ppb	MTBE out ppb	TBA in ppb	TBA out ppb	Method
1/08/03	11	280	ND<0.5	1,600	ND<5	(8260B)
2/04/03	11	120	ND<0.5	1,100	ND<5	
3/05/03	11	77	ND<0.5	830	ND<5	
4/02/03	12	110	ND<0.5	670	ND<5	
5/08/03	9	49	ND<0.5	570	ND<5	
6/03/03	10	31	ND<0.5	360	ND<20	
7/15/03	12	29	ND<0.5	180	ND<20	
8/06/03	11	23	ND<0.5	150	ND<5	

System shut down and relocated – clean-up sufficient for this site

Bedford, New Hampshire

Challenging System

- Bedrock groundwater
- Weather proof enclosure
- Influent groundwater
  - BTEX (30,000 ppb)
  - MTBE (80,000 ppb)
  - TBA (8,000 ppb)
  - Iron (up to 13 ppm)
  - Manganese (up to 30 ppm)
- Suggest large bioreactor
- System includes:
  - Iron pretreatment
  - Air stripper
  - Small bioreactor
  - 500# carbon polishers
  - Discharge to infiltration gallery i source area

Air Stripper

Stripper – 4 Trays 250-300 cfm
Water to Stripper – up to 5 gpm

BIOREACTOR SYSTEM

- Bio-500 bioreactor – green
- Oxygenation tower - white
- Nutrient feed drum - blue
- Spa heater loop – gray

- Stripper effective for BTEX, MTBE, TAME
- TBA is removed in bioreactor
- Fe comes out in stripper and must be water blasted off
  - Fe pretreatment added 8/06
- Mn comes out in the Bio-500 - much can be siphoned off as a slurry

Carbon Vessels

Bedford NH Data

Date	Flow (gpm)	Temperature (degrees F)	Bioreactor TBA (ug/l) Influent	Bioreactor TBA (ug/l) Effluent	Notes
2/15/05	1.4	65	6,440	<20	
2/22/05	1.5	63	4,930	27	
2/28/05	1.4	65	5,820	<20	
3/7/05	1.4	80	6,320	<20	
3/14/05	0.5	77	3,570	<20	
4/5/05	0.9	72	2,770	<20	
5/2/05	0.8	67	4,230	<20	
6/28/05	1.5	81	1,230	<20	
7/19/05	2.0	86	608	<20	
7/20/05	1.0	79	574	<20	
8/12/05	2.0	76	<20	<20	
8/22/05	1.8	73	890	<20	
9/20/05	0.9	75	374	<20	

Bedford NH Data

Date	Flow (gpm)	Temperature (degrees F)	Bioreactor TBA (ug/l) Influent	Effluent	Notes
10/22/05	1.7	60	3,930	<20	Record rainfall; new well
11/4/05	4.9	54	7,210	4,030	on line; increase loading
11/5/05	4.9	54	4,590	1,820	5-fold; decreased temp.
11/28/05	4.9	56	1,940	540	
12/31/05	2.7	57	490	<20	
1/20/06	3.9	56	1,600	34	
2/13/06	3.3	51	1,480	<20	
3/13/06	4.3	55	245	<20	
4/14/06	4.4	57	276	<20	
5/19/06	2.2	65	70	<20	
6/5/06	4.6	59	185	<20	
6/26/06	5.8	64	912	<20	25% stripper bypass
7/10/06	5.1	64	417	<20	50% stripper bypass
7/21/06	4.5	65	258	<20	75% stripper bypass
8/4/06	4.2	61	<160	<20	100% stripper bypass
9/8/06	4.3	64	NA	<20	100% stripper bypass
10/16/06	4.3	61	<20	<20	100% stripper bypass
10/30/06	4.8	63	277	<20	100% stripper bypass
12/11/06	4.1	59	140	<20	100% stripper bypass
1/29/07	4.9	57	<20	44	100% stripper bypass
3/30/07	3.4	54	<20	<20	0% stripper bypass

Bedford NH – Recent MTBE and BTEX Data

Date	Bioreactor MTBE (ug/l) Influent	Effluent	Bioreactor BTEX (ug/l) Influent	Effluent	Notes
6/5/06	51	19	ND	ND	0% stripper bypass
6/26/06	530	46	663	ND	25% stripper bypass
7/10/06	>1,900	16	707	ND	50% stripper bypass
7/21/06	2,990	29	579	ND	75% stripper bypass
8/4/06	2,410	42	562	ND	100% stripper bypass
9/8/06	NA	104	NA	ND	100% stripper bypass
10/16/06	1,340	414	922	ND	100% stripper bypass
10/30/06	>1,810	53	4,369	ND	100% stripper bypass
12/11/06	863	453	4,829	ND	100% stripper bypass
1/29/07	562	543	3,912	265	100% stripper bypass
3/30/07	<2	<2	ND	ND	0% stripper bypass

Air stripper was turned back on on 2/12/07 because influent now mostly BTEX:

MTBE 450 ug/l
TBA <1,000 ug/l
BTEX 6,191 ug/l

After 3/30/07, trickle air stripper bypass to feed the bugs in bioreactor

Bedford NH Other Parameters (mg/l)

Date	Stripper Influent	Bioreactor Influent	Bioreactor Effluent
		Manganese	
3/14/05	13	12	<1
5/05/05	13	12	6.5
		Iron	
3/14/05	13	4	<1
5/05/05	10	5	4
		Dissolved Oxygen	
5/05/05		20	5

Bedford NH

- Bioreactor effectively destroyed TBA to below standard (40 ug/l) except in 11/05 during period of:
  - Drastically increased TBA mass loading to bioreactor
  - Decreased temperature
  - Malfunctioning iron/manganese pretreatment system
- Air stripper and GAC were bypassed until recently
  - Bioreactor can treat ethers, alcohols, aromatics
  - Effluent with oxygen and bugs discharged to groundwater to promote in situ bioremediation
- Dissolved oxygen concentrations up to 38 mg/l have been achieved by oxygen booster
- Water was heated initially but not this past winter
- MTBE and TBA concentrations in site GW are down; BTEX contamination remains
  - Oxygenated effluent is flushing smear zone at source

Maryland Site

- Larger bioreactor (ERI-4000)
- Incoming well water accumulated in frac tanks
- Filtration to remove solids
- Treating BTEX, MTBE, TBA
- Carbon (3 plus spare) for final polish
- Final water accumulated for analysis
- Currently discharge effluent to surface water
- May reinject to groundwater in the future

Maryland Site Startup Data

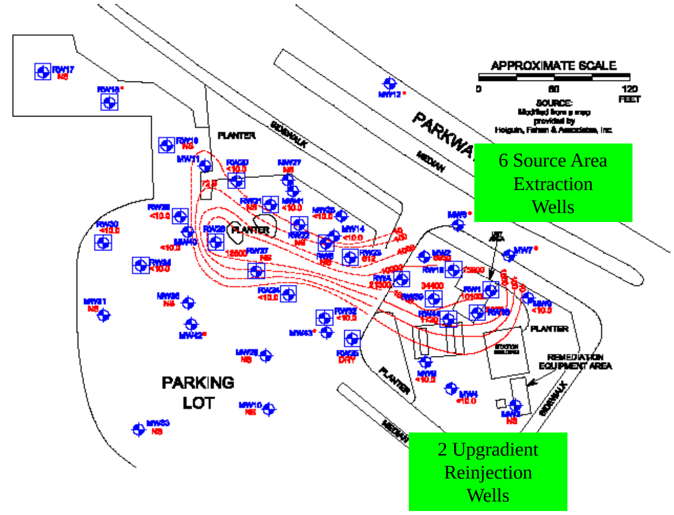
Sample Date	Flow (gpm)	Benzene (ug/l) in	Benzene (ug/l) out	MTBE (ug/l) in	MTBE (ug/l) out	TBA (ug/l) in	TBA (ug/l) out
8/1/06	4.5	64	0.6	9,450	50	1,290	<25
8/11/06	10.0	4	<1	5,670	1,580	792	<25
8/14/06	10.0	7	<1	9,490	327	522	<25
8/18/06	10.5	5	<1	3,420	4	429	<25
8/29/06	13.0	12	<1	4,790	23	557	<25
9/20/06	13.0	7	<1	3,610	188	431	<25

They stopped analyzing because they accumulate water in frac tank and analyze it prior to discharge - always ND

California Site

- Maximum groundwater concentrations:
  - TBA: 80,000 ug/l
  - MTBE: 100 ug/l
  - BTEX: negligible
- Treated effluent reinjected upgradient of source
- Regional Water Quality Control Board:
  - Limits reinjection to 3 gpm total
  - Requires increased monitoring of downgradient wells
- Potential concerns to track:
  - Clogging of reinjection wells
  - Pushing impacted GW off-site
- As TBA concentrations decrease:
  - Extraction will ramp up to ~1 gpm/well

California Site Plan and TBA in Groundwater



California Site Startup Data

Date	Flow (gpm)	TBA (ug/l) Influent	TBA (ug/l) Effluent	MTBE (ug/l) Influent	MTBE (ug/l) Effluent	Notes
01/04/07	0.00	<200	<10	3300	<1	
01/10/07	0.00	37000	ND	18	0.21	
01/16/07	0.03	47000	ND<10	38	ND<0.5	
01/23/07	0.06	43000	ND<10	ND<100	ND<1.0	
01/30/07	0.17	15000	ND<10	26	0.52	
02/06/07	0.36	69000	36000	260	88	Lost circ
02/08/07	0.35	91000	920	250	13	Lost circ
02/12/07	0.00	55000	1300	160	15	Lost circ
02/13/07	0.00	NT	NT	NT	NT	
02/20/07	0.29	98000	18	130	3.1	
02/27/07	0.10	58000	ND	140	ND	
03/06/07	0.06	68000	ND	200	0.38	
03/16/07	0.12	43000	ND	150	1.2	

Bioreactor Sizing

Based on loading of VOCs

- **Standard Size FBR – 5’ diameter x 11.5’ tall**
  - **On 6’ x 10’ skid**
  - **Design loading = 100,000 ppb-gpm**
  - **Or with O_2 booster = 250,000 ppb-gpm**
- **Small Size FBR – 2’ diameter x 11.5’ tall**
  - **On 4’ x 4’ skid**
  - **Design loading = 20,000 ppb-gpm**
  - **Or with O_2 booster = 40,000 ppb-gpm**

Startup

- **Initial startup phase - ERI will:**
  - Add the biomass and start up the bioreactor
  - Operate the bioreactor during initial startup phase
  - Train site personnel on O&M
- **First several months of operation – ERI will:**
  - Review site O&M data
  - Advise on optimizing bioreactor performance

O&M

- **Weekly:**
  - Measure DO, pH, temperature, pressures, flow
  - Gauge depth to sand
  - Backwash bead filter
  - Fill nutrient drum
- **Periodically:**
  - Influent and effluent sampling for VOCs
  - Clean particulate filters
- **Respond if recirculation stops**

ERI-4000 Costs

Capital Costs

• Bioreactor/biomass purchase	$65,000
• Oxygen booster (optional)	$3,500
• Transport/install/startup and GAC/pumps/tanks/piping/elec.	site-specific

O&M Costs

• On-site labor	2-3 hr/wk
• Electricity for bioreactor only	1.5 KW
• Materials/chemicals/parts/ sludge disposal	$200/month

ERI-500 Costs

Capital Costs

• Bioreactor/biomass purchase	$35,000
• Oxygen booster (optional)	$3,500
• Transport/install/startup and GAC/pumps/tanks/piping/elec.	site-specific

O&M Costs

• On-site labor	1.5-2.5 hr/wk
• Electricity for bioreactor only	0.9 KW
• Materials/chemicals/parts/ sludge disposal	$100/month

Small BioReactor
Huntington Beach

- 2x500 lb Liq. Carbons
- Fluidized Bed Tower
- Clean Water Surge Tank
- Nutrient Feed Drum
- Filters

Comparison with Other Technologies

- AS/SVE slightly effective for MTBE and ineffective for TBA
- MTBE – medium to high concentrations
  - Competitive with GAC
  - Competitive with chemical oxidation
  - Competitive with air stripping w/vapor-phase treatment
  - Not competitive with air stripping w/no vapor-phase treatment
  - Competitive with bioGAC – FBR advantages:
    - Can handle higher concentrations
    - More reliable and controllable
    - Less clogging problems
    - Don't need H_2O_2 – safety issues
- TBA – medium to high concentrations
  - Hard to separate TBA from water
  - Cost-effective technologies limited to biodegradation and chemical oxidation
  - Major advantage over chemical oxidation
    - Hazardous chemicals not used (e.g., H_2O_2, O_3)

Conclusions

- Contaminant destruction – alcohols, ethers, aromatics
- Low effluent concentrations – can use oxygenated effluent containing bacteria to promote in situ bio
  - Discharge effluent back to groundwater
- Hydraulic control possible
- Good performance at cool temperatures
- Can tolerate high manganese concentrations
- Small volumes of wastes generated
- Bioreactor can be reused at next site