TETRA TECH

Concentrate Management Utilizing Brine Bulb Technology (BBT)

2013 Industrial Water Reuse Specialty Conference

December 10, 2013

Long Beach, CA

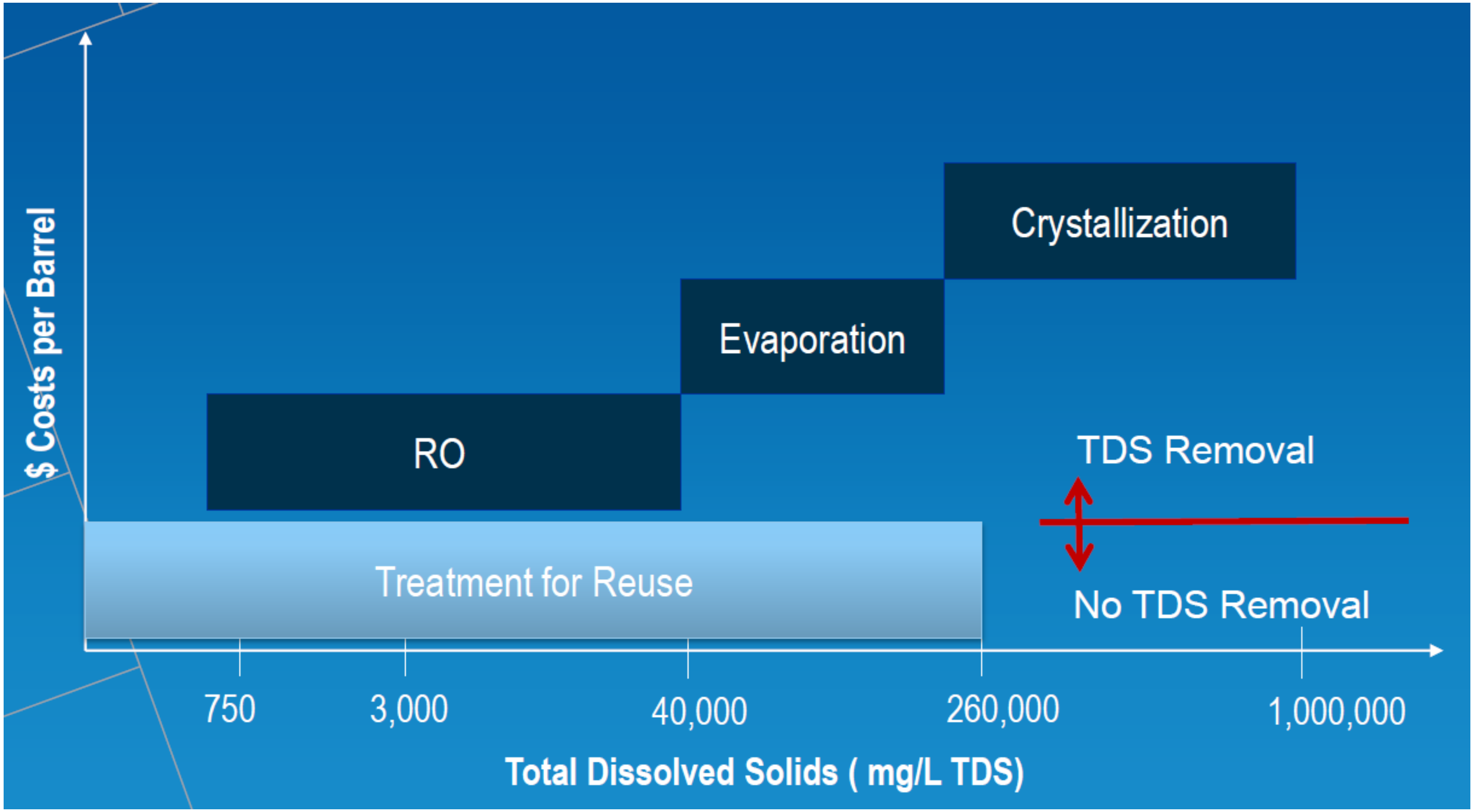
Presentation Prepared by:
Eric Dole, PE,
Sr. Water/Wastewater Energy Engineer
Tetra Tech, Inc.

US Patent No. 8,273,156

The Problem

- What to do with aggressive, high TDS wastewater/brine
  - Concentrate stream from Reverse Osmosis (RO)
  - Spent regenerate stream from IX resin
  - Flowback / produced water from frac operations (oil/gas industry)
  - Agricultural liquid waste stream
  - Cooling tower blow-down
- May be **> 10 x** the cost of bulk water treatment to treat brine
  - Brine is typically between 10-30% of bulk flow

The Problem



Courtesy of CDM Smith Presentation “Key Considerations for Frac Flowback / Produced Water Reuse and Treatment”

Brine Background

- Concentrate stream contains all of the constituents removed in the RO process:
  - High TDS concentration
    - 2,000 to > 40,000 mg/L for brackish applications
      - @ 75% recovery
    - 60,000 to >80,000 mg/L for seawater applications
      - @ 50% recovery
    - Depends on RO feed pressure, pre-treatment, membrane recovery and raw water quality
- Spent brine stream in IX resin regeneration process contains:
  - High TDS concentration
    - 100,000 to 200,000 mg/L depending on brine strength
  - Plus all cations and anions removed in IX process

Brine Background

- Typical Raw Flowback WQ

Contaminate	Min Value (mg/L)	Max Value (mg/L)
TDS	40,000	185,000
Sodium	10,000	55,000
Calcium	2,200	34,000
Magnesium	200	5,200
Iron	20	600
Chloride	20,000	110,000
Sulfate	10	80
Barium	30	6,000
Strontium	100	4,300

Brine Disposal Issues & Concerns

- **SEWER DISPOSAL** - Brine is not removed in conventional activated sludge WWTPs
  - High TDS water passes through to end user (golf courses, streams and rivers)
  - Causes osmotic stress on plants / grass.
- **DEEP WELL INJECTION** – Faces significant regulatory concerns…max allowable TDS of 8,000 mg/L
  - Well Classification Delay Until Hydrogeology and Water Chemistry are Characterized…must be in confined aquifer with no transmissivity to other aquifers
  - Permit (Extensive Public Participation)

Brine Disposal Issues & Concerns

- **EVAPORATION PONDS** – Land acquisition is costly and generally only used in arid regions.
  - Turbo Misters help removal but only 15-20% efficient and require excessive kWh/gal costs
  - Require HDPE liners, or impermeable clay, and leak detection
- **PRETREATMENT + RO + EVAP POND** – Lime softening and nanofiltration to increase RO recovery…further concentrate brine (10-15% of feed flow)
  - Lime Softening = costly settling basins, storage silos, chemical addition, pumps, filter press
  - NF membranes = feed pumps chemicals and additional controls are costly.

Brine Disposal Issues & Concerns

- **BRINE CONCENTRATOR/CRYSTALLIZERS** – Utilizes thermal vapor recompression and multiple effects to thermally evaporate brine
  - Relatively large footprint : flow ratio
  - Capital & operation cost intensive

Brine Disposal Issues & Concerns

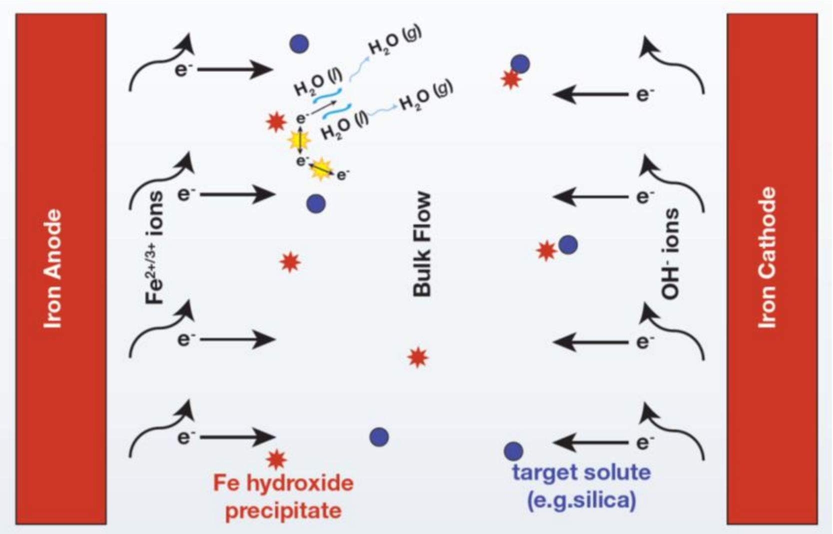
- **OCEAN OUTFALL** – Not practical for land-locked applications.
  - Falling out of favor due to environmental concerns.
  - Brine salt concentration = 20% denser than ambient seawater concentration which makes it sink to ocean floor… kills sea grass habitats
- **WETLAND TREATMENT** – Currently in development.
  - Utilizes salt tolerant wetland plants to remove challenging contaminates.

A Solution - BBT

- BBT utilizes:
  - Multiple Effect Vacuum Distillation + Electro-coagulation (EC)
    - Constant vacuum technology w/ no moving parts
      - Allows depressed boiling point = less thermal input
    - Up to 3 effects achieved
      - Promotes efficient use of heating / cooling process

Brine Bulb Technology Introduction

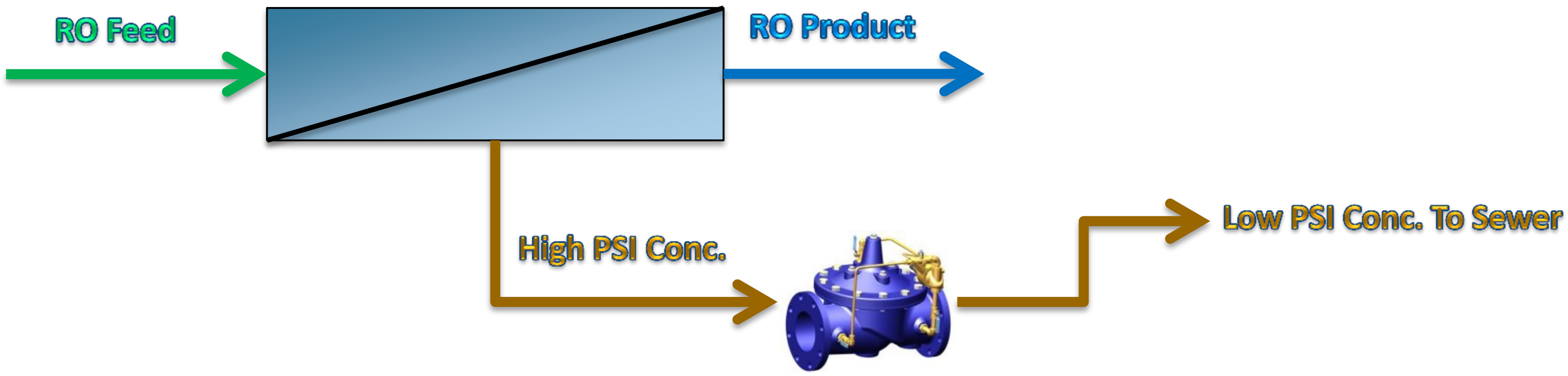
- BBT utilizes:
  - Multiple Effect Vacuum Distillation + Electro-coagulation (EC)
    - Alternating current EC
      - Floods water w/ electrons, Fe+ and OH-; neutralizes charged particles; drives precipitation of cations and anions w/out adding salts
      - Electrons excite water molecules and breaks surface tension bonds that result in 35% reduction in specific heat and 84% reduction in latent heat of vaporization
      - Provides 3-5 log virus removal in 76oF water
      - Creates hydrophobic sludge (see ALPHA Prototype Study)



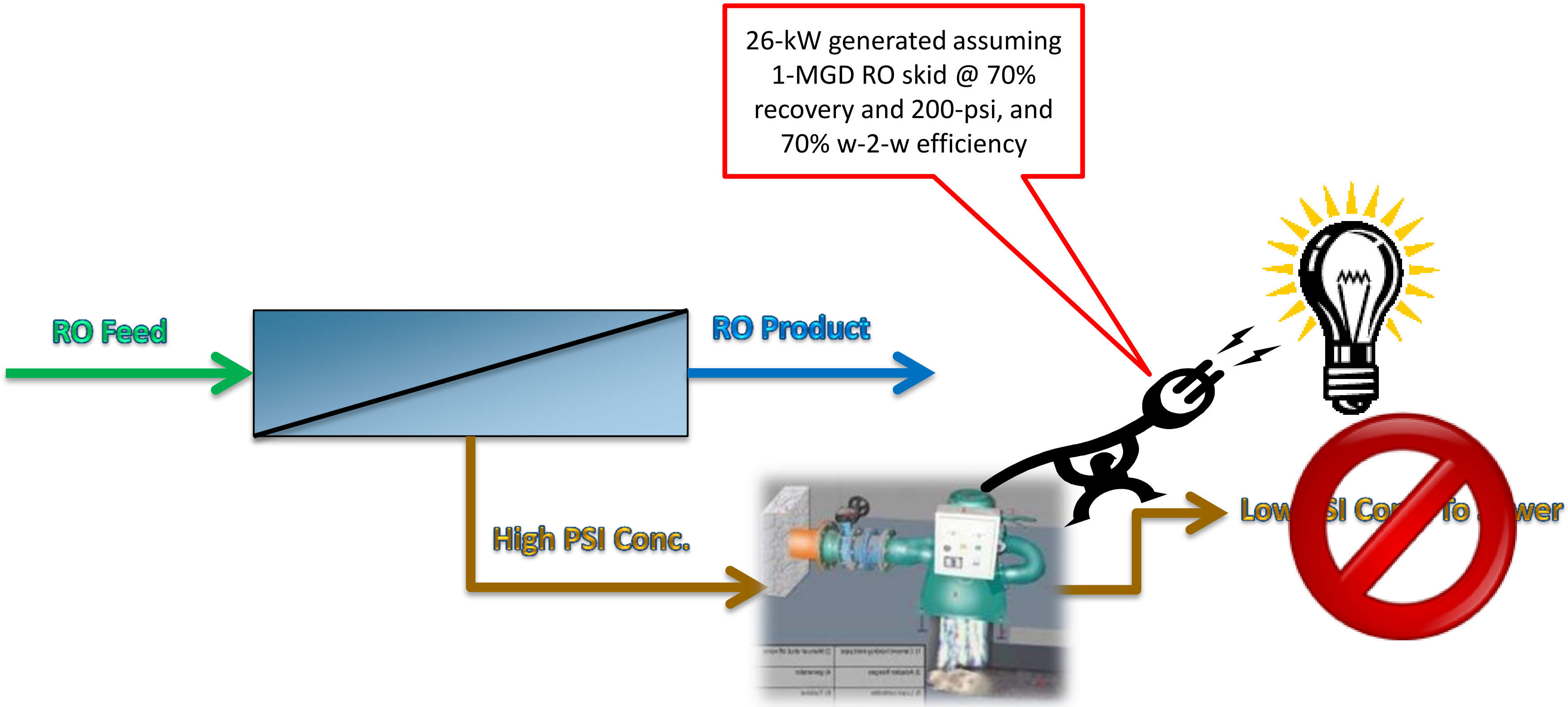
 Portion of slide courtesy of PW

Brine Bulb Technology Introduction

- BBT^{TM} utilizes:
  - Micro-turbine technology to replace RO concentrate valve
    - Produces significant "green energy" otherwise wasted through concentrate valve
    - Reduces electrical requirement of BBT
    - Accomplishes pressure sustaining feature of concentrate valve



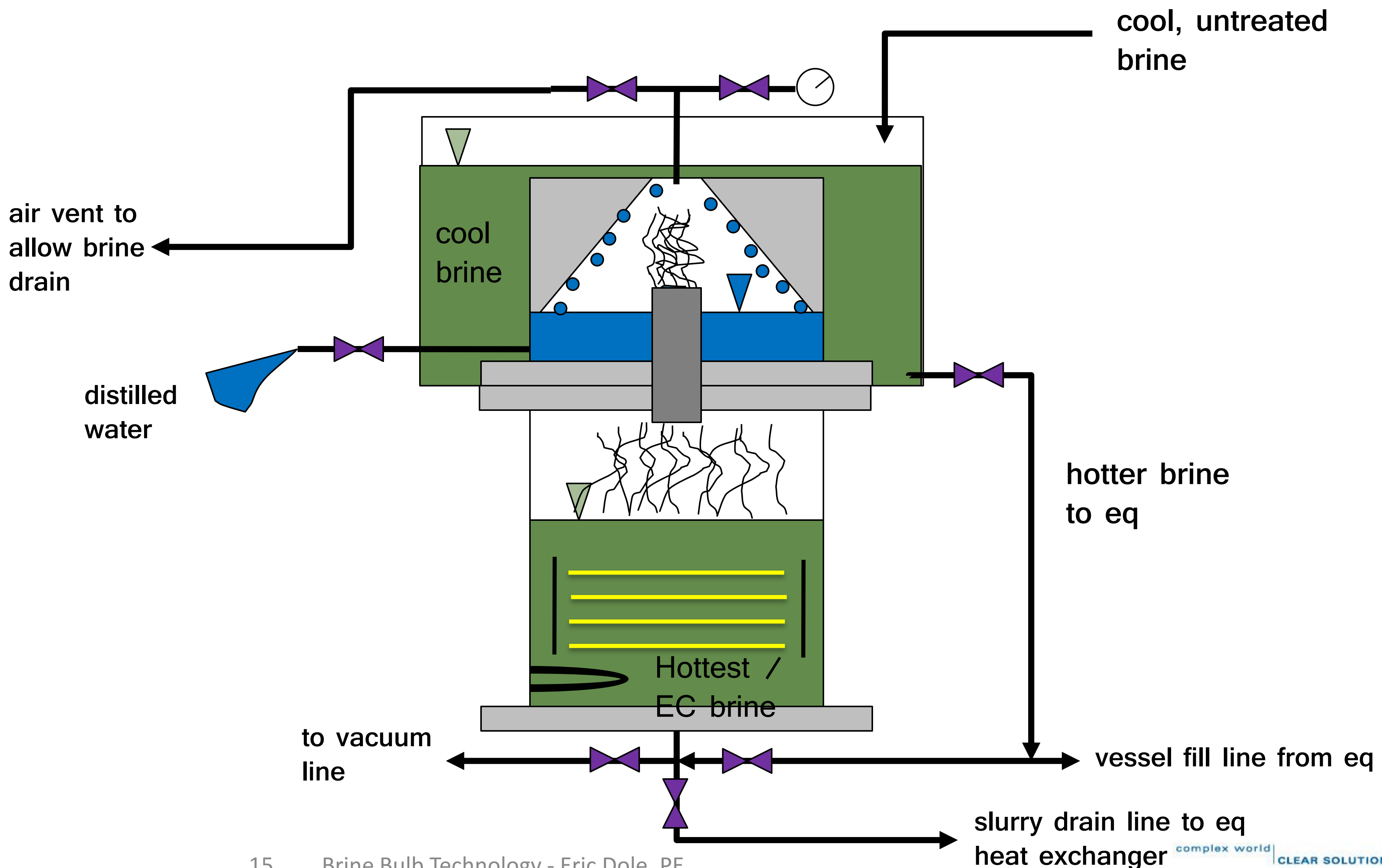
Brine Bulb Technology Introduction



Brine Bulb Technology Introduction

- BBT^{TM} can be used as a stand-alone unit or in parallel w/ RO
- BBT^{TM} achieves high removal efficiencies:
  - Suspended / dissolved solids
  - Colloidal solids
  - FOG
  - Bacteria / viruses
  - Heavy metals
  - Organics / inorganics

BBT Typical Schematic - Flashing Chamber



Water Boiling Points at Various Pressures

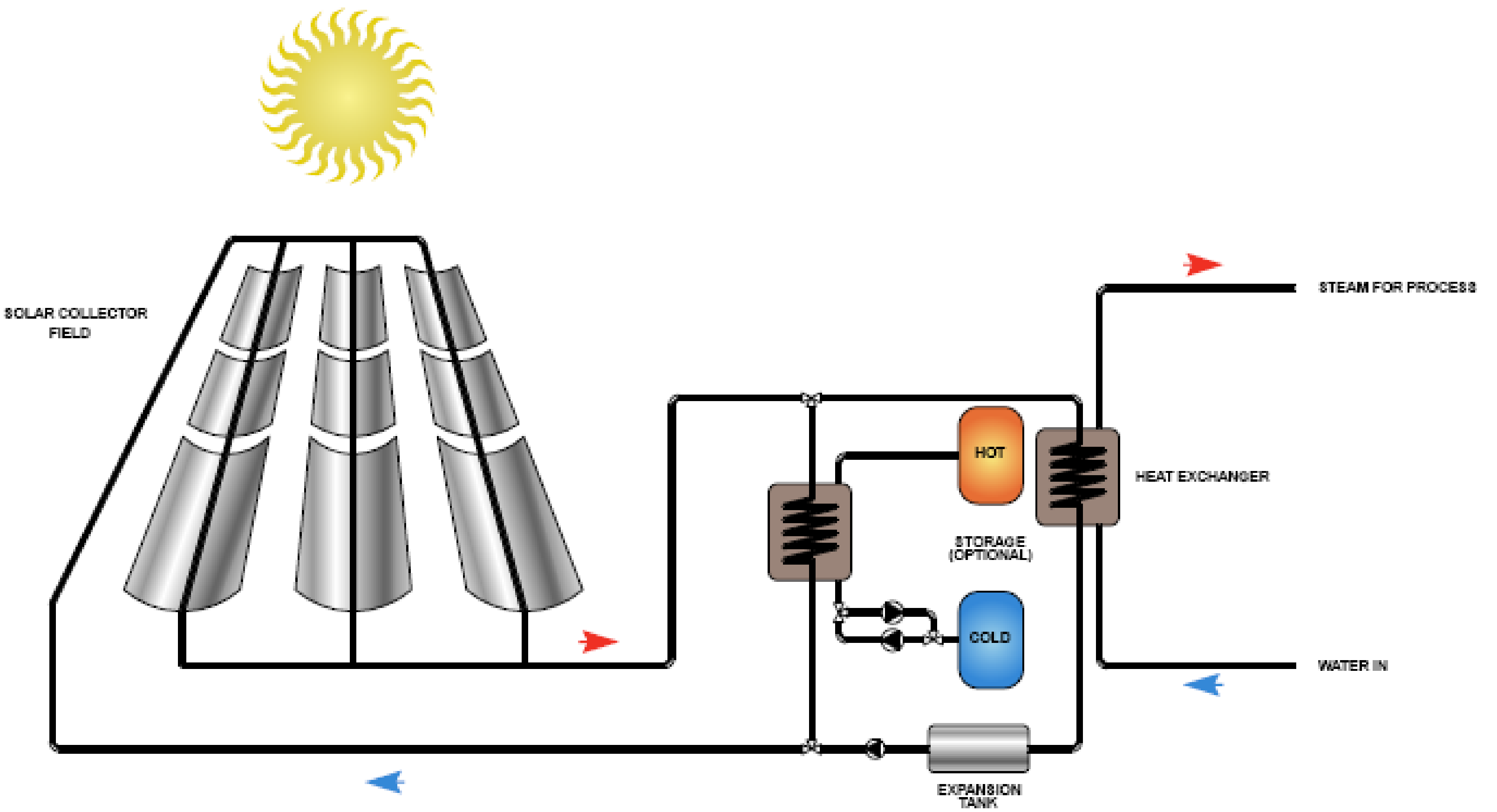
Video of BBT boiling RO concentrate (later in presentation) at 95 deg F at 23” Hg…35% lower than indicated in table due to patented heating system.

Water Boiling Points at Various Pressures

Vacuum (In/Hg	Boiling Point		Vacuum (In/Hg)	Boiling Point
29	76.62		7	198.87
28	99.93		6	200.96
27	114.22		5	202.25
26	124.77		4	204.85
25	133.22		3	206.70
24	140.31		2	208.50
23	146.45		1	210.25
22	151.87		Gauge Lbs.	
21	156.75		0	212.0
20	161.19		1	215.6
19	165.24		2	218.5
18	169.00		4	224.4
17	172.51		6	229.8
16	175.80		8	234.8
15	178.91		10	239.4
14	181.82		15	249.8
13	184.61		25	266.8
12	187.21		50	297.7
11	189.75		75	320.1
10	192.19		100	337.9
9	194.50		125	352.9
8	196.73		200	387.9

BBT ™ Concentrated Solar Heat Source Schematic

Figure 3: Process Heat (Steam) Flow Chart

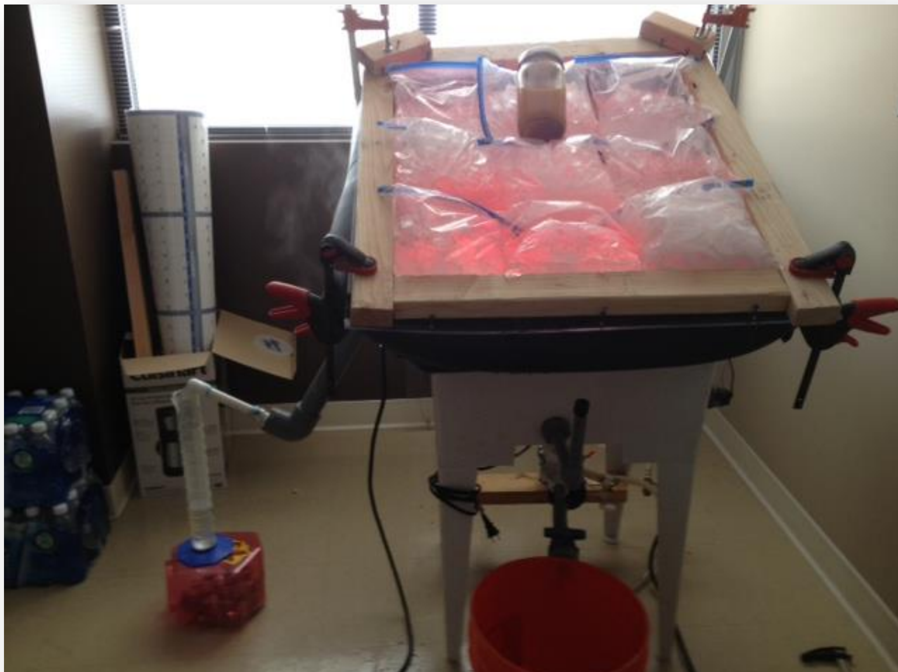


BBT™ ALPHA Prototype

- Raw water consisted of 10 gal mixture of saturated salt brine and RO concentrate from Scottsdale AZ WWTP + 1 cup of flowback (as seen in mason jar). Raw Water TDS > 300,000 mg/L

BBT™ ALPHA Prototype

- Distilled water in graduated cylinder to left at TDS = 550 mg/L



BBT™ ALPHA Prototype

- Electro-coagulated solids after 35 min of runtime at 120 V / 13 amps / 60Hz

BBT™ ALPHA Prototype

- Settled solids after 5 min

BBT ™ Removal Efficiencies (ALPHA Prototype)

- RO concentrate grab sample collected on 3/23/11 from AZ WRF tertiary treatment

RW = raw water; TW1 = unpurged treated water; TW2 = purged treated water

ANALYTE	RW	TW_1 % Rem	TW_1	TW_2 % Rem	TW_2	MDL	UNIT
Alkalinity, Bicarb	436	94.5%	24	95.4%	ND	20	mg/L
Alkalinity, Total	436	94.5%	24	95.4%	ND	20	mg/L
Arsenic, As	0.0086	-33.7%	0.0115	73.3%	0.0023	0.0050	mg/L
Barium, Ba	0.588	92.7%	0.0427	98.4%	0.0096	0.0050	mg/L
Boron, B	1.24	29.7%	0.872	73.7%	0.326	0.050	mg/L
Calcium, Ca	550	99.5%	2.57	99.8%	0.92	0.50	mg/L
DOC	39.8	57.8%	16.8	89.6%	4.15	5.0	mg/L
Chloride, Cl	2350	98.0%	47.4	99.6%	ND	10	mg/L
Conductivity, Lab	20900	98.8%	260	99.6%	83.2	2	µmho
Copper, Cu	0.0180	46.7%	0.0096	86.1%	0.0025	0.0050	mg/L
Fluoride, F	2.2	90.9%	ND	90.9%	ND	0.2	mg/L
Iron, Fe	0.288	92.4%	0.022	82.6%	ND	0.050	mg/L
Magnesium, Mg	186	99.5%	0.93	99.8%	0.44	0.500	mg/L
Manganese, Mn	0.126	76.9%	0.0291	95.9%	0.0052	0.0050	mg/L
Molybdenum, Mo	0.0315	84.1%	ND	84.1%	ND	0.0050	mg/L
Nickel, Ni	0.0120	75.0%	0.0030	58.3%	ND	0.0050	mg/L
Nitrate, NO3	45.7	99.1%	0.4	99.6%	ND	0.2	mg/L
Nitrite, NO2	0.2	0.0%	ND	0.0%	ND	0.2	mg/L
Phosphorus, Ortho, P	19.6	97.4%	ND	96.8%	0.627	0.5	mg/L
Potassium, K	216	99.4%	1.40	99.8%	0.36	0.50	mg/L
TDS	7730	98.4%	120	99.6%	32	20	mg/L
Selenium, Se	0.0076	34.2%	ND	34.2%	ND	0.0050	mg/L
Silica, SiO2	75.8	92.1%	6.00	97.7%	1.77	1.05	mg/L
Sodium, Na	1650	99.2%	13.2	99.8%	3.36	0.50	mg/L
Strontium, Sr	7.25	99.6%	0.0326	99.9%	0.0101	0.0050	mg/L
Sulfate, SO4	1930	99.5%	ND	99.5%	ND	10	mg/L
Uranium, U	0.0084	40.5%	ND	40.5%	ND	0.0050	mg/L
Vanadium, V	0.0070	28.6%	ND	28.6%	ND	0.0050	mg/L

TETRA TECH

BBT TM Removal Efficiencies (ALPHA Prototype)

- Demo conducted on 12/27/12 - Raw water consisted of 10 gal mixture of saturated salt brine + RO concentrate seed from AZ WRF + 1 cup of flowback

ANALYTE	RW	TW	TW % Removal	MDL	UNIT
Ag	0.00022	0.00022	0%	0.0002	mg/L
Al	40.8	0.116	100%	0.0138	mg/L
As	0.0041	0.0131	-222%	0.0041	mg/L
B	**0.136**	**1.91**	-1300%	**0.1362**	**mg/L**
Ba	0.391	0.110	72%	8E-05	mg/L
Be	**0.00015**	**0.00015**	0%	**0.0001**	**mg/L**
Ca	181.4	19.46	89%	0.0041	mg/L
Cd	**0.00010**	**0.00010**	0%	**0.0001**	**mg/L**
Co	0.000134	0.000138	-3%	0.0001	µmho
Cr	0.00027	0.00027	0%	0.0003	mg/L
Cu	0.280	0.0231	92%	0.0009	mg/L
Fe	**0.0004**	**0.011**	-2788%	**0.0004**	**mg/L**
K	**230.6**	**2.935**	99%	**0.0315**	**mg/L**
Li	0.005	0.05208	-865%	0.0054	mg/L
Mg	50.92	6.64	87%	0.0003	mg/L
Mg	52.176	6.57814	87%	0.0004	mg/L
Mn	0.371	0.16325	56%	9E-05	mg/L
Na	94243.5	198.1	100%	0.0211	mg/L
Ni	0.0008	0.00474	-459%	0.0008	mg/L

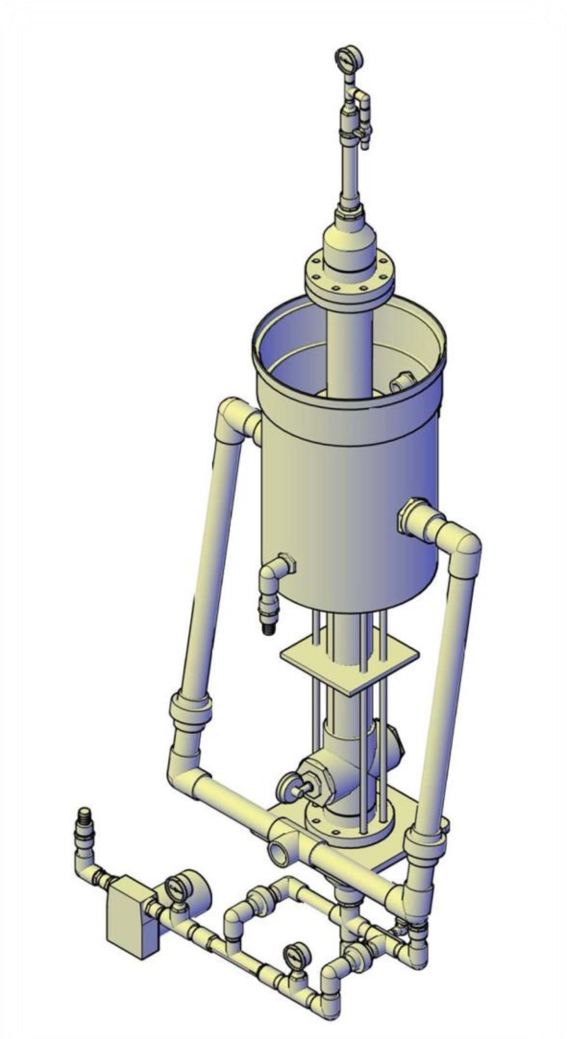
RW = MDL = instrument noise

Approx. [TDS RW] = [Na] + [Cl] + [Mg] + [Ca] + [HCO3] + [SO4] = 247,000 mg/L
Approx. [TDS TW] = [Na] + [Cl] + [Mg] + [Ca] + [HCO3] + [SO4] = 570 mg/L
% [TDS] Removal = 99.8%

P	144.233	2.48944	98%	0.0197	mg/L
Pb	**2.037**	**0.00156**	100%	**0.0015**	**mg/L**
S	250.741	8.88491	96%	0.0061	mg/L
Se	4.476	0.00429	100%	0.0043	mg/L
Si	**0.219**	**7.25370**	-3205%	**0.2195**	**mg/L**
Sr	**1.471**	**0.13534**	91%	**8E-05**	**mg/L**
Tl	**0.00145**	**0.00145**	0%	**0.0015**	**mg/L**
U	1.676	1.676	0%	1.6762	mg/L
V	0.000	0.00093	-212%	0.0003	mg/L
Zn	129.137	7.25370	94%	0.0003	mg/L
Sn	0.003	0.13534	-4295%	0.0031	mg/L
Mo	0.0020	0.0020	0%	0.002	mg/L
Sb	0.00331	0.00331	0%	0.0033	mg/L
Ti	0.001	0.00093	-56%	0.0006	mg/L
F	0.050	0.050	0%	0.0500	mg/L
Cl	152508.5	345.2	100%	0.1000	mg/L
Br	0.100	0.10703	-7%	0.1000	mg/L
NO3	26.814	2.57500	90%	0.1000	mg/L
PO4	0.5	0.5	0%	0.5000	mg/L
SO4	1.00	20.16	-1916%	1.0000	mg/L

BBT™ BETA Prototype

- 1 gpm unit completed in April 2013
- Processed
  - RO concentrate from TX nitrate removal facility
  - Flowback / produced water
- Produce distilled water quality
- Purpose: Validate kWh/1,000 gal and removal efficiencies



BBT^{TM} BETA Prototype - Processing RO Concentrate

Video

BBT^{TM} BETA Prototype - Lab Analysis Results

RW Results of TX RO concentrate sampled 5/30/13

Customer Sample ID TXRO-CONC-RW-53013
Sample Date/Time: 5/30/13 10:50 AM
Lab Number: 130530056-05

Test	Result	Method	LQL	Date Analyzed	Analyzed By
Total Dissolved Solids	**4381 mg/L**	SM 2540-C	5	6/3/13	ISG
Total Selenium	**0.0532 mg/L**	EPA 200.8	0.0008	6/4/13	VDB

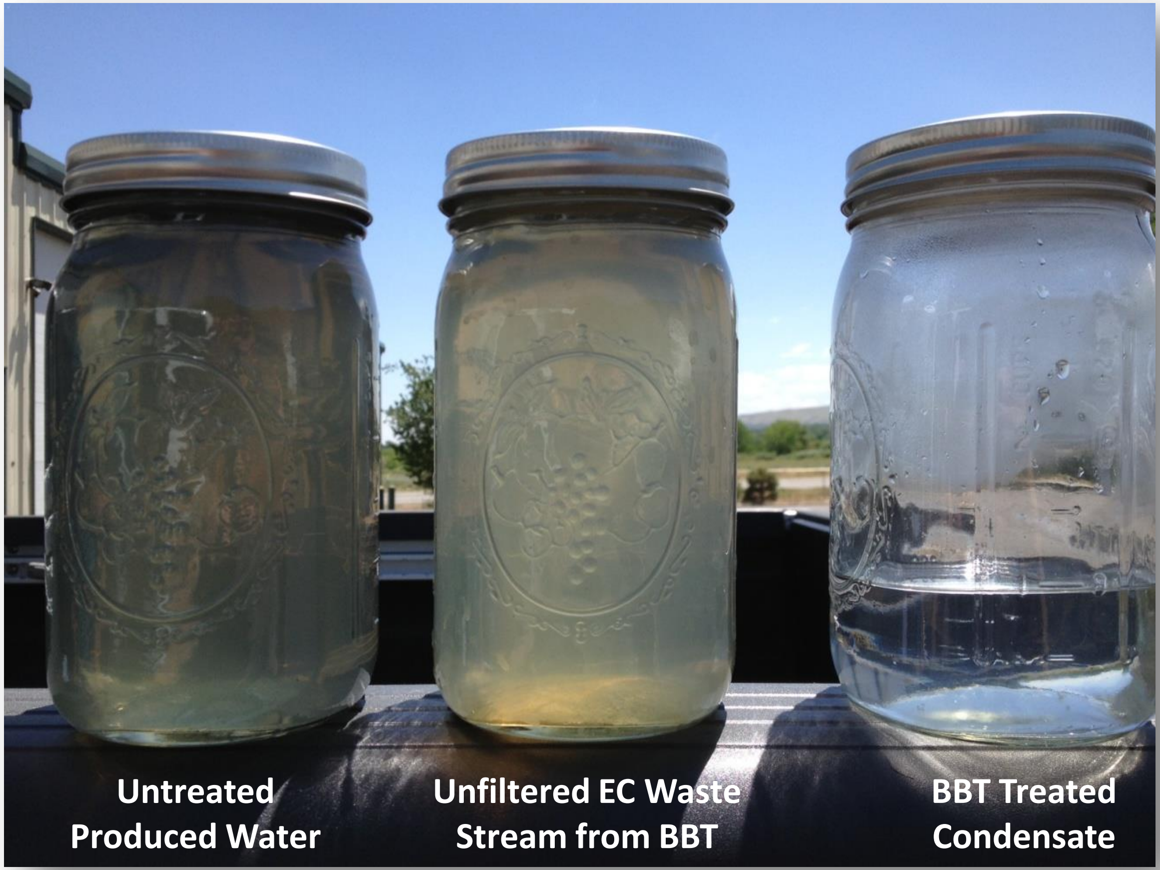
TW Results of BBT on TX RO concentrate sampled 5/30/13

- Accidentally allowed RW to enter distilled water collection trough. Did not purge full volume of RW prior to grab sample. This led to lower than normal removal efficiency.

Customer Sample ID TXRO-CONC-TWBBT-53013
Sample Date/Time: 5/30/13 11:20 AM
Lab Number: 130530056-07

Test	Result	Method	LQL	Date Analyzed	Analyzed By
Total Dissolved Solids	**1058 mg/L**	SM 2540-C	5	6/3/13	ISG
Total Selenium	**0.0098 mg/L**	EPA 200.8	0.0008	6/4/13	VDB

BBT BETA Prototype - Processing Produced H2O from Colorado O&G Well



BBT BETA Prototype
- Processing Produced H2O from Colorado O&G Well

BBT BETA Prototype
- Processing Produced H2O from Colorado O&G Well

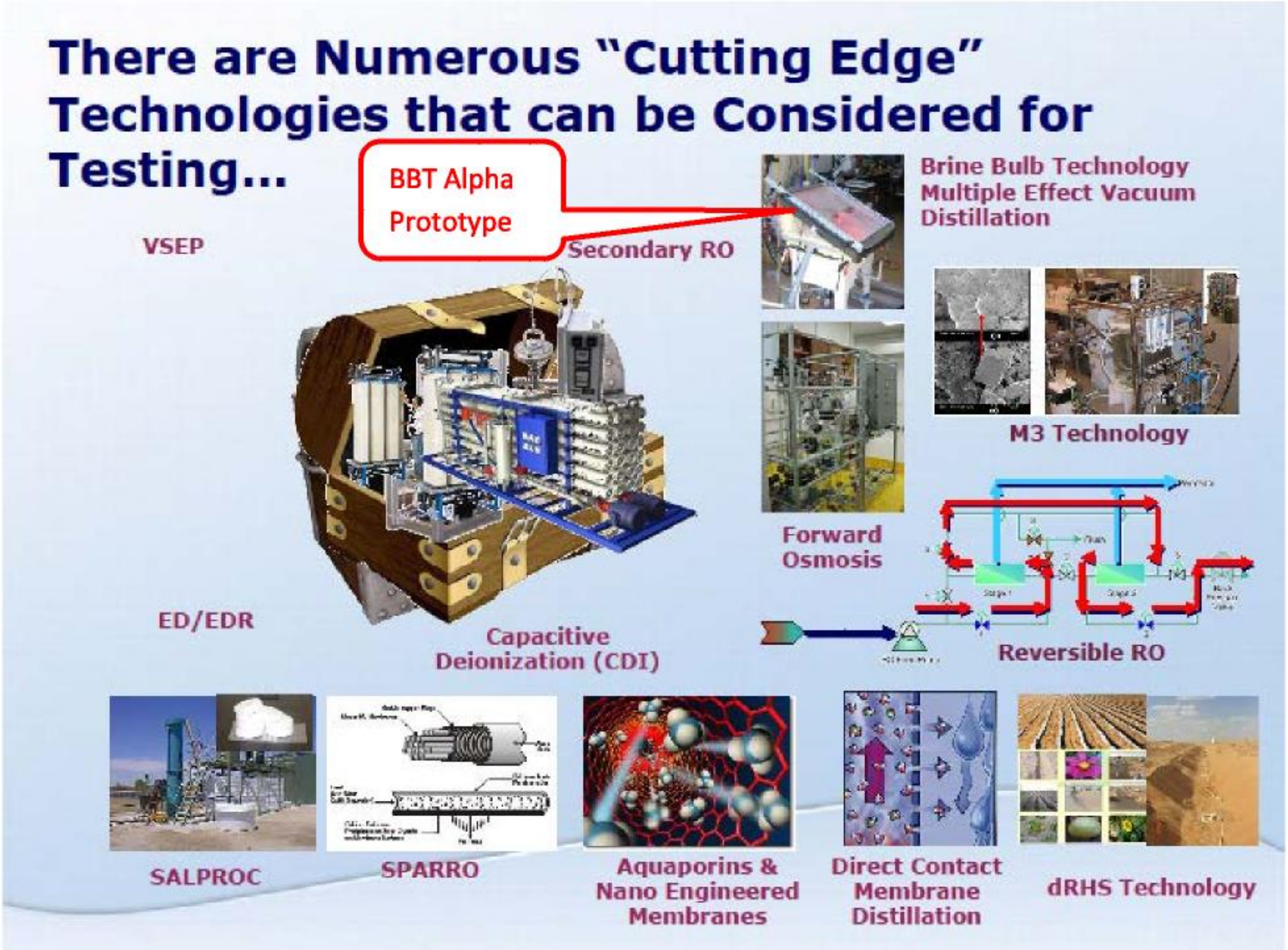
BBT BETA Prototype - Produced Water Test Run ICP Results from CSM

DATE: 6/27/13	Sample Location: Produced Water from CO O&G Well				Removal Efficiency	
Analyte	Detection Limit (mg/L)	Raw Water (mg/L)	EC Blowdown filtered (mg/L)	Condensate unfiltered (mg/L)	RW to EC Blowdown	RW to Condensate
As	0.00200	0.3531		0.0061		98%
B	0.03994	3.2097	2.6393	0.1443	18%	96%
Ba	0.00011	12.7207	8.3054	0.1292	35%	99%
Ca	0.00299	81.091	31.6769	33.4257	61%	59%
Cu	0.00034	0.3222	0.1764	0.0064	45%	98%
Fe	0.00254	0.5257		0.0454		91%
K	0.01531	19.4505	14.0707	2.3062	28%	88%
Li	0.00042	1.1100	0.8009	0.0275	28%	98%
Mg	0.00029	5.0190	5.0960	19.5400	-2%	-289%
Mn	0.00005	0.0633		0.0041		93%
Na	0.00655	1233.119	1139.6283	106.2194	8%	91%
Ni	0.00022	0.1469		0.0041		97%
P	0.00165	30.7996	1.0538	0.1747	97%	99%
Pb	0.00045	0.1672	0.0808	0.0011	52%	99%
S	0.01211	5.3540	4.5102	50.1457	16%	-837%
Se	0.00118	0.3126		0.0100		97%
Si	0.03926	18.1066	18.3608	6.9044	-1%	62%
Sr	0.00003	8.6041	6.1086	0.5315	29%	94%
Zn	0.00016	1.1795	1.2457	0.3041	-6%	

BBT^{TM} BETA Prototype Conclusions

- Incorporates MEVD, EC and MT into one unit process to achieve high quality water at low kWh/1,000 gal
- Patented heating element results in
  - 35% reduction in specific heat capacity
  - 84% reduction in latent heat of vaporization
- Approximately 0.2 lb/1,000 gal of iron blade consumption
- Removal efficiency is a function of amp density, time, blade material, pH and solids separation technique.
- Operates better at higher TDS
- Condensation continues with unit off until system reaches equillibrium

BBT "Emerging Technology"



"Recovery & Concentrate Management – A Look at 3 Local Projects"; Author: Guy Carpenter, PE, Carollo Engineering that was presented at the WRRC 2011 Annual Conference.
AND
"Demonstrating Innovative Inland Concentrate Management Solutions"; Author: Guy Carpenter, PE Carollo Engineers and Brandy Kelso PE, City of Phoenix Water Dept. that was presented at the 2011 26th Annual Water Reuse Symposium Presentation.

BBT "Emerging Technology"

Recent Proven Technologies

- Capacitive Dionization, (Carbon Aerogel Anode and Cathodes, LLNL Technology)
- Brine Bulb Technology, energy recovery from RO system for heating and further concentrating RO Brine (Hydrosystems Engineering)
- DewVaporation – (Alta)

BBT citation

"Advances in Concentrate Minimization and Disposal"; Author: Kevin Alexander, P.E. Separation Process Inc. and presented at the International Water Association Annual Conference 2008.

BBT Next Steps

- Currently in negotiations with investors for future prototypes
  - Tetra Tech to assist with design
- Need further R&D to substantiate prelim findings
- Liquid waste streams like
  - RO concentrate
  - Flowback or produced water
  - Mine waste
  - Cooling tower blowdown
  - Desalination
  - Municipal / industrial waste
  - High TDS waters

Acknowledgments

- Dr. Tzahi Cath, Colorado School of Mines
- Central AZ Salinity Study
- Wife

QUESTIONS

<u>Contact:</u>
Eric Dole, PE
email: eric.dole@tetratech.com
Phone: 720-409-2432