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Disposal of Concentrate from Treatment of Water for Beneficial Reuse

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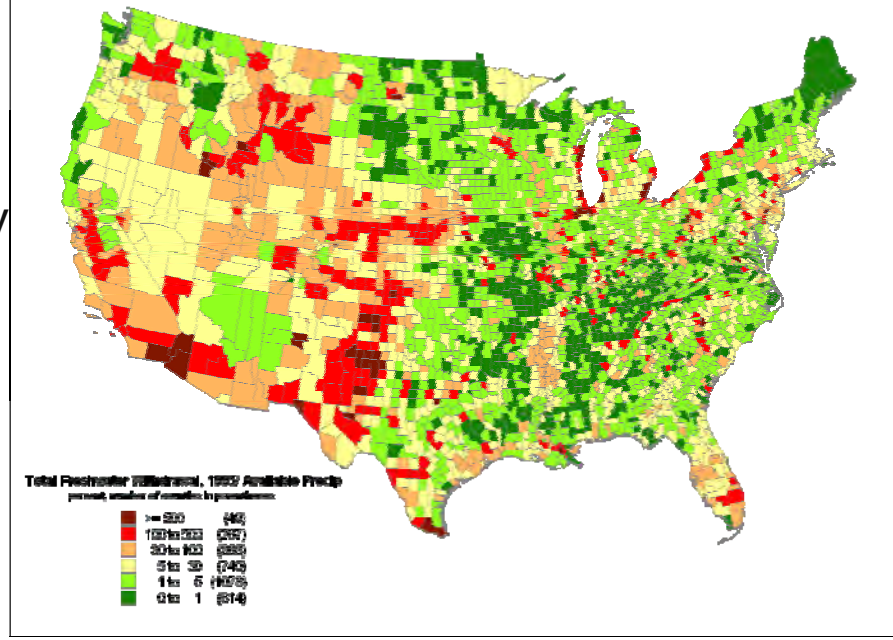
Contents of Presentation

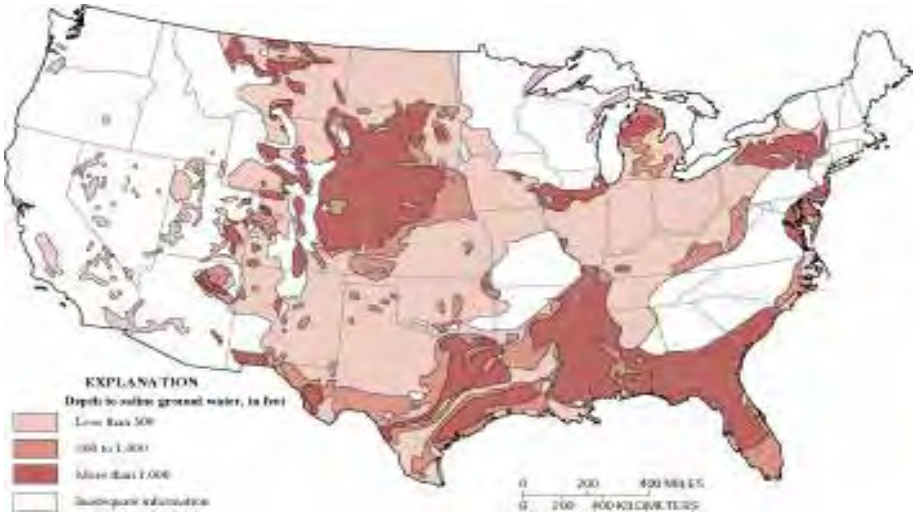
- Overview of water treatment processes
- SDWA drinking water standards
- CWA water quality criteria
- RCRA toxicity characteristic criteria
- Comparison
- What do the different regulatory programs and approaches mean?
- Some actual data

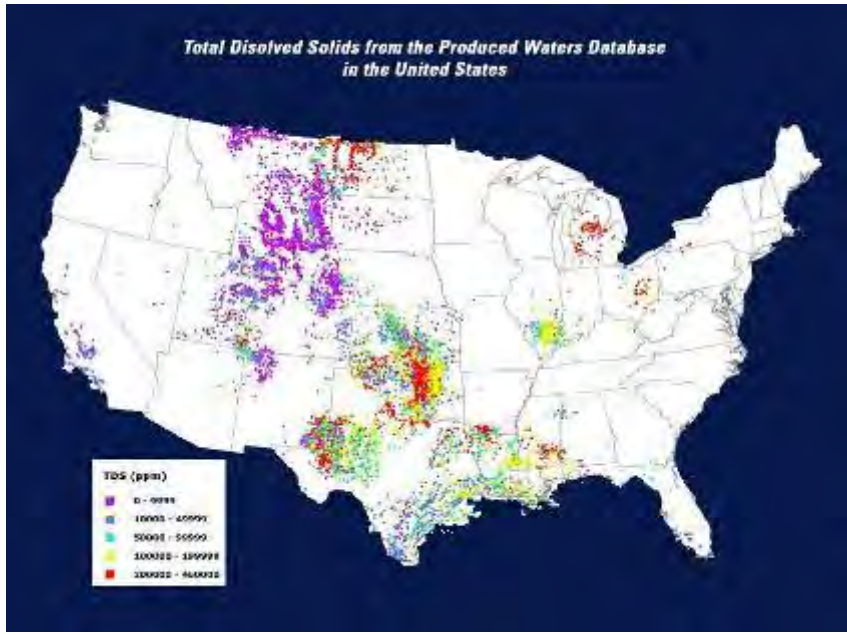
Fresh Water Availability

- Insufficient fresh water resources in many parts of U.S. (and world)

- Many of these areas have access to sources of saline water
  - Saline ground water
  - Produced water

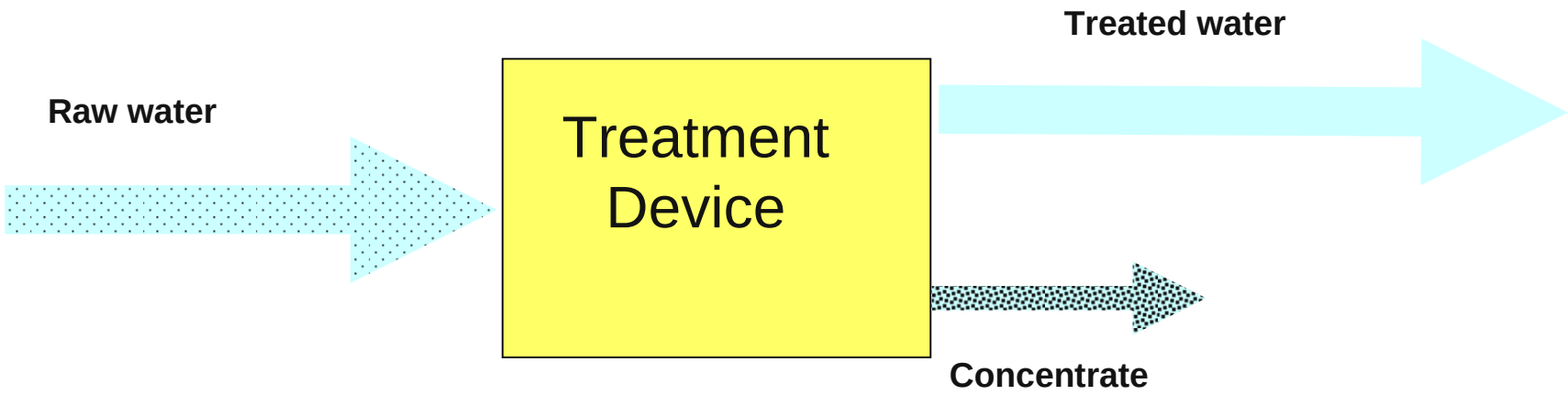






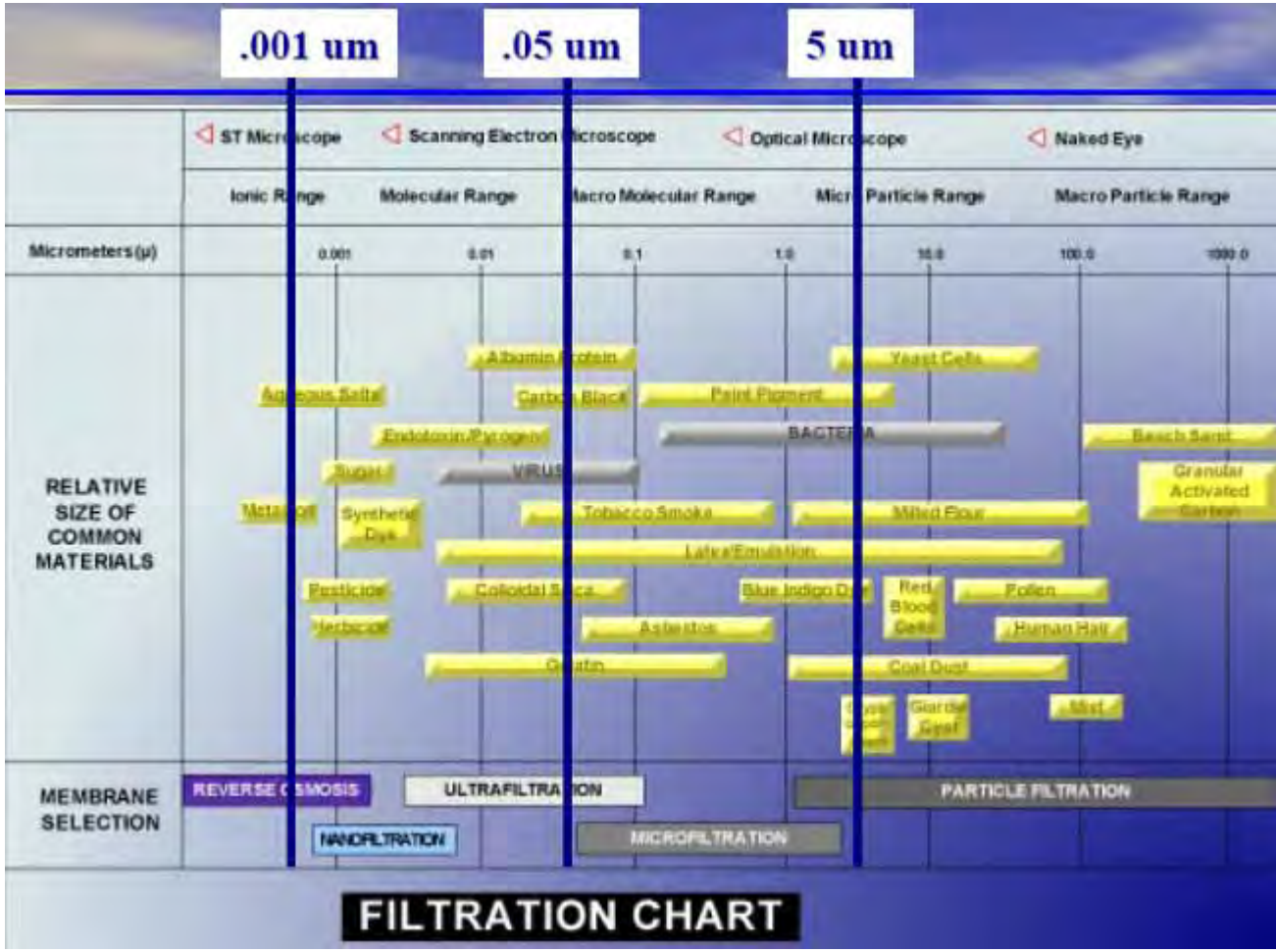
Several Technologies Exist to Remove Salinity

- Treatment results in two byproduct streams
  - Treated water
    - *In filtration systems this may be called permeate*
  - Concentrated solution containing removed constituents
    - *Called concentrate*



Processes Used to Treat Saline Water

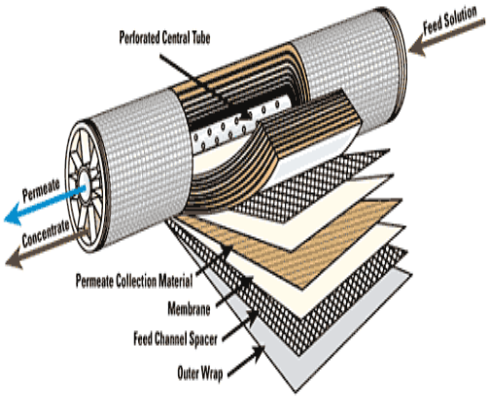
- Membrane processes
  - Microfiltration
  - Ultrafiltration
  - Nanofiltration
  - Reverse osmosis
- Electrodialysis
- Ion exchange
- Thermal distallation



Source: Ben Gould, Ashbrook Simon-Hartley

What membrane systems look like

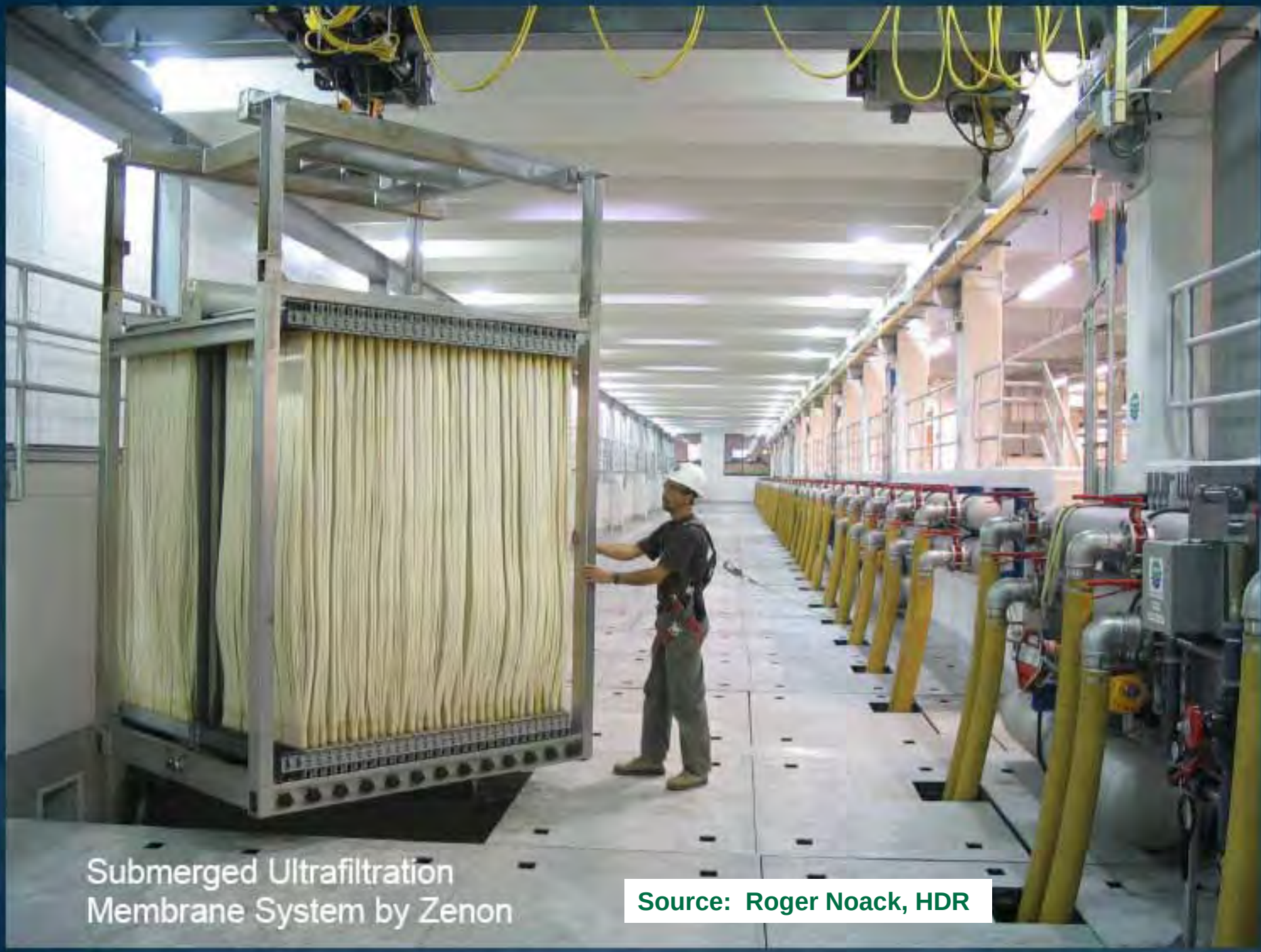
- Cross flow
  - Flat sheet membrane
    - Spiral wound
    - Plate and frame
  - Tubular membrane
    - Fine fiber
    - Capillary fiber
    - Hollow tube
- Dead end
  - Cartridges
    - Pleated
  - Tubular membrane
    - Fine fiber
    - Capillary fiber



Source: Anders Hallsby, Nalco

Source: Roger Noack, HDR

Microfiltration System by US Filter


Submerged Ultrafiltration
Membrane System by Zenon
Source: Roger Noack, HDR

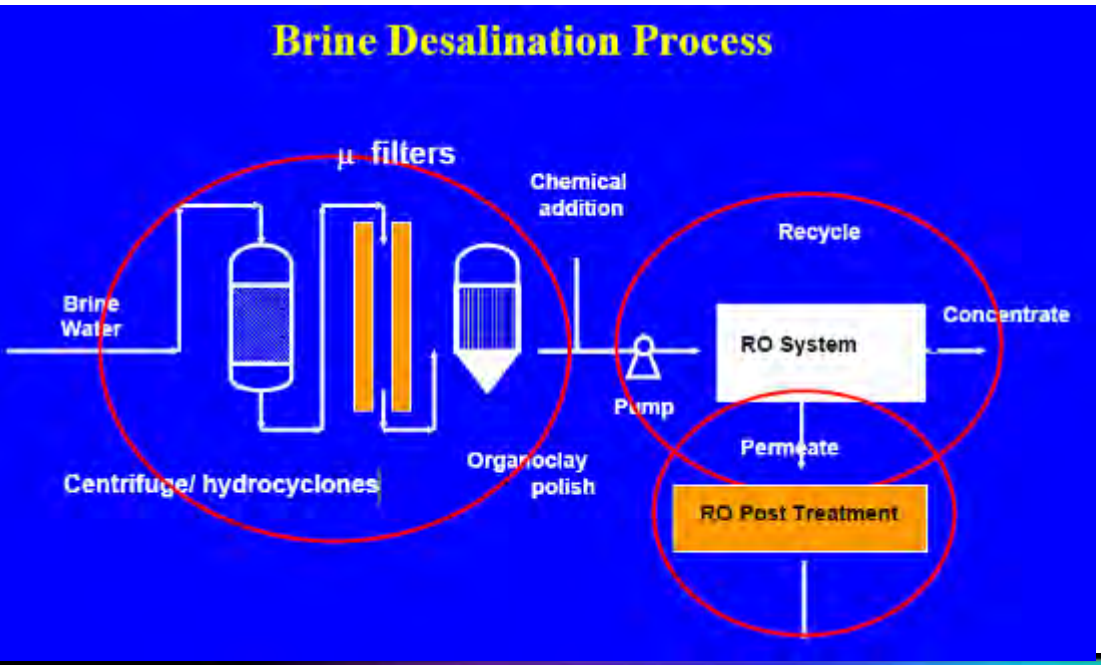
Reverse Osmosis

EDR System by GE/Ionics

Source: Roger Noack, HDR

Water Treatment System Must Remove a Variety of Constituents

- Different pretreatment steps are used to first remove:
  - Larger-sized materials (e.g., sand, microbes)
  - Constituents that would impair additional treatment (e.g., oil and grease)



Texas A&M Treatment Trailer

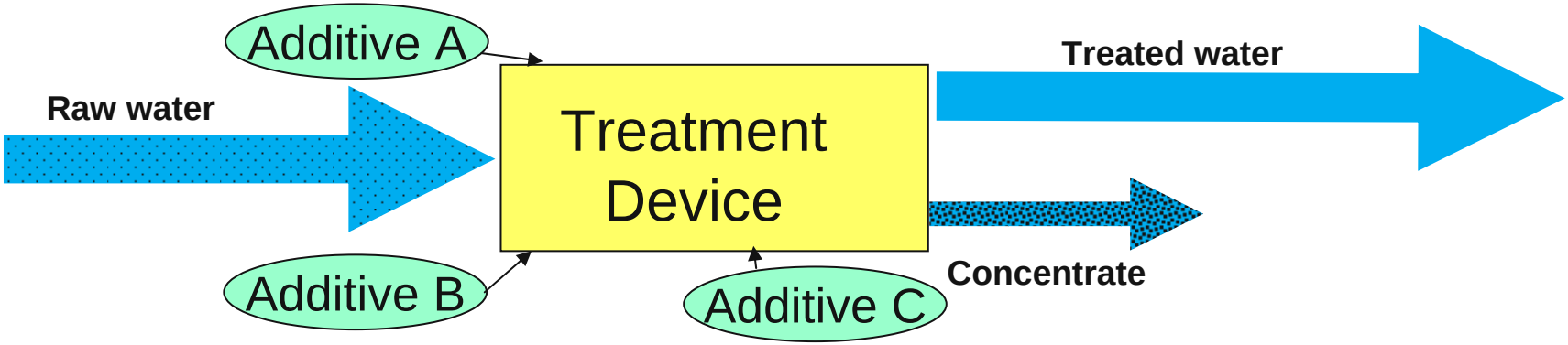
Four pillars of successful RO membrane operation …

Source: Anders Hallsby, Nalco

- Prevent Mineral scaling
  - Antiscalants
- Prevent Colloidal fouling
  - Particulate filtration
    - Improve efficacy with filter aid
- Prevent Microbial fouling
  - Control microbial activity in the feed
  - Minimize AOC (TOC)
  - Equipment design
    - Nowhere for bugs to hide
  - Equipment operation
    - Remove biofilm before it is "too late"
    - No inadvertent re-inoculation

- All of these steps add constituents to the water that may end up in the concentrate

How Is the Concentrate Disposed of/Managed?



- Volume and parameter concentration of concentrate stream are determined by operating parameters
  - Low volume means high energy input and high parameter concentrations
- Options:
  - Inject concentrate underground
    - *Disposal*
    - *Use for enhanced oil recovery*
  - Discharge to surface water body
  - Dispose of by land application
- Each of these practices is governed by different set of rules

Inject Concentrate Underground

- Safe Drinking Water Act (SDWA) establishes the Underground Injection Control (UIC) program
- Concentrate is injected for promoting additional oil and gas production (enhanced recovery):
  - Most states and EPA consider the injection well to be a Class II well
- Concentrate is injected solely for disposal:
  - States and EPA are not consistent of type of injection well
  - Raw water is produced water
    - *The resulting injection well is usually a Class II well*
  - Raw water is other than produced water (e.g., saline ground water)
    - *The resulting injection well could be Class I, II, or V*
    - *Depends on the situation and philosophy of agency*

Standards often Used for Injection

- SDWA directs EPA to develop two types of standards for drinking water quality:
  - Maximum Contaminant Levels (MCLs)
    - *Enforceable*
    - *Based on affordable treatment methods*
  - Maximum Contaminant Level Goals (MCLGs)
    - *Non-enforceable*
    - *Represents the public health goal*
- These are available for more than 75 contaminants
- http://www.epa.gov/safewater/consumer/pdf/mcl.pdf
- UIC permits other than Class II may require injectate to meet MCLs

Excerpt from EPA Drinking Water Standard Table

Contaminant	MCL or TT[1] (mg/L)[2]	Potential health effects from exposure above the MCL	Common sources of contaminant in drinking water	Public Health Goal
Chlordane	0.002	Liver or nervous system problems; increased risk of cancer	Residue of banned termiticide	zero
Chlorine (as Cl_2)	MRDL=4.0[1]	Eye/nose irritation; stomach discomfort	Water additive used to control microbes	MRDLG=4[1]
Chlorine dioxide (as ClO_2)	MRDL=0.8[1]	Anemia; infants & young children: nervous system effects	Water additive used to control microbes	MRDLG=0.8[1]
Chlorite	1.0	Anemia; infants & young children: nervous system effects	Byproduct of drinking water disinfection	0.8
Chlorobenzene	0.1	Liver or kidney problems	Discharge from chemical and agricultural chemical factories	0.1
Chromium (total)	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits	0.1
Copper	TT[7]; Action Level = 1.3	Short term exposure: Gastrointestinal distress. Long term exposure: Liver or kidney damage. People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level	Corrosion of household plumbing systems; erosion of natural deposits	1.3
Cryptosporidium	TT[3]	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and fecal animal waste	zero
Cyanide (as free cyanide)	0.2	Nerve damage or thyroid problems	Discharge from steel/metal factories; discharge from plastic and fertilizer factories	0.2

Discharge of Concentrate and Relevant Standards

- Discharge of concentrate would require an NPDES permit
  - Permit includes limits that would ensure compliance with state water quality standards (WQS)
- Clean Water Act (CWA) directs each state to adopt enforceable WQS
- To help the states, EPA develops non-enforceable, technical recommendations called water quality criteria (WQC)
  - Aquatic life protection
    - *Fresh and salt water*
    - *Acute and chronic exposure*
  - Human health protection
    - *Eating fish/seafood from water*
    - *Drinking water and eating fish/seafood from water*
- These are available for about 150 substances

http://www.epa.gov/waterscience/criteria/nrwqc-2006.pdf

Excerpt from EPA WQ Criteria Table

NATIONAL RECOMMENDED WATER QUALITY CRITERIA FOR PRIORITY TOXIC POLLUTANTS

	Priority Pollutant	CAS Number	Freshwater CMC (µg/L)	Freshwater CCC (µg/L)	Saltwater CMC (µg/L)	Saltwater CCC (µg/L)	Human Health For Consumption of: Water + Organism (µg/L)	Human Health For Consumption of: Organism Only (µg/L)	FR Cite/ Source
1	Antimony	7440360					5.6 B	640 B	65FR66443
2	Arsenic	7440382	340 A,D,E	150 A,D,K	69 A,D,bb	36 A,D,bb	0.018 C,M,S	0.14 C,M,S	65FR31682 57FR60848
3	Beryllium	7440417					Z		65FR31682
4	Cadmium	7440439	2.0 D,E,K,bb	0.25 D,E,K,bb	40 D,bb	8.8 D,bb	Z		EPA-822-R-01-001 65FR31682
5a	Chromium (III)	16065831	570 D,E,K	74 D,E,K			Z Total		EPA820/B-96-001 65FR31682
5b	Chromium (VI)	18540299	16 D,K	11 D,K	1,100 D,bb	50 D,bb	Z Total		65FR31682
6	Copper	7440508	13 D,E,K,cc	9.0 D,E,K,cc	4.8 D,cc,ff	3.1 D,cc,ff	1,300 U		65FR31682
7	Lead	7439921	65 D,E,bb,gg	2.5 D,E,bb,gg	210 D,bb	8.1 D,bb			65FR31682
8a 8b	Mercury Methylmercury	7439976 22967926	1.4 D,E,hh	0.77 D,E,hh	1.8 D,ee,hh	0.94 D,ee,hh		0.3 mg/kg J	62FR42160 EPA823-R-01-001
9	Nickel	7440020	470 D,E,K	52 D,E,K	74 D,bb	8.2 D,bb	610 B	4,600 B	65FR31682
10	Selenium	7782492	L,R,T	5.0 T	290 D,bb,dd	71 D,bb,dd	170 Z	4200	62FR42160 65FR31682 65FR66443

Other Standards for Management of Concentrate

- Resource Conservation and Recovery Act (RCRA) includes various criteria for determining if a substance is subject to the hazardous waste program
- The toxicity characteristic is based on a leaching procedure
- Waste samples exceeding the regulatory limit meet EPA's definition of characteristic hazardous wastes
- Toxicity thresholds are often set at 100 times the MCL
- If concentrate constituents exceed hazardous waste thresholds
  - This could affect the class of UIC injection well used and could restrict other methods of managing the concentrate

Toxicity Characteristic Regulatory Thresholds (mg/L)

Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresol	200.0
m-Cresol	200.0
p-Cresol	200.0
Cresol	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13
Endrin	0.02
Heptachlor and its epoxide	0.008

Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane.	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentrachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

Comparison of Different Threshold Values (mg/L)

Type of Criterion	Benzene	Mercury
SDWA – MCL	0.005	0.002
SDWA - MCLG	0	0.002
CWA - Acute WQC – freshwater	No criterion	0.0014
CWA - Chronic WQC – fresh	No criterion	0.00077
CWA - Human Health WQC – fish	0.0022	0.3 mg/kg
CWA - Human Health WQC – water and fish	0.051	No criterion
RCRA toxicity	0.5	0.2

What Do These Different Standards Mean to the Regulators?

- For most drinking water concentrate in arid areas, surface water discharge is not a viable option
  - Therefore, CWA WQC are not applicable
- For concentrate injection, regulators will want to know if the concentrations are:
  - < MCL
  - > MCL but < RCRA toxicity threshold
  - > MCL and RCRA toxicity threshold
- This information will allow them to decide what class of well can be used for injection
  - At this time, there is not a uniform approach to determining the classification of concentrate disposal wells

Examples of Data from Treatment of Produced Water

- The Texas A&M desalination trailer has been operated on several produced water samples
- Various analytical results of the raw water, treated water (permeate), and concentrate are shown in the following slides

Production Well - Brazos County TX, August 4th, 2006
Water Treated by Texas A&M Trailer

Constituent	Raw Water	Reject*	Permeate
TDS	13,320	14,021	323
Sodium	4,490	4,726	127
Chlorides	7,494	7,888	184
Potassium	76	80	1.2

*Estimated at 95% reject volume

Units are mg/L

Comparison of Desalinated Produced Water with Municipal Water from College Station. TX

		College Station Municipal Water (1)	Desalinated Produced Water (2)	Desalinated Produced Water (3)
	Substance	Amount	Amount	Amount
Agronomic Properties				
	pH	7.8	7.1	6.2
Physical Properties				
	Conductivity	882	2270	17
	TDS	523	1290	17
	SAR		23	0.1
Major Ions				
	Alkalinity (CaCo3)		34	5
	Bicarbonate (HCO3)	450	41	6
	Chloride	54	706	1
	Sulfate	9	3	ND
	Ca, Mg, K, Na, B	203	94 ppm	1.3
Metals, Dissolved				
	Barium, etc	2 ug/L	0.9 mg/L	ND
Volatile Organics				
	Chloroform, +	14 ug/L	3.4 ug/L	85 ug/L

(1) College Station municipal treatment plant

(2) Neuman gas well – treated by A&M trailer

(3) Fife #3 oil well – treated by A&M trailer

Detailed Data from Fife #3 Oil Well

- The A&M Desalination Unit was towed to the Fife Well site in Washington Co, TX
- Produced water from the Buda Lime was treated and desalted with a single stage one-pass RO configuration
  - Concentrate stream = 76% of volume

Units are mg/L

Analyte	Raw Feed	microfilter pass-through	microfilter reject	RO filter pass-through	Reduction
Alkalinity, Total as CaCO3	188	187	235	34	82%
Bicarbonate as HCO3	230	229	287	41	81%
Carbonate as CO3	< 1.2	1	1	1	n/d
Hydroxide as OH	< 1	1	1	1	n/d
Conductivity	33000	36500	46000	2270	93%
Magnesium	73	72	93	1	99%
Silicon	78	77	85	2	97%
Calcium	1055	1039	1363	23	98%
Potassium	124	126	172	5	96%
Sodium	11570	12480	16240	416	96%
Boron	87	87	105	34	61%
Silica	1664	162	181	4	99%
pH	6.1	6	7	7	
Solids, Total Dissolved TDS @ 180 C	38300	37700	49740	1291	97%

Preliminary Results - Darst Field Pilot Plant Test

&Analyte	Raw Feed	Concentrate	RO Perm.	RO Perm	RO Perm
Phosphorus, Dissolved Orthophosphate as P	< 2.25			1.156	< 0.15
Fluoride	8.82	9.07	0.456	0.311	0.448
Chloride	14588	16504	624	530	790
Sulfate	1118	1276	10	10	13
Bromide	88.4	100	5.19	4.74	7.04
Potassium	272	310	26.2	22.2	31.3
Magnesium	547	610	2.66	2.26	2.89
Silicon	12.5	12.5	0.258	0.255	0.328
Calcium	1692	1876	8.096	5.75	8.67
Sodium	6850	7490	402.4	341.6	488.8
Boron	16.8	16.8	11.1	10.6	11.4
Silica	26.6	26.8	0.552	0.545	0.701
Solids, Total Dissolved TDS @ 180 C	28780	31720	1215	1051	1458
Solids, Total Suspended TSS @ 105 C	2	< 4	< 4	<4	<4
Total Petroleum Hydrocarbons	5.24	0.311	< 1.1	< 1.1	<1.1
Nitrogen, Nitrate as N		34.2	3.28	6.48	16.1
SAR	52.4			43.2	
			No filter	Old C filter	New C filter

Detailed Data from Neuman Gas Well

Parameter	Units	Raw Water	Microfiltr-ation Permeate	RO Permeate	RO Concentrate	
pH	SU	7.1	7.2	6.8	8.3	
Conductivity	umhos/cm	536	478	23	3,130	
Solids, Total Dissolved	mg/L	149	135	ND	924	
Sodium Adsorption Ratio	unitless	5	5	0.9	13	
Solids, Total Suspended	mg/l	9	4	ND	ND	
Alkalinity	mg/L	126	110	9	677	
Bicarbonate	mg/l	154	134	11	826	
Carbonate	mg/l	ND	ND	ND	ND	
Chloride	mg/L	65	58	ND	404	
Sulfate	mg/L	1	1	ND	9	
Calcium	mg/L	14	12	ND	87	
Magnesium	mg/L	ND	ND	ND	4	

Detailed Data from Neuman Gas Well - continued

Parameter	Units	Raw Water	Microfiltration Permeate	RO Permeate	RO Concentrate
Potassium	mg/L	ND	ND	ND	6
Sodium	mg/L	70	64	1	471
Boron	mg/L	7.67	6.8	1.47	28.2
Silicon	mg/L	1.36	1.48	ND	11.2
Silica	mg/L	2.9	3.2	ND	24
Anions	meq/l	4.4	3.8	0.21	25
Cations	meq/l	3.8	3.4	0.049	25
Benzene	ug/l	498	290	8.3	30
Ethylbenzene	ug/l	9.3	4.6	ND	ND
Toluene	ug/l	290	149	0.5	17
Total Xylenes	ug/l	44	14	ND	4
Total Petroleum Hydrocarbon	mg/l	8.15	1.38	ND	4.85

Questions?