
Arsenic Removal from Water using Iron Oxide Ceramic Membranes
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May 1, 2007

Problem

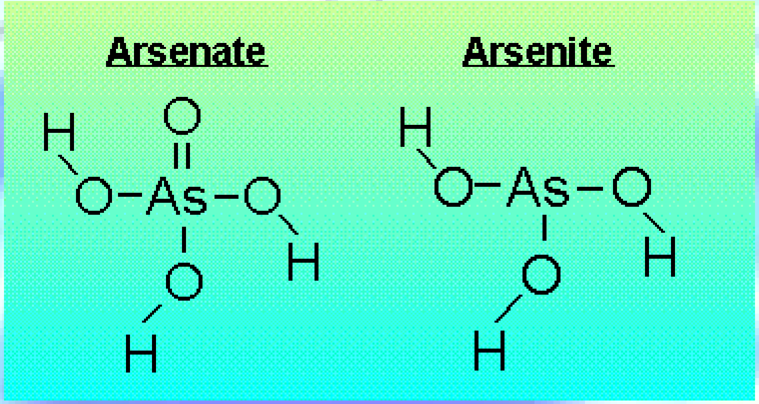
- Norman pays Oklahoma City $3.10/1000 gallons for drinking water
- Previously from Lake Thunderbird and Norman wells (Well flow rates of 1500 m^3/day)
- Arsenic (As) concentrations range from 1 to 42 parts per billion (ppb)
- Lung, skin, urinary, bladder, and kidney cancers caused by As poisoning

Challenge

- Reduce concentrations to World Health Organization (WHO) standards of
  10 ppb
- Evaluate iron oxide ceramic membranes to remove this arsenic
- Design treatment system using membranes

Background

- Arsenate and arsenite are common forms of arsenic found in water



- Research at UT-El Paso found that these two forms adsorbed to iron oxide coated stones

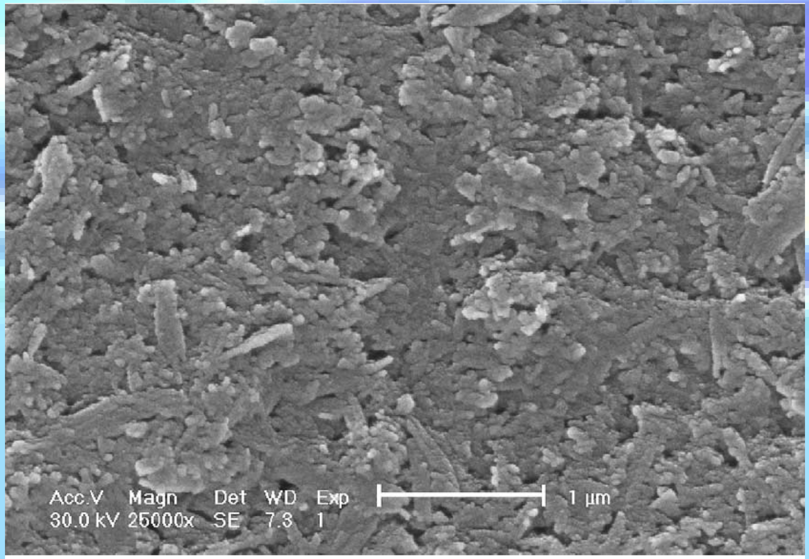
Background

- Under Dr. Maria Fidalgo de Cortalezzi, current research is being performed on iron oxide membranes at El Instituto Tecnólogico de Buenos Aires

Saturation Limit:	0.00011	kg As/kg Fe_2O_3
Porosity:	0.4	
Fe_2O_3 on pilot membrane:	0.002	kg
Membrane thickness, l_m:	50	µm
Pore diameter:	24	nm
Flux:	9.02×10^{-5}	m^3/m^2s
BET Surface Area:	120	m^2/g

Background

- Pressure difference across membrane drives contaminated water across membrane
- Arsenic adsorbs to iron oxide membrane



SEM image of top the top surface of an iron oxide membrane

From Cortalezzi, et al.

Challenge

- Must treat 8 contaminated wells with an iron oxide membrane system
  - Membrane Design Limitations:
    - Size (Brittleness, transporting…)
    - Porosity
    - Thickness
    - Saturation time

Design Proposals

Municipal Treatment System

1. Large membrane to place inside 33” pipe

    -Too brittle

    -Cannot transport

    -High production costs

2. Small membranes to make up 33” pipe

    - Sturdy

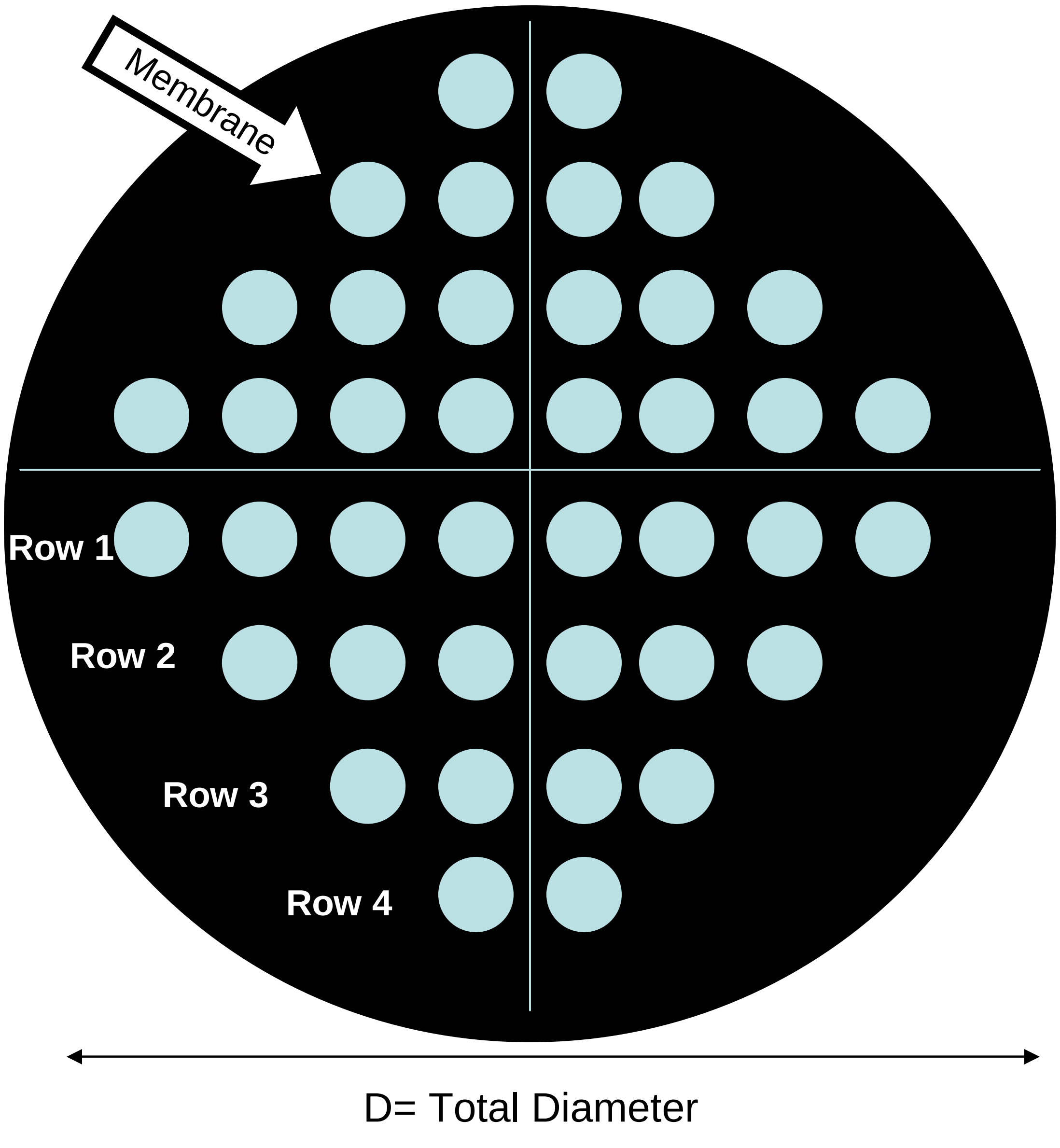
    - Low production costs

At-Home Treatment System

3. Membrane size of faucet

    - High consumer costs

Scale Up



D= Total diameter of support (inches)

$D_{membrane}$ + Clearance= 3 inches

n=number of membranes

Looking at 1 quadrant of support:

Row 1: n=D/(2*($D_{membrane}$+Clearance))

Row 2: n=(D/6)-1

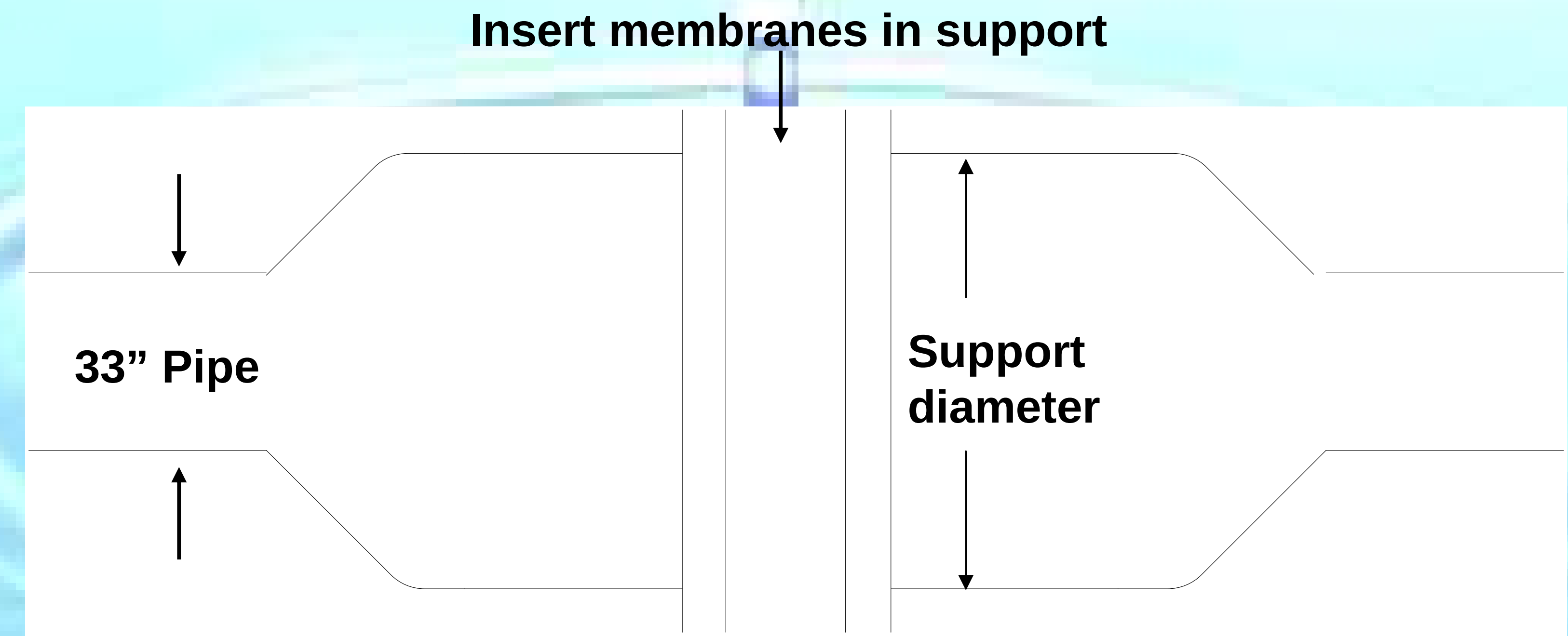
Row 3: n=(D/6)-2

Row 4: n=(D/6)-3=(D/6)-((D/6)-1)

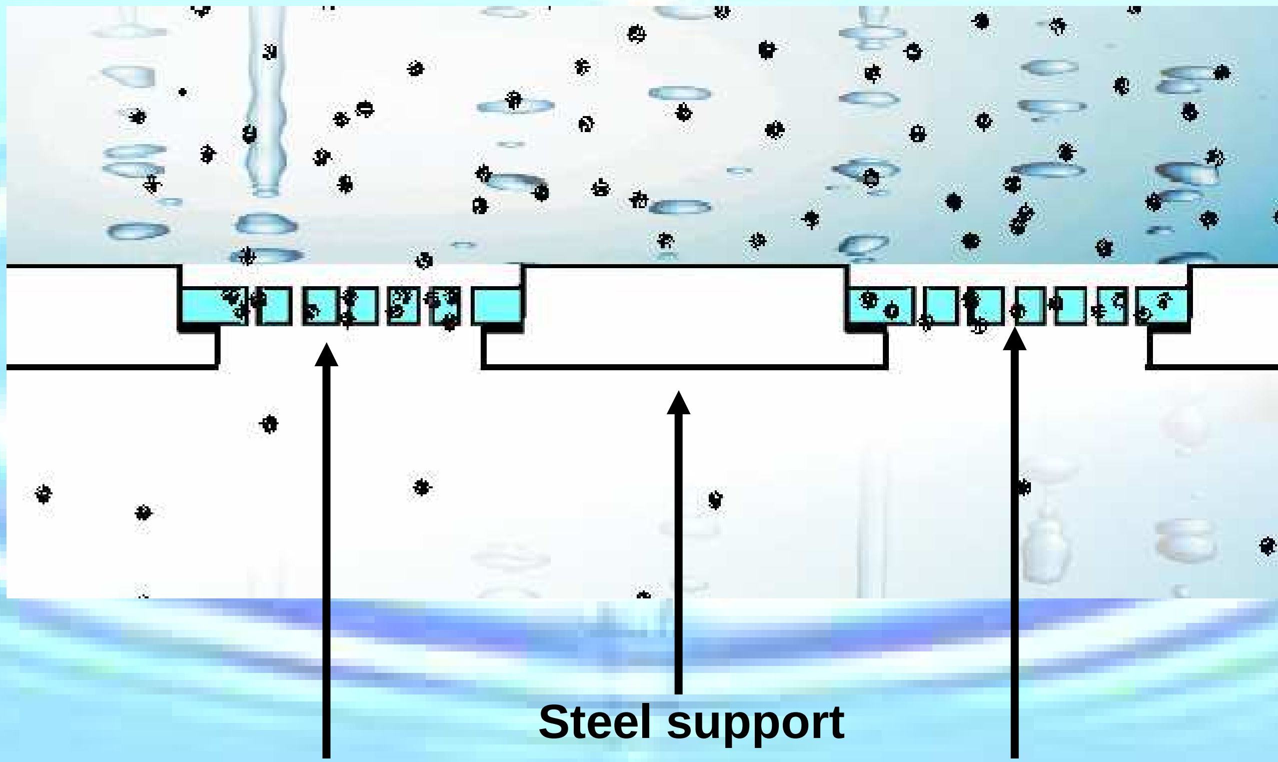
Continue for any diameter and multiply by four for number of quadrants:

$$n = 4 * \sum_{x=0}^{\frac{D}{6}-1} \left(\frac{D}{6} - x \right)$$

Chosen Design



Chosen Design



Pressure Drop Across Membrane

Modified Ergun Equation, derived from Darcy's Law for dead-end filtration, laminar flow of spherical particles (arsenic) in solution (water) into a porous membrane

$$\rho Q_{well} = \frac{\rho \varepsilon^3 (P_{in} - P_{out})}{(150/36)(1-\varepsilon)^2 a_v^2 \mu l_M}$$

Bernoulli Equation for work of the pump

$$\frac{\Delta P}{\rho} + \frac{\Delta(v^2)}{2} + g\Delta z = \frac{W}{\rho Q_{well}} \Rightarrow W = Q_{well}\Delta P$$

Required Pump Work

$$W = Q_{well}\Delta P = \frac{Q_{well}^{2}((150/36)(1-\varepsilon)^{2} a_v^{2} \mu l_M)}{\varepsilon^{3}}$$

Where Q_{well}= volumetric flow rate of water

ε= porosity

D_{pore}= pore diameter

n= number of pores

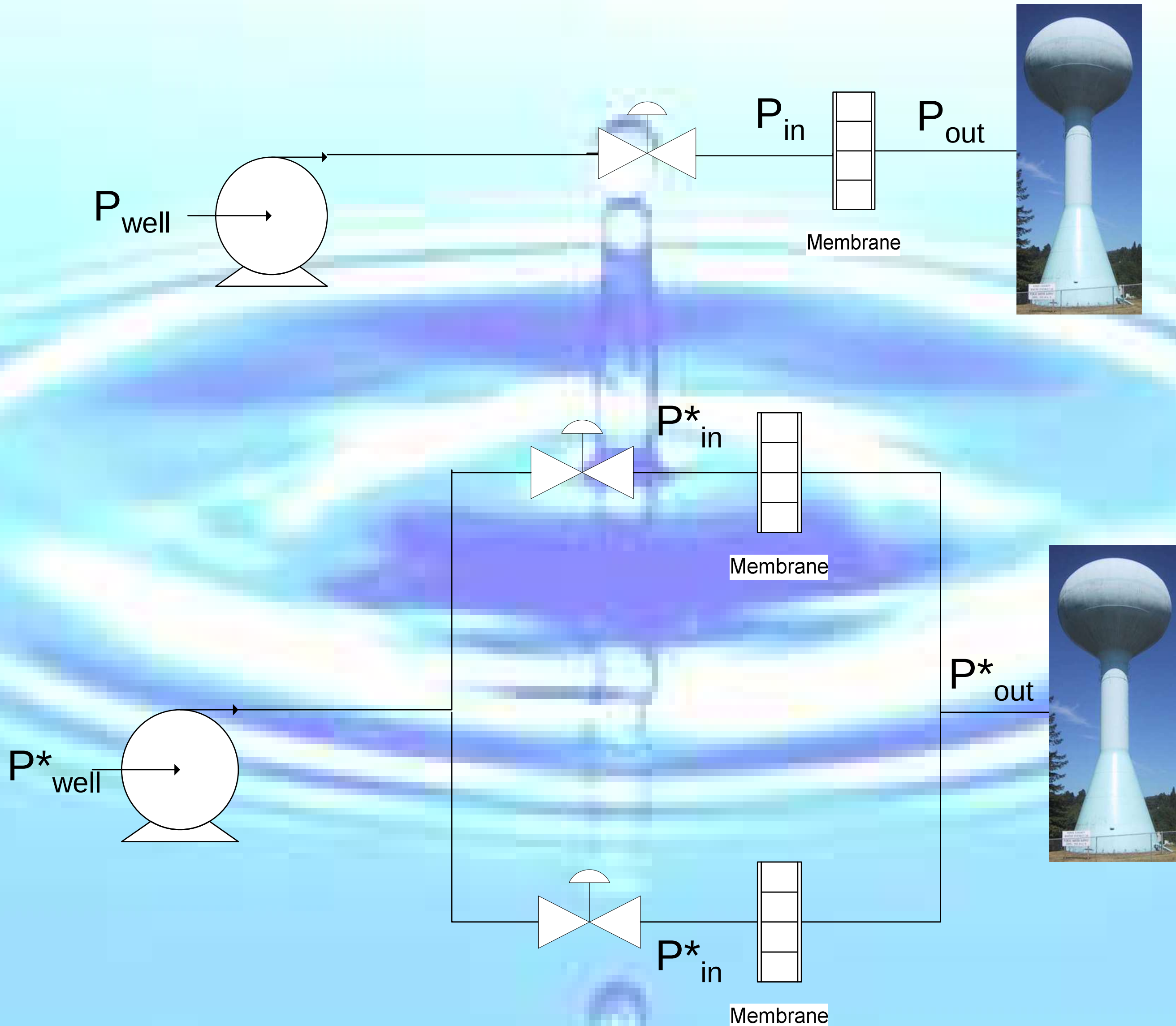
a_v= specific surface area of membrane

μ= fluid viscosity

l_M= membrane thickness

150/36= 2*tortuosity

Municipal System



Pump Work Comparison

$$\rho Q_{well} = \frac{\rho \varepsilon^3 (P_{in} - P_{out})}{(150/36)(1-\varepsilon)^2 a_v^2 \mu l_M} \Rightarrow P_{in} = Q_{well}\alpha + P_{out}$$

Full Flow

$P_{in} = Q_{well}\alpha + P_{out}$

$\Delta P = P_{in} - P_{out} = Q_{well}\alpha$

$W_{pump} = Q_{well}(P_{in} - P_{well})$

$= Q_{well}(Q_{well}\alpha + P_{out} - P_{well})$

$P_{out} = P_{well}$

$W_{pump} = Q_{well}(Q_{well}\alpha)$

$\boxed{\mathbf{W_{pump} = Q_{well}^2\alpha}}$

Split Flow

$P^*_{in} = (Q_{well}/2)\alpha + P^*_{out}$

$\Delta P^* = P^*_{in} - P^*_{out} = (Q_{well}/2)\alpha$

$W^*_{pump} = Q_{well}(P^*_{in} - P^*_{well})$

$= Q_{well}[(Q_{well}/2)\alpha + P^*_{out} - P^*_{well}]$

$P^*_{out} = P^*_{well}$

$W^*_{pump} = Q_{well}[(Q_{well}/2)\alpha]$

$\boxed{\mathbf{W^*_{pump} = Q_{well}^2\alpha/2}}$

Work to Remove Water from Well and Pump to Holding Tanks

- Each well supplies water at 1500 m^3/day
- Assume this same flow rate to holding tanks approximately 10 miles away
- Bernoulli Equation with frictional losses through 33” pipe

$$\frac{\Delta P}{\rho} + \frac{\Delta(v^2)}{2} + g\Delta z + \sum F = W$$

Turbulent Flow

$$f = \frac{0.079}{\mathrm{Re}^{0.25}} \qquad F = \frac{2fV^2L}{D}$$

Time of Saturation

$$t_{saturation} = \frac{(0.00011 kgAs / kgFe_2O_3) * x_{kg,ironoxide}}{As_{flow}}$$

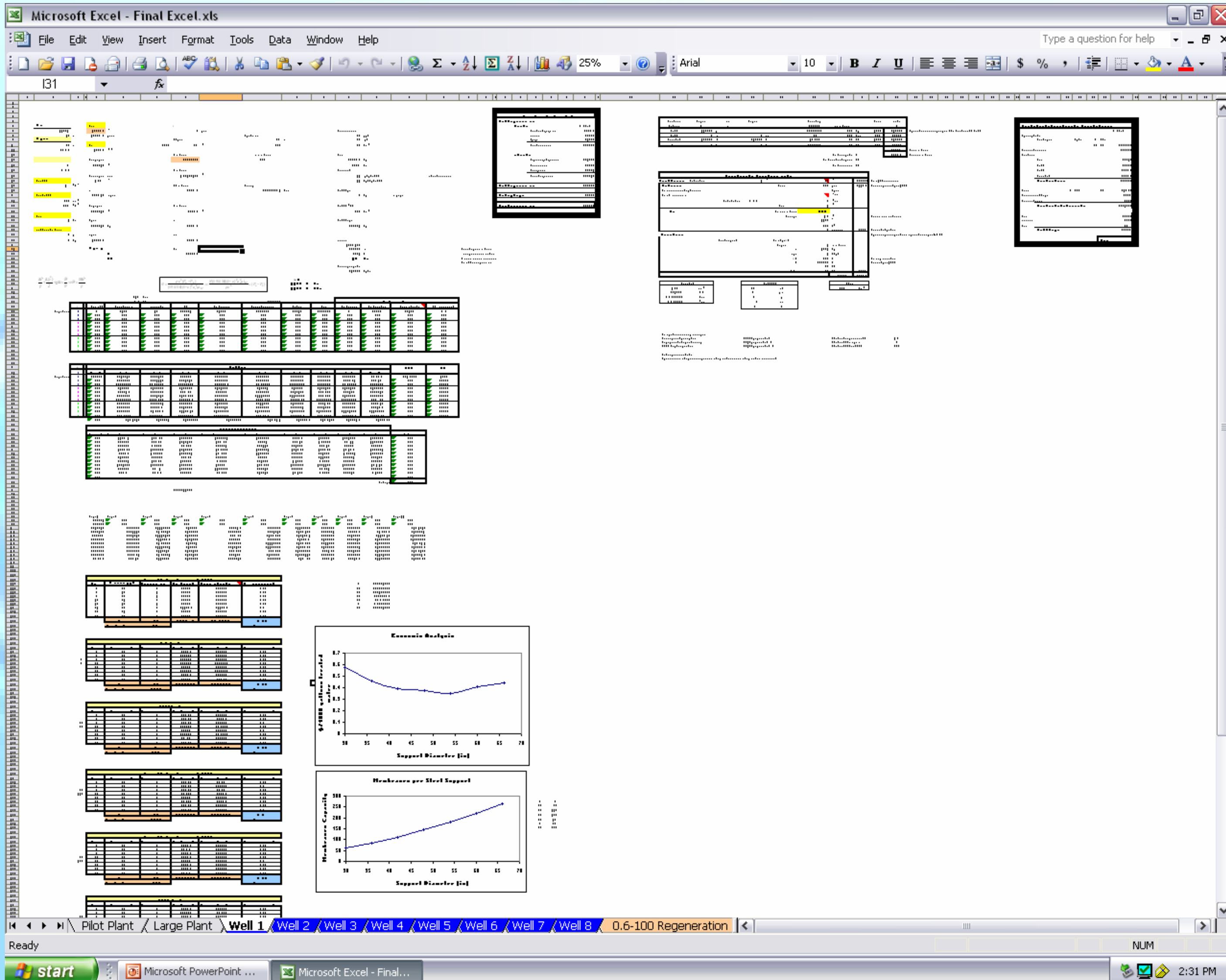
Regeneration with Basic Wash

1st flush: $t_{saturation} = t_{saturation} + 0.5t_{saturation}$

2nd flush: $t_{saturation} = t_{saturation} + 0.5t_{saturation} + 0.25t_{saturation}$

3rd flush: $t_{saturation} = t_{saturation} + 0.5t_{saturation} + 0.25t_{saturation} + 0.125t_{saturation}$

Scale Up



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Arial
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Economic Analysis
Membranes per Steel Support
Pilot Plant
Large Plant
Well 1
Well 2
Well 3
Well 4
Well 5
Well 6
Well 7
Well 8
0.6-100 Regeneration
Ready
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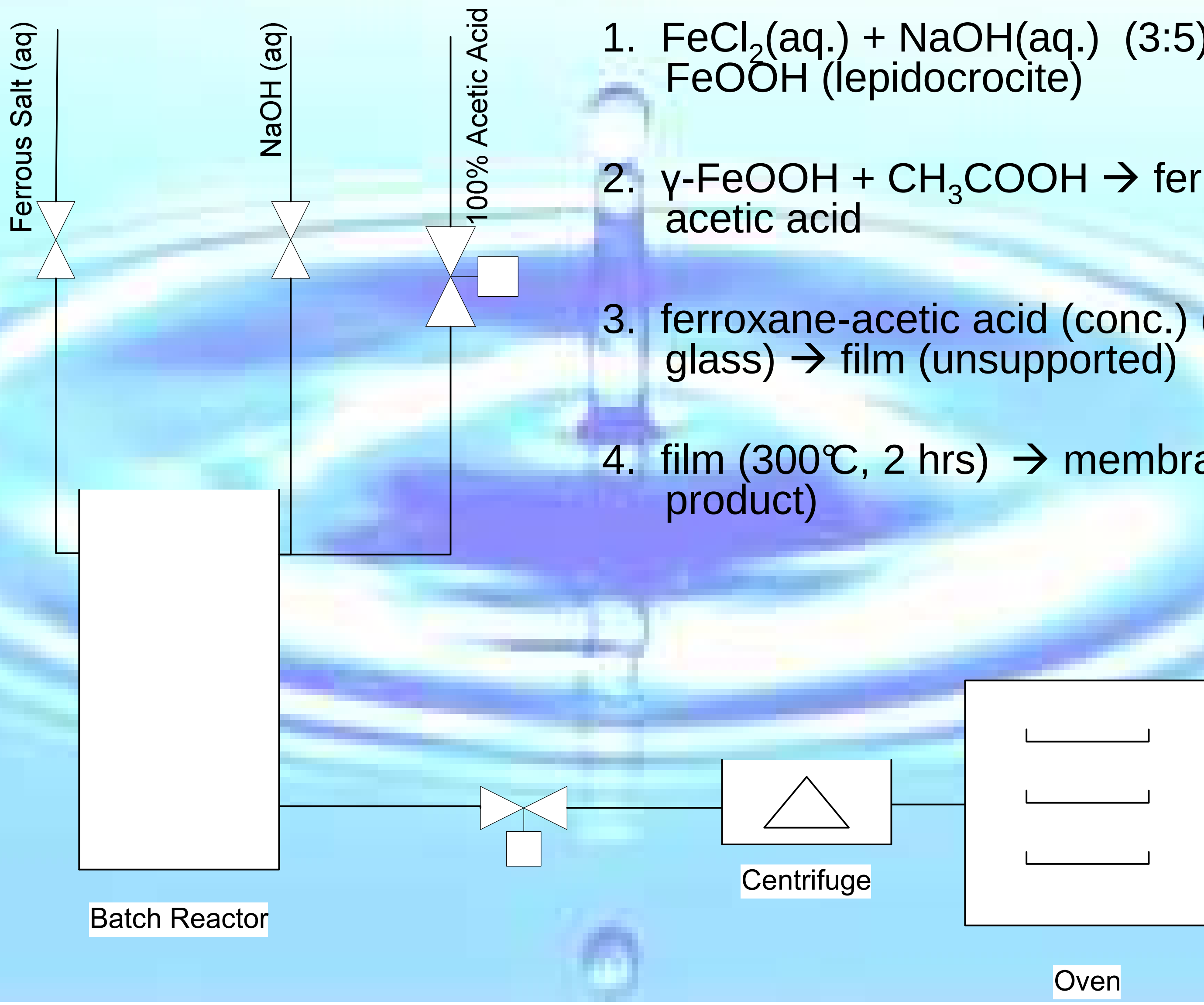
Pump Work and Saturation Time

- Chose to vary following parameters:
  - Support diameter
  - Arsenic concentration
  - Flow rate from well
- With more research, in the future, can vary:
  - Pore diameter
  - Membrane thickness
  - Membrane diameter
  - Porosity

Pump Work and Saturation Time

D_{as}			Q_{well}			ε			$As_{concentration}$	
1.15E-10	(m)		0.0174	(m^3/s)		0.4	porosity		32	(ppb)
0.12	(nm)		1.45E+08	gal/year		SA_{pores}			0.032	(mg/L)
D_{pore}			**Flux**			240	(m^2)		0.000032	(kg/m^3)
24	(nm)		0.016	(m^3/m^2s)		$R_{membrane}$			As_{flow}	
2.40E-08	(m)		$A_{cs\ single\ pore}$			0.035786997			5.556E-07	(kg/s)
l_m			4.52E-16	(m^2)		$A_{membrane}$			17.52	(kg/yr)
50	(μm)		$A_{cs\ every\ pore}$	flow/flux		1.062195148	(m^2)		**Saturation Limit**	
5.00E-05	(m)		1.06E+00	(m^2)		$SA_{membrane}$			0.11	(mg As/g Fe_2O_3)
			n			8.85E+03			0.00011	(kg As/kg Fe_2O_3)
Denisty H_2O			2.35E+15	(# of pores)		$V_{membrane}$			**Fe_2O_3/m^2 SA**	
1000	(kg/m^3)		$Q_{single\ pore}$			5.31E-05	(m^3)		1.24	(kg/m^2)
Denisty Fe_2O_3			7.394E-18	(m^3/s)					**Fe_2O_3 needed**	
5.26	(g/cm^3)		N_{pore}			Ergun Parameters			78738.1	(kg)
5260	(kg/m^3)		7.394E-15	(kg/s)		**a**				
Viscosity			v_{pore}			4.52E+06	(m^2)			
0.001	(Pa-s)		**1.634E-02**	(m/s)		a_v				
Fe_2O_3 on Membrane						7.53E+06	(m^2)			
2	(g)					**Re**				
0.002	(kg)					3.923E-04				
Support diameter			ΔP			W_{pump}			$t_{saturation}$	
66.0	(in)		1154063.95	(Pa)		20035.82	(W)		15590149	(s)
1.68	(m)		**1154.06**	**(kPa)**		**20.04**	**(kW)**		259836	(min)
									4331	(hr)
# of membranes within support									**180**	**(days)**
264										

Production of Membrane

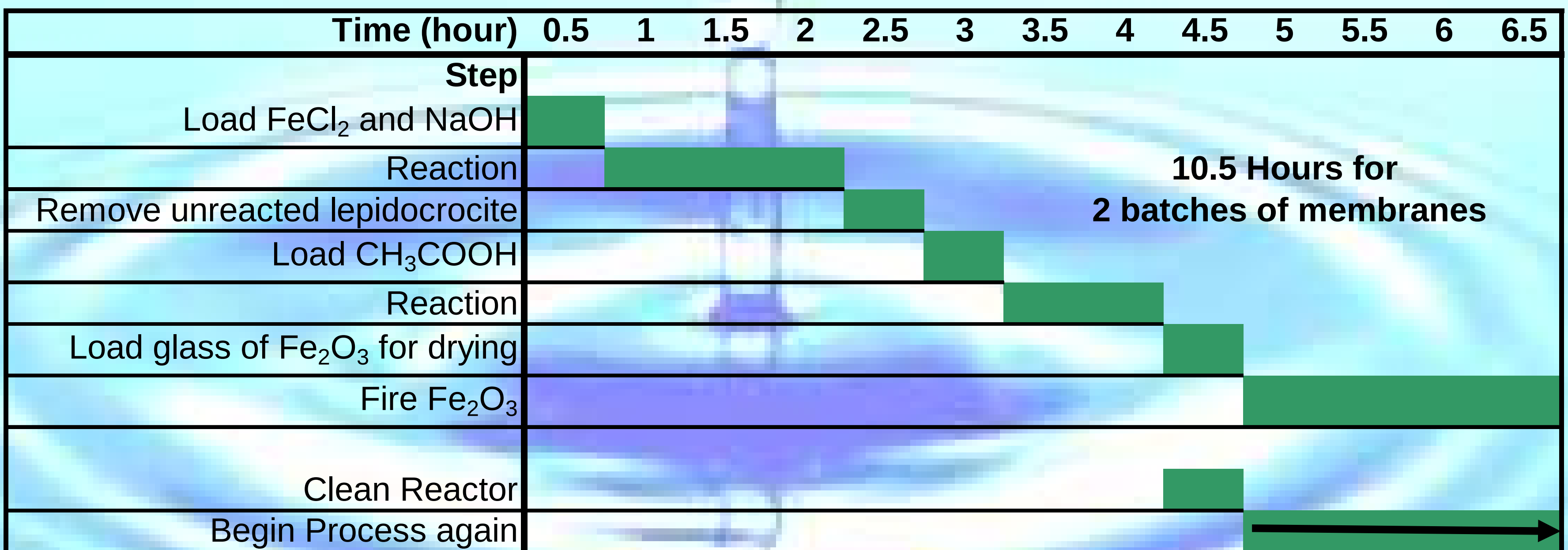


1. $FeCl_2$(aq.) + NaOH(aq.) (3:5) → γ-FeOOH (lepidocrocite)
2. γ-FeOOH + CH_3COOH → ferroxane-acetic acid
3. ferroxane-acetic acid (conc.) (on glass) → film (unsupported)
4. film (300℃, 2 hrs) → membrane (final product)

Membrane Synthesis

- Equipment required
  - 1 carbon steel batch reactor (size based on capacity)
  - Centrifuge to remove unreacted lepidocrocite
  - Glass for membrane drying
  - Batch Oven

Production Time



Plant Capacity

Chose steel support of D=30 inches

$D_{membrane}$ + Clearance= 3 inches

$$n = 4 * \sum_{x=0}^{\frac{D}{6}-1} \left(\frac{D}{6} - x \right)$$

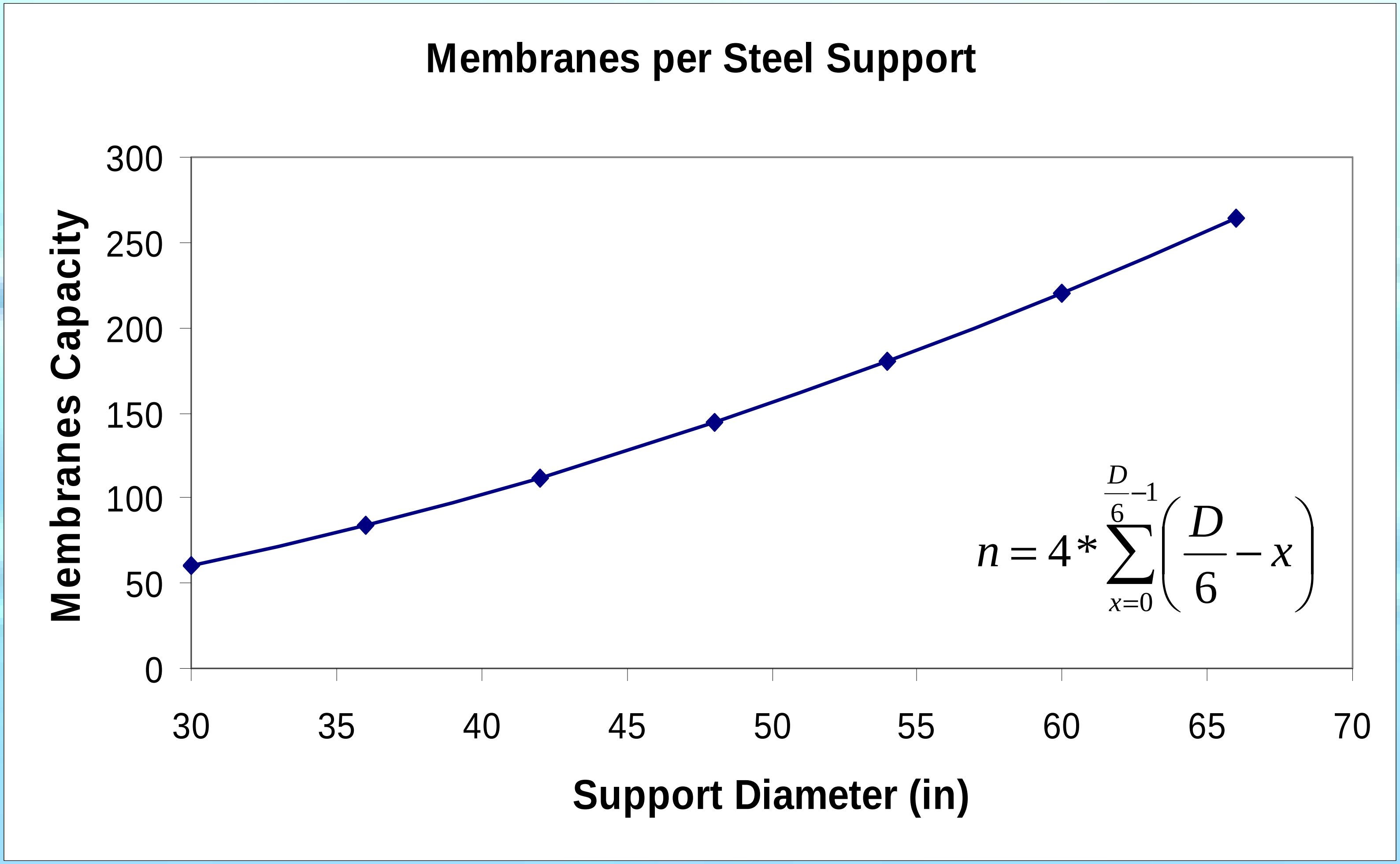
$$n = 4 * \sum_{x=0}^{\frac{30}{6}-1=4} \left(\frac{30}{6} - x \right) = 60 membranes$$

Norman Water Wells

Well #	Asconc (ppb)	Replacements/yr
4	29	12
6	16	4
7	24	8
15	41	18
18	13	2
31	42	18
32	31	12
36	12	2
	Total:	**76**
	Total Membranes:	**3800**

Plant Capacity: Produce 3800+10 membranes per year

Membranes per Steel Support



Raw Materials

Raw Materials									
Produces									
$FeCl_2$	1.19286	g	--	--	59643	0.000374	$/g	22.3	$22.31
NaOH	0.01	mol	4E-07	ton	0.02	165	$/ton	3.3	$3.30
Acetic Acid	1.35688	mL	0.003138	lb	157	0.25	$/lb	19.6	$19.61
Water	0.1	L	0.1	kg	5000	0.00055	$/kg	2.8	$2.75
								Batch of membranes	$47.97

Equipment

Batch Oven Specifications

-Reach temperature of 400^{o}C

-Hold two glass shelves with area of total membranes on support

-Electrically heated

-Blower to circulate air

-Ventilation to remove evaporating water

Equipment Costs

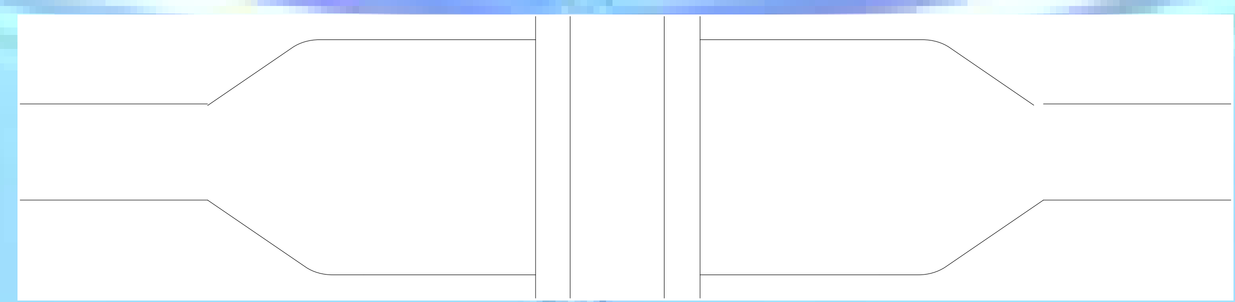
Membrane Equipment Costs						
Batch Reactor	Carbon Steel	0.000	m^3/s	0.05	m^3	$1,200
Centrifuge						$5,500
*Remove unreacted lepidocrocite by centrifuging for 30 minutes						
Glass		Total diameter of membranes:		***0.91***	m	
		Area of glass:		0.66	m^2	
				7.07	ft^2	
				15.75	$\$/ft^2$	
				2	levels of glass	$223
Furnace & Blower						
	Inside dimensions	Recirculated Air Volume		Output		
	WxLxH	1600	ft^3/min	500000	Btu/hr	
	3'x3'x4'	45.3	m^3/min	147	kW	
						$7,000
					TOTAL:	$13,923

Fixed Capital Investment

Fixed Capital Investment		
Direct Costs		2007 Costs ($)
	Purchased equipment	$13,811
	Installation	$2,762
	Piping	$552
	Total direct plant cost	**$17,126**
Indirect Costs		
	Engineering & supervision	$11,049
	Legal expenses	$3,729
	Contingency	$2,072
	Total indirect plant cost	**$16,850**
Fixed Capital Investment		**$33,976**

Working Capital

Working Capital	**$47,425**
Steel Support (36 inches)	$1,325
Additional 33" Pipe ($225/meter)	$2,250
Increased Piping at Well ($300meter)	$2,400
Pipe Preparation	$1,250
Flanged Valve	$5,000
Raw Materials	$7,100
Labor & Installation	$13,000
Engineer	$7,500
Installation Equipment Rental	$4,500
Taxes	$3,100



Production Costs

Total Product Cost - Large Scale Membrane Production

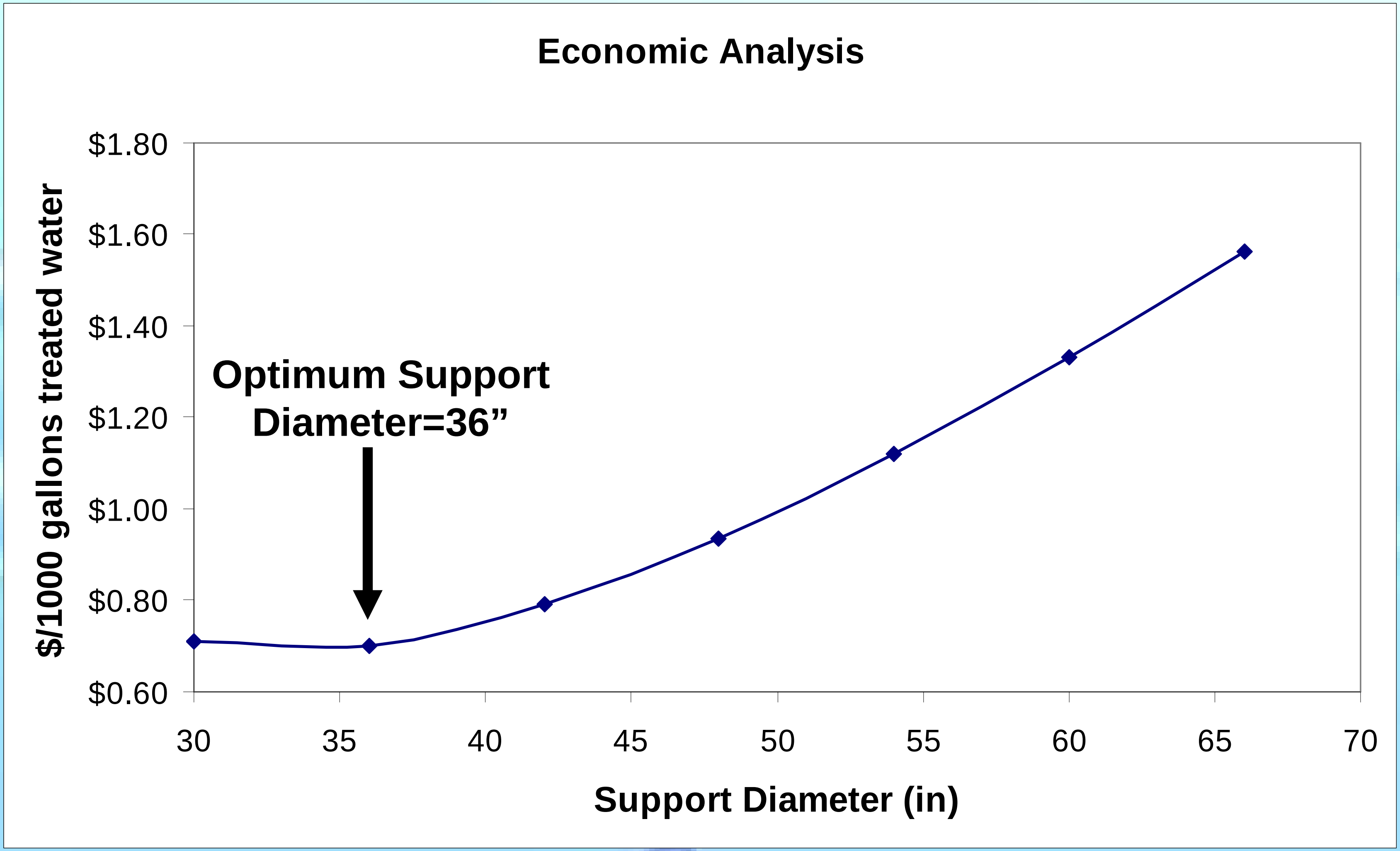
				2007 Costs ($)
Operating Labor				
	Plant Capacity		30 (hr/day)	
			21 ($/hr)	$195,458
Operating Supervision				$78,183
Raw Materials				
	Water			$828
	NaOH			$993
	$FeCl_2$			$6,714
	Acetic Acid			$5,903
	Total Raw Materials			$14,439
Electricity		0.05 ($/kW)	90925 (kW)	$4,092
Maintenance & Repairs				$2,039
Operating Supplies				$306
	Total Variable Production Costs			$294,515
Royalties	(membrane patent)			$2,166
Taxes				$4,077
Insurance				$3,398
Rent				$30,000
	Fixed Charges			$39,640
			Total:	**$334,156**

Vary Support Diameters

36"-84 Membranes/support						
Well #	Asconc (ppb)	Replacements/yr	Membrane $/yr	Elec $/yr from ground + to holding tanks	Consumer Total Cost/yr	$/1000 gallons treated
4	29	8	$72,839	$33,029	$105,868	$0.73
6	16	4	$36,420	$33,029	$69,449	$0.48
7	24	6	$54,629	$33,029	$87,659	$0.61
15	41	14	$127,468	$33,029	$160,498	$1.11
18	13	2	$18,210	$33,029	$51,239	$0.35
31	42	14	$127,468	$33,029	$160,498	$1.11
32	31	10	$91,049	$33,029	$124,078	$0.86
36	12	2	$18,210	$33,029	$51,239	$0.35
	Total:	**60**	**$546,293**	**$264,235**	**$810,528**	**$0.70 Average**
	Total Membranes:	**3000**				

42"-112 Membranes/support						
Well #	Asconc (ppb)	Replacements/yr	Membrane $/yr	Elec $/yr from ground + to holding tanks	Consumer Total Cost/yr	$/1000 gallons treated
4	29	6	$94,721	$23,548	$118,269	$0.82
6	16	2	$31,574	$23,548	$55,122	$0.38
7	24	6	$94,721	$23,548	$118,269	$0.82
15	41	10	$157,868	$23,548	$181,416	$1.25
18	13	2	$31,574	$23,548	$55,122	$0.38
31	42	10	$157,868	$23,548	$181,416	$1.25
32	31	8	$126,294	$23,548	$149,843	$1.04
36	12	2	$31,574	$23,548	$55,122	$0.38
	Total:	**46**	**$726,191**	**$188,388**	**$914,579**	**$0.79 Average**
	Total Membranes:	**2300**				

Cost Analysis



Norman Savings

36"-84 Membranes/support						
Well #	Asconc (ppb)	Replacements/yr	Membrane $/yr	Elec $/yr from ground + to holding tanks	Consumer Total Cost/yr	$/1000 gallons treated
4	29	8	$72,839	$33,029	$105,868	$0.73
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	Total:	**60**	**$546,293**	**$264,235**	**$810,528**	**$0.70 Average**
	Total Membranes:	**3000**				

Consumer Total Cost/yr includes:

- **Membrane $/yr found from dividing production costs per year by membranes produced in year plus a 15% mark-up**
- **Total electricity costs to pump water from well to holding tank**

Save $2.40/1000 galllons of water treated

Save $2.5 million per year!!!

At Home System

Average household water consumption (drinking water only): 7 gallons per day

Diameter of membrane: 1 inch (Size of faucet head)

ε	l_m (μm)	W_{pump} (kW)	Energy $ of pump/yr	$t_{saturation}$ (day)	TCI	Membrane cost	Total product cost/year	Unit Price	Sales	Revenue
0.4	100	332	17	41	$198,297	2.04	$711,139	2.15	$746,696	$35,557
0.5	100	170	9	41	$198,297	1.99	$692,685	2.09	$727,319	$34,634
0.6	100	99	5	41	$198,297	1.94	$674,426	2.04	$708,148	$33,721

Treat 1 household per year
$23.18

Average # of households
38,834

Cost to treat for all houses
$900,077

Water treated for all households (gal/yr)
99,220,870

$/1000 gallons of treated water
$9.07

Conclusions

•36 inch steel support of membranes proves most economically feasible

•Saves City of Norman $2.5 million per year

•At home system is not economical

•Norman now in compliance with WHO regulations

Recommendations

- Increase Product Markup
  - Norman only saves $500,000/yr
- Consider On-Site Regeneration Services
- Expand to Other Cities with Arsenic Problems
- Research Membrane Mechanics
  - Increase Porosity
  - Increase Thickness
  - Study Mechanical Integrity


Questions?