

# Review and Evaluation of Water Detritiation Technologies for Watts Bar Primary Cooling Water

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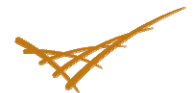
*May 10, 2017  
EMSL Auditorium, PNNL*



**PNNL-SA-125901**

# Background

- ▶ Tritium in the primary cooling water of the Watts Bar Nuclear Reactor
  - not captured nor treated but released to the river
  - Tritiated water concentration is well below the EPA's drinking water standard of 20 pCi/g met after mixed with the river
- ▶ Increased number of TPBARs may increase the amount of tritium in the cooling water
  - reactor contains 368 TPBARs, but 1504 will be used during the "equilibrium" phase
  - higher tritium levels may necessitate other pathways for tritiated water disposition



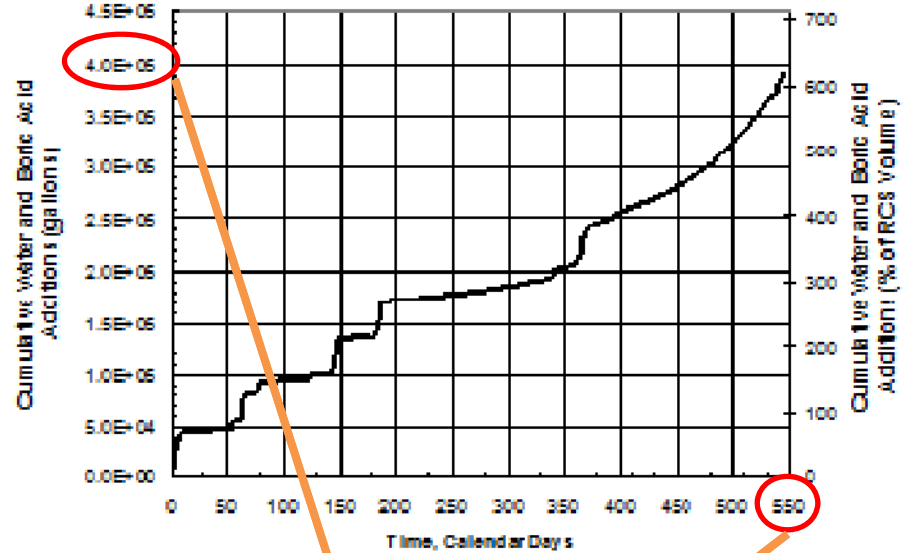
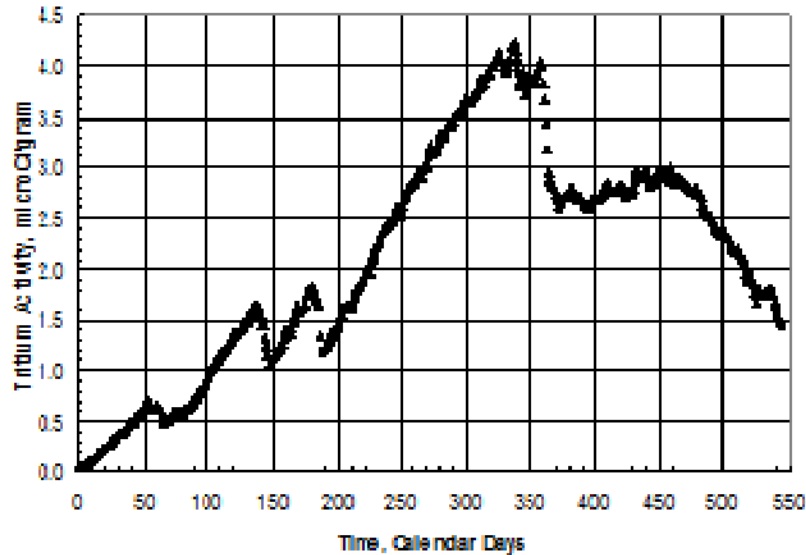
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# Report Purpose

- ▶ Identify and evaluate disposal pathways for disposition of tritium-containing primary cooling water from Watts Bar
  - include the current approach of direct disposal into the Tennessee River
  - consider alternatives to reduce tritium prior to discharge
  - concentrated tritium stream will be grouted and disposed of in a commercial near-surface burial site
  - costs are rough order of magnitude estimates only

# Conditions Considered



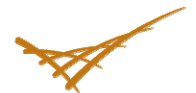
Tritium activity and water discharge volume for Cycle 9, Watts Bar Unit 1

Overall Assumptions		
Total Volume	390,000	gallons
Processing Duration	550	days
Operating Efficiency	80%	--
Average <sup>3</sup> H Conc.	14	uCi/g
Target Decontamination Factor	140	--
Target Concentration Factor	100	--



# Previous Work

- ▶ This work is based previous tritium mitigation alternatives analyses:
  - Hanford Site Wastewaters (1997, 2004, 2009)
  - Savannah River Site (1998)
  - CANDU Reactors (1984, 1990)
  - Fukushima Daiichi Nuclear Plant (2013, 2014)
  - Recent literature
- ▶ Use of previous cost estimates from literature:
  - adjusted to 2015 dollars
  - system sizing based on six-tenths-factor rule
  - processes for isotope enrichment are “in most instances . . . indifferent to the feed concentration.” (Miller 1998)
  - 10 year lifetime, linear depreciation



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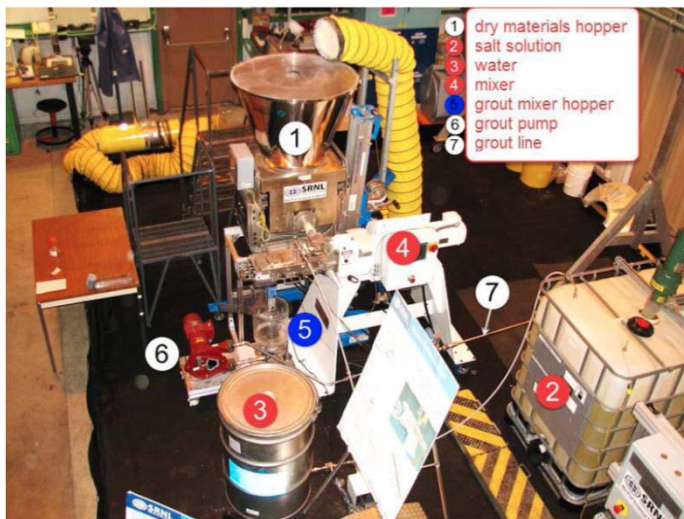
# Approach

- ▶ When Literature Cost Not Available
  - Operating costs based on electricity and natural gas costs
  - Facility footprint for nuclear facility estimate \$3500/ft<sup>2</sup>
  - Use available current cost data from DOE Energy Efficiency and Renewable Energy (EERE)
    - Electrolysis, Hydrogen Liquefaction, Fuel Cells
- ▶ Estimate of Technology Readiness (TRL) from DOE EM

TRL Level	Scale of Testing	Fidelity	Environment
9	Full	Identical	Operational (Full Range)
8	Full	Identical	Operational (Limited Range)
7	Full	Similar	Relevant
6	Engineering/Pilot	Similar	Relevant
5	Lab/Bench	Similar	Relevant
3-4	Lab	Pieces	Simulated
1-2	None	Paper	Simulated

# Tritium Disposal Alternatives— No Tritium Separation

- ▶ Direct Disposal into the River (**\$0.7/gallon**)
  - Only analysis and sampling required
- ▶ Grout Disposal of Tritiated Water (**\$12/gallon**)
  - Use phosphate/sulfate waste grout (high water)
  - 2018 disposal costs for Waste Control Specialists (WCS)
  - Equipment cost based on grouting study and SRS Engineering Scale Continuous Processing Facility (ESCPF)



ESCPF

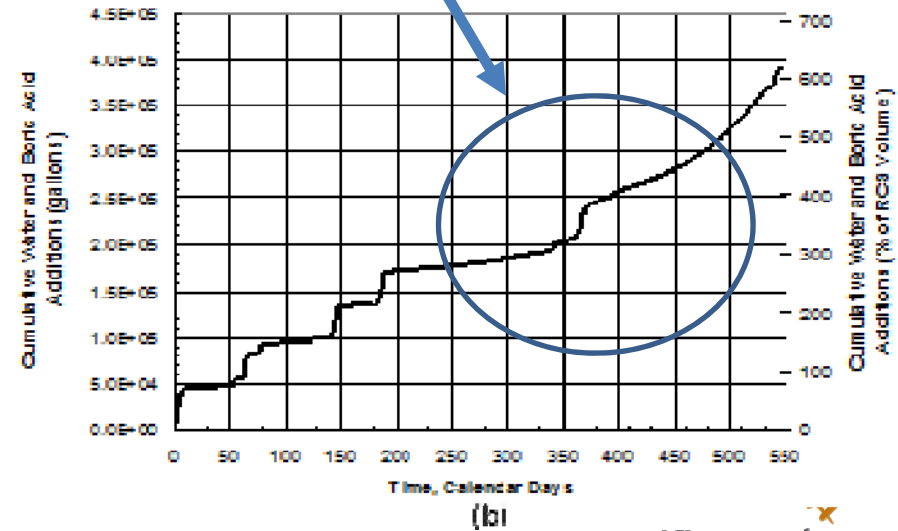
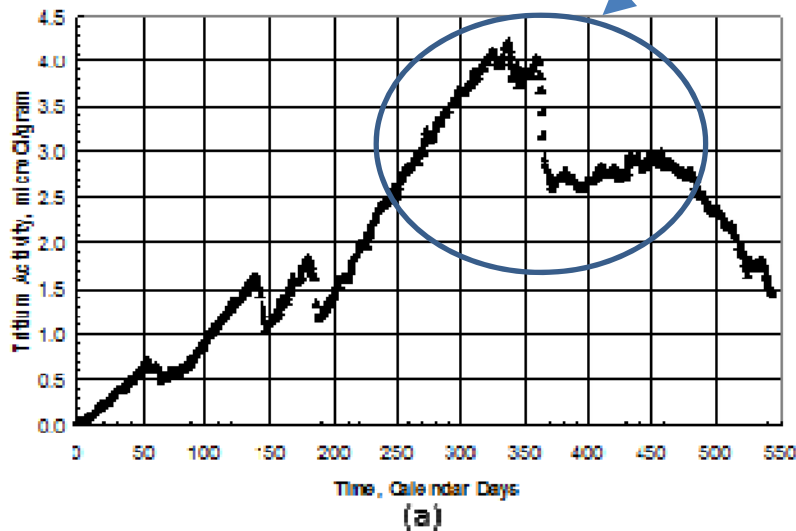
Characteristic	Cost	Units
Type of Grout	Phosphate/Sulfate Waste	
Ratio cement to water	7.5	lb/gallon water
Density of Cement	11.7	lb/gallon grout
Composition of Solids	41 wt% Portland cement 40 wt% Fly Ash 11 wt% Attapulgite clay 8 wt% Indian Red Pottery Clay	
WCS Class A LLW Base Disposal Cost	\$876	\$/cubic yard
WCS Class A LLW Drum Surcharge	\$417	\$/cubic yard
Water Shipping Cost	\$2.50	\$/gallon
* WCS costs area based on Year 5 (2018)		

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# Combined Direct Disposal and Grout Disposal

- ▶ Assume 1/3 of water is grouted and 2/3 disposed of into river
- ▶ Reduced cost: **\$5.5/gallon**

High Concentration  
Tritium for Grout  
Disposal

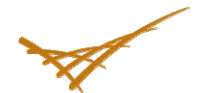




# Tritium: Hydrogen Separation Factors for Developed Tritium Removal Technologies

Dual Temperatures Processes	Low Temperature		High Temperature	
	T (°C)	T/H	T (°C)	T/H
Water Bithermal	60	5.289	150	2.918
Girdler Sulfide	32	3.599	130	2.563
Ammonia Bithermal	-30	16.1	40	8.6
Single Temperature Processes	T (°C)	T/H		
Catalytic Exchange	60	5.289		
Water Distillation	50	1.059		
Electrolysis	50-80	15		
Cryogenic Distillation	-250	1.8		
Graphene Oxide Membrane	100	1.6		
Adsorption Processes	RT	1.4		

Operating and Capital Costs Estimated for these Technologies



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# Water Distillation

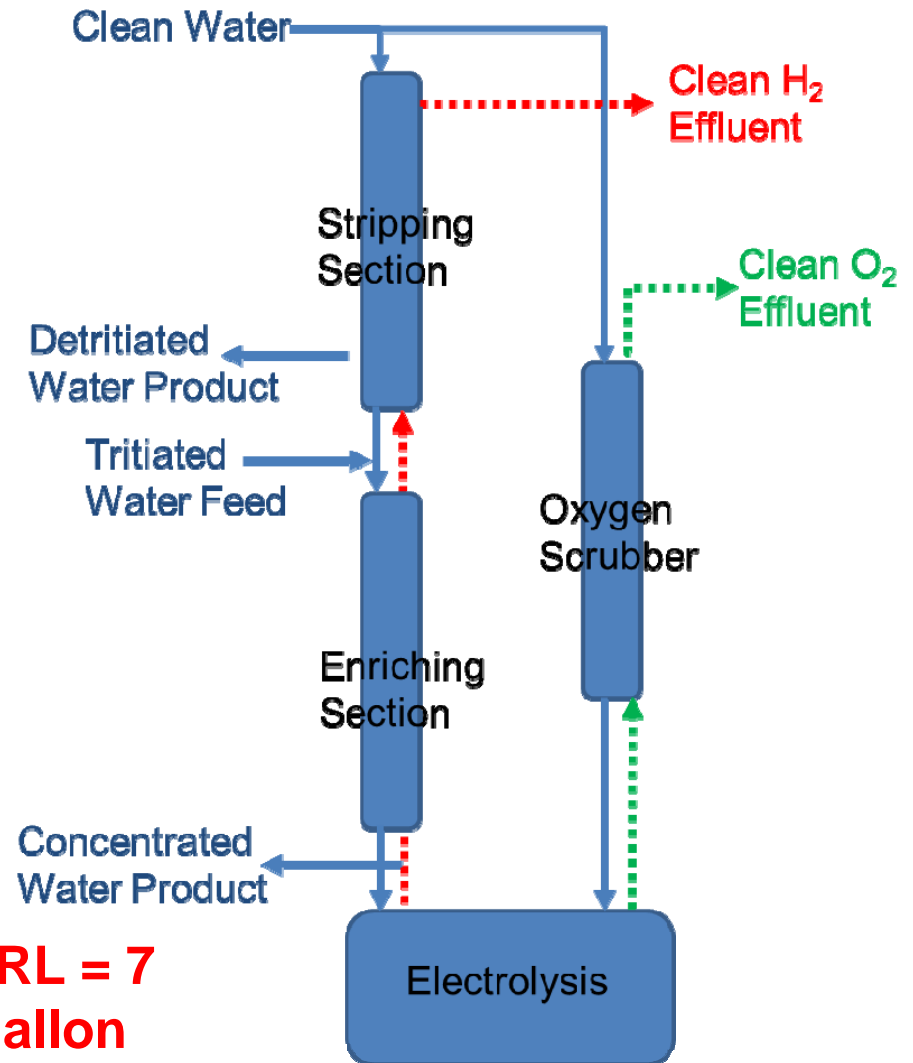
- ▶ Lowest separation factor
  - High reflux → high heat usage + large diameter columns
  - > 200 theoretical plates → tall columns
- ▶ Use of heat pump and improved packing address column size and heat requirements
- ▶ Well developed technology
- ▶ Working with water → Very safe

**Capital + Operating = \$19/gallon**  
**TRL = 7**

# Water/Gas Catalytic Exchange: Vapor Phase, Liquid Phase, or Combined Electrolysis

- ▶ VPCE, LPCE and CECE all based on the equation
  - $\text{HT(g)} + \text{H}_2\text{O(l)} \leftrightarrow \text{HTO(l)} + \text{H}_2\text{(g)}$
- ▶ VPCE and LPCE processes well developed
  - DF = 25-35
- ▶ CECE plants have achieved higher DFs
  - DF = 30,000 - 50,000
  - Commercial at ~1 kg/hr scales
  - 30X scale-up required

**CECE: TRL = 6    VPCE/LPCE: TRL = 7**  
**CECE: Capital + Operating = \$7/gallon**



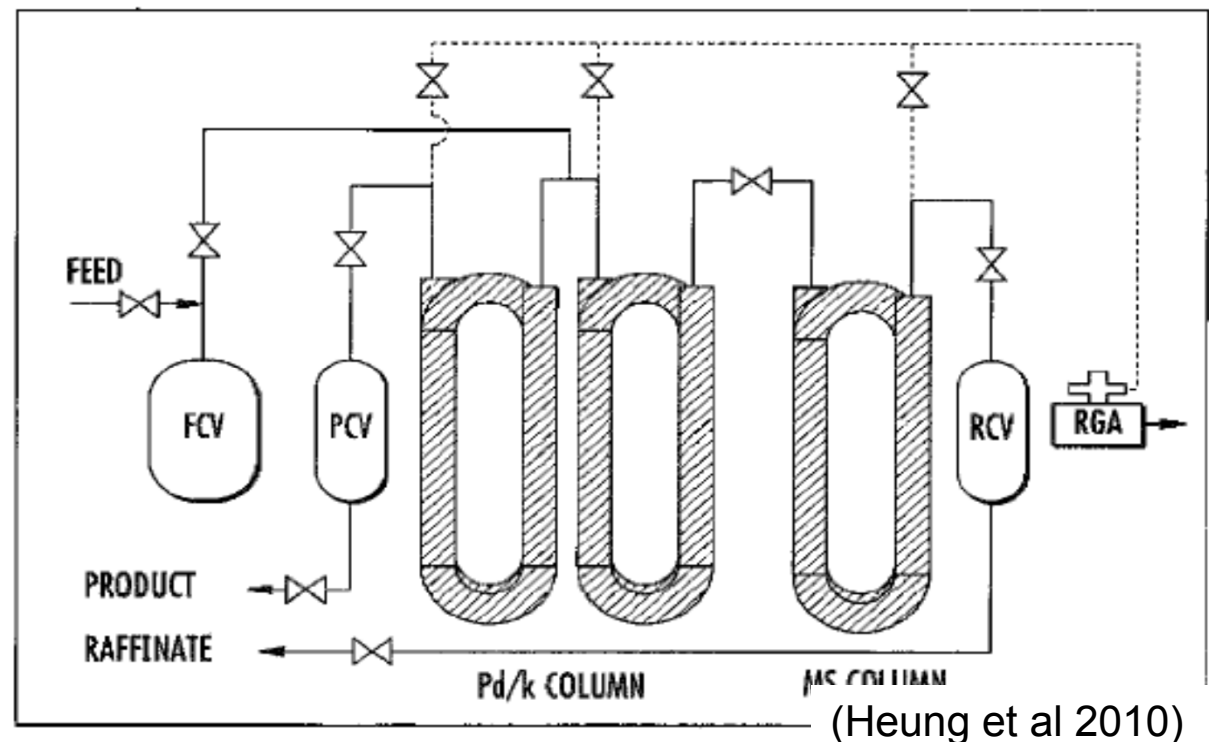
# Facilities Use Water/Gas Catalytic Exchange

Facility	Technologies	Input Capacity, gpm	Input $^3\text{H}$ , $\mu\text{Ci/g}$
Darlington, TRF	VPCE	1.6	30,000
Grenoble	VPCE	0.1	3000
AECL Test	LPCE	0.03	23,000
Chalk River, TEP	LPCE	0.09	35,000
Wolsung	LPCE	0.44	10,000-60,000
Mound	CECE	0.09	Unknown
Mol	CECE	0.007	$2 \times 10^{-3}$
KFK	CECE	0.004	100
FUGEN	CECE	0.004	4000

**Watts Bar Application:**  
**Flow Required = 0.6 gpm**  
**Input  $^3\text{H}$ ,  $\mu\text{Ci/g}$  = 14**

# Thermal Cycle Adsorption Process (TCAP) + Electrolysis

- ▶ Semi-continuous temperature swing chromatographic process
- ▶ Tritium concentrates at far end of Pd/k column & protium concentrates at far end of MS column
- ▶ Used for tritium purification



# TCAP-E Cost Estimate

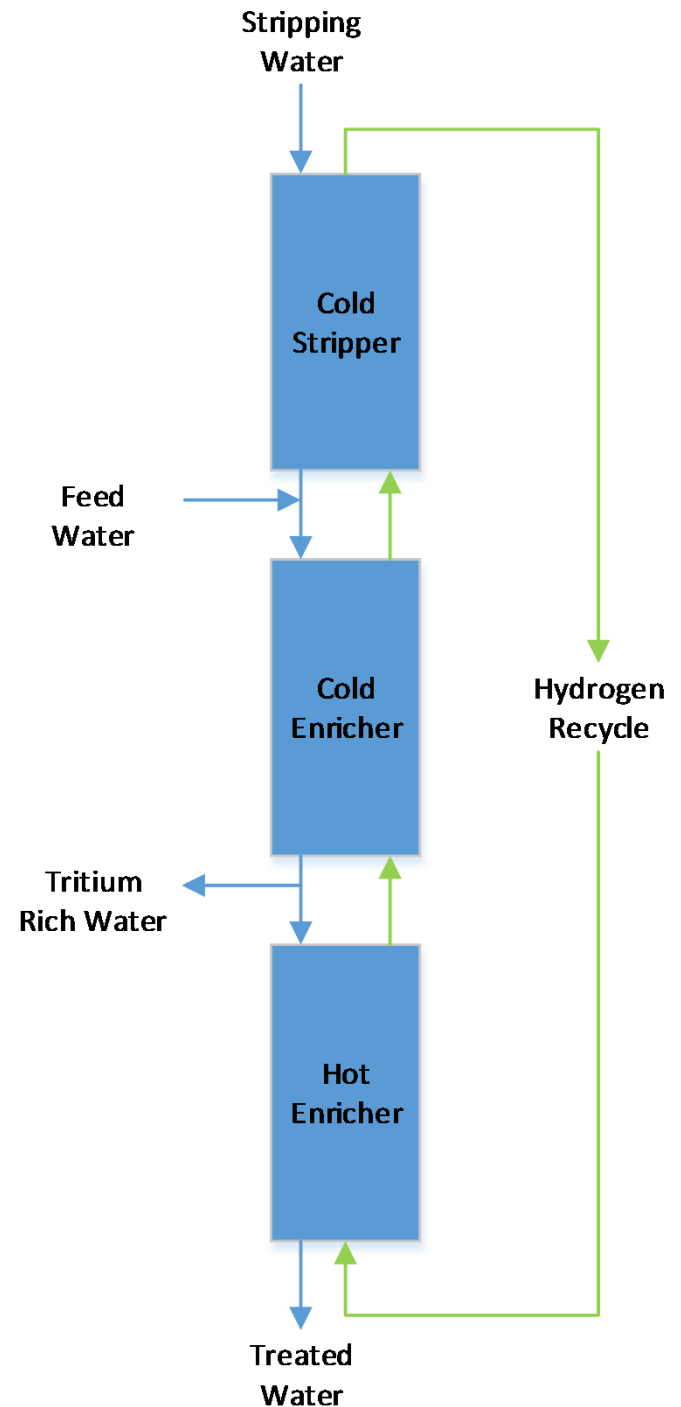
- ▶ Estimate includes cost of electrolysis, electricity and heat for cooling and heating, Pd metal cost, facility cost, and tritium disposal

	Pd/k Column	MS Column	Units
Throughput Rate	12.8	40.4	L H <sub>2</sub> / kg bed / cycle
Mass fraction Pd	27%	0%	--
Temperature Differential Pd/k Bed	200	90	°C
Cycle time	16		min/cycle
Absorbent Fractional Heat Load	50%		--
COP for Cryocooling	0.5		--
Footprint of Mini-TCAP (4 sl/cycle)	18		ft <sup>2</sup>

**Capital + Operating = \$17/gallon**  
**TRL = 6**

# Bithermal Processes

- ▶ Hydrogen-Water ( $H_2$ )
  - 50 to 170°C, 5 MPa
  - **\$7/gallon + TRL 6**
- ▶ Girdler Sulfide ( $H_2S$ )
  - $H_2S$  toxic, corrosive, flammable
  - 32 to 130°C, 2 MPa
  - **\$11/gallon + TRL 7**
- ▶ Ammonia-Hydrogen ( $NH_3$ )
  - -30 to 40°C, 15 MPa
  - **\$165/gallon + TRU 7**



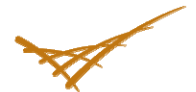
# Other Processes Evaluated

- ▶ Multiple Electrolysis Cycle Process
  - Feed electrolyzed **9 times** for DF = 10,000, CF = 100
  - Use fuel cells to recover some electricity
  - *Cell concentration =  $\frac{1}{\sqrt{\alpha}}$  \* H2 Product Concentration*
  - **\$22/gallon + TRL 5**
- ▶ Cryogenic Distillation
  - Issues with safety, purification, liquefaction
  - **\$9/gallon + TRL 6**
- ▶ Graphene Oxide Membrane
  - Direct tritiated water clean-up
  - Low energy, but extremely high capital cost
  - **\$227/gallon + TRL 3**



# Separation Techniques Not Costed

- ▶ Low TRL / Research Level Techniques
  - Selective Laser Excitation (fluoro- and chloro-alkanes)
  - Freeze concentration ( $\Delta T_{\text{melt}} = 4.49^{\circ}\text{C}$ )
  - Pressure swing adsorption (synthetic zeolites)
  - Palladium membrane reactor (alternative electrolysis)
  - Chromatographic adsorption (isotopically swamping of tritium loaded molecular sieve bed)
  - Thermal diffusion (T gradient)
  - Formic acid electrolysis (8X faster kinetics than water)
  - Functionalized Zn and Cu MOF adsorption (increased cryogenic temperature)

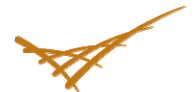


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# Summary of Results

Proposed Technology	Technology Readiness Level	Estimated Cost (\$/gallon)	Estimated Cost				
			< \$1	\$ 1-10	\$ 1-20	\$20-100	> \$100
Direct River Disposal	8	\$0.7					
Grout High Tritium Water	7	\$5.5					
Girdler Sulfide Process	7	\$11					
Grout Entire Volume	7	\$12					
Water Distillation	7	\$19					
Ammonia-Hydrogen Bithermal Process	7	> \$165					
Combined Electrolysis Catalytic Exchange	6	\$6.6					
Bithermal Hydrogen-Water Process	6	\$7.3					
Cryogenic Distillation Process	6	\$8.9					
Thermal Cycle Adsorption Process	6	\$17					
Multiple Electrolysis Cycle Process	5	\$22					
Graphene Oxide Membrane Process	3	> \$227					

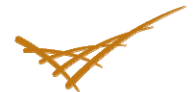


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# Conclusions and Recommendations

- ▶ As expected, direct disposal of tritiated water into the river is least expensive
- ▶ Grouting 1/3 tritiated water with higher concentration significant reduces the overall cost of disposal
- ▶ Separating the tritium with CECE or bithermal  $H_2-H_2O$  may be less expensive than grouting entire volume
- ▶ Estimates are only rough order of magnitude. Additional design and costing analysis is needed.



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