NITEK USA, Inc.
8439 Leeward Air Ranch CIR
Ocala, FL 34472-9261
U.S.A.

Tel: (352) 537-0864
Email: abusigin@nitek.com

Comparison of Water-Hydrogen Catalytic Exchange Processes versus Water Distillation for Water Detritiation

A. Busigin, Ph.D., P.Eng.

April 22, 2014

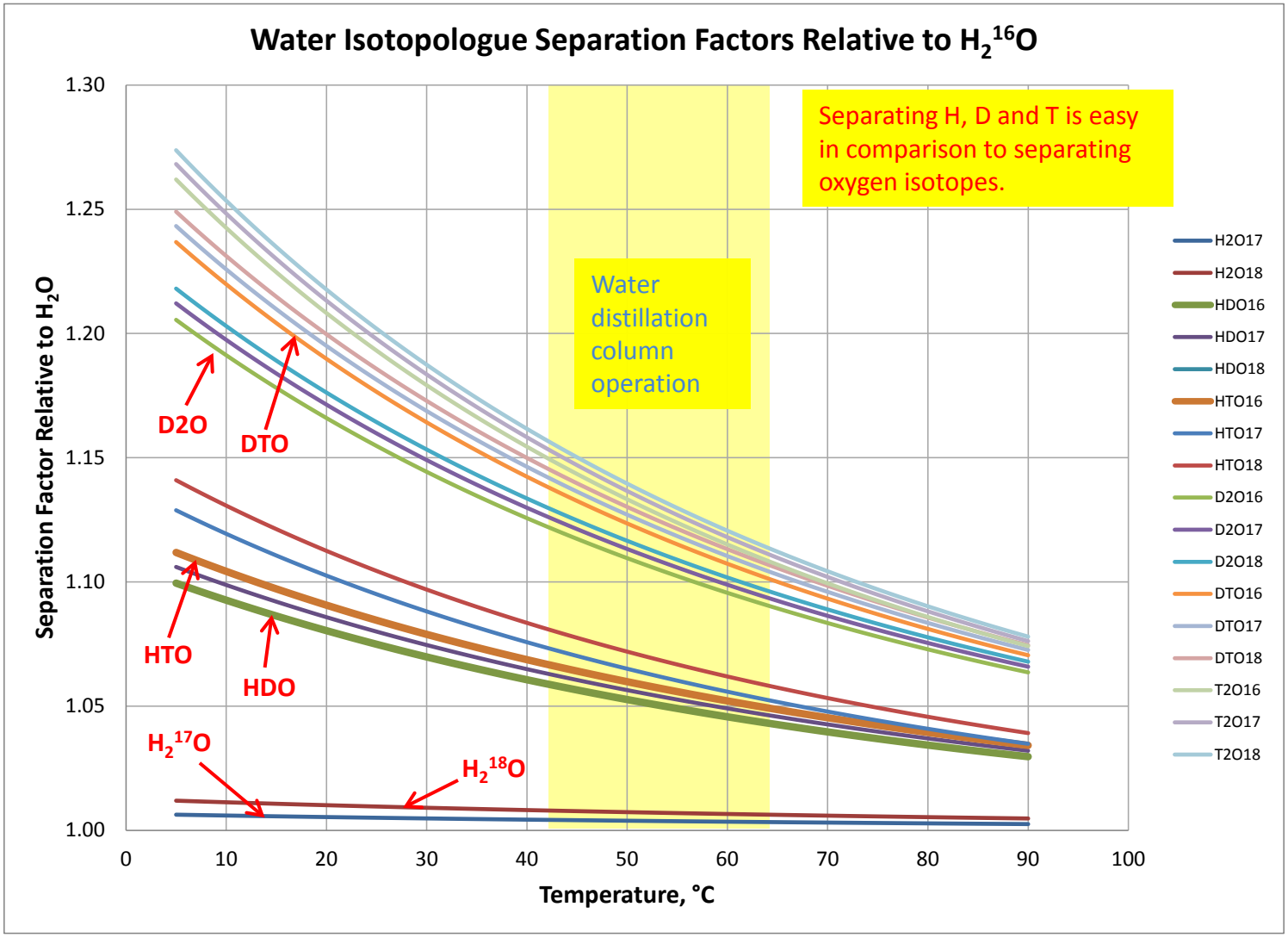
Presented at Tritium Focus Group Meeting, April 22-24, 2014, Aiken, SC

Presentation Objectives

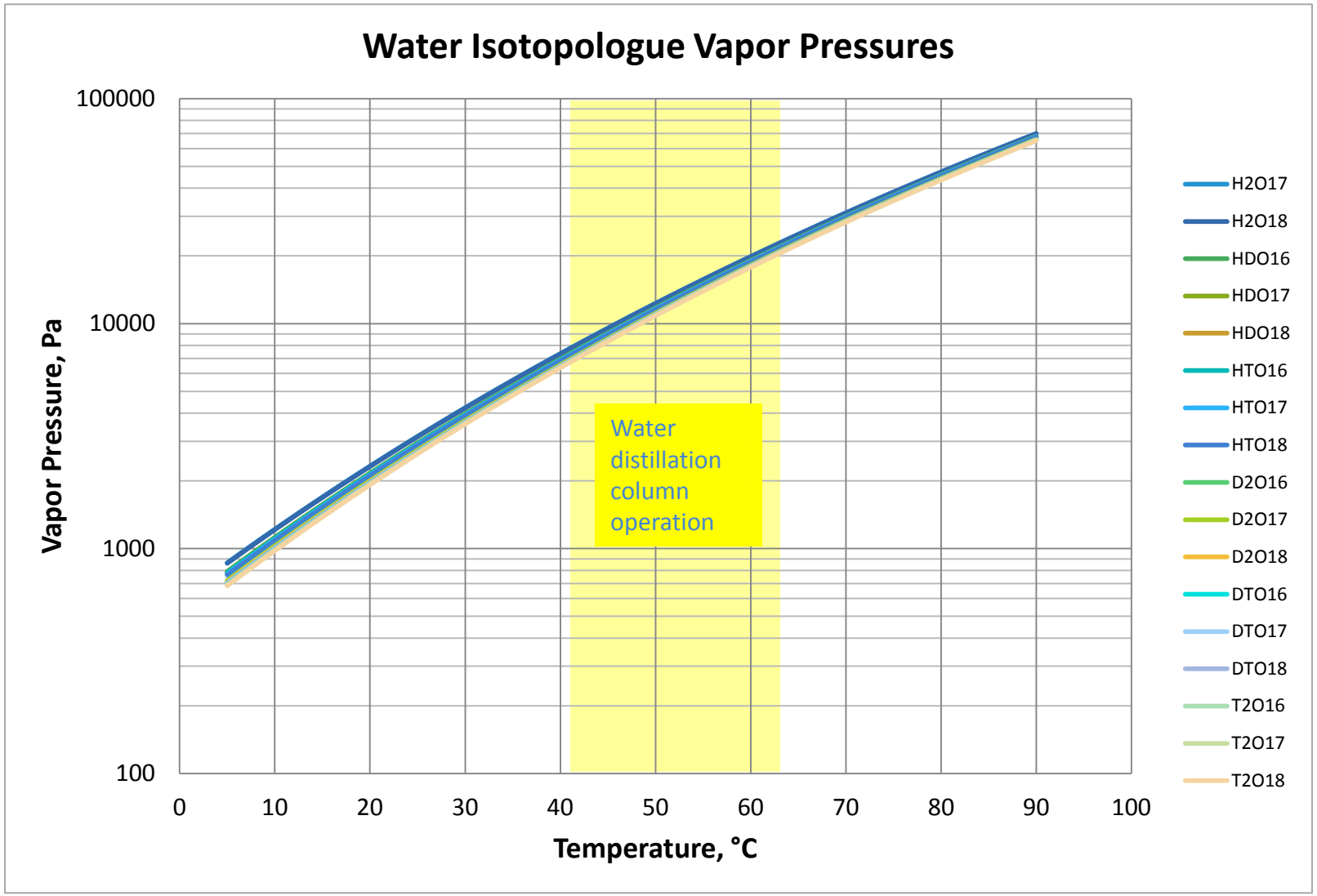
- ***Principles of operation***
  - Elementary separation factors
- ***Historical overview of technology***
  - Distillation and chemical exchange technologies for hydrogen isotope separation are 60+ years old
  - Focus will be on Water Distillation versus Combined Electrolysis and Chemical Exchange (CECE).
- ***Operational experience***
  - H/D, H/T and D/T separations
- ***Current technology characteristics***
  - Size, complexity, operation, safety, level of expertise required
- ***Applications for water detritiation:***
  - "lab-scale" (nominally 0.5 kg/h feed)
  - "industrial scale" (25 to 500 kg/h feed – CANDU scale)
- ***Relative size, cost, complexity, and scalability***

Water Distillation

Water Distillation Separation Factors



Water Distillation Operating Pressure

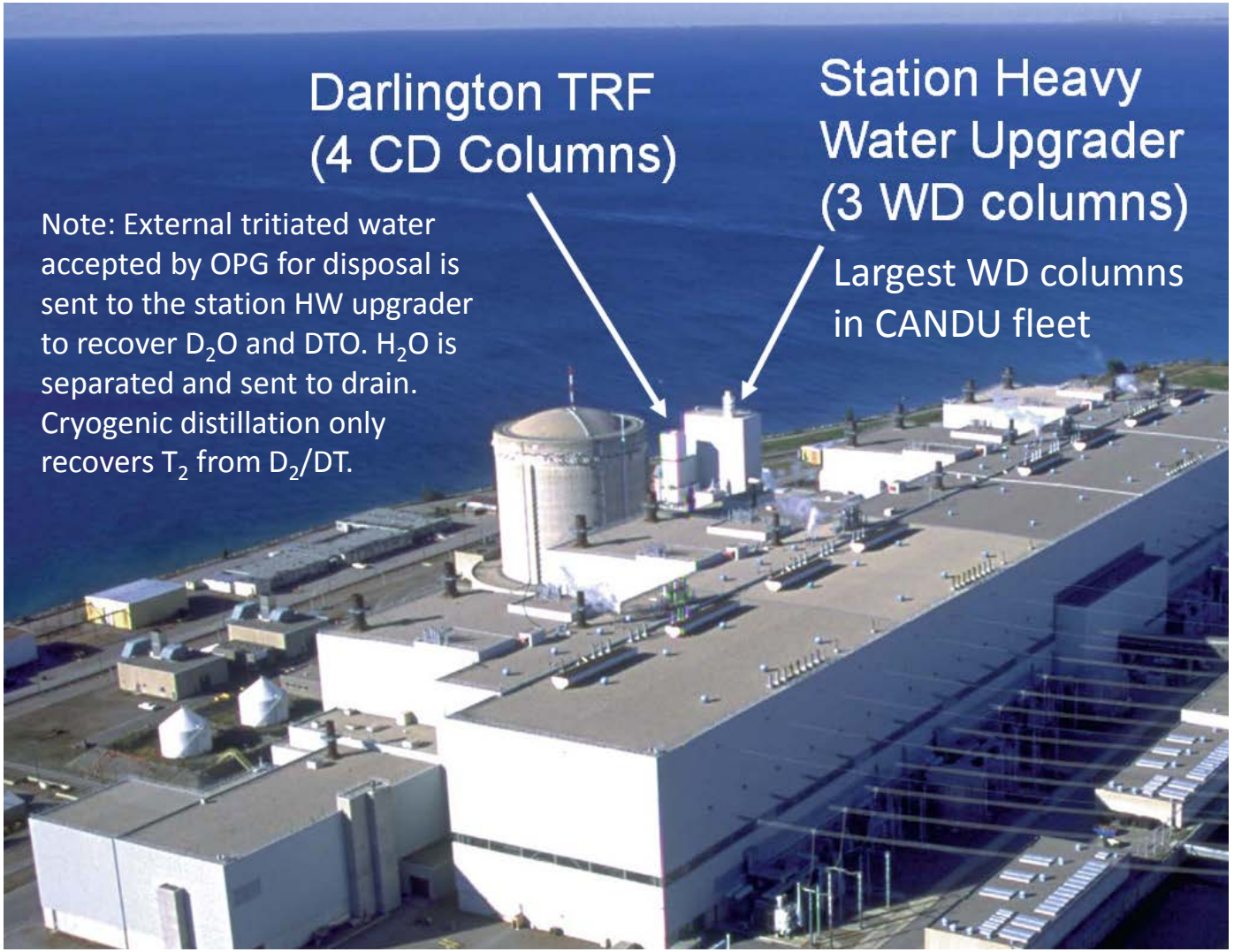


As Part of Overall Manhattan Project, Heavy Water Production was referred to as the "P-9 Project"

- Most of the heavy water produced during WW II was by water distillation.
- DuPont built heavy water production facilities at:
  - Morgantown Ordnance Works, near Morgantown, West Virginia;
  - Wabash River Ordnance Works, near Dana and Newport, Indiana;
  - Alabama Ordnance Works, near Childersburg and Sylacauga, Alabama
- ***WW II era water distillation systems were largest ever built***. They used bubble plate columns, which are much larger than current high efficiency packing technology.
- ***Design and construction was very fast***. For example, Morgantown decision to build was made December 1942, and equilibrium concentration levels were achieve in May 1944. **About two years for design, build, commission and startup!**

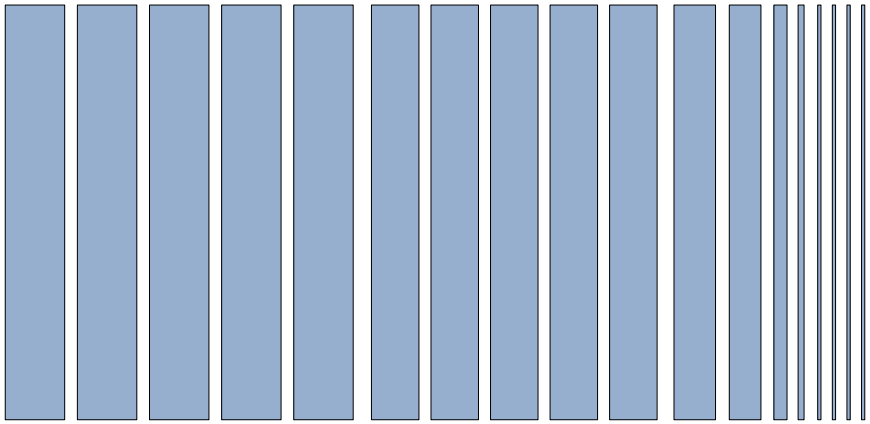
Morgantown, West Virginia, 1943

Modern (1980s) CANDU CD + WD



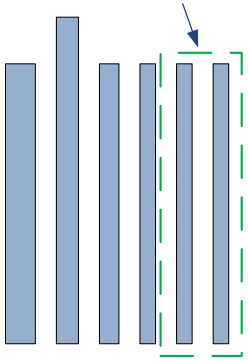
Industrial Scale Water Distillation

Built 1943-1944



Morgantown, W. VA., Distillation Plant for Heavy Water

Savannah River individual columns were similar in size to current large CANDU heavy water upgraders. ***However, CANDU upgraders use only two or three columns.***



Built Early 1950s

Used to upgrade heavy water from 20% to 90%.

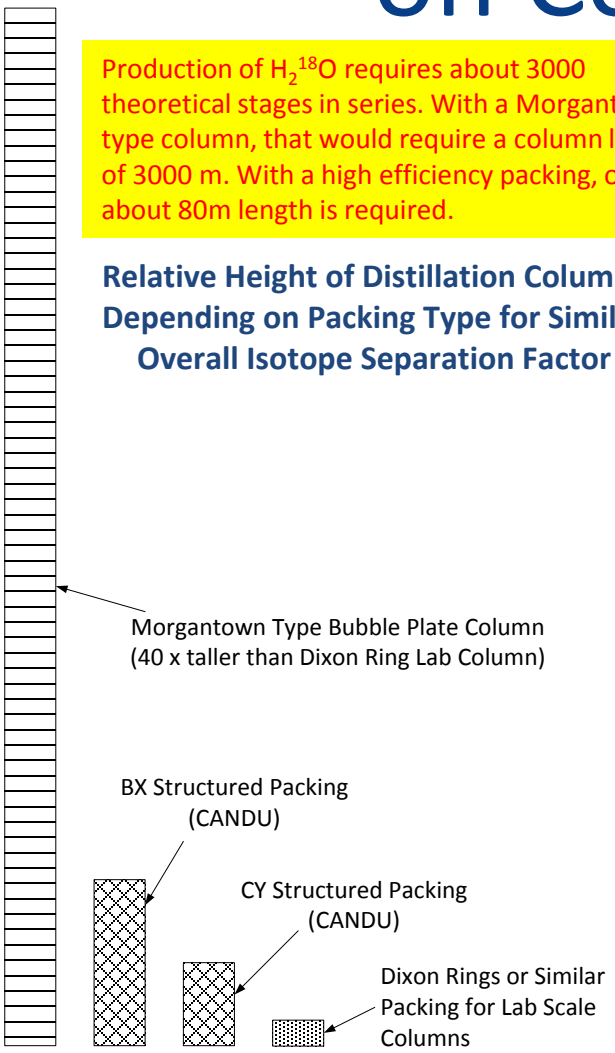
Savannah River Water Distillation Plant

- Large industrial columns create the impression that water distillation equipment is always very large and very expensive. ***However, the technology is much more compact at lab-scale throughput.***
- CANDU Heat Transport Upgraders routinely recover tritium and deuterium from mostly light water (typical feed is 70% light water, 30% heavy water, and about 1 Ci/kg tritium in the heavy water component).
- **CANDU Heat Transport Upgraders have been in continuous use since the 1960s, and are the most proven and successful method of large scale light water detritiation.**

WD High Efficiency Packing – Effect on Column Height

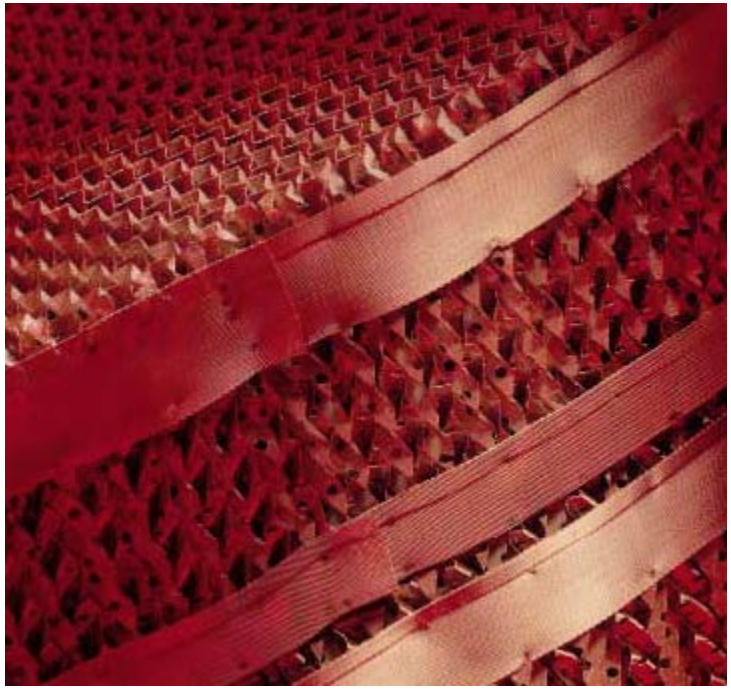
Production of $H_2{}^{18}O$ requires about 3000 theoretical stages in series. With a Morgantown type column, that would require a column length of 3000 m. With a high efficiency packing, only about 80m length is required.

Relative Height of Distillation Columns Depending on Packing Type for Similar Overall Isotope Separation Factor



- At small scale, up to about 0.1m diameter, packed columns can have very small Height Equivalent to a Theoretical Plate (HETP), in the range of 1.5 to 3 cm.
- Small diameter packed columns do not require liquid redistributors and manholes for maintenance of liquid redistributors, which further reduces height.
- ***Water distillation columns work really well at small diameter and small throughput!***

WD Structured Packing



- Wire gauze structured packing helps spread liquid by capillarity effect of wire gauze
- Structured packing performance scales well to large diameter columns, but it has greater HETP than high efficiency packing in small diameter laboratory columns.
- *Oxidized phosphor bronze packing is black in appearance*.

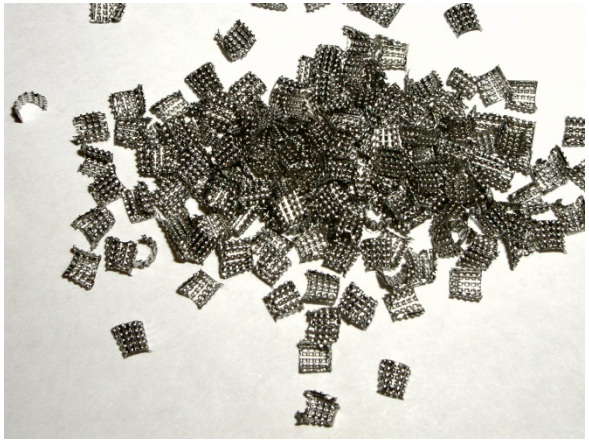
- **Sulzer CY type packing is the most proven packing for large scale water distillation.**
- **Koch Glitsch manufactures CY type packing in Wichita Kansas. They originally manufactured CY packing under license from Sulzer.**
- **Both Sulzer and Koch Glitsch manufacture high efficiency DX and EX structured packing for laboratory scale columns.**

Examples of High Efficiency WD Random Packing for Small Columns

Dixon Rings. For water distillation the material would be phosphor bronze, oxidized to have a black CuO coating.

Dixon Rings characteristics for water distillation were published from late 1940s to 1970s by I. Dostrovsky. Dixon Rings have been used commercially in water distillation to separate oxygen isotopes – a much more difficult separation than H/D/T separation.

Heli-Pack. Has high pressure drop for vacuum distillation, but small HETP.



Pro-Pack. Also used in commercial CO distillation for ^{13}C isotope separation.

Russian Spiral Prismatic Packing. Characterized and tested for water distillation at Petersburg Nuclear Physics Institute (PNPI). Performance characteristics such as HETP, pressure drop and liquid holdup published in 1990s, I. Alexeev et al.

Oxidized phosphor bronze packing (top) and stainless steel packing (bottom).

Scale-up of High Efficiency Small Columns, 1 of 2

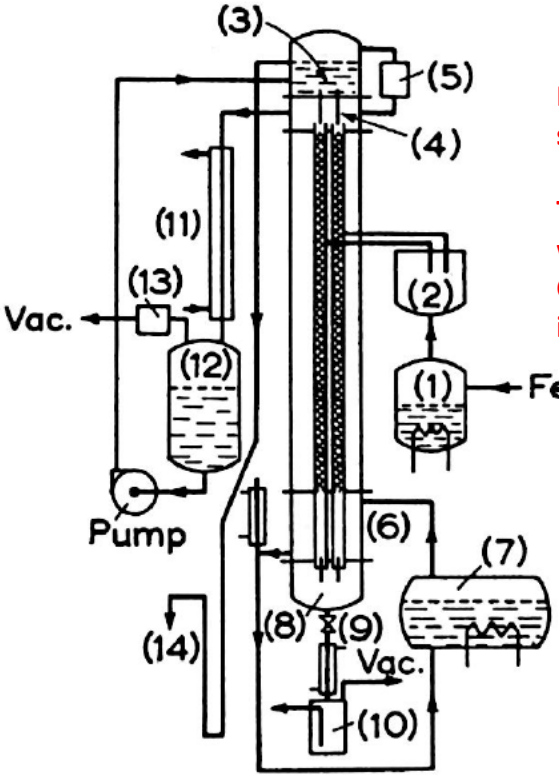


FIG. 2.—Pilot plant for the final concentration of D_2O (first stage).

Multiple columns in a single assembly.

The individual columns were called "Kuhn Columns" after the inventor.

Werner Kuhn, 1950s

P. Baertschi and W. Kuhn, 1956. Assembled multiple parallel small high efficiency columns at University of Basle, Zurich, Switzerland. Each column had a throughput of 0.1 kg/h and had 50 to 60 theoretical stages per meter. Prof. Kuhn worked with Sulzer Bros., Ltd., Winterthur on large assemblies of multiple columns. The approach was abandoned upon development of structured packing for large columns.

Multiple small single columns were used for many years for oxygen isotope separation at the Weizmann Institute and later Rotem Industries in Israel.

Prof. Israel Dostrovsky was a contemporary of Prof. Werner Kuhn. Most of the basic R&D work was done in the 1940s and 1950s.

Multiple columns connected together in series and parallel.

Almost all the ^{18}O produced in the world today uses water distillation for isotope separation.

Scale-up of High Efficiency Small Columns, 2 of 2

GST Plant 1, Sosnovy Bor, Russia – water distillation for oxygen isotopes.

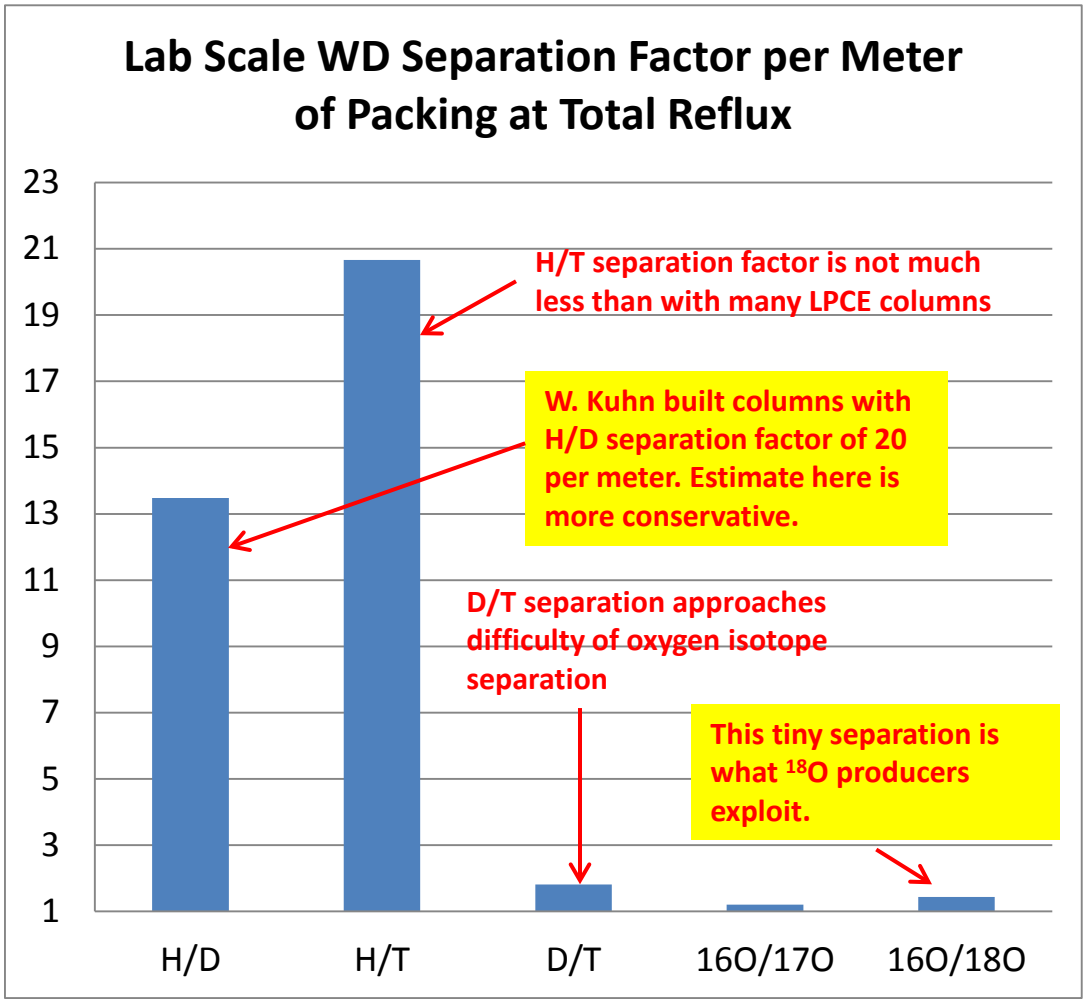
Multiple individual columns connected together.

GST Plant 2, Sosnovy Bor, Russia – water distillation for oxygen isotopes.

Global Scientific Technologies in St. Petersburg, Russia area is one of the world's largest producers of ^{18}O by water distillation.

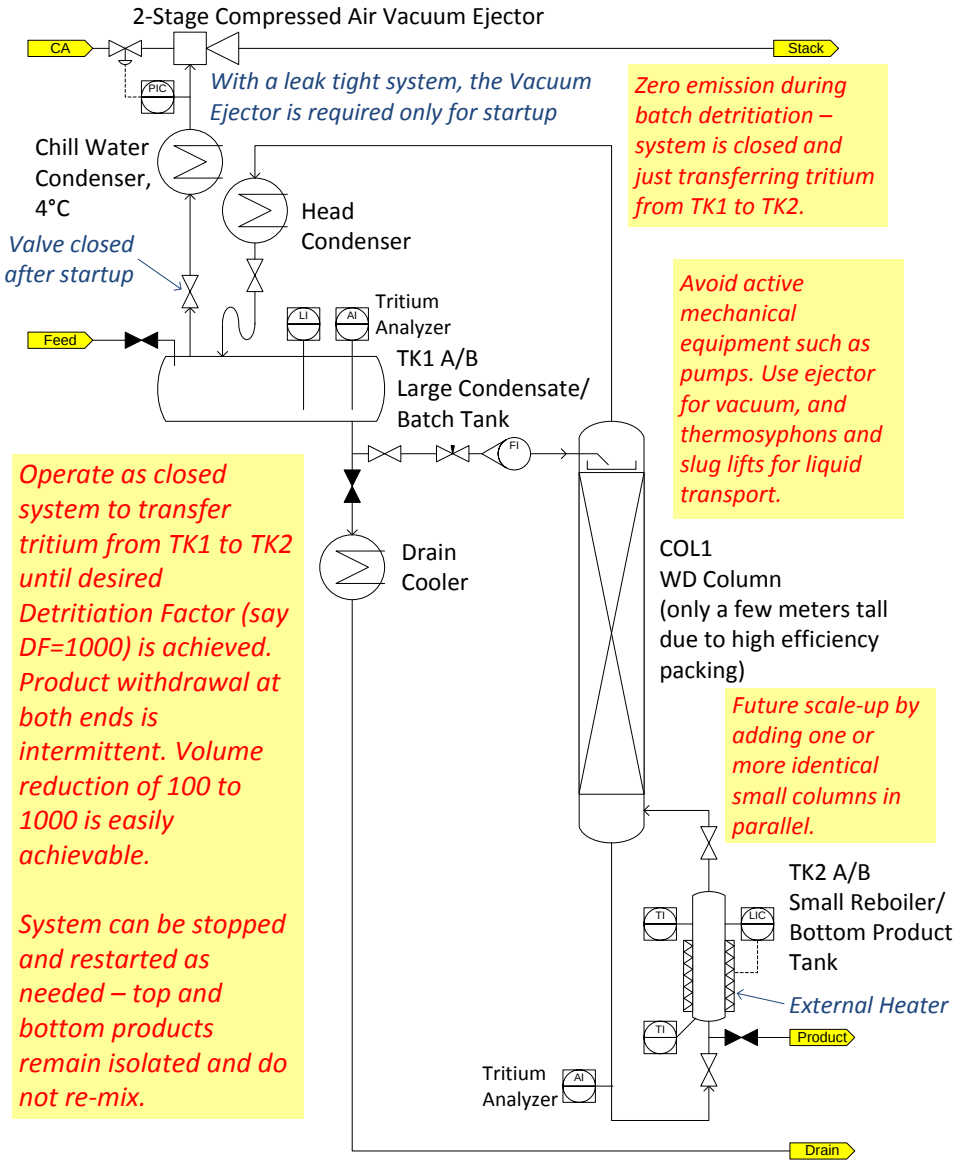
From: G. Vasaru, "SEPARATION OF HEAVY OXYGEN ISOTOPES"

Characteristic of High Efficiency Water Distillation for Isotope Separation



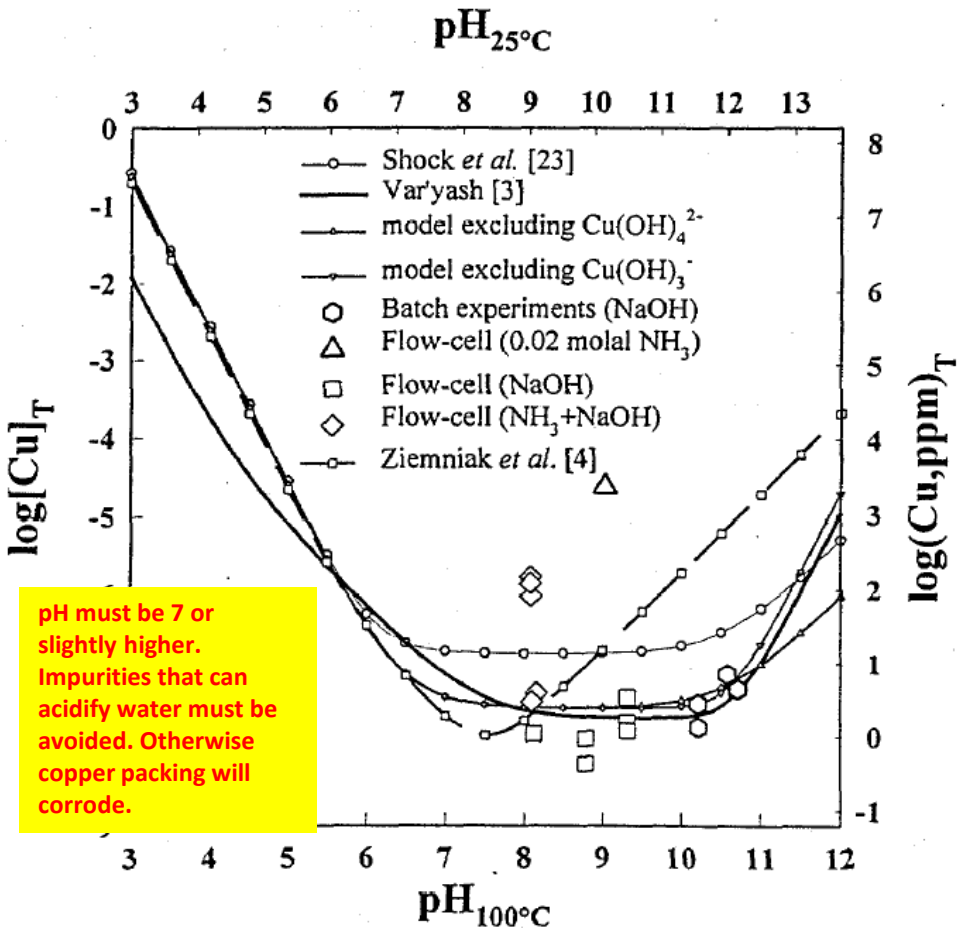
- Energy cost ≈ 20 kWh (thermal) per kg of water feed - simplest system for H/D or H/T separation
- Energy cost ≈ 2 kWh per kg of water feed with heat pump
- Vacuum distillation is practically emission free
- There are no cryogens, no flammable gases, benign temperature and pressure, and no hazardous chemicals
- Light water detritiation can enrich T by a factor of 2000 before D significantly interferes
- Throughput for D_2O/DTO separation is 1/5-th that for H_2O/HDO separation. Also, more column height is required for the same overall separation factor.

Simplest Lab Scale WD Detritiation System



- Batch operation is simplest for unattended operation. A practical system may have DF = 100 to 1000 times, and volume reduction of 100 to 2000 times.
- Passive operation with no moving parts
- Zero emission during the batch operation – evacuation required only at start-up.
- No tritium permeation into metal as with elemental tritium. Simple decontamination.
- System can be stopped and restarted (i.e. power outage) without remixing of products
- No chemistry or electrolyte handling – a pure water system. Water purity can be tested before starting a batch.

Water Distillation – R&D



pH must be 7 or slightly higher. Impurities that can acidify water must be avoided. Otherwise copper packing will corrode.

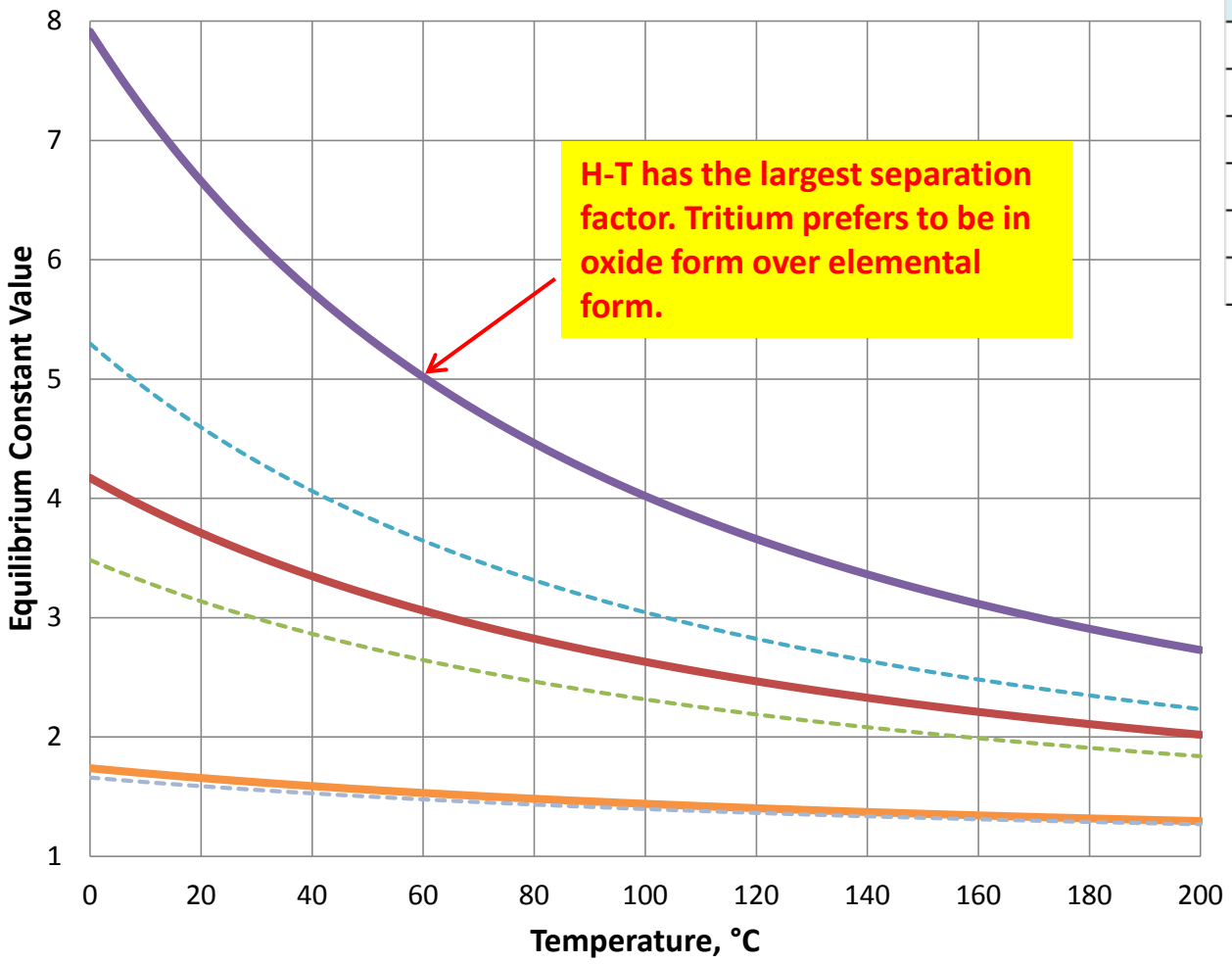
The solubility profile of CuO at 100°C and infinite dilution.

From: D. A. Palmer, P. Benezeth, J. M. Simonson, A. Petrov, "Transport and Chemistry of Copper in Power Plants as Determined by Laboratory Experiments", available at http://www.ntis.gov/search/product.aspx?ABBR=DE2001771414

- Technology is proven – little new work has been done in the last 40 years. Operational experience continues to accumulate with CANDU heavy water upgraders using Sulzer structured packing. There have been no new projects in Canada since the 1980s. There is little incentive for design improvements. since the technology works well.
- The only significant technical issue is feed water purity. CANDU heavy water upgraders have excellent reliability as long as the feed water is very pure.
- Occasional performance problems have been due to poor chemistry control, with the result that packing corrosion products block liquid redistributor holes.
- ***Small, high efficiency columns don't require internal liquid redistributors, so they don't have the same susceptibility as CANDU upgraders. The liquid distributor for condensate at top of column is not exposed to packing corrosion products***.

Combined Electrolysis and Chemical Exchange (CECE)

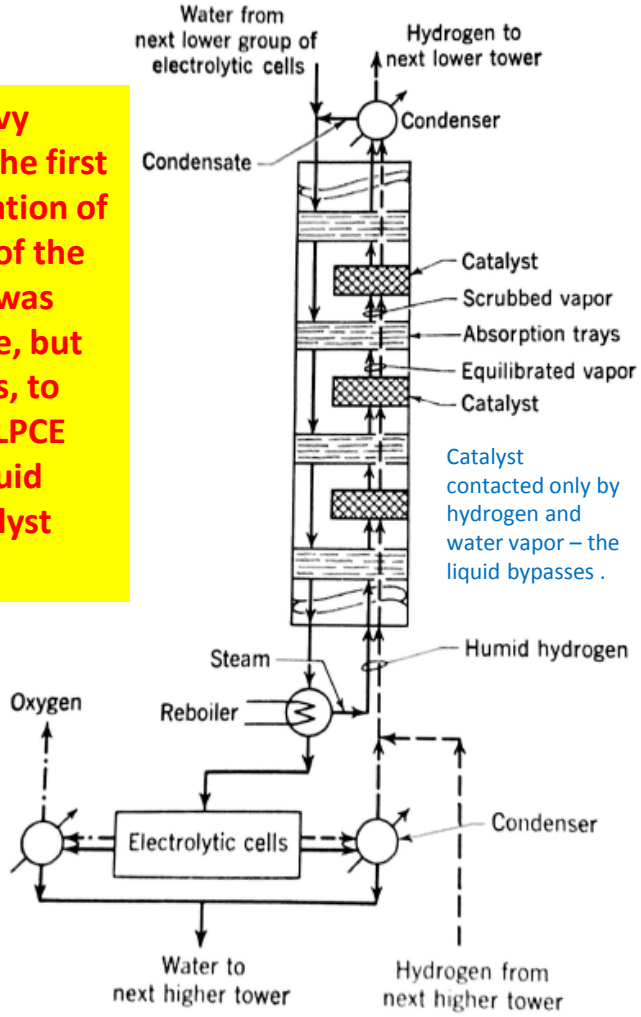
Chemical Exchange Separation Factors



Reaction	K Name
$H_2O + HD = HDO + H_2$	$K_{HD,HDO}$
$HDO + D_2 = D_2O + HD$	$K_{DH,DHO}$
$H_2O + HT = HTO + H_2$	$K_{HT,HTO}$
$HTO + T_2 = T_2O + HT$	$K_{TH,THO}$
$D_2O + DT = DTO + D_2$	$K_{DT,DTO}$
$DTO + T_2 = T_2O + DT$	$K_{TD,TDO}$

Trail, British Columbia, Canada, 1945 Cominco, Manhattan Project

The Trail B.C. Heavy Water Plant was the first large scale application of CECE. The design of the column internals was similar in principle, but different in details, to the Wolsong TRF LPCE column where liquid bypasses the catalyst beds.



Source: http://www.waymarking.com/gallery/image.aspx?f=1&guid=ae0900d3-d0f3-4b78-af0c-0e6fa455d384

Development of Hydrophobic Catalyst, 1970s

Novel Catalysts for Isotopic Exchange between Hydrogen and Liquid Water

J. P. BUTLER, J. H. ROLSTON, and W. H. STEVENS

Atomic Energy of Canada Ltd., Chalk River Nuclear Laboratories, Physical Chemistry Branch, Chalk River, Ontario K0J 1J0

Catalytic Detritiation of Water

M. L. ROGERS, P. H. LAMBERGER, R. E. ELLIS, and T. K. MILLS

Monsanto Research Corp., Mound Laboratory*, Miamisburg, OH 45342

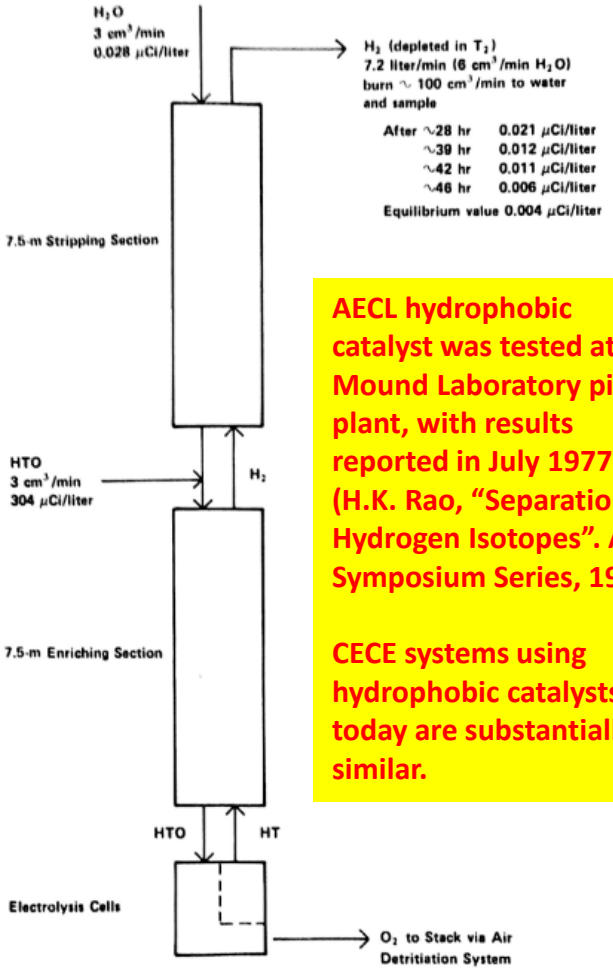


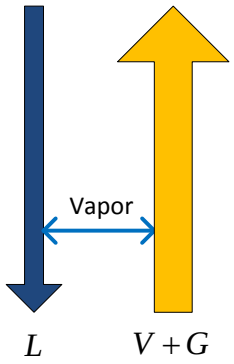
Figure 3. Preliminary results combined electrolysis catalytic exchange system (CECE)

AECL hydrophobic catalyst was tested at Mound Laboratory pilot plant, with results reported in July 1977. (H.K. Rao, "Separation of Hydrogen Isotopes". ACS Symposium Series, 1977)

CECE systems using hydrophobic catalysts today are substantially similar.

LPCE Overall Mass Transfer Coefficient Film Theory

Deuterium or Tritium Removal from Gas by Water Scrubber



$$V\frac{dy_{\text{vap},i}}{dz}=\left(\frac{\theta}{1-\theta}\right)G\frac{dy_{\text{vap},i}}{dz}=K_y a\left(y_{\text{vap},i}-y^*_{\text{vap},i}\right)=K_y a\left(y_{\text{vap},i}-m_D x_i\right)$$

$$\frac{1}{K_y a}=\frac{1}{k_y a}+\frac{m_D}{k_x a}$$

$$\frac{1}{K_x a}=\frac{1}{m_D k_y a}+\frac{1}{k_x a}$$

$i =$ H, D or T

$y_i =$ atom fraction of i in Q_2 gas

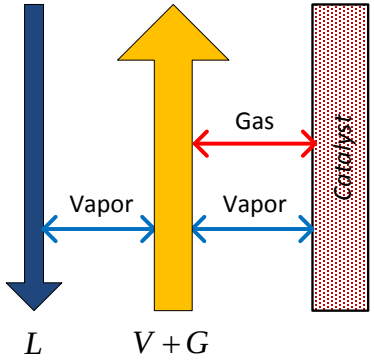
$y_{\text{vap},i} =$ atom fraction of i in Q_2O vapor

$a =$ surface area of liquid vapor/gas interface, m^2/m^3

$\theta = V/(V+G)$ and $V = G\theta/(1-\theta)$

LPCE mass transfer modeling is more complicated than simple countercurrent exchange between liquid and gas/ vapor.

Liquid Phase Catalytic Exchange Column



Effect of water vapor back-mixing. This is an exact expression, not an approximation.

$$G\frac{dy_i}{dz}=\left[1-\frac{m_{D,i}V}{L}\right]K_{y,i}\bar{a}\left(y^*_{\text{vap},R,i}-y^*_{\text{vap},D,i}\right)$$

$$=\underbrace{\frac{1}{m_{R,i}}\left[1-\frac{m_{D,i}V}{L}\right]K_{y,i}\bar{a}}_{k_i}\left(y_i-\underbrace{\frac{m_{D,i}}{m_{R,i}}}_{m_i}x_i\right)$$

Slope of equilibrium line

The "overall" mass transfer coefficient

$$=k_i\left(y_i-m_i x_i\right)=\frac{k_i'}{m_{R,i}}\left(y_i-m_i x_i\right)$$

Overall mass transfer coefficient - water vapor basis.

$$y^*_{\text{vap},D,i}=m_{D,i}x_i$$

$$y_i=m_{R,i}y^*_{\text{vap},R,i}$$

$$y^*_{\text{vap},R,i}=\frac{y_i}{m_{R,i}}$$

$$\frac{1}{\bar{a}}=\frac{1}{a_D}+\frac{1}{a_C}$$

Catalyst area a_C is actually not the whole picture of what's happening. If there is a catalyst reaction rate limitation, a_C will appear to decrease with increased flow, because reaction rate cannot increase as we decrease fluid mass transfer resistance with flow/velocity.

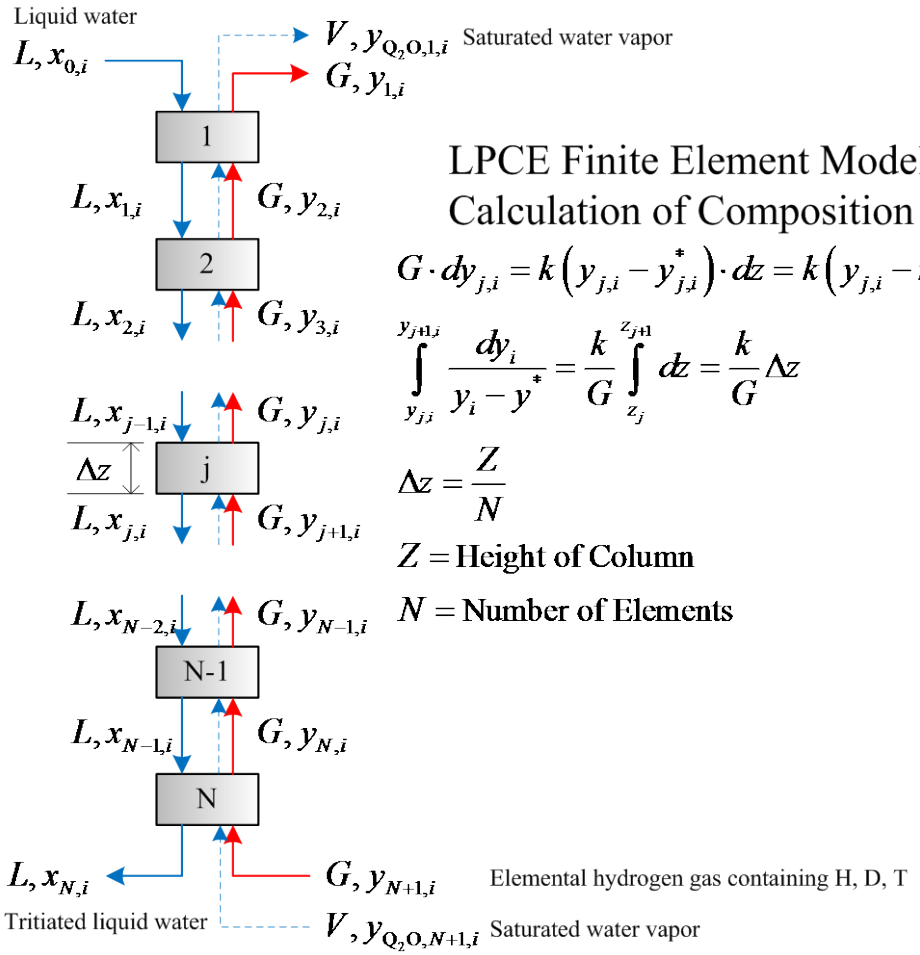
$m_D =$ slope of equilibrium line at liquid-vapor/gas interface

$m_T =$ slope of equilibrium line at vapor/gas-catalyst interface

$a_D =$ surface area of liquid vapor interface, m^2/m^3

$a_C =$ surface area of catalyst, m^2/m^3

Solving Differential Equations for Column Composition Profiles – Finite Element Method



LPCE Finite Element Model
Calculation of Composition Change

$$G \cdot dy_{j,i} = k\left(y_{j,i} - y^*_{j,i}\right) \cdot dz = k\left(y_{j,i} - \bar{m}_{j,i} x_{j,i}\right)$$

$$\int_{y_{j,i}}^{y_{j+1,i}} \frac{dy_i}{y_i - y^*} = \frac{k}{G} \int_{z_j}^{z_{j+1}} dz = \frac{k}{G} \Delta z$$

$$\Delta z = \frac{Z}{N}$$

Z = Height of Column

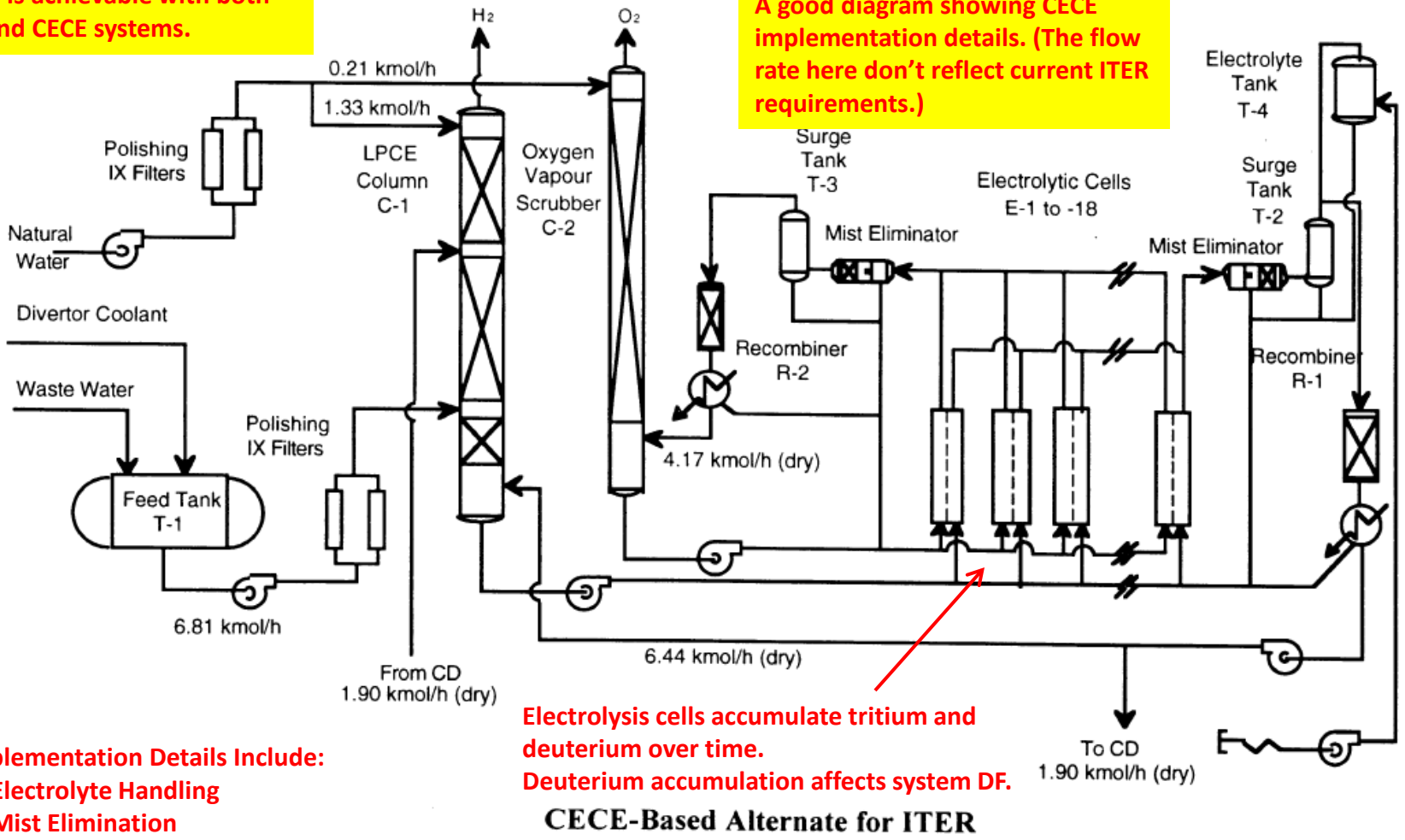
N = Number of Elements

- Replace derivatives in differential equations by finite difference approximations.
- Differential equations are converted to a system of algebraic equations.
- Each increment of column height $\Delta z = Z/N$ (m) is a finite element. Here, Z is column height, and N is the number of finite elements.
- In the limit $N \to \infty$, the finite element solution converges to the exact solution, subject to round-off error.

The main advantage of CECE over WD is smaller size of the LPCE column versus a WD column. A very high detritiation factor is achievable with both WD and CECE systems.

CECE System Details

A good diagram showing CECE implementation details. (The flow rate here don't reflect current ITER requirements.)



Electrolysis cells accumulate tritium and deuterium over time.
Deuterium accumulation affects system DF.

CECE-Based Alternate for ITER

D.A. Spagnolo and A.I. Miller, Fusion Technology, Vol 28, 748-754 (1995)

Implementation Details Include:

- Electrolyte Handling
- Mist Elimination
- Recombination of trace O_2 in hydrogen and trace Q_2 (Q = H, D or T) in oxygen
- Liquid pumps
- Gas Circulation Pump

CECE – R&D

- NSSI in Texas has recently operated a CECE plant for heavy water detritiation in campaigns. NSSI's accumulating experience is very helpful to demonstrate CECE technology with current catalyst and electrolysers.

- AECL has successfully demonstrated CECE in pilot plants over many years, and has proven wet-proof catalyst. AECL has proposed CECE for CANDU heavy water upgrading in future nuclear power stations as well as for ITER.

- ITER will use CECE for their Water Detritiation System and has supported R&D into catalyst testing, electrolyser testing, and CECE operation.

- R&D continues into improved catalysts (Canada, Russia, South Korea, China, etc.)

- Long term electrolyser tritium compatibility at high tritium levels requires more demonstration.

WD vs CECE Column Packing/Catalyst Size, 1 of 2

F = liquid water feed rate to column (kg h^{-1})

$N_{min} = \frac{\ln(S)}{\alpha} =$ minimum number of equilibrium stages to achieve separation factor S

$N_{ideal} = 2N_{min} =$ number of stages in an ideal cascade/column

$H = \text{HETP} \times N_{ideal} =$ height of column (m)

(HETP = height equivalent to a theoretical plate – a measured value (m))

$R_{min,WD} \approx \frac{1}{\alpha_{WD} - 1} =$ WD minimum reflux ratio required to strip all tritium from feed liquid

$R_{min,LPCE} \approx \frac{1}{1-\theta} \times \frac{1}{\alpha_{LPCE} - 1} =$ LPCE minimum reflux ratio, accounting for vapor fraction θ

$R = 2 \times R_{min} =$ practical reflux ratio for column/cascade

$D = \left[\frac{4RF}{\pi L}\right]^{\frac{1}{2}} =$ column diameter (m), where $L =$ liquid loading (kg $h^{-1}m^{-2}$)

$V = H \times \frac{\pi}{4} D^2 =$ packing or catalyst volume (m^3)

WD vs CECE Column Packing/Catalyst Size, 2 of 2
Lab Scale WD vs CECE Relative Column Sizes

$$\frac{H_{\mathrm{WD}}}{H_{\mathrm{LPCE}}} \approx 1.9$$

$$\frac{D_{\mathrm{WD}}}{D_{\mathrm{LPCE}}} \approx 3.9$$

$$\frac{V_{\mathrm{WD}}}{V_{\mathrm{LPCE}}} \approx 29$$

Energy consumption of WD and CECE is of the same order of magnitude.
With heat pumping, WD energy consumption is lower.

Due to a larger separation factor an LPCE column is shorter and narrower in comparison to a WD column.

But the WD column is simpler:

- **no electrolyser**
- **no electrolyte management**
- **can have no pumps**
- **no oxygen scrubbing**
- **no hydrogen explosion hazard**
- **can operate emission free in batch mode as closed system**
- **decommissioning and decontamination is easier since there is no tritium permeation into metal**
- **WD column is taller, but floor footprint for CECE is larger due to more equipment**

Which is better for a given application?

- **It's a judgment call**
- **So far, CANDU power stations have preferred WD to CECE. Reduced column size at the expense of complexity is a tough sell for nuclear plant operators.**
- **^{18}O producers have also preferred WD to more complex chemical exchange systems or cryogenic distillation with larger elementary separation factors.**
- **ITER has selected CECE technology for their WDS.**

Cost and lifetime:

- **WD overall cost may be less because packing doesn't use platinum catalyst and lifetime operation and maintenance is less.**
- **WD packing can be expected to last 50 years. LPCE catalyst in contact with liquid water may need to be replaced every 5 to 10 years? Spent catalyst will be tritiated, making recovery of platinum difficult.**

Summary and Conclusions

- Both WD and CECE originated as heavy water production technology in the 1940s.
- The largest light water detritiation systems in the world are CANDU heat transport system heavy water upgraders, although detritiation is not their primary function.
- The LPCE columns in CECE systems are considerably smaller than similar throughput WD columns, but CECE systems are much more complex – the tradeoff is size versus complexity.
- **Choice of technology needs to weight the pros and cons of each technology – WD and CECE are both competitive technologies.**