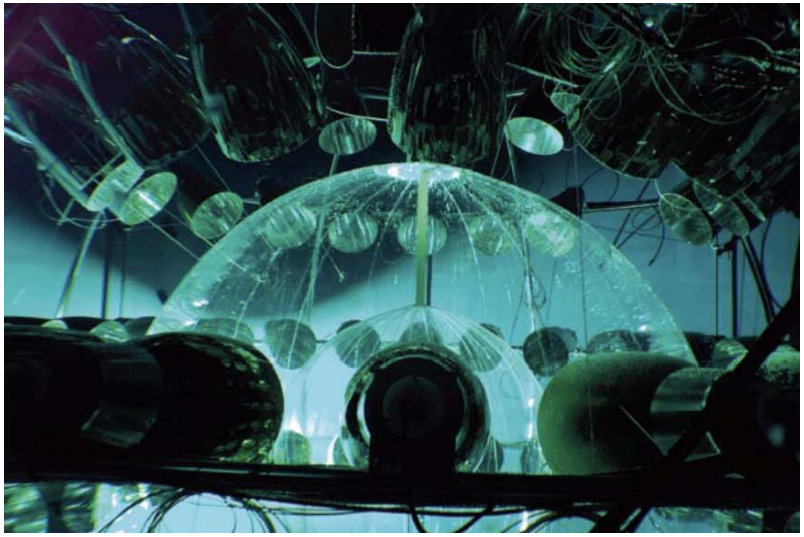
Organic Liquid Scintillators and Purification for Large Low-Background Detectors

LRT2019 Jaca, Spain

Richard Ford
SNOLAB

20th May 2019

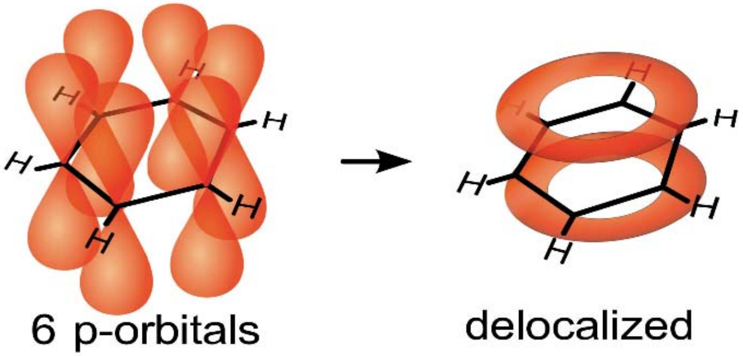


Borexino CTF

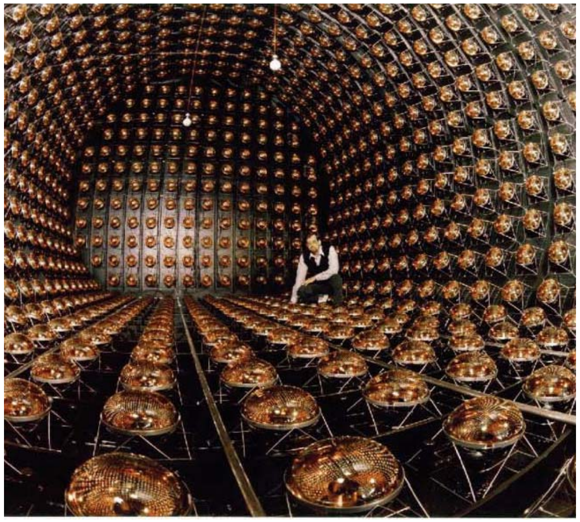
Why Use Liquid Organic Scintillator?

For rare-event detectors - the detector is the target, or active shield (either electrons, nucleons, or nuclei)

Best organic scintillators are aromatic hydrocarbons. The delocalized electron ring structure has high density of states to efficiently absorb ionizing radiation into optical transitions.



- Good light yield (compared to Cerenkov):
  - ✓ Low threshold
  - ✓ Good energy resolution
- Fast response:
  - ✓ Low dead time, less pile-up
  - ✓ Good position resolution → bigger fiducial volume
  - ✓ Pulse-shape discrimination → background discrimination



Other features:

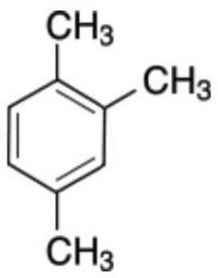
- ➢ Good attenuation length → good detector light yield
- ➢ Light nuclei (C, N, O, H) → no cosmic ray activation
- ➢ Hydrocarbons don't leach/dissolve heavy metals → high purity
- ➢ Relatively inexpensive to get very large detector mass
- ➢ As solvent, can add/change fluors, double-beta isotopes etc.
- ➢ As liquid:
  - ✓ Easy to fill and empty detector, and recirculate to purify
  - ✓ Several options for chemical processing and purification

But …

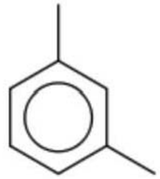
- ❑ Hydrocarbon solvents are typically:
  - ▪ Flammable, and low flashpoint
  - ▪ OH&S issues – Carcinogenic
  - ▪ Harmful to environment
- ❑ Susceptible to impurities, eg. O_2 – electronegative and can quench light emission. Also can oxidize solvent resulting in attenuation.

Liquid Scintillator Components

- Luminescent solvent

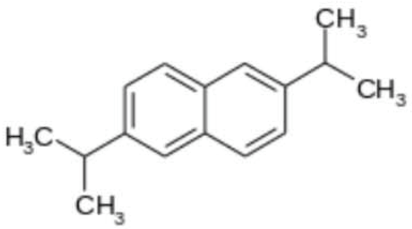


pseudocumene

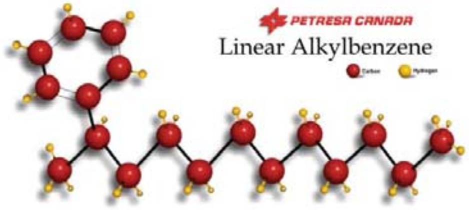


1,3-dimethylbenzene
(*meta*-xylene)

xylene

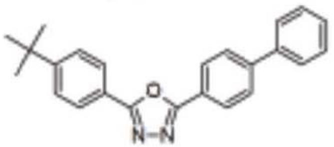


DIN

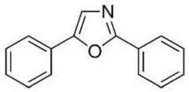


LAB

- Primary Fluor (wavelength shifter – none radiative transfer)

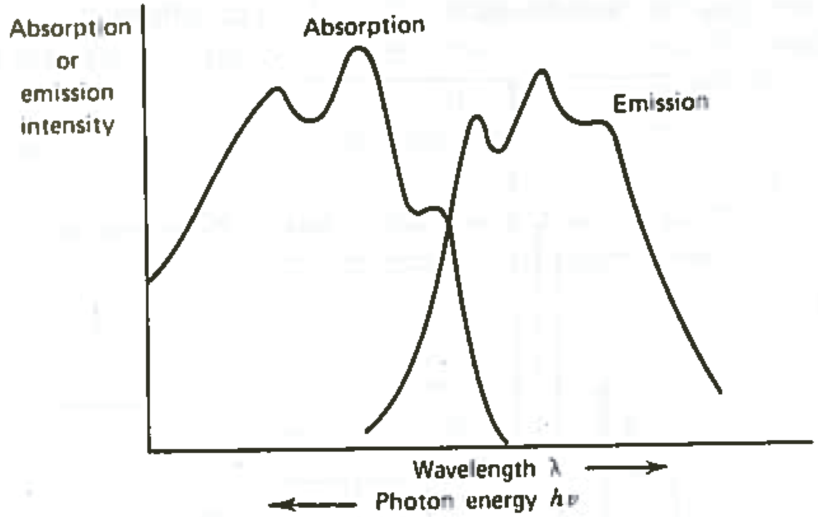


butyl-PBD



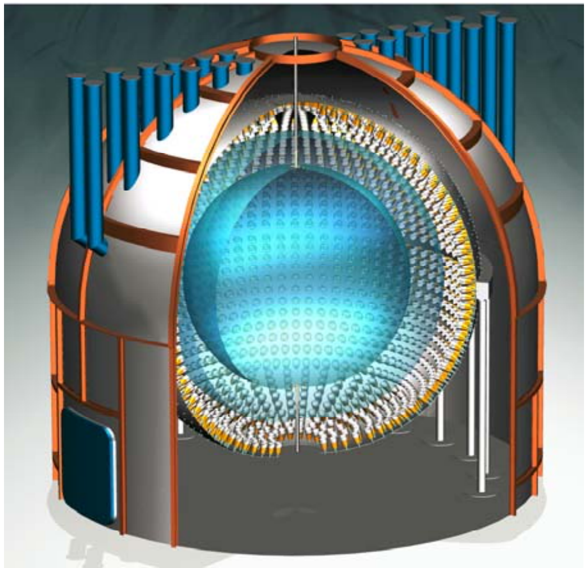
PPO

p-terphenyl



- Secondary Fluor – eg. bis-MSB

Large Low-Background Liquid Scintillator Detectors

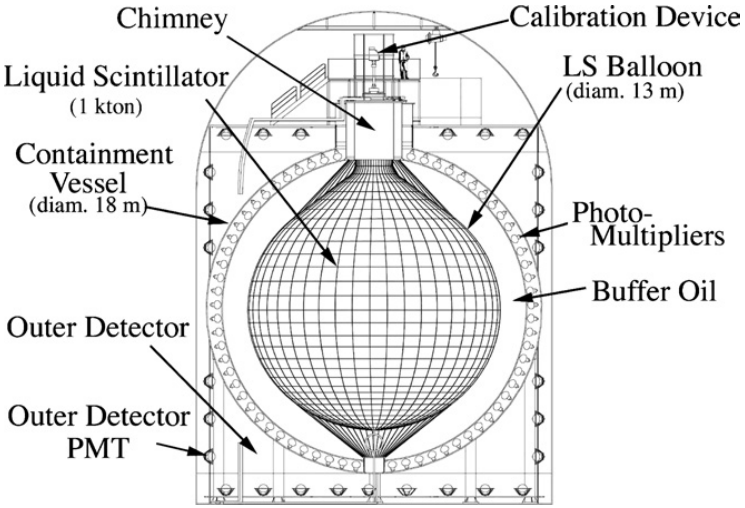


Borexino

Solar Neutrino Detector

Scintillator:

Pseudocumine (PC) + PPO



Kamland

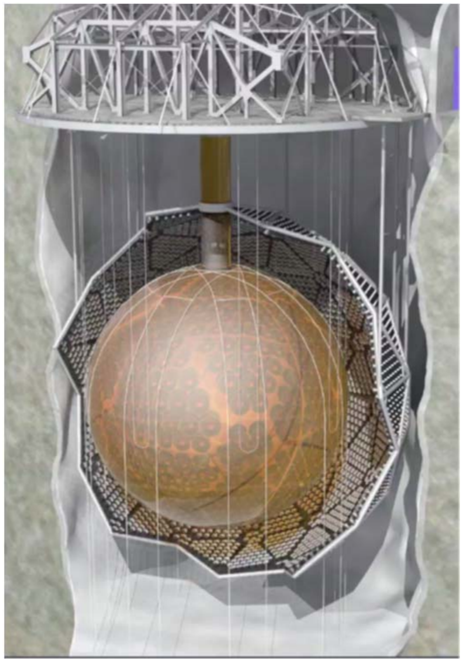
Reactor Anti-Neutrino Detector

and $0\nu\beta\beta$ with ^{136}Xe

Scintillator:

Pseudocumine (PC) + PPO

+ Dodocane



SNO+

Solar Neutrino Detector

and $0\nu\beta\beta$ with ^{130}Te

Scintillator:

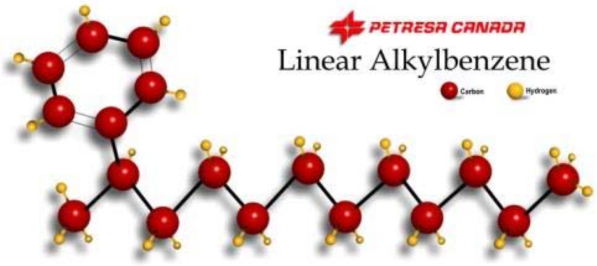
Linear Alkylbenzene (LAB)

+ PPO

SNO+ Scintillator

- Linear alkylbenzene (LAB) for the liquid scintillator solvent:
  - Chemical compatibility with acrylic
  - High light yield
  - High purity available
  - Safe
    - Low toxicity
    - High flash point 140°C
    - Boiling point 278-314°C
    - Environmentally safe (bio-degrades)
    - Low solubility in water 0.041 mg/L
  - Inexpensive
  - Suitable density $\rho = 0.86$ g/cm^3

- PPO for the wavelength shifter:
  - Common “whitening” or marker dye
  - Low toxicity
  - Melting point 72°C, boiling point 360°C



Cepsa Plant – Bécancour, QC

SNO+ Scintillator Purification

Purification processes:

- Distillation
  - ✓ Improve optical transparency and remove heavy metals
- Gas stripping
  - ✓ Remove dissolved gases (oxygen, radon, argon, krypton)
- Solvent-solvent extraction with water
  - ✓ Remove ionic radioactive metals
- Metal scavenger
  - ✓ Functional chelation of heavy metals
- Micro-filtration
  - ✓ Remove suspended particulate

Target levels:

Th: 10^{-17} g/g

U (Rn): 10^{-17} g/g

^{40}K: 1.3×10^{-18} g/g

^{85}Kr, ^{39}Ar: < 100 cpd

Plant Design Constraints

The challenge was to design and build a plant similar to a small hydrocarbon/chemical refinery (160/1250 bpd), except in a mine ……

Requirements:

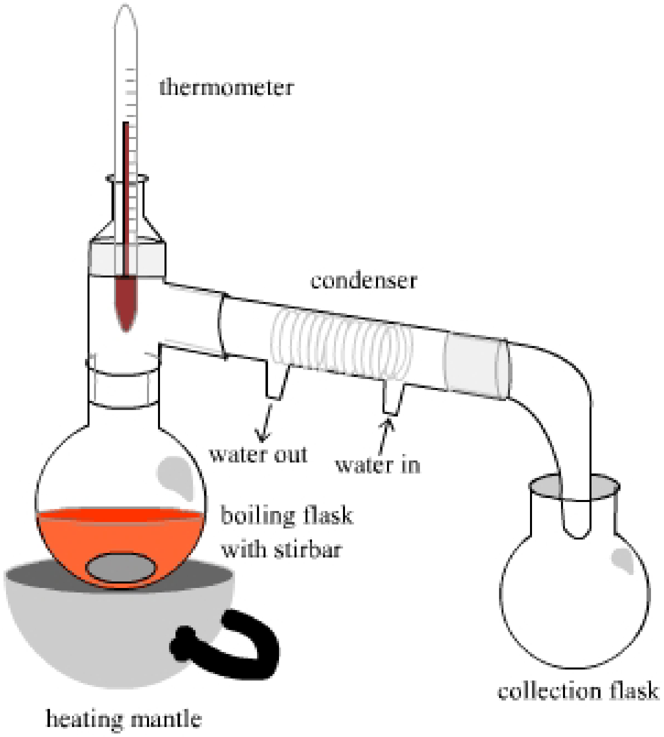
- High chemical process efficiency needed to obtain ~10^{-6} purification.
- High flow capacity (process detector in ~1 week)
- Stringent materials of construction requirement to obtain purity.
- Clean construction and high purity cleaning to obtain process purity.
- Design and maintain plant as high-vacuum system for Rn, Kr, Ar ingress.
- Do all this underground!!

Some of the constraints:

- Space available is highly constrained.
- Vertical height constraint (for equilibrium stages, pumps NPSH, etc).
- Power available constraint (realistically <500kW at SNOLAB).
- Cooling constraint – all process cooling goes to the SNOLAB chiller.
- Fire protection challenge unique in a mine.
- Liquid nitrogen limited by logistics of delivery underground.
- Seismicity – must be safe in case of earth-quake and rock burst events.

Distillation: benchtop vs column

"Bench-top" (laboratory scale) distillation is quite different from continuous multistage tower distillation. A small batch distillation cannot show the efficacy of the fractionating distillation process.



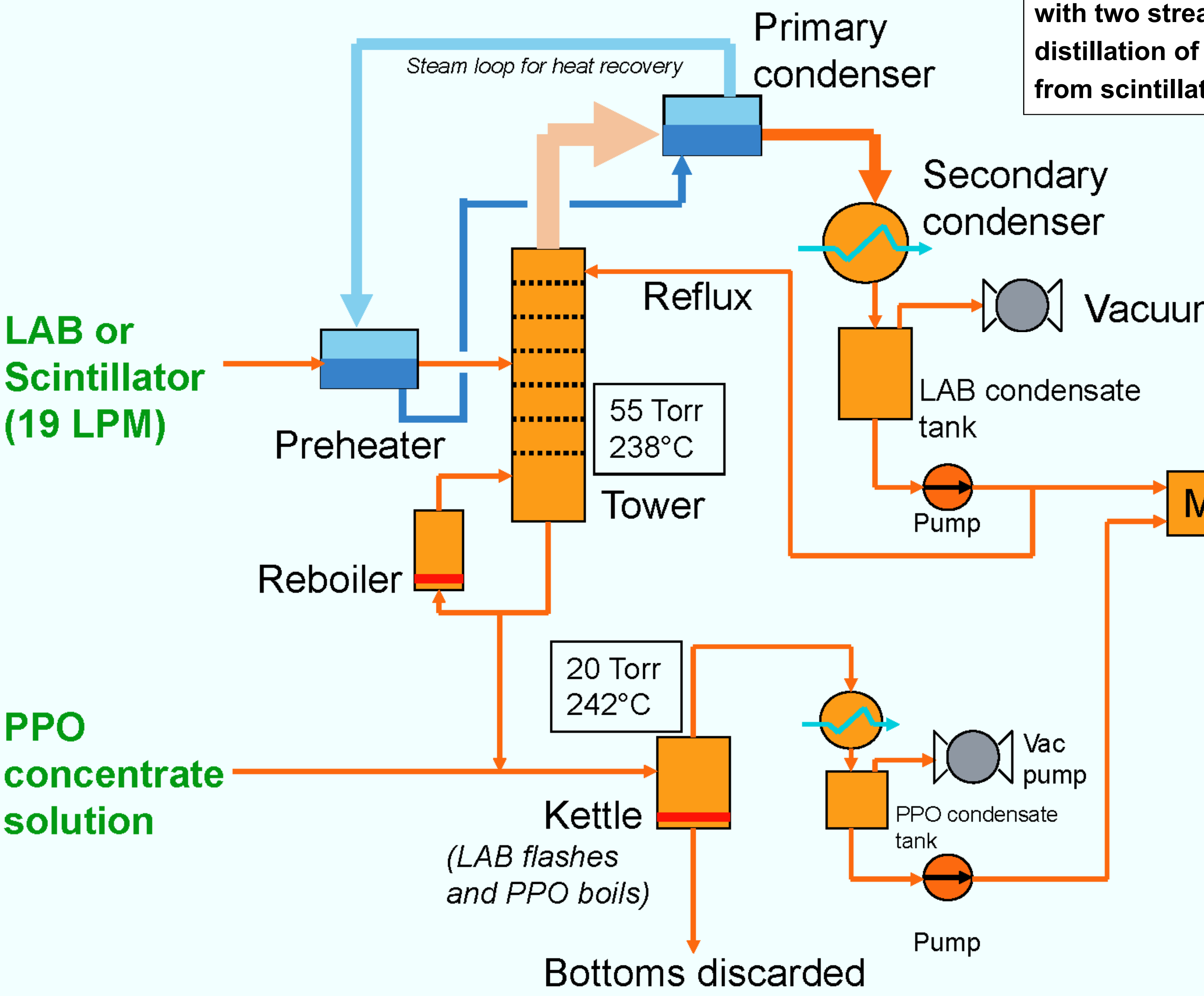
VS.

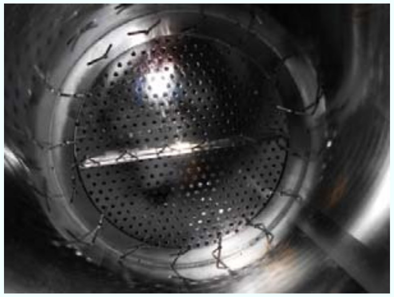
Distillation is also an equilibrium stage process – but you need the stages!!!

$$V_{n+1}y_{n+1} = L_n x_n + D x_D \Rightarrow y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{D}{V_{n+1}} x_D$$

Distillation System

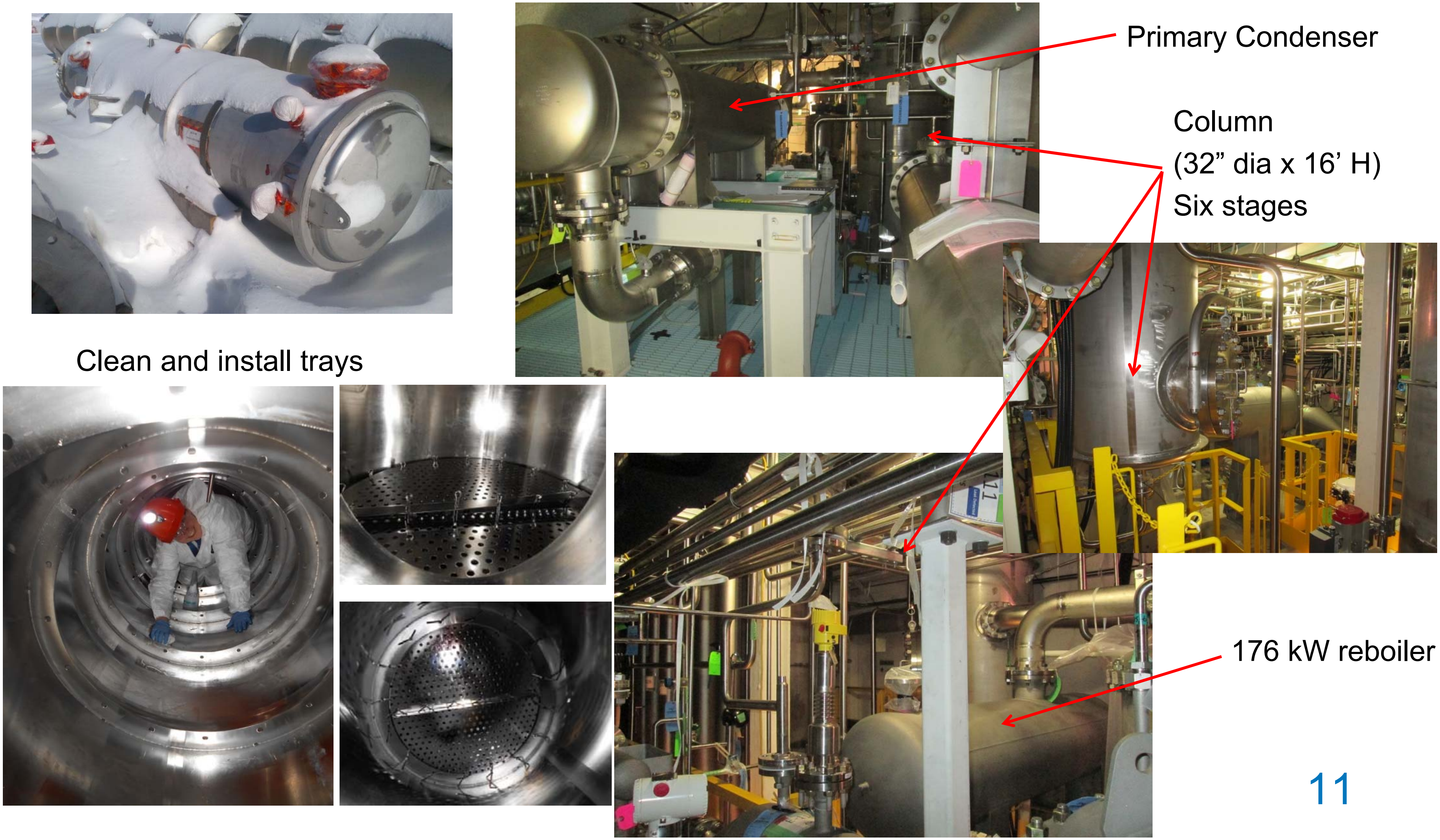
Multi-stage vacuum distillation with two streams to provide distillation of PPO solution from scintillator bottoms.





Tower uses custom dual-flow trays

Distillation Equipment



Clean and install trays

Primary Condenser

Column
(32” dia x 16’ H)
Six stages

176 kW reboiler

Distillation Challenges

- Although heavy metals are expected to have very low volatility, some organic optical contaminants can have volatilities close to LAB. Need to maximize number of stages.

However …

- To increase effective stages need to increase the column pressure, or increase the column diameter, or the column height.

Also …

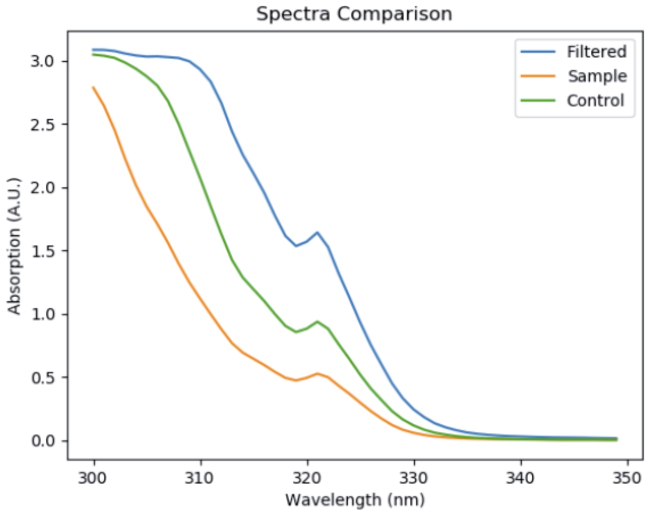
- Need to limit the operating temperature of the column
  - ➢ Due to fire safety operating above Auto-Ignition Temperature,
  - ➢ Due to Pyrolysis (heat cracking) → optical degradation,
  - ➢ Due to difficulty getting gaskets, valves, instrumentation etc for very high temperatures.

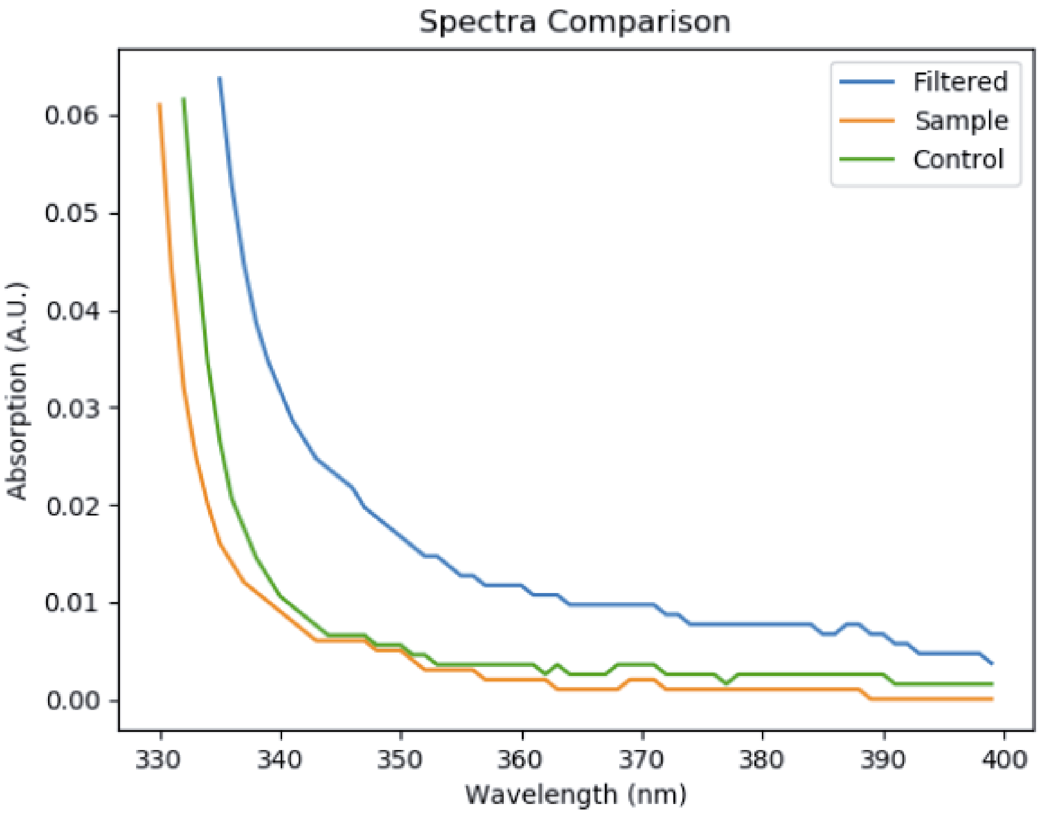
Then …

- To reduce boiler temperature need to reduce stage dP and number of stages. Used dual-flow trays instead of downcomers for minimum dP and best stage efficiency.
- Designing for low dP gives limited turn-down capacity – must operate to design.

Distillation

Optical Improvement:





Another comment: many authors describe purification effectiveness by a reduction factor:

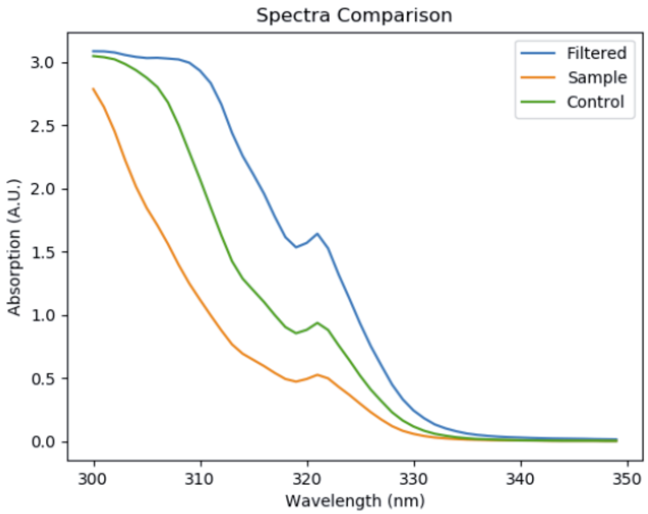
$$R = \frac{A_I}{A_F}$$

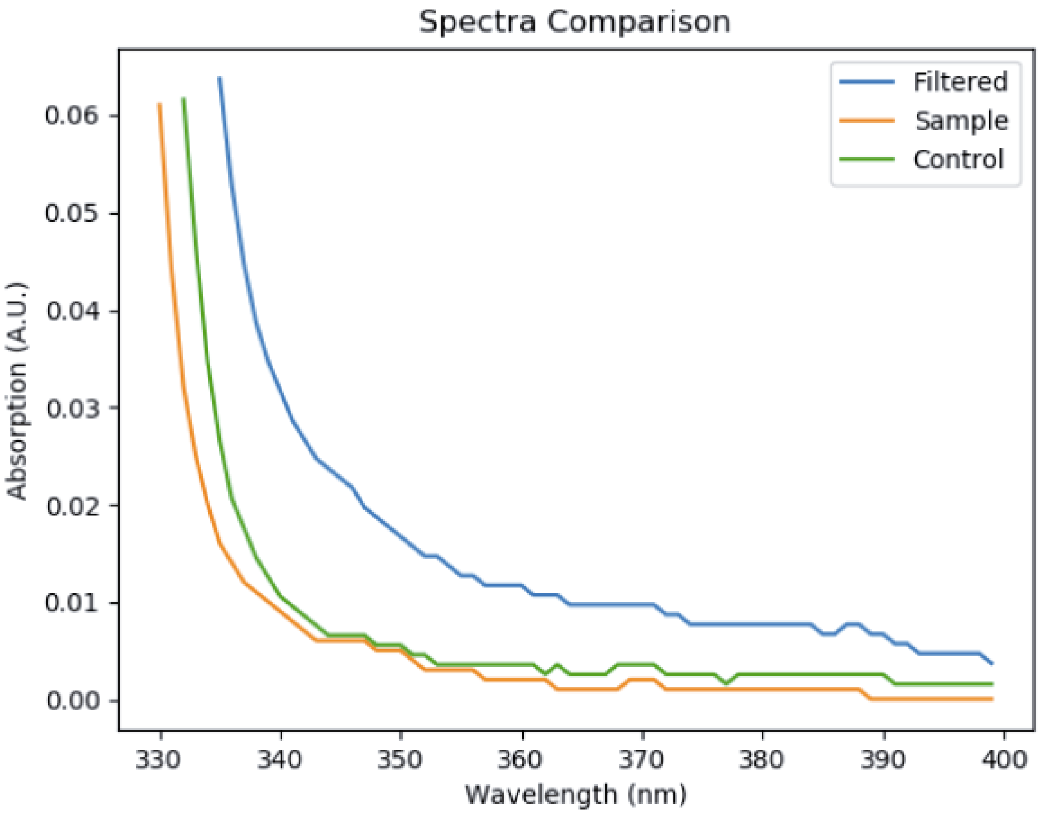
This is implying the reduction is reproducible on same sample to achieve any reduction needed. The is justified on basis that thermodynamics is same on each pass since to contamination is only trace quantity, ie.

$$R_2 = \frac{A_I}{A_{F2}} = R\frac{A_I}{A_{F1}} = R^2 \qquad R_N = R^N$$

Distillation

Optical Improvement:





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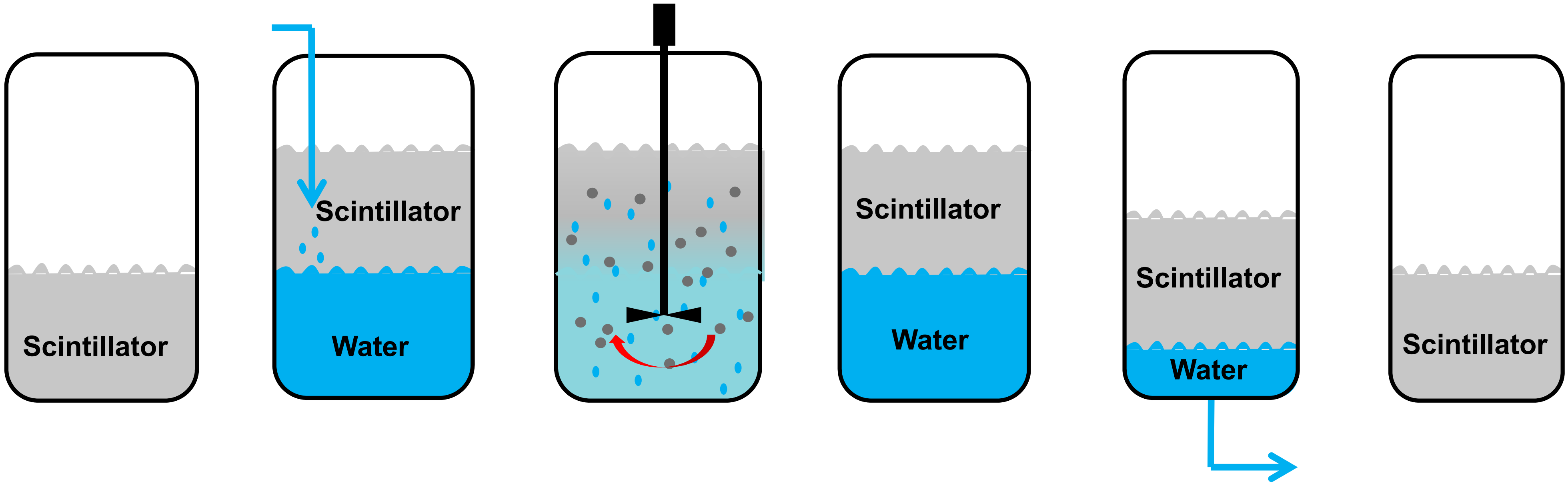
$$R_2 = \frac{A_I}{A_{F2}} = R\frac{A_I}{A_{F1}} = R^2$$

$$\cancel{R_N = R^N}$$

What remains is chemically different

Water Extraction – Single Equilibrium Stage

Illustrative Example of Steps for Single Batch-wise Stage of Water-Extraction



Step 1

Start with scintillator in tank

Step 2

Add equal volume of high purity water

Step 3

Mix with sufficient vigour and/or time to ensure high degree of phase contact

Step 4

Allow time for phases to separate

Step 5

Drain water to be wasted or repurified

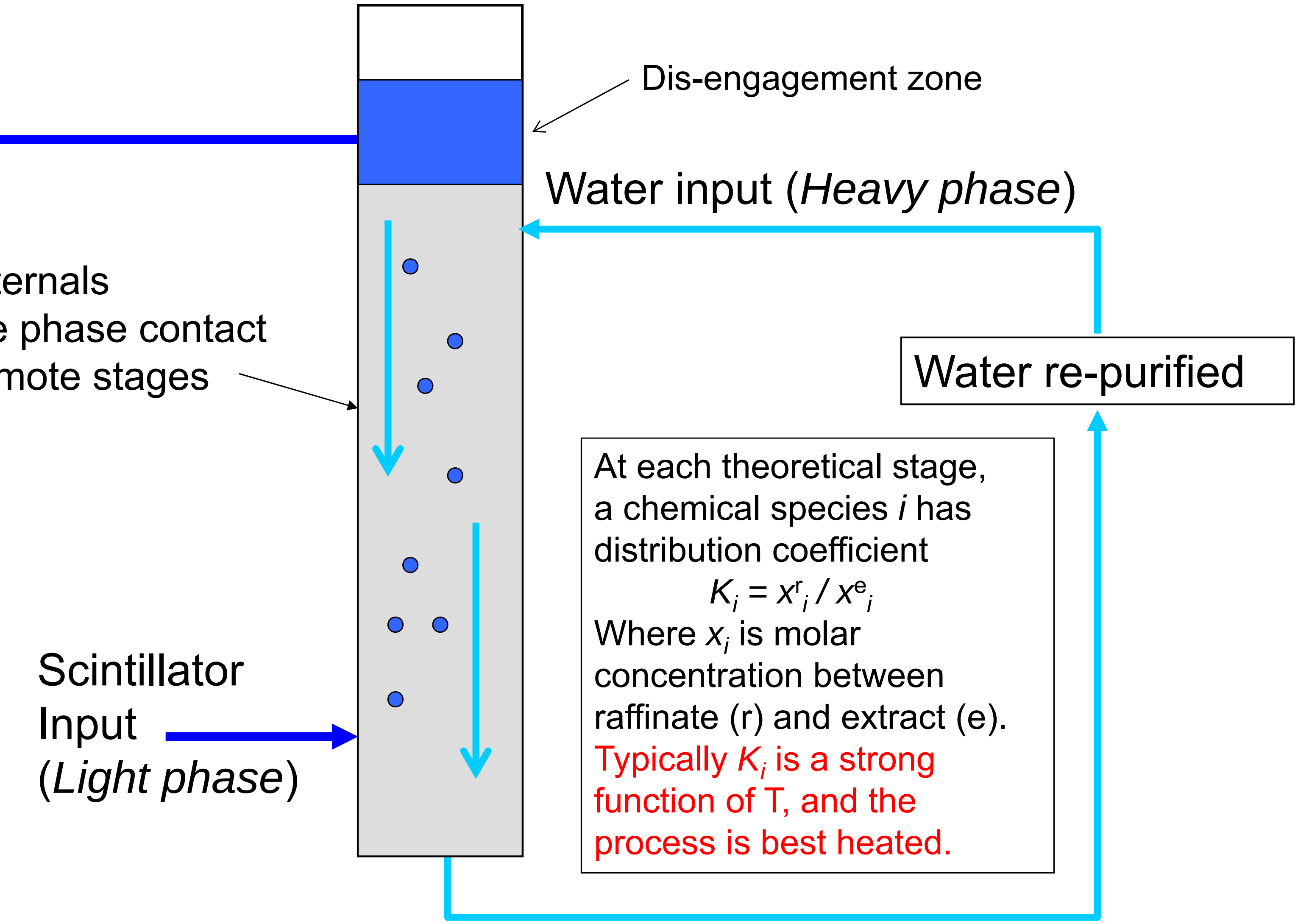
Step 6

End of single-stage water extraction

Repeat batch process for multiple stages

For removal of ionic species Ra, Pb, K, Bi

Counter-Current Water Extraction



Scintillator Output (*Raffinate*)

Dis-engagement zone

Water input (*Heavy phase*)

Column internals
to enhance phase contact
and/or promote stages

Water re-purified

At each theoretical stage, a chemical species *i* has distribution coefficient

$$K_i = x^r_i / x^e_i$$

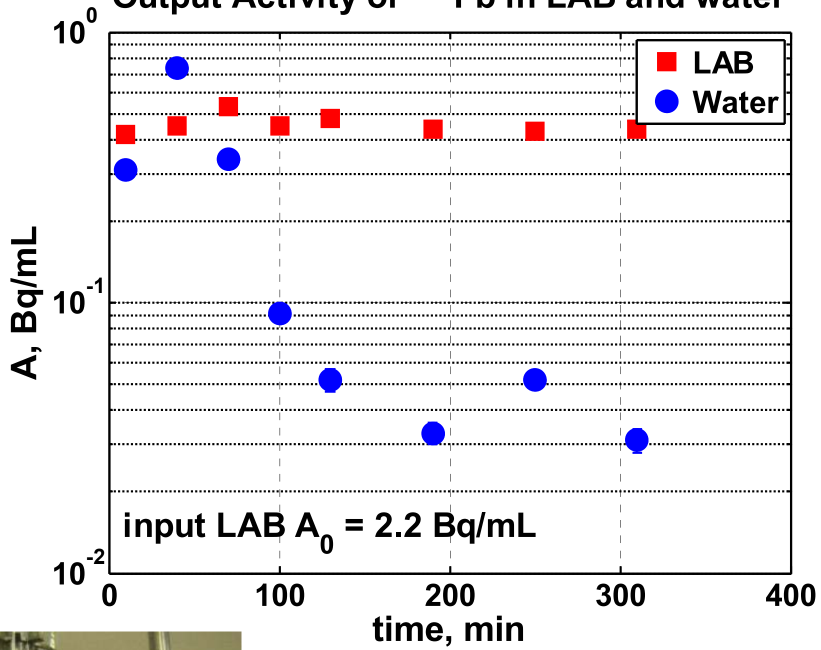
Where x_i is molar concentration between raffinate (r) and extract (e). Typically K_i is a strong function of T, and the process is best heated.

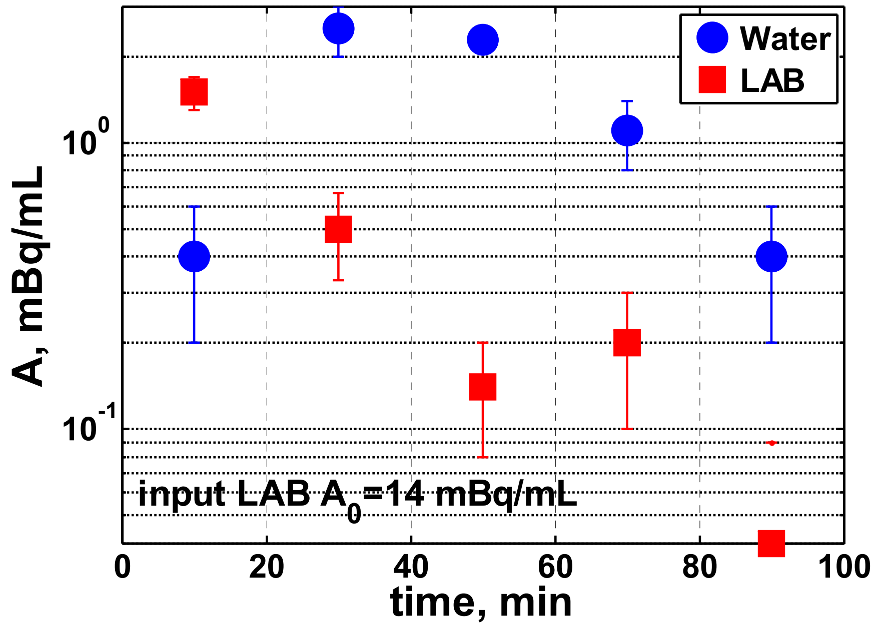
Scintillator Input (*Light phase*)

Water out (*extract phase*)

Water Extraction Bench-top Spike Tests

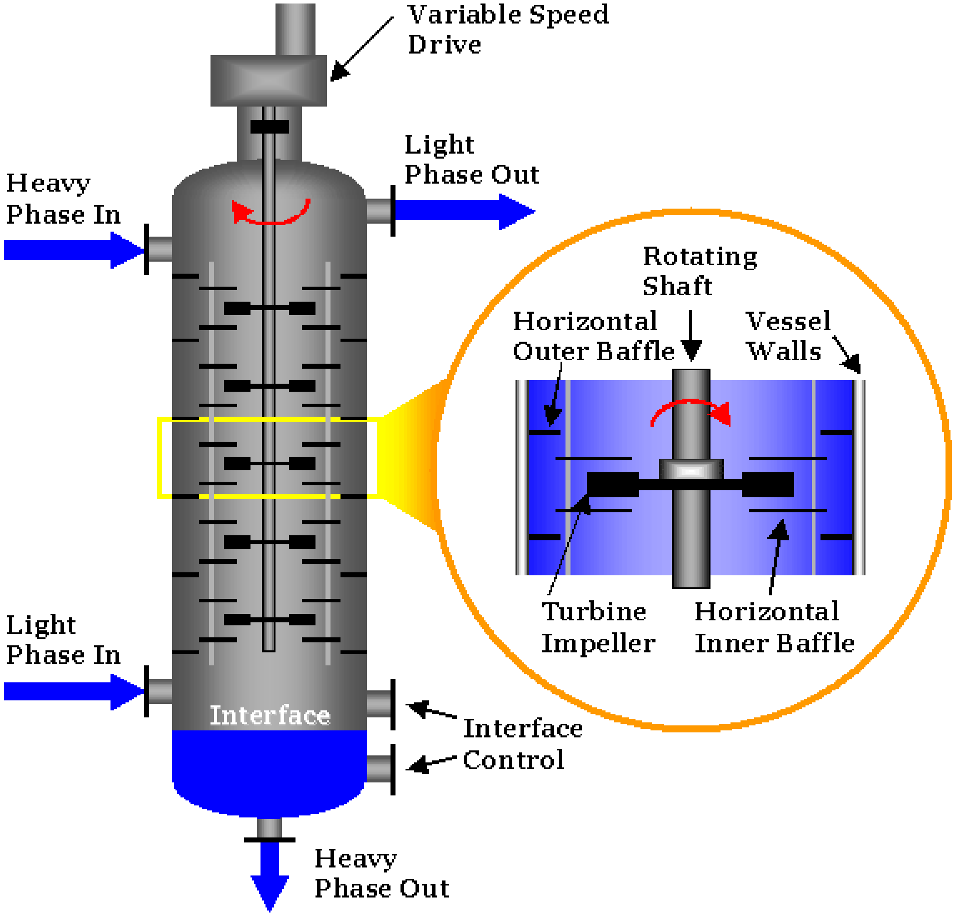
- WE efficiency of ^{212}Pb removal from LAB is 87%.
- Tests with ^{224}Ra show a high removal efficiency 98%.
- There is a lead component in LAB, irremovable by WE.


Output Activity of ^{212}Pb in LAB and water


Output Activity of ^{224}Ra in Water and LAB

Water Extraction Scheibel Column

Scheibel column is 30” dia x 23’ H. Flow 150 LPM raffinate, 30 LPM extract with 30 equilibrium stages.



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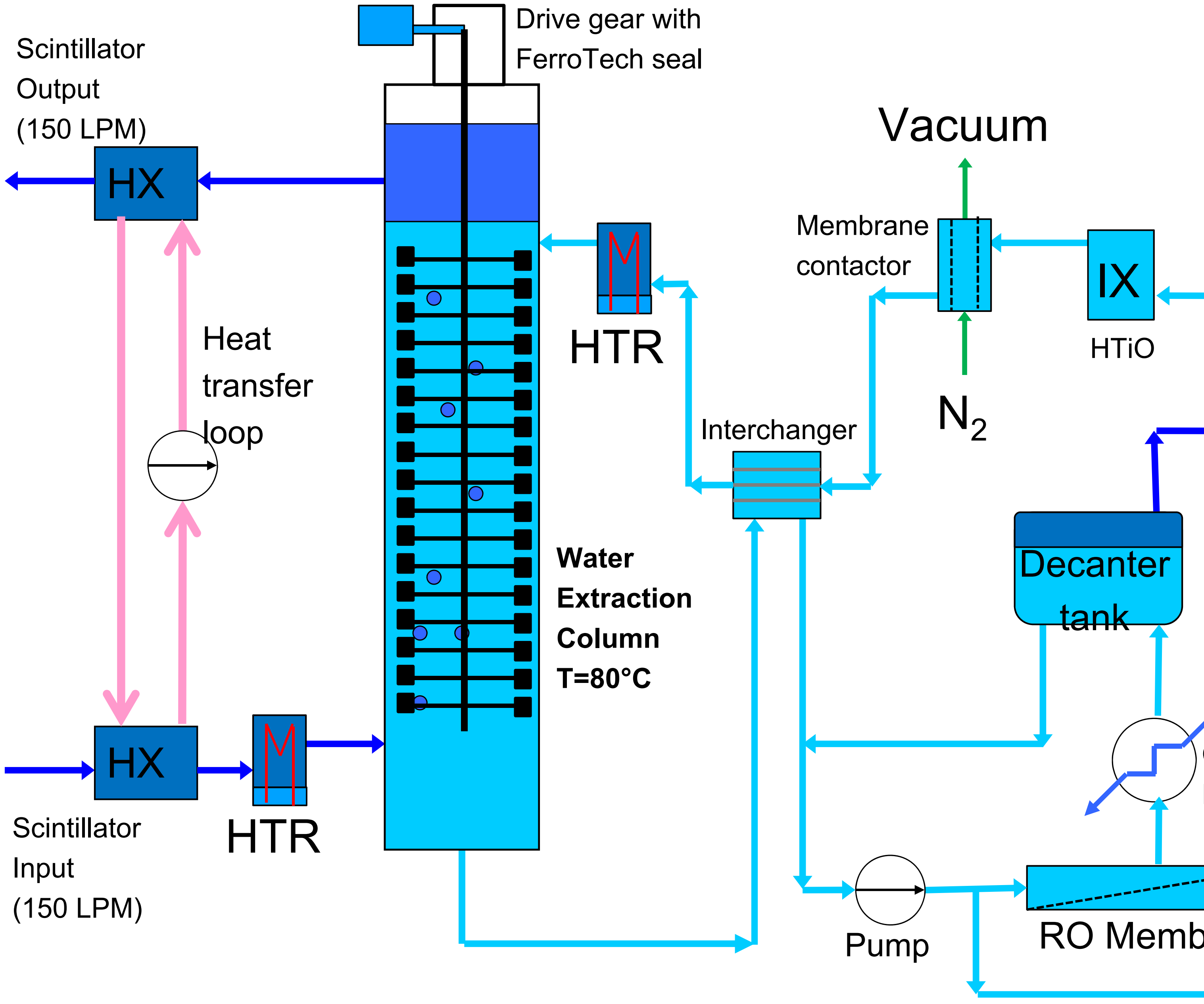
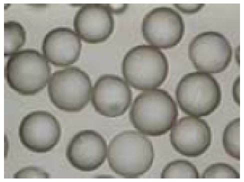
Water Extraction process loop



Metal Scavenger Columns

QuadraSil
spherical silica beads:

- average particle size 54 μm
- zero swell in solvents
- extremely fast scavenging



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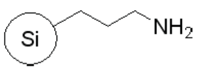
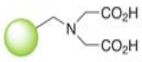
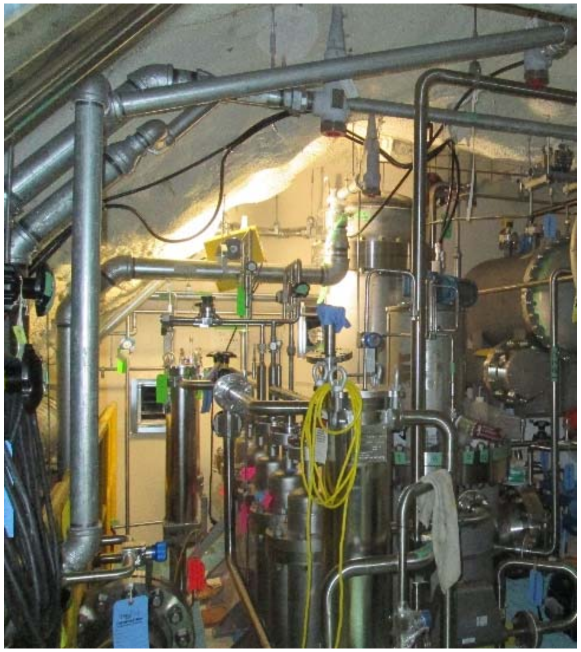


TA

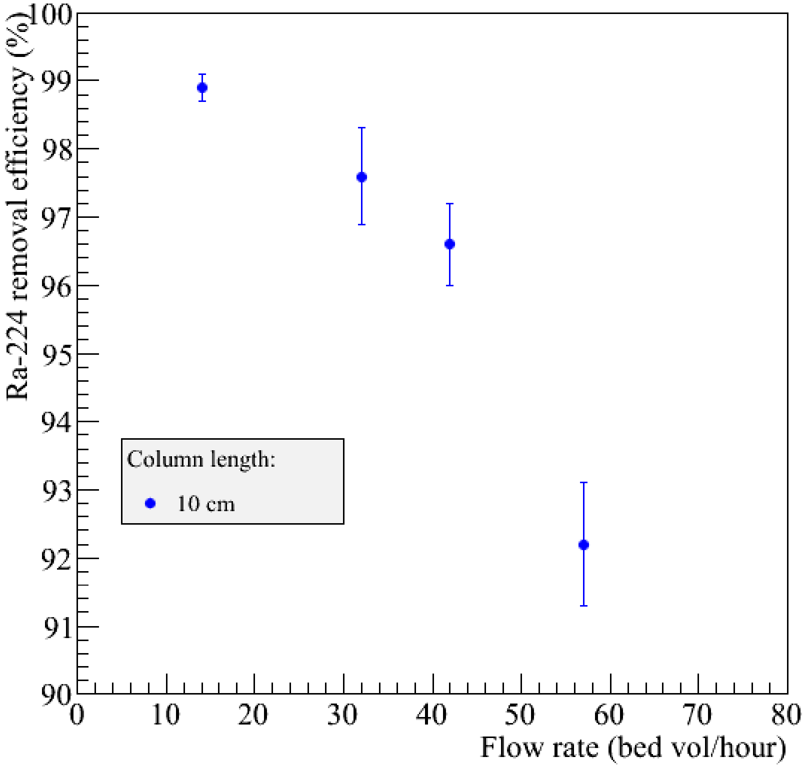




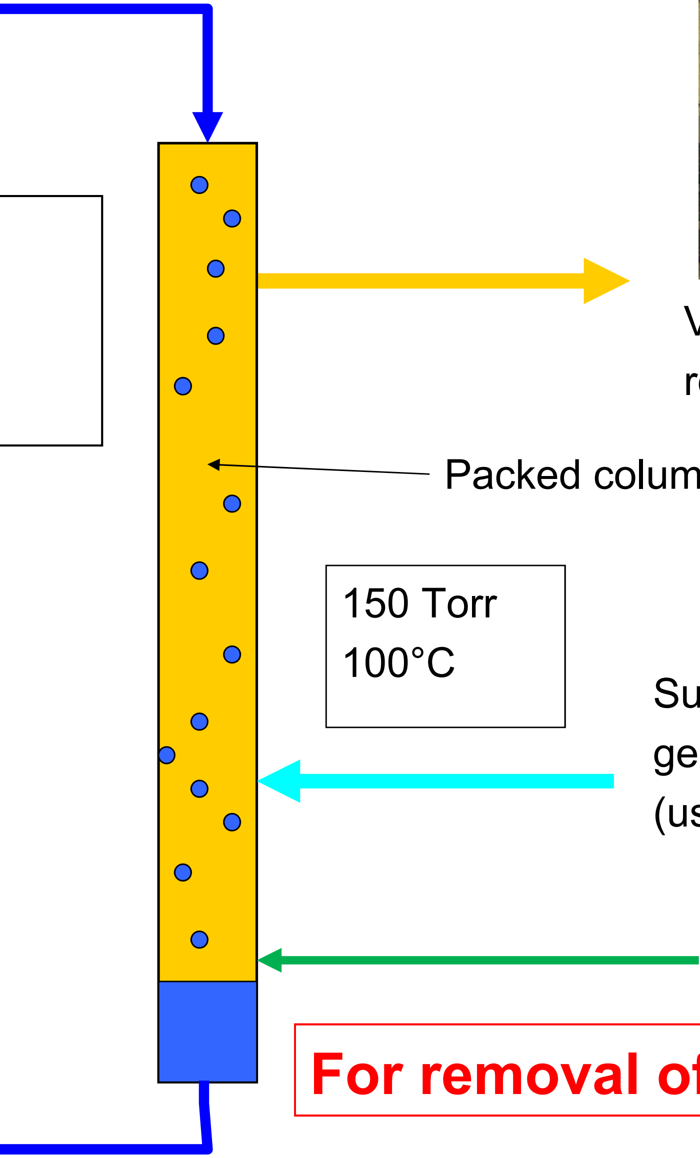
Chemical adsorption on functional group allows regeneration and recovery of metals for off-line assay (Ra, Pb, Bi)

Method to break ^{210}Bi degeneracy with CNO neutrinos

Six columns
6” dia x 16’-8” H



Gas Stripping (N2/steam)



Scintillator
Input
(150 LPM)

SNO+ column is 24” dia x 24’ H.
Flow 150 LPM.
- 95% Rn removal eff.
- 99% O_2 removal eff.

Vacuum pump to vapour recovery and vent header

Packed column

150 Torr
100°C

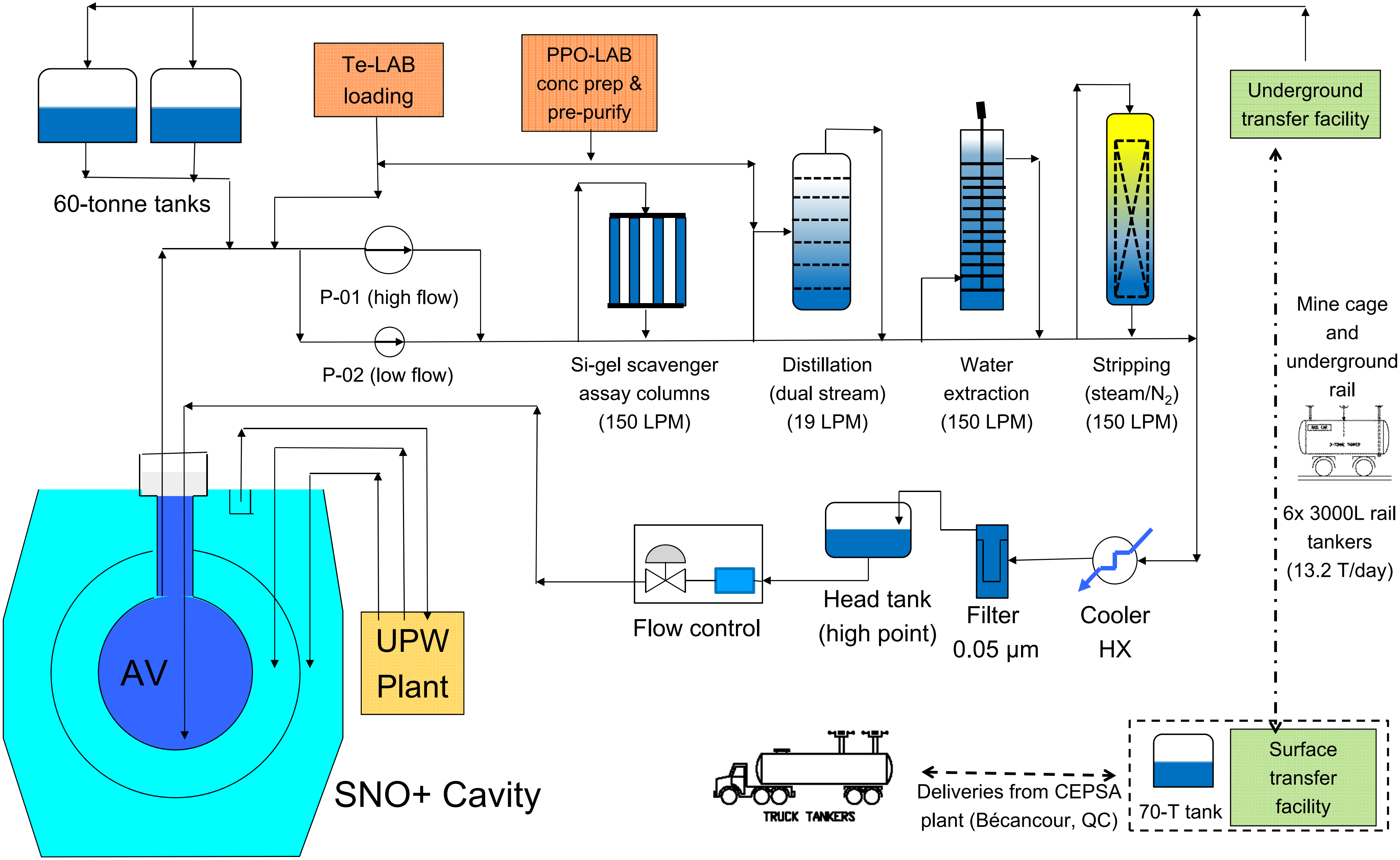
Super-heated steam generator (10 kg/hr) (using Rn stripped H_2O)

N_2 (3 kg/hr)

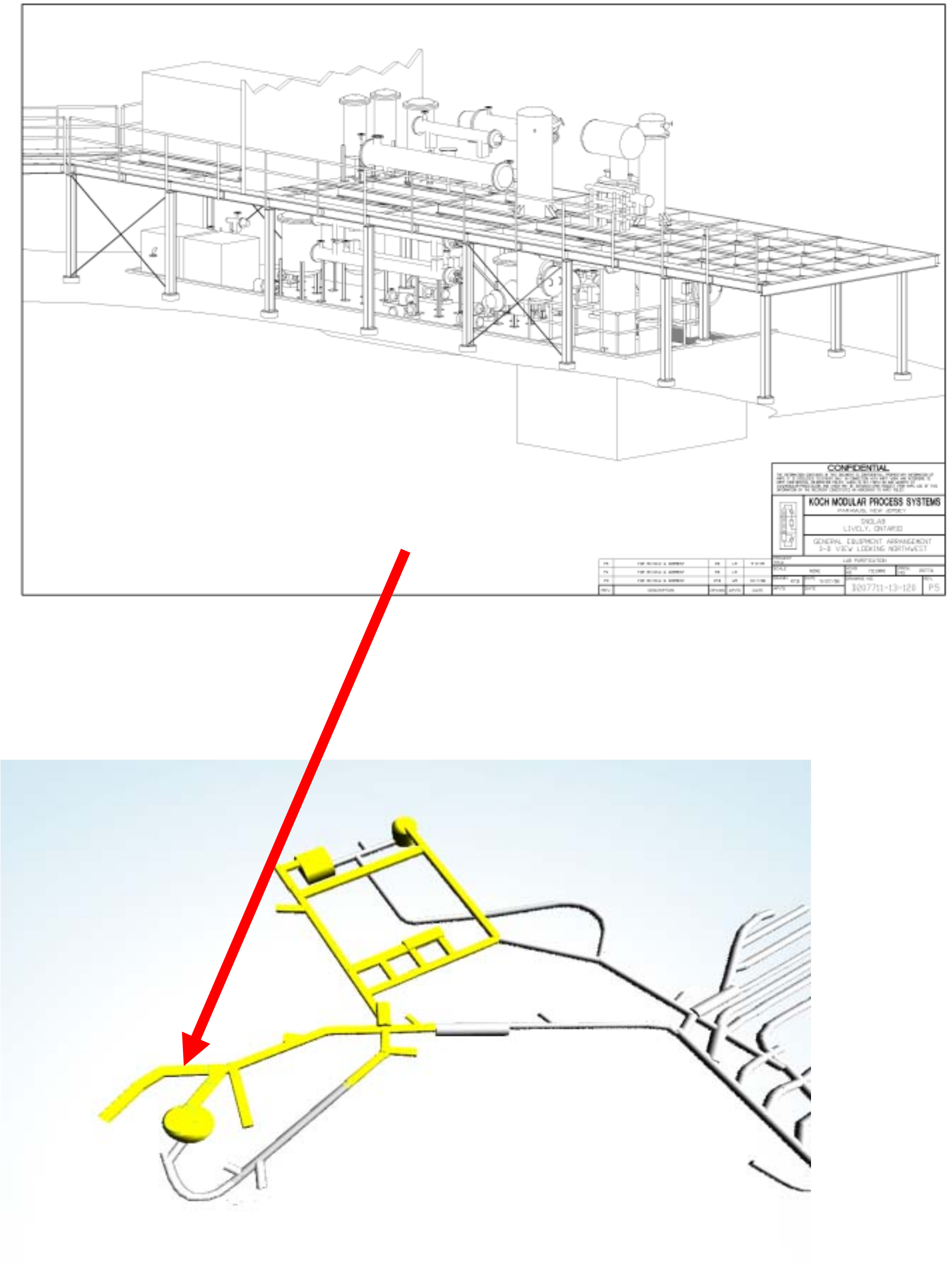
Scintillator
Output
(150 LPM)

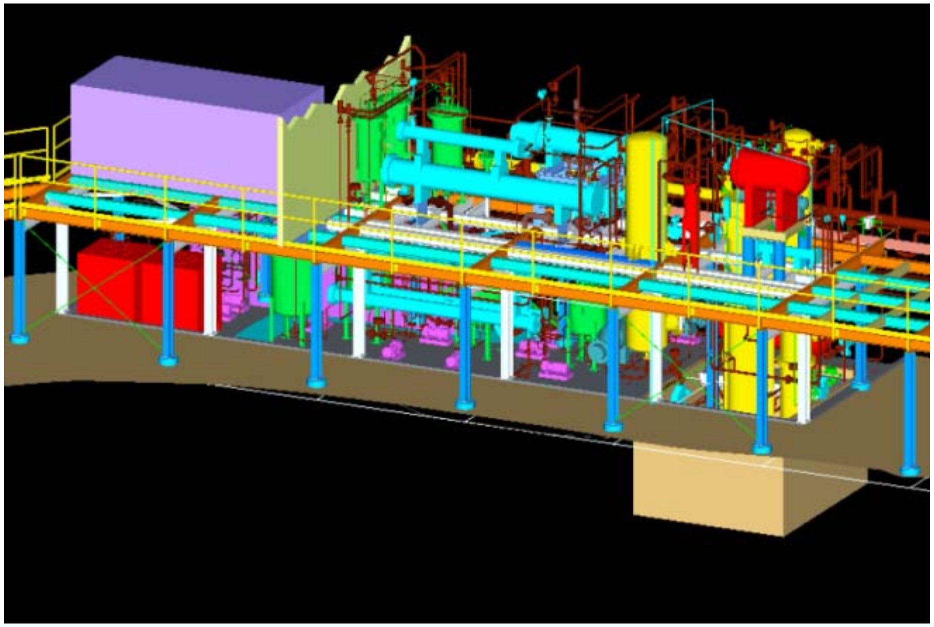
For removal of Rn, O_2, Ar, Kr, H_2O

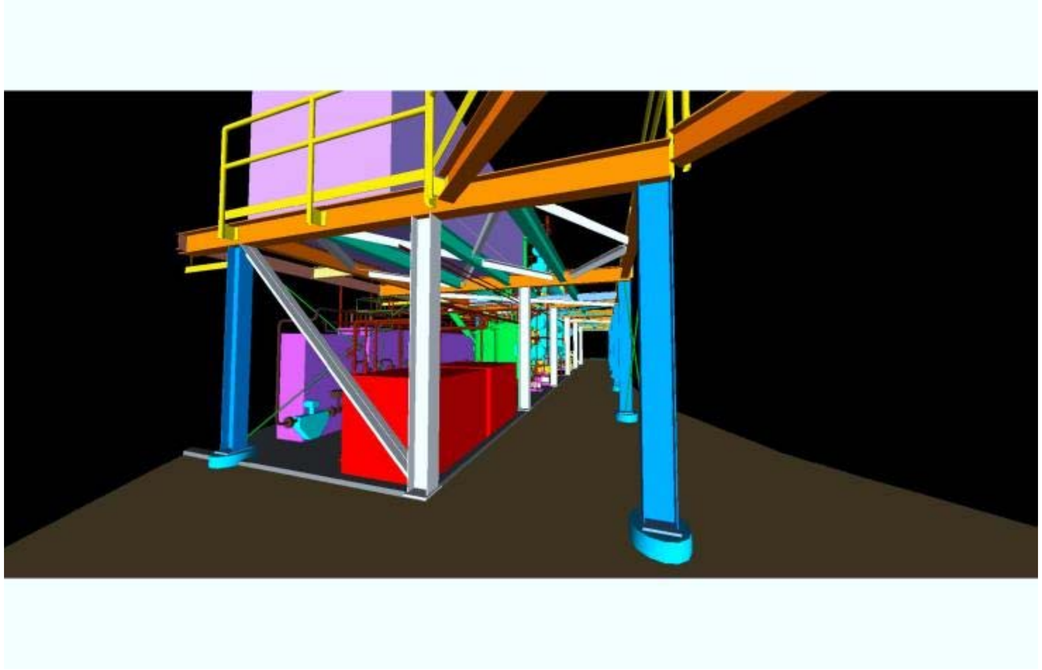
SNO+ Simplified Process Flow Diagram



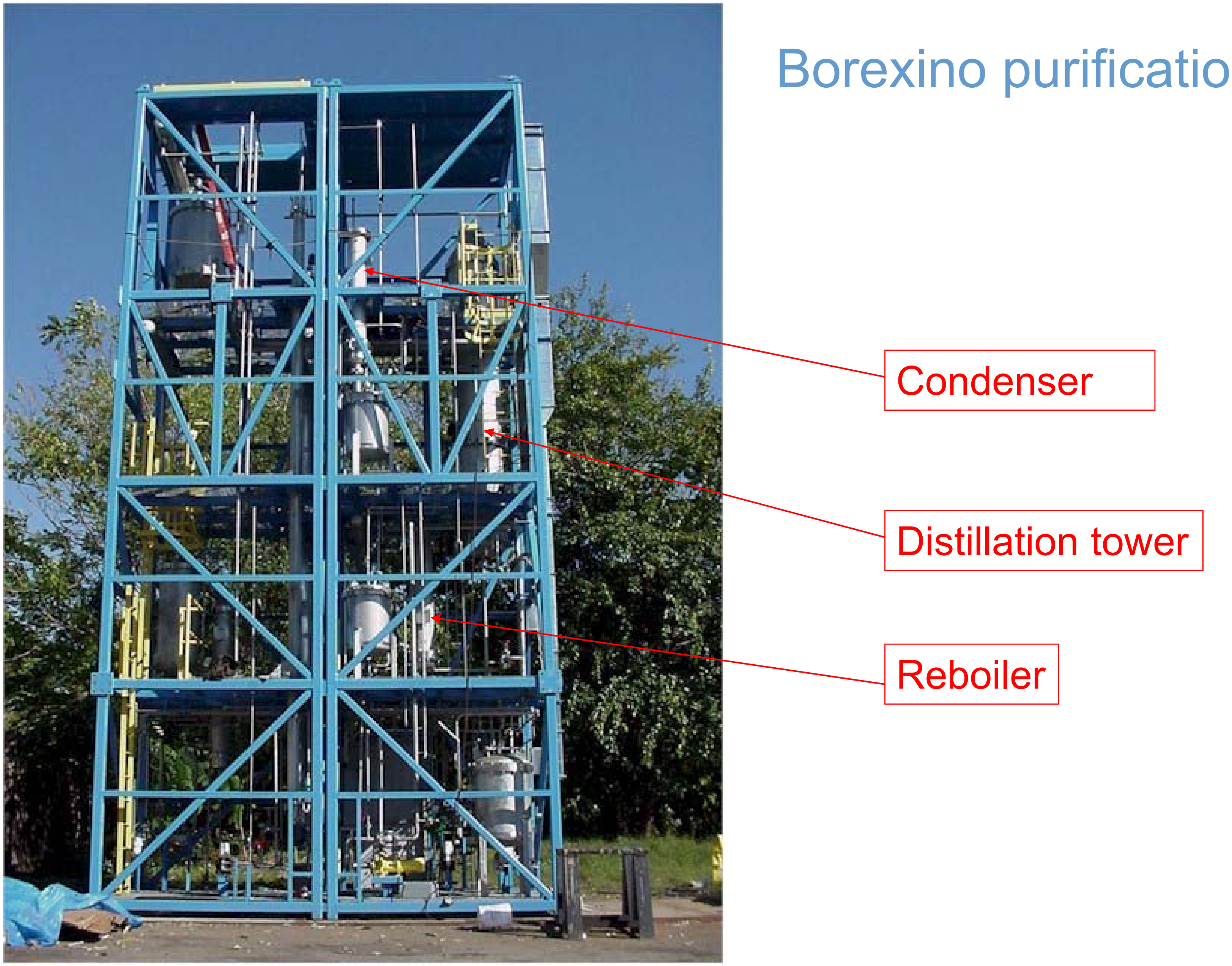
Scintillator plants







Borexino purification skids



Condenser

Distillation tower

Reboiler

Conclusions

Effective methods of liquid organic scintillator purification:

- Distillation
  - Need to optimize design for maximum stages at reduced P and T
  - Strip or degas first to remove oxygen avoid oxidation
- Water-extraction
  - Counter-flow columns can be challenging to control
  - Effectiveness depends on water supply and purity
- Gas stripping
  - Dependent on nitrogen gas purity
  - Steam stripping effective to reduce radon, need to use vacuum/N2 to control humidity
- Adsorption columns
  - Silica Gel or functional metal scavengers
  - Column aspect ratio critical for flow and breakthrough characteristics

Plant design considerations:

- Flow requirements for both filling and recirculation
- Power, cooling, and heat recovery
- Column size constraints, and impact on pressure, temperature, and number of stages
- Requirements for nitrogen supply and purity, and ultra-pure water
- Materials and piping specification for high-vacuum and high-purity
- Fire safety and plant HAZOP analysis
- Structural requirements, eg. seismicity

The End


SCINTILLATOR
SCINTILLATOR 1042
E-101
E-3


E-301A
E-201B
SCINTILLATOR 1109
E-301B
SCINTILLATOR 1042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Considerations for Plant Design

- Require capacity to purify full detector volume in ~4 days, for reduced equilibrium level of potential ^{222}Rn and ^{224}Ra sources (both ~4 day half-lives). Also, due to mining company logistical and access issues, we require ability to turn-over the detector within 5 days.
- Purification processes are equilibrium stage processes with require high temperatures to gain stage efficiencies, and tall columns for more stages.
- Being underground we are severely constrained by space and height.
- Limited electrical power available. Plant has ~0.75 MW installed, but limited to ~0.5 MW operating (SNOLAB has two 1500 kVA MPCs).
- Limited cooling capacity available. SNOLAB has 320 tons (1.1 MW), of which about 400 kW needed for climate control (13 AHUs) and 400 kW for other experiments, leaving 300kW baseline (can peak higher).
- Limited LN_2 boil-off available due to logistics to ship LN_2 dewars underground. Limited to about 5 kg/hr for cover gas and stripping.
- Plant and equipment must meet code for earthquake and near-field seismic events due to mining “rock-bursts”.
- LAB is combustible and must have all risk of fire mitigated due to unique life-safety hazards being located within a mine.

Stripping Challenges/Solutions

- ☐ Solubility of noble gases (Rn, Ar, Kr) high in aromatic solvent (eg. Henry coefficient for Rn in LAB is ~10, which means Rn partitions ~87% into LAB at 1 atm). Need more stages, and reduced pressure.
- ☐ Flow rate 150 LPM, hence need large flow rate of low-radon stripping gas to obtain the required stages. However, logistically it is very difficult to ship sufficient liquid nitrogen into the mine. Solution to use steam as stripping gas, where water is low in Rn from UPW plant degasser/regasser.
- ☐ Kremser equation (trace quantity limit):

$$N = \frac{\ln\left[\left(1 - L/mV\right)\left(x_0/x_N\right) + L/mV\right]}{\ln\left[mV/L\right]} \approx 4 \quad \text{Stages}$$

For *m* ≈ 80 at 150 Torr, with 3 kg/hr N_2 and 10 kg/hr steam, to obtain x_0/x_N = 20 for Rn.

Purification strategies:

- ***Multi-stage distillation***
  - Initial LAB cleanup for high radio-purity and optical clarity
  - Dual-stream PPO distillation for scintillator recirculation
- ***Pre-purification of PPO concentrated solution***
  - N2 sparging, batch water extraction, followed by “flash”-distillation
- ***Pre-purification of Te-salt solution and “loading agent” chemicals***
  - pH-controlled precipitation or thermal re-crystalization of Te-salt solution
  - Thin-film evaporation or silica-gel purification of “loading agent” chemicals
- ***Steam/N2 stripping under vacuum***
  - Removes Rn, O_2, Kr, Ar and provides LAB humidity control
- ***Water extraction (liquid-liquid extraction)***
  - Provides high-flow recirculation polishing stage
  - Effective for ionic metals (K, Pb, Ra) and partially effective for Th and Po
  - Cannot be used with Te-loaded scintillator, however equipment can be used to unload Te
- ***Functional metal scavengers (on silica gel matrix)***
  - High-flow columns effective for Pb, Bi and Ra
  - Can be regenerated with acid wash
  - Processing and assay of the acid wash provides a method for radio-assay of scintillator
- ***Filtration***
  - Ultra-fine (0.05μm) filtration for “ultra-fine” suspended contamination

PPO Concentrated Solution

- The PPO will be dissolved and pre-purified as a concentrated solution at 120 g/L.
- To match 19 LPM LAB fill rate 55 kg/day of PPO will be mixed into 450 L LAB.
- Will mix 1 batch per day, which will be water extracted 3 times, sparged and filtered, then transferred to surge tank.
- The PPO conc solution will distilled in a flash kettle in parallel with the LAB.

Future Planning WS 2019

SNOLAB Future Planning Workshop 2019

Dates: 14-17 July 2019

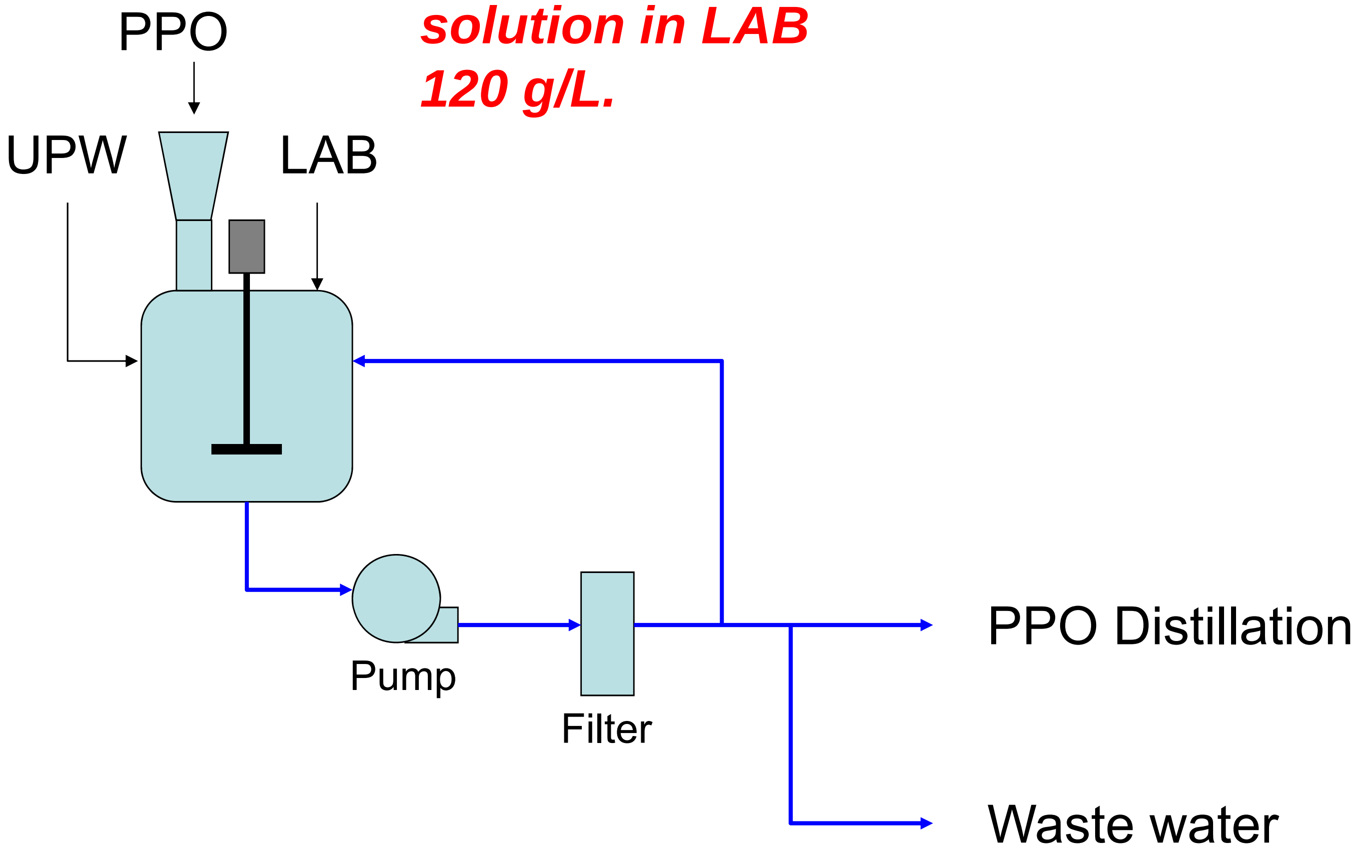
The objective of the Future Planning workshop is to provide SNOLAB with a road-map of potential large scale projects that may require its experimental areas on a five to ten year timescale. It is understood that projects will be at various stages of development, and this is not a final selection meeting. Following discussion with the Experiment Advisory Committee, SNOLAB resources could be made available on request to potential projects, to help develop plans and determine suitability and achievability.

Registration is open for presentations on the SNOLAB website:

http://www.snolab.ca/science/meetings-and-workshops/workshops/2019-future-planning-workshop

www.snolab.ca → SCIENCE → MEETINGS&WORKSHOPS

PPO Concentrated Solution Preparation



Dissolve PPO in concentrated solution in LAB 120 g/L.

Pre-purifiy PPO solution with batch water-extraction process