Water Radiolysis Issues

T. Sekiguchi

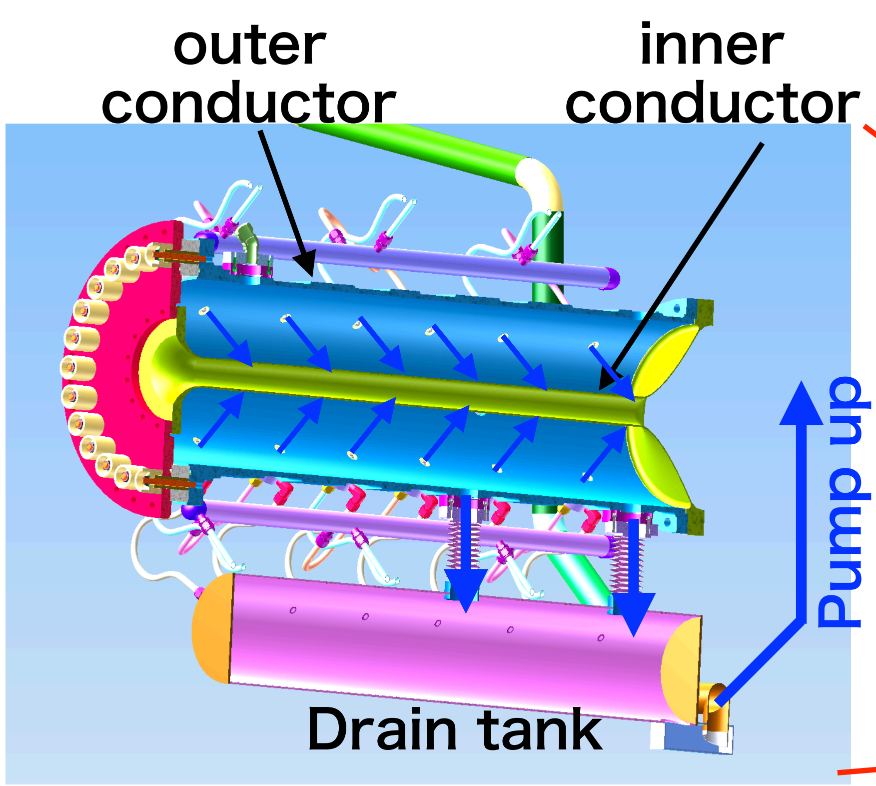
2019. 10. 24

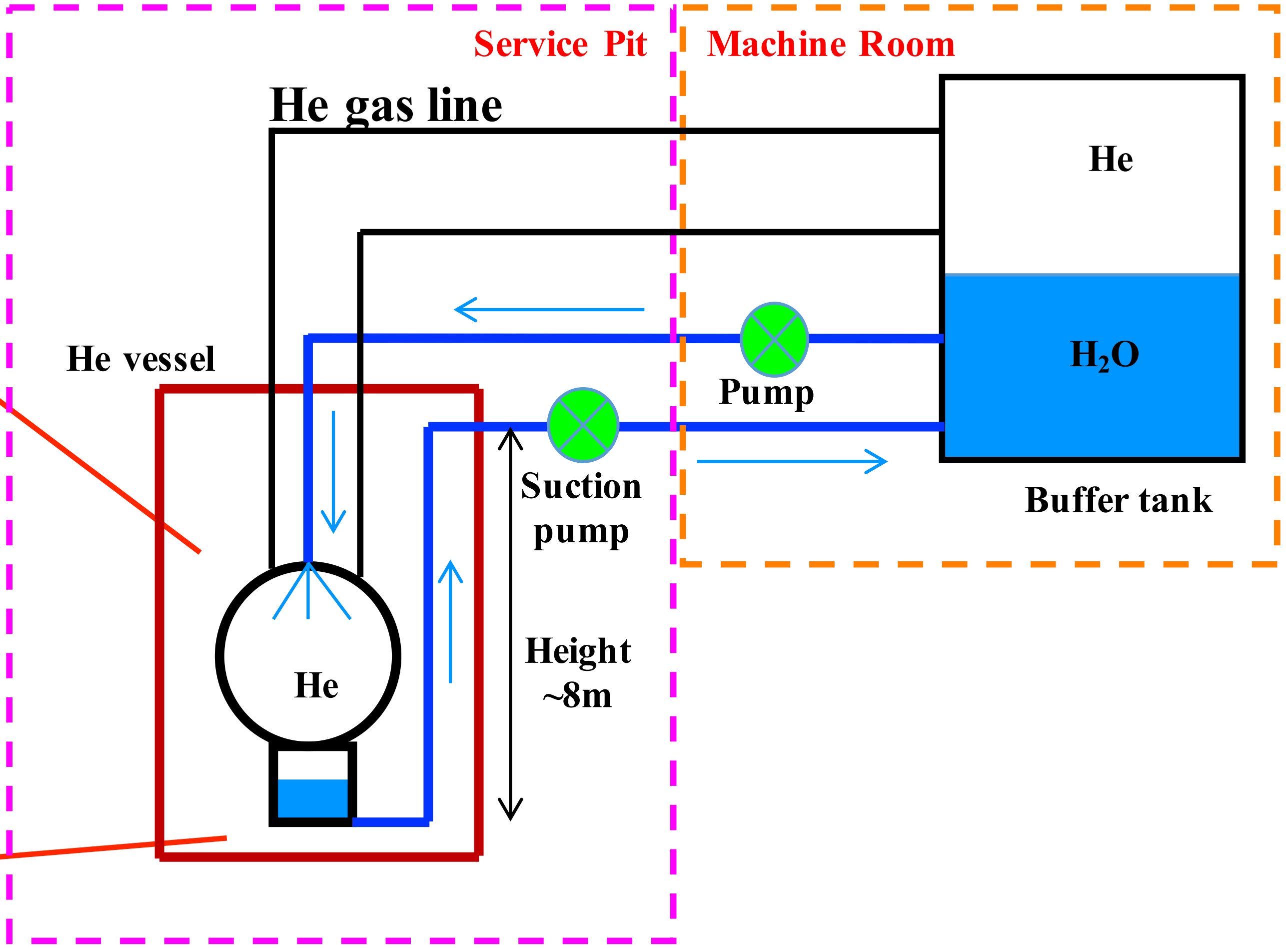
Contents

- Water radiolysis
- Hydrogen recombination system
    - Operation status
    - Issues
- Summary

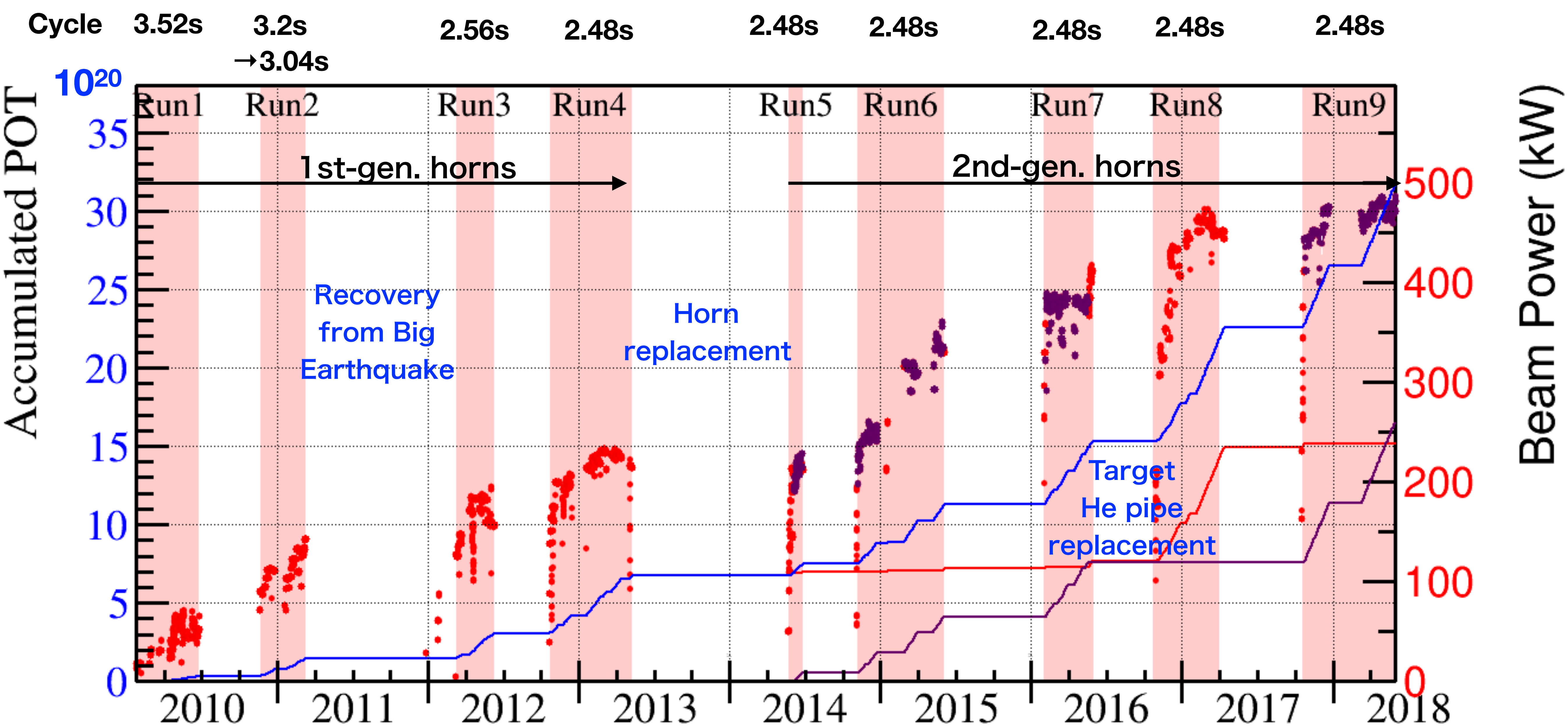
Horn Cooling Water System

- **Water cooling of horn conductors**
  - Water spray onto IC ⇒ collected in drain tank ⇒ pump up
- **Two independent pumps for water circulation**
  - Water supply pump
  - Water suction pump @ 7~8 m above horns
  - Supply and suction flow rates are balanced manually





Horn Operation History



horn pulse

0.2x10⁷ 0.5x10⁷ 0.8x10⁷ 1.2x10⁷ 0.1x10⁷ 0.5x10⁷ 0.8x10⁷ 1.3x10⁷ 1.7x10⁷

Hydrogen problem (2010.Mar)

Power supply problem (2011.Dec)

Corrosion problem (2012.Jun)

Water drop problem (2012.Oct)

Neutral grounding problem (2014.Oct)

Neutral grounding problem (2016.Feb.&Apr.)

Capacitor problem (2017.Mar)

Hydrogen problem (2017.Oct)

Water drop problem (2018.Mar)

Water Radiolysis

- **Beam exposure to horn cooling water produces hydrogen gas**
- **Water radiolysis**
  - Ionization and excitation of H_2O molecule by beam exposure
    - Primary products : e_{aq}^-, OH, H, H_2, H_2O_2 ⇒ Final products : H_2, O_2, H_2O_2
  - Production ratio : H_2, O_2, H_2O_2 = 1.3 : 0.1 : 0.99 ⇒ very small O_2 production
  - H_2O_2 naturally decomposes, yielding O_2
    - $2H_2O_2 \rightarrow 2H_2O + O_2$

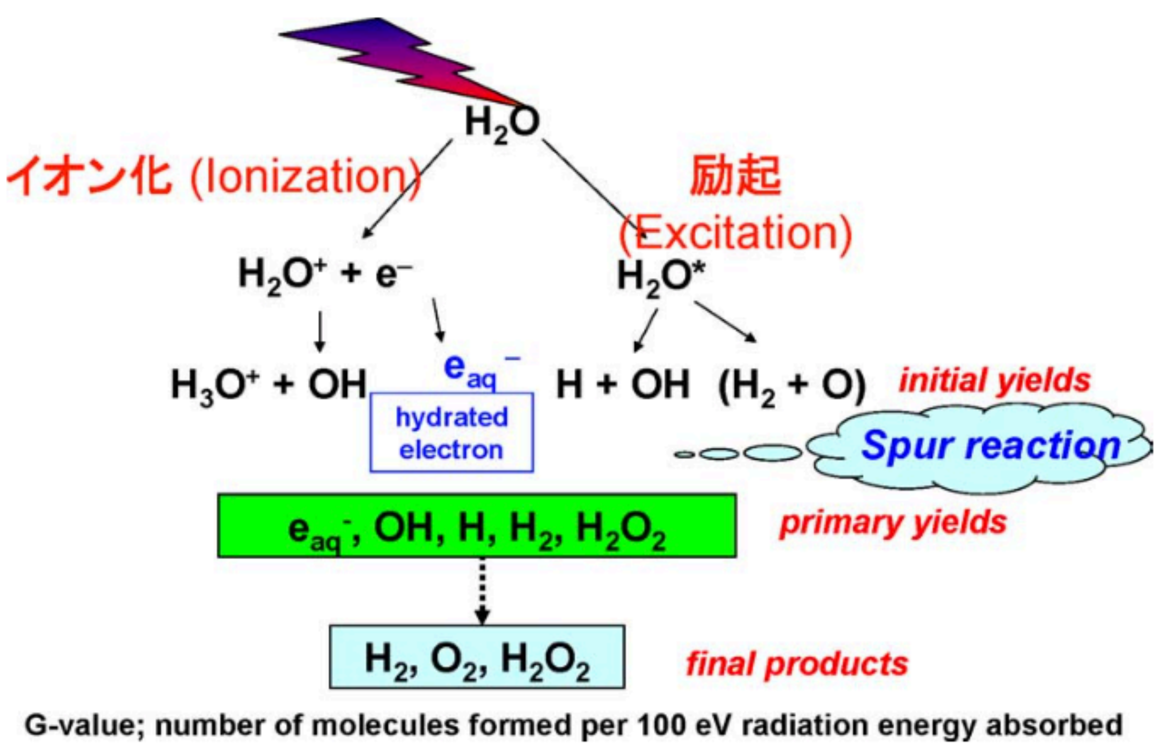
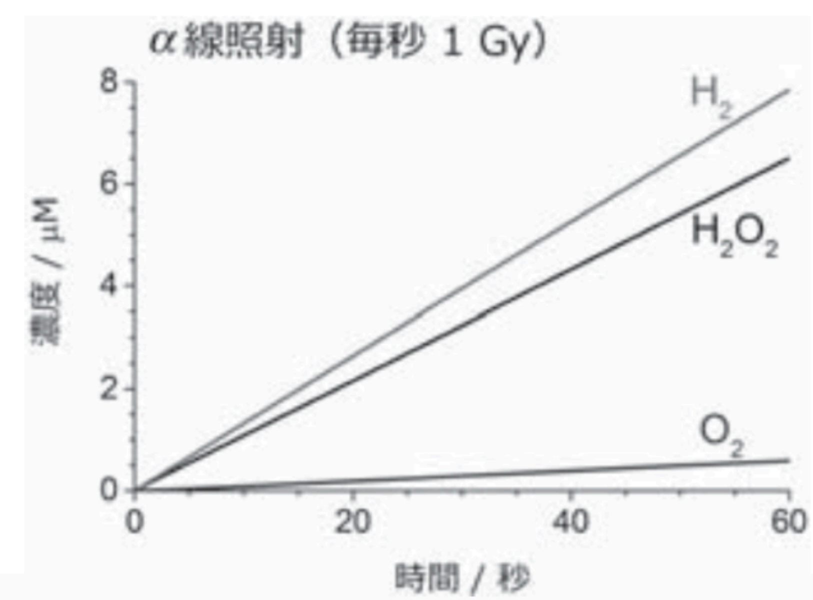


図 2　水の放射線分解スキーム

Y. Katsumura, Radiation Chemistry, No.81, 2-7 (2006)

表 1　γ(X) 線と α 線照射時の水の放射線分解で生じる化学種の G 値（個/100 eV）[2, 3]

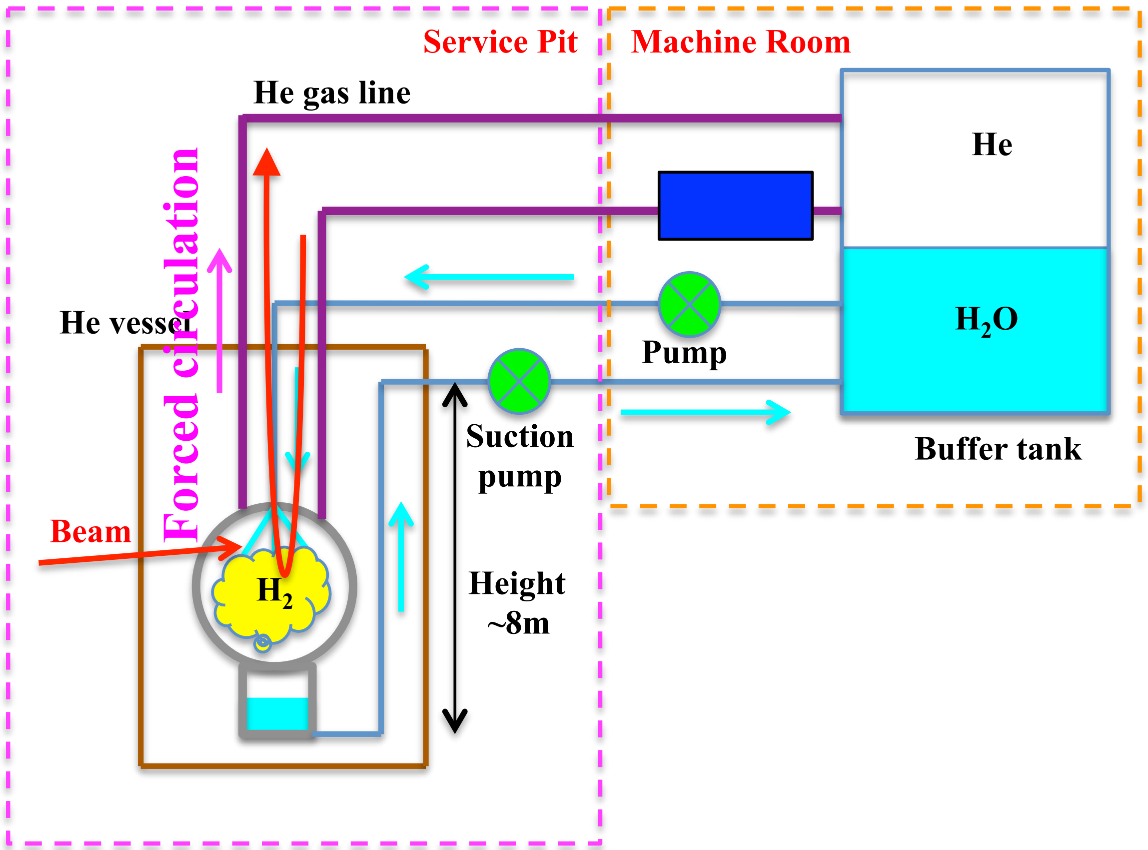
G-values	$-H_2O$	e^-_{aq}	OH	H	H_2O_2	H_2	HO_2
γ(X)-ray	4.11	2.64	2.82	0.57	0.645	0.45	—
α-ray	2.65	0.06	0.24	0.21	0.985	1.3	0.22



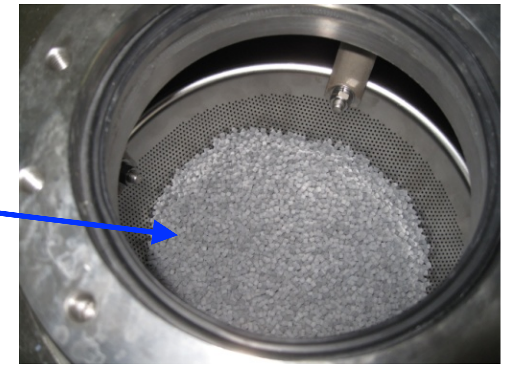
Y. Katsumura, Isotope News, No.746, 48-49 (2016)

Hydrogen Production and Recombination

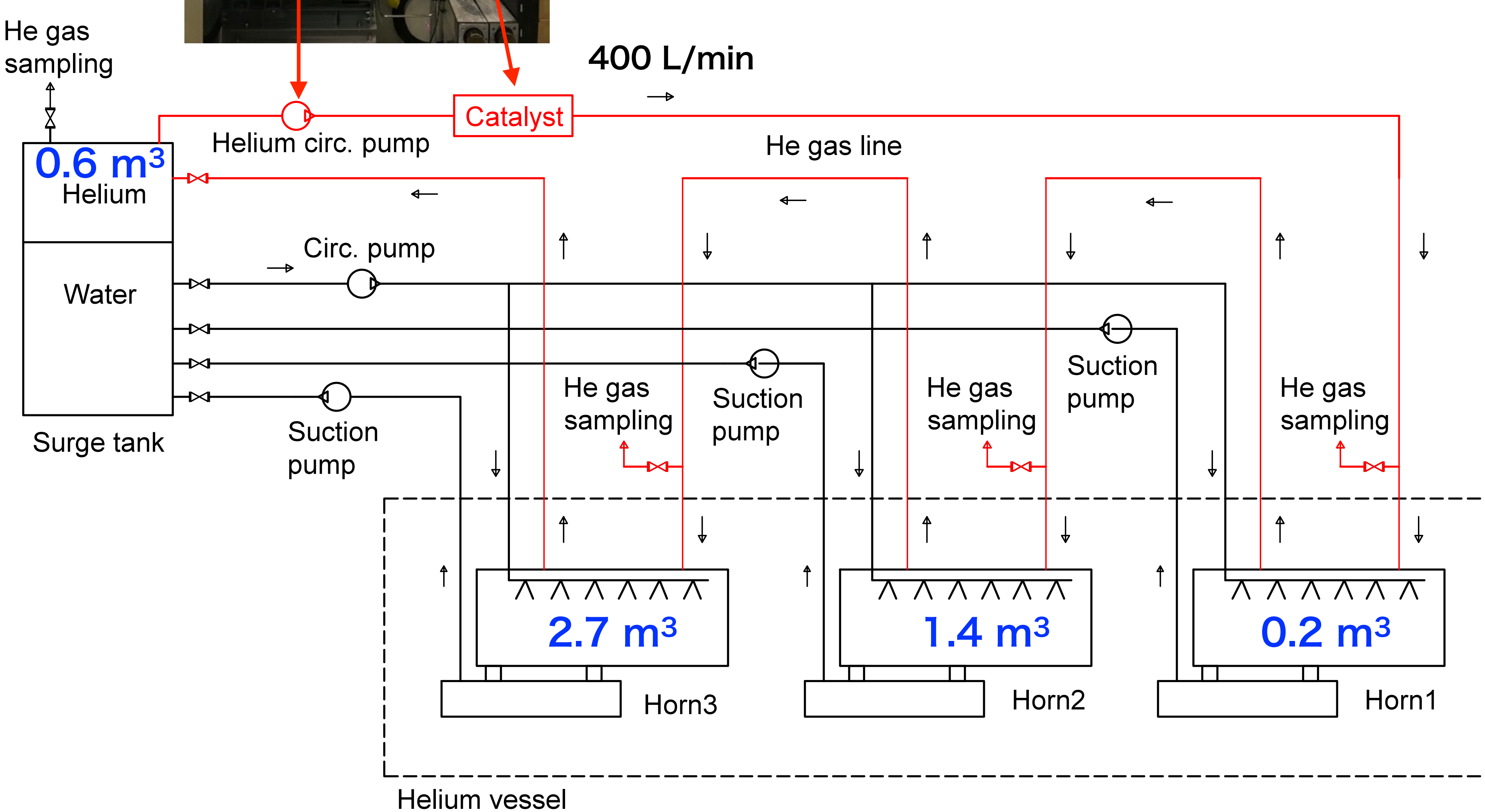
- **Measured production rate**
  - ~260 L (4.7%) / 10^{19} POT @ 485 kW
- **Hydrogen removal by recombination : $2H_2 + O_2 \rightarrow 2H_2O$**
  - Catalyst : Alumina pellet with 0.5% Pd
  - H_2 produced inside horns → Forced He (+H_2) circulation through catalyst
  - H_2 production rate greatly reduces to 5.8 L (0.1%) / 10^{19} POT
  - However, H_2 still gradually increases → He flushing once per 1~2 weeks
    - H_2 concentration : 1%→0.1%



Hydrogen Removal System

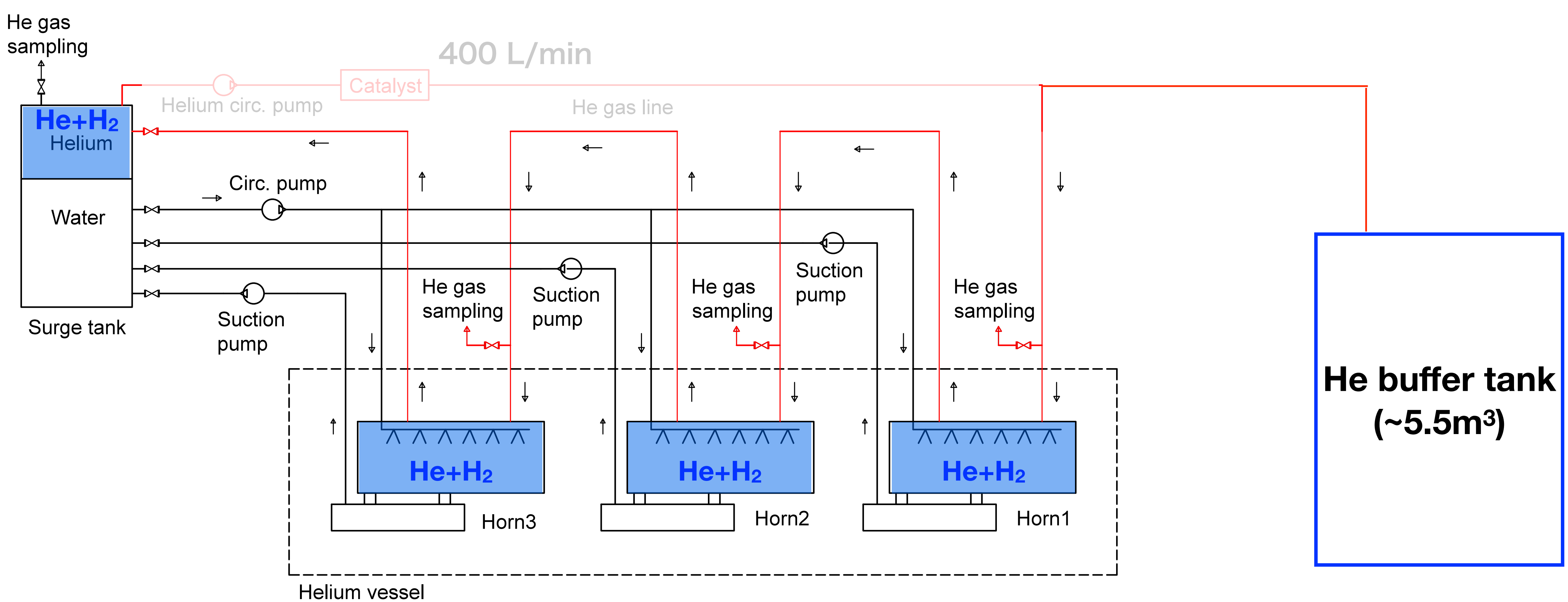


H_2 recombination catalyst
Alumina pellet with 0.5% Pd



Hydrogen Removal System

- **He flushing to be performed once a week (or two weeks)**
- **He flushing system**
    - He buffer tank (~5.5m³) in TS machine room
    - Pure He gas injected to water tank ⇒ Horns ⇒ He buffer tank
    - Old He gas stored for a week and exhausted to outside ⇒ short-lived nuclei to decay
    - One He flushing ⇒ 2/3 of entire He gas can be replaced with flesh He gas



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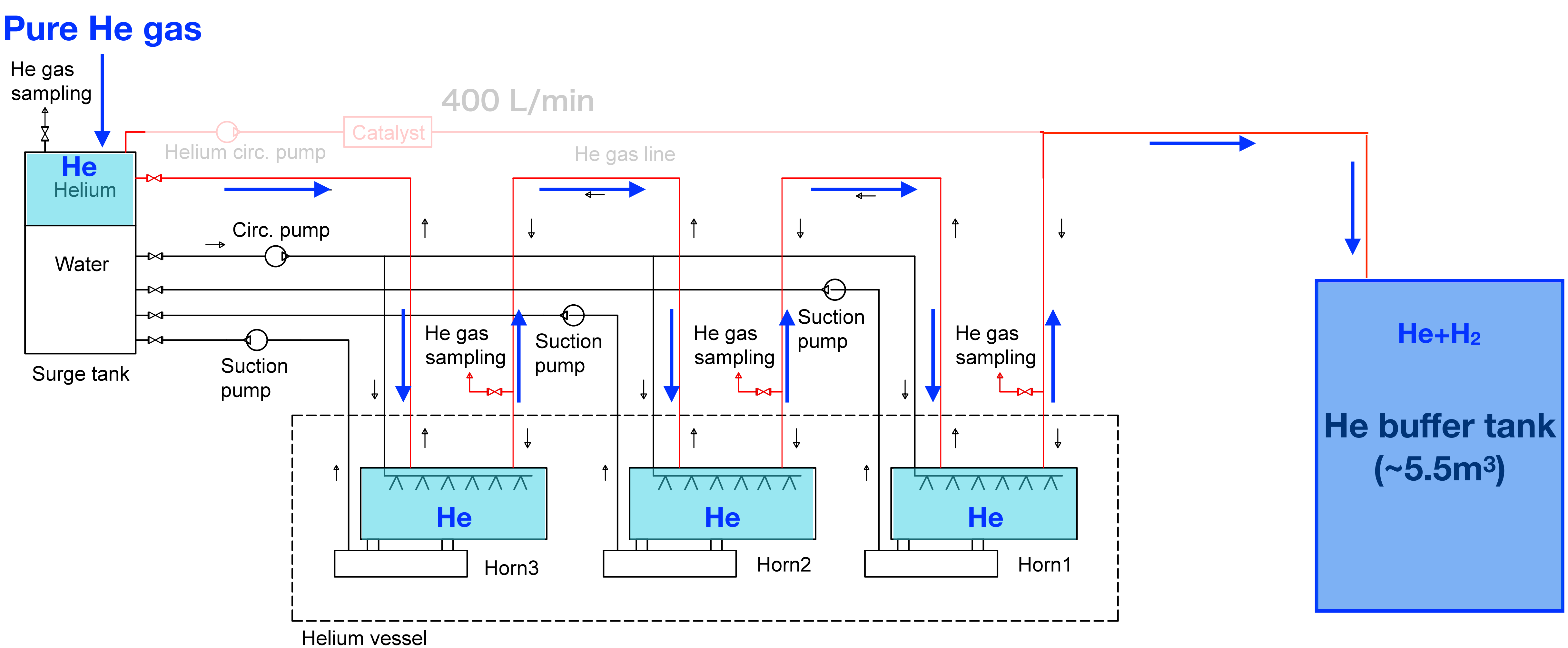

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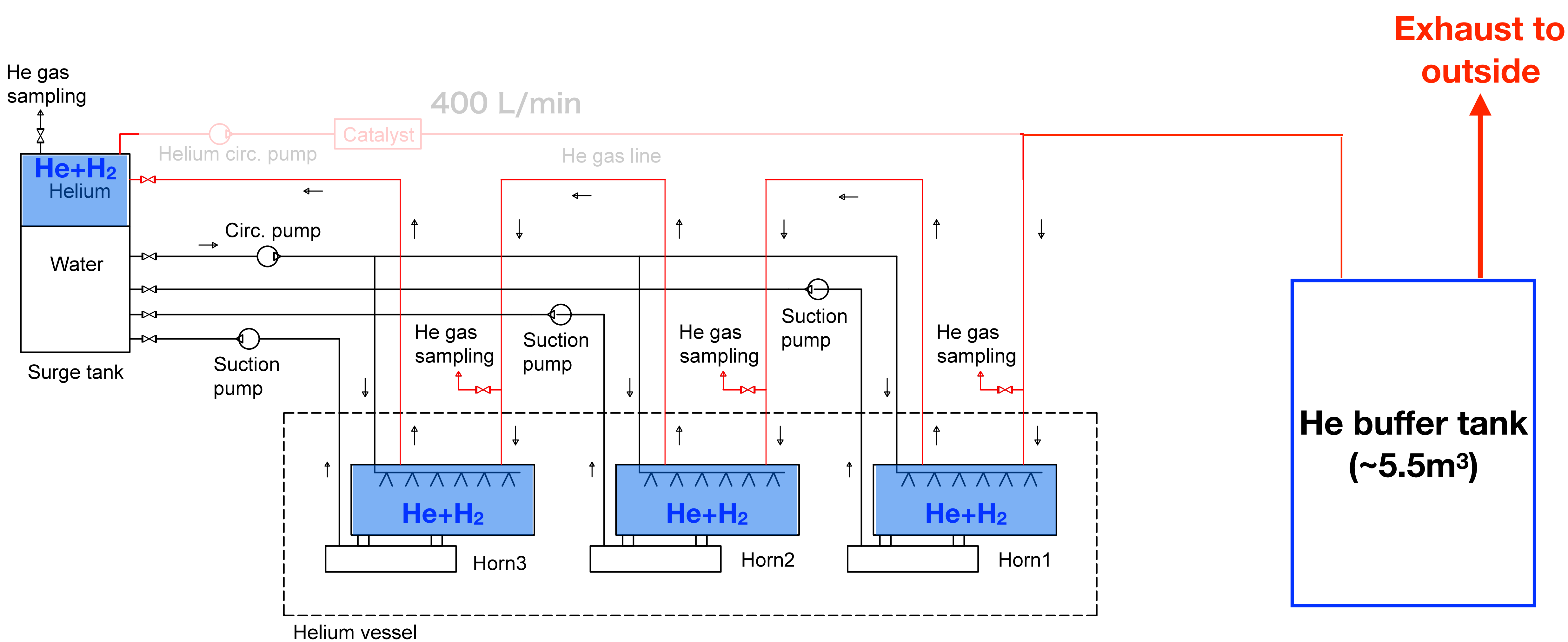
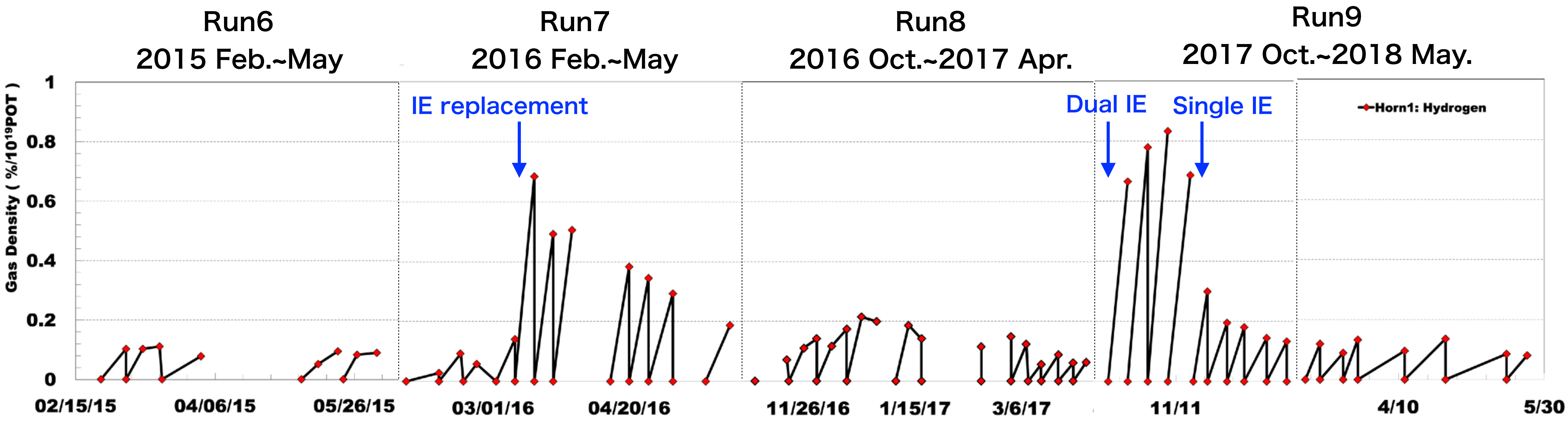


Prospect for 1.3 MW

- **Operation criteria**
  - Keep H_2 concentration below 3%
    - H_2 explosion limit in air = 4%
- **Prospect for 1.3 MW**
  - H_2 concentration < 1% in 1 week operation @ 485 kW ⇒ **< 3% @ 1.3 MW**
  - **Current production rate can be acceptable even with 1.3 MW beam**
    - But there exists some problems that need to be solved for a safe operation

Ion Exchanger Effect on H_2 Concentration

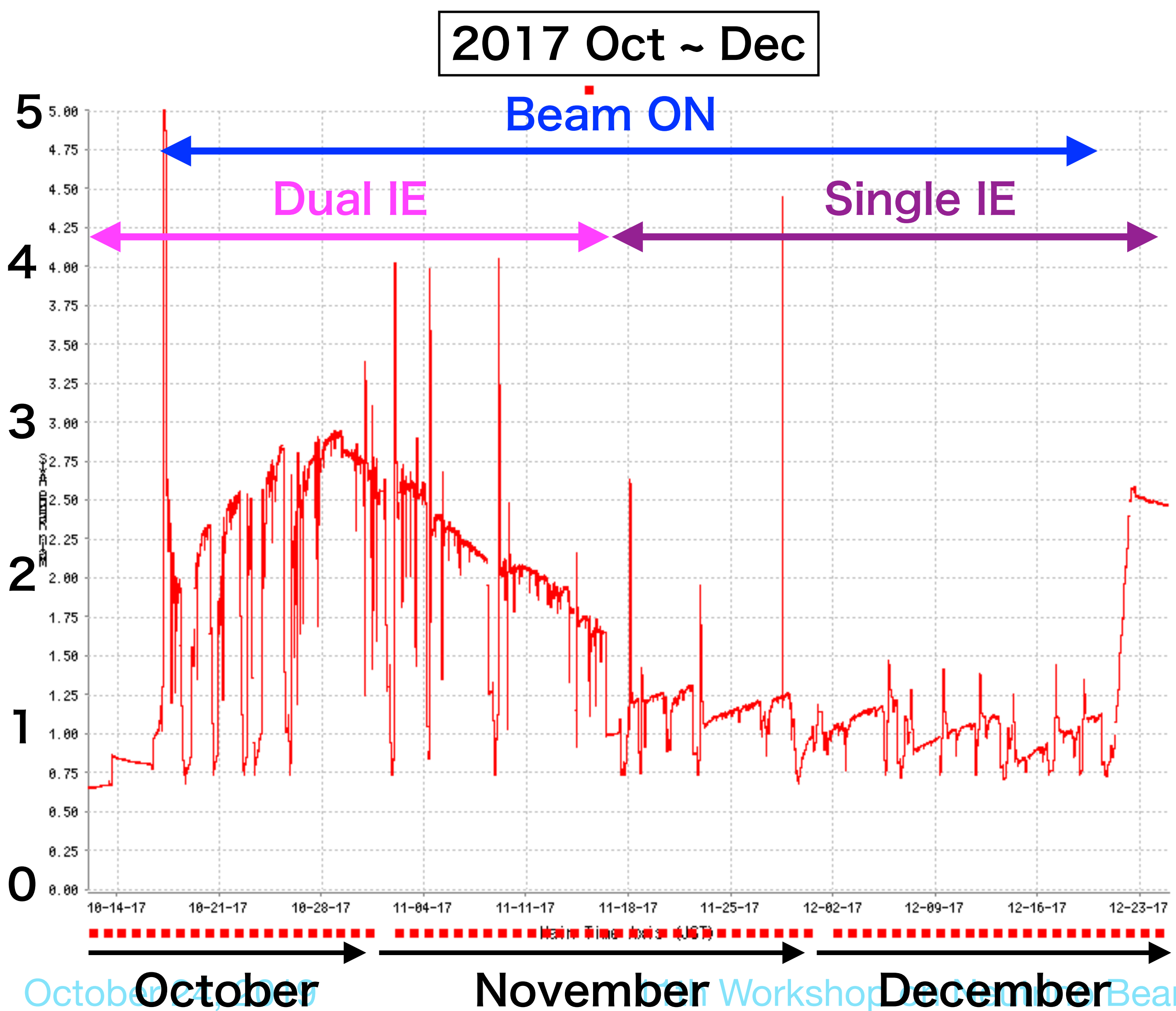


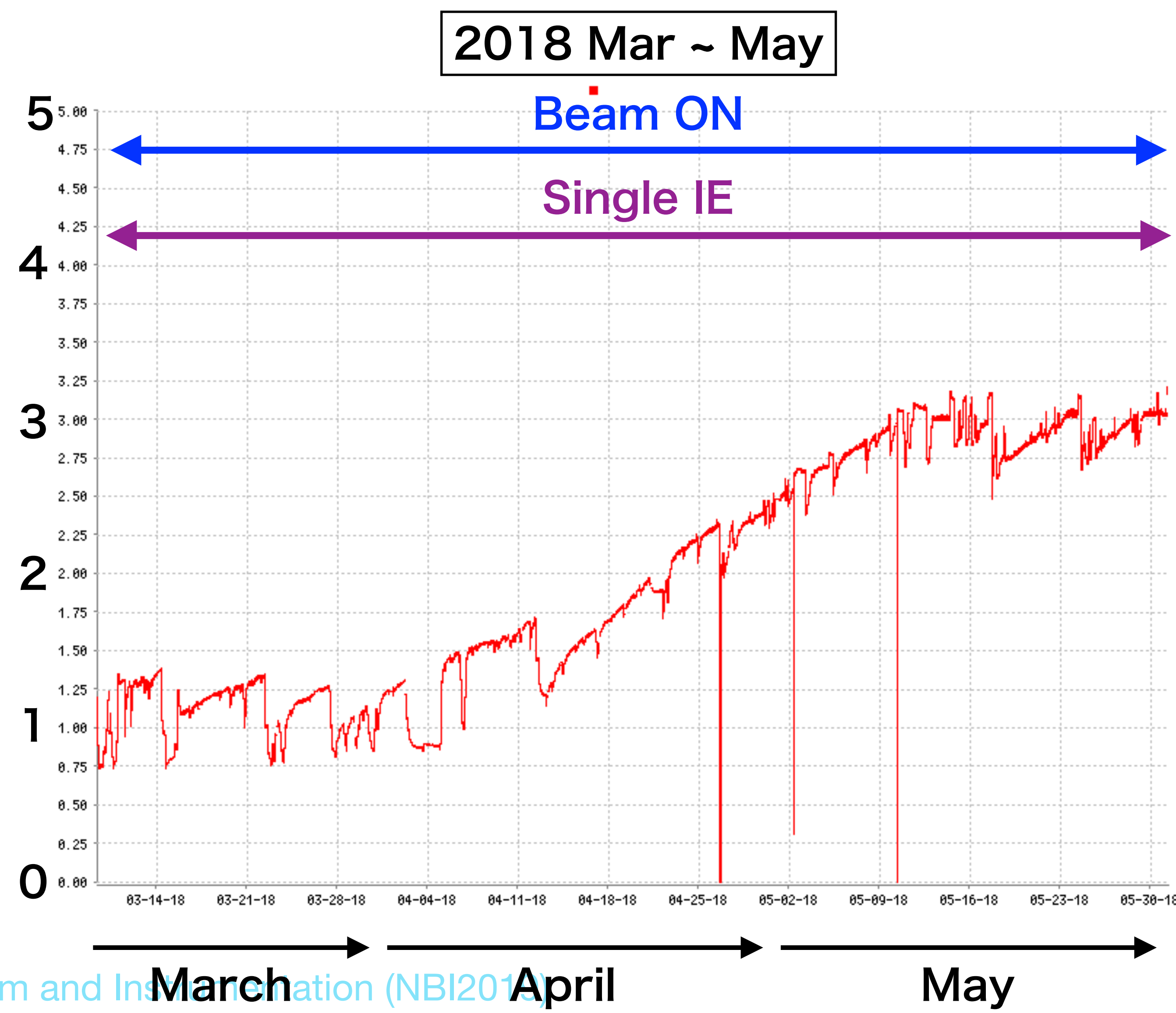
Run period	Run6	Run7	Run8	Run9-1	Run9-2	Run9-3
Configuration	Single (old)	Single (new)	Single (old)	Dual (new)	Single (new)	Single (new)
Beam power (kW)	330	390	470	450	475	485
H_2 concentration (%)	0.4	2.5	1.5	4.0	1.0	2.4
Production rate (% / 10^{19} POT)	0.173	0.683	0.215	0.832	0.299	0.137

- H_2 production rate rapidly increased after Ion exchanger replacement
- Moderate production rate for old IE, but water conductivity increased ⇒ IE's lifetime
- IE resins may be degraded due to oxidization by H_2O_2

Water Conductivity Trend

- **Water conductivity**
  - A strange behavior during dual IE operation
  - Low conductivity during single IE operation
  - Conductivity got increased around middle of April
    - This indicates lifetime of IE ⇒ **~6.0 x 10^{20} POT (or 2~3 months)**

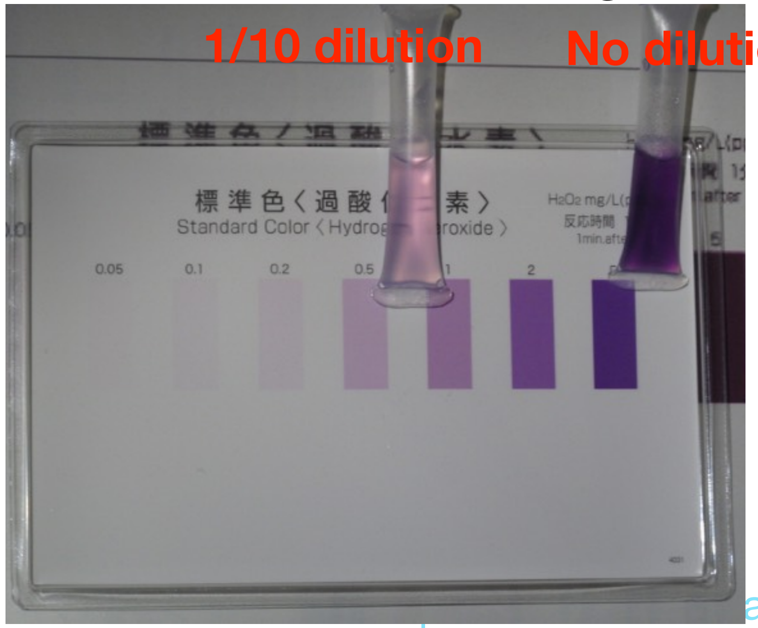




Effect of H_2O_2

- **Hydrogen peroxide (H_2O_2)**
  - Production rate is close to that of H_2 ($H_2 : H_2O_2 = 1.3 : 1$)
  - It **corrodes** IE resins ⇒ degradation of IE with presence of H_2O_2
  - Can be **decomposed naturally** : $2H_2O_2 \Rightarrow 2H_2O + O_2$
    - Catalyst can accelerate the decomposition
    - Resultant O_2 can work as a source O_2 for the recombination
- **Measurement of H_2O_2 concentration**
  - **~10 mg/L** ⇔ estimated : **~500 mg/L** @ 3.9×10^{20} POT
    - This indicates that most of H_2O_2 produced was decomposed
  - Even this small concentration of H_2O_2 can affect the IE resins

Sensitive to 0.05-5mg/L



Sensitive to 3-700mg/L

Problems and Countermeasures

- **Problems**
  - Short lifetime of IE due to H_2O_2 ⇒ IE replacement causes high H_2 production rate
  - H_2 gradually increases due to small O_2 concentration
    - Dissolved O_2 in cooling water (~1.9mg/L)
      - Can create superoxide O_2^- ($e_{aq}^- + O_2 \rightarrow O_2^-$), which can accelerate water radiolysis ⇒ dissolved O_2 should be removed
- **Countermeasures**
  - Need ion exchanger resins which are tolerant to H_2O_2
  - O_2 degasifier to remove dissolved O_2
  - Inject O_2 gas to solve the lack of O_2 for recombination ⇒ Safety control is an issue

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  To be considered

  - Inject O_2 gas to solve the lack of O_2 for recombination ⇒ Safety control is an issue

H_2O_2 Resistant Ion Exchanger

- **H_2O_2 is problematic for nuclear reactor business**
  - H_2O_2 resistant ion exchanger developed for nuclear reactor
  - Pd-doped ion exchanger can decompose H_2O_2 and ⇒ Pd works as a catalyst
    - therefore can extend lifetime of ion exchanger

Award Paper

Prolongation Technology of Life Time of Ion Exchange Resins in Nuclear Power Plants

T. Izumi et al (2018)

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(Manuscript accepted July 20, 2018)

Abstract

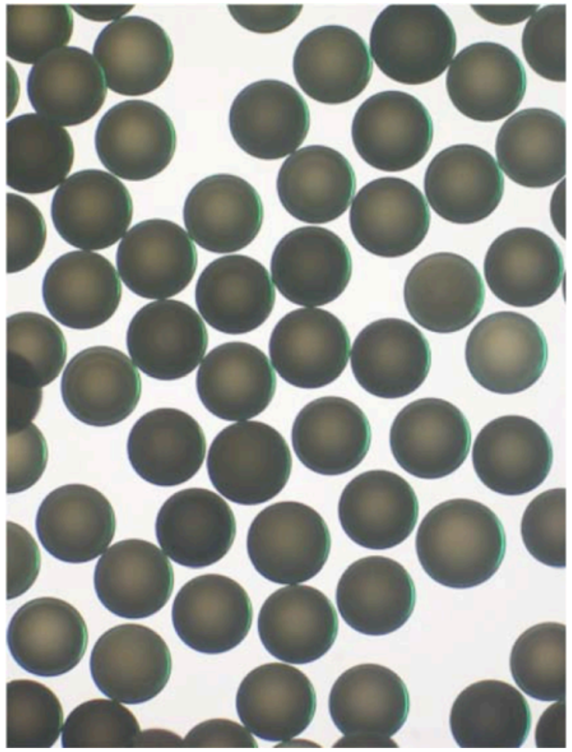
From the viewpoint of the minimizing the corrosion of the reactor's structural material in the nuclear power plants, the ion exchange resins are generally used as one of purification system in order to keep water quality clean. Hydrogen peroxide generated by the radiolysis of water exists in the reactor water and it accelerates the oxidation decomposition of the ion exchange resins and finally, it becomes the cause to shorten the resin life. To solve this problem, the application of Pd doped resins which can decompose hydrogen peroxide catalytically at the surface has been considered. It was confirmed by the cold test that Pd doped resins overlaid on the ion exchange resins or mixed with the ion exchange resins decomposed hydrogen peroxide contained in the reactor water and inhibited the oxidative degradation of the ion exchange resins. We report the results of these tests.

Keywords: Pd doped resins, Hydrogen peroxide, Ion exchange resins, Nuclear power plants

H_2O_2 Resistant Ion Exchanger

• New resin

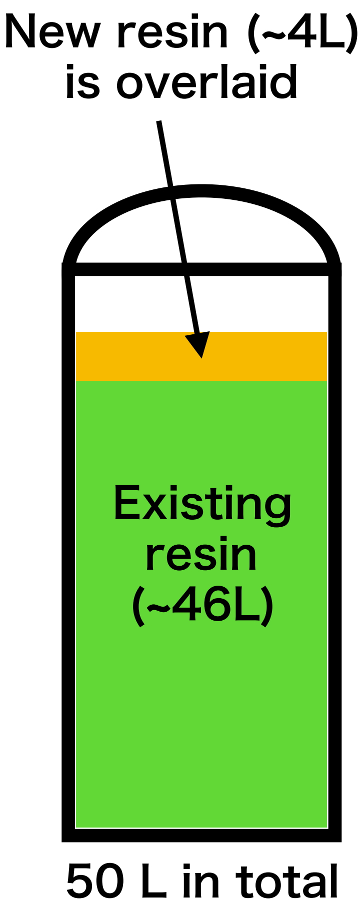
- Resins produced by LANXESS and its performance proved by EBARA
- I contacted the person in charge of the new resin and he was very interested in the application of this resin
- As a trial, this resin was put into one IE bottle for a test
  - 4L of the old resins were replaced with new ones
- To be tested during next beam time



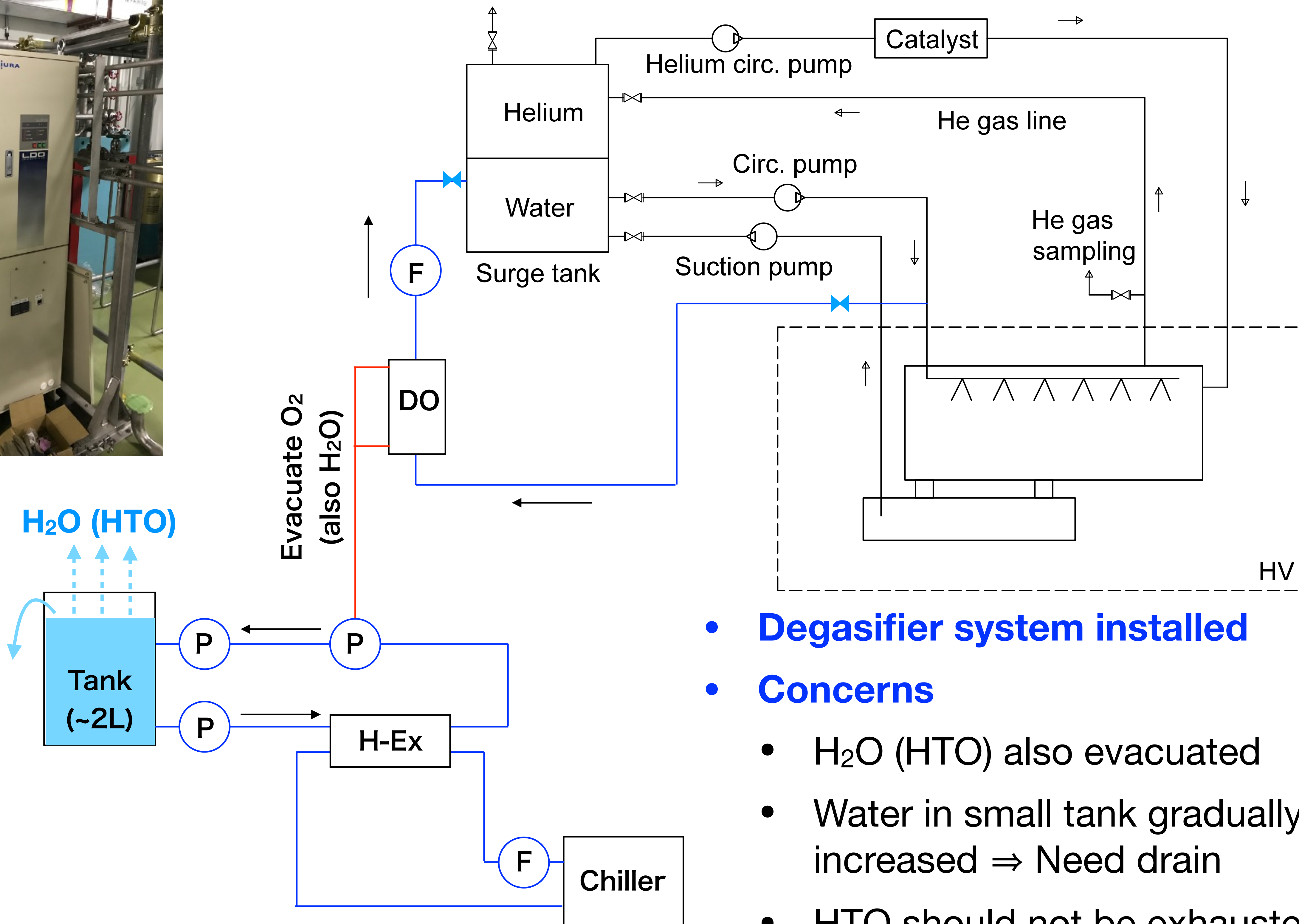
Remove existing resins

Put new resins

Completed IE bottle

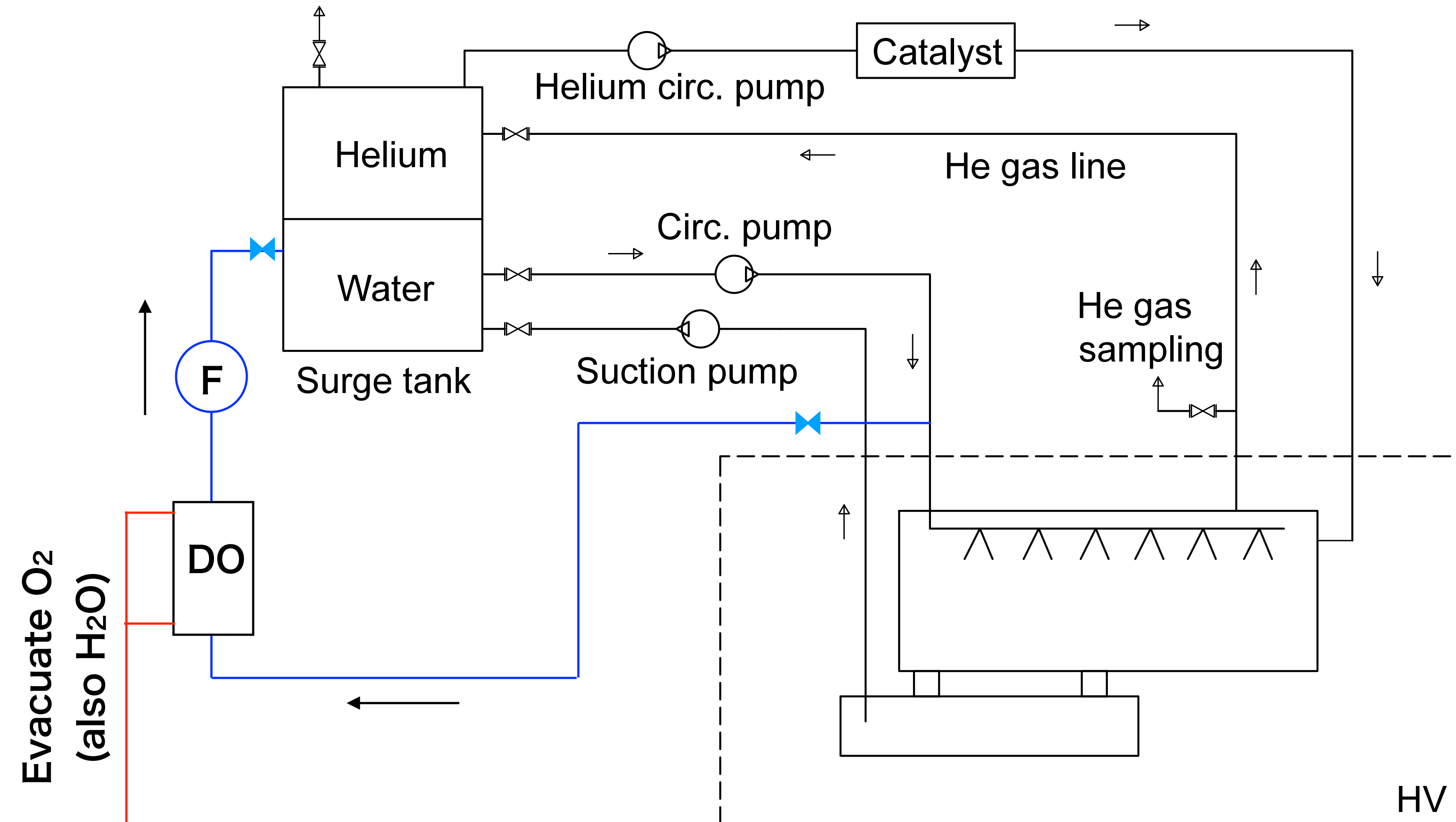


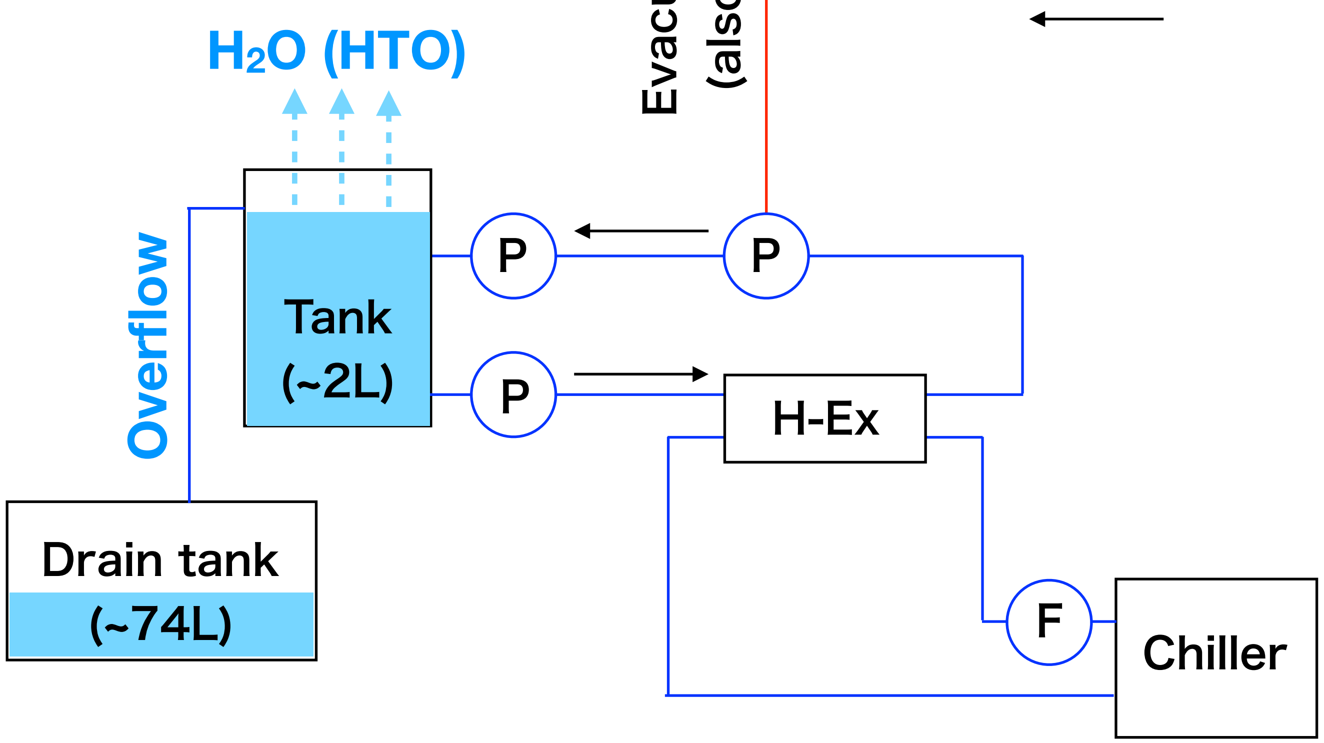
O_2 Degasifier System



- **Degasifier system installed**
- **Concerns**
  - H_2O (HTO) also evacuated
  - Water in small tank gradually increased ⇒ Need drain
  - HTO should not be exhausted to the air

O_2 Degasifier System





- **Degasifier system installed**
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  - Water in small tank gradually increased ⇒ **Drain tank added**
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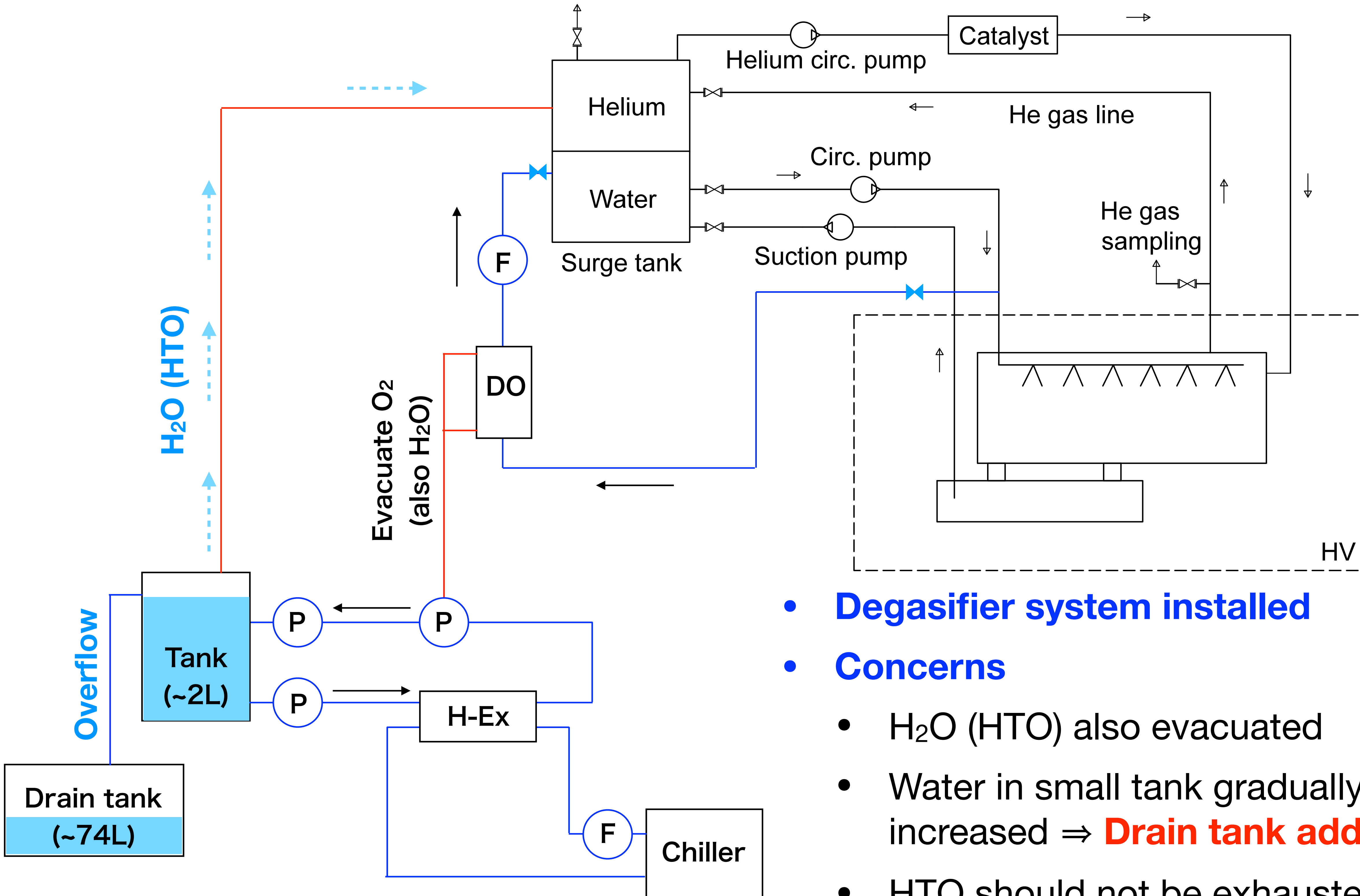

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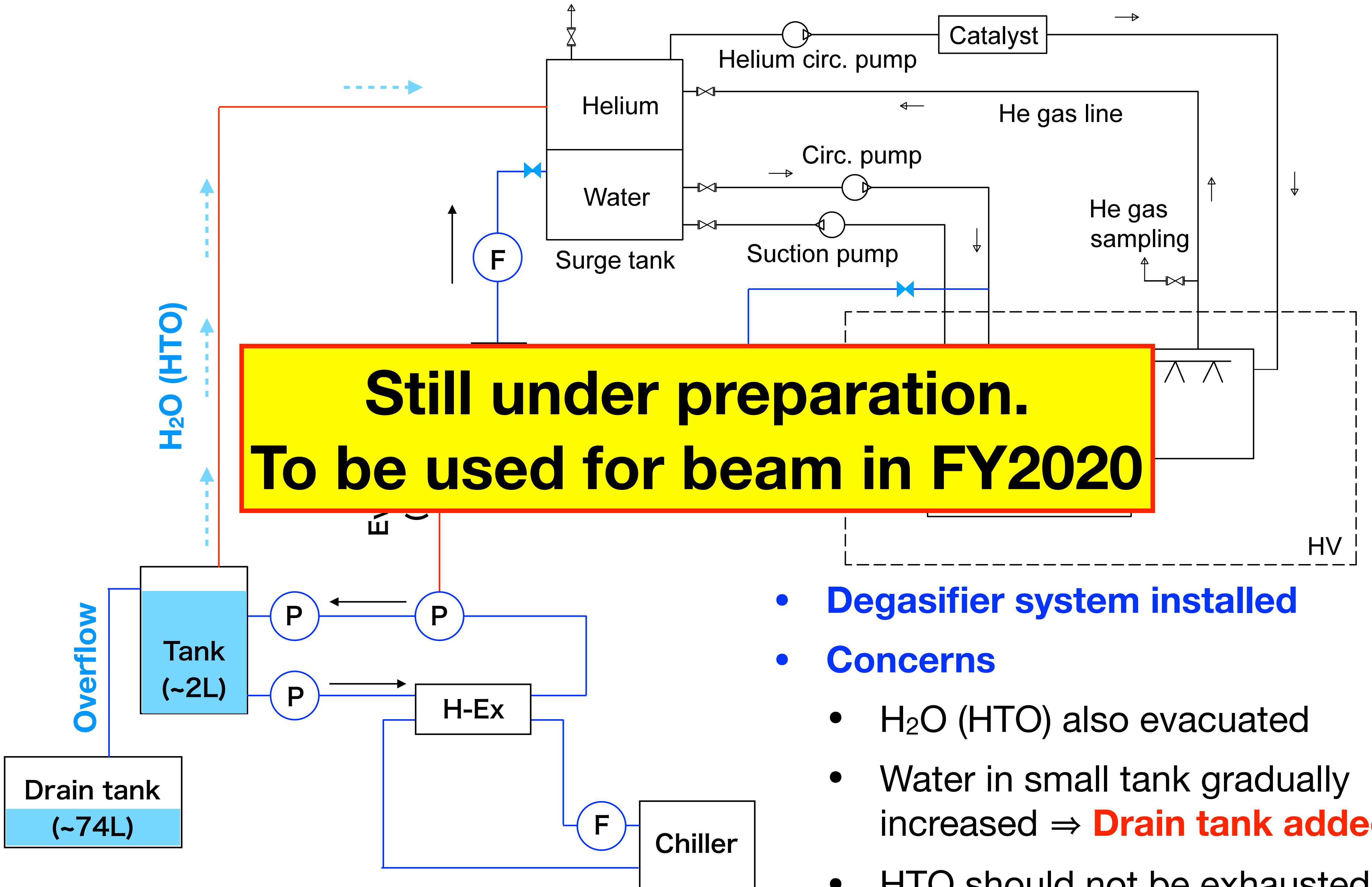
O_2 Degasifier System



Still under preparation.
To be used for beam in FY2020

- **Degasifier system installed**
- **Concerns**
  - H_2O (HTO) also evacuated
  - Water in small tank gradually increased ⇒ **Drain tank added**
  - HTO should not be exhausted to the air ⇒ **Return to water tank**

Summary

- Beam exposure to the horn cooling water creates H_2, O_2, H_2O_2
- H_2 is removed by H_2 recombination using catalyst
- H_2 concentration is currently < 1% per week @ 485 kW, which can indicates < 3% even at 1.3 MW
- It is likely that ion exchanger resins are oxidized by H_2O_2 and lifetime is 2~3 months
- New ion exchanger resins tolerant to H_2O_2 are introduced and will be tested in next beam time
- Dissolved O_2 in the water can affect H_2 production rate. O_2 degasifier is under preparation.