Comparison of excess heat evolution from zirconia-supported Pd-Ni nanocomposite samples with different Pd/Ni ratio under exposure to hydrogen isotope gases

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Abstract

Hydrogen isotope absorption by palladium and nickel-based nanocomposite samples has been examined as a collaborative work using the experimental apparatuses installed at Kobe University and Tohoku University in order to share scientific understanding of the anomalous heat effects both at room temperature (RT) and elevated temperatures (ET). In the present paper we discuss D (or H) gas charging and heat release characteristics of PNZ6, PNZ6r and PNZ7k tested in Kobe.

These samples consist of Pd-Ni nanocomposites embedded in ZrO_2 particles that had been formed by milling of calcined amorphous ribbons of Pd, Ni and Zr mixture made by melt-spinning method. The calcination was performed in atmospheric air for 60 hours at 450 °C. The PNZ6r sample is a re-oxidized sample of PNZ6 after finishing a series of D(H) gas charging/calorification experimental runs at RT and ET with repeated sample baking. The PNZ6 and PNZ6r samples contain Pd and Ni with atomic ratio of Pd/Ni = 1/10, while the PNZ7k sample contains them with Pd/Ni = 1/7. About 100 gram of the sample containing about 20 gram of Ni was used in each case.

The samples have been characterized by XRD, SEM-EDX and TEM analyses to reveal existence of $NiZr_2$ phase and formation of $NiZr_2D_x$ under exposure to D_2 gas. The samples have also been subjected to ERDA analyses to examine hydrogen isotope distribution in the near surface region.

The results of the gas charging/calorification measurements are summarized as follows:

(1) Similarly to other PNZ samples tested so far, in the initial phases at RT (#1-1) for virgin PNZ6 and PNZ7k samples, hydrogen absorption and heat evolution are characterized by large amount of the loading ratio $L_M \equiv$ D/(Pd·Ni) ~ 3.4 and the specific absorption energy η_{av} ~ 0.6 eV/D.

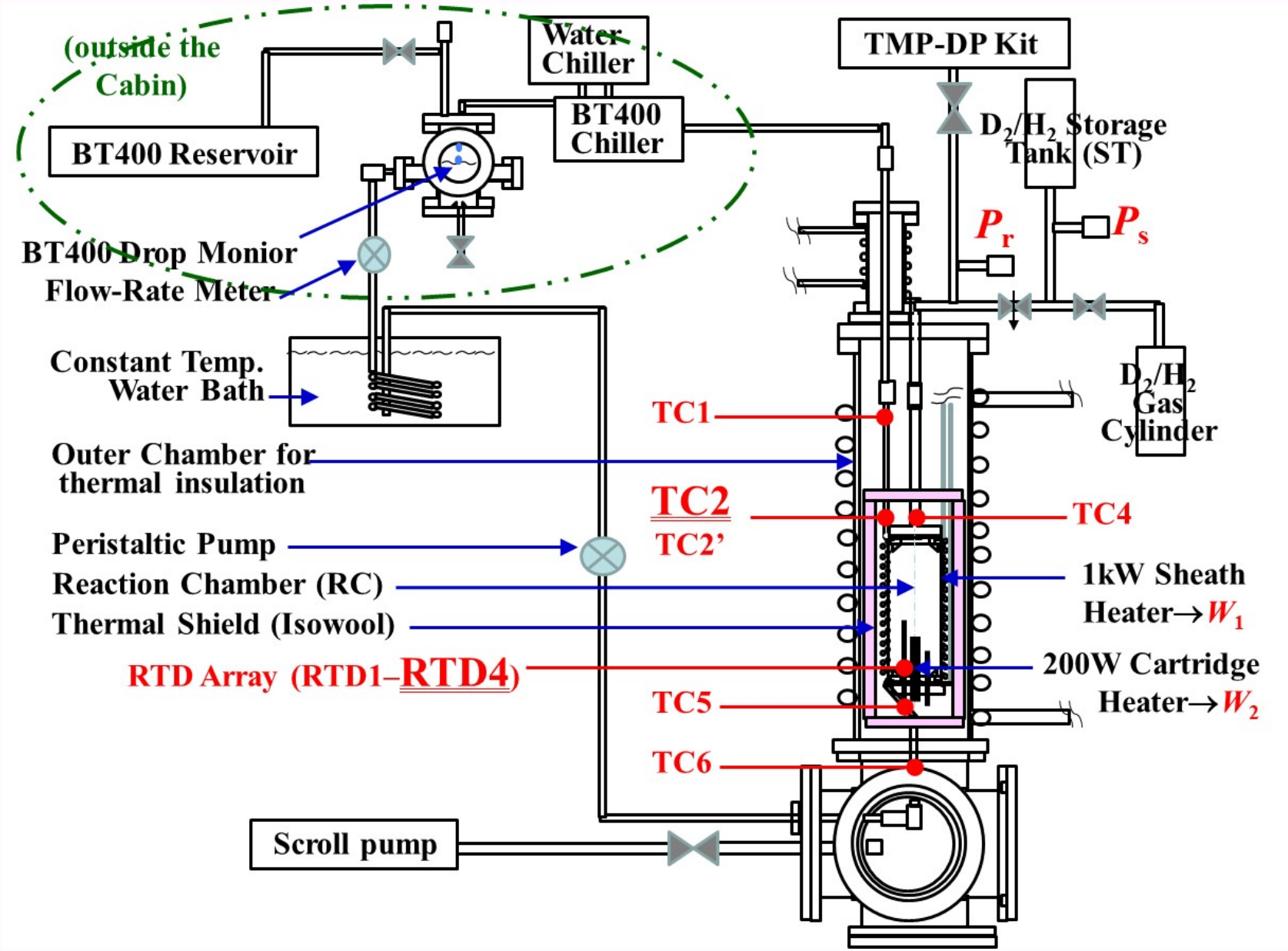
(2) On the other hand, in #*n*-1 ($n \geq 2$) phases at RT for these samples after the cycle of RT-ET D(H)-gas charging phases followed by vacuum baking between #(*n*-1) and #*n* runs, the values reduces to $L_M \equiv$ D/(Pd·Ni) ~ 1.3 and η_{av} ~ 0.3 – 0.4 eV/D, to which formation of PdD/NiD and $NiZr_2D_x$ contributes.

(3) In the ET phases, the excess power W_{ex} continuing for several weeks with the maximum reaching 24 W and slowly decreasing to around 10 W has been recorded for PNZ6, while W_{ex} ~ 7 - 8 W for PNZ6r, and 3 - 4 W for PNZ7k.

(4) The fact that the samples with Pd/Ni = 1/10 showed much higher excess power than the sample with Pd/Ni = 1/7 suggests that the atomic ratio is one of the key factors to improve the COP.

(5) The maximum integrated excess energy amounts to 40 MJ/mol-Ni or 200 MJ/mol-H without any observable change in the sample composition, which cannot be explained by any chemical process.

Experimental system C_1 with oil-flow calorimetry for nano-metal H(D) energy

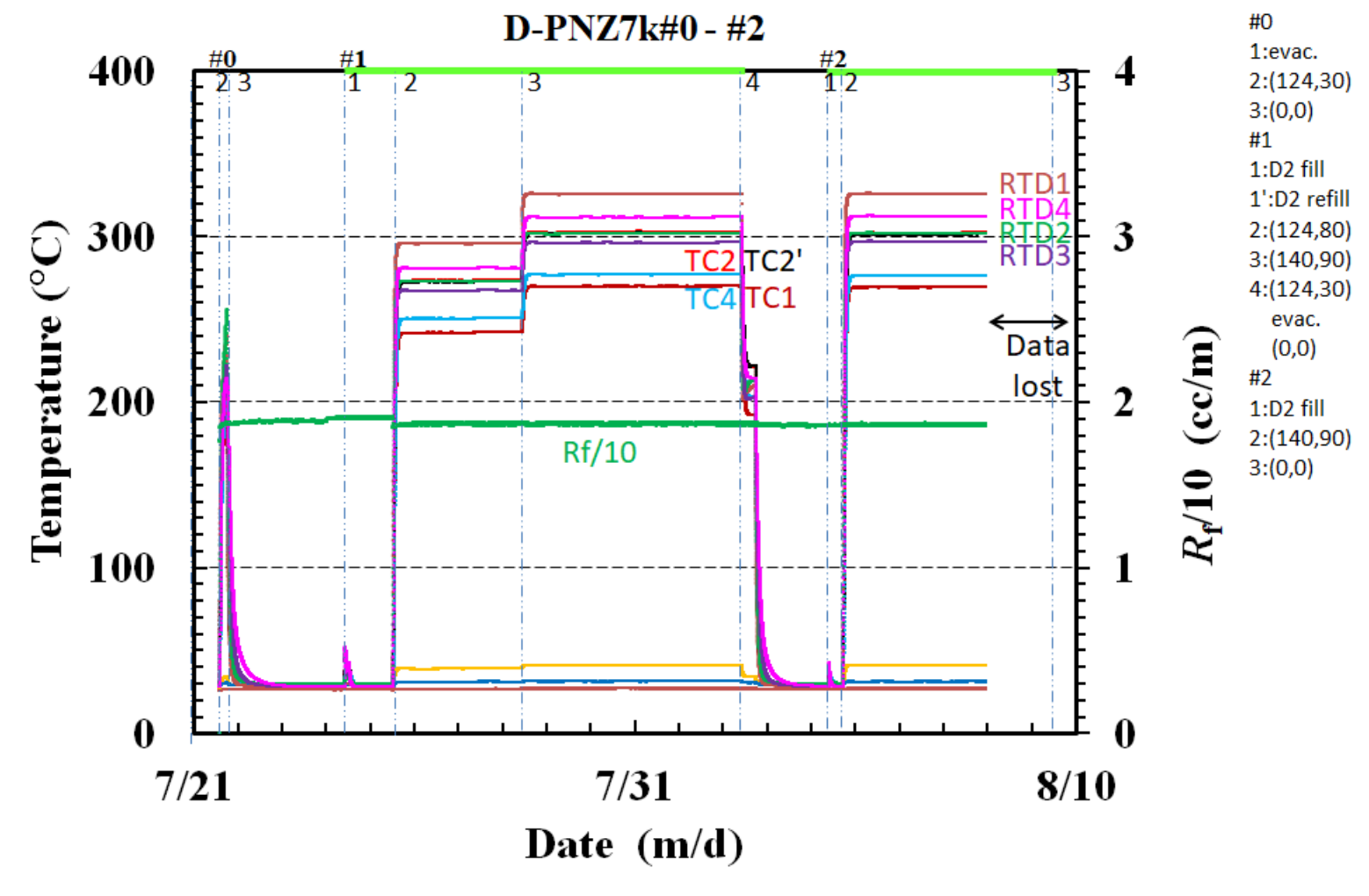


Atomic composition for Pd_1Ni_{10}/ZrO_2 (PNZ6, PNZ6r) and Pd_1Ni_7/ZrO_2 (PNZ7k)

Sample	Mass (g)	Molar ratio				ZrO_2 filler mass (g)
		Ni	Pd	Zr	O	
PNZ6	124.2	**0.318**	**0.032**	**0.650**	0.240	1377
calcined at 450°C·60h		10 : 1				
PNZ6r	131.9	**0.318**	**0.032**	**0.650**	1.03	1378
recalcined at 450°C·60h		10 : 1				
PNZ7k	99.8	**0.306**	**0.044**	**0.650**	0.274	1531
calcined at 450°C·60h		7 : 1				

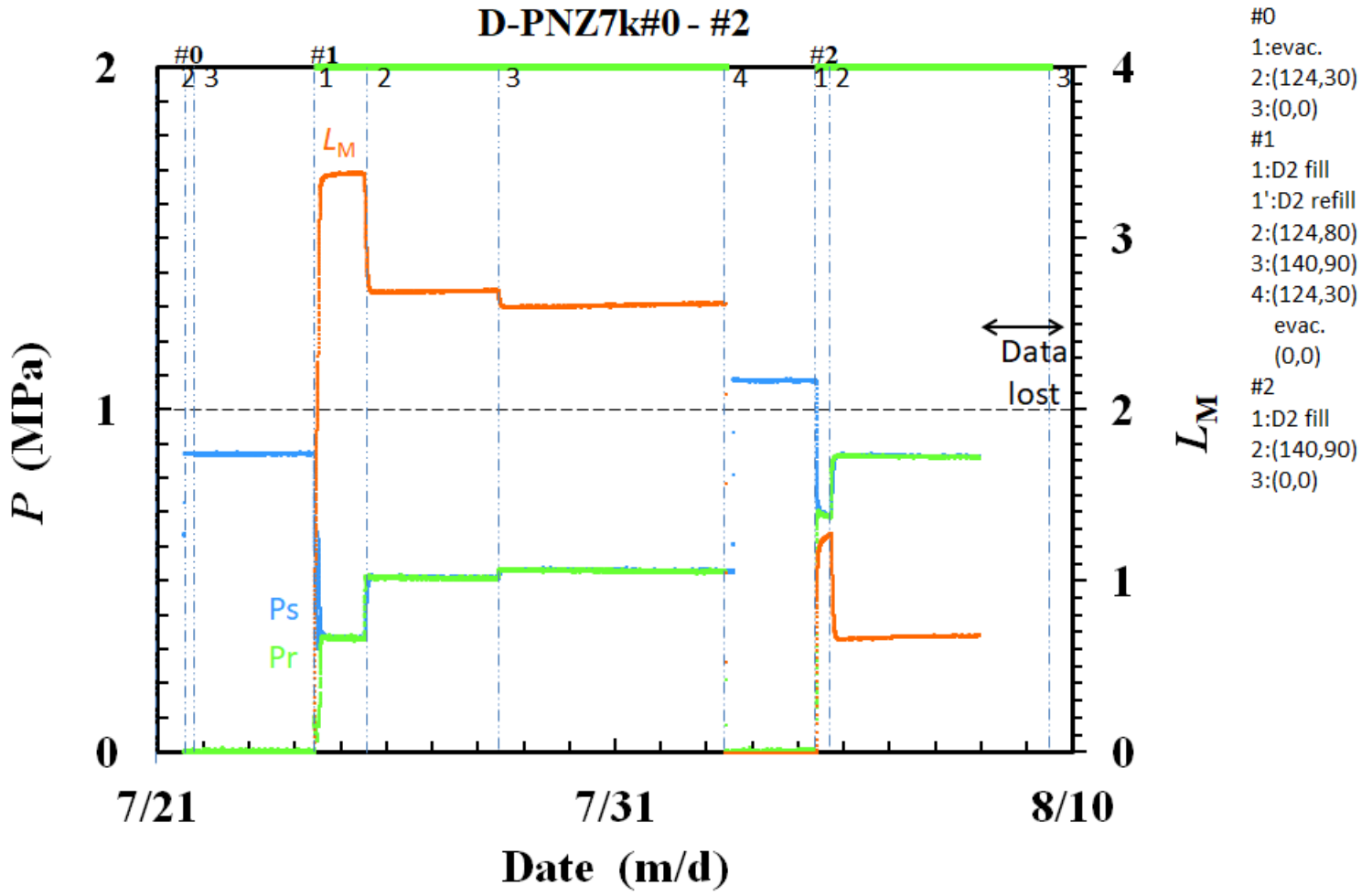
95% of 500-cc RC was filled with ZrO_2 filler

Temperature data and oil flow rate (R_f) data in PNZ7k#0 through #2 runs



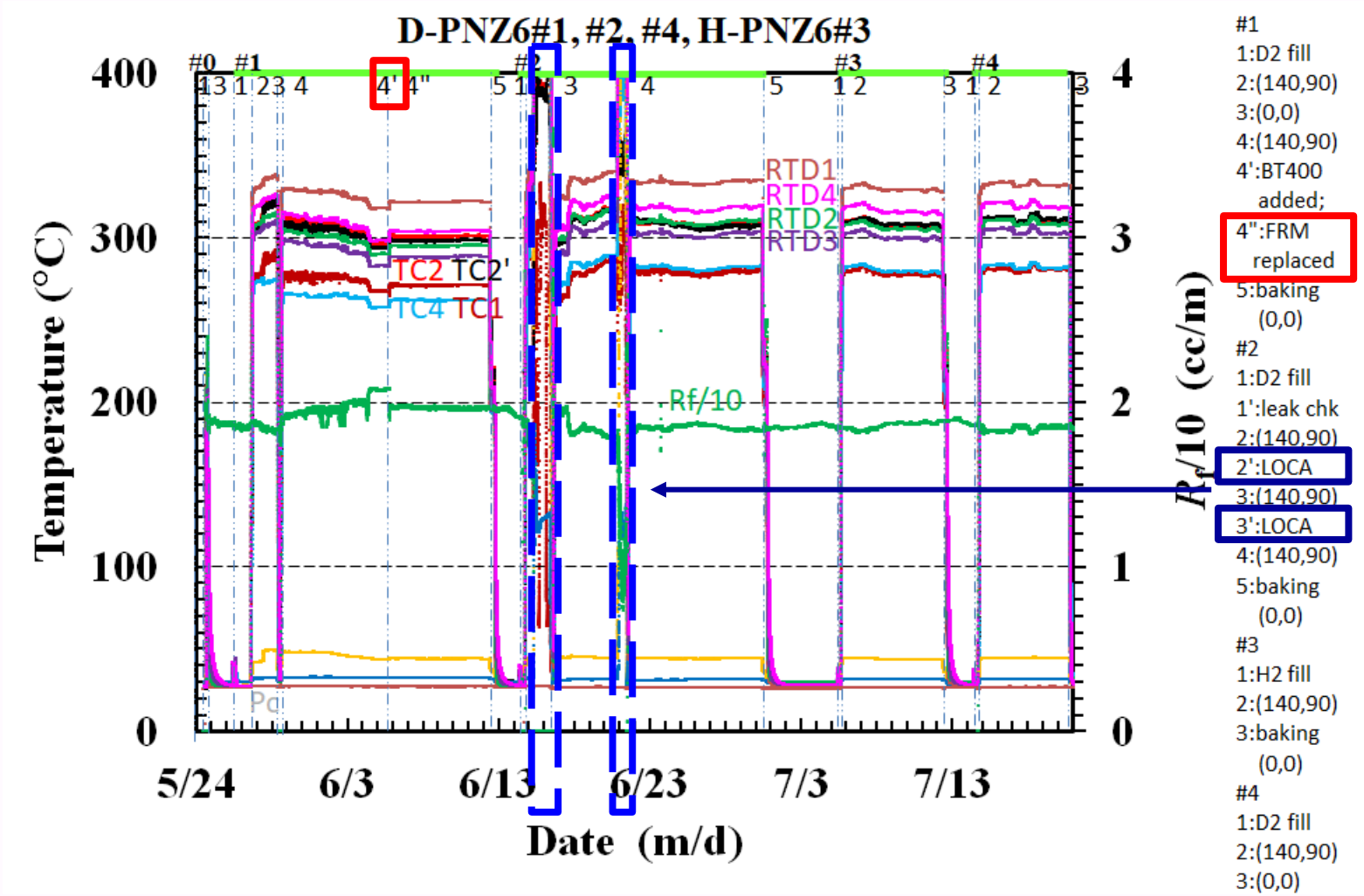
- Rather uniform temperature distribution in RC : 300~320°C
- Coolant flow rate R_f is stable.

Hydrogen loading ratio L_M(≡D/M) derived from pressures and volumes of the reaction chamber (RC) and the storage tube (ST) in PNZ7k#1~#2 runs



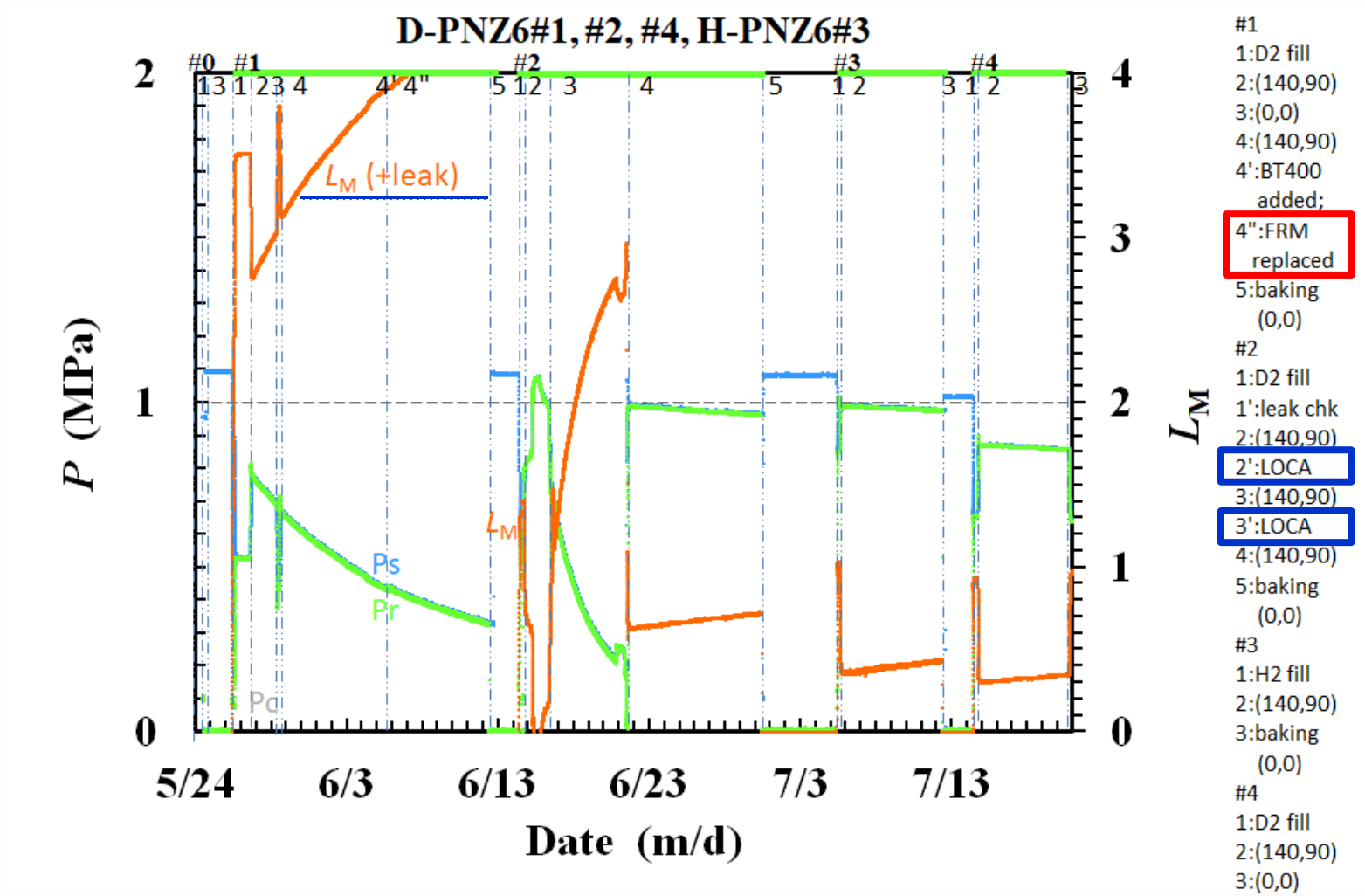
- L_M is a decreasing function of temperature due to desorption.
- After re-baking at #1-4, L_M dropped drastically at #2-1 and later.

Temperature evolution and oil flow rate R_f in PNZ6#0 through #4 runs



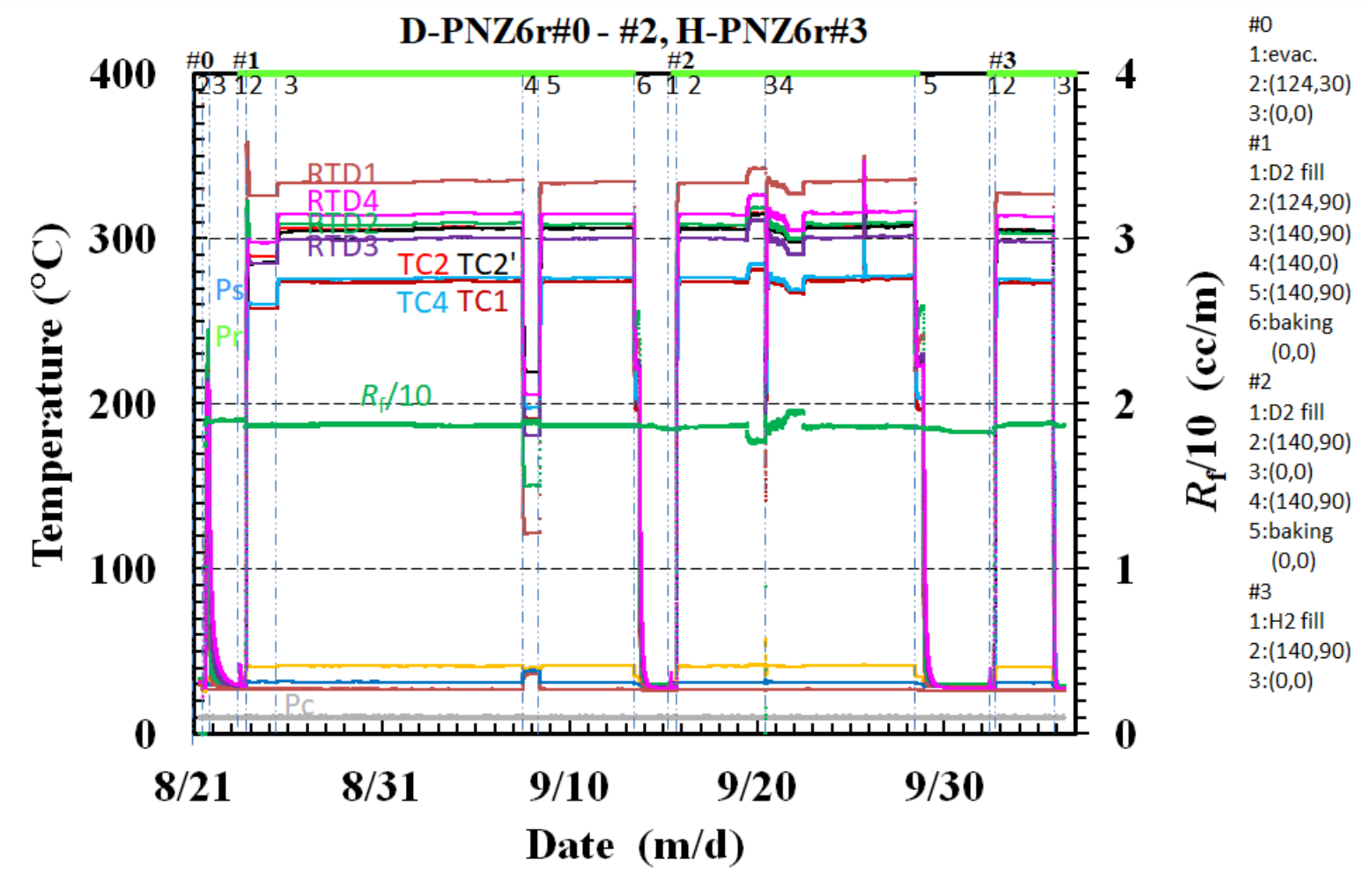
- Considerable time-variation of temperature evolution in RC, measured by RTDs : 300~340°C by constant heater input of 230 (140, 90) W

Hydrogen loading ratio L_M (=D/M) and D(H)-gas pressure in PNZ6#1~#4 runs



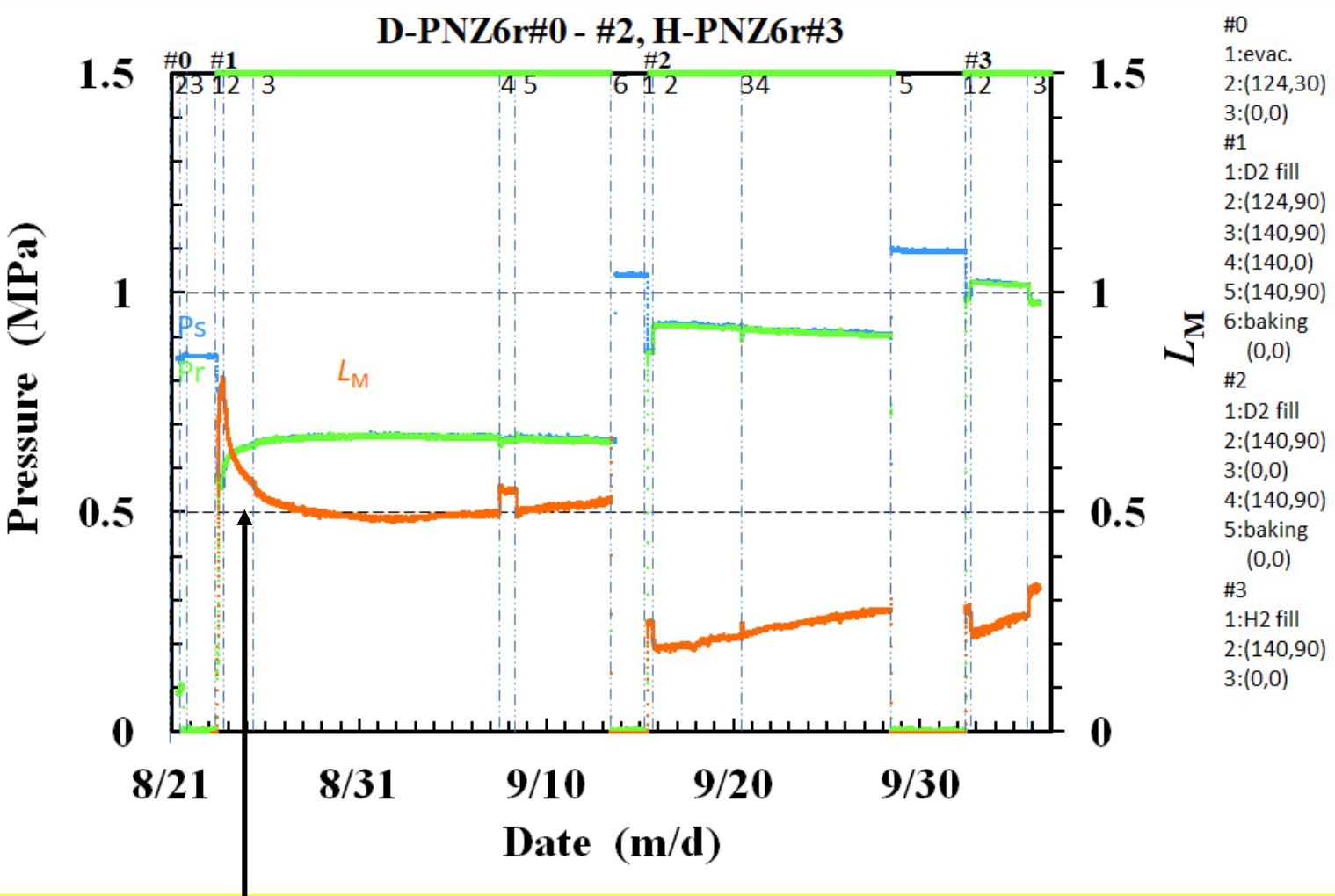
- Appreciable gas-leak from RC, but with little influence on L_M data at RT

Temperature evolution and oil flow rate in PNZ6r#0 through #3 runs



Small time variation of the RC temperatures at RTDs shows rather steady excess power evolution in the re-oxidized PNZ6r sample.

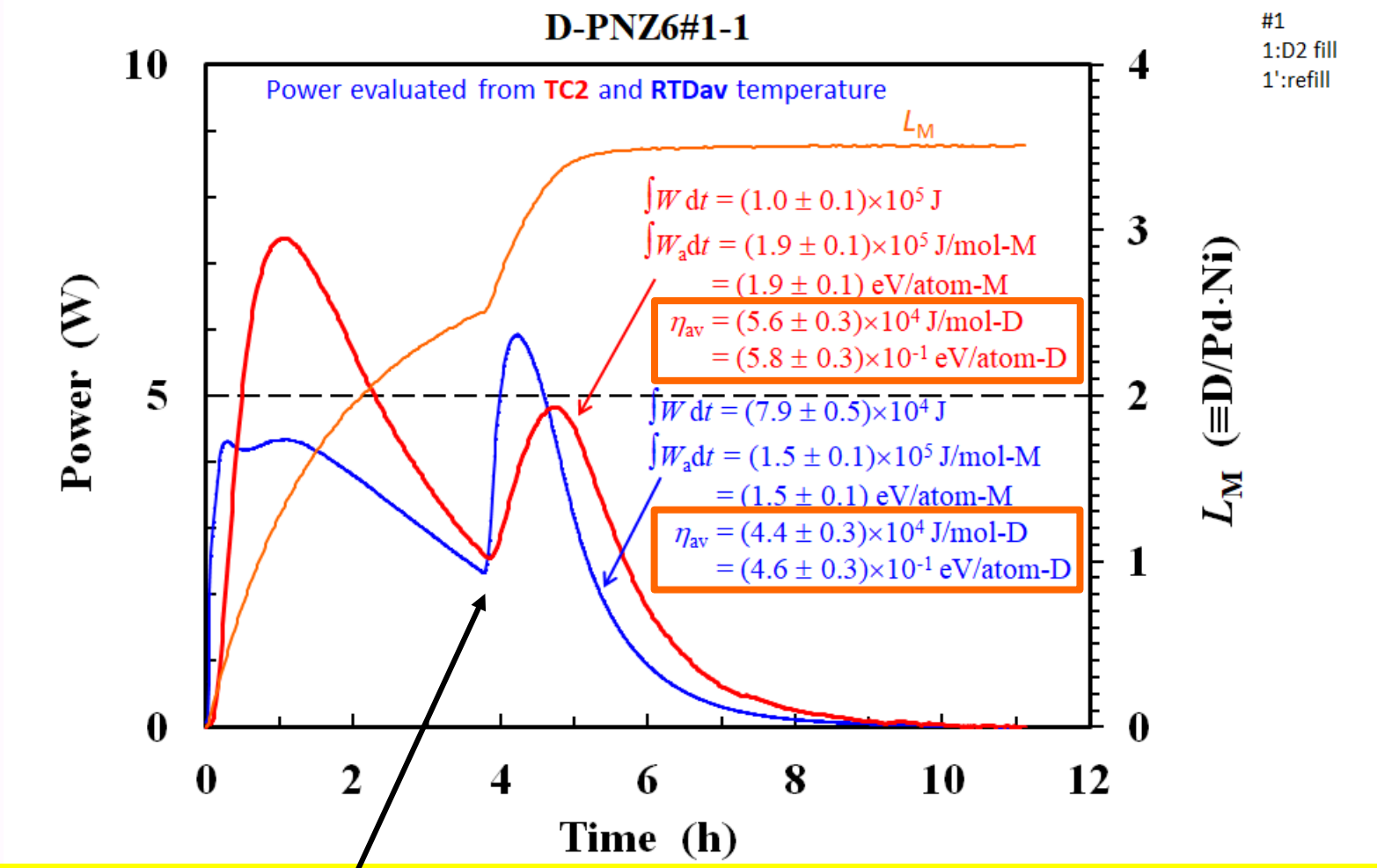
Hydrogen loading ratio L_M (=D/M) and gas pressure in PNZ6r#1~#3 runs



- Desorption under elevated temperatures similar to other samples, but with exceptionally large time constant
- Under such desorption, excess heat was observed (see p.21).

Absorption and heat evolution at room temperature (RT)

Typical hydrogen evolution of L_M and power in PNZ6#1-1 phase at RT



- **Deuterium resupplied to ST**
- **20% difference between the integrated values evaluated from TC2 and those from RTDav : due to inhomogeneity of the 124.2-g sample distributed in the ZrO_2 filer**

(cf.: 1 eV/atom-M = 0.96E+05 J/mol-M)

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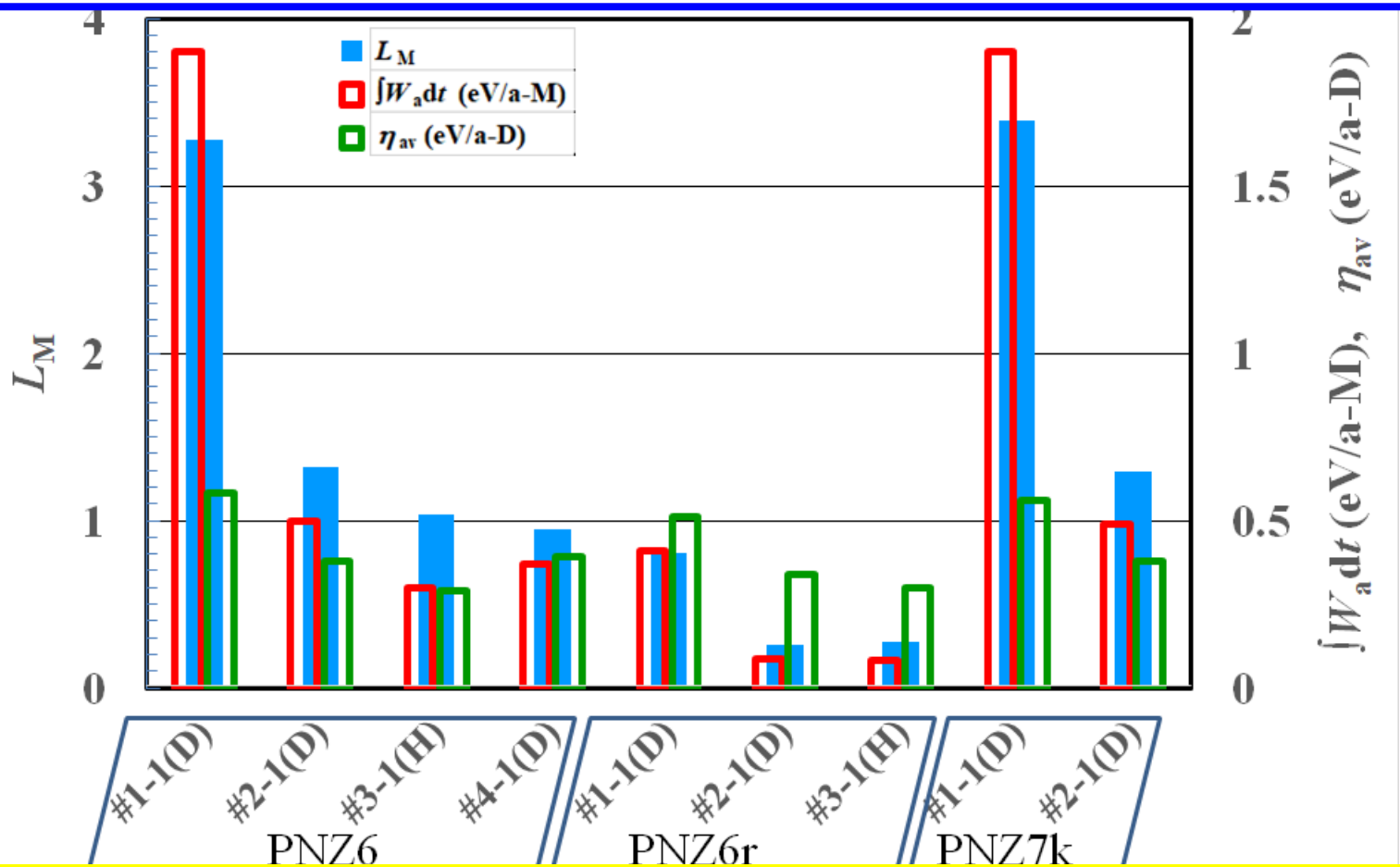
Comparison of L_M, $\int W_a dt$ and η_{av} in RT phases



- All quantities for PNZ7k are similar to those for PNZ6.
- All quantities for PNZ6 are similar to those for other PNZ* samples.

} Implying the same physics

- η_{av} for PNZ6r#*n*-1 are similar to those for PNZ6#*n*-1.
- L_M and $\int W_a dt$ for PNZ6r#1-1 succeed the tendency of those for PNZ6#1-1 ~ #4-1, and decrease to very small values in PNZ6r#2-1 and PNZ6r#3-1.

(cf.: 1 eV/atom-M = 0.96E+05 J/mol-M)

Known chemistry to be considered for PNZ* exposed to $D_2(H_2)$

Composition after #0 baking : ZrO_2 +(1-*x*)$NiZr_2$ +*x*(NiO +PdO)

#1-1:

reduction $PdO + D_2(H_2) \rightarrow Pd + D_2O(H_2O)\downarrow$ + 1.77(1.63) eV/atom-Pd, (1)

$NiO + D_2(H_2) \rightarrow Ni + D_2O(H_2O)\downarrow$ + 0.176 (0.033) eV/atom-Ni. (L_M=2.0) (2)

absorption $Pd + (a/2)D_2(H_2) \rightarrow PdD_a(H_a)$ + 0.2 (0.18) eV/atom-Pd, (3)

$Ni + (b/2)D_2(H_2) \rightarrow NiD_b(H_b)$ + (0.1~0.2) eV/atom-Ni. (L_M=*a*+*b*) (4)

absorption $NiZr_2 + (3.7/2)D(H)_2 \rightarrow (0.7NiZr_2D(H)_{2.23}+0.3NiZr_2D(H)_{7.16})$ + (? eV). (5)

(3.7=0.7×2.23+0.3×7.16; 0.7/0.3; cf. XRD spectra (NISSAN) (L_M=3.7)

#1-*n*(*n*≥2):

desorption (reversed (5)) $NiZr_2H_{3.7} \rightarrow NiZr_2 + (3.7/2)H_2\uparrow$, (5')

desorption (reversed (3)&(4)) $Ni(Pd)D_b(H_b) \rightarrow Ni(Pd) + (b/2)D_2(H_2)\uparrow$. (3'4')

Composition after #1 baking : ZrO_2 +*x*(Pd +Ni) +(1-*x*-*y*)$NiZr_2H_{3.7}$ +*y*$NiZr_2$

#*n*-1:

reduction $Pd + (a/2)D_2(H_2) \rightarrow PdD_a(H_a)$ + 0.2 (0.18) eV/atom-Pd, (3)

$Ni + (b/2)D_2(H_2) \rightarrow NiD_b(H_b)$ + (0.1~0.2) eV/atom-Ni. (L_M=*a*+*b*) (4)

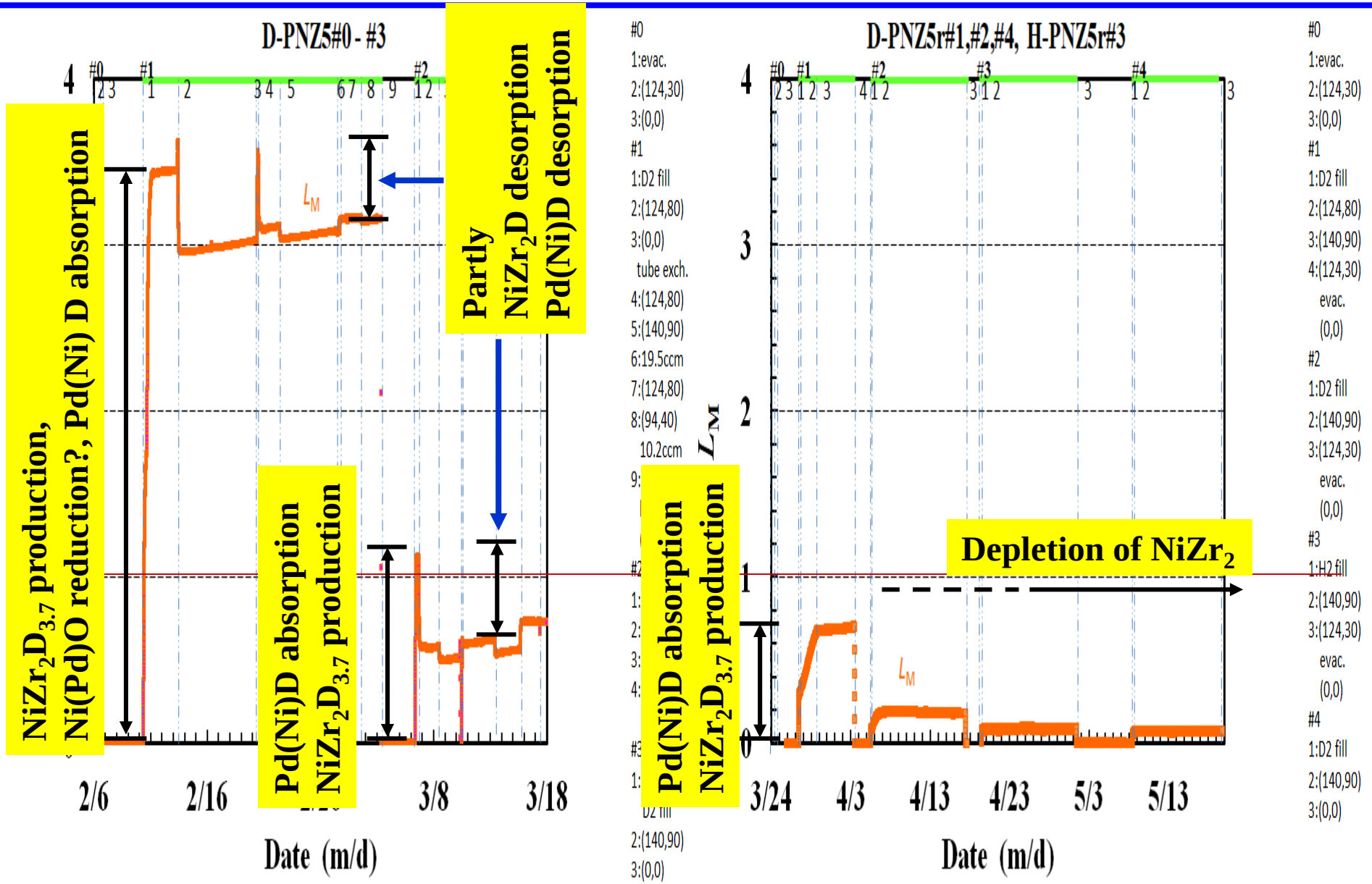
absorption $NiZr_2 + (3.7/2)H_2 \rightarrow NiZr_2H_{3.7}$ + (? eV). (L_M=3.7) (5)

#*n*-*n*(*n*≥2):

desorption (reversed (5)) $NiZr_2H_{3.7} \rightarrow NiZr_2 + (3.7/2)H_2\uparrow$ – (? eV), (5')

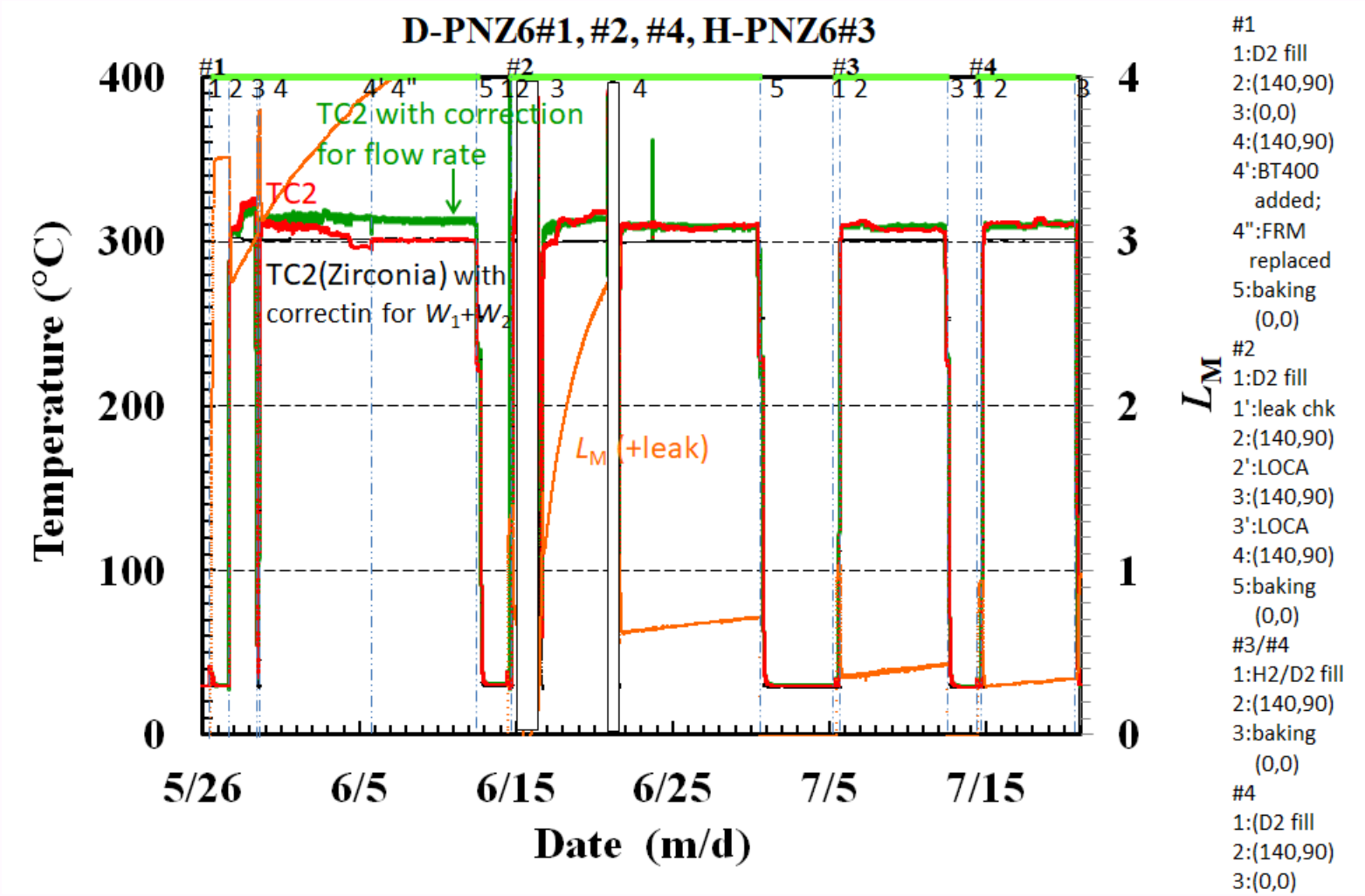
desorption (reversed (3)&(4)) $Ni(Pd)D_b(H_b) \rightarrow Ni(Pd) + (b/2)D_2(H_2)\uparrow$. (3'4')

In-situ characterization is necessary to quantitatively discuss the RT data



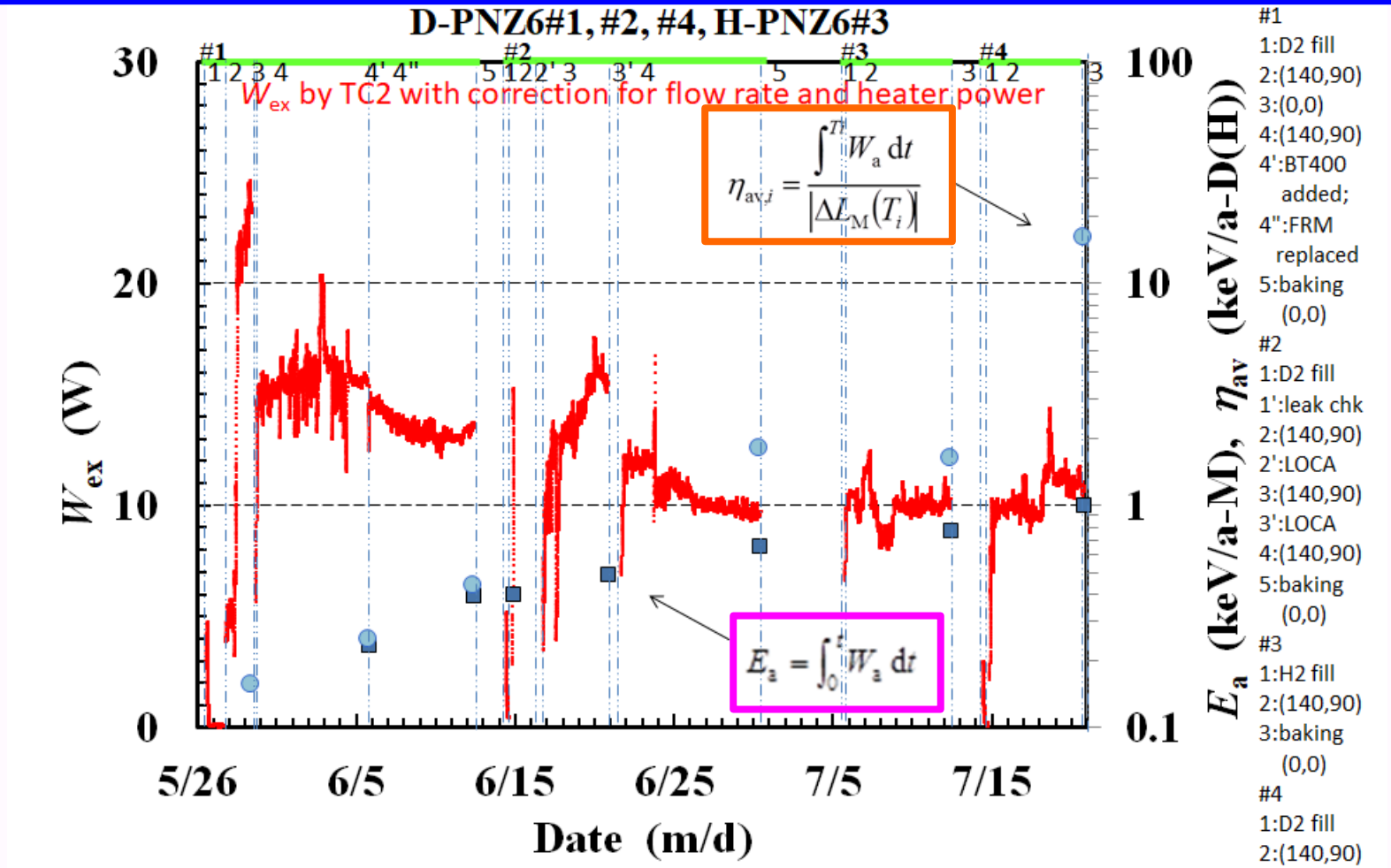
Heat evolution in elevated temperature (ET) phases

Difference between foreground run and blank (zirconia) run → Excess power



▪ Corrections for heater power and flow rate of BT400 are necessary, but the flow-rate correction is small for #2 through #4 runs.

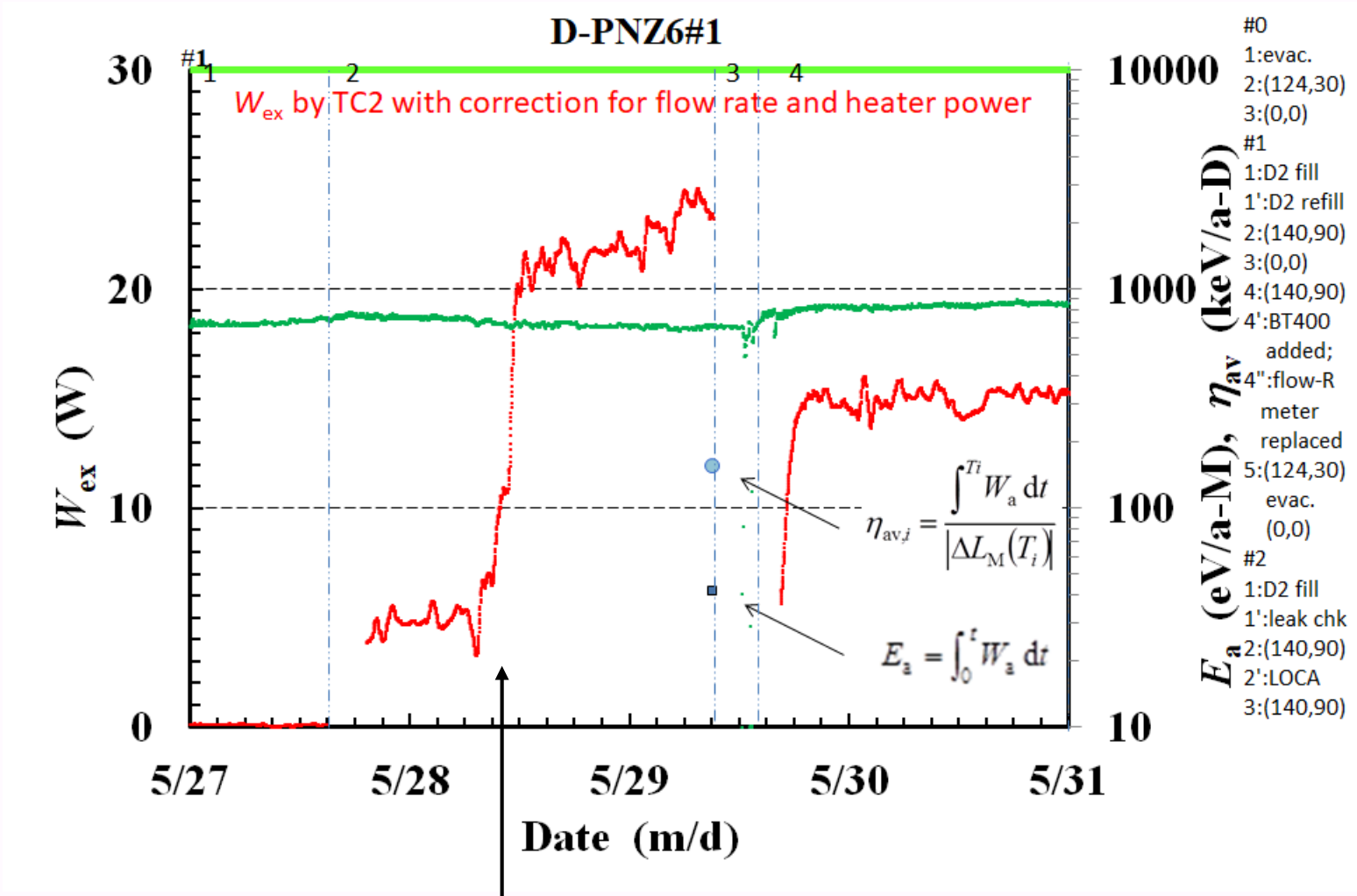
Excess power, W_{ex}, integrated excess heat per metal atom, E_a (keV/a-M), and excess energy per hydrogen isotope atom absorbed/desorbed, $\eta_{av,j}$ (keV/a-D(H)), in RT and ET phases evaluated by TC2 temperature.



- Excess power W_{ex} exceeding 10 W continued 45 days
- $\eta_{av,j}$ exceeded 10 keV/a-D, and E_a reached 1 keV/a-M.

(cf.: 1 eV/atom-M = 0.96E+05 J/mol-M)

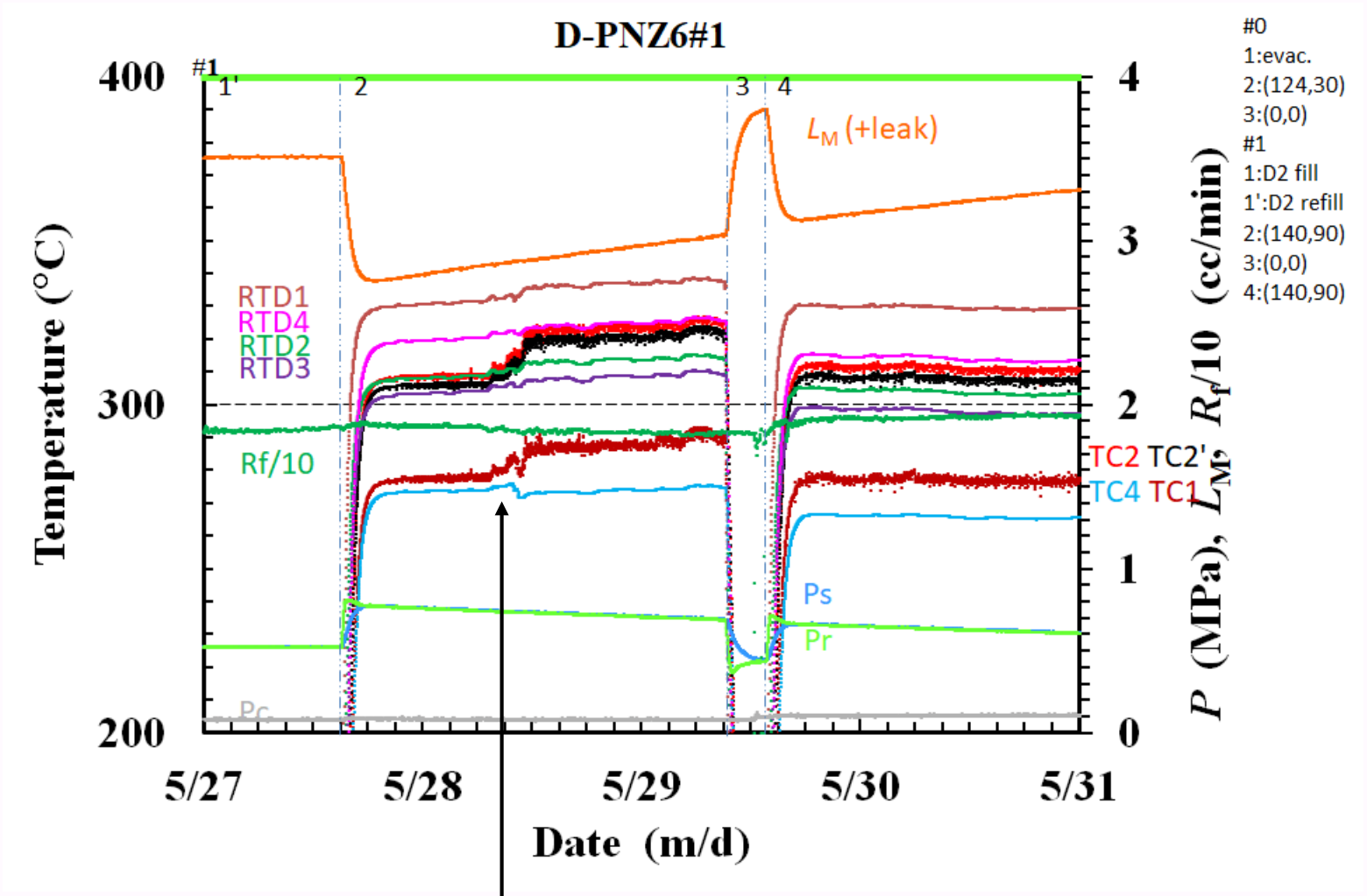
Excess power in D-PNZ6#1-2 phase is largest among all sample runs tested so far.



- **Unexpected, unintended evolution of excess power with no correlation with the flow rate**

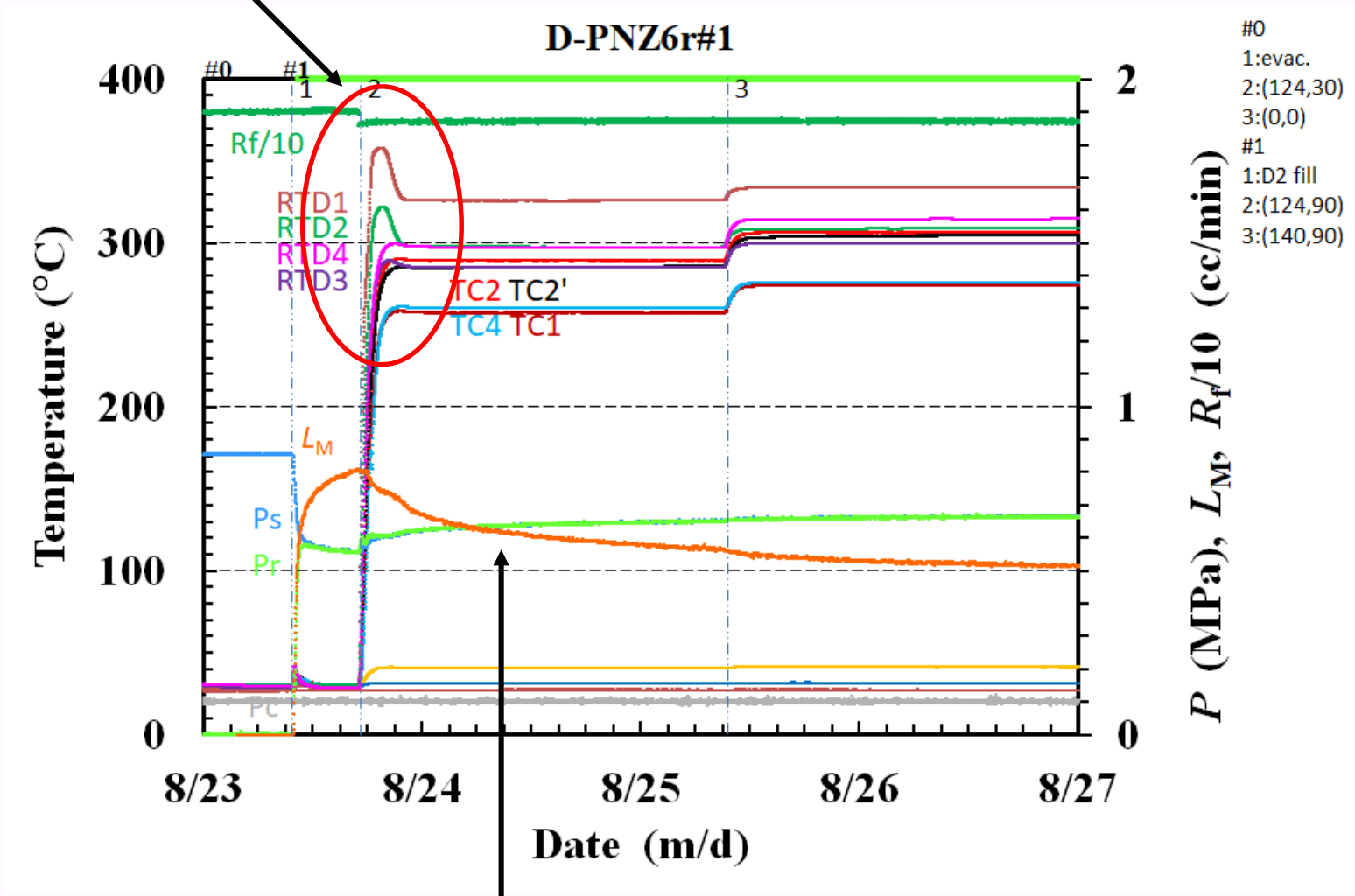
(cf.: 1 eV/atom-M = 0.96E+05 J/mol-M)

Temperature at each TC and RTD, when the large excess power emerged



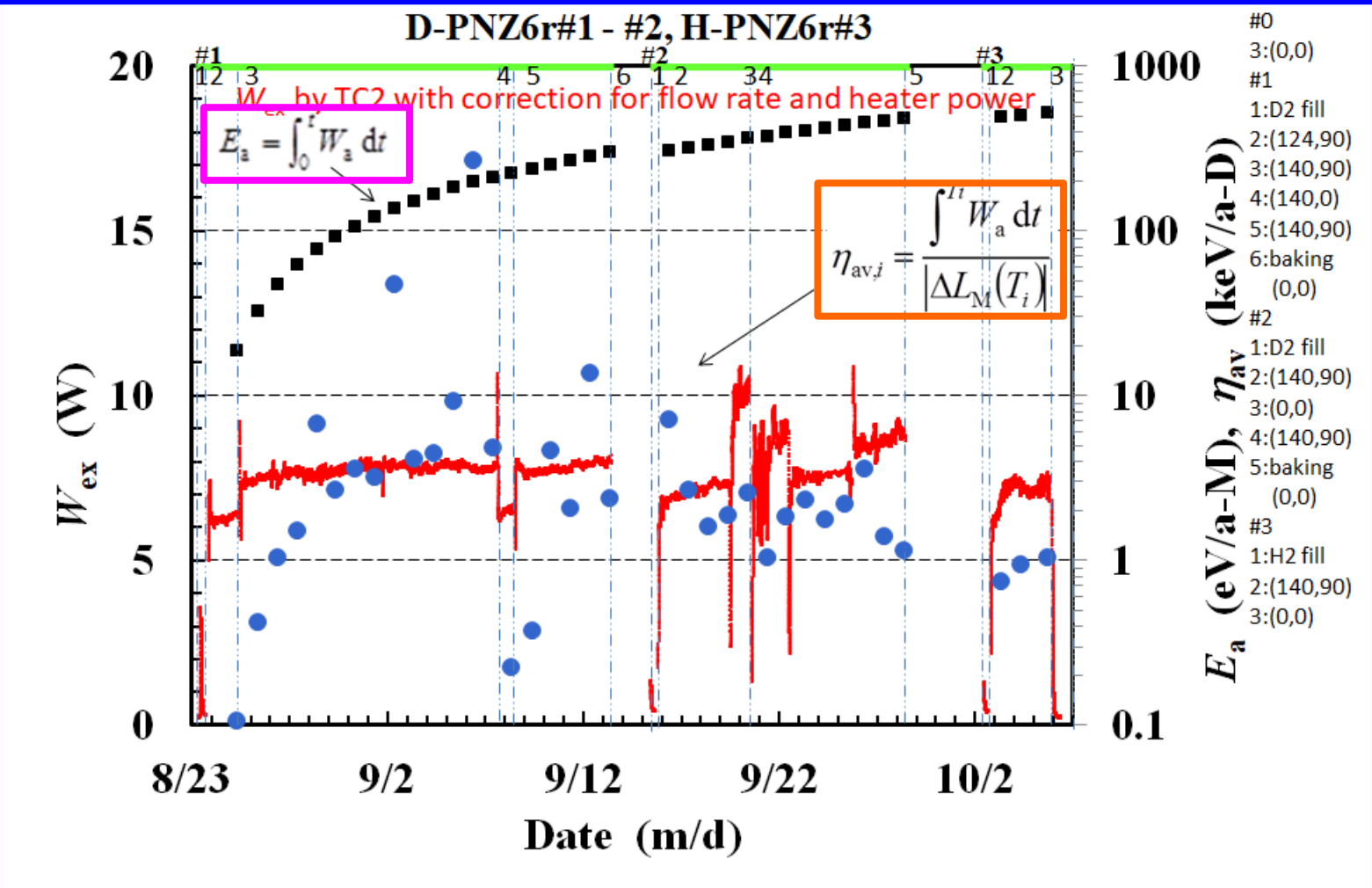
▪ **Unexpected, unintended evolution of excess power originates in the peripheral region of RC. (RTD's are insensitive to the temperature there.)**

Peculiar evolution of temperature in D-PNZ6r#1-2 phase



- **Desorption under elevated temperatures similar to other samples, but with exceptionally large time constant**

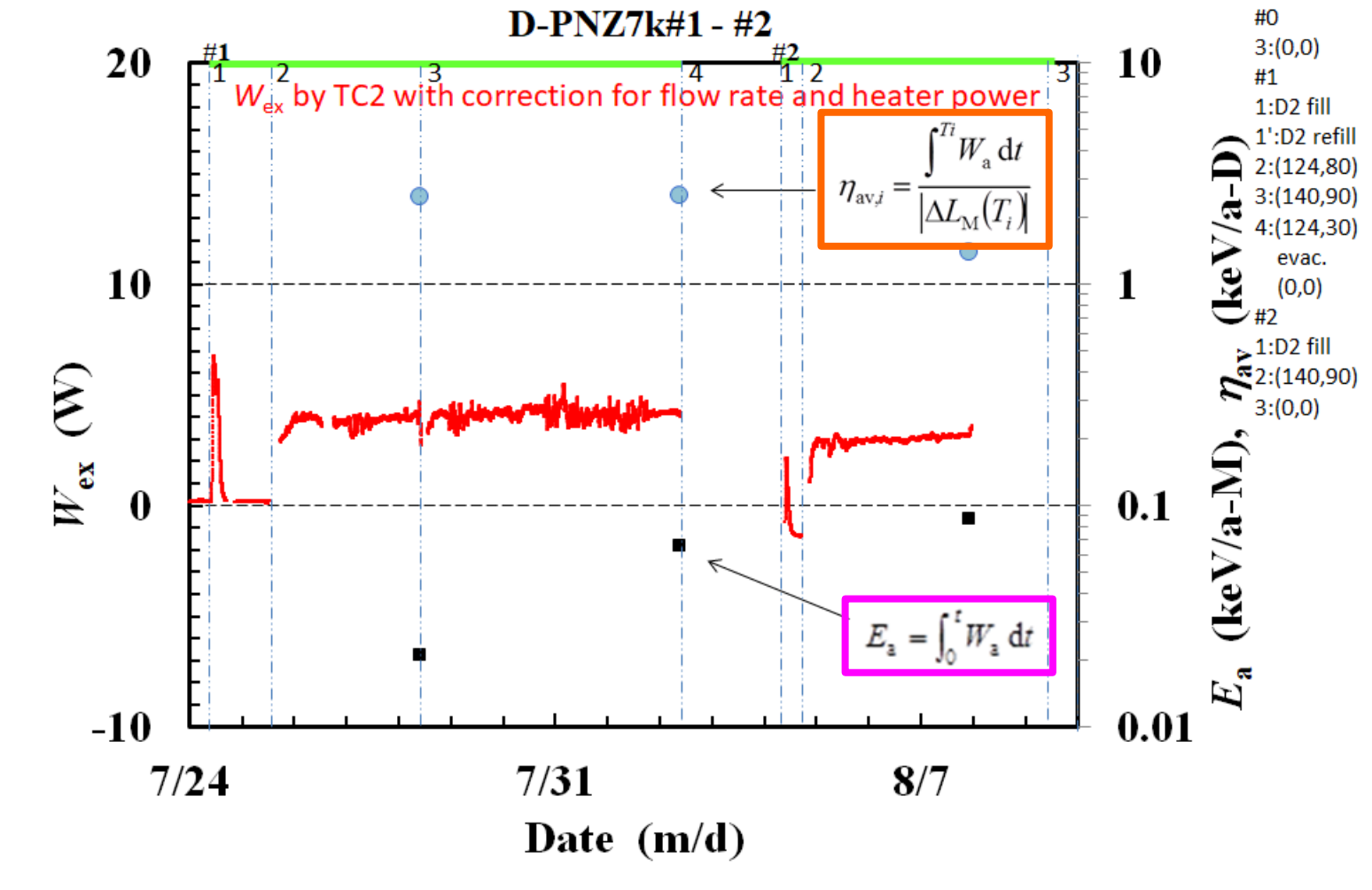
Excess power, W_{ex}, integrated excess heat per metal atom, E_a (keV/a-M), and excess energy per hydrogen isotope atom absorbed/desorbed, $\eta_{av,j}$ (keV/a-D(H)), in RT and ET phases evaluated by TC2 temp.



- large values of η_{av} making it realistic to assume nuclear origin of the excess heat

(cf.: 1 eV/atom-M = 0.96E+05 J/mol-M)

Excess power, W_{ex}, integrated excess heat per metal atom, E_a (keV/a-M), and excess energy per hydrogen isotope atom absorbed/desorbed, $\eta_{av,j}$ (keV/a-D(H)), evaluated by TC2 temp.

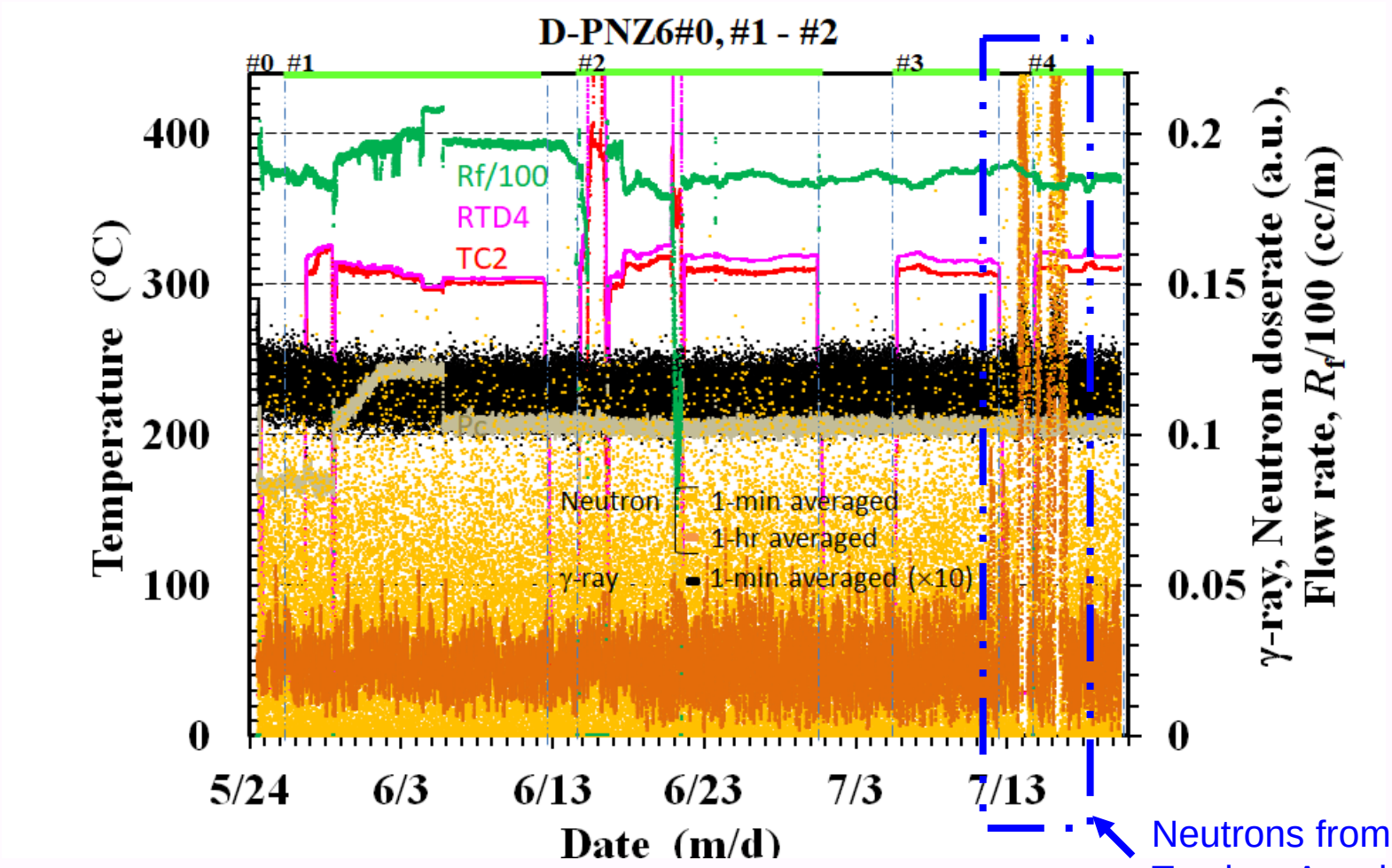


- Appreciably small excess power compared with that for PNZ6 and PNZ6r

(cf.: 1 eV/atom-M = 0.96E+05 J/mol-M)

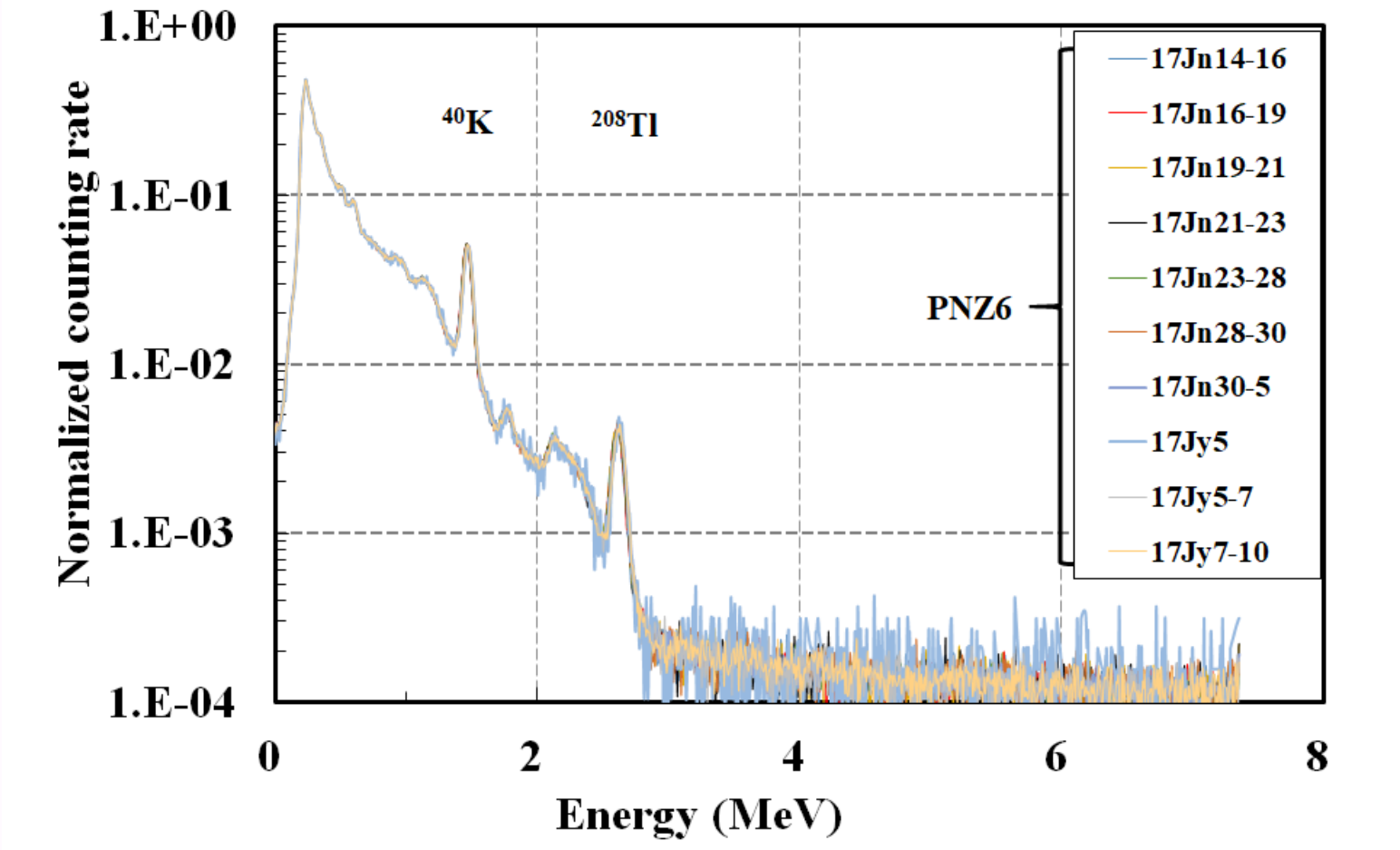
Radiations

Radiations and flow rate of coolant BT400



- **Radiation dose rates during large-excess-power phases are almost the same as those during inactive phases, *e.g.*, Jn. 30 – Jy. 5.**

γ-ray spectra



- Spectra during large excess phases are almost the same as those during inactive phases, *e.g.*, Jn. 30 – Jy. 5.

Summary

Hydrogen isotope absorption and heat evolution have been examined for three kinds of ZrO_2-supported Pd·Ni nanocomposites, PNZ6, PNZ6r, and PNZ7k

- Excess power of 3~24W at elevated temperature of 200~300°C continued for several weeks.
- PNZ6 and PNZ6r samples with Pd/Ni=1/10 generated much higher excess power than PNZ7k with Pd/Ni=1/7
  : Pd/Ni ratio is one of the keys to increase the excess power.
- Maximum specific energy η_{av} > 16 keV/D (1.6 GJ/mol-D), Integrated excess energy = 1 keV/Ni (100 MJ/mol-Ni)
- Impossible to attribute to any chemical reaction, possibly radiation-free nuclear process