Collaborative Examination on Anomalous Heat Effect Using Nickel-Based Binary Nanocomposites Supported by ZirconiaEnter title

Presentation · October 2016

DOI: 10.13140/RG.2.2.27005.15844

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Collaborative Examination on Anomalous Heat Effect Using Nickel-Based Binary Nanocomposites Supported by Zirconia

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(1) Introduction: sample and apparatus

(2) PNZ3 – absorption and heat evolution at room temp. (R.T.)

(3) PNZ3 – heat evolution at elevated temperatures (E.T.)

(4) PNZ3r - absorption and heat evolution at R.T. and E.T.

(5) CNZ5 – absorption and heat evolution at R.T. and E.T.

(6) Summary

Hydrogen isotope absorption by nickel-based nanocomposite samples

- Anomalous heat effects both at room temperature (R.T.) and elevated temperatures (E.T.) up to 300 °C
- Collaborative work using experimental apparatuses at Kobe Univ.
  and at Tohoku Univ. (next presentation),
  by the joint-team of 6 Japanese groups
- Reaction chamber with a capacity of 500 cc
- Flow-calorimetry system at elevated temperatures up to 300 °C
- Samples: amorphous mixture of the metal elements prepared by melt spinning method, and oxidized/annealed in air at a temperature of 450 °C for 100 hr ~ 60 hr
  $Pd_{0.044}Ni_{0.31}Zr_{0.65}$ ("PNZ3", "PNZ4/PNZ4s" and recalcinated "PNZ3r")
  $Cu_{0.044}Ni_{0.31}Zr_{0.65}$ ("CNZ5/CNZ5s")
- Preferential oxidation of Zr to ZrO_2 is expected with formation of nanoparticles of Ni and Pd or Cu embedded in it.

Sample composition

		Weight (g)	Molar fraction (%)					Duration of oxidation at 450 °C
			Cu	Pd	Ni	Zr/Si	O	
PNZ3	Kobe	95.5	---	3.5	24.5	52.0	20.0*	100 hr
PNZ3r	Kobe	113.2	---	1.7	11.6	24.5	62.3**	200 hr
CNZ5	Kobe	130.4	1.7	---	11.6	24.5	62.3*	60 hr
	Sendai	130.0						
PNZ4	Kobe	109.4	---	3.6	25.2	53.4	17.8*	60 hr
	Sendai	109.4						

Tested at Tohoku Univ. giving essentially the same result (next presentation by Iwamura et al.)

Oxygen content:

(*): estimated from weight gain during oxidation of the amorphous ribbon

(**): from weight gain, which is consistent with STEM/EDS and XRD

Material characterization

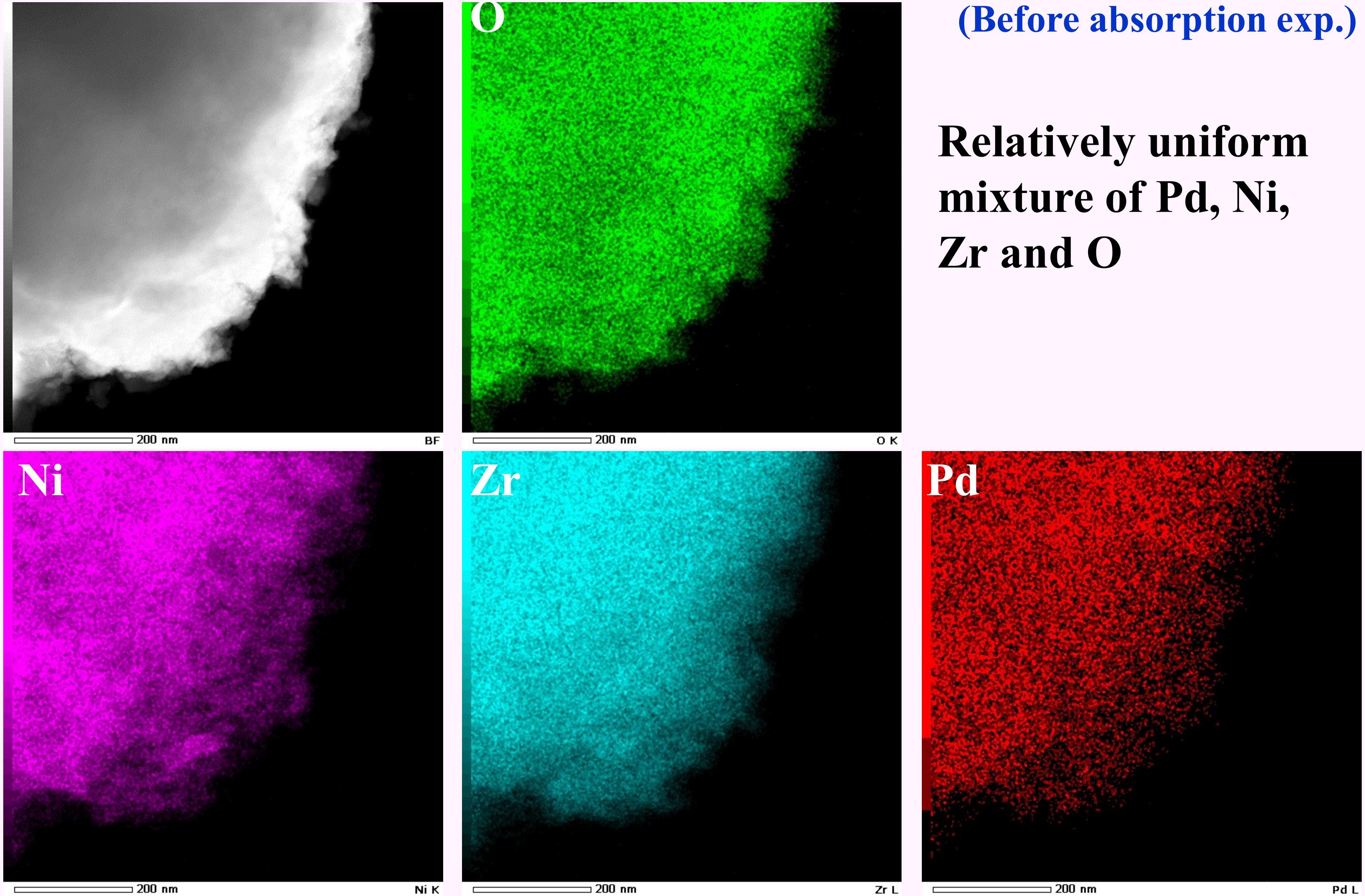
- ICP-AES and XRD analyses done at Nissan Motor Co. Ltd., Kyushu Univ., and Nagoya Univ.

  A lot of interesting features including crystalline phases of **$NiZr_2$**, **ZrO_2**, etc. have been revealed, which will be published independently elsewhere.
- STEM/EDS at Kobe Univ. showed features of nano-structure

PNZ3	Amorphous ribbon calcinated at 450 °C for 100 hr	• Mostly, relatively uniform mixture of Pd, Ni, Zr and O, but partly nonuniform distribution of Ni and Pd is recognized. • Most Pd and Ni atoms are occupying the same position. • After absorption runs, $NiZr_2$ decreased, and ZrO_2 increased, and some reduced Ni atoms is forming a block.
PNZ3r	Used PNZ3 re-calcinated at 450 °C for 200 hr	• The assumed majority is ZrO_2 + NiO + PdO. • O atoms have increased. • NiO and PdO appear to be separated from ZrO_2. • Nonuniform distribution of Ni and Pd atoms developed further. • After absorption runs, NiO and PdO appear to be reduced.

One of the typical examples of STEM/EDS pictures : PNZ3-B_010

(Before absorption exp.)

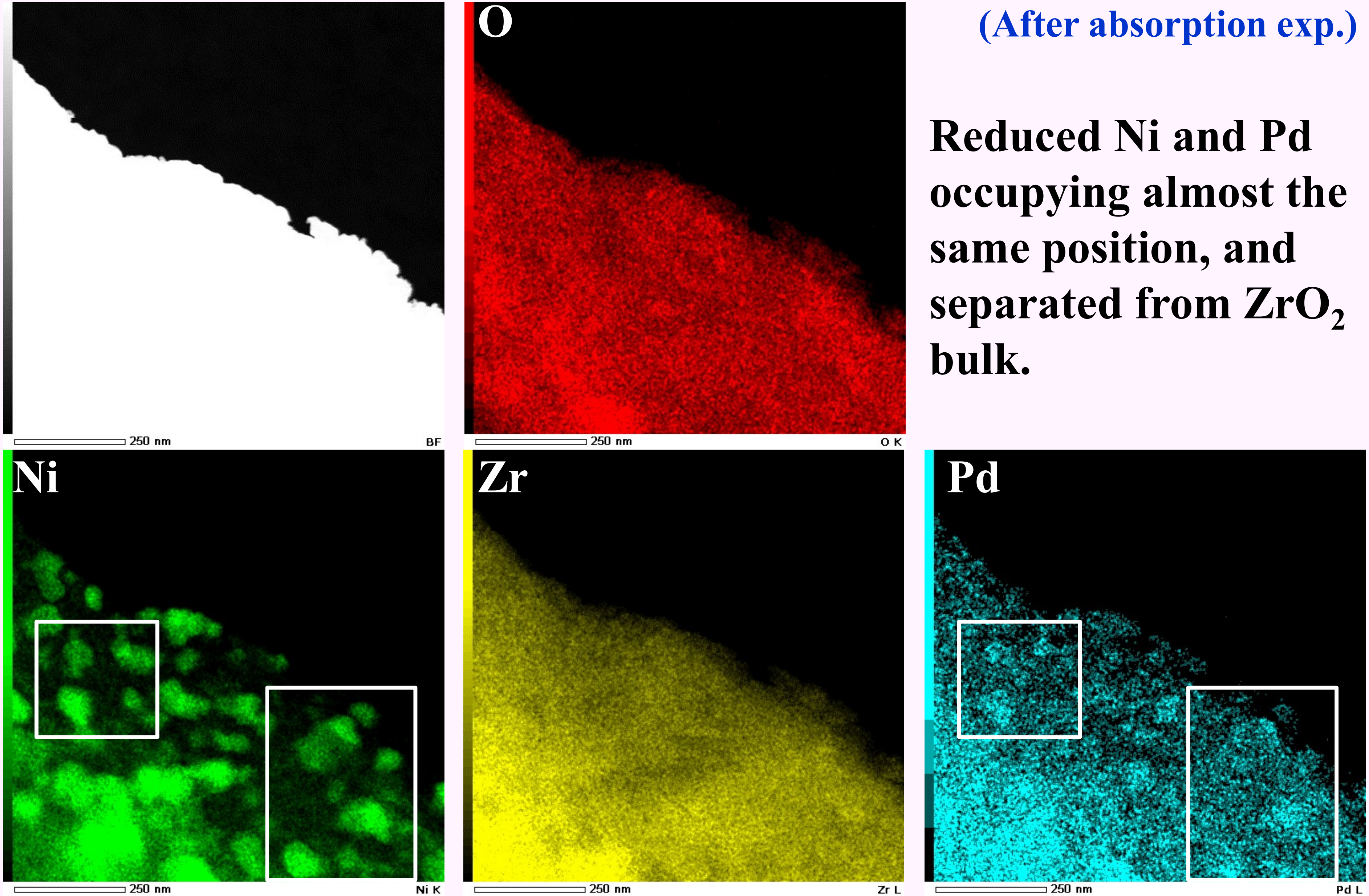


Relatively uniform mixture of Pd, Ni, Zr and O

200nm

One of the typical examples of STEM/EDS pictures : PNZ3r-A_000

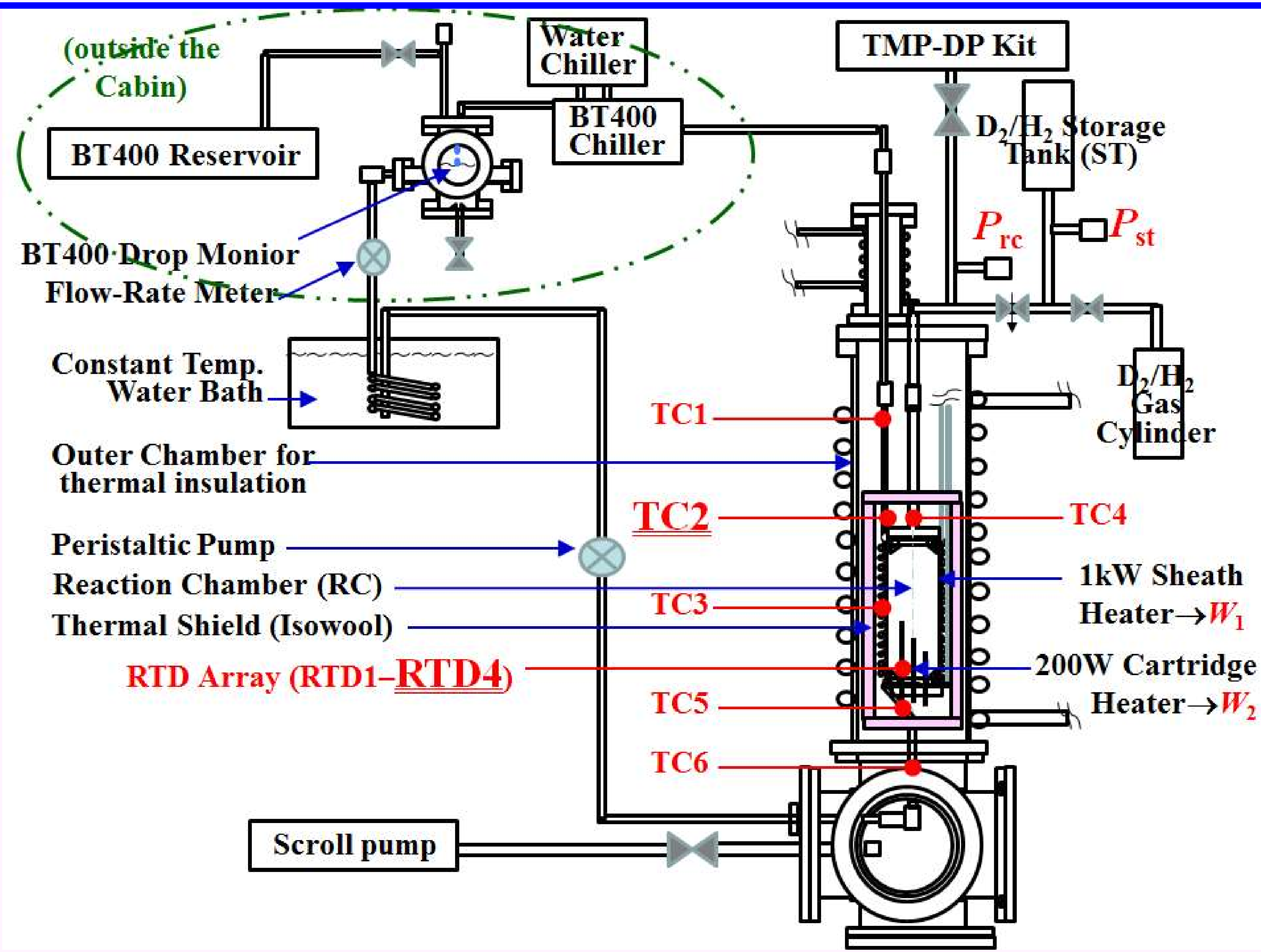
(After absorption exp.)



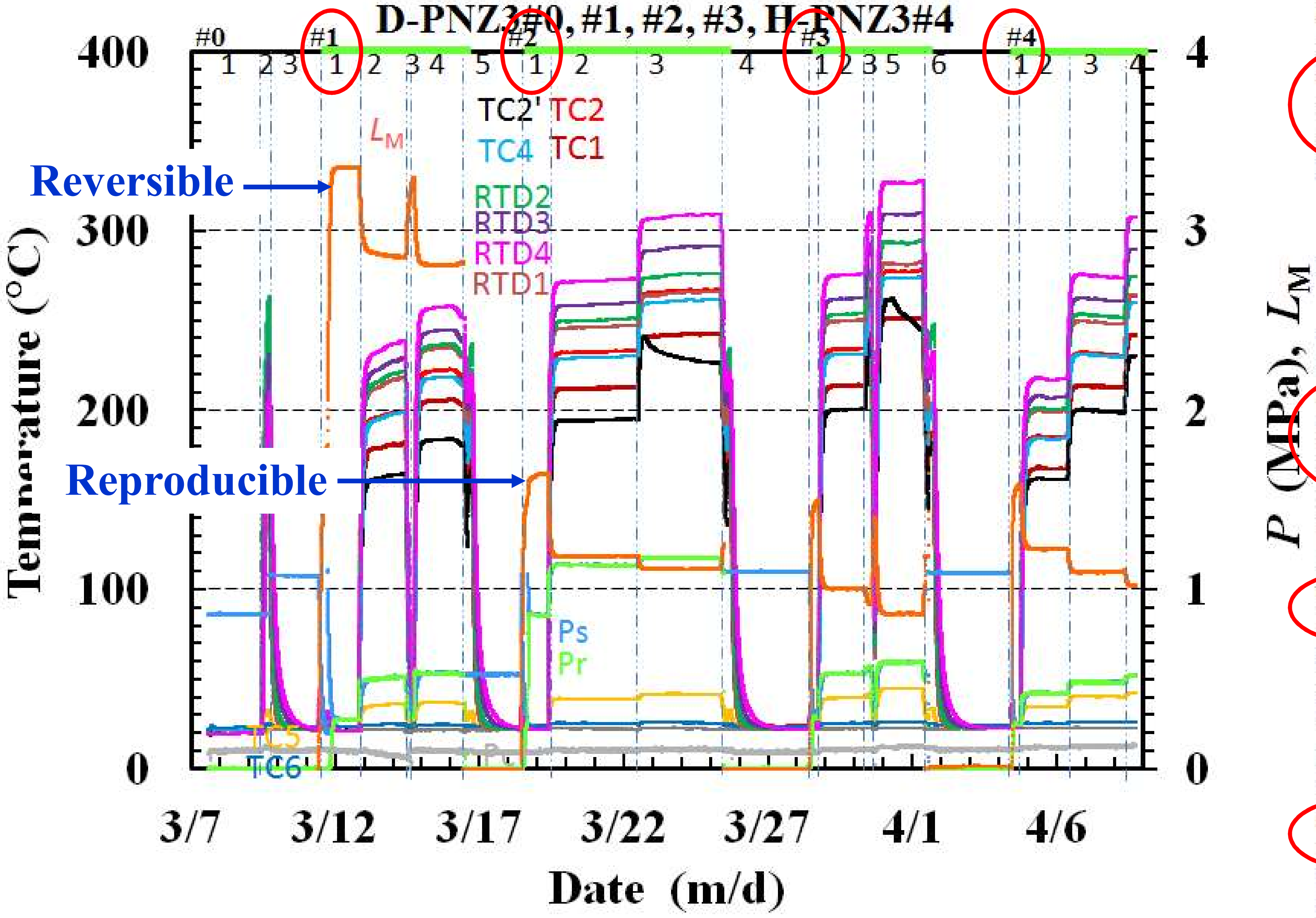
Reduced Ni and Pd occupying almost the same position, and separated from ZrO_2 bulk.

250nm

Schematic of the C_1 system: D(H)-absorption and oil-mass-flow calorimetry



PNZ3 sample: baking (#0) followed by #1 through #4 runs



#0
1-3:baking
#1
1:D2 fill
1a: refill
2:(50,30)
BT400
leak
3:(0,0)
ex. tube
4:(69,40)
5:baking
#2
1:D2 fill
1a: refill
2:(69,40)
3:(94,40)
4:baking
#3
1:D2 fill
2:(69,40)
3:(94,40)
4:(0,0)
5:(94,40)
6:baking
#4
1:H2 fill
2:(50,30)
3:(69,40)
4:(94,40)

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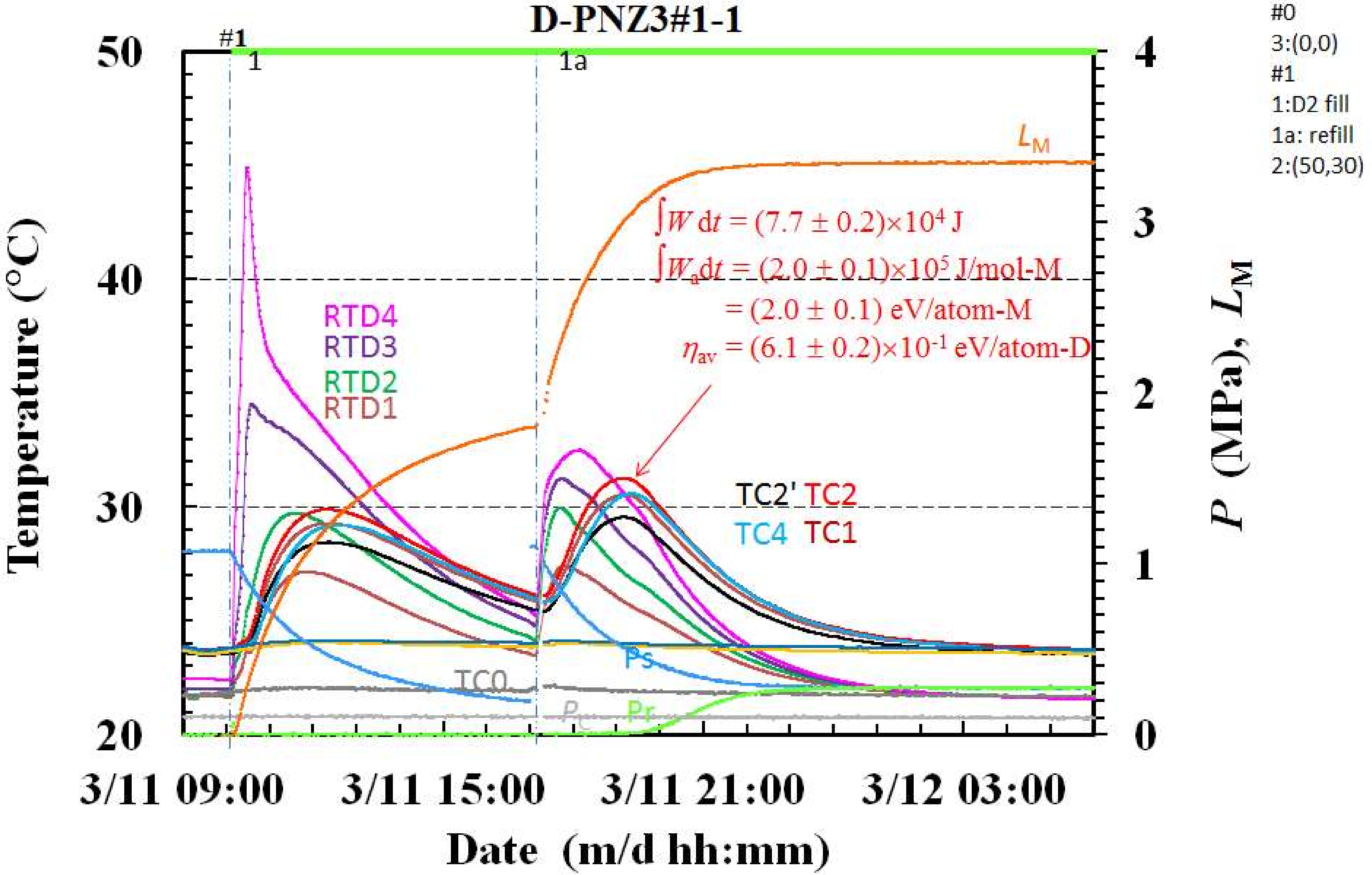
(4) PNZ3r - absorption and heat evolution at R.T. and E.T.

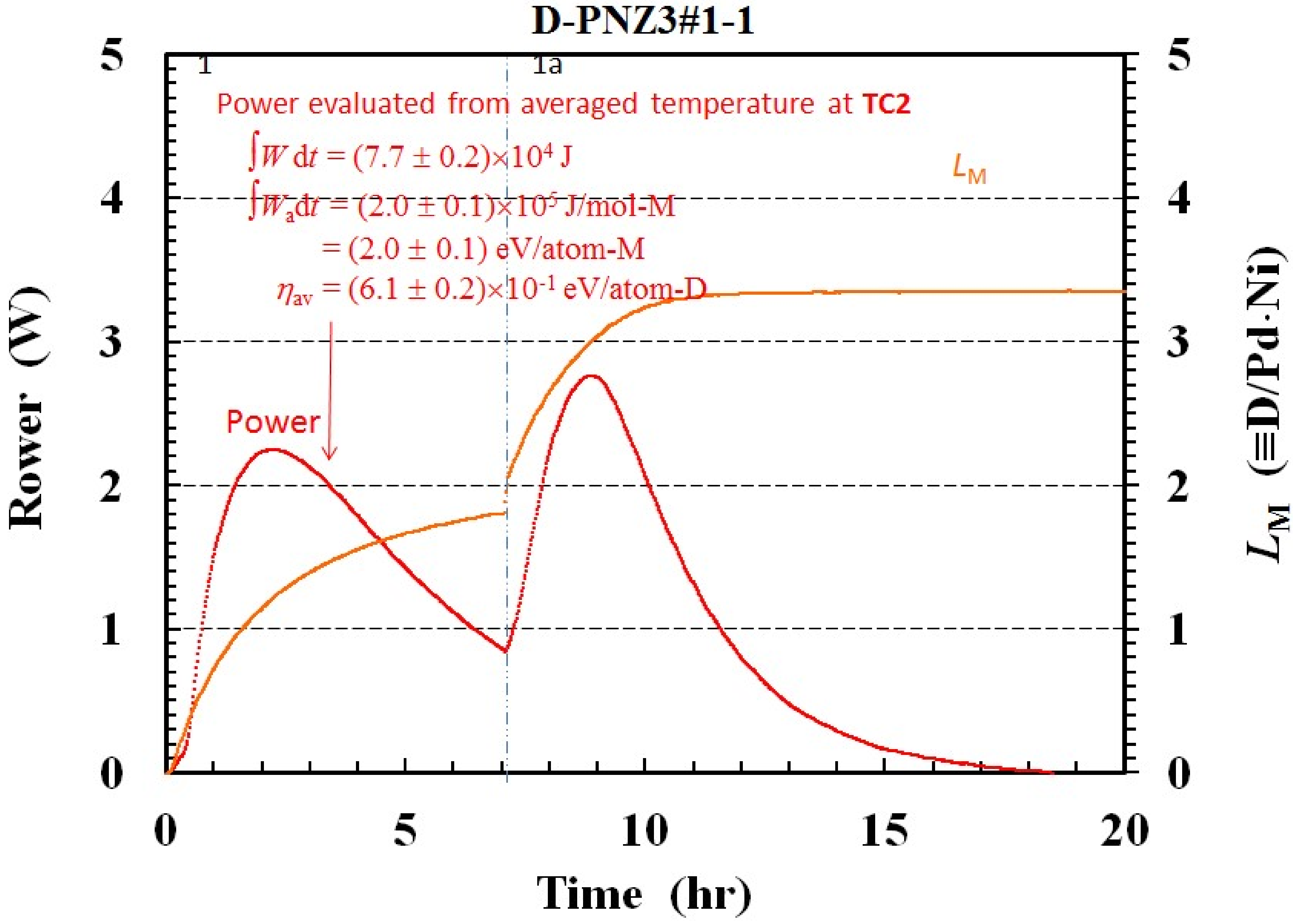
(5) CNZ5 – absorption and heat evolution at R.T. and E.T.

(6) Summary

Initial burst of heat in the PNZ3#1-1~1a phases at R.T.

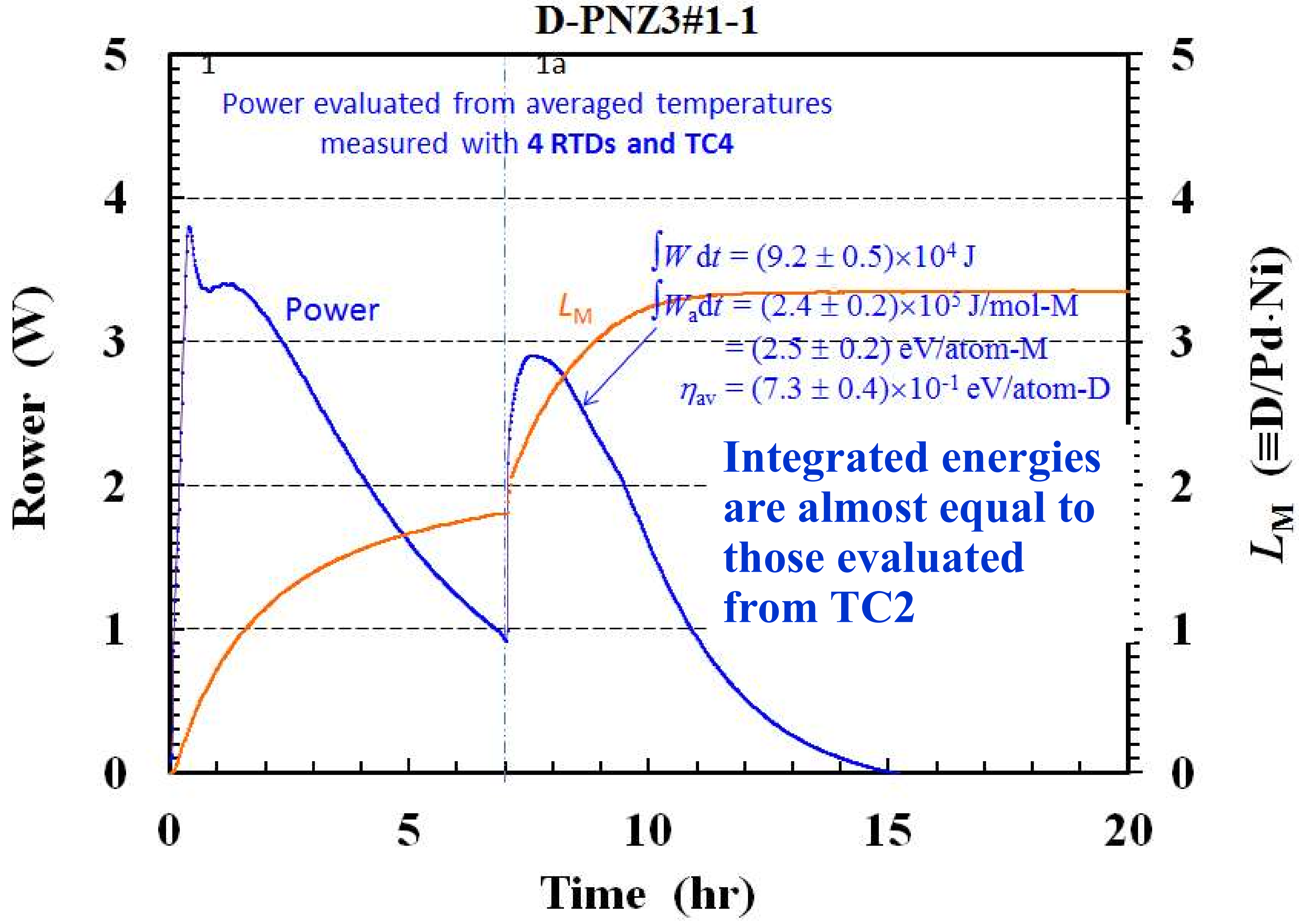


Power evaluated from TC2 & loading ratio in the PNZ3#1-1~1a



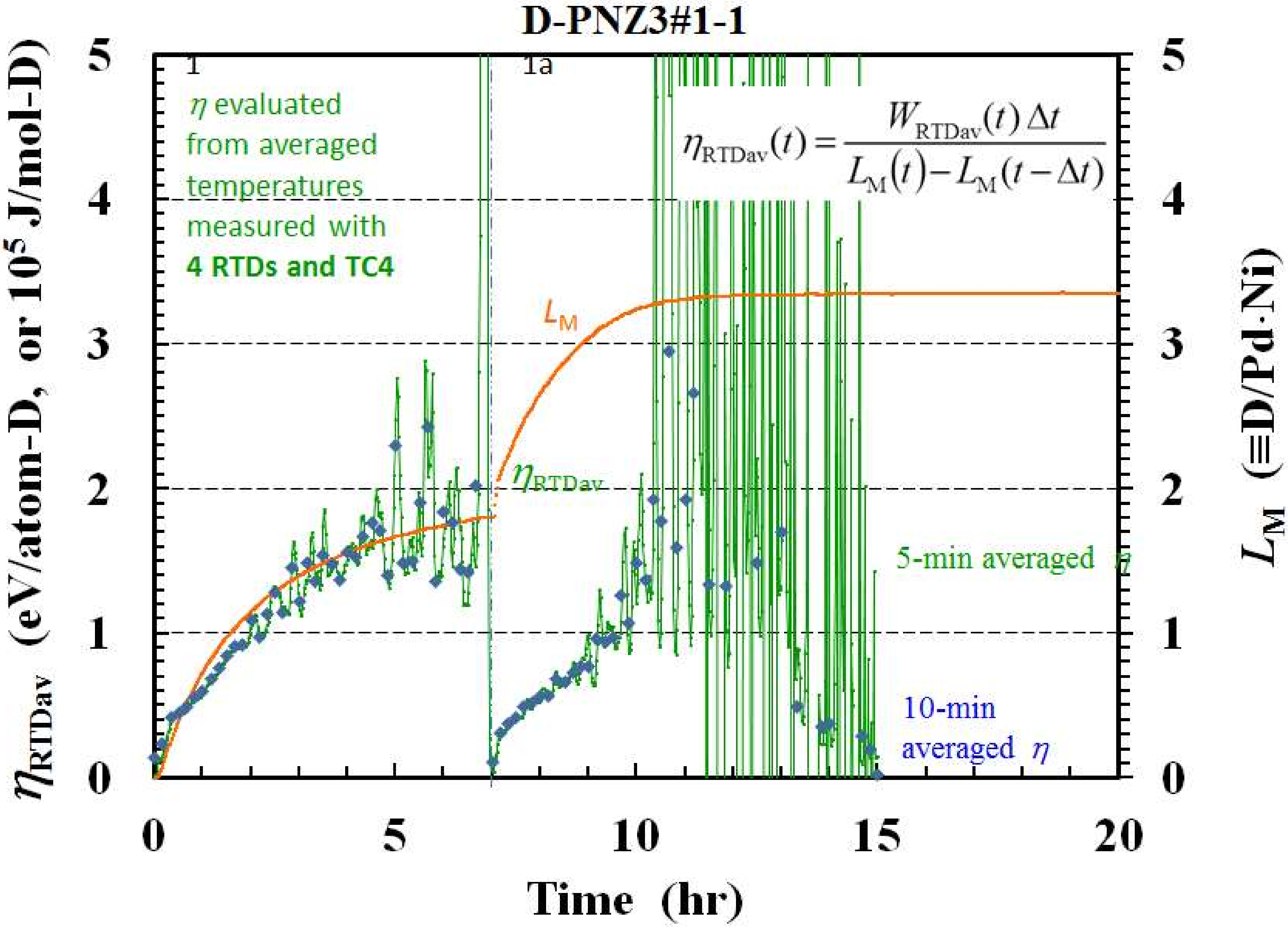
#0
3:(0,0)
#1
1:D2 fill
1a: refill

Power evaluated from RTDs & loading ratio in the PNZ3#1-1~1a



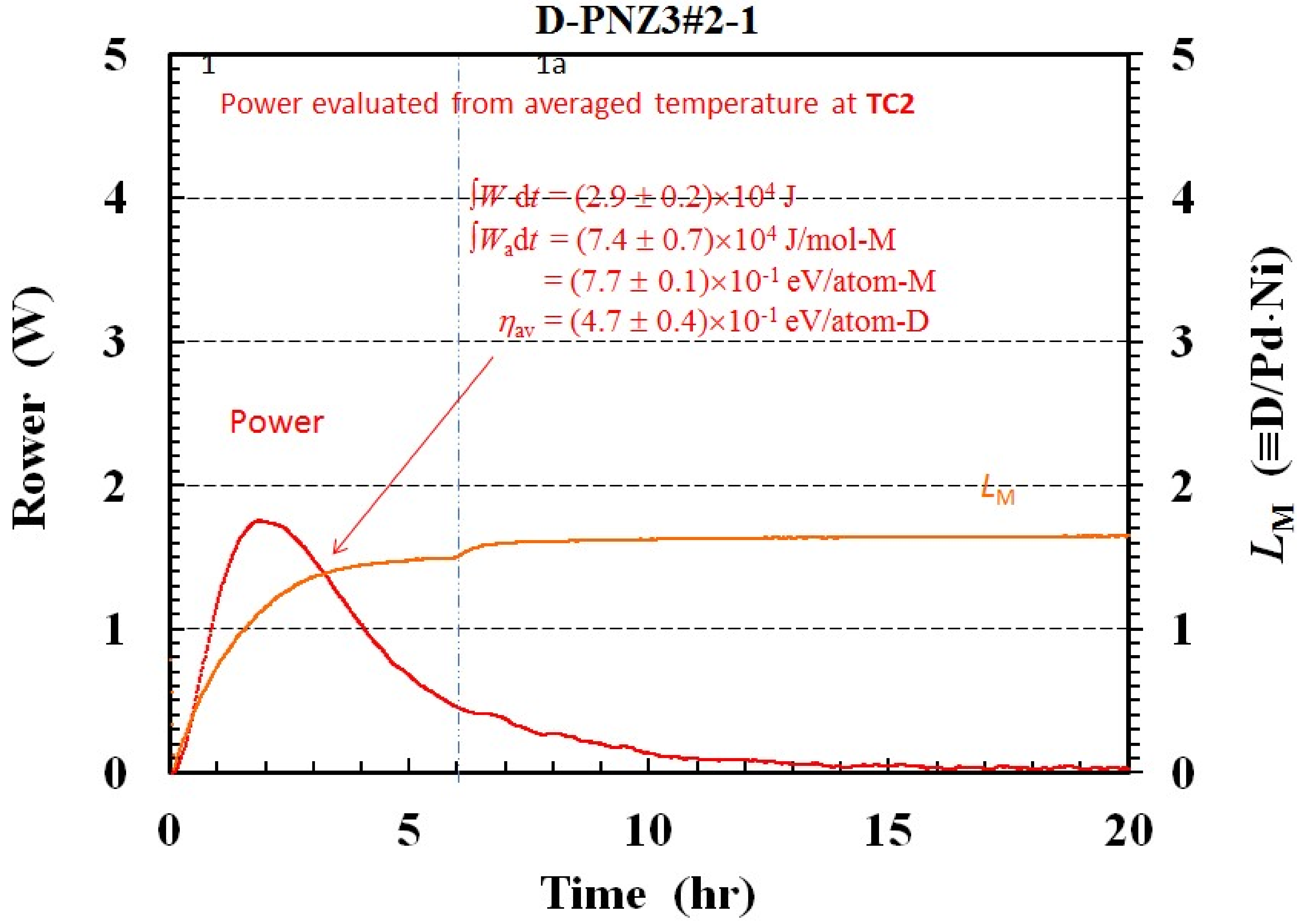
#0
3:(0,0)
#1
1:D2 fill
1a: refill

Specific absorption energy η reaches almost 2 eV/atom-D



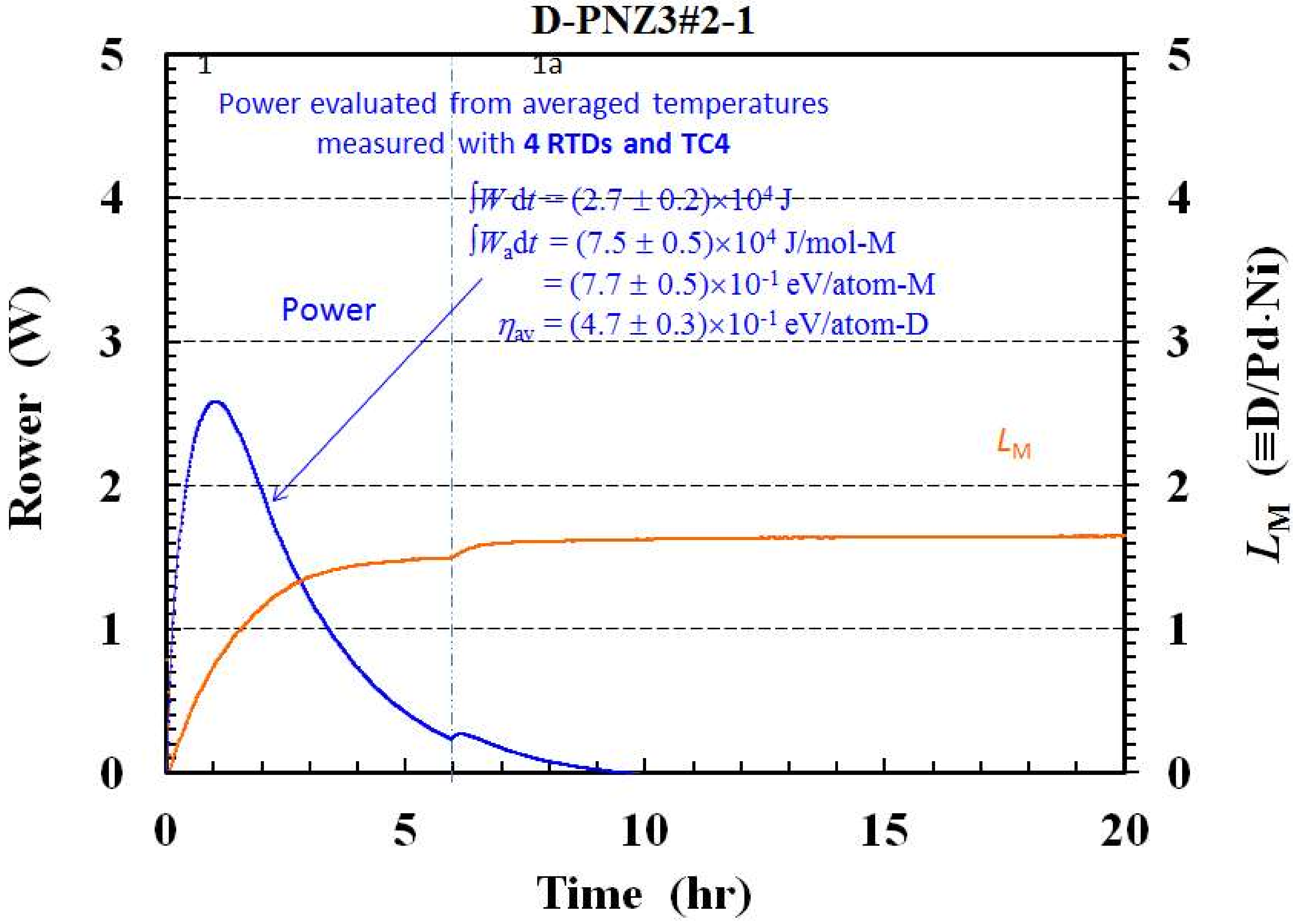
#0
3:(0,0)
#1
1:D2 fill
1a: refill

Approximate equality of TC2 and RTD is also true for runs #2 and later.



#1
5:(69,20)
evac.
(0,0)
#2
1:D2 fill
1a: refill

Approximate equality of TC2 and RTD is also true for runs #2 and later.

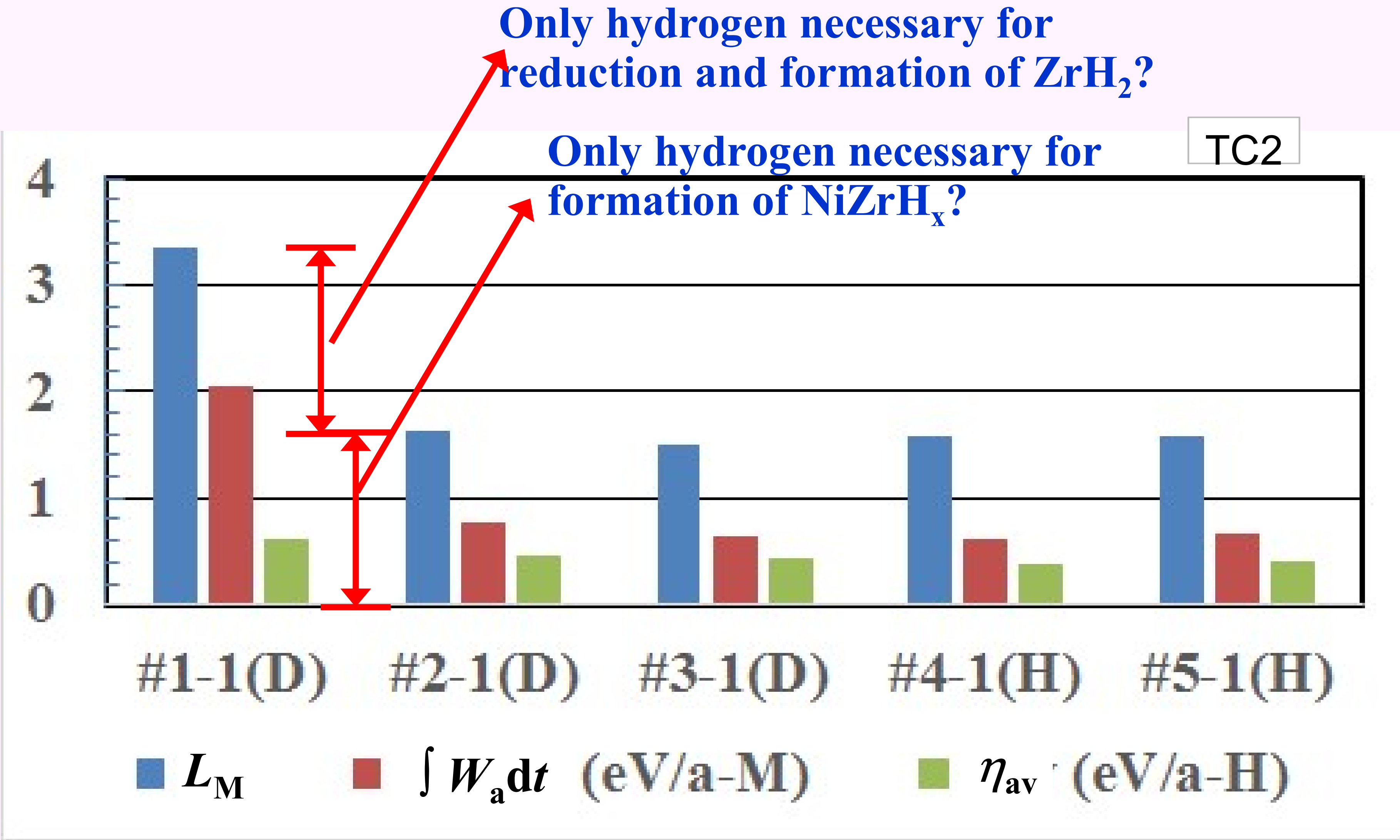


#1
5:(69,20)
evac.
(0,0)
#2
1:D2 fill
1a: refill

Loading ratio and output energy in the first phases at R.T. (PNZ3#*n*-1)

TC2						
		#1-1(D)	#2-1(D)	#3-1(D)	#4-1(H)	#5-1(H)
L_M		3.35E+00	1.64E+00	1.50E+00	1.59E+00	1.57E+00
$\int W_a dt$	(eV/a-M)	2.04E+00	7.68E-01	6.48E-01	6.17E-01	6.63E-01
η_{av}	(eV/a-H)	6.09E-01	4.67E-01	4.32E-01	3.89E-01	4.22E-01
RTDav						
		#1-1(D)	#2-1(D)	#3-1(D)	#4-1(H)	#5-1(H)
L_M		3.35E+00	1.64E+00	1.50E+00	1.59E+00	1.57E+00
$\int W_a dt$	(eV/a-M)	2.45E+00	7.74E-01	7.22E-01	6.91E-01	6.74E-01
η_{av}	(eV/a-H)	7.31E-01	4.70E-01	4.81E-01	4.35E-01	4.29E-01

Loading ratio and output energy in the first phases at R.T. (PNZ3#*n*-1)



Possible reactions with hydrogen isotopes

- Hydrogen pickup reactions

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

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

- Hydrogenation and hydrogen storage reaction

$NiZr_2 + (4.5/2)H_2 \rightarrow ZrH_2 + ZrNiH_{2.5} + 2.85$ eV/atom-Ni,
(0.63 eV/atom-H) (3)*

irreversible (ZrH_2) **reversible?** ($ZrNiH_{2.5}$)

- Others ? **Nuclear one ?**

To discuss this issue quantitatively, the amount of **$NiZr_2$** in the sample must be known.

* P. Dantzer, W. Luo, Ted B. Flanagan and J.d. Clewley; Calorimetrically Measured Enthalpies for the Reaction of H_2 (g) with Zr and Zr Alloys; Metallurgical Transactions A, **24A** (1993) 1471-1479.

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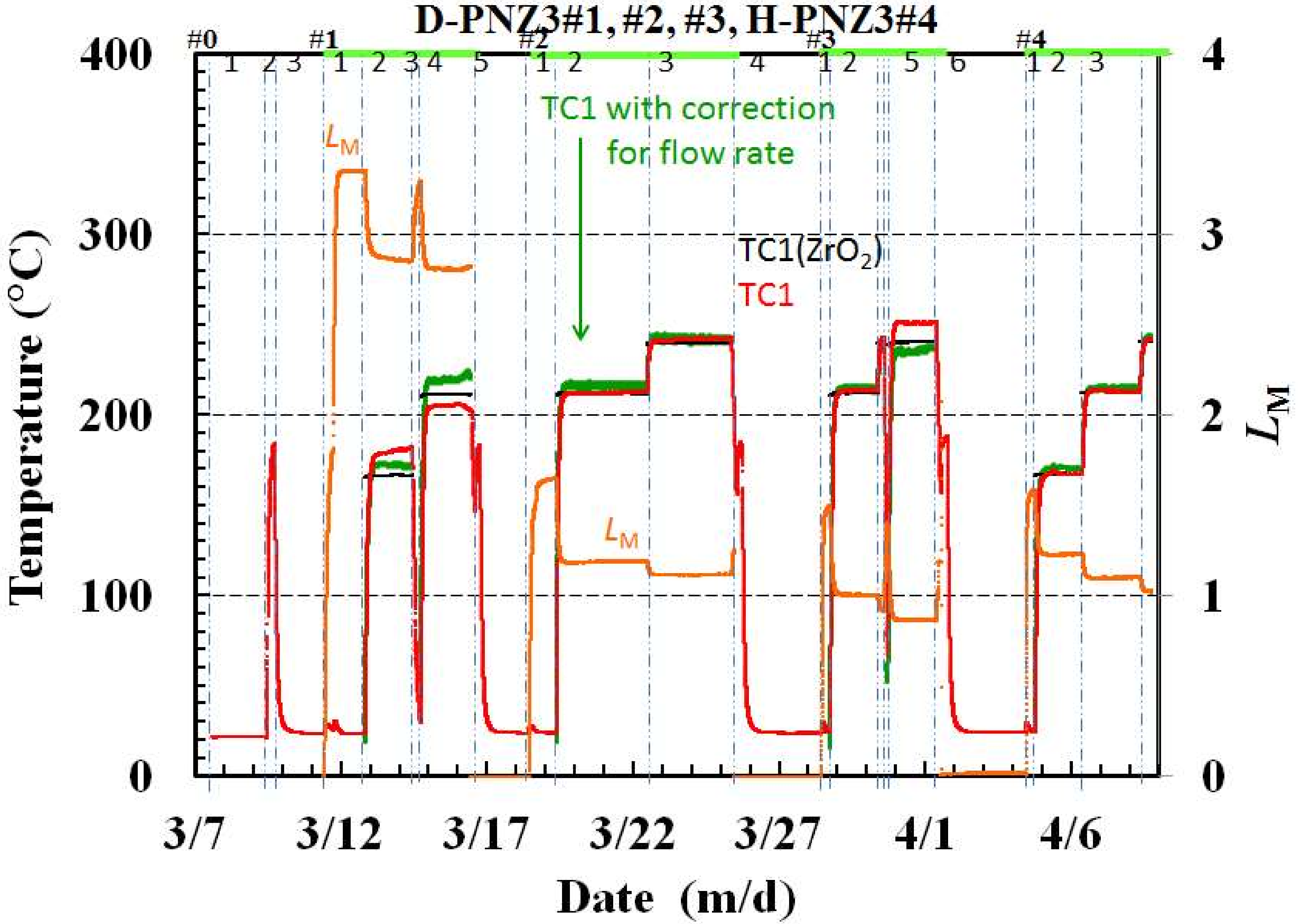
(5) CNZ5 – absorption and heat evolution at R.T. and E.T.

(6) Summary

Raw data for PNZ3 runs, virgin (#1), after baking (#2) and after 2nd baking (#3)



#0
1-3:baking (0,0)

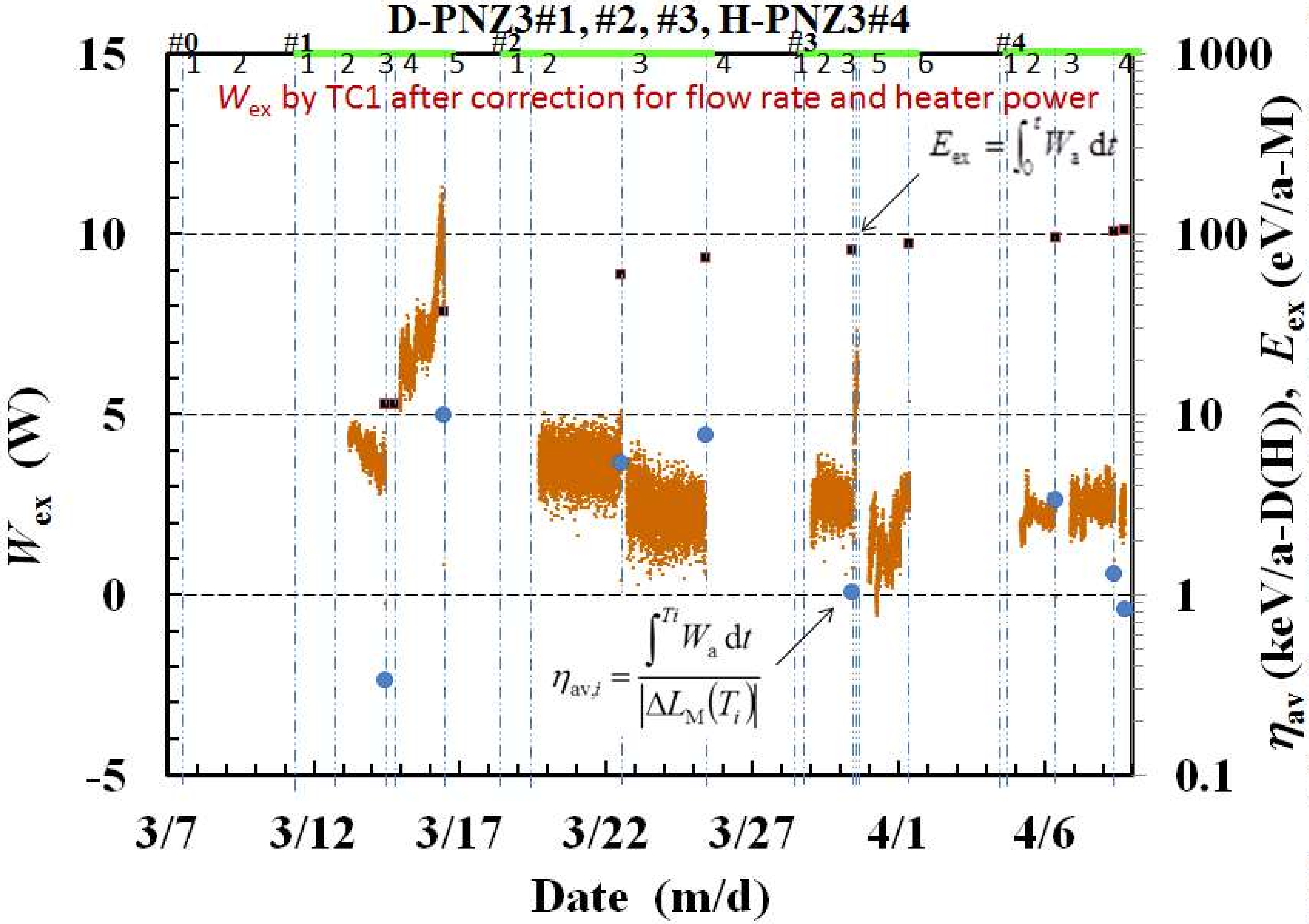
#1
1:D2 fill
1a: refill
2:(50,30) cool. leak
3:(0,0) ex. tube
4:(69,40)
5:baking (0,0)

#2
1:D2 fill
1a: refill
2:(69,40)
3:(94,40)
4:baking (0,0)

#3
1:D2 fill
2:(69,40)
3,5:(94,40)
6:baking (0,0)

#4
1:H2 fill
2:(50,30)
3:(69.40)

Excess power calculated with use of TC1 for elevated temperature runs



#0
1-3:baking (0,0)
#1
1:D2 fill
1a: refill
2:(50,30) cool. leak
3:(0,0) ex. tube
4:(69,40)
5:baking (0,0)
#2
1:D2 fill
1a: refill
2:(69,40)
3:(94,40)
4:baking (0,0)
#3
1:D2 fill
2:(69,40)
3,5:(94,40)
6:baking (0,0)
#4
1:H2 fill
2:(50,30)
3:(69.40)

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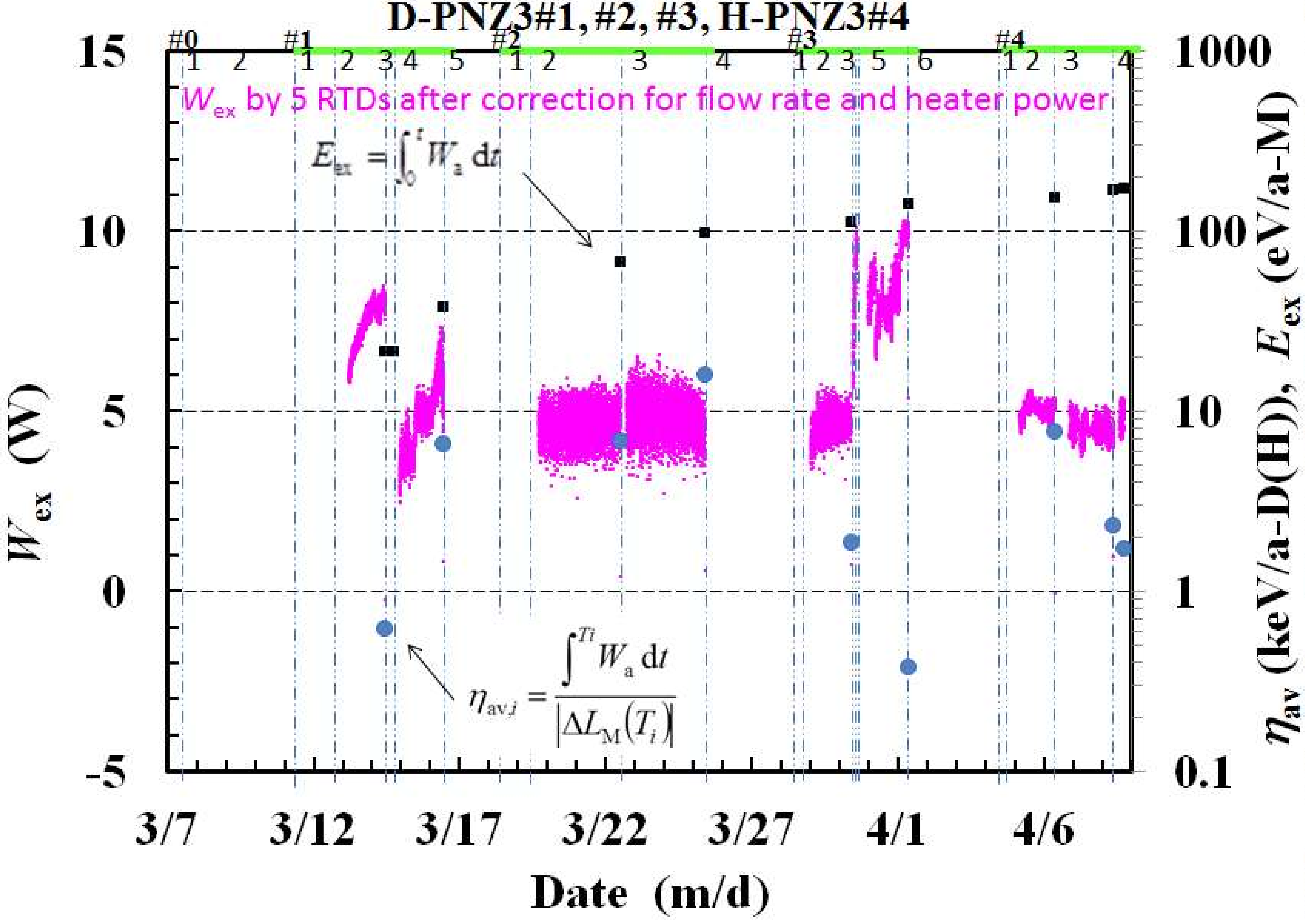
Excess power calculated with use of RTD temperatures (renewed reference)



#0
1-3:baking (0,0)
#1
1:D2 fill
1a: refill
2:(50,30) cool. leak
3:(0,0) ex. tube
4:(69,40)
5:baking (0,0)
#2
1:D2 fill
1a: refill
2:(69,40)
3:(94,40)
4:baking (0,0)
#3
1:D2 fill
2:(69,40)
3,5:(94,40)
6:baking (0,0)
#4
1:H2 fill
2:(50,30)
3:(69.40)

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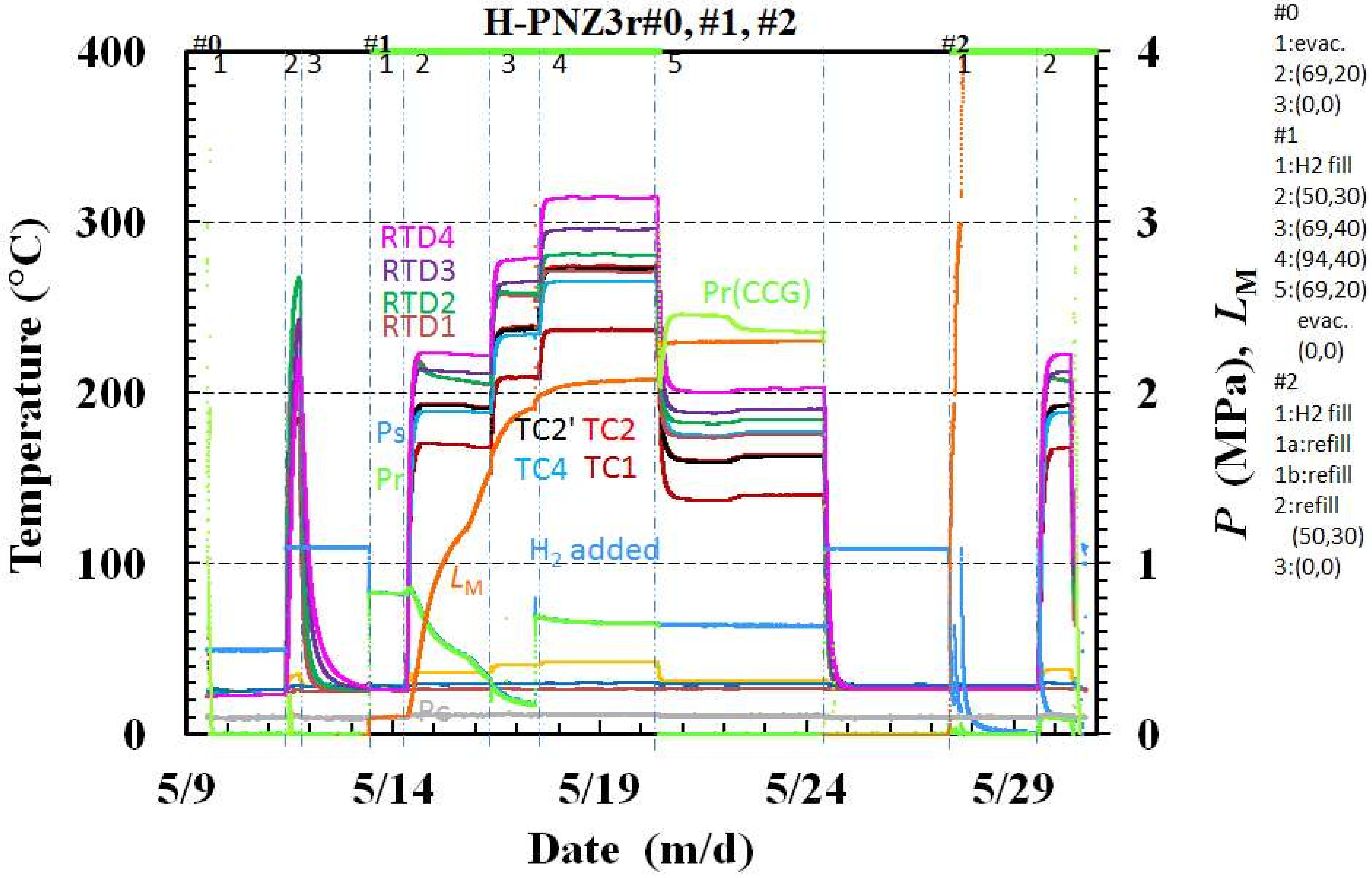
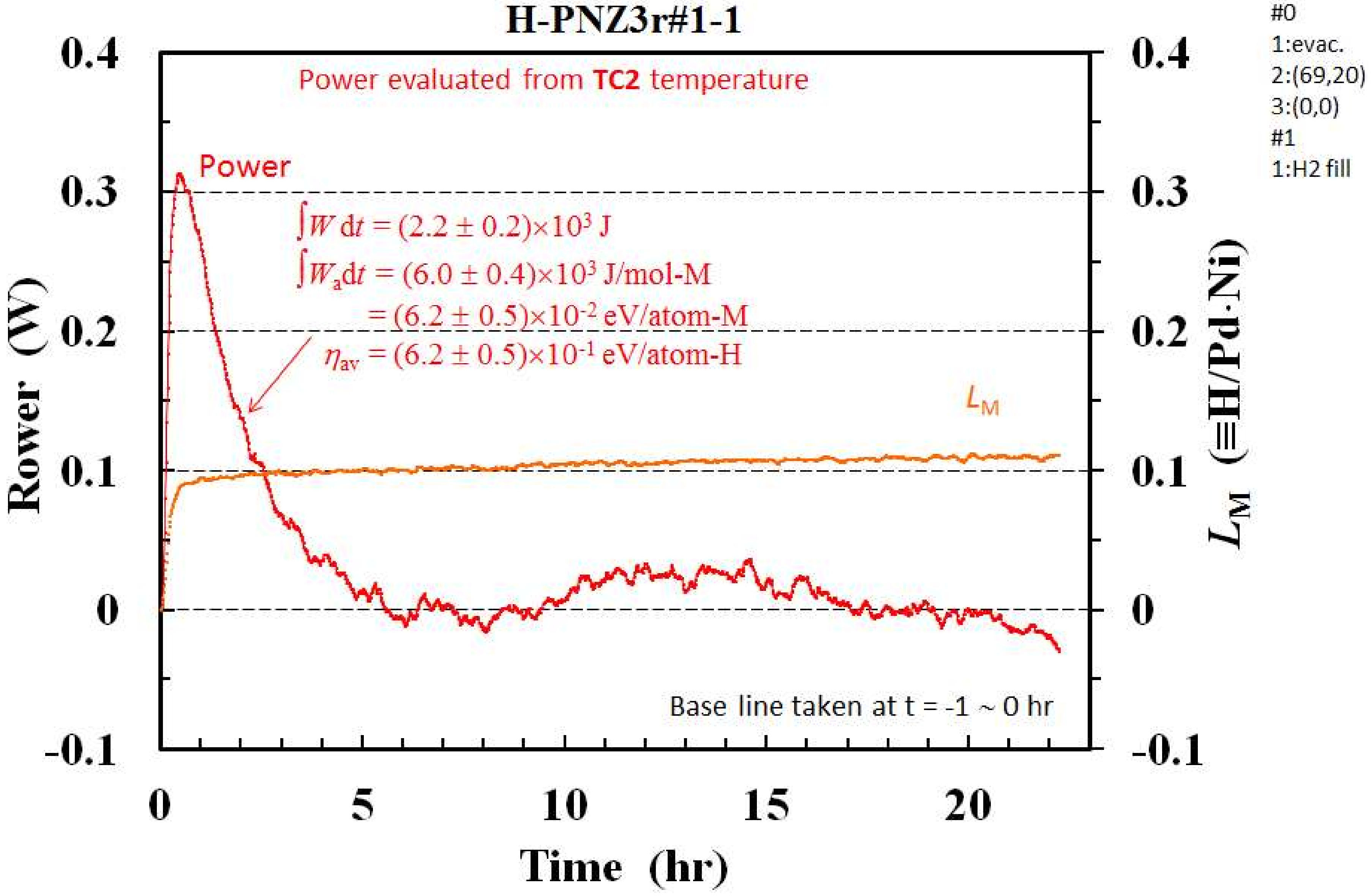
(5) CNZ5 – absorption and heat evolution at R.T. and E.T.

(6) Summary

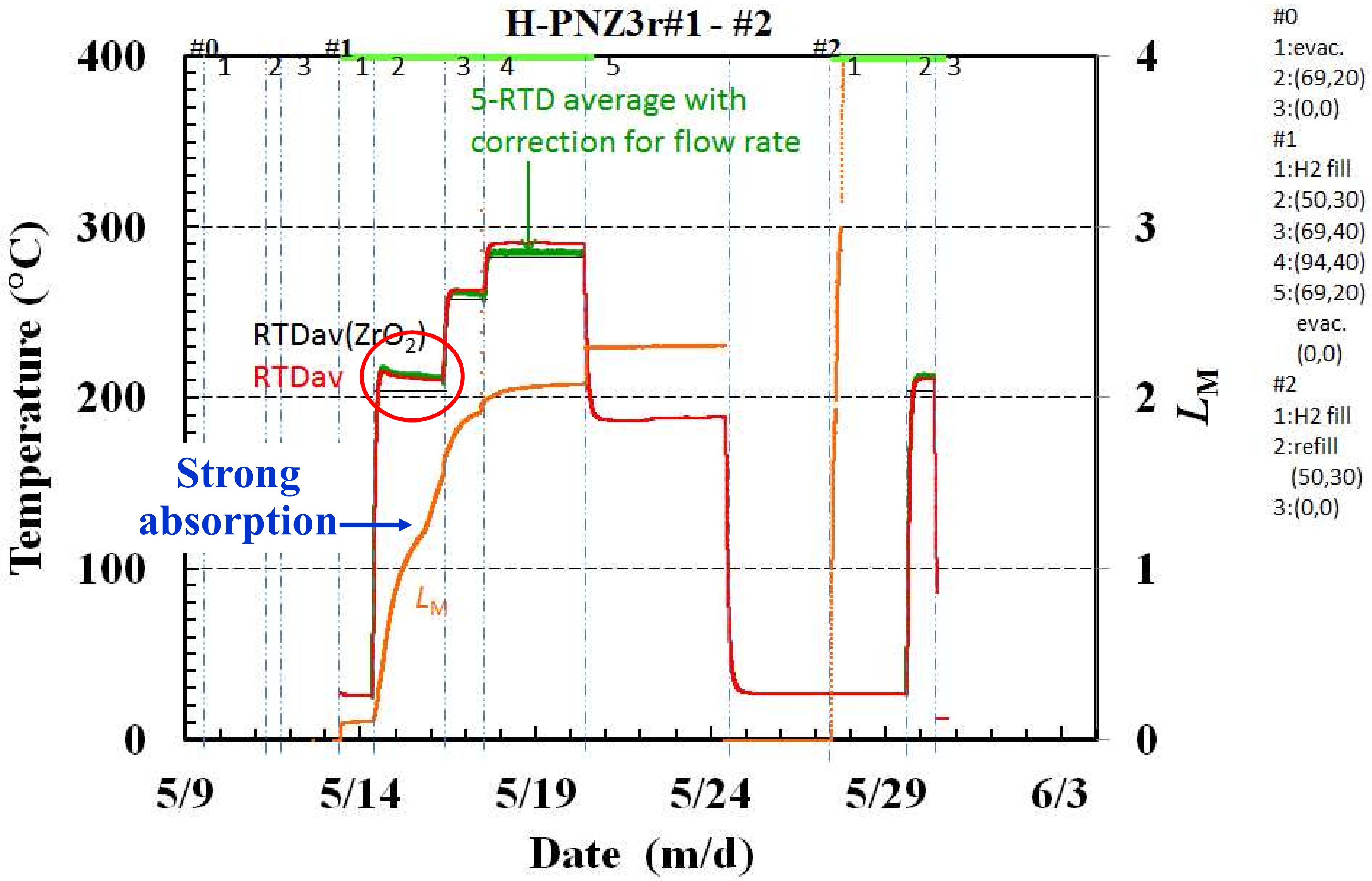
PNZ3r sample: baking (#0) followed by #1 run and #2 run with some leak



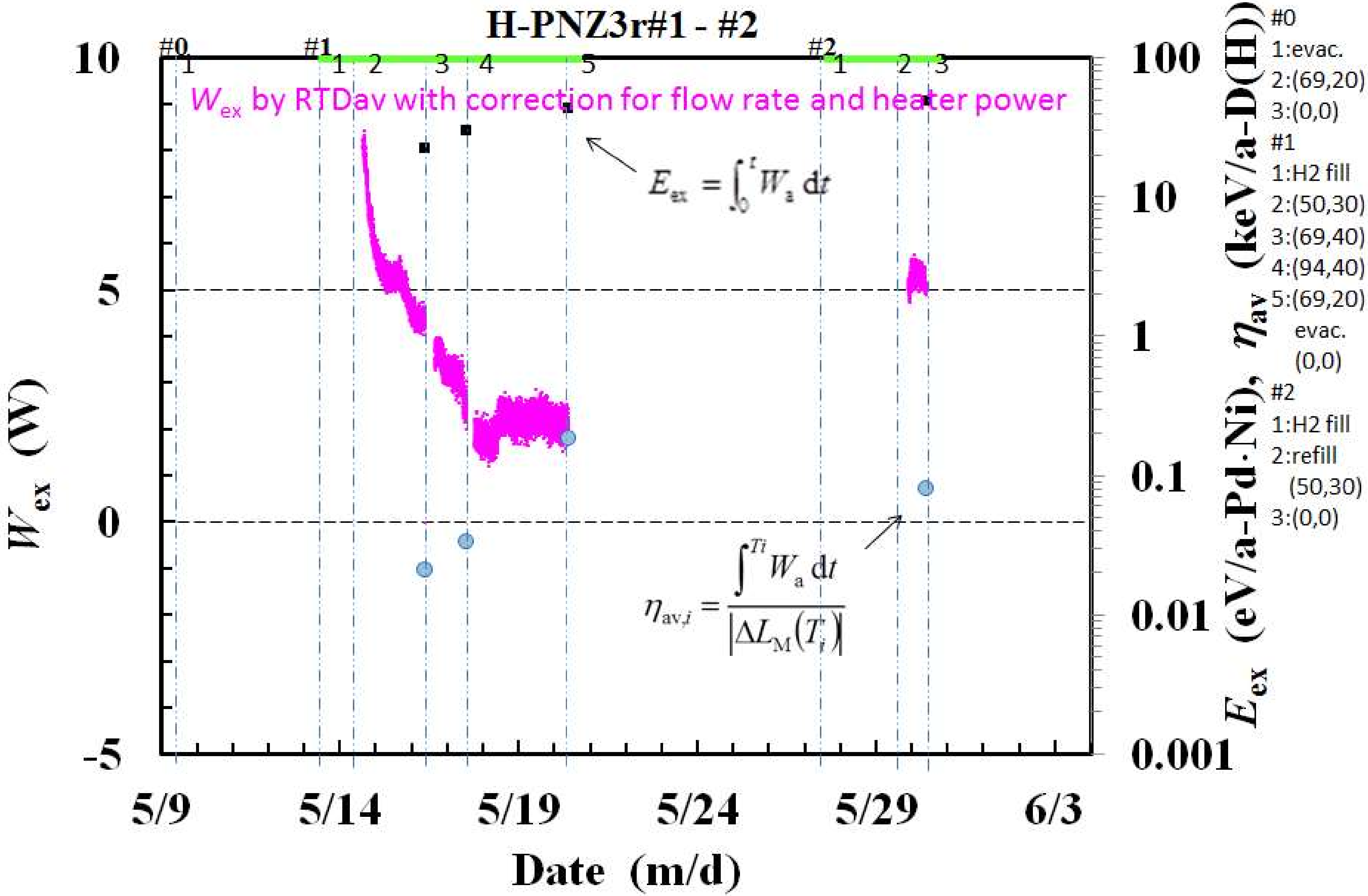
Very low L_M at R.T., but with η_{av} ~ 0.6 eV/a-H equal to that for PNZ3



Strong absorption at ~200 °C with appreciable temperature hump



Excess power calculated with use of RTD



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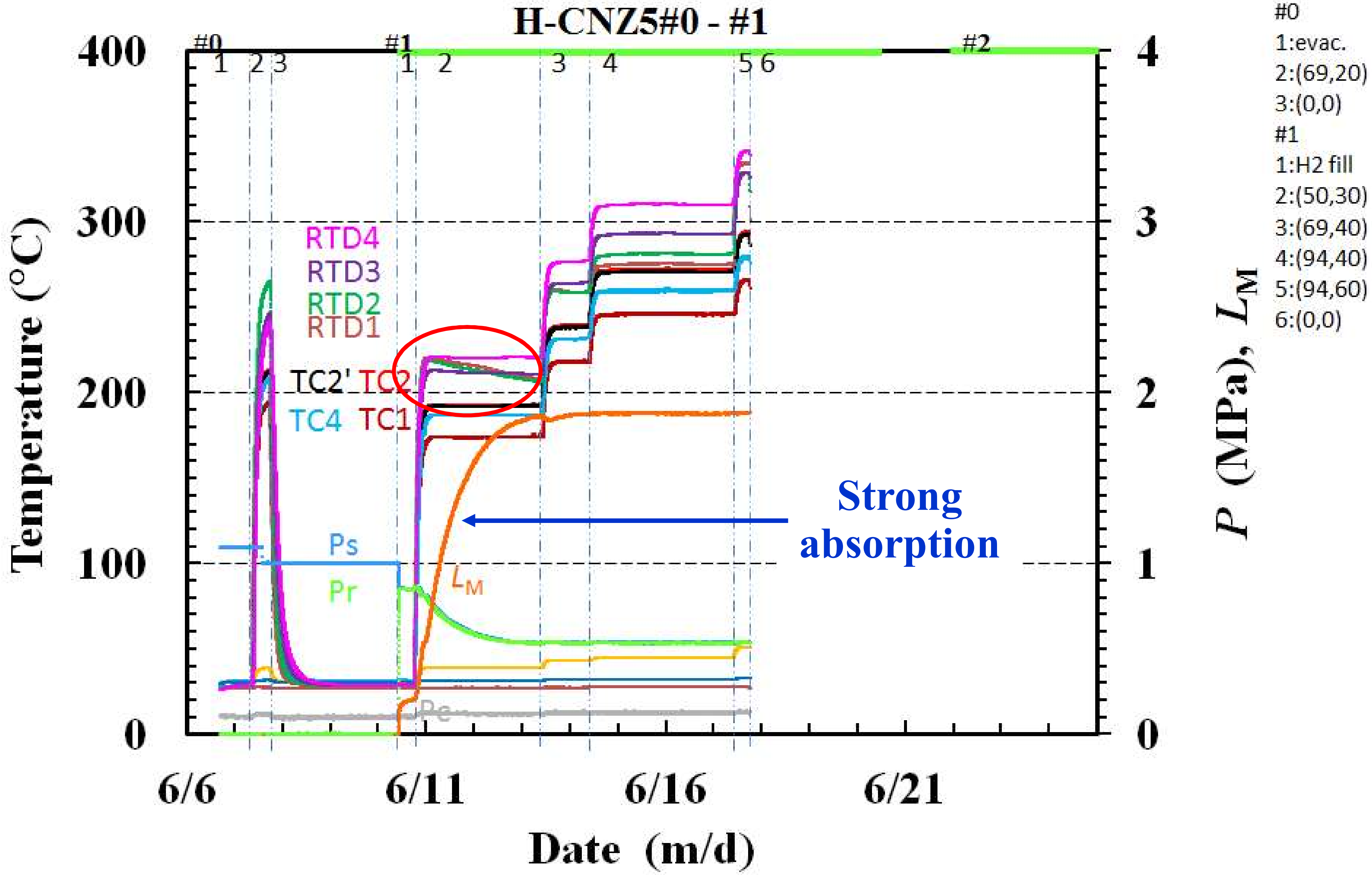
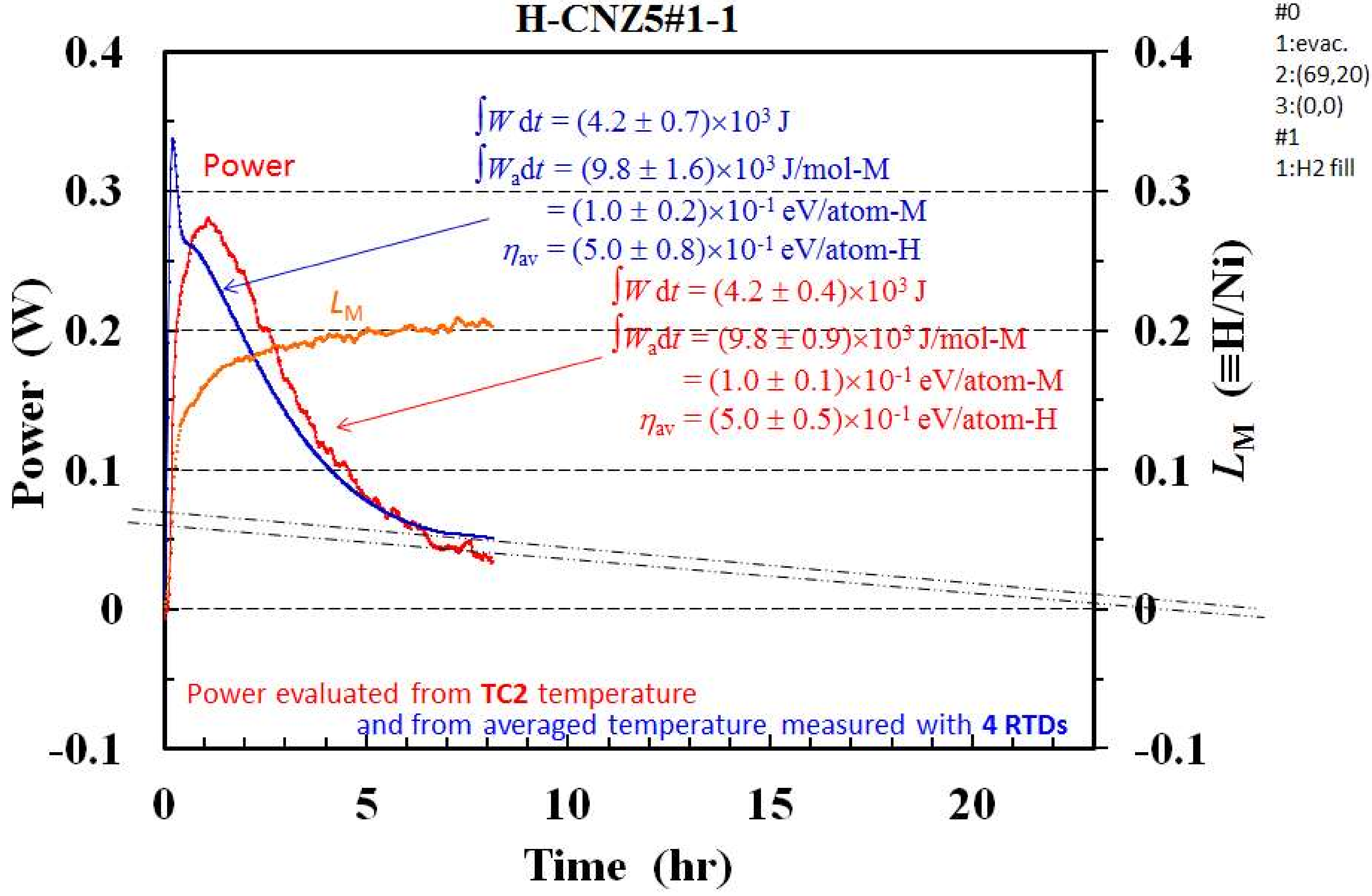
(6) Summary

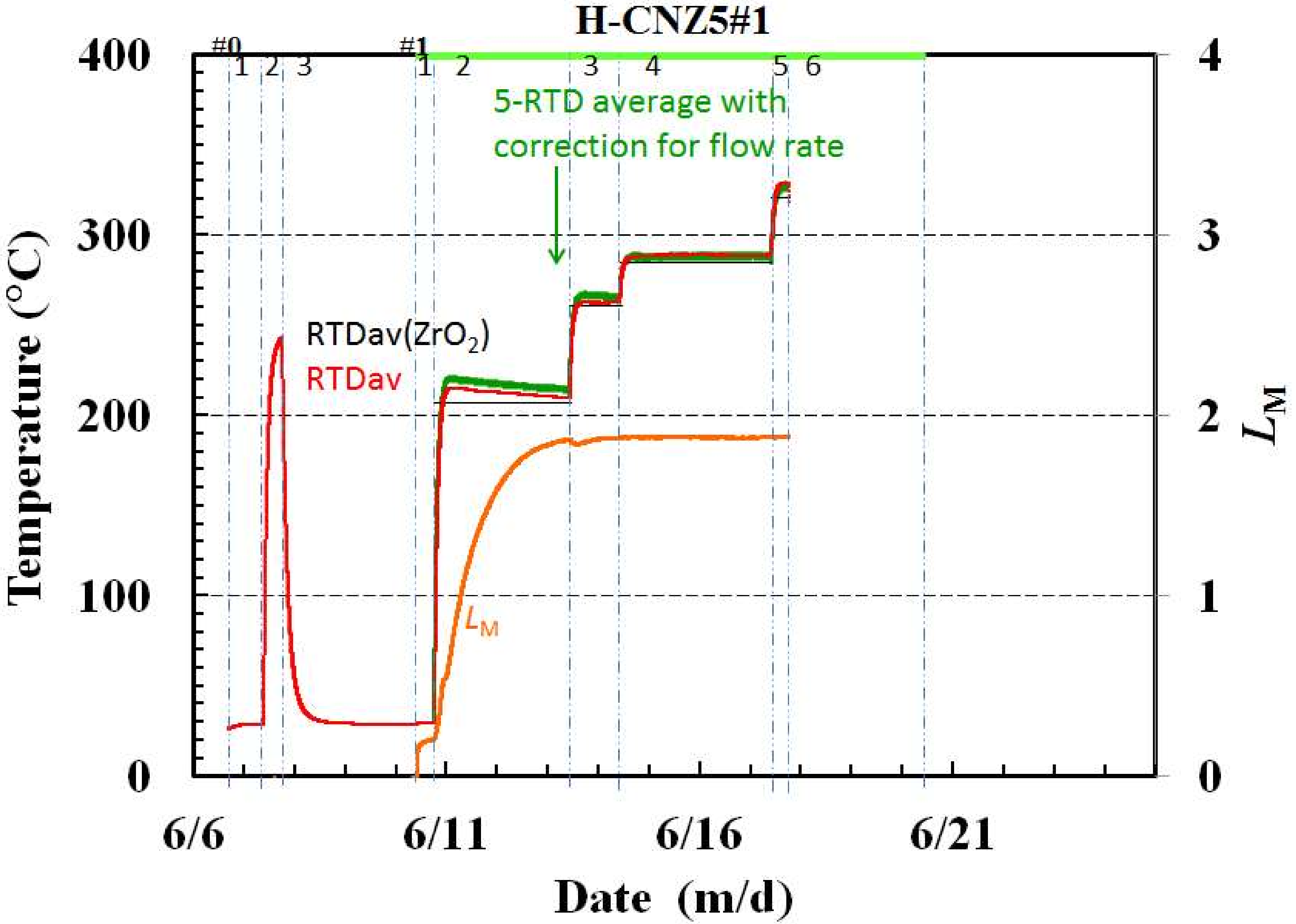
CNZ5 sample: Behavior of L_M and RTD temperatures similar to PNZ3r



Modest power and η with modest L_M, also similar to PNZ3r at RT

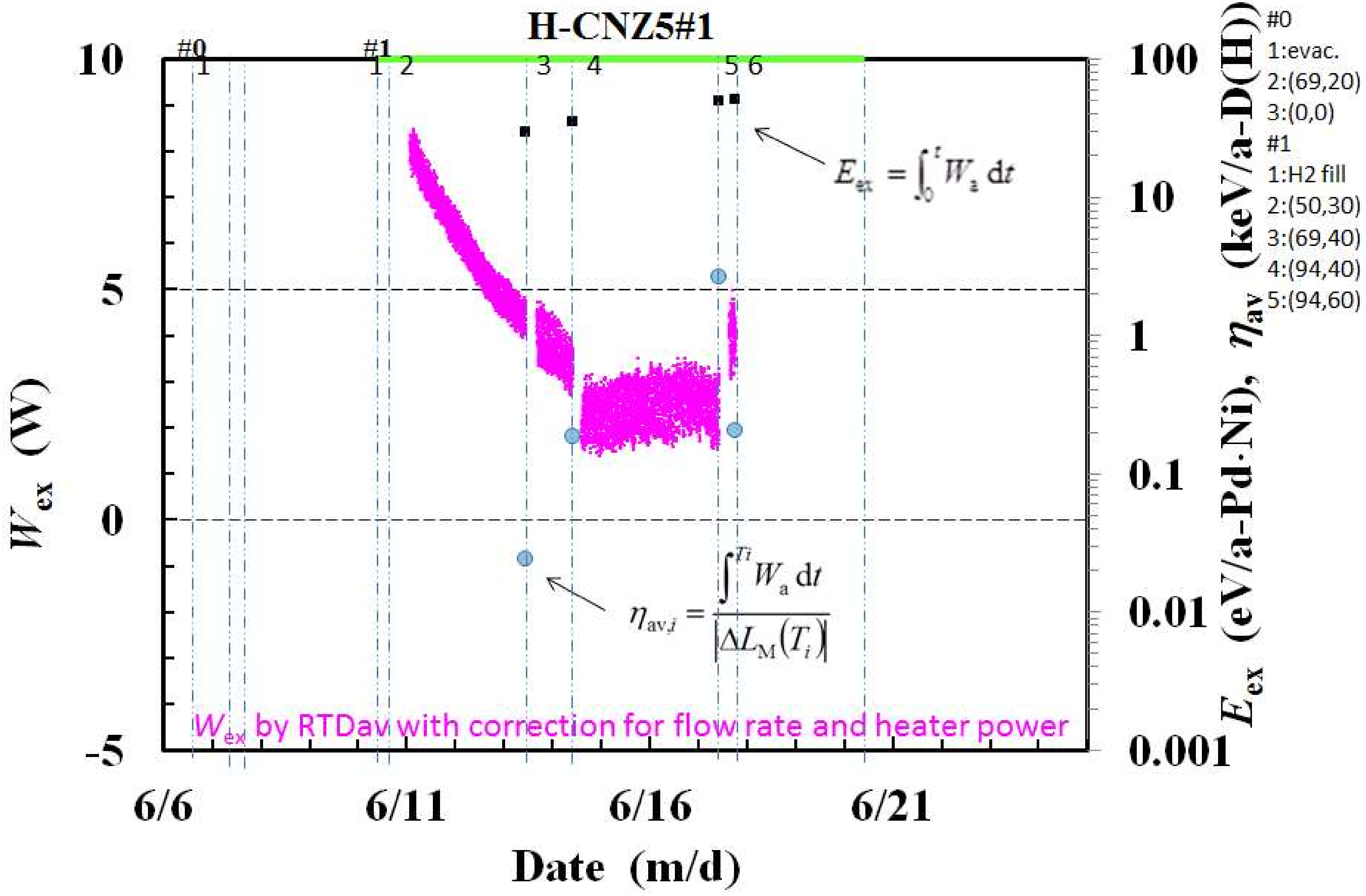


Excess temperature also at RT (#1-1) and above 200 °C (#1-2,3,3,5)



#0
1:evac.
2:(69,20)
3:(0,0)
#1
1:H2 fill
2:(50,30)
3:(69,40)
4:(94,40)
5:(94,60)
6:(0,0)

Excess power calculated with use of RTD temperatures



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(6) Summary

Summary: L_M, η and W_{ex} compared with other samples

	Room Temp.				Elevated Temp.	
	#1		#2, #3, …		L_M at 200°C / hump on RTD	Excess power
	L_M	η (eV/a-D(H))	L_M	η (eV/a-D(H))		
PNZt	(1)	2	2	0.4	---	6W/9W (TC2/RTD)
CNZt	0.2	0.4	0.15	0.2	1.6 / hump	5W (TC2)
CNZtr	0.15	~0	0.15	~0	2.0 / hump	~0
PS3	2	0.7	0.7	0.4	---	~0
PNZ3	3.4	0.6	1.6	0.4	---	10W (RTD,TC1)
PNZ3r	0.1	0.6	---	---	2.0 / hump	8W (RTD)
CNZ5	0.2	0.5	---	---	1.9 / hump	8W (RTD)
PNZ4	3.5	0.6	1.7	0.4	---	(malfunctioning)

Implying common physics

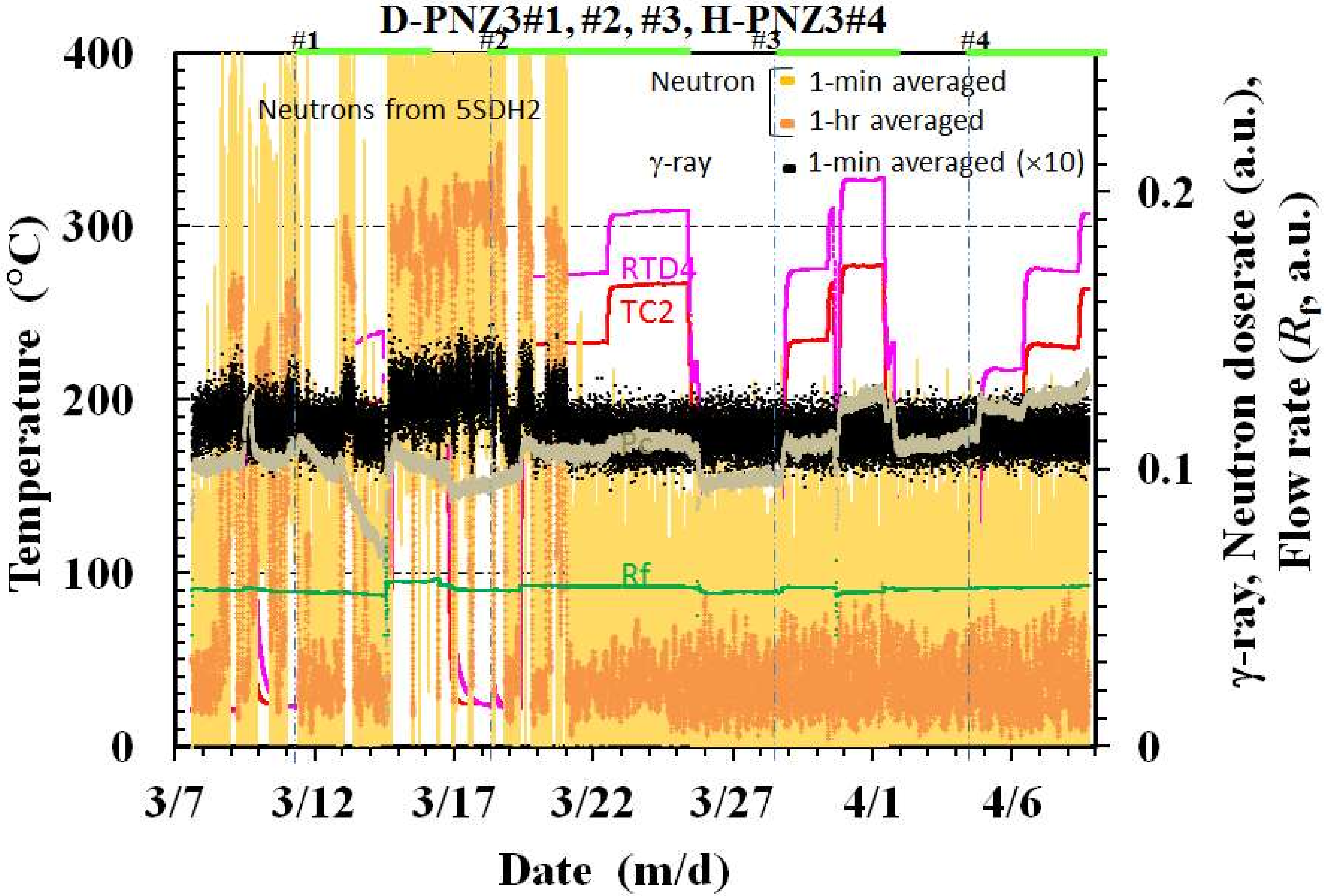
Also tested at Tohoku Univ. (see the next presentation by Y. Iwamura)

Concluding remarks

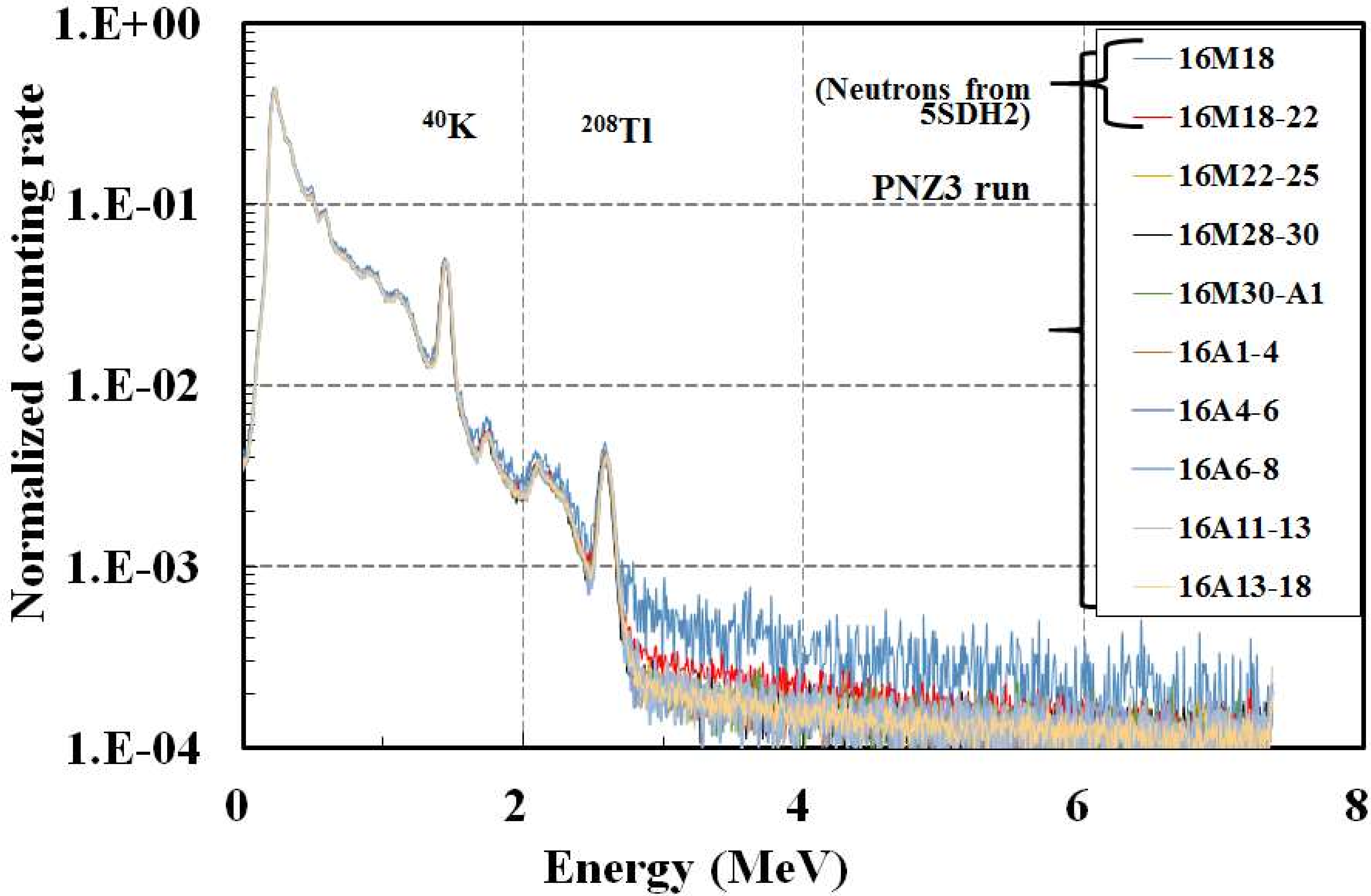
- **Material characterization : XRD, ICP and STEM/EDS**
  Crystalline phases of $NiZr_2$, ZrO_2, etc. identified
- **PNZi samples (PNZ3, PNZ4) at R.T. :**
  very strong absorption with rather large thermal output
  $L_M \equiv$ D(H)/Pd·Ni ~ 3.5, η_{av} ~ 0.6 eV/D (virgin PNZi)
  L_M ~ 1.7, η_{av} ~ 0.4 eV/D (after degassing following E.T. runs)
- **CNZ5 and PNZ3r at R.T. : little absorption but with comparable η_{av}**
  $L_M \equiv$ H/Ni ~ 0.2 and η_{av} ~ 0.5 eV/H at R.T.
- **To discuss whether nuclear process is involved or not, the amount of $NiZr_2$ in the sample must be known for the data at RT.**
- **CNZ5 and PNZ3r at E.T. (~ 200 °C) : a strong absorption similar to PNZ3 at R.T.**
- **All samples at E.T. (200 ~ 300 °C) showed Anomalous Heat: Basis for Clean Energy Device Application**
  Excess power W_{ex} ~ 5 - 10 W for several days
  Excess energy E_{ex} ~ 5 keV/atom-D(H)
  =0.5 GJ/mol-D(H)

Thank you for your attention.

Radiations and flow rate of the coolant



Gamma-ray spectra



Malfunctioning cooling system

Degradation of the coolant BT400 causing change in characteristics

Used BT400

New BT400