Effect of Supporter Material on Heat Evolution from Ni-based Nano-Composite Samples under Exposure to Hydrogen Isotope Gas

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Oct. 2015, **Collaborative Research Project**

launched by six research institutes; Technova Inc., Tohoku Univ., Nissan Motor Co. Ltd., Nagoya Univ., Kobe Univ., Kyushu Univ.

"Analysis and control of novel heat-reaction between metal-nanoparticles and hydrogen"

Objective:

- to verify the presence of the anomalous heat effect (**AHE**) generation phenomena
- to find guiding principles of power control
- to extend research activity as a national project, etc.

High-precision flow calorimetry systems;

one installed at Kobe U., Jun. 2013,

and new similar one installed at Tohoku U, Apr. 2016.

2016~2017, collaborative exam. at Kobe using 4 kinds of samples

Collaborative experiments done at Kobe-U, 2016~2017

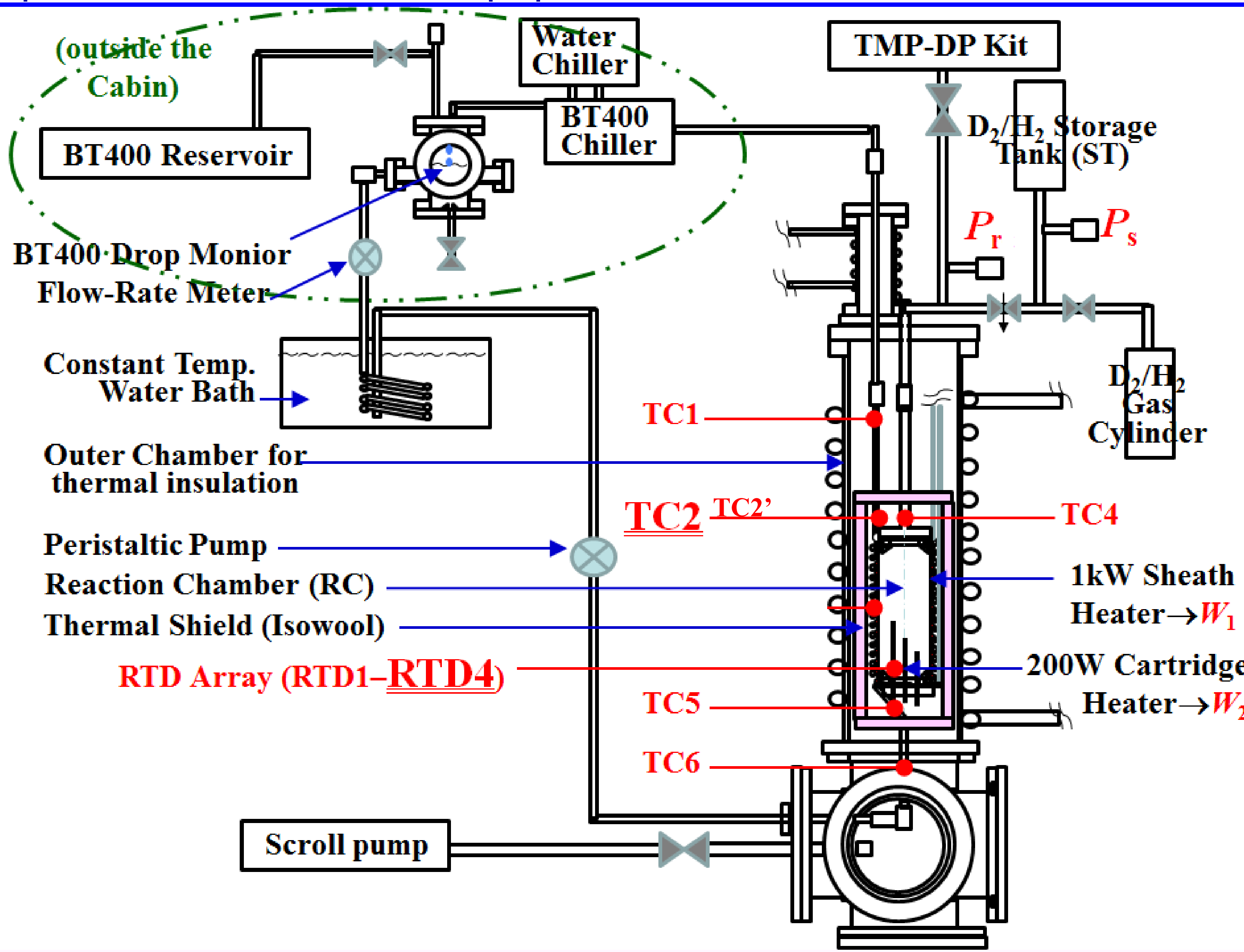
(a) $Pd_{0.044}Ni_{0.31}Zr_{0.65}$; PN**Z**3, PN**Z**4, PN**Z**5
(b) $Cu_{0.044}Ni_{0.31}Zr_{0.65}$; CN**Z**5
- Amorphous mixture of Pd (or Cu), Ni & Zr by melt-spinning method
  ⇒ Calcination at 450 °C for 100~60 h
  ⇒ Formation of binary nanocomposite of Pd·Ni (or Cu·Ni) in **ZrO_2**
- Oct. 2016, at ICCF20 (J. Cond. Matter Nucl. Phys.)

(c) $Cu_{0.008}Ni_{0.079}$ supported by **mesoporous silica** (mp-S); CN**S**3
- NH_3aq solution of $PdCl_2$ & $NiCl_2$ with mp-S suspended
  ⇒ binary nanocomposite of Cu·Ni adsorbed on the pore surfaces

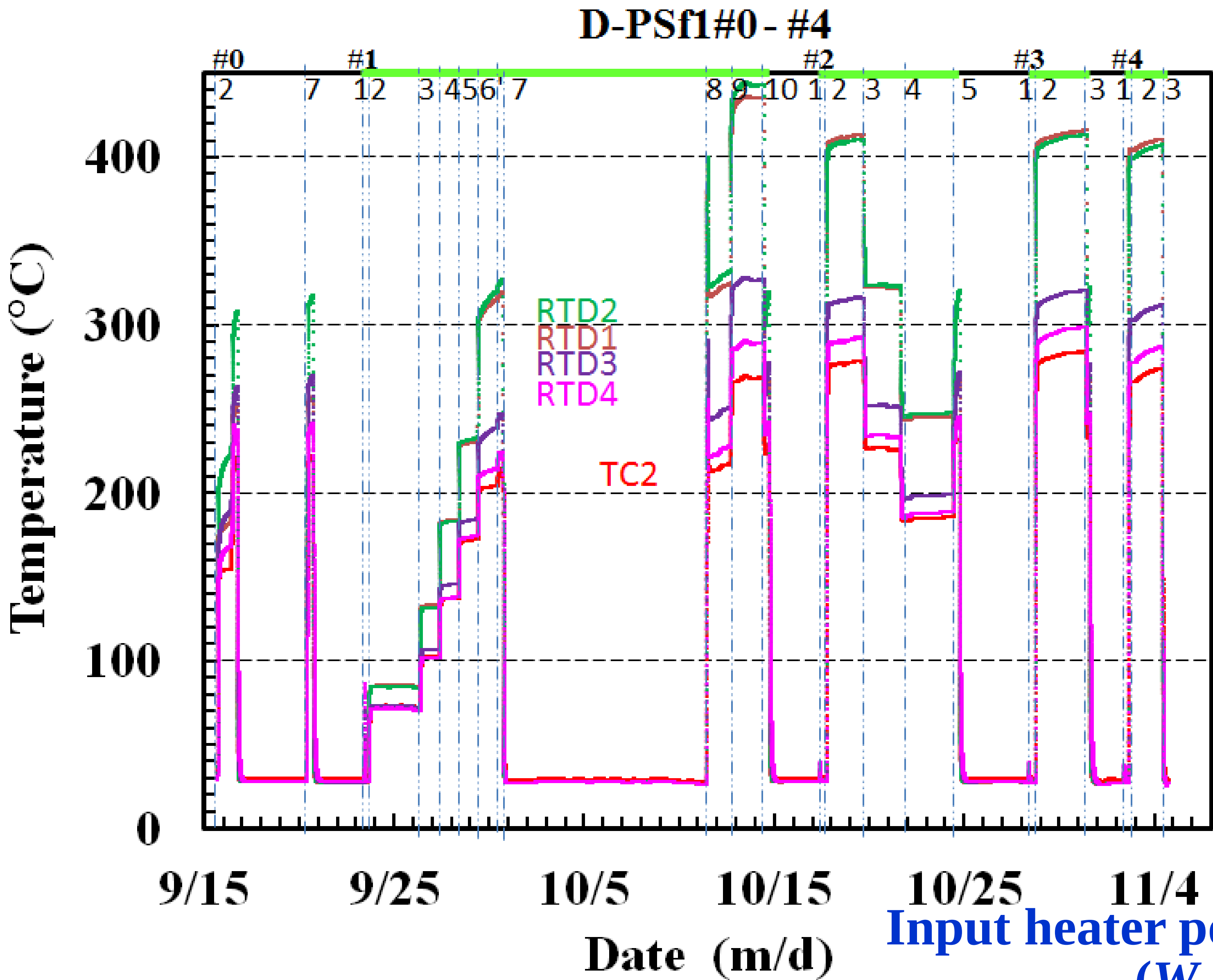
(d) Pd nanoparticles embedded in mesoscopic **SiO_2**; P**S**f1
- Developed at Kyushu Univ.
- Mar. 2017, at JCF17 (Proc. JCF17)

Results
- Excess power at elevated temperatures around 300 °C observed only for binary-metal nanoparticle samples
- Excess power of 3 ~ 10 W lasting for a few weeks at elevated temperatures 200 ~ 300 °C, to result in integrated heat-energy of 20 MJ/mol-Ni, or 90 MJ/mol-H
- Unexplainable by any known chemical reaction

High-precision evaluation equipment for anomalous heat effect



Temperature history in D-PSf1#1 through #4 runs

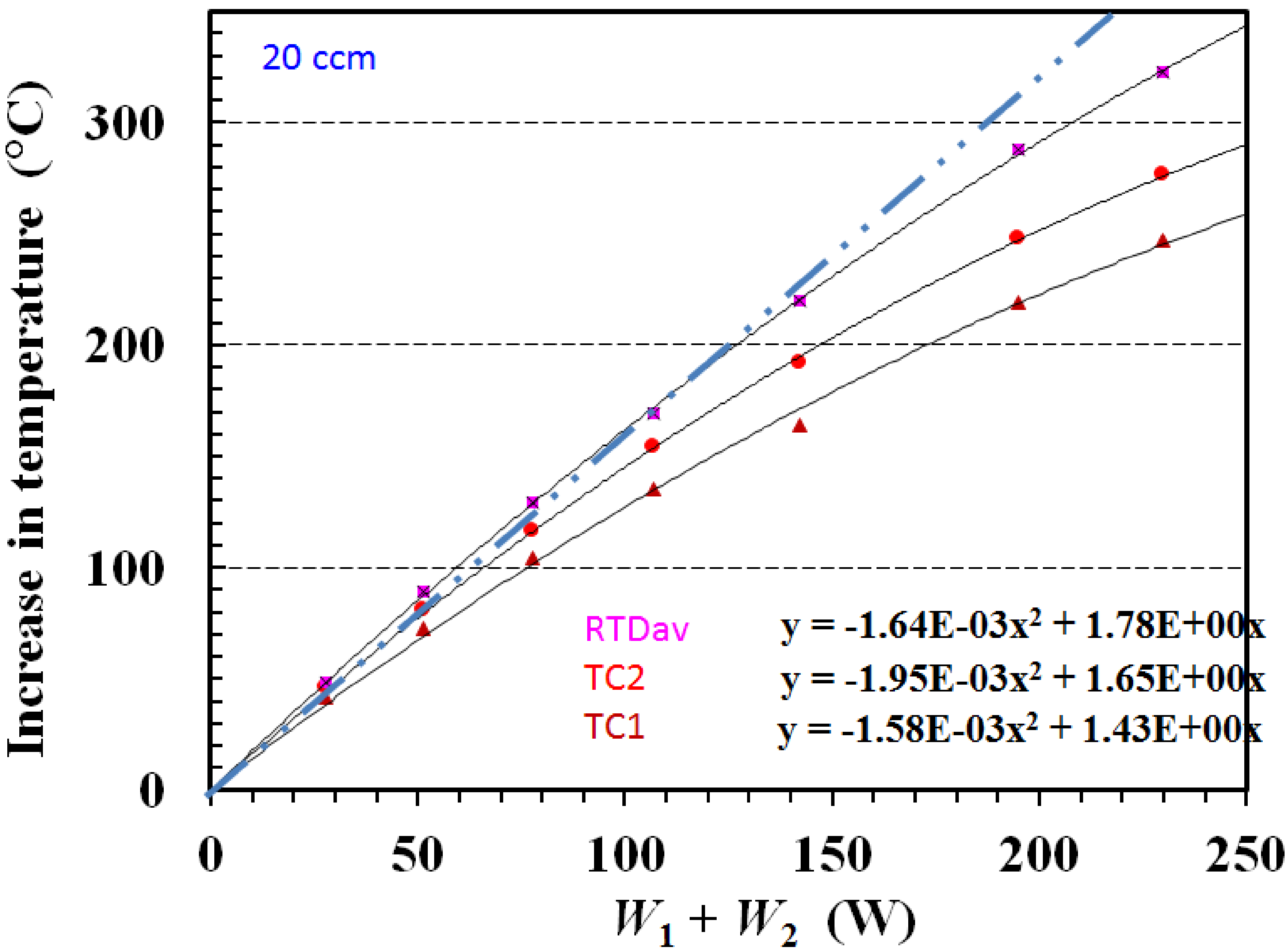


Input heater power (W_1, W_2)

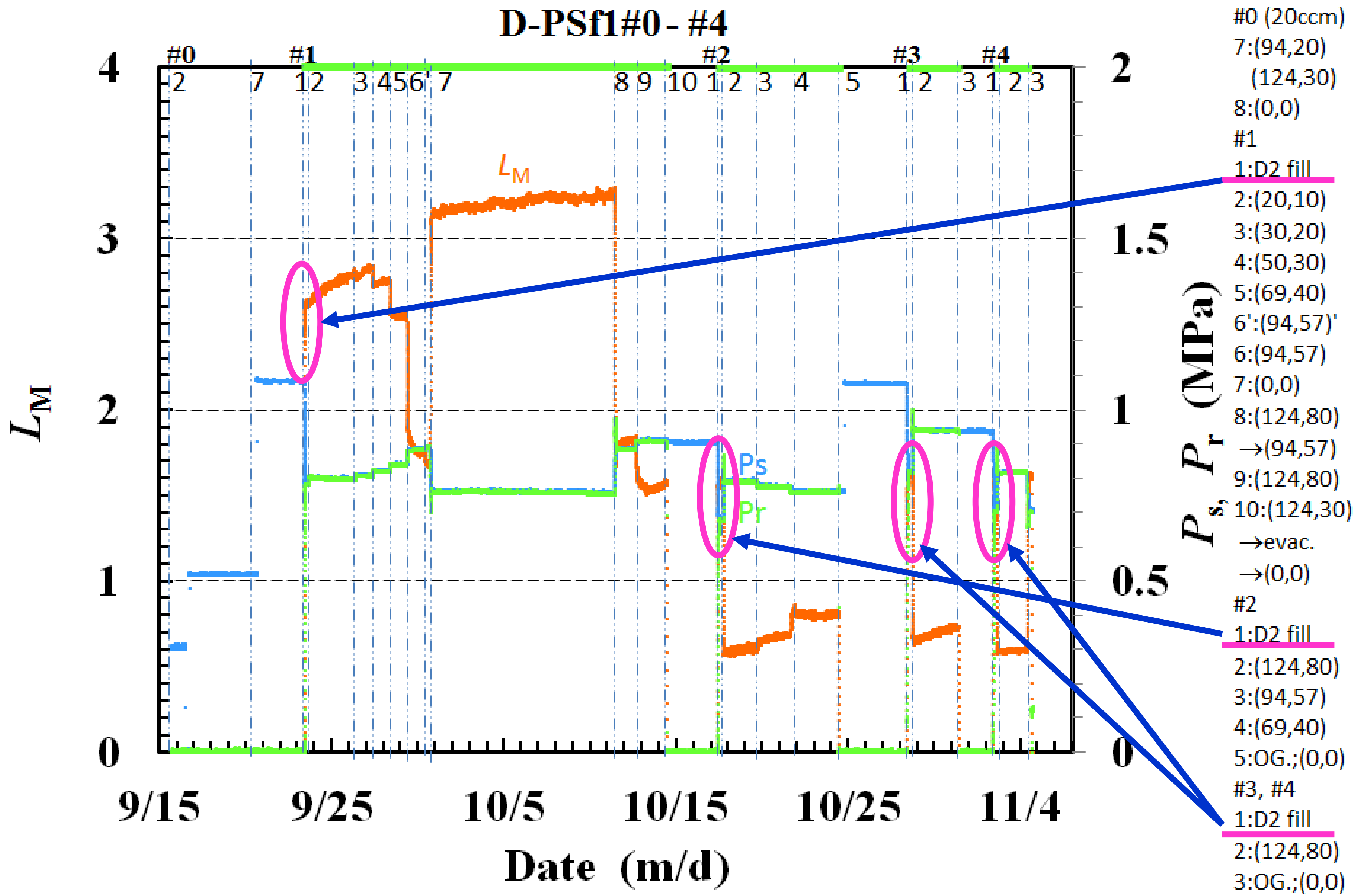
#0 (20ccm)
7:(94,20)
(124,30)
8:(0,0)
#1
1:D2 fill
2:(20,10)
3:(30,20)
4:(50,30)
5:(69,40)
6':(94,57)'
6:(94,57)
7:(0,0)
8:(124,80)
→(94,57)
9:(124,80)
10:(124,30)
→evac.
→(0,0)
#2
1:D2 fill
2:(124,80)
3:(94,57)
4:(69,40)
5:OG.;(0,0)
#3, #4
1:D2 fill
2:(124,80)
3:OG.;(0,0)

Conversion of temperature to power produced in RC: Calibration

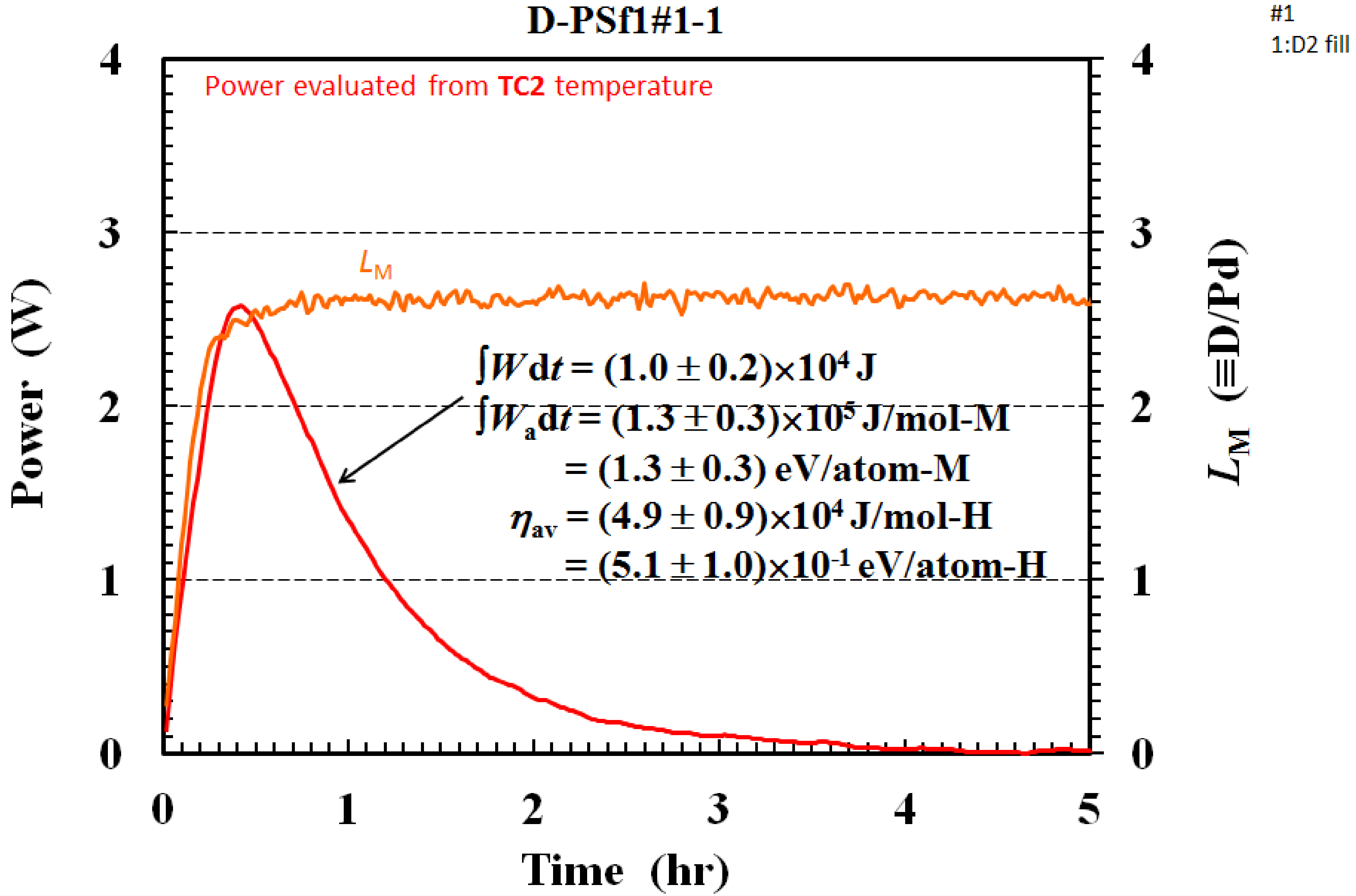
(control sample: mp-silica) H-S2#1



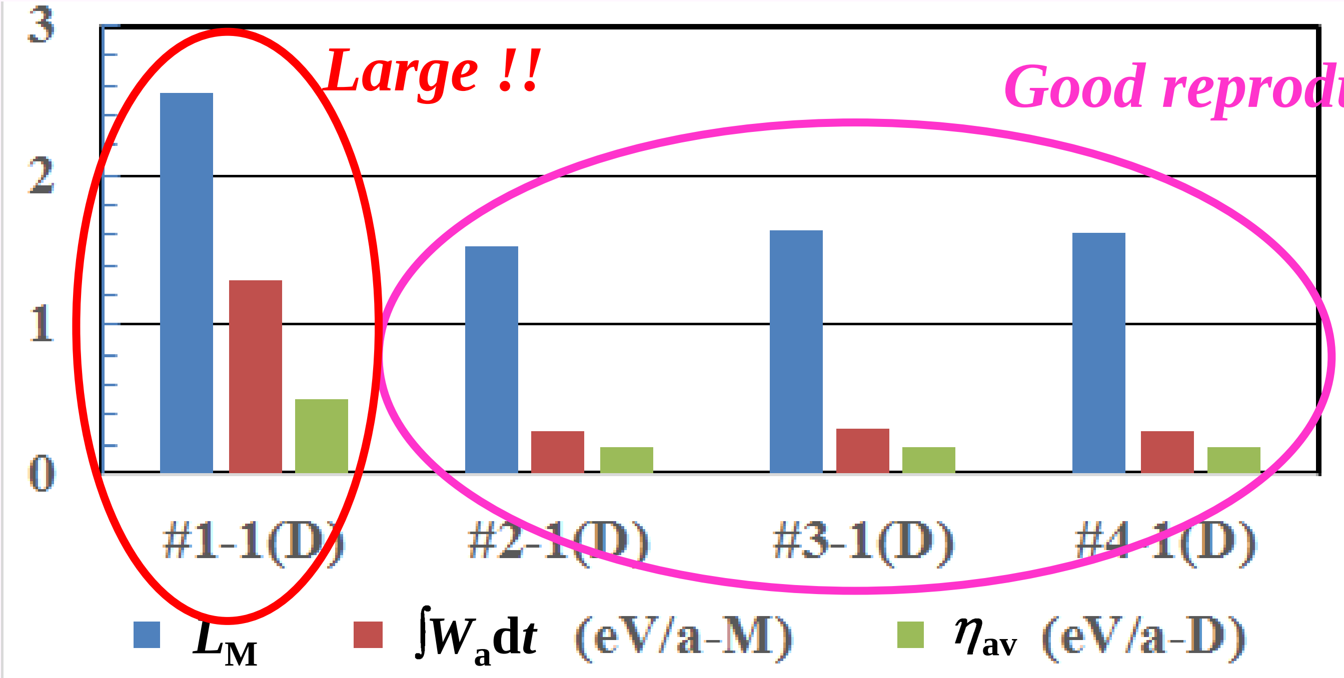
Variation of deuterium-loading ratios, L_M≡D/M (M=Pd), in PSf1



Emerging power and integrated heat under D_2 exposure of virgin PSf1 at room temperature (R.T.), and evolution of D-loading ratio L_M



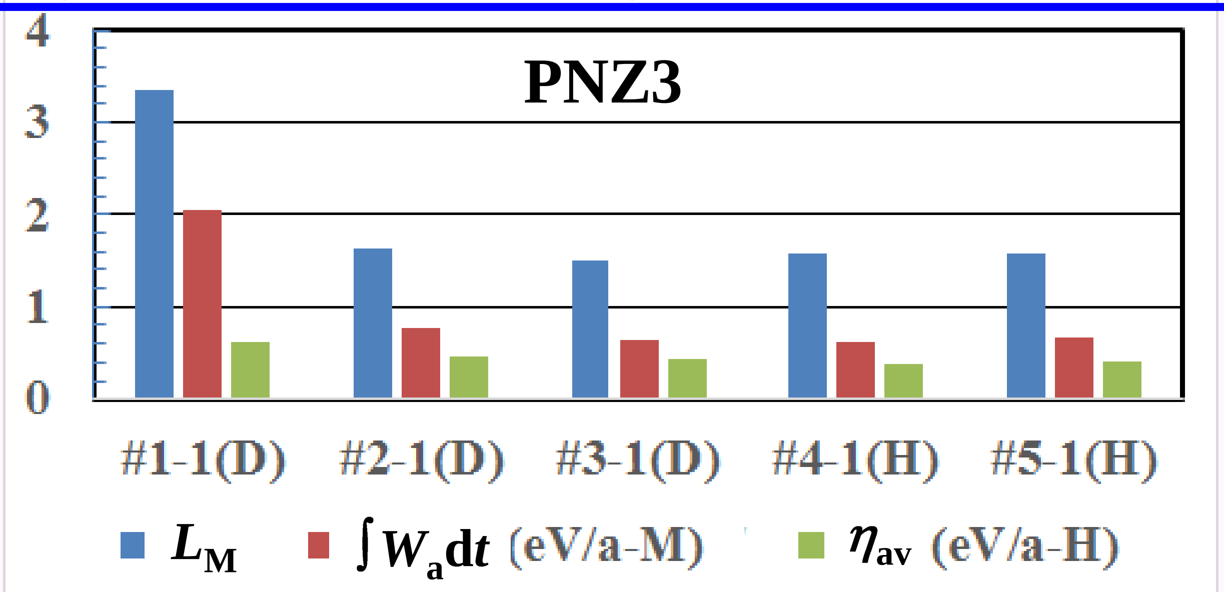
Thermal energy output and D-loading ratio in R.T. phases, PSf1#*n*-1



		#1-1(D)	#2-1(D)	#3-1(D)	#4-1(D)
L_M	"M"=Pd	2.55E+00	1.53E+00	1.63E+00	1.61E+00
E_a ($\equiv \int W_a dt$)	(eV/a-M)	1.3E+00	2.9E-01	3.1E-01	2.9E-01
η_{av}	(eV/a-D)	5.1E-01	1.9E-01	1.9E-01	1.8E-01

may be explainable by known chemical reactions.

Thermal energy output and loading ratios in R.T. phases, PNZ3#n-1



	PNZ3	#1-1(D)	#2-1(D)	#3-1(D)	#4-1(H)	#5-1(H)
L_M	"M"=Pd·Ni	3.35E+00	1.64E+00	1.50E+00	1.59E+00	1.57E+00
$E_a \equiv \int W_a dt$	(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

Ni absorbs at R.T.
(Catalytic effect of Pd)

Very large
L_M, E_a, η_{av}

Fairly large L_M, E_a, η_{av} :
$NiZrD_{2.5} \leftrightarrow ZrNi+D_2$

Plausible chemistry for D(H)-absorption and energy release in PNZ samples at R.T.: Existence of $NiZr_2$ phase may be the key.

$PdO + D_2(H_2) \rightarrow Pd + D_2O(H_2O)$ + 1.77 (1.63) eV/atom-Pd, (4)

$NiO + D_2(H_2) \rightarrow Ni + D_2O(H_2O)$ + 0.176 (0.033) eV/atom-Ni. (5)

$NiZr_2 + (4.5/2)H_2 \rightarrow ZrH_2 + ZrNiH_{2.5}$ + 274.4 kJ. (6)*

(L_M(=H/Ni)=4.5) (2.85 eV/a-Ni) = (0.63 eV/a-H)

(: *Main reaction in #1-1?*)

(*Reaction in #n-1*（*n*≥2）?: *reversible*)

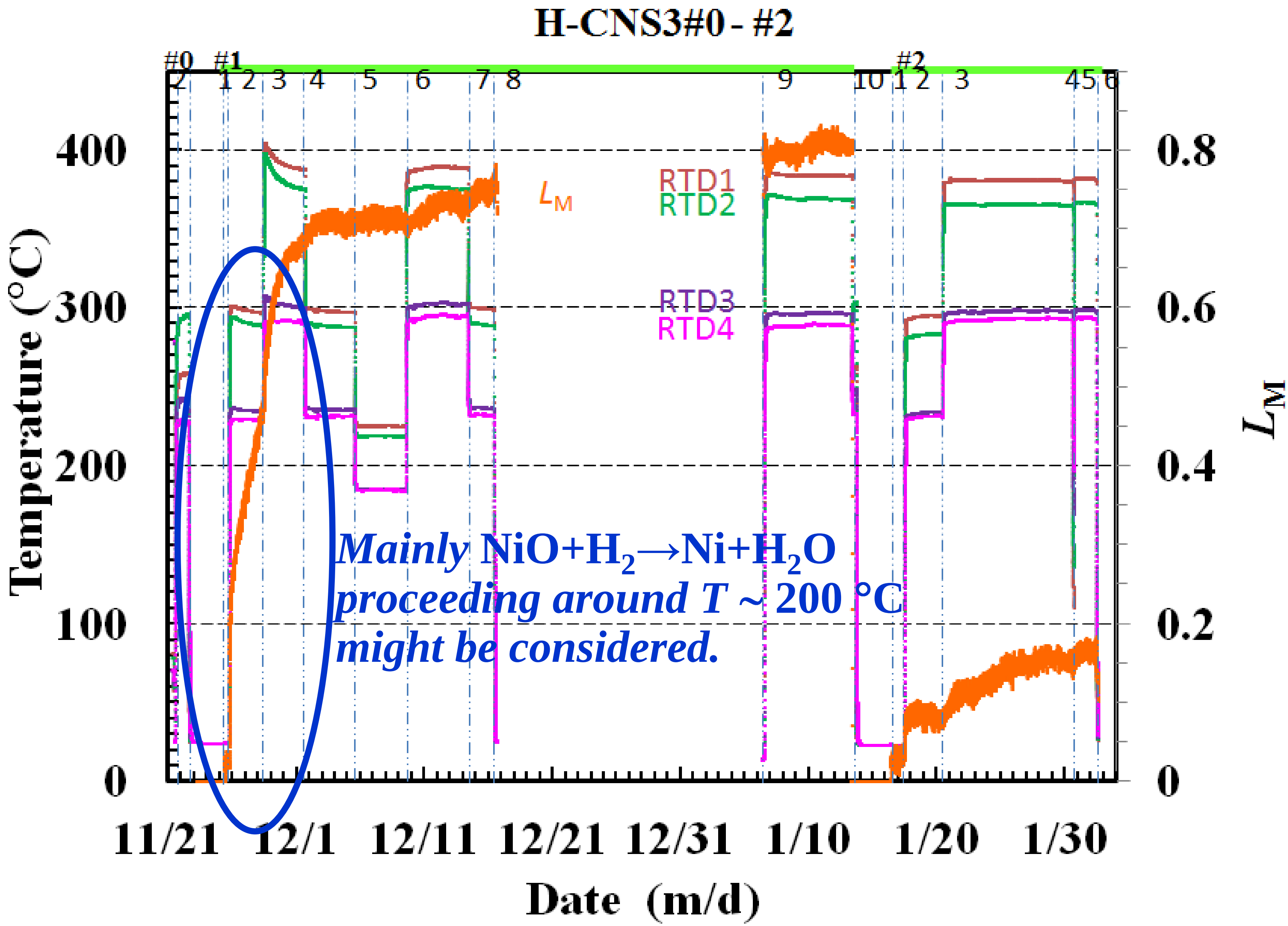
$ZrNi + (2.5/2)H_2$ + (~0.3 eV)

(*After re-calcination in air*)

$ZrO_2 + NiO$ （Mass buildup = 32%: *consistent with exp.*)

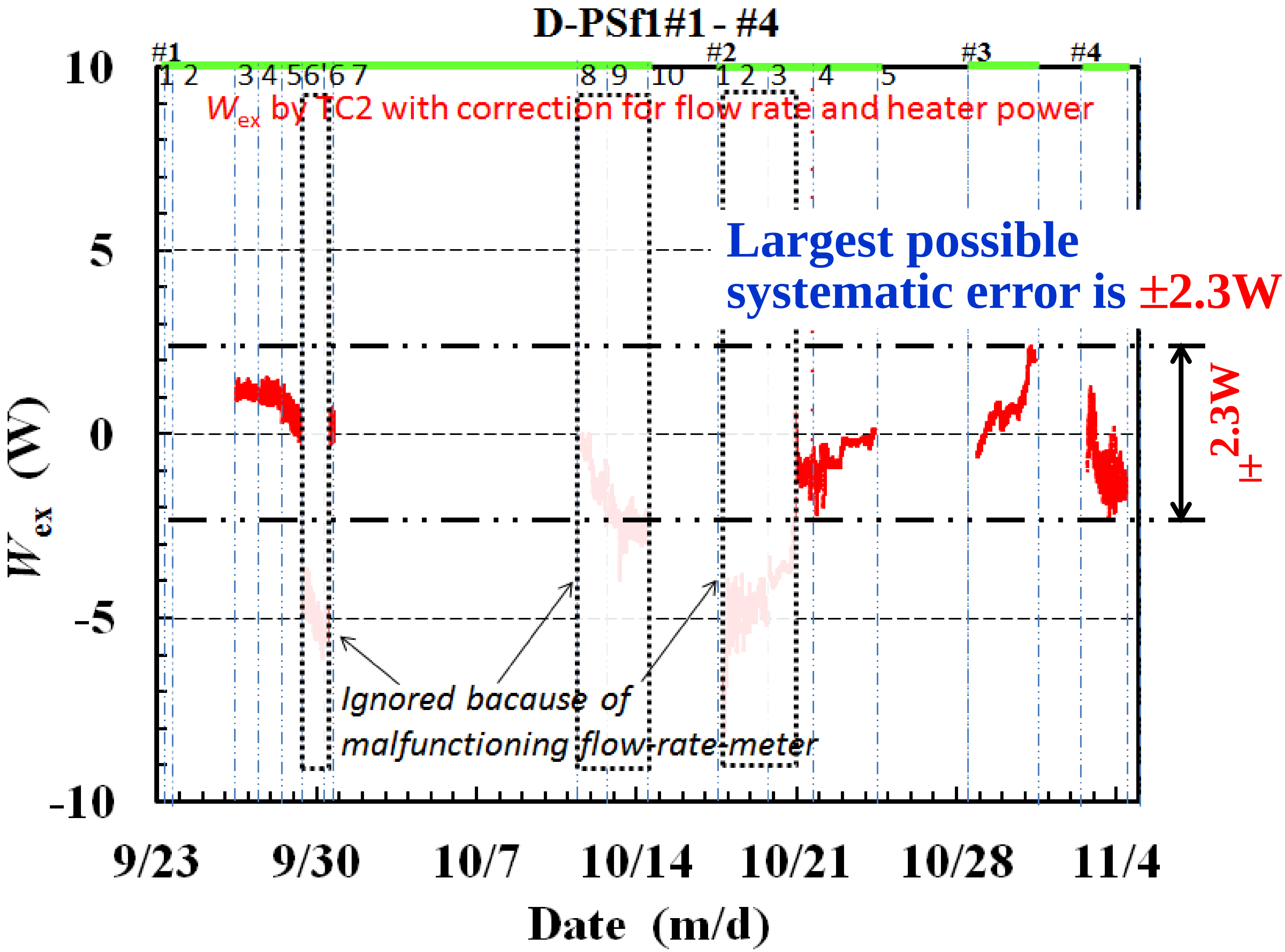
* P. Dantzer, W. Luo, Ted B. Flanagan and J.d. Clewley; Calorimetrically Measured Enthalpies for the Reaction of H_2 (g) with Zr and Zr Alloys; Metallurgical Transactions A, **24A** (1993) 1471-1479.

Hydrogen absorption/consumption of CNS3 ($L_M \equiv$ H/Pd)



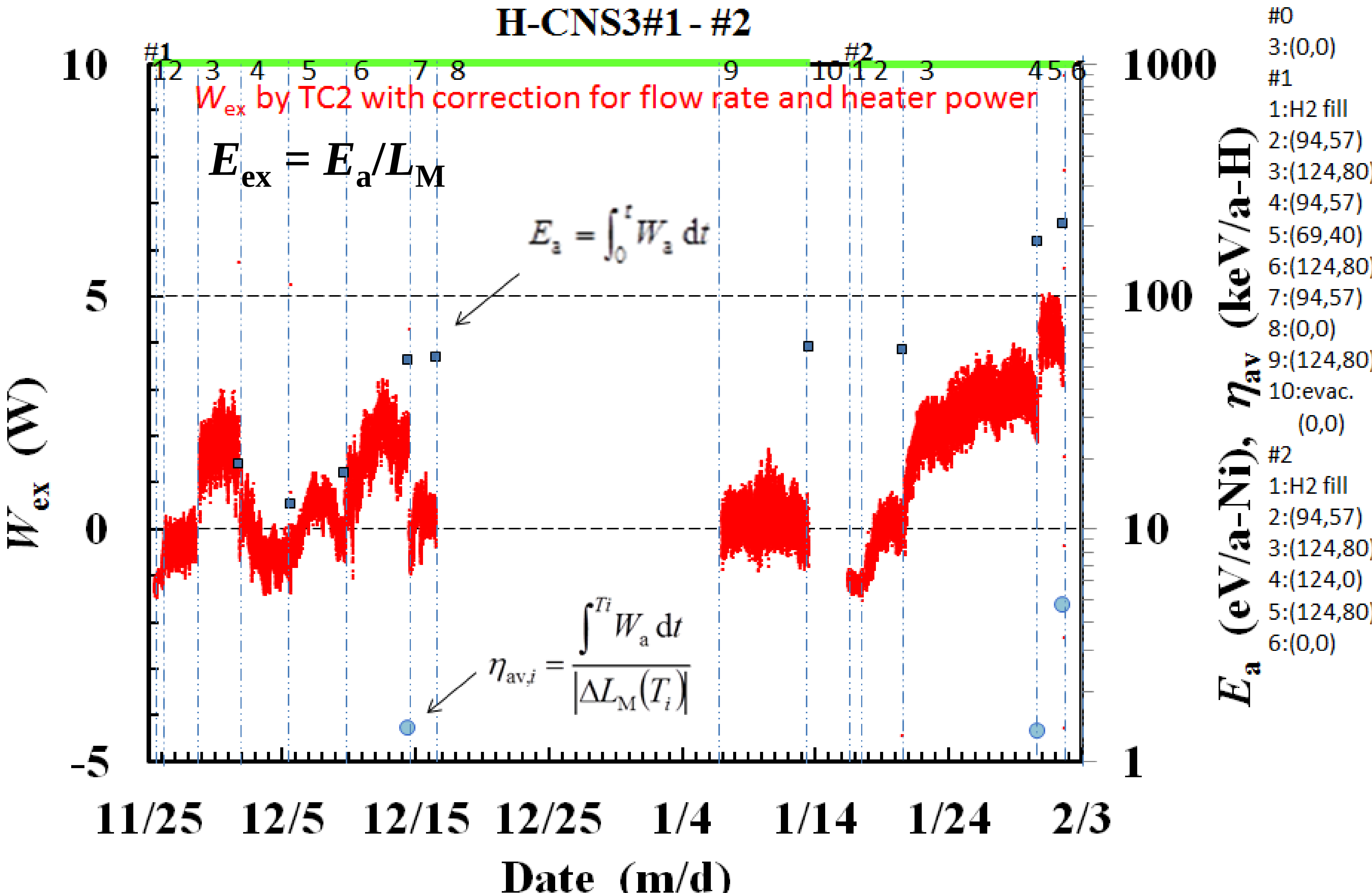
#0
1:evac.
2:(124,30)
3:(0,0)
#1
1:H2 fill
2:(94,57)
3:(124,80)
4:(94,57)
5:(69,40)
6:(124,80)
7:(94,57)
8:(0,0)
9:(124,80)
10:evac.
(0,0)
#2
1:H2 fill
2:(94,57)
3:(124,80)
4:(124,0)
5:(124,80)
6:(0,0)

Excess power ($T_{C2;PSf1}$-$T_{C2;mp-S}$) at elevated temp.: No excess for PSf1

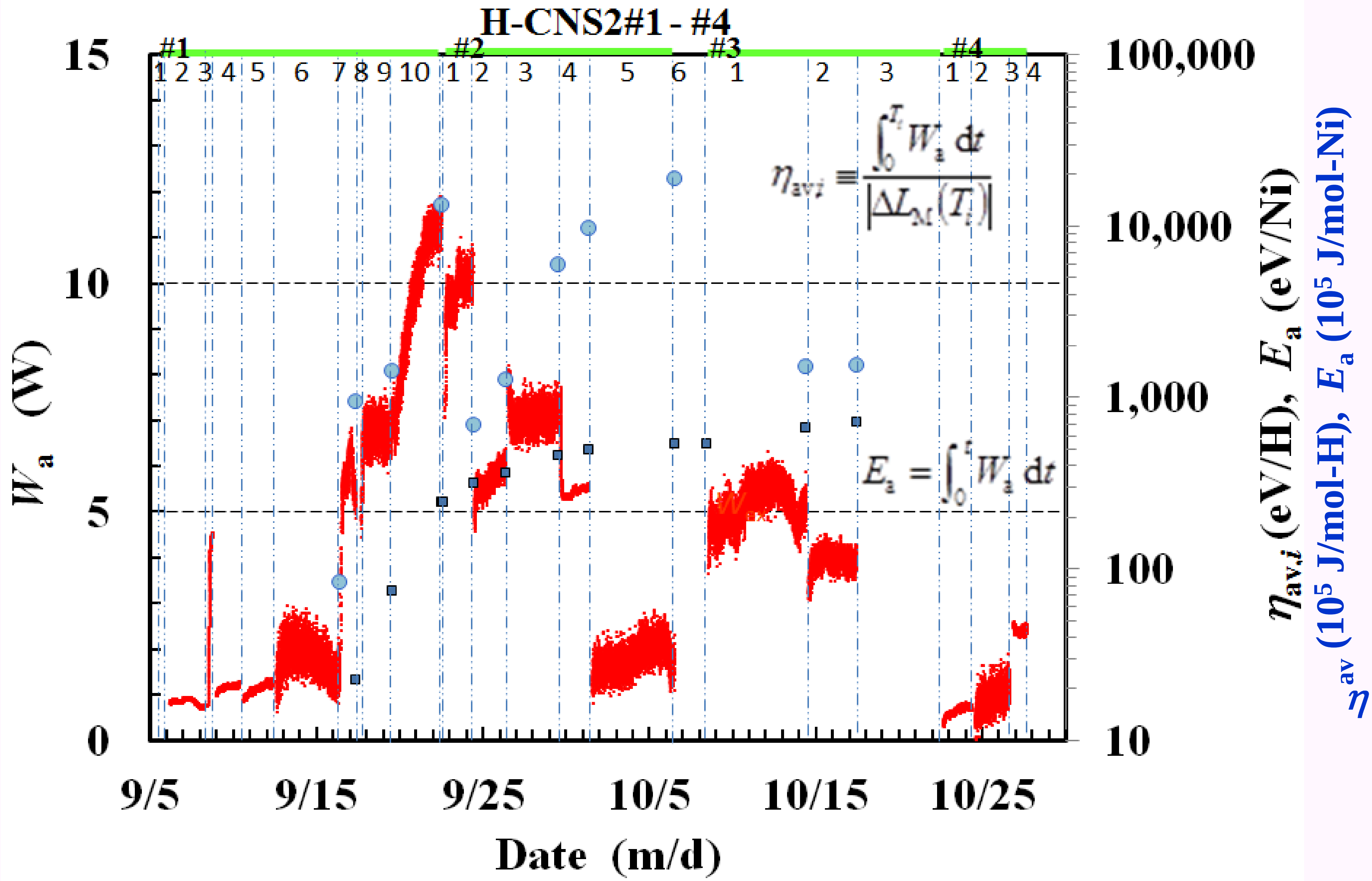


#1
1:D2 fill
2:(20,10)
3:(30,20)
4:(50,30)
5:(69,40)
6':(94,57)'
6:(94,57)
7:(0,0)
8:(124,80)
→(94,57)
9:(124,80)
10:(124,30)
→evac.
→(0,0)
#2
1:D2 fill
2:(124,80)
3:(94,57)
4:(69,40)
5:OG.;(0,0)
#3
1:D2 fill
2:(124,80)
3:evac.(0,0)
#4
1:D2 fill
2:(124,80)
3:(0,0);evac

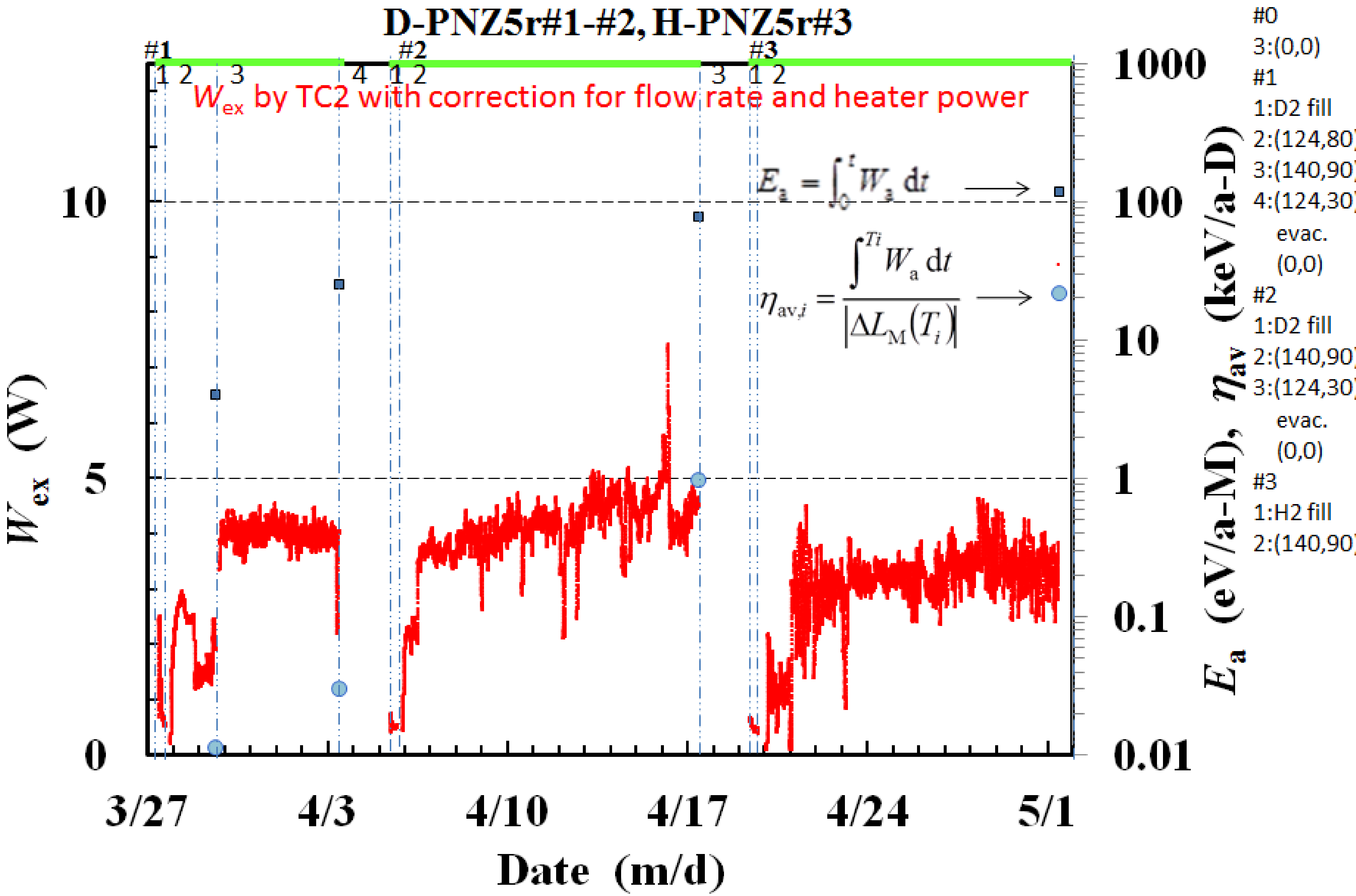
Excess power for CNS3: 4.5 W with $E_{ex} \equiv E_a/L_M$ ~ 90 MJ/mol-H.



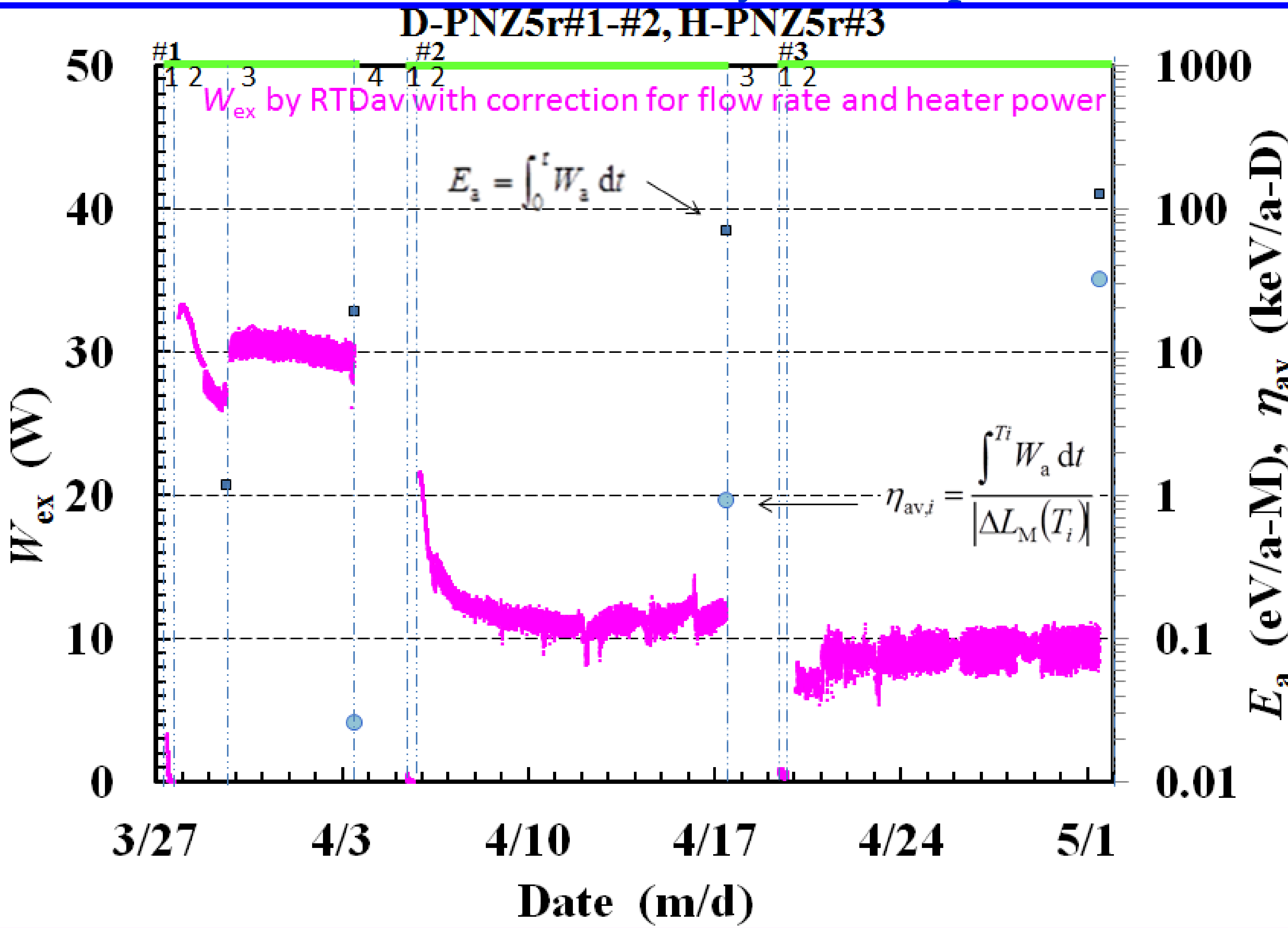
Excess power is reproducible; 11 W for CNS2 with E_{ex} 190 MJ/mol-H.



Excess power evolution for PNZ5r: 4 ~ 5W with E_{ex} ~ 9 MJ/mol-D



Excess power for PNZ5r calculated with RTDav：
Uniformalization is one of the keys for the power enhancement.

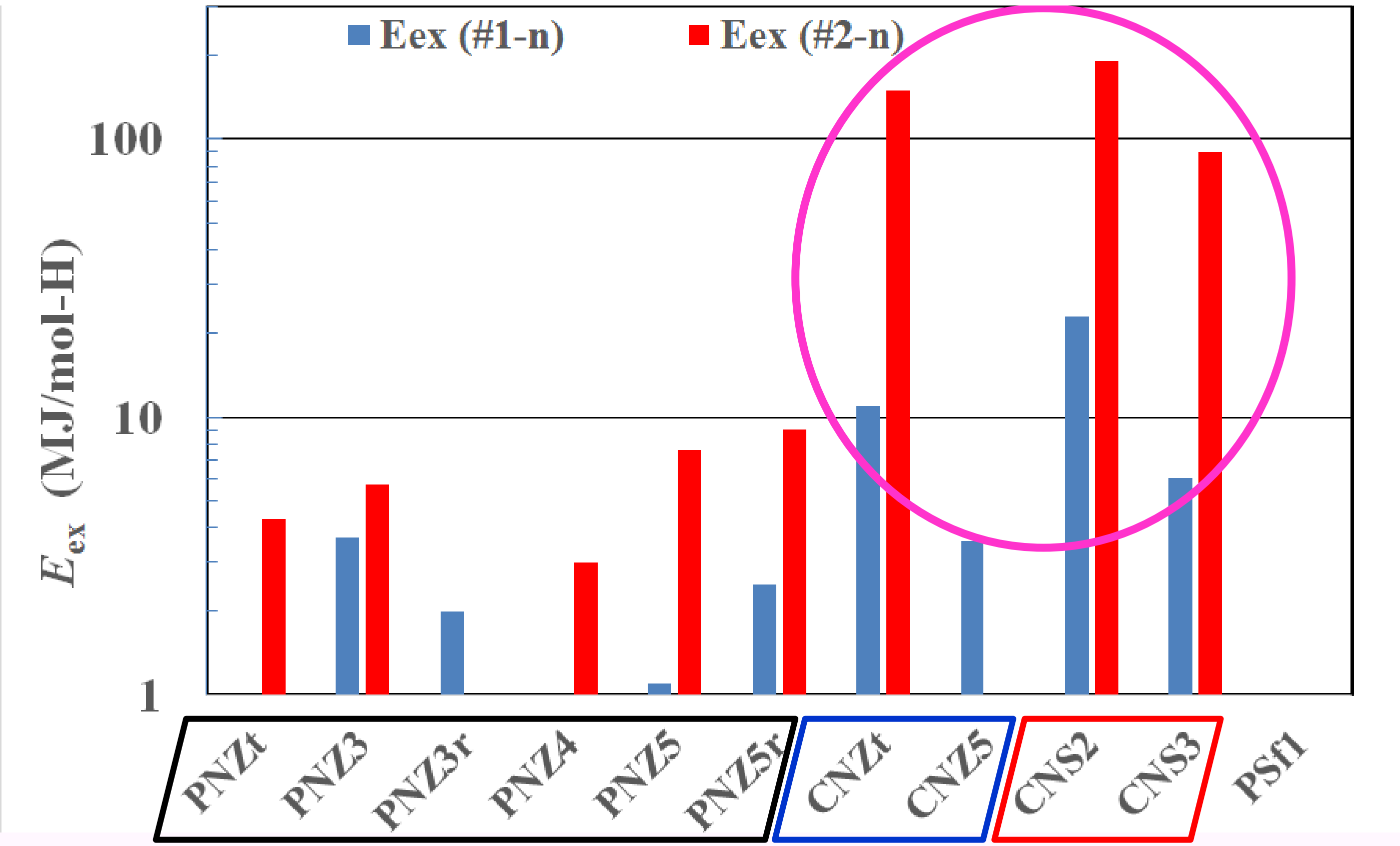


#0
3:(0,0)
#1
1:D2 fill
2:(124,80)
3:(140,90)
4:(124,30)
evac.
(0,0)
#2
1:D2 fill
2:(140,90)
3:(124,30)
evac.
(0,0)
#3
1:H2 fill
2:(140,90)

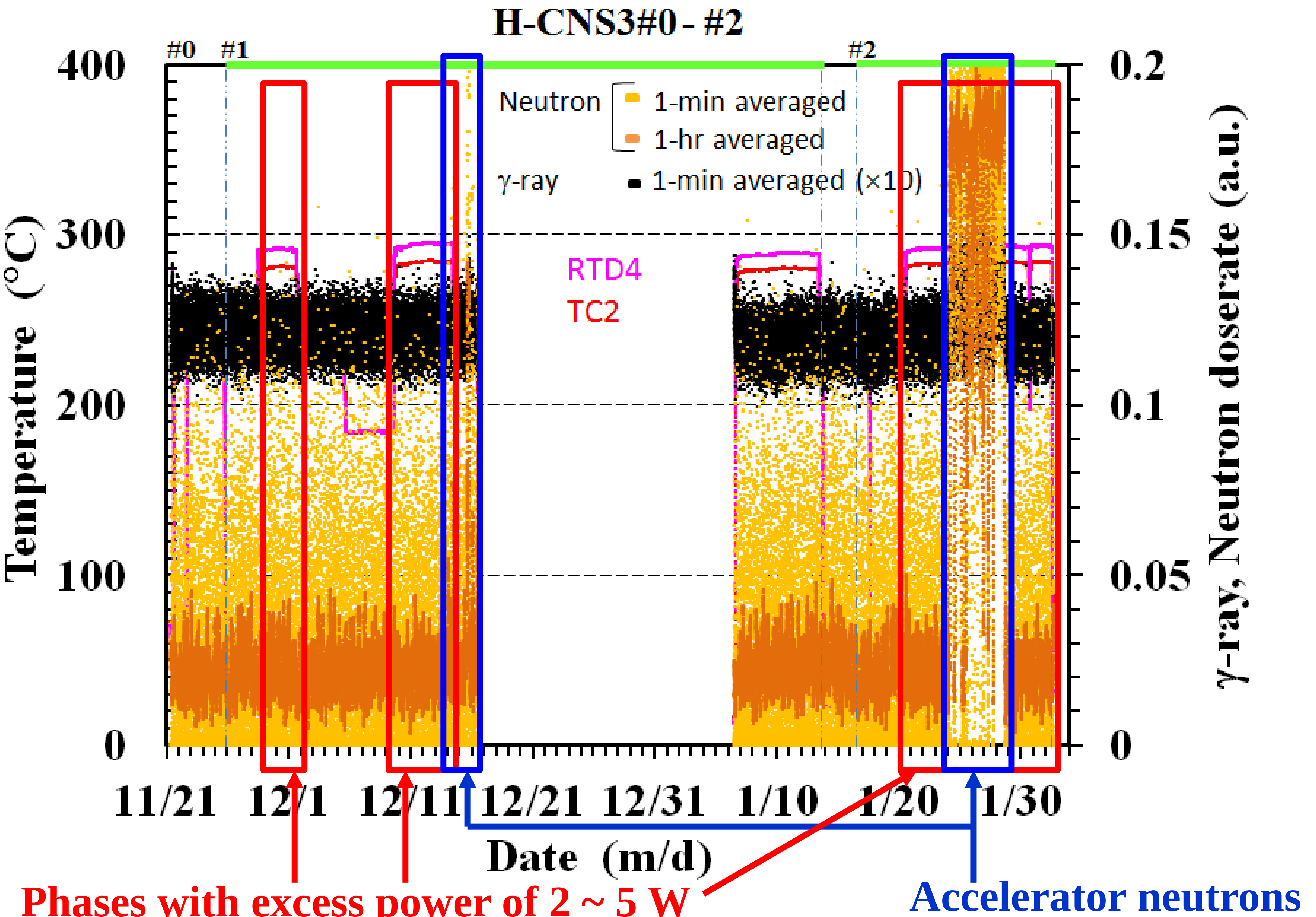
Comparison of integrated excess heat at elevated temperatures

It appears that;

- **CuNi is better than PdNi as the binary metal nanocomposites.**
- **ZrO_2 is better than SiO_2 as the supporter material, when compared in terms of excess energy per unit sample mass.** (c.f. mass of CNZt is 54 g, while CNS3 150 g)



Excess power accompanied by no hard radiations (neutrons and γ rays)



Summary of cooperative exp. at Kobe, 2016~2017

ZrO$_2$-supported

(a) $Pd_{0.044}Ni_{0.31}Zr_{0.65}$; PNZ3, PNZ4, PNZ5

(b) $Cu_{0.044}Ni_{0.31}Zr_{0.65}$; CNZ5

SiO$_2$-supported

(c) $Cu_{0.008}Ni_{0.079}$ (mesoporous silica supported); CNS3

(d) Pd nanoparticles (mesoscopic SiO_2 supported); PSf1

- AHE at elevated temperatures around 300 °C were observed only for binary-metal nanoparticle samples ; no AHE for single-element-metal nanoparticles
- Observed both in D-Pd system and H-Ni system
- Excess power of 3 ~ 10 W for weeks at 200 ~ 300 °C
- Integrated released energy of 3 ~ 30 MJ/mol-Ni, or 4 ~ 90 MJ/mol-H
- ZrO_2 is advantageous as the supporter material, when compared in terms of excess energy per sample mass.
- Anyway, unexplainable by any known chemical reaction.

Short-term tasks for further research

(1) find optimum conditions (duration of calcination, particle size, etc.) for making binary metal nano-fabricated samples

(2) make temperature distribution in RC uniform

(3) find optimum molar ratio for binary samples

(4) find optimum combination of the metal elements for binary samples

(5) establish a scaling law of the output power

(6) examine effectivity of ternary nanocomposites

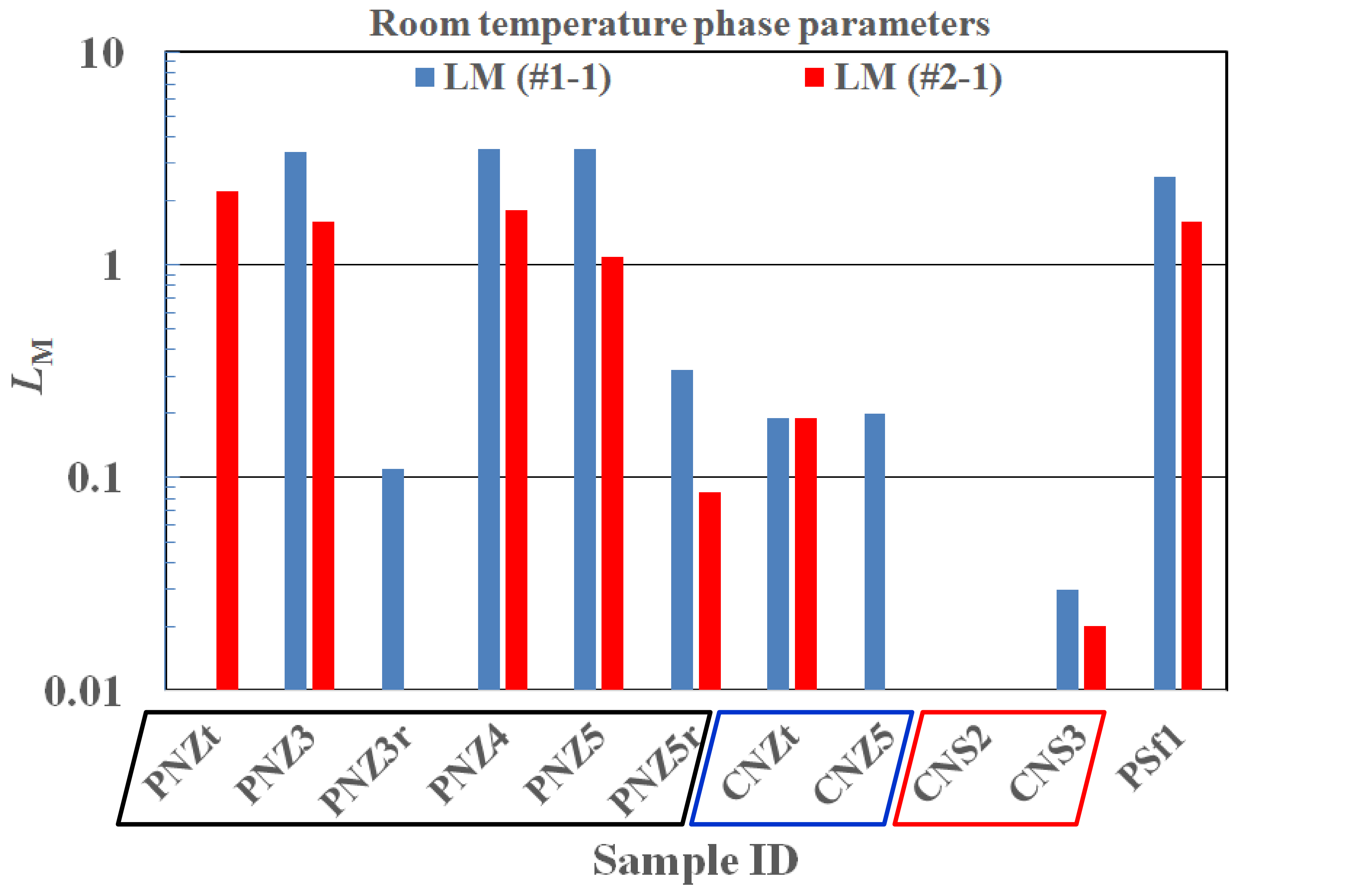
(7) design and make a prototype reactor with 1-kW output power

Supplement

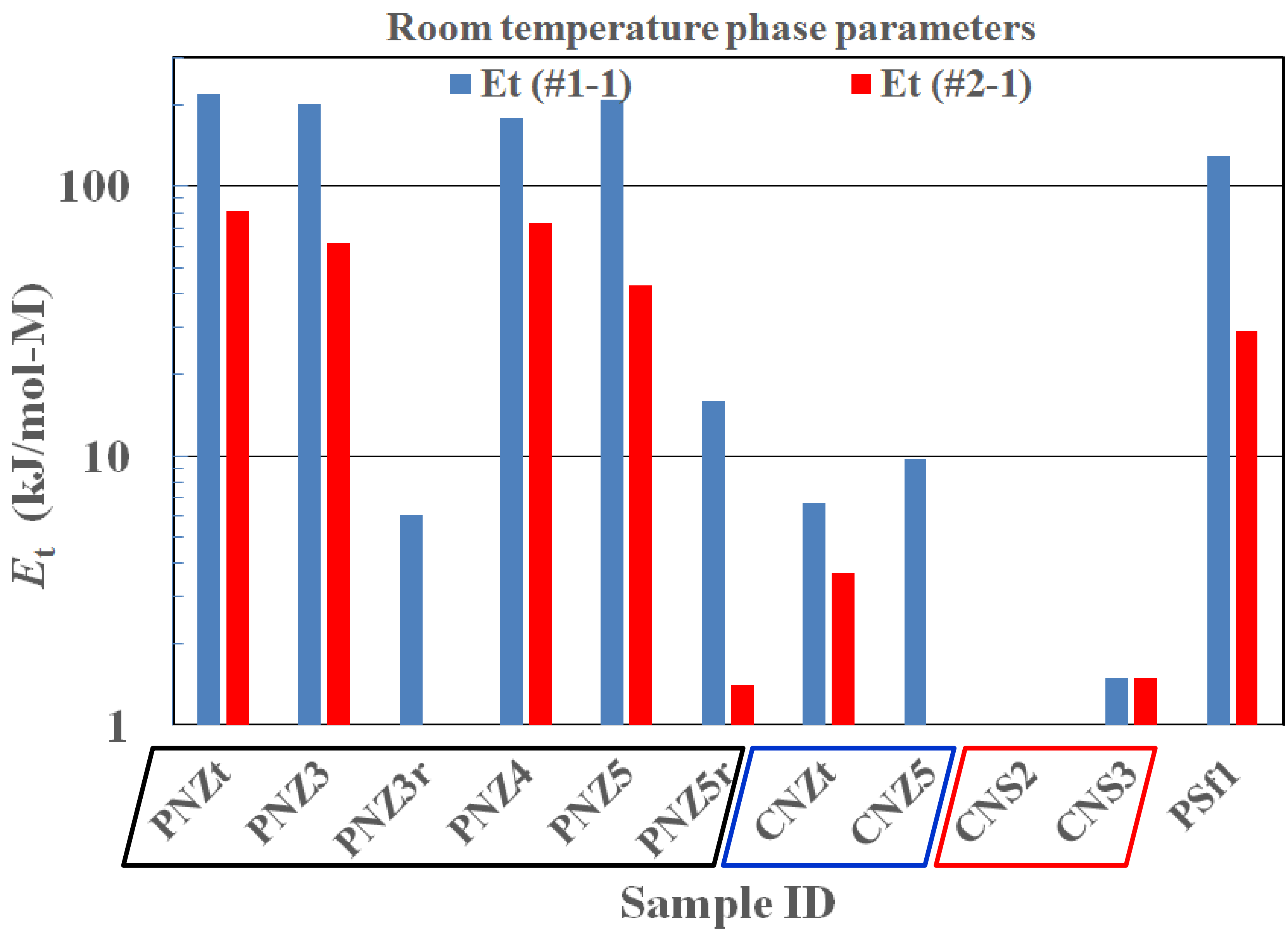
Summary of the results in the past 3 years

Sample ID	M (Ni or Pd) content	H (D or H)	RT						ET (> 250°C)								Remarks			
			L_M		$E_t \equiv \int W dt$		η_{av}		L_M		W		η_{av}		$E_{ex} \equiv \int W dt / L_M$		RC	ref	α	
	(g)				(kJ/m-M)		(eV/H)				(W)		(keV/H)		(MJ/m-H)		old /new	fitting func	variable	
(NEDO)			#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2				
PNZt	6.4	D(H)	(1.1)	2.2	220	81	(2.1)	0.39	1.5	0.15	5.9	2.6	(0.29)	0.77	(7.8)	4.3	o			leak
PNZ3	20.0	D	3.4	1.6	200	62	0.61	0.43	2.8	1.1	8.0	10	6.5	16	3.7	5.7	o			RTDav
PNZ3r	18.8	H	0.11	(5.3)	6.0	0	0.62	0	2.1	(7.4)	8.0	---	0.19	---	2.0	---	o			RTDav,leak reoxid. 200 h
PNZ4	23.0	D	3.5	1.8	180	73	0.56	0.43	3.1	1.1	---	4.5	---	4.4	---	3.0	o		v	malf. (#1)
PNZ5	41.1	D	3.5	1.1	210	43	0.63	0.4	3.1	0.55	3.5	4.2	0.4	1.3	1.1	7.6		f	v	
PNZ5r	40.7	D	0.32	0.085	16	1.4	0.53	0.17	0.7	0.2	3.7	4.5	0.025	1.0	2.5	9.0		f	v	reoxid. 100 h
CNZt	9.1	H(D)	0.19	0.19	6.7	3.7	0.37	0.2	1.7	0.2	4.0	2.2	1.7	0.83	11	150	o			
CNZ5	22.0	H	0.2	===	9.8	===	0.5	===	1.9	===	3.3	===	3.4	===	3.6	===	o		v	RTDav
CNS2	12.1	H	0.01	===	0	===	0	===	1.1	0.15	11	7.2	11	20	23	190	o			
CNS3	11.4	H	0.03	0.02	1.5	1.5	0.57	0.65	0.8	0.16	2.4	4.4	1.4	4.7	6.0	90		f	v	
PSf1	8.4	D	2.6	1.6	130	29	0.51	0.19	1.6	0.7	< 1	< 2.2	0	0	0	0		f	v	

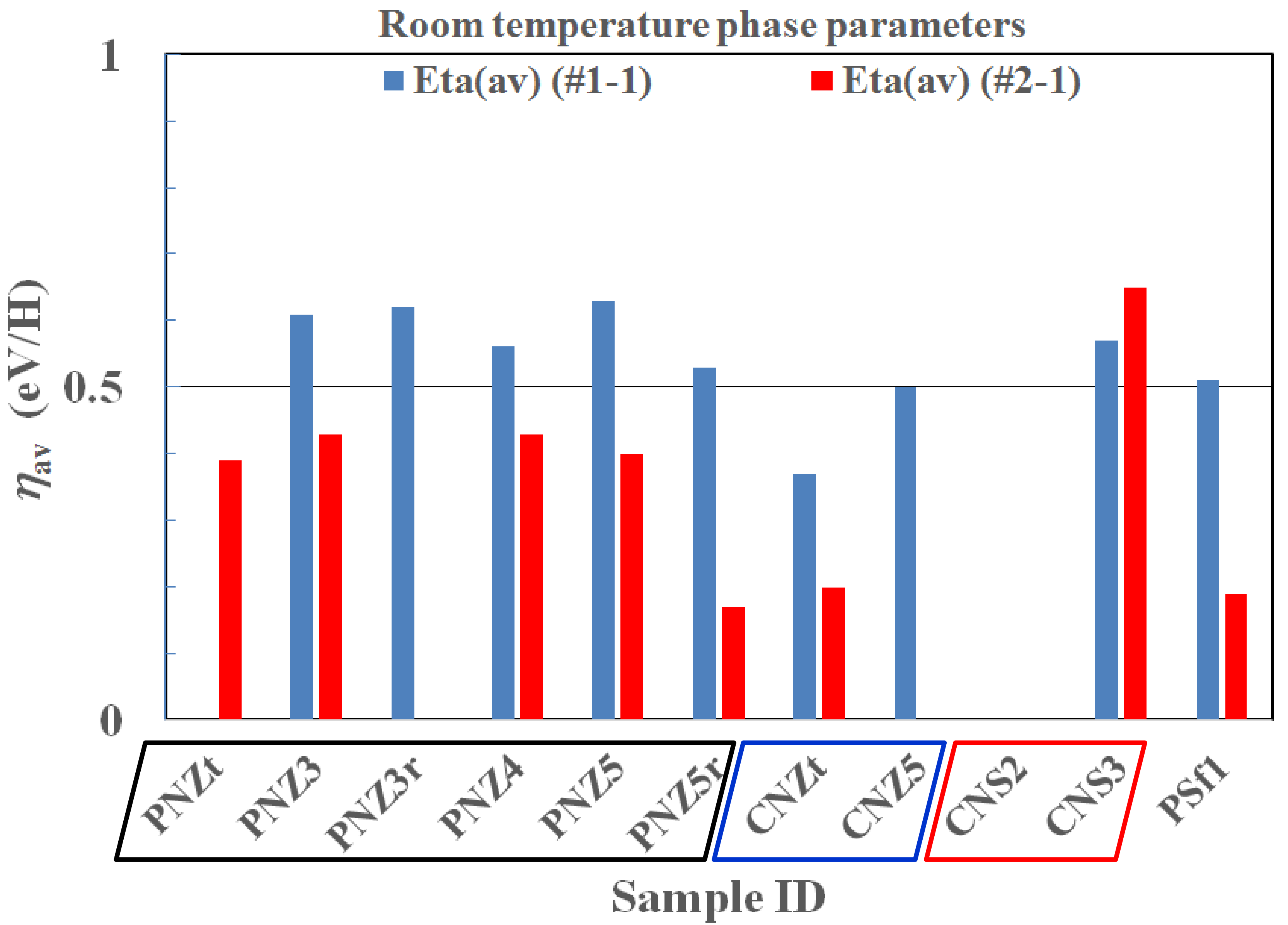
Loading ratio L_M at R.T.



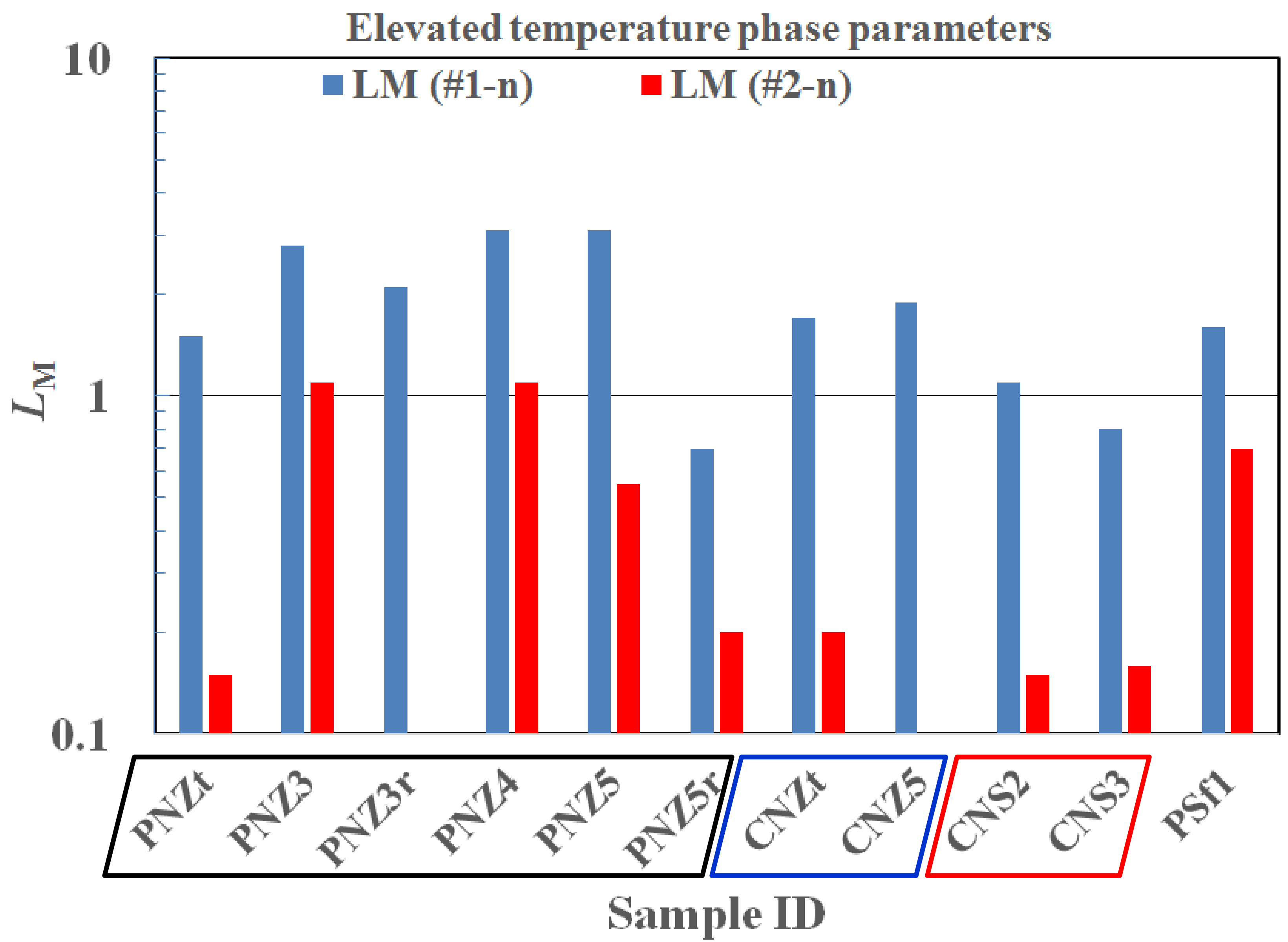
Absorption energy E_t at R.T.



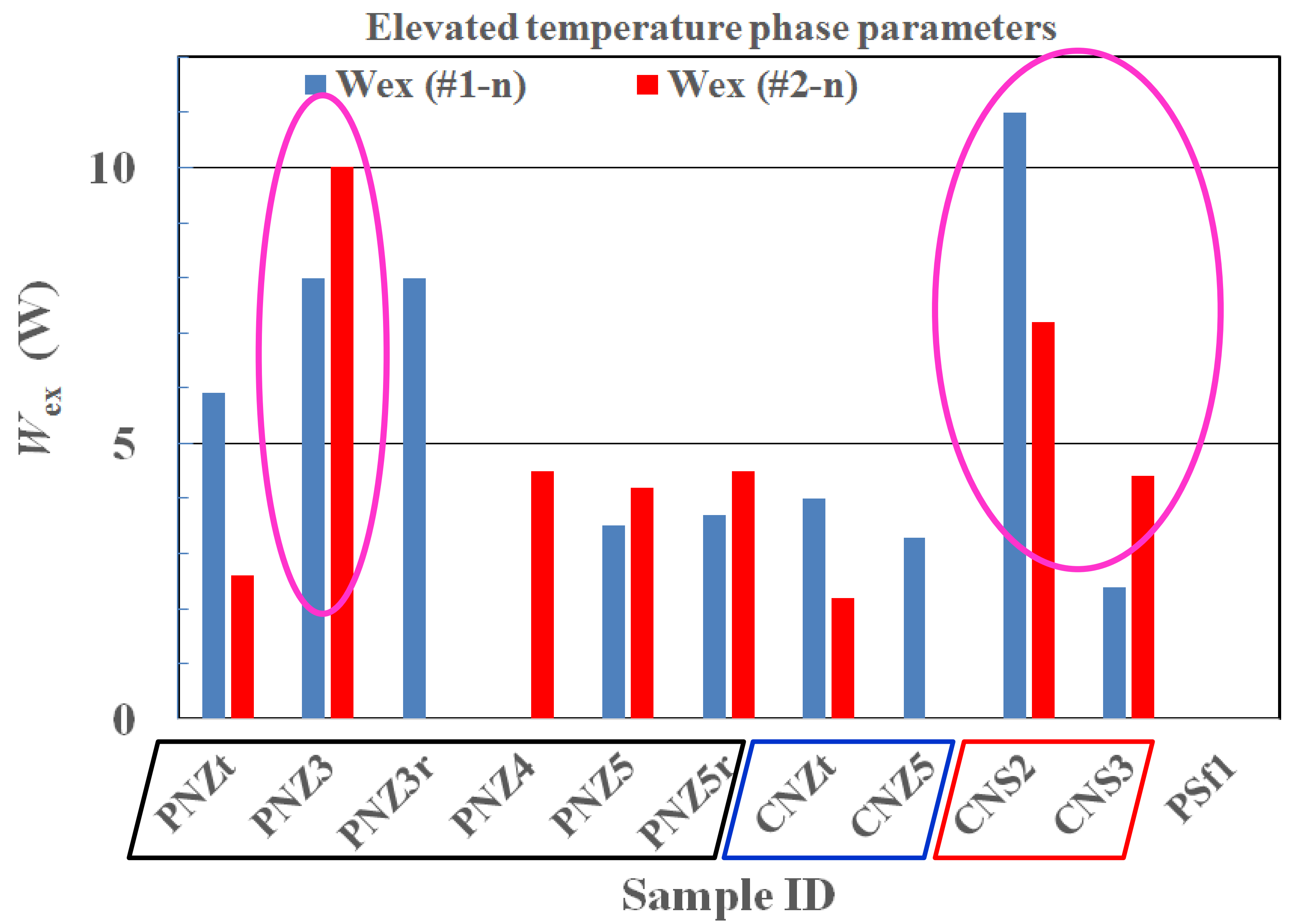
Specific absorption energy η_{av} at R.T.



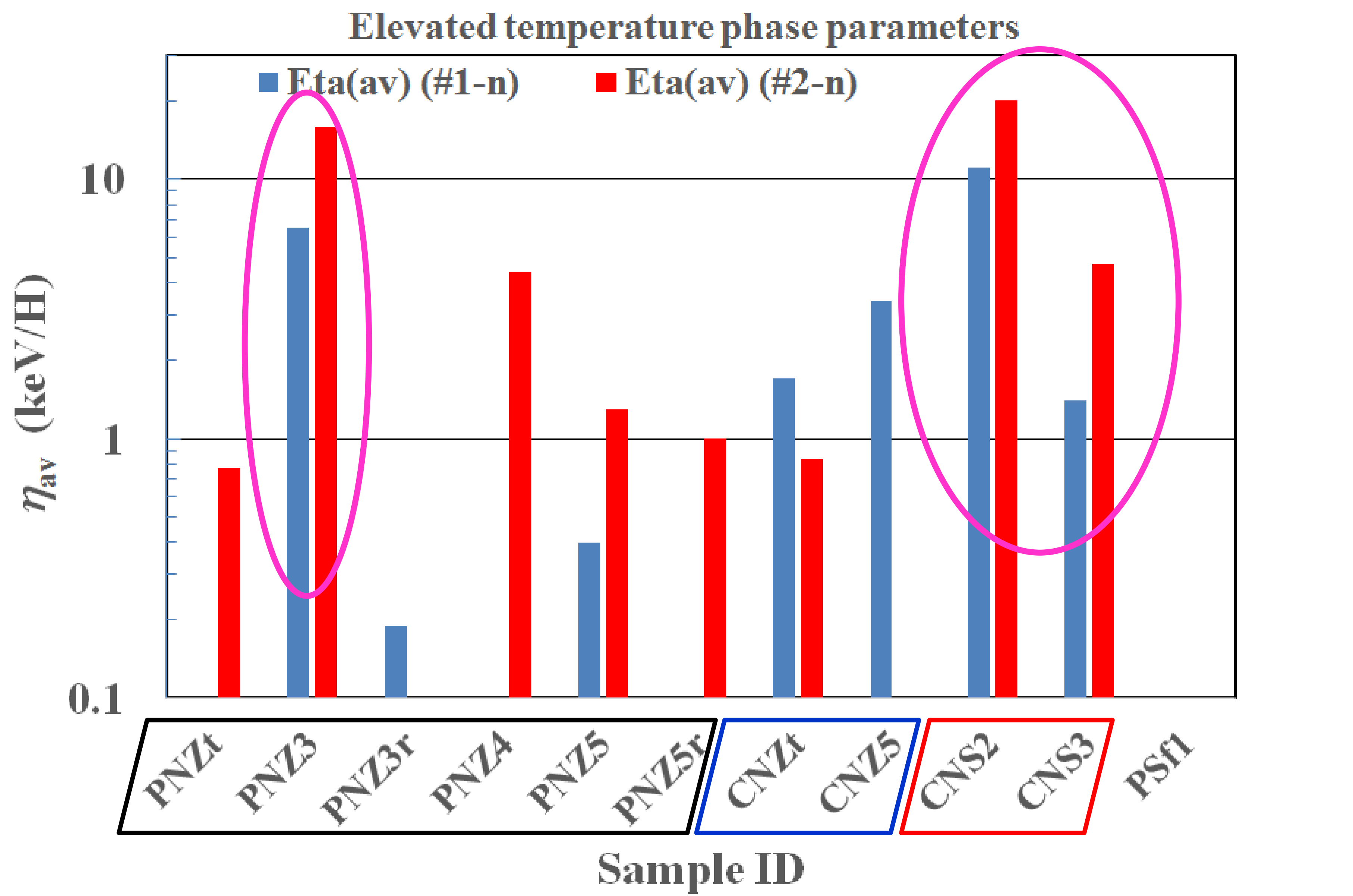
Loading ratio L_M at E.T.



Excess power W_{ex} at E.T.



Specific sorption energy η_{av} at E.T.



Earlier results by Technova-Kobe group

Proc. ICCF14 (2011) 400-408
Proc. JCF9 (2009) 23-28/ ibid. 29-35
Proc. ICCF15 (2011) 216-220/ ibid. 94-99/ ibid. 297-302
Phys. Lett. A **373** (2009) 3109–3112
J. Condensed Matter Nucl. Sci. **4** (2011) 56-68
Proc. JCF10 (2010) 14-19/ ibid. 20-25/ ibid. 46-53
LENR-NET SB **3** (2010) ACS
J. Condensed Matter Nucl. Sci. **5** (2011) 42-51/ ibid. 17-33
Proc. JCF11 (2011) 10-15/ 16-22/ ibid. 47-52
J. Condensed Matter Nucl. Sci. **10** (2013) 46-62
Proc. JCF12 (2012) 1-9/ ibid. 10-18
J. Condensed Matter Nucl. Sci. **13** (2014) 471–484/ ibid. 277-289
Proc. JCF13 (2013) 214-229/ ibid. 230-241
J. Condensed Matter Nucl. Sci. **15** (2015) 23-32/ ibid. 231-239
Proc. JCF14 (2014) 1-13
Proc. JCF15 (2015) 1-19
Current Science, **108** (2015) 589-593
J. Condensed Matter Nucl. Sci. **19** (2015) 135-144
Proc. JCF16 (2016) 135-144

Equations used for correction for flow rate fluctuation

$$R_h = F^{\alpha} \cdot \rho \cdot C \cdot (T_{C2} - T_{C6})/(W_1 + W_2), \quad (1)$$

$$\Delta T_{C2} = (dT_{C2}/dF) \cdot \Delta F$$

$$= (-\Delta F/F) \cdot (W_1 + W_2) \cdot (dT_{C2}/dW) \cdot \alpha. \quad (2)$$

$$\alpha = 1.9 \times 10^{-2} \cdot \exp[4.0 \cdot (F/F_0)]. \quad (3)$$