Review of experimental measurements involving dd reactions

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Outline

1. Contributors
2. How this all started?
3. Issues of Pd/D Loading
4. Calorimetric results
5. Nuclear effects
6. Conclusions

Primary Contributors and Collaborators

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- Consultants: W. B. Clarke, L. Case, R. George, B. Oliver, K. Wolf
- EPRI: J. Chao, T. Passell, J. Santucci , M. Schreiber
- Lockheed: J. Pronko, D. Kohler
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- MIT: **P. Hagelstein**, L. Smullin
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- Project Cobalt: K. Mullican, M. Trevithick
- Osaka Univ.: Y. Arata, Y. Zhang

Low temperature nuclear activity in solids

The recent phase of attention was stimulated by two publications in 1989:

Fleischmann and Pons:

Principal claim is excess heat from Pd cathode electrolyzed in heavy water

Jones *et al*:

Neutrons claimed as evidence of low-level dd-fusion reactions from Ti cathode electrolyzed in heavy water

Hypothesis 1

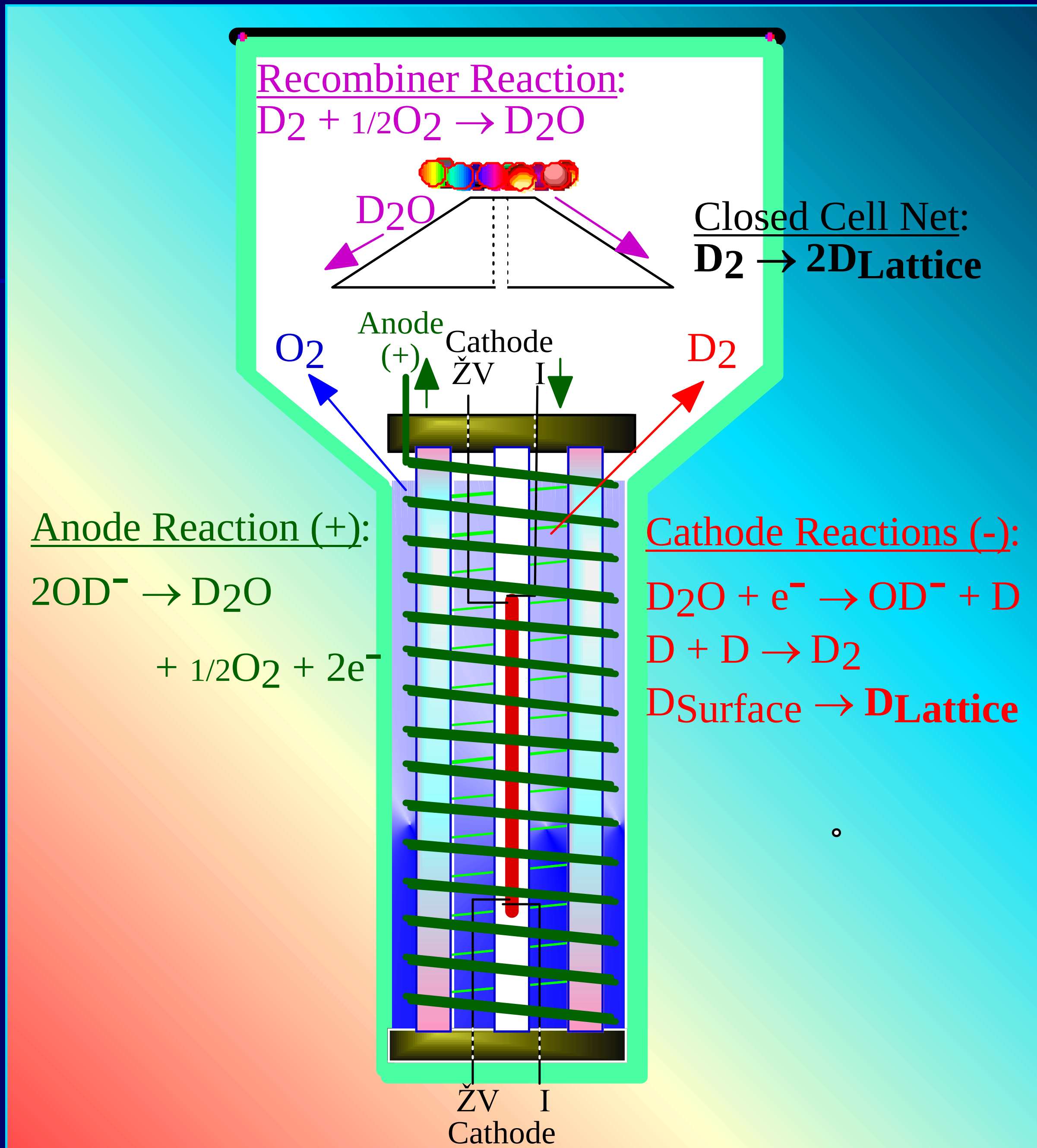
"There is an unexpected and unexplained source of heat in the D/Pd System that may be observed when Deuterium is loaded electrochemically into the Palladium Lattice, to a sufficient degree."

Experiments:

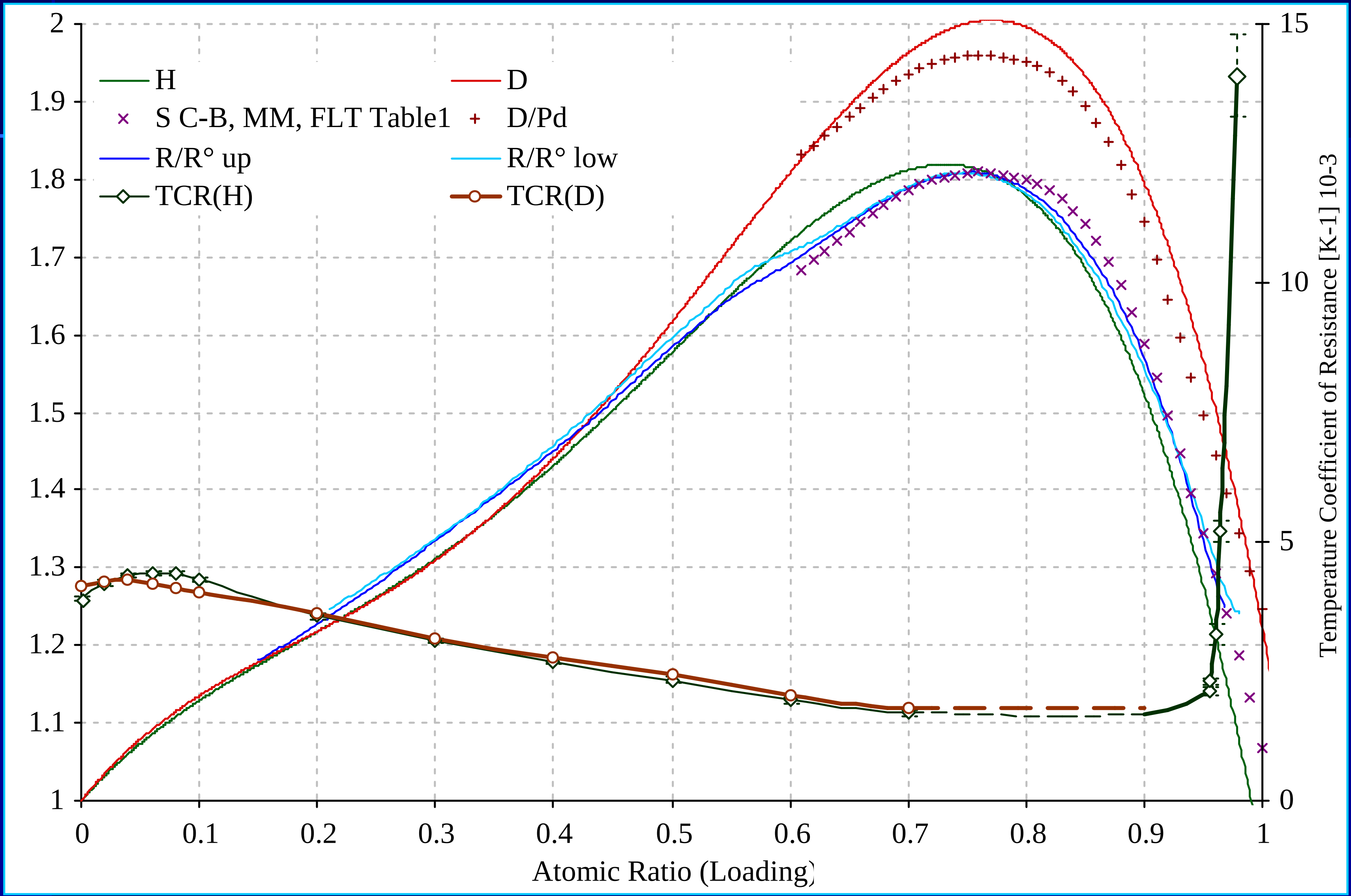
- D/Pd Loading studies (R/R°, interfacial Z).
  - Electrochemical Impedance (kinetics & mechanism)
  - Resistance Ratio (extent of loading)

- Calorimetry
  - first principles closed-cell, mass-flow calorimeter,
  - > 98% heat recovery
  - absolute accuracy < ±0.4%

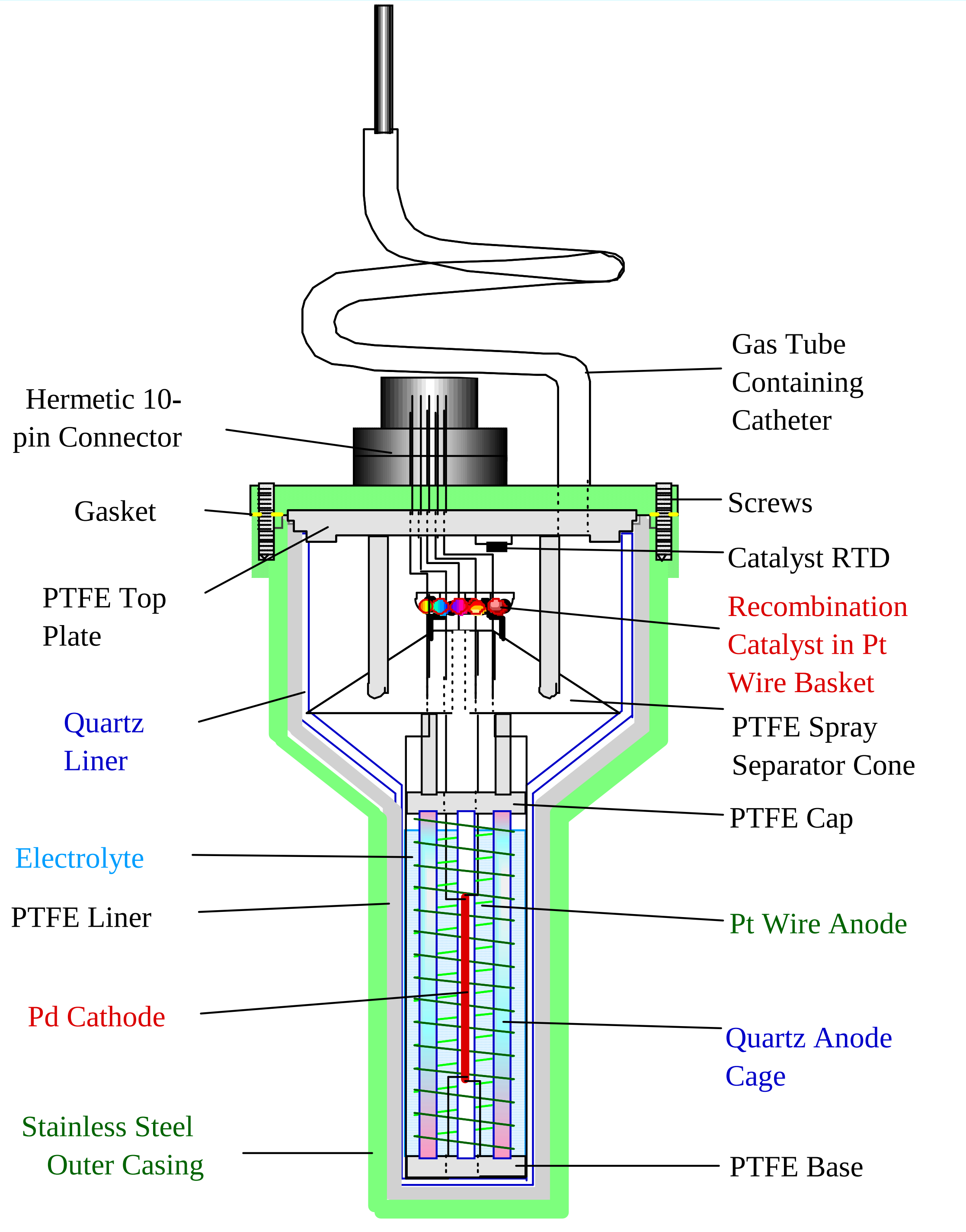
Electro-chemical Loading of Pd in a Thermo-dynamically Closed Cell:



Loading and Temperature coefficient (2)



SRI Quartz Calorimeter *and* DoL Cell



Requirements of a (*CF*) Calorimeter (*1989*)

- Conceptually simple system based on first principles
- Maintain control of operating parameters (including T_{Cell})
- On-line monitoring of all relevant variables including D/Pd
- Multiply redundant measurement of parameters critical to calorimetry
- Accommodate large dynamic range of P_{in} and P_{out} (0.1 - 100W)
- Closed and isolated electrochemical system to retain all products
- High accuracy and precision (< 1 ppt)
- Known sources of systematic error yield conservative estimates of output heat

Flow Calorimetry (*1989*): Advantages

All the heat evolved by electrochemical cell is absorbed by the heat transfer fluid

Control temperature of electrochemical cell by controlling heat transfer fluid flow rate and temperature

Can accommodate large inputs of electrochemical power and large dynamic range of heat input and output

Calibration not required

Flow Calorimetry (*1989*): Potential Problems

Flow rate must be measured on-line for high accuracy

Calibration desirable for high accuracy

Flow streamlining at points of temperature measurement can lead to errors

Heat Relationships

$$P_{heater} + P_{electrochem} = (C_p\,\delta m/\delta t + k')\,(T_{out} - T_{in})$$

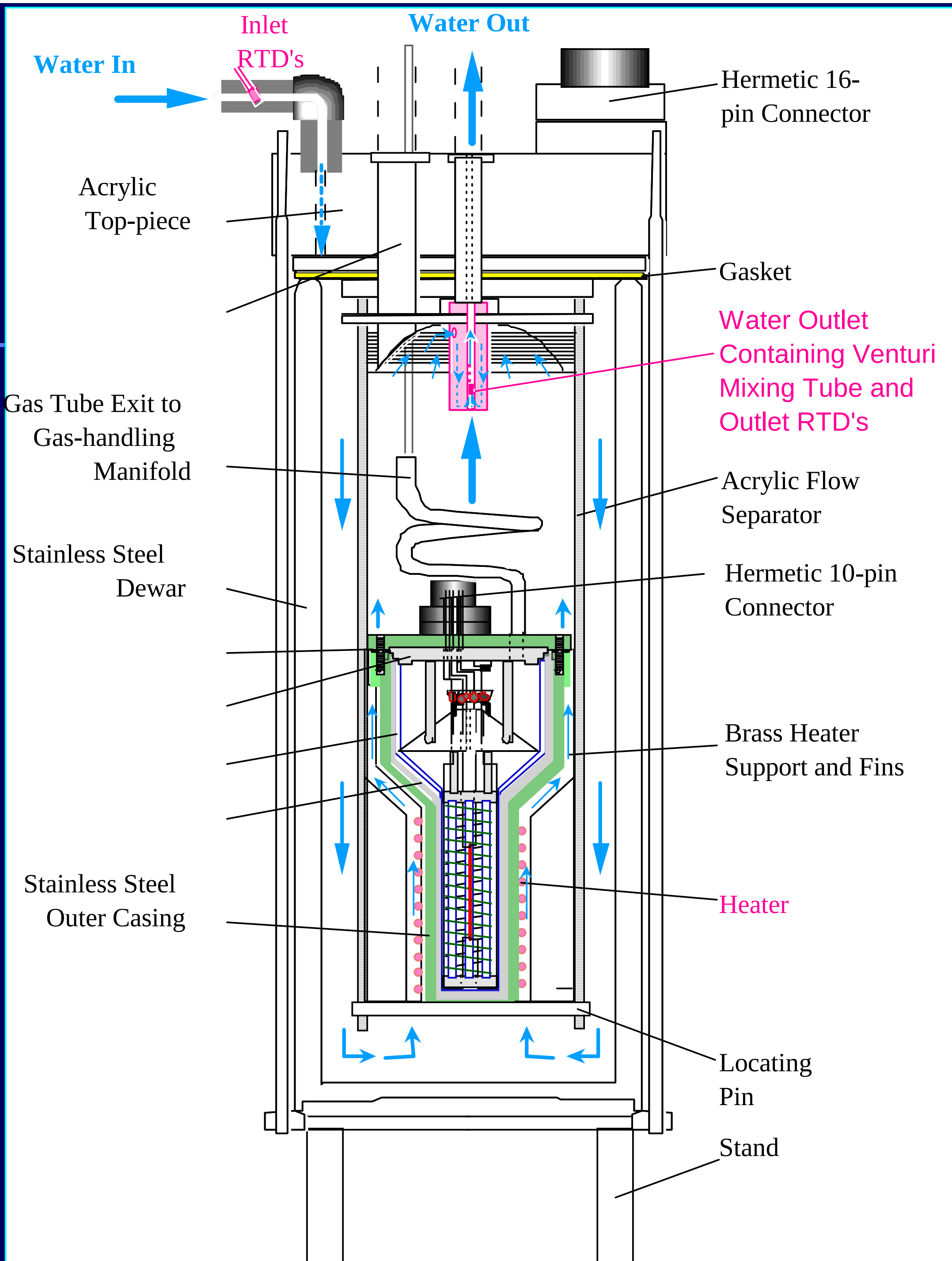
C_p = heat capacity of heat transfer fluid

$\delta m/\delta t$ = mass flow rate

k' = effective heat loss constant

T_{in} and T_{out} are inlet and outlet sensor temperatures

SRI LL Calorimeter and Cell



First 25 Pd		l	d	A	mM	Electrolyte:	Conc.	Add.	T °C	P (psi)	Max. I: A	/ cm^2	Min. R/R°	Max. D/Pd	Expt (h)	Init. (h)	P_{XS} (W)	%	Inpu MJ	Output-Input MJ	%	eV	#
Differential Calorimeter (High pressure, Low temperature)															*2.2*	*Years*						Pd atom	
P1a	AECL	5.0	0.7	11	217	LiOD	1.0	none	**7**	**650**	7.5	0.68	**1.20**	**1+**	696	369	1.8	**52%**	3.4	0.07	**2.1%**	3.4	5
P1b	*	5.0	0.7	11	4E-4	LiOD	1.0	none	**7**	**650**	7.5	0.68	Cu Substr.		696	299	0.2	**7%**		0.01		4.E+05	2
P2 Series (High pressure flow Calorimeter)																							
P2	Engel.	4.5	0.3	4.2	36	LiOD	1.0	none	**4**	**1000**	2.1	0.50	1.65	0.95	1393	504	2.0	**53%**	50	1.07	**2.1%**	310	4
P3	Engel.	4.5	0.3	4.2	36	LiOD	1.0	none	4	1000	1.5	0.35	1.70	0.90	1250				18				
P7	Engel.	4.5	0.3	4.2	36	LiOD	1.0	none	8	1000	1.1	**0.26**	Contact Prob.		145				2.1				
P10	Engel.	4.5	0.3	4.2	36	LiOD	1.0	none	35	900	0.2	**0.05**	Contact Prob.		18				0.3				
P11	Engel.	4.5	0.3	4.2	36	LiOD	1.0	none	35	1050	5.0	1.18	1.65	0.95	85				1.2				
P4 Series (Medium Pressure)																							
P4	Engel.	5.0	0.3	4.7	40	LiOD	**0.1**	none	15	100	2.4	0.51	1.80	0.80	1165				17				
P5	Engel.	5.0	0.3	4.7	40	Li_2SO_4	**0.5**	none	16	100	4.0	0.85	1.70	0.90	287				4.1				
P6	Engel.	5.0	0.3	4.7	40	Li_2SO_4	**0.5**	As_2O_3	8	100	2.7	0.57	1.70	0.90	649				9.3				
P8	Engel.	3.0	0.3	2.8	24	LiOD	**0.1**	none	15	100	1.8	0.64	1.65	**0.95**	**186**				2.7				
P9	Engel.	3.0	0.3	2.8	24	LiOD	1.0	none	35	50	1.5	0.53	1.65	**0.95**	**597**				22				
P12 Series (Al & Si)																							
P12	Engel.	3.0	0.3	2.8	24	LiOD	1.0	**^{4}He,Al**	30	50	2.5	0.88	1.55	**0.98**	1631	316	1.0	**10%**	59	0.80	1.4%	**346**	4
P13	Engel.	3.0	0.3	2.8	24	LiOH	1.0	Al	30	50	2.5	0.88	1.1*	**0.98**	815				12				
P14	Engel.	3.0	0.3	2.8	24	LiOD	1.0	**^{3}He,Al**	30	50	2.5	0.88	1.60	0.94	692	184	0.5	5%	10	0.20	**2.0%**	84	2
P15	Engel.	3.0	0.3	2.8	24	LiOD	1.0	**Al**	35	40	2.5	0.88	1.58	**0.97**	1104	684	2.4	**24%**	40	0.55	1.4%	**238**	3
P16	Engel.	3.0	0.3	2.8	24	LiOD	1.0	**^{3}He,Al**	35	40	2.5	0.88	1.70	0.90	1104	948	0.4	4%	40	0.10	0.2%	42	4
P17	Engel.	3.0	0.3	2.8	24	LiOD	1.0	**Si**	29	40	1.1	0.39	1.29	**1+**	1202	1040	0.2	2%	13	0.10	0.7%	42	2
P18	Engel.	3.0	0.3	2.8	24	LiOD	1.0		35	40	Failed early due to electrical contact												
P20	Engel.	3.0	0.3	2.8	24	LiOD	1.0	**Al**	35	40	2.0	0.71	1.55	**0.98**	954	650	0.3	2%	17	0.16	1.0%	71	3
P19 Series (Boron)		Outlet; 2 RTD & 2 thermistors									B effect, multi-humped R response												
P19	Engel.	3.0	0.3	2.8	24	LiOD	1.0	**B**	35	40	1.9	0.67	1.45	**0.99**	1287	261	0.9	340%	23	0.41	1.8%	**180**	4
P21	Engel.	3.0	0.3	2.8	24	LiOD	1.0	**B**	30	40	2.0	0.71	1.60	0.94	764	390	0.6	6%	14	0.04	0.3%	17	2
P22	Engel.	3.0	0.3	2.8	24	LiOD	1.0	**B**	30	40	2.0	0.71	1.30	**1+**	1480	378	0.1	**30%**	21	0.27	1.3%	**119**	3*
C Series (Large Area)																	Last event terminated by H_2O addition *						
C1	JM	30	0.1	9.4	27	LiOD	1.0	Al	30	50	7.2	0.76	1.65	0.93	866	390	1.4	3%	49	1.12	**2.3%**	**437**	1
C2	JM foil	25	μm	60	3	LiOD	1.0	Al	30	50	7.2	0.12	1.60	0.94	356	190	3.0	**10%**	14	0.56	**3.9%**	**2076**	1

SRI First 25

Excess Power *vs.* Maximum Loading (1)

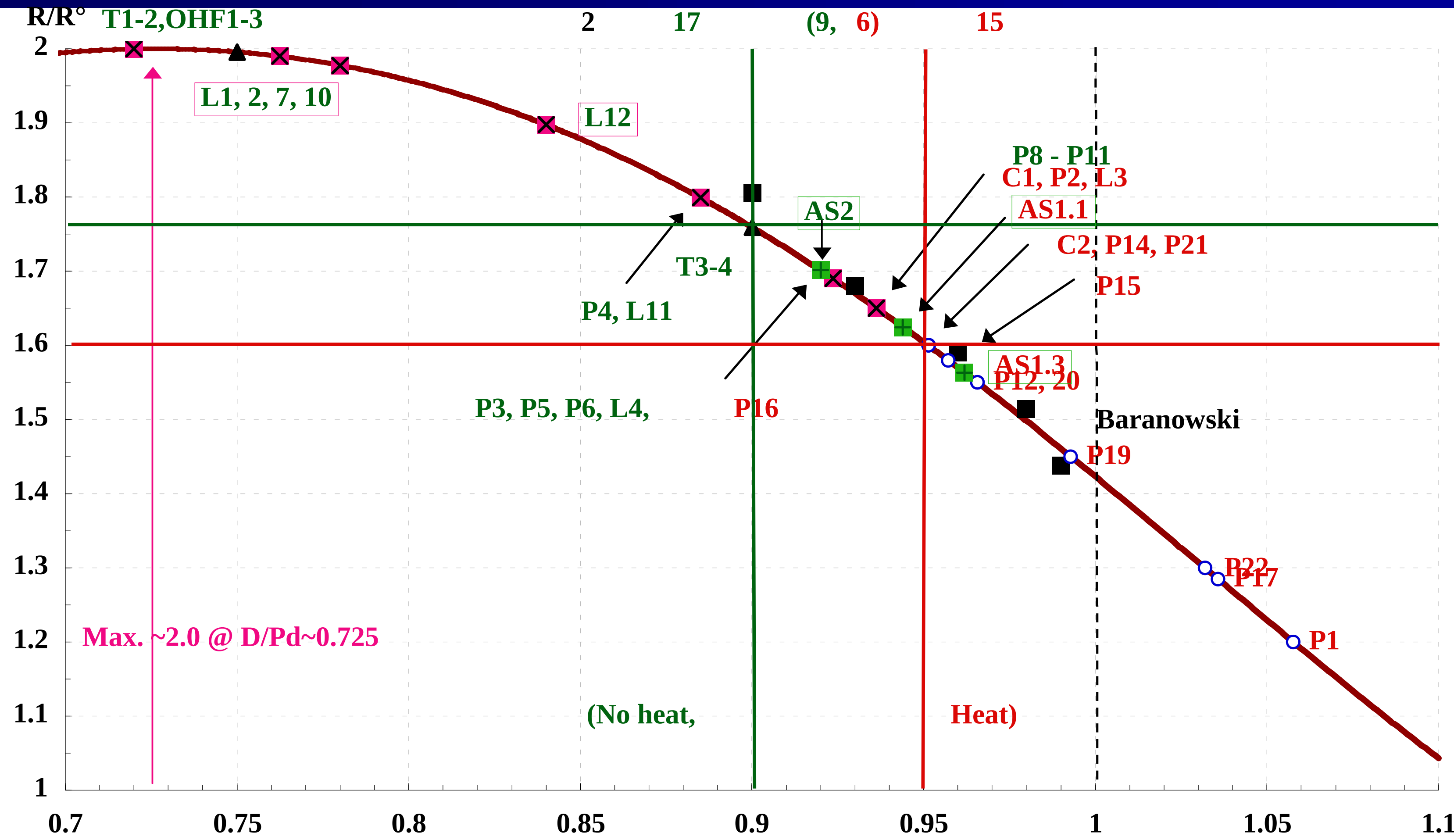
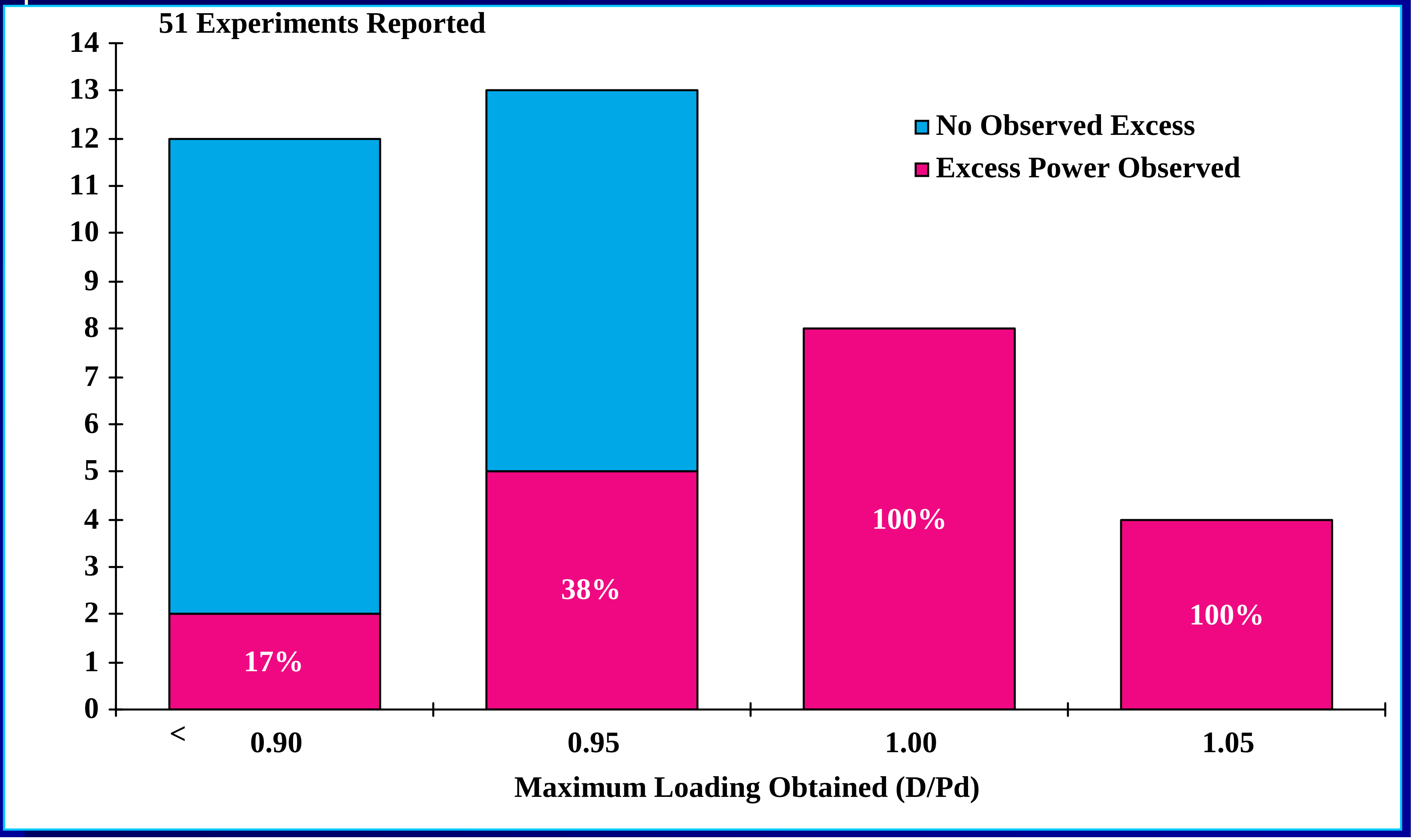
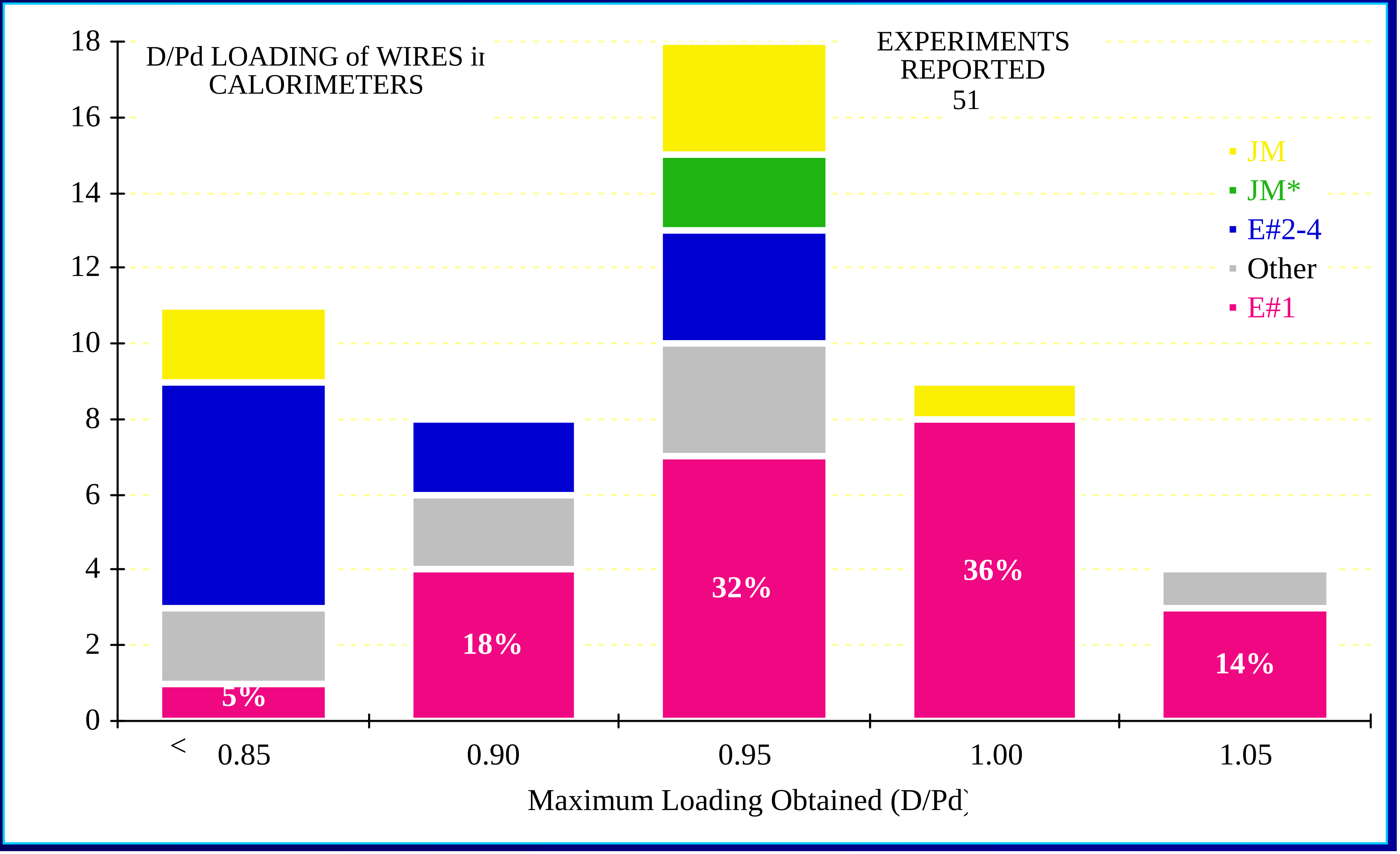


Figure 1 Maximum loading, D/Pd, attained in experiment; determined by R/R°.

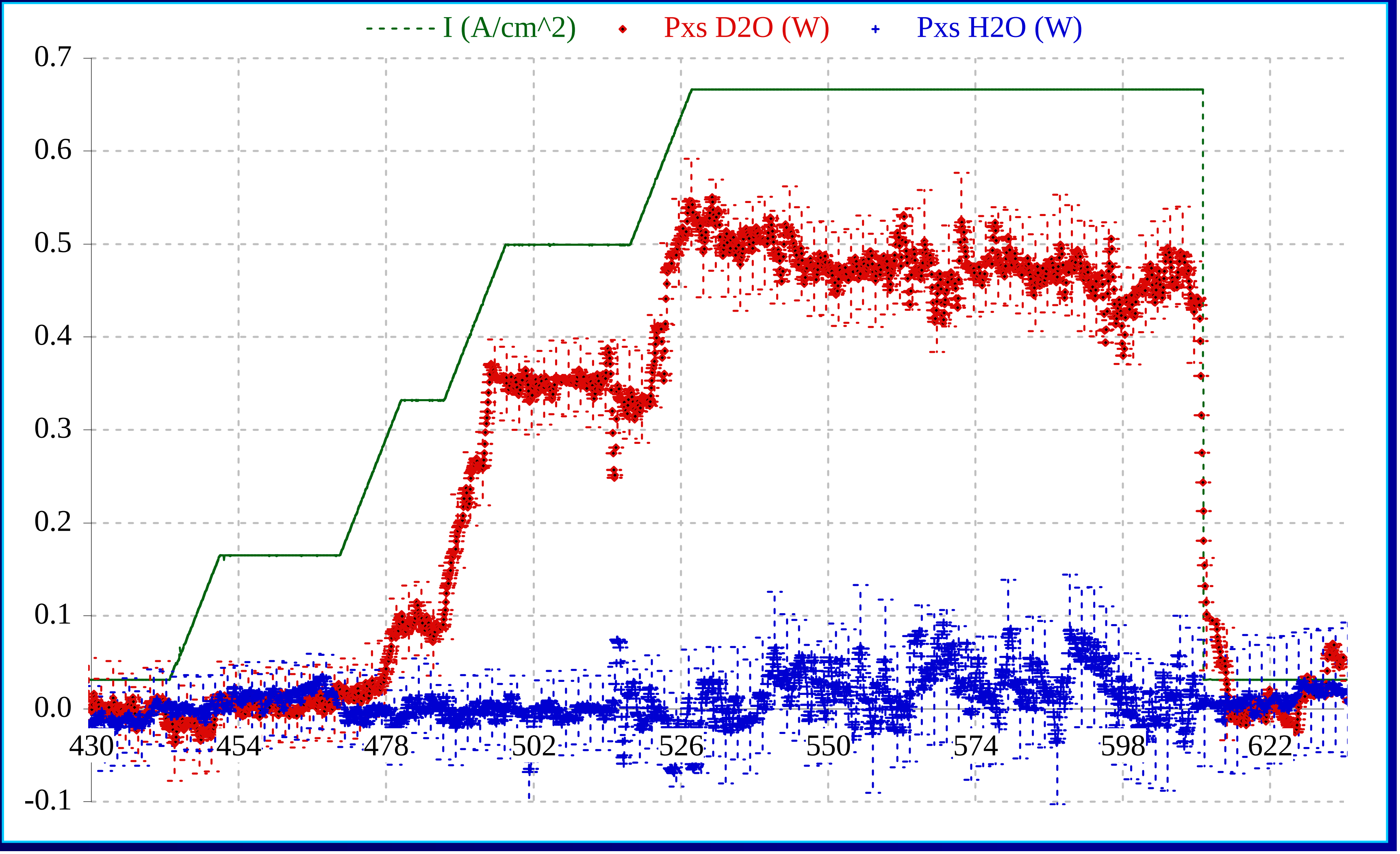
Excess Power *vs.* Maximum Loading (2)



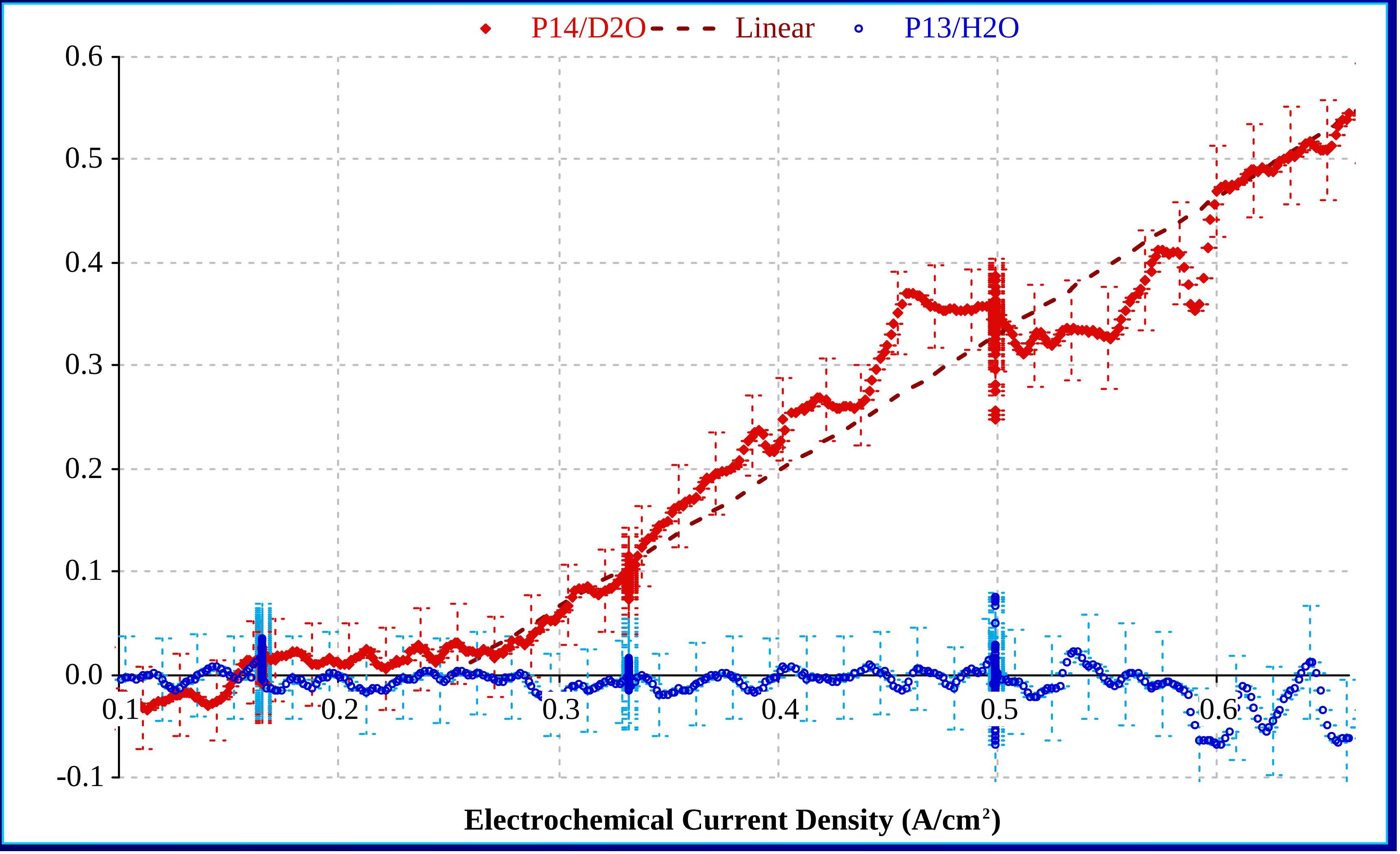
Excess Power *vs.* Palladium Source



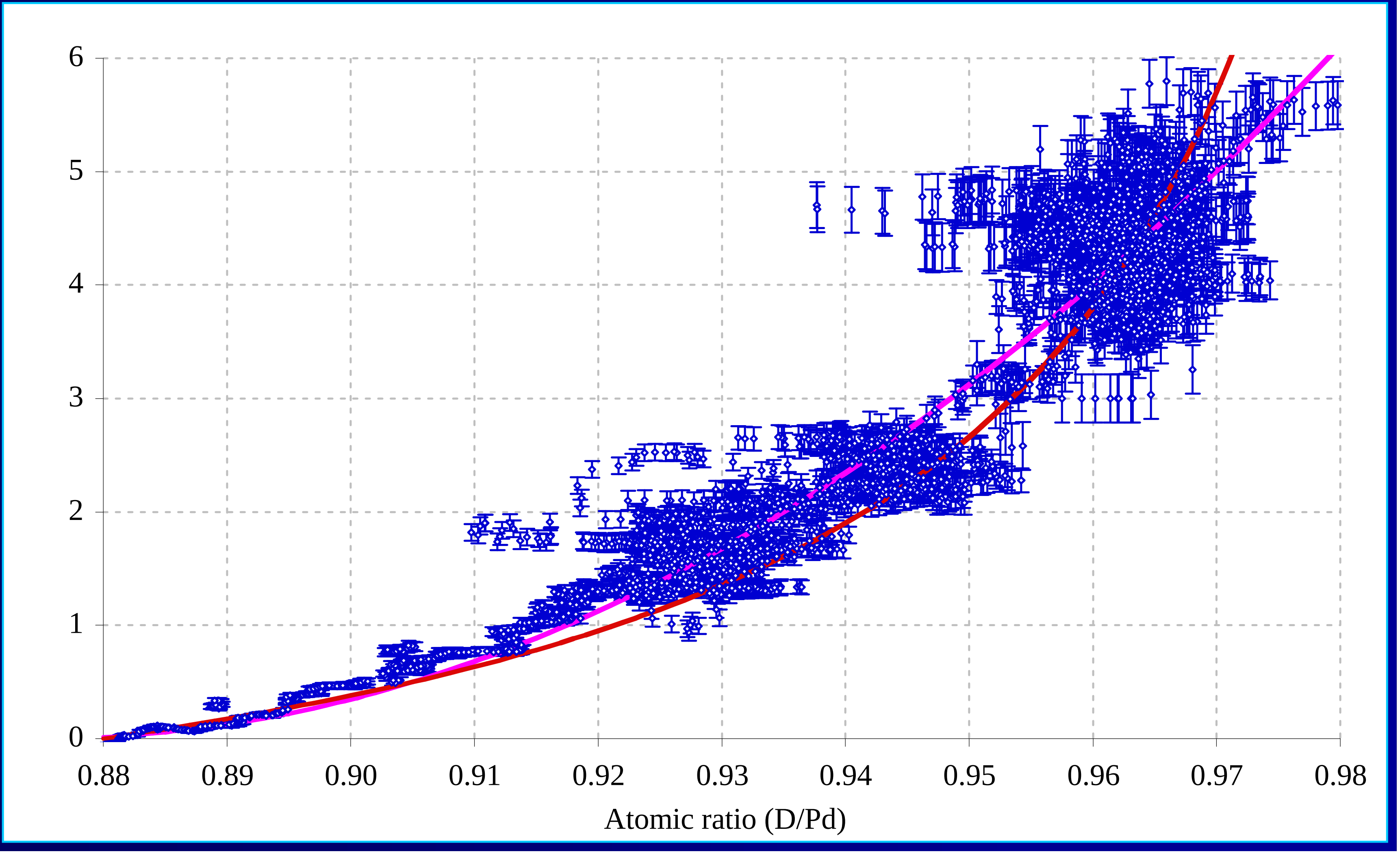
P13/14 Simultaneous Series Operation of Light & Heavy Water Cells;
Excess Power & Current Density vs. Time



<u>P13/14</u> Simultaneous Series Operation of Light & Heavy Water Cells; ***Excess Power vs. Current Density***



C1: Excess Power *vs.* D/Pd



Conclusions regarding Excess Heat Production in Bulk Pd Cathodes Electrolytically Loaded with D:

- Effect Evidenced on numerous occasions (>***50***)
- Typical P_{xs} 3 - 30% (±0.5%) of Total P_{in} (340%)
- Up to 90σ observation of excess power effect
- Duration several hours to 1 week
- 100's to 1000's of eV's / Pd (D) atom (2076)
- Sustained, unidirectional heat burst exhibit an integrated energy at least 10x greater than the sum of all possible chemical reactions within a closed cell
- Heat effects are observed with D, but not H, under similar (or more extreme) conditions

McKubre *et al*, ***"Developpment of Advanced Concepts…",*** EPRI, TR-104195 (**1994**)

Necessary Conditions for Excess Heat Production in Bulk Pd Cathodes Electrolytically Loaded with D:

- Maintain High Average D/Pd Ratio (Loading)
- For times >>20-50x $\tau_{D/D}$ (Initiation)
- At electrolytic i >250-500mA cm^{-2} (Activation)
- With imposed D Flux (Disequilibrium)

For 1mm dia. Pd wire cathodes:

- $P_{xs} = M (x-x°)^2 (i-i°) \partial x/\partial t$
- x°=0.84-0.88, i°=350-425mA cm^{-2}, t°>200 $\tau_{D/D}$

McKubre *et al*, ***"Energy Production Processes in Deuterated Metals",*** EPRI, TR-107843-V1 (**1998**)

Hypothesis 2

"The observed excess heat originates in a hitherto unexpected and presently unexplained Nuclear Effect and that is a property of Crystalline Metals strongly loaded with Deuterium."

Experiments:

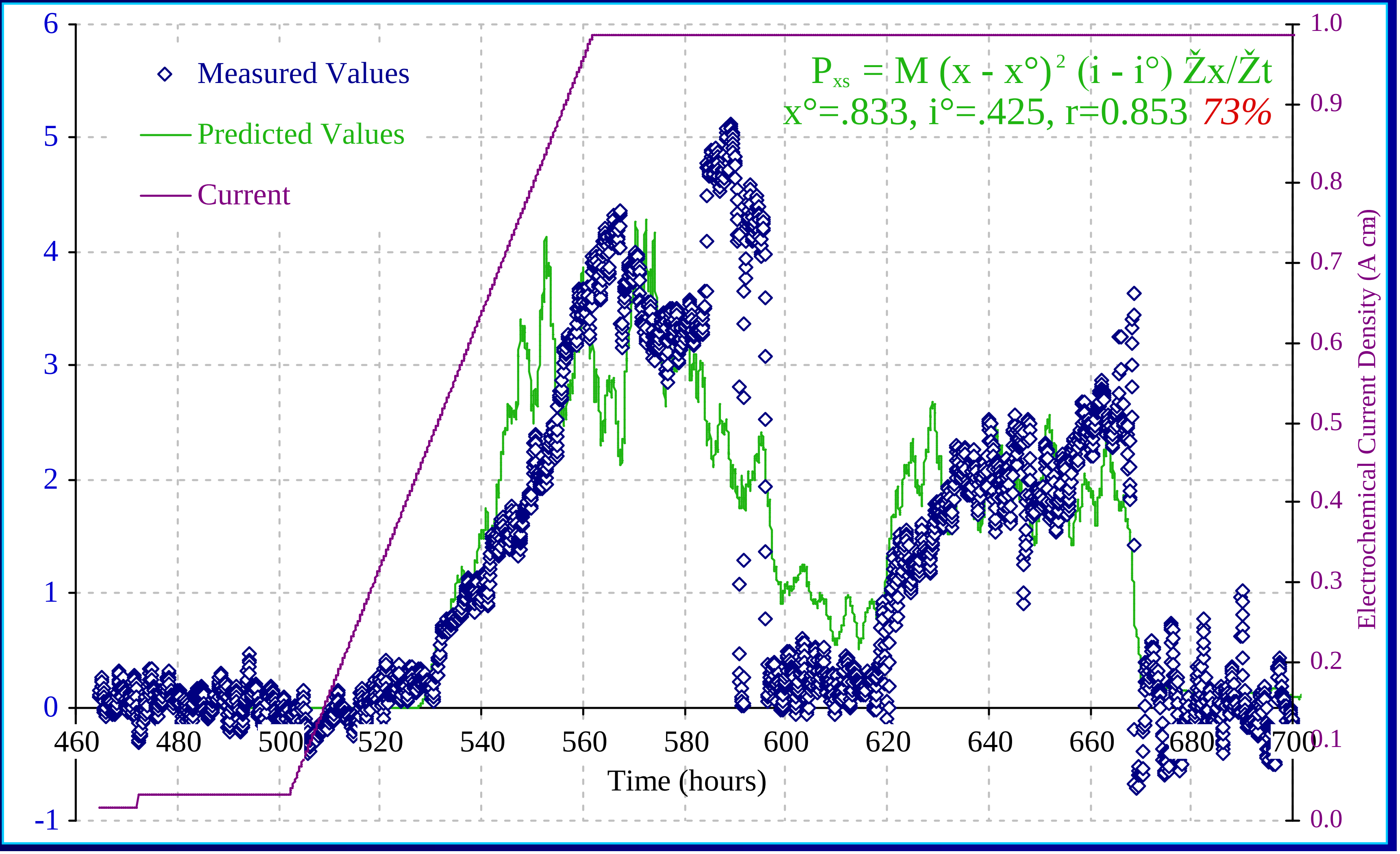
- 2π, real time, "*in situ*" X-ray detector (Lockheed)
- Gamma and X-ray spectrometer (K. Wolf)
- Neutron spectrometer (K. Wolf)
- Charged particles: α, β, p^+ (MIT)
- Tritium
- Helium: ^3He and ^4He (Amarillo, PNNL & Clarke)

Results:

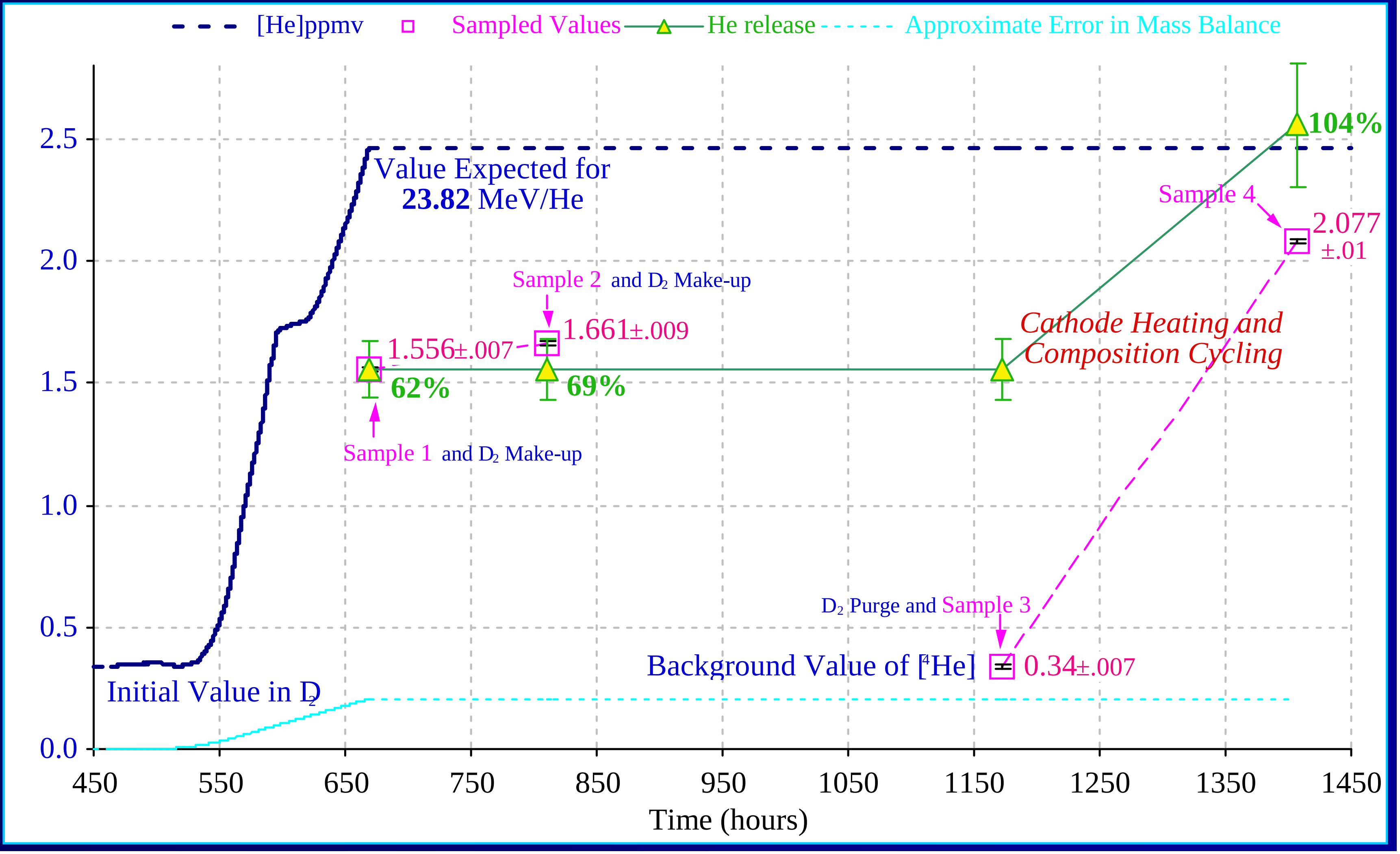
- Correlated heat and ^4He.
- Evidence of Tritium. ___

M4: Excess Power Correlation function

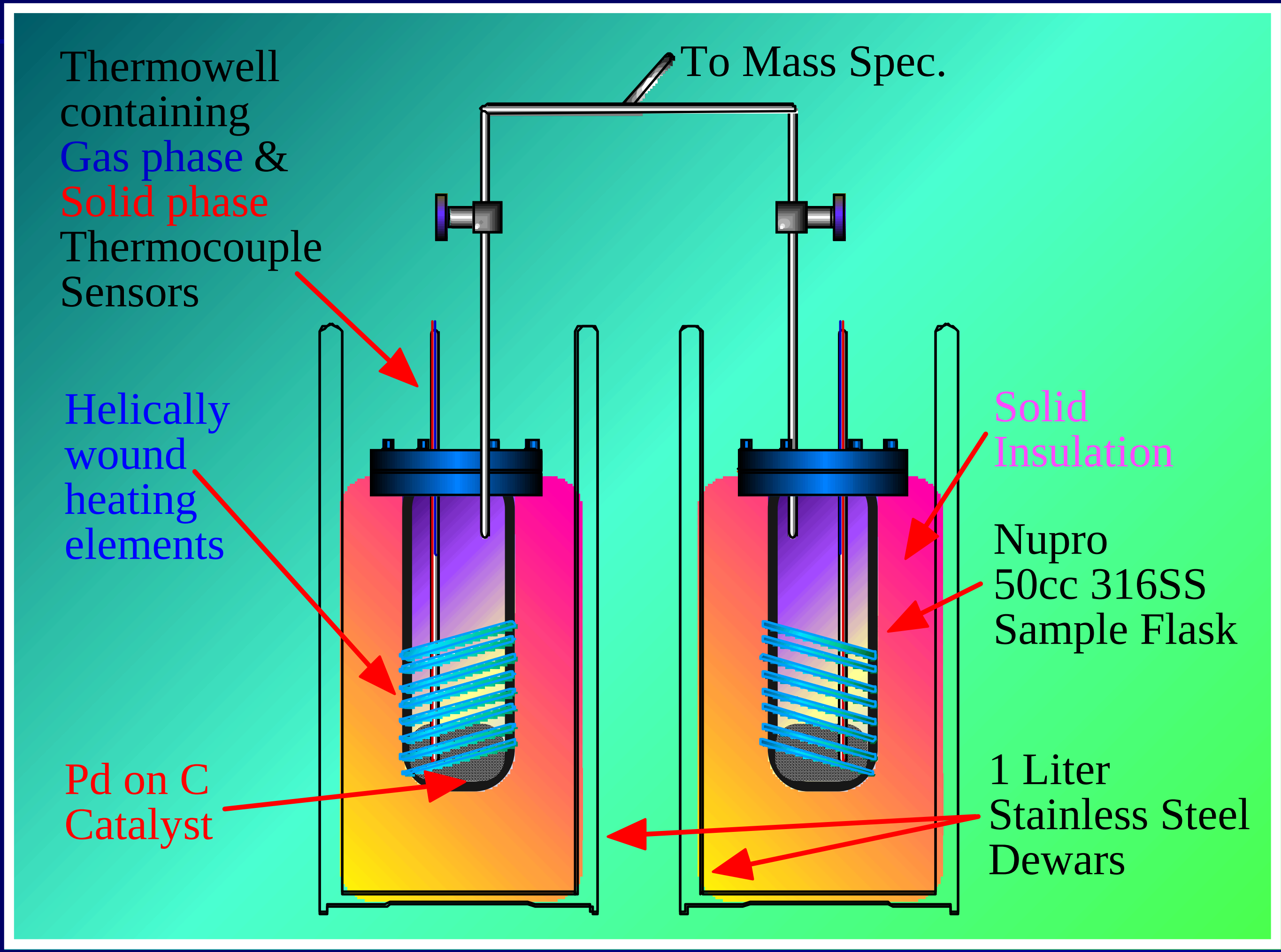
[Closed, He-leak tight, Mass-Flow Calorimeter, Accuracy ±0.35%]



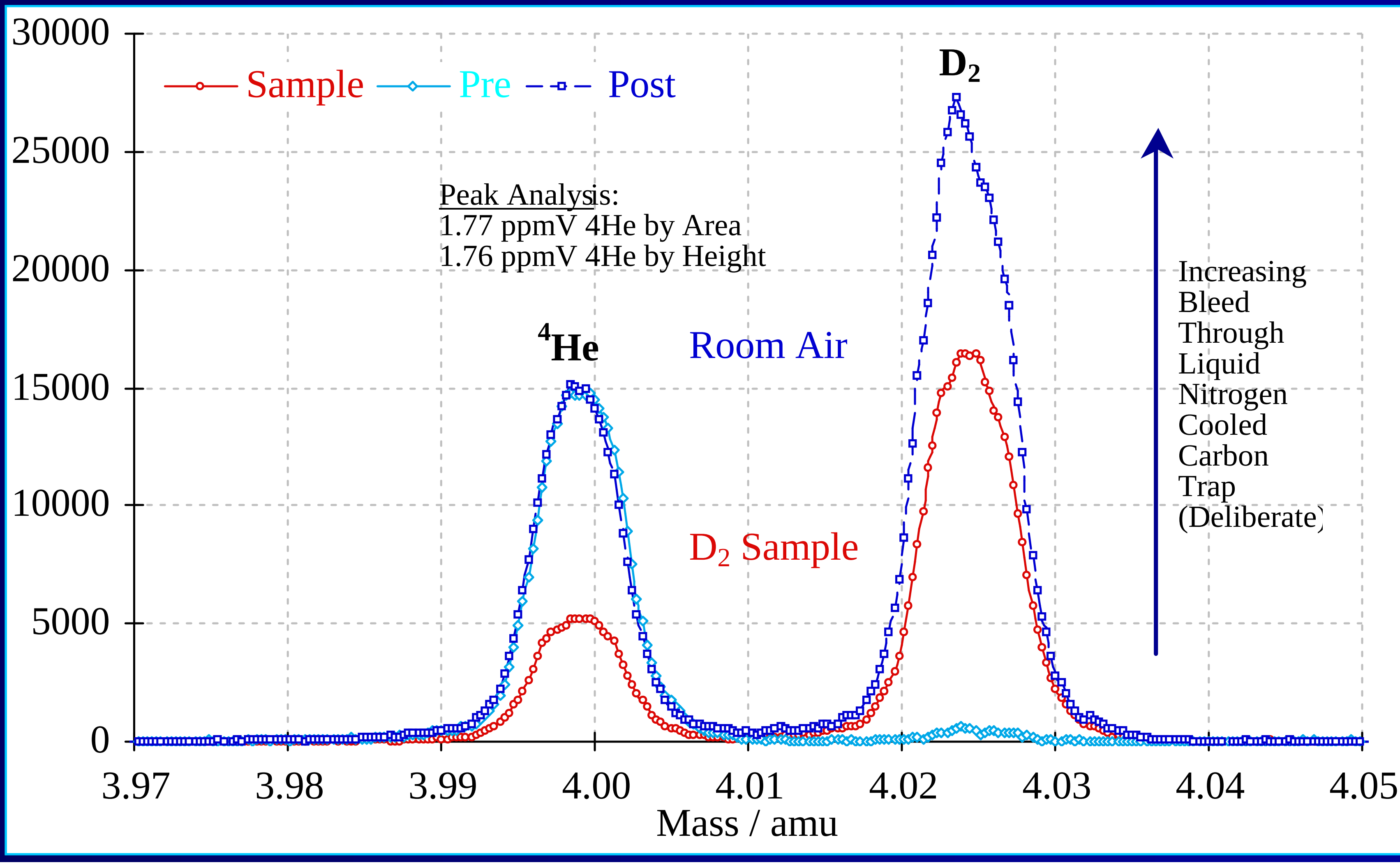
M4: Correlation of Heat with Helium



Case cell Studies:
D_2 Gas with Pd/C Catalyst



Extrel QMS: resolution of D_2 & ^4He



SRI Micro-Mass 5400
Noble Gas Mass Spectrometer

Specifications:

- Magnetic Sector Analyzer with 90° extended geometry ion optics
  giving a dispersion length of 54cm

- Helium Sensitivity

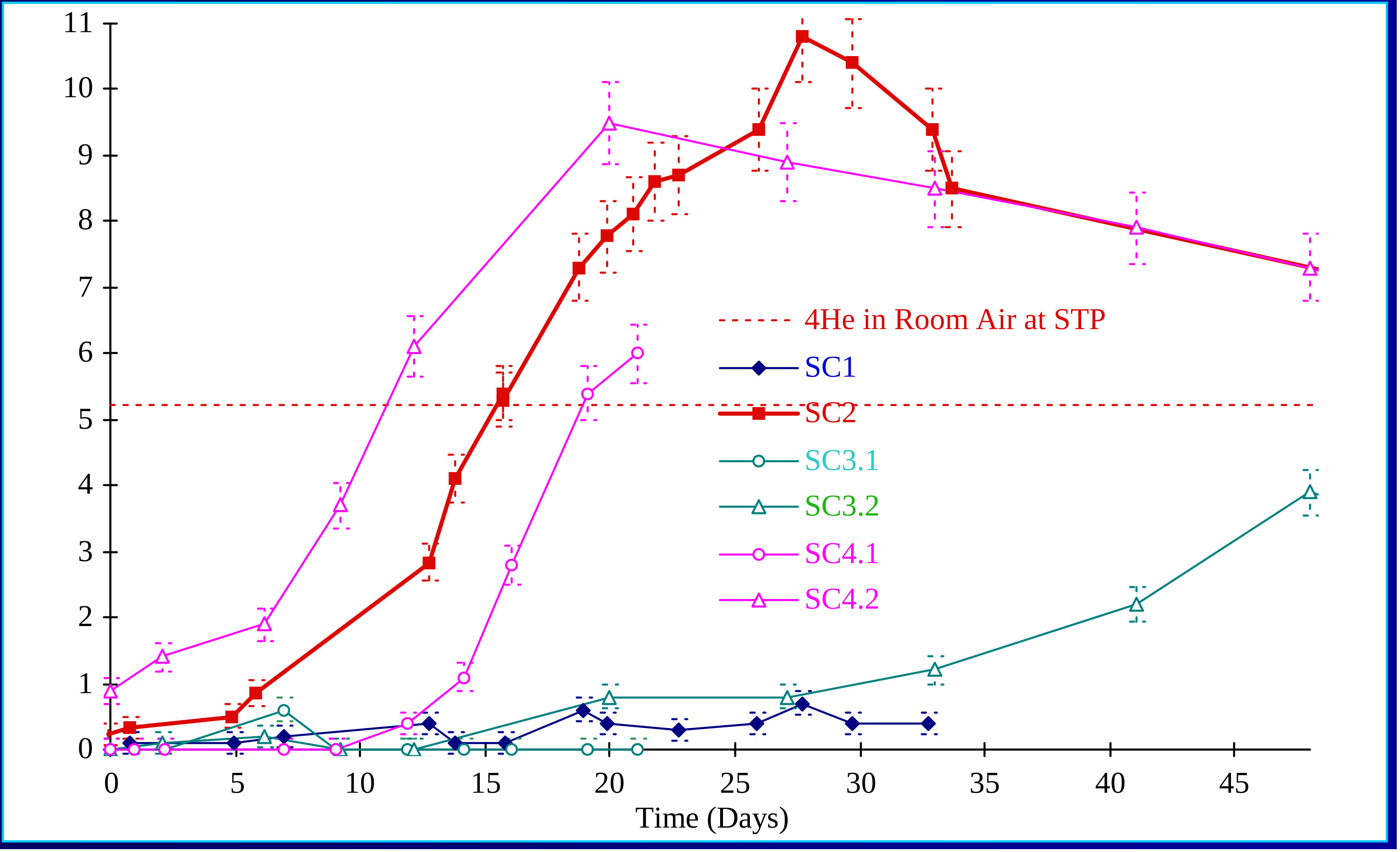
Isotope	Faraday	Channeltron	Absolute resolution
^4He	3ppb	2.0pptr	$1.0x10^7$ atoms*
^3He	3ppb	0.05pptr	$2.5x10^5$ atoms**

* Limited by background

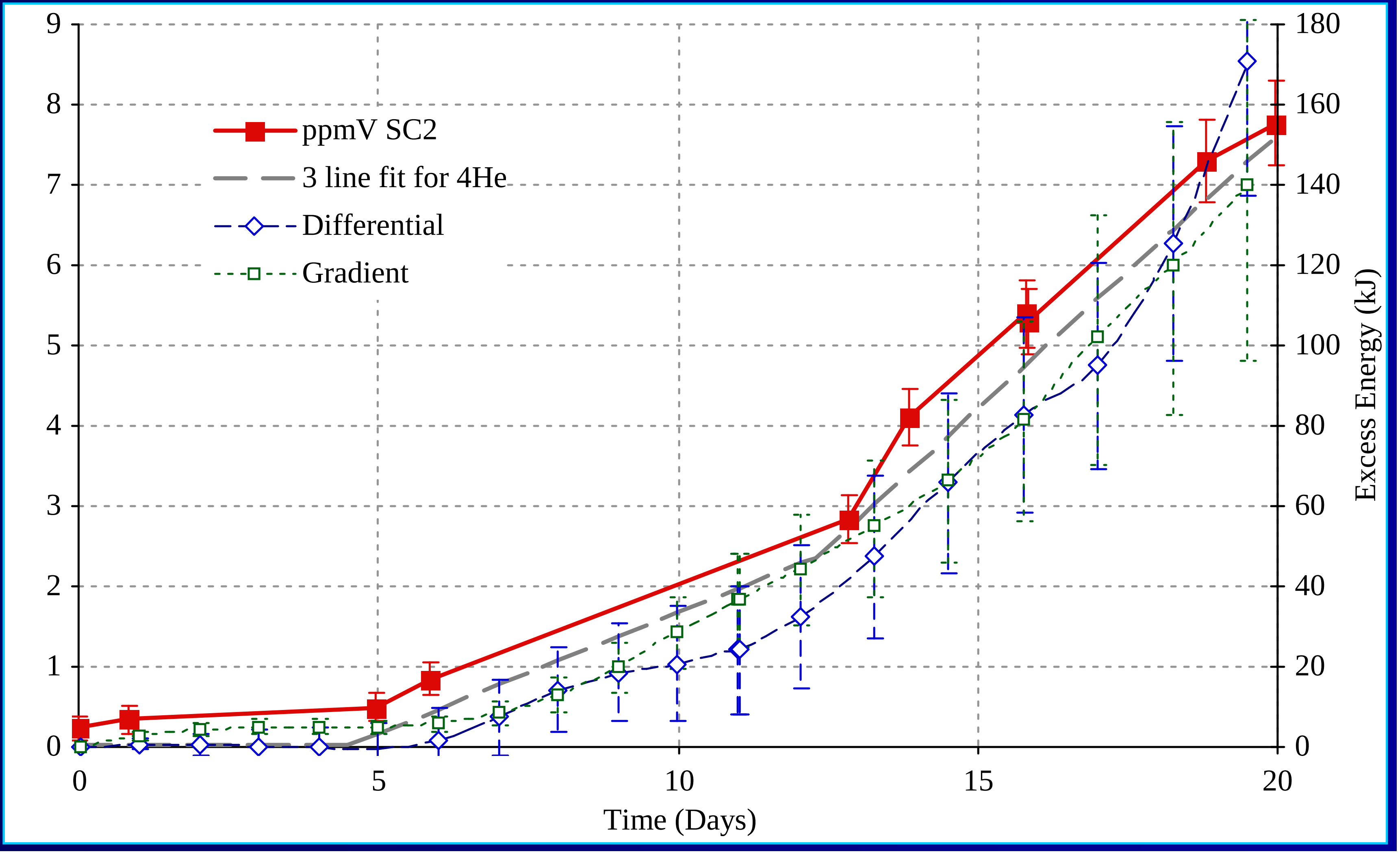
** May be reduced using different method

- Metal Analyses
  - still under development

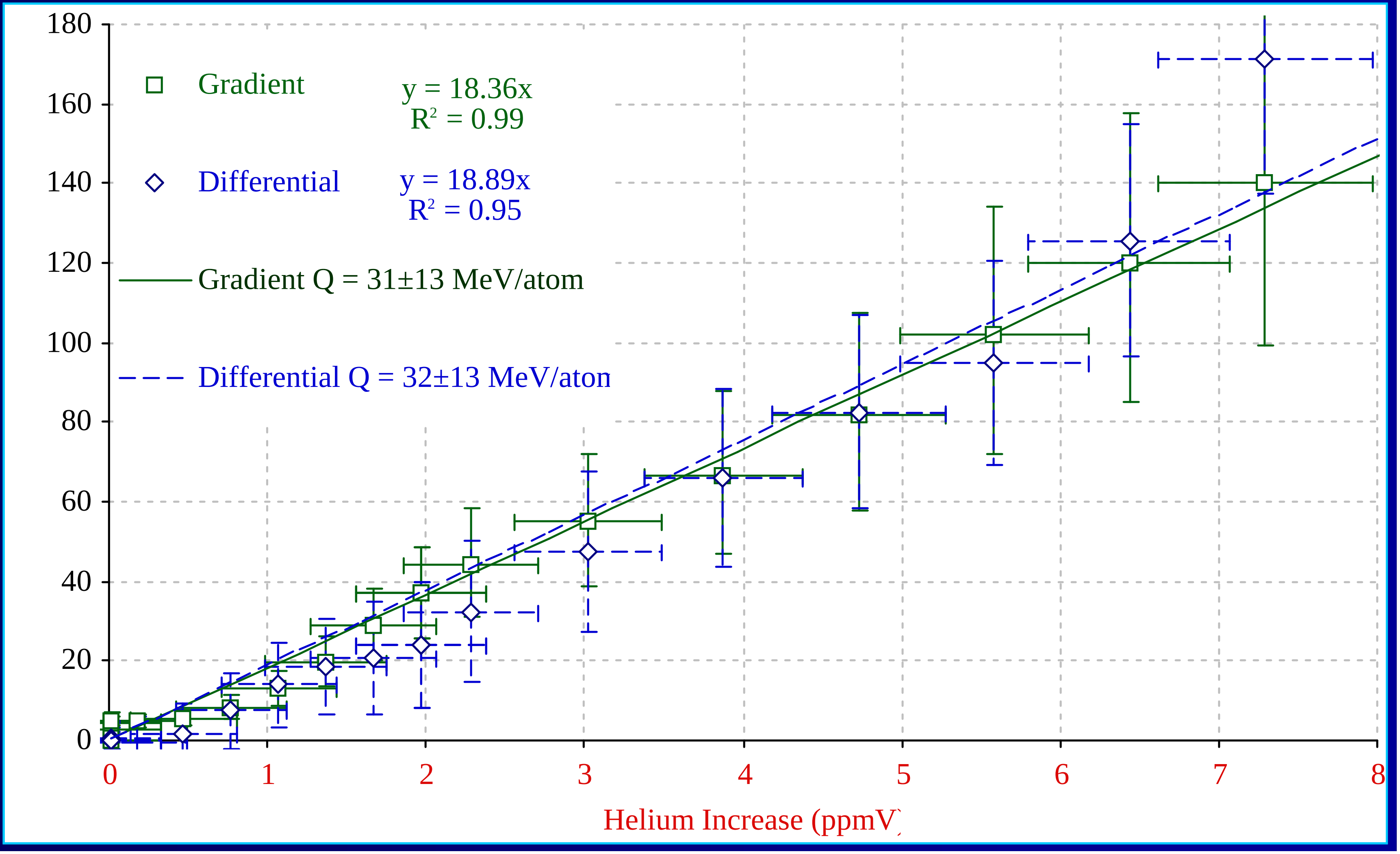
Case: ^{4}He *vs.* time



Case: ^{4}He and Heat *vs.* time



Case: "Q"-Value - Energy *vs.* ^{4}He



Case Conclusions

- Near quantitative correlation between Heat and ^4He production according to:

Predicted: $d + d \rightarrow {}^4He + \sim 24MeV_{(lattice)}$

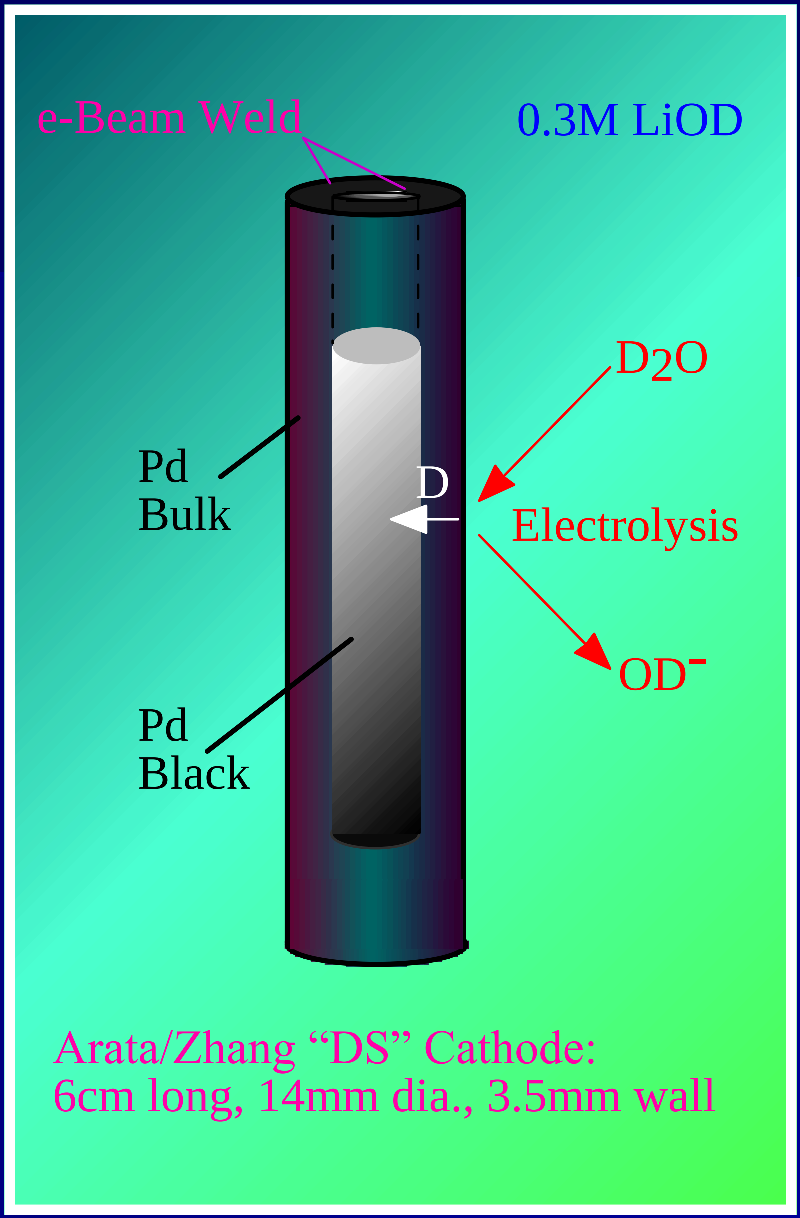
Measured: $Q = 31 \pm 13$ MeV/atom

- Discrepancy may be due to solid phase retention of ^4He
- Substantial initiation time >> D diffusion.
- Max $[^4He]_{Sample} / [^4He]_{Air} > 2$

Production of Tritium in a Sealed Pd cavity

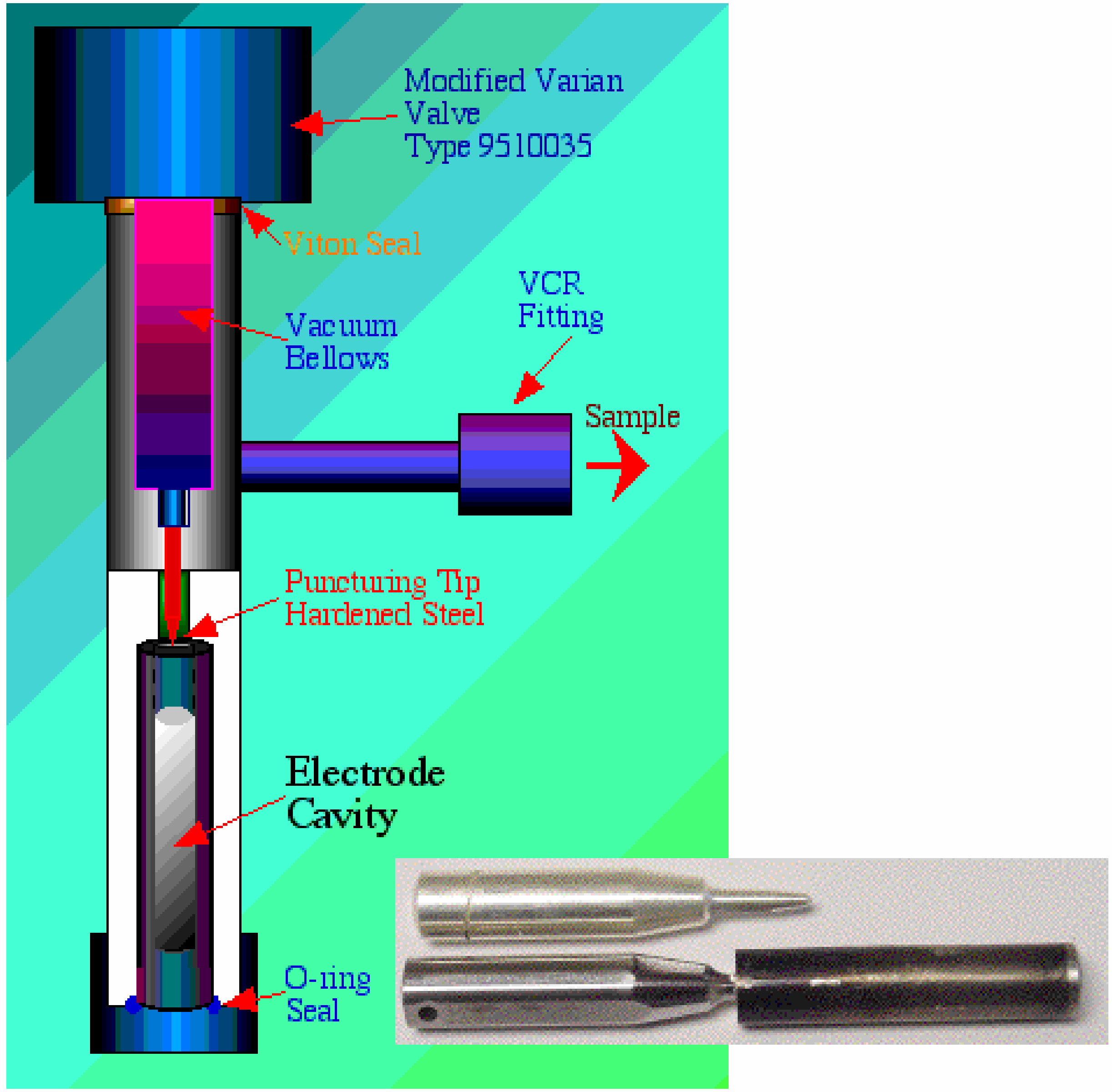
AZ1 0.3M LiOD, AZ2 0.3M LiOH
Cathodic Current 5 - 7.5A
Current Density 170-255mA cm^{-2}
P_{in} 50-317 W, Duration <u>120</u> Days
$P_{xs,Max}$ = 10 ±1.5%, P_{xs} 0 ±1.5%,

Deloaded:
open circuit and at 2V Anodic
for a further <u>100</u> Days.



Gas Sampling Method for Sealed Cathodes

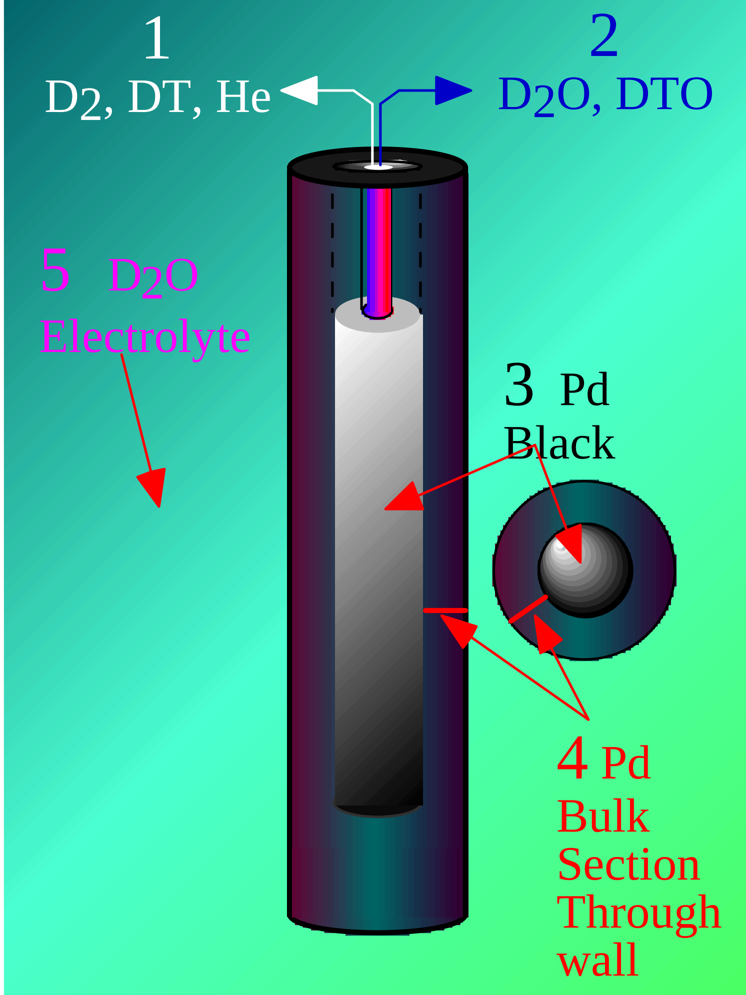
[B. Oliver, PNNL, analyses performed by:
B. Oliver, PNNL,
W. B. Clarke, McMaster, Ontario,
and by
V. Violante, ENEA]



AZ1: Measurements of ^{3}He and ^{3}H

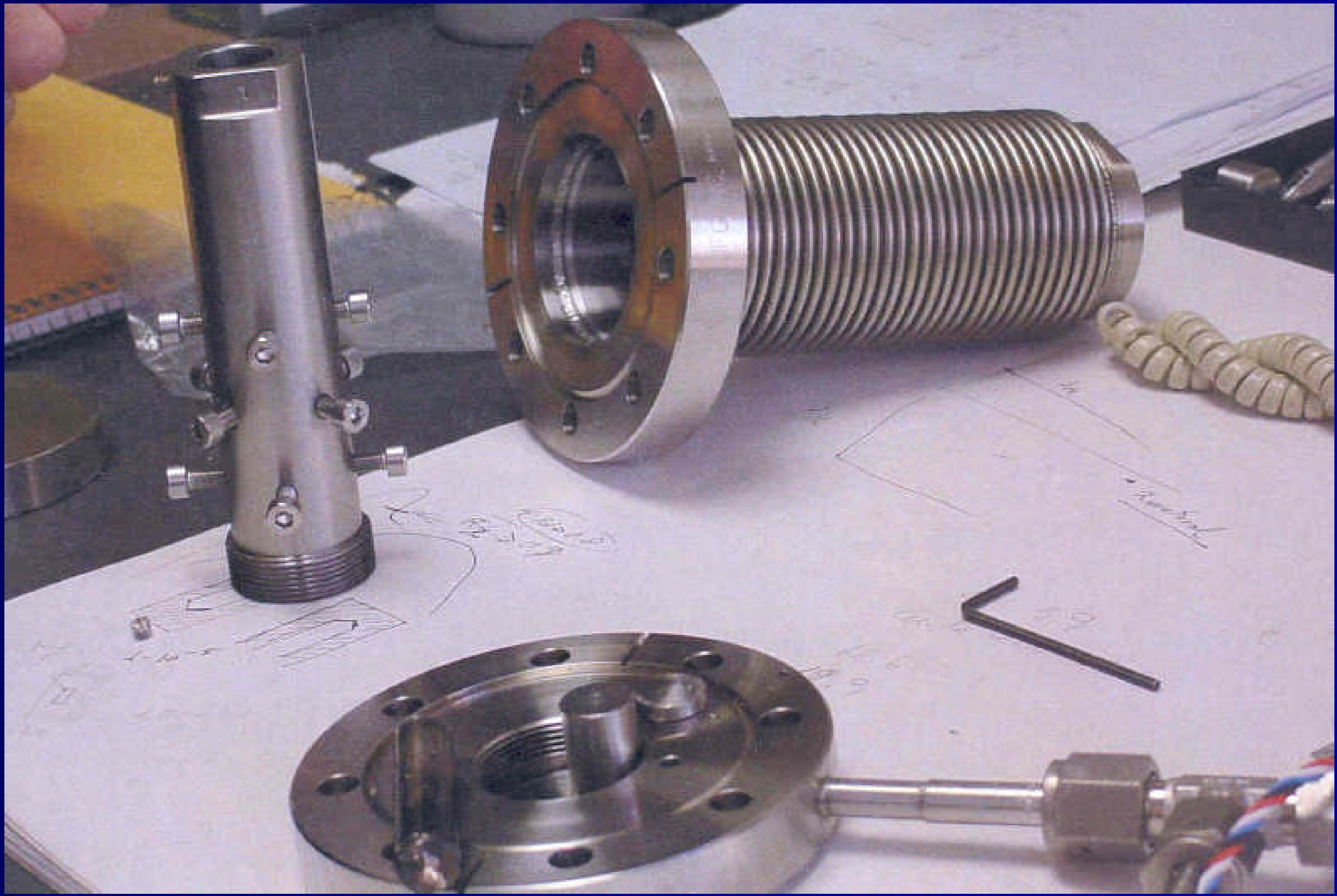
T measured as ∂^3He/∂t at McMaster in Phases 1-4

T measured by scintillation at SRI in electrolyte (Phase 5)



Arata/Zhang "DS" Cathode:
6cm long, 14mm dia., 3.5mm wall

ENEA/AZ1:
Apparatus for Gas sampling in sealed cathode Void



ENEA/AZ1: Press and Bellows

ENEA/AZ1:
Puncturing tip and cathode

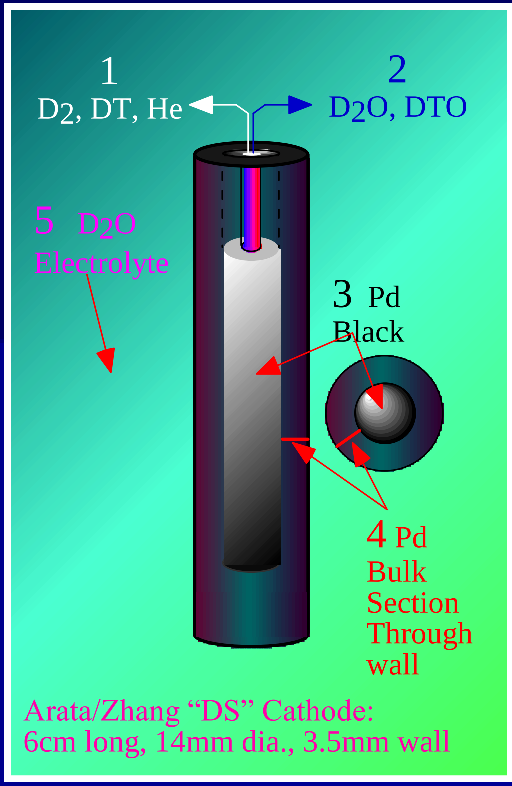
Tip and Cathode

QuickTime™ and a
Photo - JPEG decompressor
are needed to see this picture.

AZ1: Tritium Results

•If Tritium was injected in a single event, this event occurred sometime during the period of cathodic electrolysis.

The total production of Tritium was between $2x10^{15}$ and $5x10^{15}$ atoms.



Tritium Fractionates between the 5 Phases as follows:

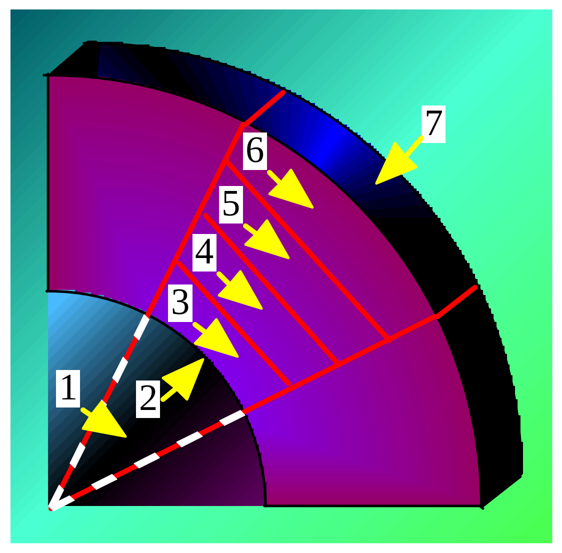
1	2	3	4	5
1.8%	97.8%	0.16%	0.24%	0.05%

Clarke, Oliver, McKubre *et al*, ***Fusion Science and Technology, Sept. (2001)***

AZ1: Radial Distribution of ^3He and ^3H:

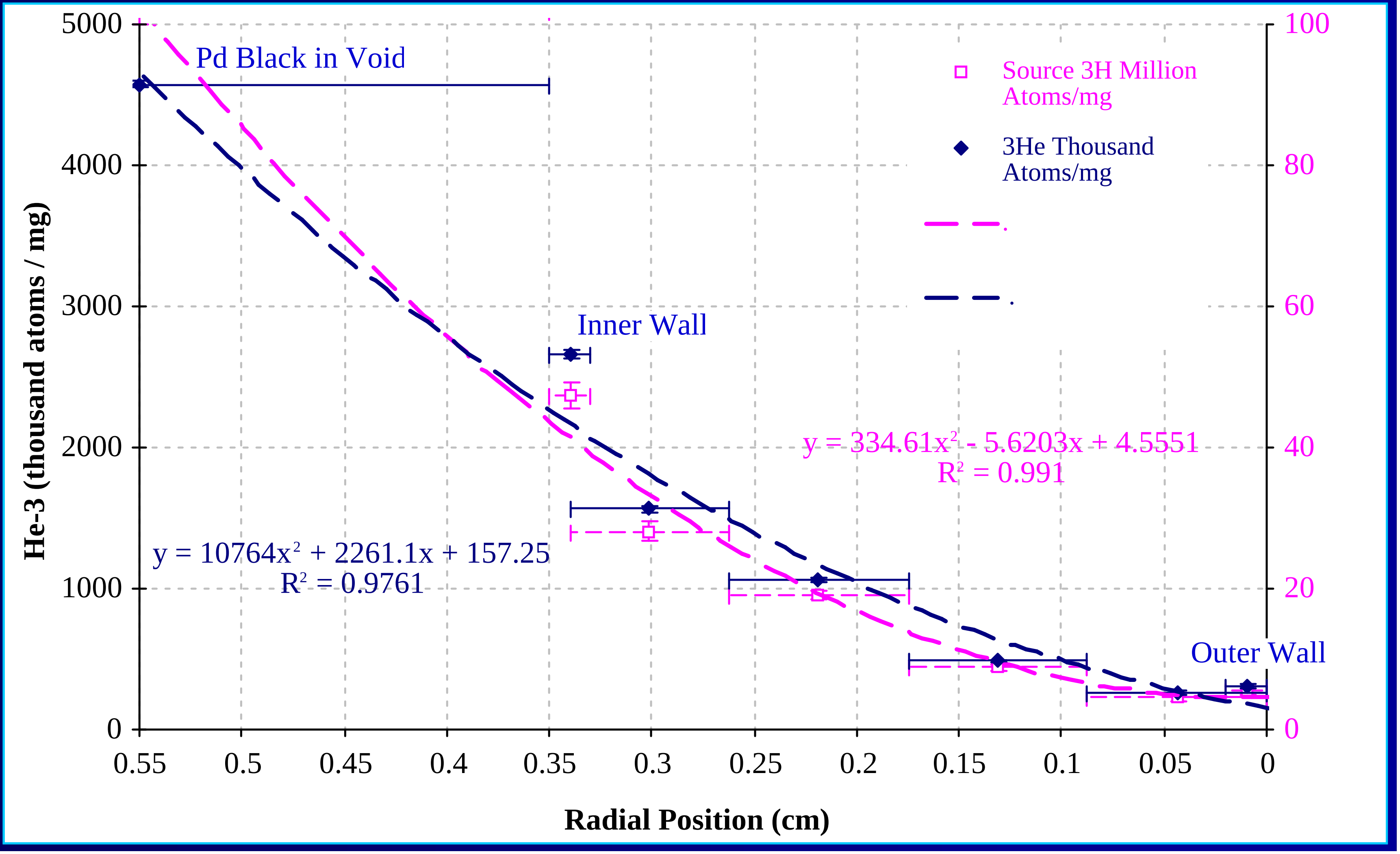
Radial Position (cm)

[^3He] Thousands of Atoms/mg Pd



1	2	3	4	5	6	7
Inside Black	Inner Wall	Inside Black	Inside Black	Inside Black	Inside Black	Outer Wall
0.525	0.345	0.301	0.219	0.131	0.044	0.005
±	±	±	±	±	±	±
0.175	0.005	0.039	0.044	0.044	0.044	0.005
4573	2656	1563	1061	486	261	307
±	±	±	±	±	±	±
21	30	21	11	9	9	10

AZ1: Radial Distribution of ^{3}He and ^{3}H



Tritium Conclusions

- Production of Tritium was between $2x10^{15}$ and $5x10^{15}$ atoms.

Modeled as a single event, this occurred during cathodic electrolysis.

There is definite evidence of excess ^{3}He from Tritium decay of all samples of Pd & Pd-black from the D_2O experiment.

Samples of Pd taken from a similar and contemporaneous H_2O electrode show low ^{3}He levels consistent with blank Pd.

Measurements of the ^{3}He gradient through the 3.5mm wall of the D_2O electrode show that the ^{3}He is the decay product of Tritium which diffused from a source inside the electrode.

No evidence for ^{4}He quantitatively consistent with excess heat.

Summary and Conclusions (1)

Experience teaches us that:

(1) There **ARE** heat effects closely correlated to the

Loading:

- Stoichiometry of D/Pd
- Chemical Potentialof D?
- New Phase formatiion?

Initiation:

- Lattice defects (vacancies and impurities)

Stimulation:

- Electromagnetic, Acoustic, Magnetic…..
- Flux effects (D^+, e^-)

Summary and Conclusions (2)

Experience teaches us that:

(2) There **ARE** (hitherto unexpected) nuclear effects:

d + d → ^{4}He + ~24 MeV (*lattice*)

- 3 metal-sealed cells
- 3 calorimetric methods
- electrochemical and gas loading experiments
- ^{4}He analyses at 4 different institutions

^{3}H production in small dimension Pd particles

Numerous other effects……

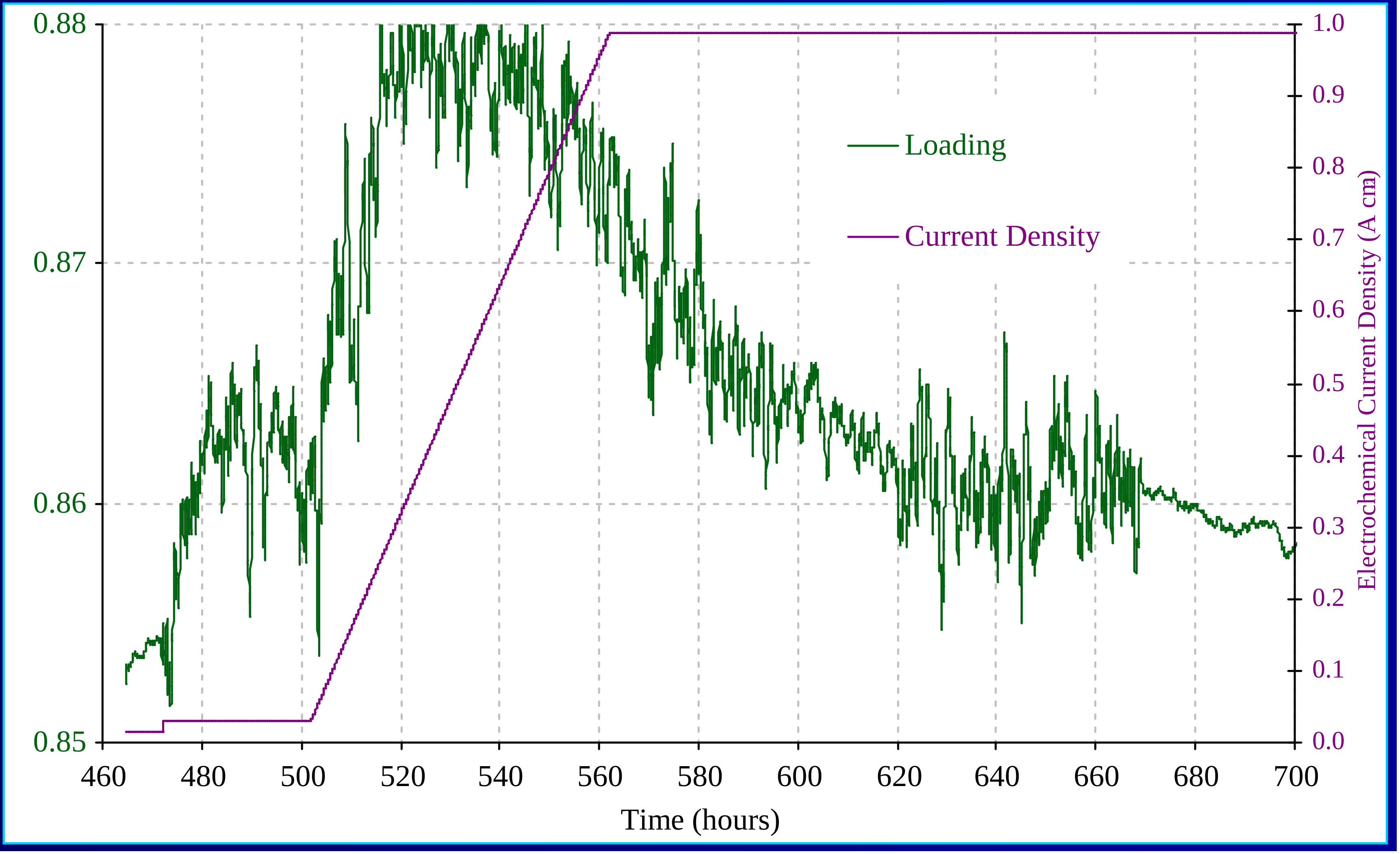
Summary and Conclusions (3)

Experience teaches us that:

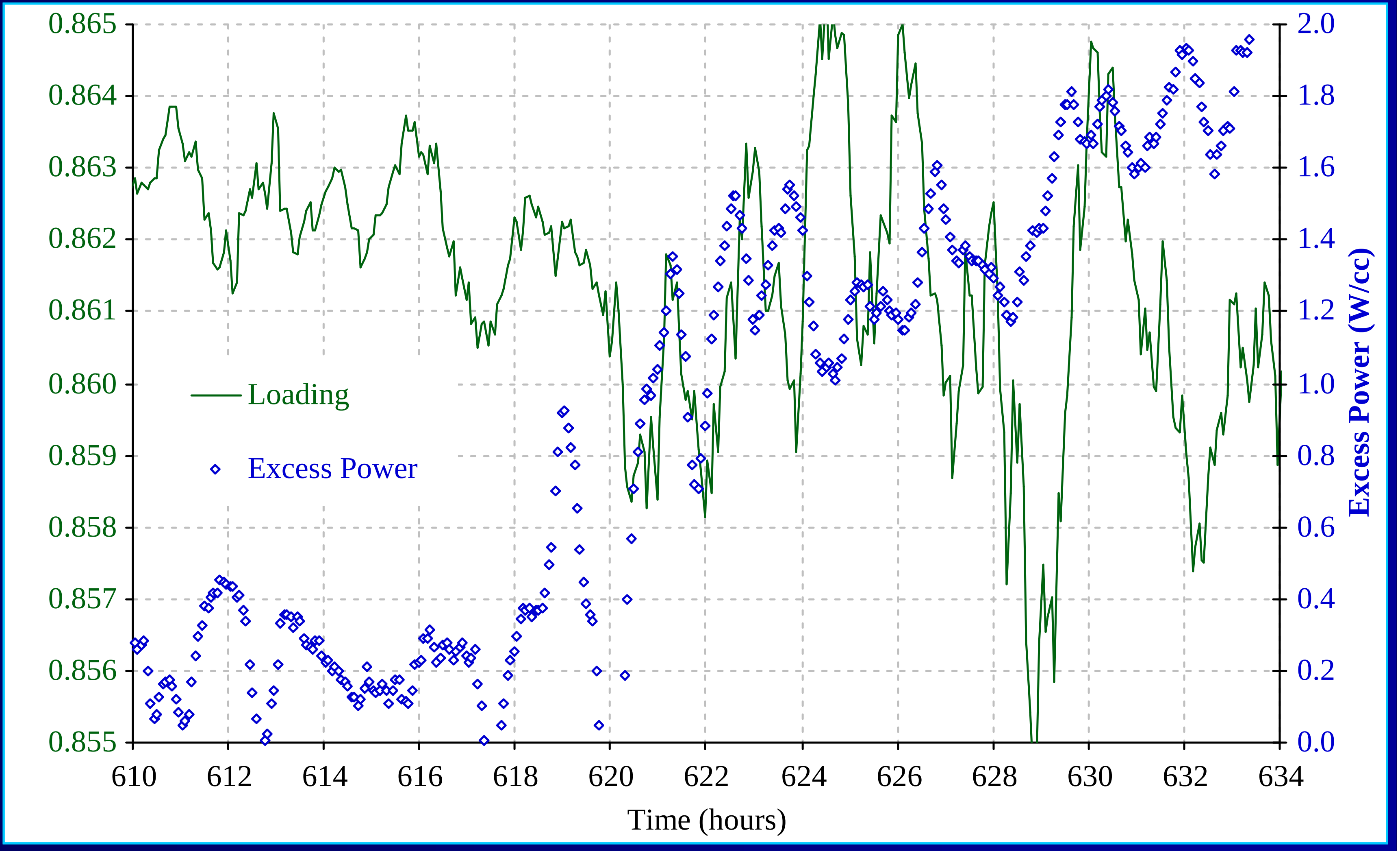
(3) Effects **ARE** amenable to conventional interpretation.

Backup Slides

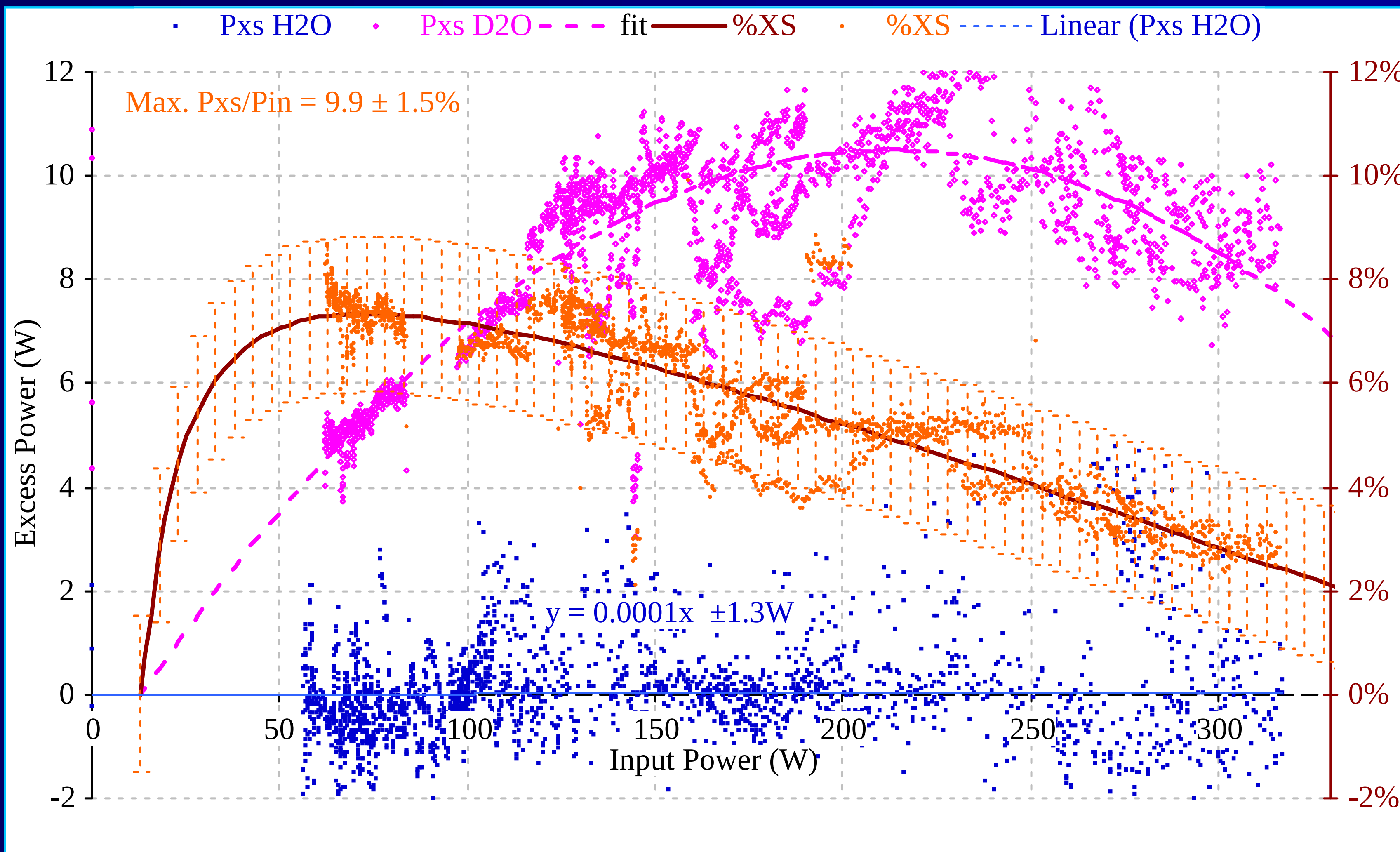
M4: The Dynamics of D Flux



M4:The Dynamics of Flux *(detail)*



AZ1,2: P_{xs} *vs.* P_{in}



The Pathway Forward:

- Predictive Theory
  - After 14 Years of Parametric Study we have learned a great deal // intuition and patience is thin
- **Simple** demonstration of a **novel** effect having an unambiguously **nuclear** origin:
  - Results are too numerous (>3000 papers) incomplete, complicated, unexpected require multi-disciplinary understanding
- Results sufficiently substantial to allow evaluation of potential technological consequences.
- Capable of independent replication.

Flow Calorimetry Details (1)

1. Operate calorimeter in constant power mode by adjusting electrochemical power and calibration heater power to be a constant sum. This maintains the calorimeter in near steady state condition.

2. Temperature sensors initially two RTD's at inlet and outlet, later two RTD's and two thermistors at the outlet.

RTD sensitivity ± 1 mK

Thermistor sensitivity ± 50 μK

3. Flow Rate Measurement on-line, gravimetric and volumetric

Flow Calorimetry Details (2)

4. Heat Transfer Fluid

Silicone oil:	low C_p, insulating, non-corrosive absorbs water (viscosity, C_p)
Water:	lower viscosity, C_p constant and well determined

All connections and wire feed throughs designed to eliminate heat transfer fluid leaks.

5. All connections and wire feed throughs designed to eliminate heat transfer fluid leaks.

6. Fluid streamlining reduced by thorough mixing of exit stream.

Flow Calorimetry Details (3)

7. Electrical leads brought in through bottom of calorimeter to reduce heat transfer along the wires (later labyrinth design).

8. Calorimeter held in constant temperature bath to minimize cooling losses and maintain them constant, also to maintain constant inlet temperature.

9. Calorimetric parameters measured via computer controlled multiplexer using a single calibrated DMM (periodically interchanged).

10. Series cell operation

SRI Micro-Mass 5400
Noble Gas Mass Spectrometer

H_3^+