## M-Series Discussion and Conclusions

***Introduction***. The purpose of the series of experiments described in this section was to determine the conditions under which the phenomenon which gives rise to calorimetrically determined excess power can be initiated and sustained. Having achieved this goal a secondary goal was to demonstrate whether or not the excess heat produced, correlated with the production of species from nuclear reactions; the primary nuclear product sought was helium, but integrating monitors were included in the M-cells for neutrons and x-rays.

In the light of these goals, the M-series experiments must be regarded as being only partially successful. The excess power observed was infrequent, and of small magnitude. The experiments, and their results summarized here, nevertheless contain a wealth of information. In this section we attempt to discuss these results, and draw conclusions from them, within the frame-work of the following four questions.

i. What can we learn from the excess power observed; can we refine the conditions necessary for its production?

ii. What can we learn from the extended periods where excess power was not observed; given the previous experience generated on this project and in the rest of the world, ought we to have observed this phenomenon more frequently or at greater amplitude under the circumstances of these experiments?

iii. What other information has been learned, in these experiments, about the D/Pd system; in what way is this information valuable?

iv. Using the information obtained, how can we achieve our goal of demonstrating conclusively whether or not nuclear processes contribute to the phenomenon of excess heat production?

***Loading.*** The D/Pd loading has been shown to be closely correlated with excess power production. Identifying the conditions under which high loadings can be achieved, and maintained has been an important, even crucial, part of our experimental program (see Section 2, Degree of Loading). Our knowledge is, as yet, incomplete; the results of the M-series experiments provides some illumination.

It is clear from past and present studies of the D/Pd system that one of the factors which controls the ability of palladium to take up and retain deuterium (and hydrogen) is contained within the metal itself. A metallurgical or mechanical property, which may vary from manufacturer-to-manufacturer, lot-to-lot, or section-to-section within a single rod, may control the rate and extent of deuterium absorption. Cathodes selected for M-cell calorimetry were from lots supplied by two manufactures, Johnson Matthey and

Engelhard, found previously to load satisfactorily. All cathodes were subjected to a single annealing process previously found to be beneficial. A considerable variation in loading was nevertheless observed; in no case was a maximum loading obtained D/Pd ≥ 0.95, a value previously observed to be necessary for reproducible excess heat production.

The M-series experiments were performed as a series of current ramps, normally followed with anodic strips, often accompanied by chemical species additions. [Other features of these experiments are discussed below under the heading *Pulses*]. Table 3-6 summarizes the loading response to successive ramps in experiment M1, M2 and M4.

In general, we observe two characteristics of loading which somewhat conflict during current ramps: an increased loading (D/Pd) with increased current density (i) - this relationship is often logarithmic; a tendency towards decreased loading with time when a cathode is held at high current densities (≥ 100 mA $cm^{-2}$).

Reviewing the data in Table 3-6 we see three different types of response for the three cathodes:

i. The 2mm JM* cathode used in M1, initially loaded quite well (D/Pd ≈ 0.927) in the presence of 200 ppm Al. This high loading was obtained at very high current densities (or, perhaps more importantly, high loading was sustained at high current densities). With successive ramps, following strips with no chemical species additions, the maximum loading obtained during a ramp declined progressively. This decrease is due to the change in slope of the Log [i] versus D/Pd relationship (see Figure 3-68). Until the addition of $H_3BO_3$ at 890 h, the M1 cathode showed very little tendency for decreased loading with time (or i during a ramp). A small (but significant) improvement in *net* loading was seen at low current densities on adding $H_3BO_3$; this improvement does not sustain to high current densities and completely changes the functional relationship between i and D/Pd.

ii. The 2.8 mm E#1 cathode used in M2 initially displayed poor loading in an electrolyte containing no deliberate additive. With anodic strips accompanied by the addition first of Al, then of Si, the maximum loading obtained during a ramp increased progressively (but not sufficiently). This cathode showed little tendency for decreased loading with time (or i during a ramp).

After hours of cycling, the surface protrusions are electrically equivalent to cylinders, 0.046 cm in diameter, 0.036 cm high and at average spacing ~ 0.2 cm. A small amount of redistribution occurs after the high current anodic/cathodic cycling is stopped. Later it appears as if the protrusions have somewhat reduced in size (or, at least, effect on $R/R^o$).

This dramatic redistribution of surface does not appear to be beneficial in facilitating deuterium uptake.

*Excess Power.* In a total of 14 current ramps in experiment M1-M4, excess power was observed on only 3 occasions: the first ramp of M1, and the first and third ramps of M4. In two instances, the amount of excess power observed was very small, not much larger than the determined accuracy of the calorimeter (~ 0.2-0.4%). Only in the case of M4 ramp 3 was excess power and energy observed with sufficient resolution to perform further analysis and draw conclusions about the causes and conditions.

Figure 3-83a shows the input, output and excess power for the period of the third ramp of experiment M4. This plot shows two "bursts" of excess power, each separated by a period of small (or no) excess power, each lasting about one day. In the first instance, excess power appears to initiate, with the current ramp, at a current density threshold of approximately 425 mA $cm^{-2}$. At constant current the excess power is highly variable. Two features of the excess power, and its variability, deserve special attention:

i. In some instances there appears to be a correlation between excess power and input power, at constant input current.

ii. There appears to be a correlation between excess power (shown in Figure 3-83b), and an apparently spontaneous variation observed in the measured cathode resistance (interpreted in Figure 3-83a as a variation in loading).

Both of these apparent correlation's warrant further scrutiny.



16

interesting effect (1.75 W). Between M4 and C1 this increase was achieved by two means: increasing $x_{max}$, and decreasing $x^o$. The former is very difficult to achieve, reproducibly. It is not at all clear why the threshold value of $x^o$ for C1 was low, or how it was lowered. Obviously it is important that we achieve such an understanding.

The product of 1.2 and 35.5 is 43. As indicated in the final row of the Table in the previous page, however, the volume (or area) weighted maximum excess power for C1 exceeded that of M4 by only 3.6. This difference is contributed, at least in part, by the much larger value of the rate of change of loading, $\delta x/\delta t$, observed in M4. If we attribute all of the difference in the specific excess power generation rate between C1 and M4 that is not due to the quantitative difference in the excess parameters $(i - i^o)$ and $(x - x^o)^2$, then the value of $\delta x/\delta t$ for M4 was 12 times larger than for C1.

A factor of 12 is the difference between one experiment and another. This also would be important as the difference between experiments in which scientifically interesting levels of excess power were observed and those which are rejected as yielding null or ambiguous results. Had this factor of 12 difference in $\delta x/\delta t$ between M4, ramp 3 and C1, ramp 1 not occurred (or in M4 it had been a factor of 12 less), then the excess power observed would have been at the threshold of calorimetric detection.

It is important to recognize that in neither case, M4 or C1, was an attempt made to maximize $\delta x/\delta t$. Quite the contrary. Both experiments were operated at constant (or slowly changing) currents, temperatures, and gas pressures; the three variables most likely to influence loading. What fluctuation in loading did occur, and in both cases it was significant and varied, occurred apparently spontaneously; we observed the effect, we did not control it.

As for the threshold values, particularly $x^o$, it is important that we understand what causes fluctuating loading, how we can control it and increase it to produce excess power more efficiently.

Attempts made to stimulate $\delta x/\delta t$ by stepping and pulsing the current at low and high (RF) frequencies were not successful. Even the very large current perturbations and oscillations, the values of $\delta x/\delta t$ induced were small compared to those which occurred apparently spontaneously during M4, ramp 3. Furthermore, large current perturbations (at least those examined so far), appear to reduce the average loading, so that neither a loading flux or excess power was observed.

**Nuclear Products.** A significant amount of excess energy was produced in experiment M4, more than can be accounted for by known chemical and mechanical processes. It is therefore appropriate to search for products of potential nuclear reactions which may give rise to excess power and energy.

The mass flow calorimeters, because of their size, complexity and the need for environmental isolation, are not provided with on-line nuclear detection capability. Instead, three integrating monitors were provided for experiment M4. These monitors had the capability of detecting integrated:

X-rays
neutrons
helium.

The capability to detect x-rays, integrated over the experiment duration, was provided by placing Kodak dental x-ray films, size 00, outside of the 1 mm PTFE liner around the electrolyte chamber. At the termination of the experiment, after 1840 hours (> 2.5 months) of operation, it was found that water damage had rendered the radiation film badges unreadable. We are therefore not able to draw conclusions regarding the production of X-rays or other penetrating radiation, and its association to excess heat production.

The capability to detect integrated neutron flux, as well as x- and gamma rays, was provided by placing commercial (Radiation Detection Company, Sunnyvale, CA) LiF Thermoluminescent Dosimeters (TLD's) inside quartz tubes in the electrolyte. Four TLD's were placed inside two quartz tubes. Two other TLD's were kept as blanks in a lead storage container during the experiment. These blanks were developed along with the TLD's from the cell. The results from the cells M1, M3 as well as the blank samples were all less than 30 mRem as shown in Appendix 2. The configurations for cells M2 and M4 were such that no TLD's could be placed in the cell. It is obvious from these results that no neutron flux was detected by this method. In fact, the output measured in these cells was always somewhat less than that measured in the blanks because the duration of time spent underwater reduced the exposure to ambient neutrons to below that seen by the blanks in a 2" thick lead cabinet.

In an attempt to measure rates of helium production, the gaseous contents of cell M4 were sampled four times during the experiment, and subjected to analysis for $^4He$. These analyses were performed by the U.S. Bureau of Mines at Amarillo, Texas. The sample times and results are presented in Table 3-7.

**Table 3-7**
**Summary of Helium Analysis**

| Sample | Duration | Date | Time | ppm |
|---|---|---|---|---|
| 1 | 669.4h | 8/16/94 | 15:07 | 1.556 |
| 2 | 810.2h | 8/22/94 | 11:55 | 1.661 |
| 3 | 1172.7h | 9/06/94 | 14:30 | 0.340 |



18

| | | | | |
|---|---|---|---|---|
| 4 | 1407.7h | 9/16/94 | 09:30 | 2.077 |

Excess power was first observed in M4 during the third current ramp at ~ 530 hours (8/10/94 19:44). At this time the current density i = 475 mA $cm^{-2}$ and the loading D/Pd = 0.88. Excess power continued with some variability, reaching a maximum of 375 mW (~ 2% of $P_{in}$), and terminated abruptly at ~ 668h. At this time the current density i = 987 mA cm-2 and the loading D/Pd = 0.86. The energy integrated from the excess power in this period was 82.45 kJ or 9.27 MJ/mole of Pd.

A sample of gas was taken almost immediately following termination of $P_{xs}$ (Sample 1, at 669 h) and found to contain 1.556 ± 0.007 ppm of $^4$He. A second sample was taken 5.9 days later (Sample 2, at 810.2 h) and found to contain 1.661 ± 0.009 ppm of $^4$He.

***Sample 1.*** If $^4$He is produced in the manner suggested by Miles and Bush via the reaction

$$D + D \rightarrow {}^4He + 22.4\ MeV$$

then from 82.45 kJ we expect

$$\Delta ppm = \frac{\delta\ atoms \times 10^6 \times 22400\ cm^3/mole\ (at\ STP)}{N \times V}$$

1,556/1.41 = 3.79
1.556/3.76 = .41

where N = Avagrodo's constant = $6.022 \times 10^{23}$ atoms/mol

V = Volume of cell plus manifold ≈ 250 $cm^3$

$$\Delta\ atoms = \frac{82.45 \times 10^3\ J}{(22.4 \times 10^6\ eV/atom)(1.6 \times 10^{-19}\ J/eV)}$$

$= 2.30 \times 10^{16}$ — number of atoms

thus

$\Delta ppm = 3.42$ ppm

Given an (assumed) starting concentration of [$^4$He] = 0.34 ppm (the value in the starting $D_2$ gas - see subsequent discussion of samples 3 and 4), then the "expected" concentration of $^4$He is

$ppm_{expected} = 3.42 + 0.34 = 3.76$ ppm

In sample 1, only 41% of this amount was found.

***Sample 2.*** The gas sampled at 669h (Sample 1) had 1.556 ppm $^4$He. The volume of this sample, reduced the system pressure by 0.73 Atm., from 0.69 to - 0.04 Atm. gauge. Using gas from the $D_2$ source, the system pressure was increased by 0.59 Atm, to 0.55 Atm. gauge.

Given a system volume of 250 cm$^3$, and a helium content of 0.34 ppm in the make-up $D_2$ gas (subsequently verified), we can calculate the expected value of $^4$He in Sample 2.

$$ppm_{expected} = \frac{0.96 \text{ Atm.} \times 1.556 + 0.59 \text{ Atm.} \times 0.34}{1.55 \text{ Atm.}}$$

$$= 1.13 \text{ ppm}$$

Sample 2 contained 1.66 ppm; 0.53 ppm more than "expected".

***Discussion of Samples 1 and 2.*** Sample 1 was lower in $^4$He, than predicted by the Miles Bush mechanism, and sample 2 was high. Two opposed hypotheses are offered:

1. Helium is not sourced with $P_{xs}$ by the mechanism of reaction [1], and the $^4$He measured originates by air in-leakage or by poor sampling procedures.

2. Reaction [1] is relevant, the integral power excess is measured accurately, but the release of $^4$He to the gas phase is subject to an appreciable delay.

These hypotheses are discussed below with reference to the analyses of Samples 3 and 4.

***Sample 3.*** Sample 3 was measured after extensively flushing the (operating) calorimeter with $D_2$ gas. This sample reflects any residual $^4$He in the cell, the $^4$He level in the $D_2$ purge gas, and any in-leakage of ambient air due to poor sampling technique. The value of 0.34 ± 0.01 ppm is consistent with samples previously taken by B. Bush of other $D_2$ gas cylinders, suggesting:

a. The gas in the cell was adequately purged

b. The sampling effectively excludes room air.

***Sample 4.*** Sample 4 was measured 9.79 days ($8.46 \times 10^5$ s) after Sample 3. During this time the cathode was ramped from 0.1 to 3.1A at 25 mA/hour, held at 3.1A for ~ 2 days,

WHERE?

and subjected to current oscillations 3.1/-0.001A with a 4 minute period twice for a total of ~ 2 days. The cell was also subjected to a "mini-boiloff", with the mass flow stopped for 76 minutes; during this time the cell electrolyte temperature rose to 57°C (from 45°C)

R8

In the period between samples there were 5 instances of rapid loading or de-loading (large $\delta x/\delta t$) and the cathode attained a maximum loading of D/Pd = 0.918.

(40ml Pav-3Pa)

Excess power was not noted during the period between samples. Under steady state conditions, $P_{xs} = 0 + 20/-50$ mW. Several features of the calorimetric balance should, however, be noted as unusual.

i. Because of the temperature step and current steps, the calorimeter was at significant remove from its steady state for long periods of time (10-20% of the between sample period).

ii. The thermal baseline was not well established. Prior to the ramp, the calorimeter was 10-20 mW above thermal balance, while at the end of the ramp the calorimeter was 40-50 mW below thermal balance even with the non-steady state correction applied.

iii. During the two periods of current oscillations the calorimeter was apparently endothermic, by as much as 100 mW.

***Hypothesis 1*** The helium sourced between purging at Sample 3 and Sample 4 can be calculated as:

$$\Delta \text{ atoms} = \frac{\Delta\text{ppm}}{10^6}\frac{350\text{cc}}{22400}\ 6.022 \times 10^{23}$$

$$= 1.17 \times 10^{16}$$

$$\Delta \text{ time} = 9.79 \text{ days} = 8.46 \times 10^5 \text{ s}$$

$$\text{Source} = 1.38 \times 10^{10} \text{ atoms/s}$$

We can imagine that the source of this helium is one of the following:

i. Diffusional in-leakage of $^4$He contained in room air.

ii. Convective in-leakage of $^4$He contained in room air, either progressively, or at the time of sampling.



21

iii. Unobserved production via D + D → $^4$He (or some other reaction)

iv. Slow release of $^4$He previously produced or occluded.

*i. Diffusion*

Diffusional flux, $F = \frac{D\,\Delta C\,A}{l}$ moles $s^{-1}$

where D = diffusion coefficient

$\Delta C$ = concentration gradient

A = available area for in-diffusion

$l$ = effective thickness of diffusing area

We can define a parameter

$$X = \frac{DA}{l} = \frac{F}{\Delta C} \quad cm^3\ s^{-1}$$

Assuming constant and uniform in-diffusion,

$$\overline{\Delta C} = C_{air} - \frac{C_{initial} + C_{final}}{2}$$

$$= C_{air} - \frac{C_{initial} + C_{final}}{2}$$

$C_{air}$ = 5.7 ppm

$C_{initial}$ = 0.34 ppm

$C_{final}$ = 2.077 ppm

$\Rightarrow$ $\overline{\Delta C}$ = 4.49 ppm

= 4.49 ppm

$$F = \frac{(\Delta ppm)\ 250\ cm^3}{\Delta t}$$

$$= \frac{(2.077 - 0.34)\ 250}{8.46 \times 10^5}$$

$$= 5.13 \times 10^{-4}$$

$$X = F / \overline{\Delta C} = 1.14 \times 10^{-4}\ cm^3\ s^{-1}$$

This diffusional rate is large. It represents ~ 0.4 $cm^3$/day which seems too much. If we ascribe all of this diffusion to the ceramic member holding the electrical feed-throughs ($A \approx 10\ cm^2$, $l \approx 0.2$ cm), then $D_{ceramic} = 2 \times 10^{-6}\ cm^2\ s^{-1}$; this is much too large a number.

*ii. Convection*

The pressure in the system varied from 0.6 to 1.05 atmospheres *above* ambient in the period between Samples 3 and 4. When corrected for temperature, the pressure was not noted to change at all. There is therefore no reason to suspect convective leakage of gas out of the system, and much less reason to suspect convective in-leakage.

Had in-leakage occurred, we can calculate how much room air (at 5.7 ppm $^4He$) would be needed to increase the concentration in 250cc from 0.34 to 2.077 ppm.

$$V_{leak} = \frac{2.077 - 0.34}{5.7} \quad 250$$

$$= 76\ cm^3$$

This value seems implausibly large.

*iii. Production*

If $^4He$ were produced by a reaction such as

$$D + D \rightarrow {}^4He + 22.4\ MeV$$

we must ask the question whether or not we should have expected to observe calorimetrically the associated power or energy.

From the previous calculation, we need to account for $1.17 \times 10^{16}$ atoms sourced in $8.46 \times 10^5$ s ($1.38 \times 10^{10}$ atoms $s^{-1}$).

For reaction [1]

$$Æ_{xs} = (1.38 \times 10^{10})\ (22.4 \times 10^6)\ (1.6 \times 10^{-19})$$

$= 4.95 \times 10^{-2}$ W

$E_{xs} = (1.17 \times 10^{16})\ (22.4 \times 10^{6})\ (1.6 \times 10^{19})$

$= 4.18 \times 10^{4}$ J

Given the state of the calorimeter and the number of transient events occurring it is possible (but not likely) that there is a baseline error of 50 mW; this reflects < 0.4% of the average input power, which is the nominal accuracy of the calorimetry. It is also possible (but not likely) that 40 kJ of excess heat could have been sourced during one or more of the calorimetric transients, and not seen.

We therefore cannot rule out the possibility that $^4$He was sourced, with excess heat, in the method reported by Miles and Bush.

*iv. Hideout*

Excess power was observed in this calorimeter, and $^4$He measured, some 20 days prior to sample 3. Immediately prior to sample 3 the cell was flushed with $D_2$ at ~ 10 cm$^3$/min. for ~ 18 hours; in this time the gas in the cell and manifold was presumed to be equilibrated with that in the $D_2$ bottle.for ~ 18 hours; in this time the gas in the cell and manifold was presumed to be equilibrated with that in the $D_2$ bottle.

Since the gas flow enters and leaves at the top of the cell, this equilibration is less likely to have taken place with the $^4$He contained in the cell electrolyte (130 cm$^3$), the cathode (0.08 cm$^3$) or the PTFE parts of the cell (~ 100 cm$^3$). We do not know what the partition coefficient for $^4$He is between $D_2$ gas, LiOD, PTFE and Pd metal. Nor do we know the effective diffusion coefficient of $^4$He in PTFE or the rate at which $^4$He sourced within Pd might be expected to leave. Given a Henry's law coefficient of 5-8 ppm for $^4$He in $D_2O$ and PTFE, however, there is certainly sufficient storage capacity to source the observed helium even with some removal during purging with $D_2$ gas. We do need to consider to what extent the cell parts, including the electrolyte, were saturated with helium (equilibrated with 5.7 ppm in the air) at the outset of the experiment.

***Hypothesis 2.*** In attempting to evaluate a $^4$He mass balance on the basis of hypothesis 2 (nuclear source), two critical pieces of information are missing: the helium content of the cell immediately before the initiation of excess heat production at 530h, and before purging at 1154h. We can make progress by assuming that, as intended (a, b) or claimed (c):

a. the system is helium leak tight

b. the initial helium content is that of the $D_2$ gas cylinder (= Sample 3)

c. helium is produced by reaction [1]

| *Sources of $^4He$* | *Atoms* |
|---|---|
| Initial inventory from $D_2$ | $3.9 \times 10^{15}$ |
| Excess power 530-658 h | $2.30 \times 10^{16}$ |
| $D_2$ top-up 690 h | $1.4 \times 10^{15}$ |
| $D_2$ top-up 815 h | $1.0 \times 10^{15}$ |
| $D_2$ fill 1173 h | $3.7 \times 10^{15}$ |
| *Sum* | *$3.30 \times 10^{16}$* |

| *Sinks of $^4He$* | *Atoms* |
|---|---|
| Sample 1 at 669 h | $7.6 \times 10^{15}$ |
| Sample 2 at 810 h | $2.2 \times 10^{15}$ |
| Purged volume before Sample 3 | Unknown |
| System volume at Sample 4 | $1.40 \times 10^{16}$ |
| *Sum* | *$2.38 \times 10^{16}$* |

Clearly, if volume purged before Sample 3 contained $\geq 9.2 \times 10^{15}$ atoms ($\geq 1.14$ ppm), then a mass balance can be achieved. The inequality is employed because we cannot be certain that all $^4He$ had been released into the gas at the time of Sample 4. This estimated concentration is entirely plausible, but not provable.

In this model, $^4He$ is created before Sample 1 (presumably in the cathode, by reaction [1]). This helium is not, however, immediately available in the gas phase where it is accessible for sampling. Instead, the helium is slowly released over a period of a month or more.

Diffusion within the metal itself, might explain this time-constant. Alternatively, hold-up in the electrolyte or PTFE parts could supply the mechanism of delay. It is possibly of significance that the large $^4He$ concentration in Sample 4, followed the extended period of temperature pulsing and a temperature step in this sample period.

## Conclusions

1. We cannot rule out the possibility that $^4He$ was sourced during the period between samples 3 and 4, or that the measured helium represents a hold-over from helium previously dissolved in $D_2O$ or PTFE.

2. In the event of delayed release, a satisfactory mass balance can be obtained for $^4He$ on the assumption that

   a. the system is helium leak tight, and

b. the helium is sourced by reaction [1].

3. Convective in-leakage during cell operation or sampling seems a very unlikely source of the measured $^4He$, and diffusional in-leakage, while possible, would be very hard to account for quantitatively.

4. The possibility of $^4He$ hide-out and slow emergence into the gas phase must be tested by experiment. This applies to both the $^4He$ thought to be produced by reaction [1] and to an initial inventory of $^4He$ in the LiOD and PTFE, due to equilibration with the ambient.

5. Definitive statements will be difficult to make about $^4He$ production in this or future experiments unless or until it is measured at several times the ambient background level.