Helium and Heat Correlation

Heat and Helium Measurements Using Palladium and Palladium Alloys in Heavy Water

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Abstract

Excess power was measured in 28 out of 94 electrochemical experiments conducted using palladium or palladium-alloy cathodes in heavy water. Reproducibility continues to be the major problem in this controversial research area. Based on our experiments, this lack of reproducibility stems from unknown variables in the palladium metal. The best reproducibility for excess power was obtained using palladium-boron alloy materials supplied by the Naval Research Laboratory (NRL), Washington, DC. A high success ratio was also obtained using Johnson-Matthey materials. Calorimeters that are capable of detecting excess power levels of 1 watt per cubic centimeter of palladium are essential for research in this field. Results from our laboratory indicate that helium-4 is the missing nuclear product accompanying the excess heat. Thirty out of 33 experiments showed a correlation between either excess power and helium production or no excess power and no excess helium. The only valid experiments that showed significant excess power but no excess helium involved a Pd-Ce cathode. The collection and analysis of the electrolysis gases place the helium-4 production rate at 10^{11} to 10^{12} atoms per second per watt of excess power. This is the correct magnitude for typical deuteron fusion reactions that yield helium-4 as a product.

1. Introduction

The objective of our program was to investigate anomalous effects in deuterated systems and answer two basic questions: (1) Is the apparent excess power real? and (2) If so, can it be reproduced regularly? The answer to the first question, based on our research is yes, but the answer to the second question is no. The lack of reproducibility has made this research exceedingly difficult. This report examines the possible production of excess power and helium-4 during the electrolysis of heavy water (D_2O) using palladium (Pd), palladium-cerium (Pd-Ce), and palladium-boron (Pd-B) alloys as cathodes.

2. Experimental

Excess power measurements involved the electrolysis of D_2O + LiOD in open isoperibolic calorimeters. A detailed discussion of this calorimetry has been published.[1] In June of 1995, Roger M. Hart, founder of Hart R and D Inc., Mapleton, Utah, and an expert in the design, construction, and testing of calorimeters visited our laboratory. After carefully examing our calorimetric design and techniques, he agreed with our stated error range of ±20 mW or ±1% of the input power, whichever is larger. This is especially true over our normal operating temperature

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range of 40 to 60°C for the cell temperature. At higher temperatures, nonlinear effects such as heat transport by radiation and by the evaporation of D_2O become larger. At low cell temperatures, the fraction of heat lost through the top of the cell becomes larger.

Three compositions of Pd-B alloy were prepared and characterized at NRL. The three alloy compositions had nominal boron concentrations of 0.75, 0.50, and 0.25 weight % boron. The glow-discharge mass spectroscopic analyses showed the three alloy compositions actually contained 0.62, 0.38, and 0.18 weight percent boron. X-ray diffraction studies showed two distinct phases of the same cubic structure in all three compositions of the alloy.[2] The palladium-cerium alloy tested was obtained from M. Fleischmann of IMRA Europe.

Experimental procedures for the collection of electrolysis gas samples and subsequent analysis for helium-4 have been previously reported.[3]

3. Results

The best reproducibility of the excess power effect was obtained using Pd-B alloys supplied by NRL. Seven out of eight experiments that used Pd-B cathodes produced excess power. The excess power measurements for our first experiment using a Pd-B cathode is shown in Figure 1. The excess power averaged about 100 mW during the second half of this experiment. This cathode was prepared as 0.75 weight % boron and had a 6-mm diameter and a 2.0 cm length with rounded ends. This Pd-B experiment was turned off and then restarted 8 days later. Excess power was again observed similar to the first experiment.[4] This demonstrates that excess power can be obtained in repeated experiments using the same cathode.

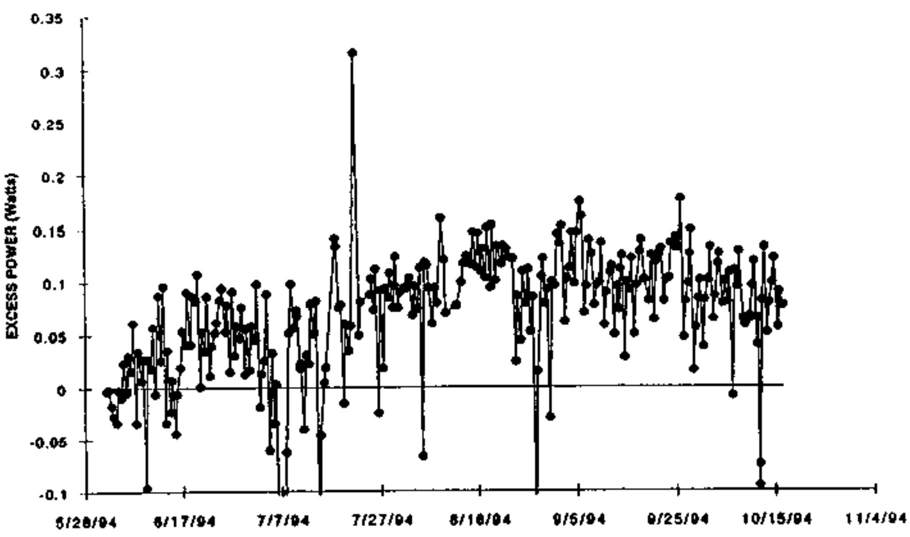

Figure 1. Excess Power Measurements for an NRL Palladium-Boron Rod (6.0 mm x 2.0 cm, 0.75 weight % boron), Cell B.

The next two studies of NRL Pd-B alloys showed excess power in one experiment, but no significant effect in the other experiment. These measurements are shown in Figures 2 and 3. The excess power for cell C showed a gradual increase with time and reached levels exceeding 300 mW (Figure 2). The second cell run in series (cell D) showed fluctuations mainly within ±50 mW and no significant production of excess power (Figure 3). There was clearly no gradual increase of excess power as shown in Figure 2. It was noted at the beginning of this experiment that the cathode in cell D was poorly aligned. This leads to an uneven current distribution and low loading of deuterium into the cathode. After this experiment, examination of the Pd-B cathode that did not produce excess power (cell D) showed an obvious flaw. Swaging of this rod had produced a large, folded-over metal region that would act as a long crack. In contrast, the heat-producing Pd-B cathode had no obvious flaws or cracks. Both cathodes consisted of 0.75 weight % B, with a rod

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diameter of 2.5 mm and a length of 2.5 cm (V = 0.12 cm^3). The end of the heat-producing electrode was left straight, while the end of the other cathode was rounded using a file. No helium measurements were performed for these experiments or for any later experiments, because we were directed to focus only on the excess-heat effect during the last year of this program.

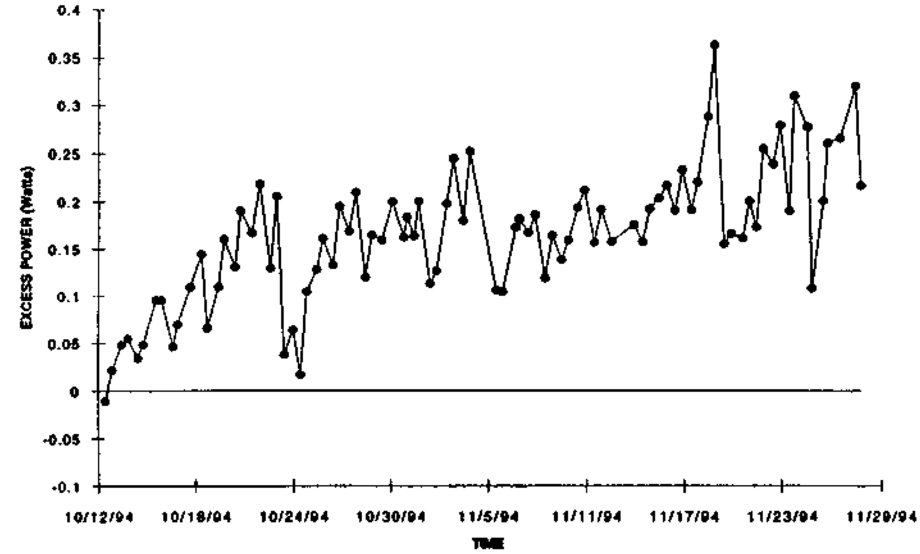

Figure 2. Excess Power Measurements for an NRL Palladium-Boron Rod (2.5 mm x 2.5 cm, 0.75 weight % boron), Cell C. A gradual increase in the excess power was observed. No flaws were visible for this cathode.

The next series of Pd-B alloy studies explored the effect of lower boron concentrations. Two studies of the 0.5 weight % boron alloy gave a fairly steady excess power effect after 11 days of electrolysis with typical levels of 50 to 100 mW.[4] Results for the 0.25 weight % boron alloys yielded excess power averages of about 100 mW for one cell with peaks of 150 to 200 mW.[4] In contrast, the other cell showed only a 5-day period of excess power early in the experiment and then no other episodes of significant excess power.[4] There was no clear relationship between the production of excess power and the boron concentration of the alloy. Results for deuterium loading into Pd-B alloys are presented elsewhere.[4,5]

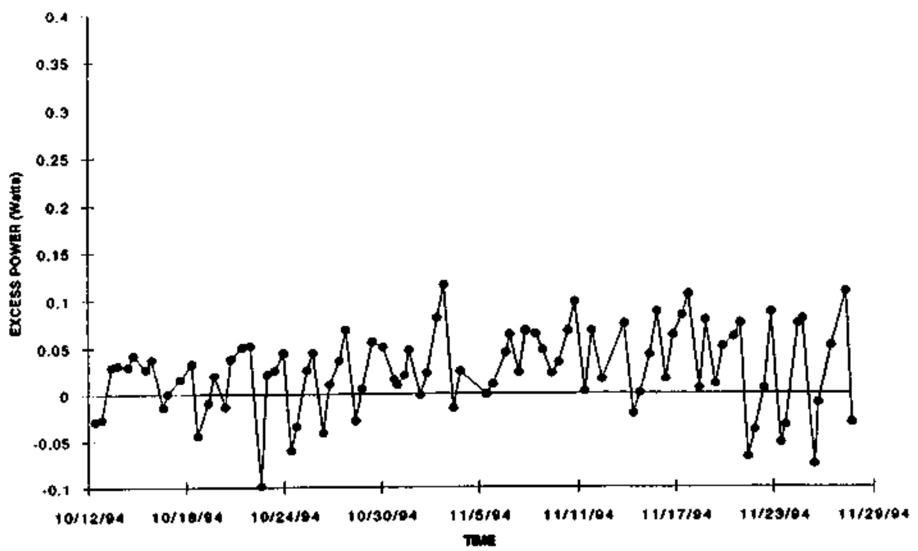

Figure 3. Experiment Showing No Significant Excess Power for an NRL Palladium-Boron Rod (2.5 mm x 2.5 cm, 0.75 weight % boron), Cell D. This rod contained a folded-over metal region that would act as a long crack.

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The 0.5 and 0.25 weight % boron alloys all had dimensions of 4 mm x 2 cm (V = 0.25 cm^3). Microscopic examinations of these four Pd-B cathodes following the experiments did not reveal any significant cracks, folded-over metal regions, or other flaws for these NRL materials. The high-success rate for excess-power production for Pd-B alloys suggests that this would be a fruitful area for further research. Perhaps the presence of B initially as an impurity in the palladium or the incorporation of B from the glass into the palladium during the experiment is a factor in the reproducibility problem for excess-heat production. It is also possible that the increased hardness of the palladium due to the added B allows it to better withstand the high stresses induced by the experiments.

A Pd-Ce alloy material was provided to us by Martin Fleischmann. The experiment using this cathode began on 15 February 1994 and the onset of excess power production was observed on 4 March 1994. The excess power versus time for the Pd-Ce cathode is displayed in Figure 4. The excess power levels for this cell reached values as high as 350 mW or 1.1 W/cm^3. The excess power production for Pd-Ce remained for over 100 days of electrolysis. A repeated run with the same Pd-Ce cathode again showed excess power levels up to 150 mW.

A puzzling helium result was obtained for the Pd-Ce cathode that produced the large excess power effect shown in Figure 4. Despite excess power measurements as large as 300 mW, no excess helium could be detected. These results are presented in Table 1. The companion cell employing a NRL Pd rod gave no excess power and almost the same amount of helium-4 (4.6 ±1.4 ppb) as found for the Pd-Ce experiment. This represents our only studies where valid excess power was measured but no excess helium was detected. An earlier experiment using a palladium cathode yielded 11% excess power (290 mW) but no detectable helium.[6] This 1990 experiment, however, was flawed due to a very low D_2O level in the cell.[6] Later experiments showed that this low D_2O level could produce a calorimetric error that would account for most of the reported excess power. There were no other palladium cathodes in 33 studies that did not show a correlation between excess power and helium production or no excess power and no excess helium.

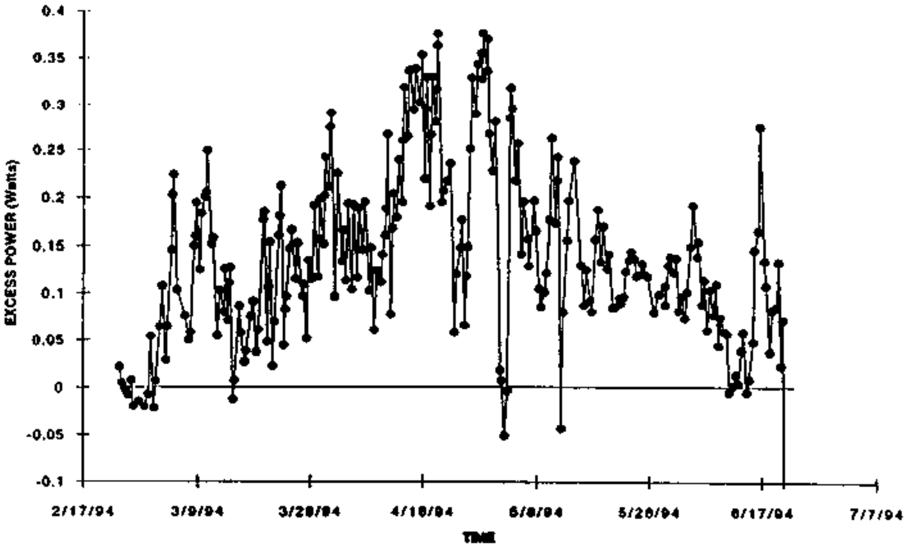

Figure 4. Excess Power Measurements for a Palladium-Cerium Alloy Rod (4.1 mm x 1.9 cm) Obtained From Martin Fleischmann, Cell C. Excess power peaks of 350 mW were observed.

TABLE 1. Excess Power and Helium Measurements in Experiments Using a Palladium-Cerium Cathode.

Electrode	Flask/cell, date	$^4He^a$, ppb	Px, W	$^4He/s\cdot W^b$
Pd-Ce Rod[c] (4.1 mm x 1.9 cm)	1/C (3/30/94)	4.6 ±1.4	0.17	0
Pd-Ce Rod[c] (4.1 mm x 1.9 cm)	4/C (4/19/94)	4.7 ±1.3	0.30	0
NRL Pd Rod[c] (4.1 mm x 1.9 cm)	3/D (3/30/94)	4.6 ±1.4	0	...
NRL Pd Rod[c] (4.1 mm x 1.9 cm)	2/D (4/19/94)	>1000[d]	0	...

[a] Metal collection flasks, analysis by U.S. Bureau of Mines, Amarillo, Texas.
[b] Corrected for background helium level of 4.5 ±0.5 ppb.
[c] D_2O + LiOD (I = 600 mA).
[d] Broken solder joint on metal flask.

One Johnson-Matthey palladium sample (1-mm wire) had previously given both excess heat and helium production at China Lake. There was an ample supply of this wire, hence the final experiments outlined for our laboratory by our sponsor were to use this wire. Four experiments using this palladium wire with our standard calorimeters were completed at China lake as the final segment of our program.[4] Excess power was obtained in one of these experiments. As shown in Figure 5, the excess power effect for this cell peaked at about 250 to 300 mW or 10% above the input power. There was a consistent excess power effect for this cell over most of the experiment. Turning the cell off for 3 days and then back on showed normal behavior, hence the excess power was not due to any calibration changes in the cell. A second calibration check was performed about 2 weeks later as shown in Figure 5. The experimental protocol used in the four Pd-wire experiments was to run at 100 mA/cm^2 for a day and then at 200 mA/cm^2 for 10 days. Calorimetric measurements were made at the normal cell operating current of 400 to 600 mA (1000 to 1500 mA/cm^2). The higher current density used for these small cathodes (A = 0.32 cm^2, V = 0.016 cm^3) is consistent with the higher power density of 15 W/cm^3 that was obtained. Most of our experiments yield about 1 watt of excess power per cubic centimeter of palladium at 100 to 200 mA/cm^2.

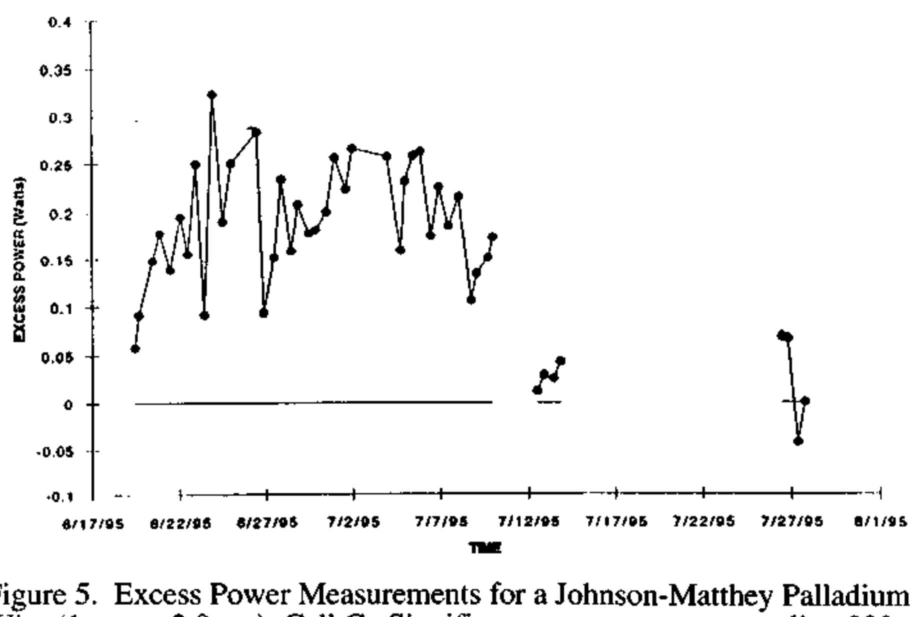

Figure 5. Excess Power Measurements for a Johnson-Matthey Palladium Wire (1 mm x 2.0 cm), Cell C. Significant excess power exceeding 200 mW was consistently observed. Calibrations checks following this experiment verify the excess power observations.

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4. Discussion
Fifteen experiments were completed where metal flasks were used in place of glass flasks to collect electrolysis gas samples for helium analysis. The use of metal flasks prevents the diffusion of atmospheric helium into the flasks after they are sealed. The valves used in these flasks were modified to effect a metal seal with a nickel gasket.

Six experiments using metal flasks where no excess power was measured are shown in Table 2. These samples were all from experiments that never produced any evidence for excess heat. The mean value of 4.5 ±0.5 ppb ^4He show that our experimental procedures are very consistent. The two Pd-Ce experiments shown in Table 1 fit in well with this mean value, hence no excess helium was produced.

In experiments producing excess power, seven helium measurements using these same four metal flasks were completed. Results for these experiments are given in Table 3. These results are all for experiments where steady, consistent excess power effects were measured. For example, the Pd-B rod results in Table 3 are for the experiment shown in Figure 1. Unlike the Pd-Ce alloy (Table 1), excess helium was measured for the Pd-B alloy. This was the only helium measurement conducted for the Pd-B alloy studies. After correcting for the background level of helium measured in Table 2 (4.5 ppb or 5.1×10^{13} atoms/500 mL), each experiment in Table 3 yields a helium-4 production rate close to 1×10^{11} ^4He/s•W. These results using metal flasks are consistent with our previous helium results using glass flasks.[6]

TABLE 2. Helium Measurements in Control Experiments Using Metal Flasks.
No excess power was measured.

Electrode	Flask/cell, date	$^4He^a$, ppb	^4He, atoms/ 500 mL
Pd Rod[b] (4 mm x 1.6 cm)	1/C (2/24/93)	4.8 ±1.1	5.5×10^{13}
Pd-Ag Rod[b] (4 mm x 1.6 cm)	2/D (2/24/93	4.6 ±1.1	5.2×10^{13}
Pd Rod[b] (4 mm x 1.6 cm)	3/C (2/28/93)	4.9 ±1.1	5.6×10^{13}
Pd-Ag Rod[b] (4 mm x 1.6 cm)	4/D (2/28/93)	3.4 ±1.1	3.9×10^{13}
Pd Rod[c] (1 mm x 1.5 cm)	3/C (7/7/93)	4.5 ±1.5	5.1×10^{13}
Pd Rod[d] (4.1 mm x 1.9 cm)	3/D (3/30/94)	4.6 ±1.4	5.2×10^{13}
(Mean)		4.5 ±0.5	($5.1 \pm 0.6 \times 10^{13}$)

[a] Helium analysis by U.S. Bureau of Mines, Amarillo, Texas.
[b] D_2O + LiOD (I = 500 mA).
[c] H_2O + LiOH (I = 500 mA).
[d] D_2O + LiOD (I = 600 mA).

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TABLE 3. Helium Measurements Using Metal Flasks.
Experiments producing excess power.

Electrode	Flask/cell, date	$^4He^a$, ppb	Px, W	$^4He/s \bullet W^b$
Pd Sheet[c] (1.0 mm x 3.2 cm x 1.6 cm)	3/A (5/21/93)	9.0 ±1.1	0.055	1.6×10^{11}
Pd Rod[c] (1 mm x 2.0 cm)	4/B (5/21/93)	9.7 ±1.1	0.040	2.5×10^{11}
Pd Rod[c] (1 mm x 1.5 cm)	1/C (5/30/93)	7.4 ±1.1	0.040	1.4×10^{11}
Pd Rod[c] (2 mm x 1.2 cm)	2/D (5/30/93)	6.7 ±1.1	0.060	7.0×10^{10}
Pd Rod[d] (4 mm x 2.3 cm)	1/A (7/7/93)	5.4 ±1.5	0.030	7.5×10^{10}
Pd Rod[d] (6.35 mm x 2.1 cm)	2/A (9/13/94)	7.9 ±1.7	0.070	1.2×10^{11}
Pd-B Rod[d] (6 mm x 2.0 cm)	3/B (9/13/94)	9.4 ±1.8	0.120	1.0×10^{11}

[a] Helium analysis by U.S. Bureau of Mines, Amarillo, Texas.
[b] Corrected for background helium level of 5.1×10^{13} ^{4}He/500 mL.
[c] D_2O + LiOD (I = 400 mA).
[d] D_2O + LiOD (I = 500 mA).

For our 33 experiments involving heat and helium measurements, excess heat was measured in 21 cases and excess helium was observed in 18 studies. Thus 12 experiments yielded no excess heat and 15 measurements gave no excess helium. If one uses these experimental results as random probabilities of $P_h = 21/33$ for excess heat and $P_{He} = 18/33$ for excess helium, then the probability of random agreement (P_a) for our heat and helium measurements would be

$$P_a = P_h \bullet P_{He} + (1 - P_h)(1 - P_{He}) = 0.512 \tag{1}$$

and the probability of random disagreement (P_d) would be $P_d = 1 - P_a = 0.488$. The presence or absence of excess heat was always recorded prior to the helium measurement and was not communicated to the helium laboratory. Based on our experimental results, the random probability of the helium measurement correlating with the calorimetric measurement is not exactly one-half. This is analogous to flipping a weighted coin where heads are more probable than tails. The probability of exactly three mismatches in 33 experiments, therefore, would be

$$P_3 = \frac{33!}{30!3!}(0.512)^{30}(0.488)^3 = 1.203 \times 10^{-6} \tag{2}$$

Similar terms can be calculated for two ($P_2 = 1.221 \times 10^{-7}$), one ($P_1 = 8.009 \times 10^{-9}$), or zero ($P_0 = 2.546 \times 10^{-10}$) mismatches in 33 experiments. The total probability of three or less mismatches in 33 studies would be

$$P = P_3 + P_2 + P_1 + P_0 = 1.333 \times 10^{-6} = \frac{1}{750{,}000} \tag{3}$$

This statistical treatment shows that the odds are approximately one in 750,000 that our complete set of heat and helium results could be this well correlated due to random experimental errors in our calorimetry and helium measurements. Furthermore, it is very unlikely that random errors would consistently yield helium-4 production rates in the appropriate range of 10^{11} - 10^{12} atoms/s per watt of excess power as given in Table 3.

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Finally, the three mismatches are the two Pd-Ce experiments given in Table 1, and the flawed 1990 calorimetric measurement where the D_2O level was much too low. Critics should carefully consider the probabilities presented in Equations 2 and 3 before dismissing this new science of anomalous effects in deuterated materials.[4,7]

TABLE 4. Summary of Palladium Materials Tested for Excess Power.

Source	d, cm	V, cm^3	Px/V, W/cm^3	Success ratio	
NRL Pd-B (0.75%)	0.6	0.57	0.6	2/2	
NRL Pd-B (0.75%)	0.25	0.12	2.1	1/2	(7/8)
NRL Pd-B (0.50%)	0.40	0.25	0.4	2/2	
NRL Pd-B (0.25%)	0.40	0.25	0.8	2/2	
JM Pd	0.63	0.36	1.4	9/14	
JM Pd	0.63	0.67	0.3	1/1	
JM Pd	0.40	0.20	0	0/2	(17/28)
JM (F/P) Pd	0.20	0.038	3.1	1/1	
JM (F/P) Pd	0.10	0.012	14.0	1/1	
JM Pd	0.10	0.02	15.0	3/7	
JM Pd-Ce (F/P)	0.41	0.25	1.1	2/2	
NRL Pd	0.40	0.25	0.4	1/2	(2/5)
Tanaka Pd sheet	...	0.05	1.2	1/3	
NRL Pd	0.40	0.25	0	0/4	
NRL Pd-Ag	0.42	0.21	0	0/3	
IMRA Pd-Ag	0.40	0.20	0	0/2	(0/19)
WESGO Pd (1989)	0.14	0.09	0	0/6	
Pd/Cu	(0.63)	0.02	0	0/2	
John Dash Pd sheet	...	0.04	0	0/2	
Co-deposition (1992)	(0.63)	0.002	75	2/34	

Most of the palladium materials investigated at China Lake are summarized in Table 4. Distinct groupings of the success ratio are readily apparent based on the source of the palladium material. A high-success ratio is found for Johnson-Matthey materials where 17 out of 28 studies gave excess heat. The highest success ratio is for NRL Pd-B materials that showed excess power in seven out of eight experiments. Other NRL materials, however, gave poor results, such as NRL Pd-Ag (0/3) and NRL Pd (1/6). The single excess-heat result for NRL Pd involved a second run of the same cathode. Several other Pd and Pd-Ag sources failed to yield any excess heat-producing experiments. This polarization of successful experiments according to the palladium source would be very difficult to explain by random calorimetric errors. These results indicate that the metallurgical preparation of palladium is a major factor for observation of the excess enthalpy effect. A similar conclusion concerning reproducibility of the excess-power production has been reported by McKubre et al.[8] Our results suggest that the presence of boron within the palladium may be a critical variable.

5. Summary

This field of anomalous effects in a deuterated system, which has come to be called "cold fusion," is a far more difficult research area than we might have thought 7 years ago. Progress at various laboratories around the world has not been as rapid as one might have hoped. Two technically challenging problems restrict progress: (1) irreproducibility and (2) scarcity of energetic (nuclear) products.

Although we have not succeeded in solving the irreproducibility problem, our results indicate that helium-4 is the missing nuclear product. This ^4He is the most likely nuclear product that could have remained so well hidden during the past 7 years.

The remarkable correlation of excess power with the source of palladium in Table 4 cannot be easily explained by any calorimetric errors. Furthermore, 30 experiments at our laboratory have shown a striking correlation between either excess power and helium production or no excess power and no excess helium. It is highly unlikely that our heat and helium correlations could be due to random errors. Finally, our calorimetric results, conclusions, and problems are practically identical to those reported by the SRI laboratory. In our opinion, these factors provide compelling evidence that the anomalous effects measured in deuterated systems are real.

This research area has the potential to provide the human race with a nearly unlimited new source of energy. Although our program is no longer funded, we hope that other scientists will continue to investigate this difficult research area until the challenging problems impeding progress are solved. It is still possible that anomalous effects in deuterated systems will prove to be one of the most important scientific discoveries of this century.

6. Acknowledgments

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