CALORIMETRY EXPERIMENTS IN THE PHYSICS DIVISION--ORNL

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September 14, 1989

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ABSTRACT

Four calorimetry experiments were performed with palladium cathode electrolysis cells to investigate the possibility of cold fusion heat production based on the reported results of Fleischmann and Pons.[1] Two of the cells contained 6.35 mm diam × 10 cm long palladium cathodes in a 0.2 M Li^{6}OD electrolyte, one cell contained a similar cathode in a 0.1 M Li^{6}OD electrolyte solution and one cell used a cast 1.27 cm diam × 10 cm palladium rod in a 0.2 M electrolyte. All four cells were constructed with platinum wire anodes. One of the cells exhibited an apparent 2-3 watt power excess for a period of approximately 300 hours of a total operating time of 1800 hours; each of the remaining cells remained in power balance for the 1800 hour period.

INTRODUCTION

Immediately following the announcement by Fleischmann and Pons at the University of Utah of the discovery of cold fusion in an electrolysis cell containing a palladium cathode, several experiments were begun at ORNL to investigate this claim. A number of electrolysis cells were constructed using palladium foil cathodes and platinum gauze anodes in an attempt to measure cold fusion produced neutrons. A neutron counter was assembled using NE213 scintillator detectors, which employed pulse shape discrimination

to reduce the effective gamma ray background. The background count rate of this detector was approximately 90 events per hour. Another detector located near the primary system was used to monitor any changes in the background level. No neutrons above the background rate were detected during these initial experiments. We then focused our attention on the report of excess heat result also made by the University of Utah group.

EXPERIMENTAL APPARATUS

Four calorimetry cells were constructed with an electrolyte volume of 300 cc in a 54 mm o.d. quartz envelope. A diagram of the calorimetry cells is shown in Fig. 1. Each cell contained a teflon plug in the top of the container with a number of penetrations for electrical connections, heavy water refilling, and sampling. Two 6.35 mm teflon rods projected through the top plug to support the palladium cathode rod in the center of the envelope. The teflon rods were spring loaded to allow for expansion of the palladium electrode during charging with deuterium. The anode was helically wound from platinum wire on the inside of a perforated quartz tube. The anode helix was wound on a mandrel and allowed to spring against the inside of the quartz tube for support. No internal recombiner was used to catalyze the recombination of the gases produced by electrolysis back into heavy water. The D_2 and O_2 gases were allowed to escape through a vent hole in the top teflon plug. The quartz cells were placed inside teflon cylinders that in turn were immersed in a temperature controlled water bath. A 2.5 mm gap between the quartz and the teflon cylinder was filled with D_2O and contained a platinum resistance
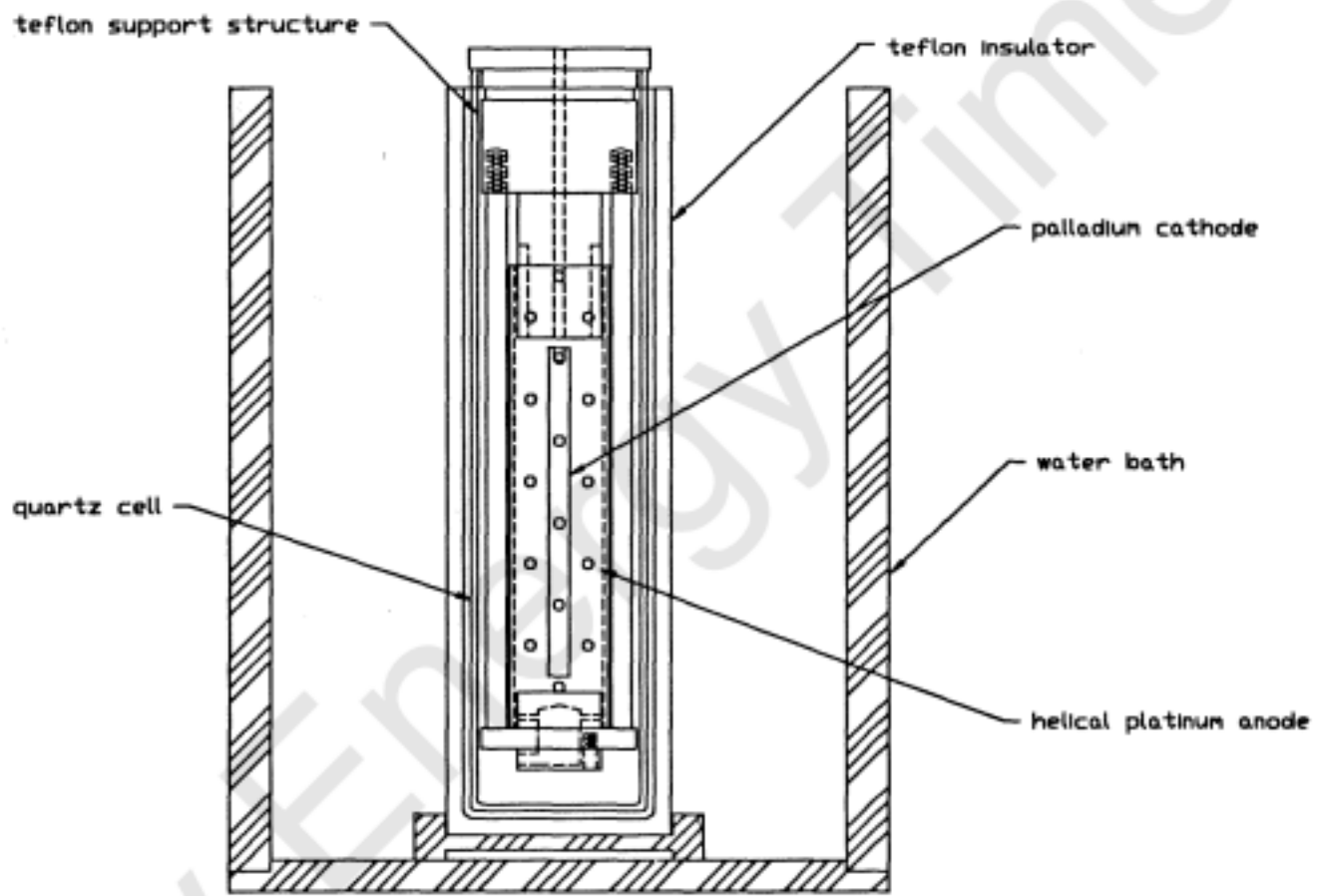
Fig. 1. Diagram of the design of the calorimetry cells.

temperature detector (RTD). Another platinum RTD was placed in the water bath adjacent to the teflon socket. A cell containing a resistance heater similar in size to the palladium cathode and identical in construction to the actual cells was placed into each teflon socket, prior to activation of the cells, for calibration. Varying amounts of electrical power were applied to the resistance heater and the temperature difference across the teflon was noted for each setting. Calibration curves for three of the cells are shown in Fig. 2. The calibration data were fitted with a fourth order polynomial for use with the cell calorimetry data. The second order term was very small and the third and fourth order terms nearly zero. The cells were periodically re-calibrated during the course of the experiments, as well as whenever the bath temperature was altered. A shielded neutron counting chamber was prepared next to the constant temperature baths to permit neutron counting of the cells during operation without interruption of the electrolysis.

ELECTRODE PREPARATION

Two of the cells contained 6.35 mm diam × 10 cm long annealed palladium cathodes, one of which was pre-charged in D_2 gas to a stoichiometry of 0.6, in a 0.2 M Li^6OD electrolyte; one cell contained a pre-charged annealed cathode in a 0.1 M Li^6OD electrolyte solution; and one cell used a cast 1.27 cm diam × 10 cm palladium rod in a 0.2 M electrolyte. Annealing was performed by heating the rods to a temperature of 900°C for 4 hours in vacuum. The cast 1.27 cm diam rod and the 6.35 mm diam non-pre-charged rod were baked at 200°C in vacuum for 24 hours to remove any residual protium before being placed in operation. The experimental parameters for the palladium
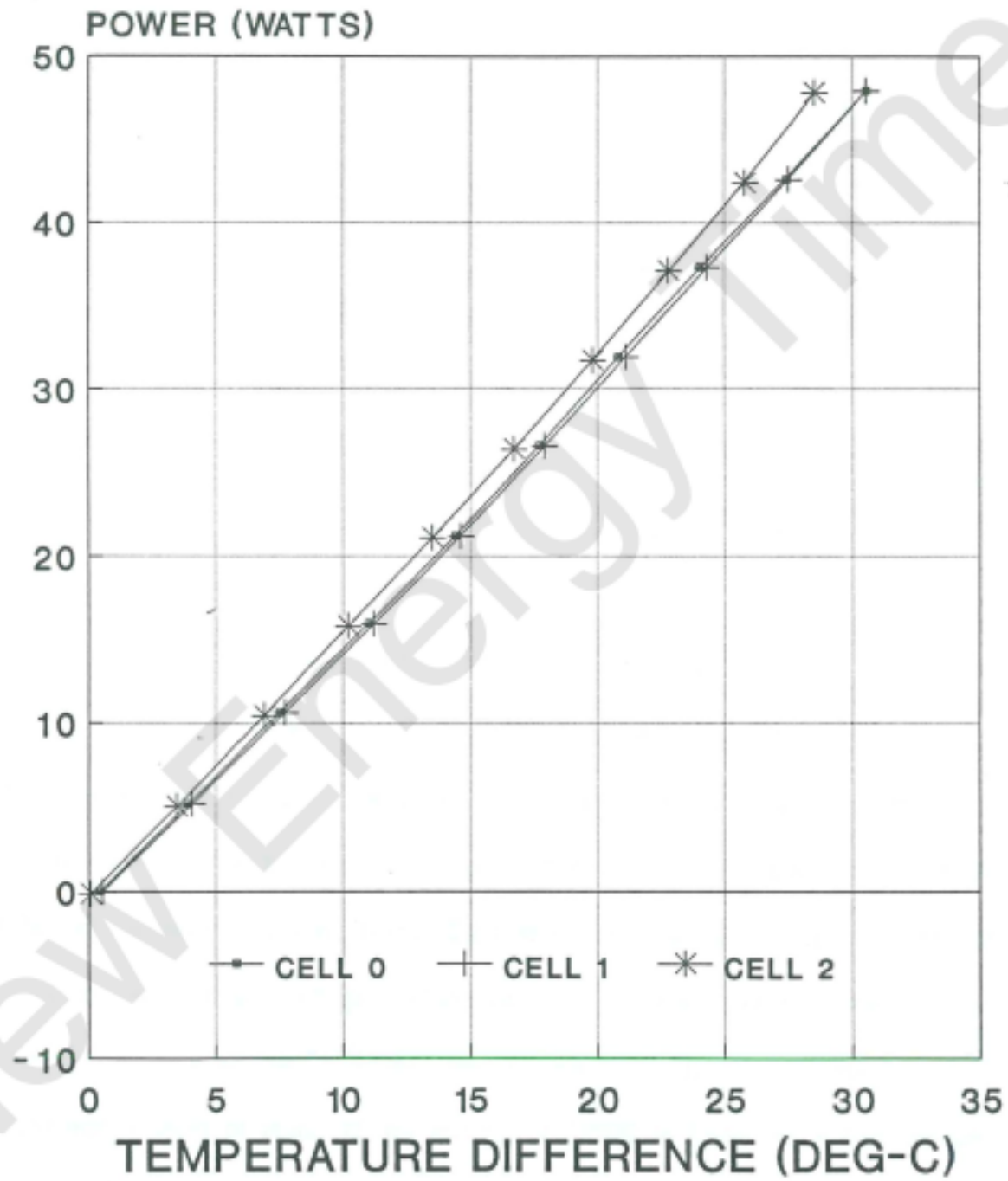
Fig. 2. Calibration curves for three of the calorimetry cells.

cathodes are summarized in Table 1. The three 6.35 mm o.d. rods were purchased from Johnson-Matthey. The cast rod was fabricated from stocks of palladium obtained at ORNL.

RESULTS

The cells were operated at an initial current density of 50 mA/cm^2 for 48 hours and then at a current density of 250 mA/cm^2 for over 1800 hours. Referring to the cell numbering from Table 1, cells #1,#2, and #3 have remained in power balance within an experimental uncertainty of ±1 watt for the duration of the experiments. However, cell #0 exhibited an apparent excess power level of approximately 3 watts for a 300 hour period beginning 180 hours after the beginning of the experiment. This imbalance was approximately 10% of the input power. Our calorimetry cells did not use an internal catalyst to promote the recombination of the electrolyzed gases back into heavy water. D$_2$O was added to the cells every twelve hours to replace the water depleted by electrolysis. By carefully recording the water usage rate, we were able to determine that no recombination was occurring in the cells.

The power balance for our cells was determined from the equation

$$P_{imbalance} = \text{heat output} + \text{electrolysis} - \text{electrical input} .$$

The heat output of the cells was measured by the calibrated platinum RTD's. The electrolysis term was determined by measuring the make-up water for the cells assuming the exhaust gases were 100% humidified. The electrical input was determined by monitoring the voltage and current going to the cells. The electrolysis cells were driven

TABLE 1
EXPERIMENTAL PARAMETERS

Cell No.	Electrode Configuration	Electrolyte Concentration	Electrode Conditioning
0	6.35 mm diam	0.2 M LiOD	Annealed
1	6.35 mm diam	0.2 M LiOD	Annealed/ pre-charged/ Arsenic added
2	6.35 mm diam	0.1 M LiOD	Annealed/ pre-charged
3	12.7 mm diam	0.2 M LiOD	Cast

Note:

1. All rods were 100 mm long.
2. The 12.7 mm diam rod was dropped cast in a chilled copper mold. The rod was x-rayed to identify any possible voids.
3. All rods were heated in vacuum to remove residual protium.
4. Current Density = 250 mA/cm2

by computer-controlled constant current sources and the voltages across the electrodes were monitored by a digital-to-analog converter in the control computer. The constant current power supplies were calibrated prior to the experiment. At an operating current density of 250 mA/cm^2, the total current to the 6.35 mm diam rod cathodes was 5.03 amps. At this current, 1.88 grams of D_2O were electrolyzed per hour of operation, resulting in volumetric water usage rate of 1.702 cc/hour. Using the value of 70.41 kcal/mole for the heat of formation of heavy water, this electrolysis rate results in 7.635 watts of power consumption. Assuming that the exhaust gases have a relative humidity of 100%, the total water consumption rate we calculate is 1.88 cc/hour corresponding to a total electrolysis power level of 7.77 watts, including power due to evaporation. The consumption of D_2O was monitored over the entire course of the experiment. Figure 3 shows a graph of the measured replenishment rate for the first 21 days of the experiment. The open circles are the measured values and the straight line is a straight line fit to the data points. The fitted value of 1.87 cc/hour is in excellent agreement with the predicted value of 1.88 cc/hour. Using this result the heat balance equation becomes

$$P_{imbalance} = heat + 7.77 \text{ watts} - V_{cell} \times I_{cell}.$$

In addition to control of the power supplies and constant monitoring of the cell parameters, the control computer was programmed to sweep the cell current once each hour. The duration of the current sweep was 5 seconds. The slope of the I-V curve is the electrolyte resistance.[2] By multiplying the square of the cell current by this quantity, the ohmic power deposited in the electrolyte may be determined. Figure 4 contains a plot of the measured parameters of cell #0 for the first 600 hours of operation. The lower
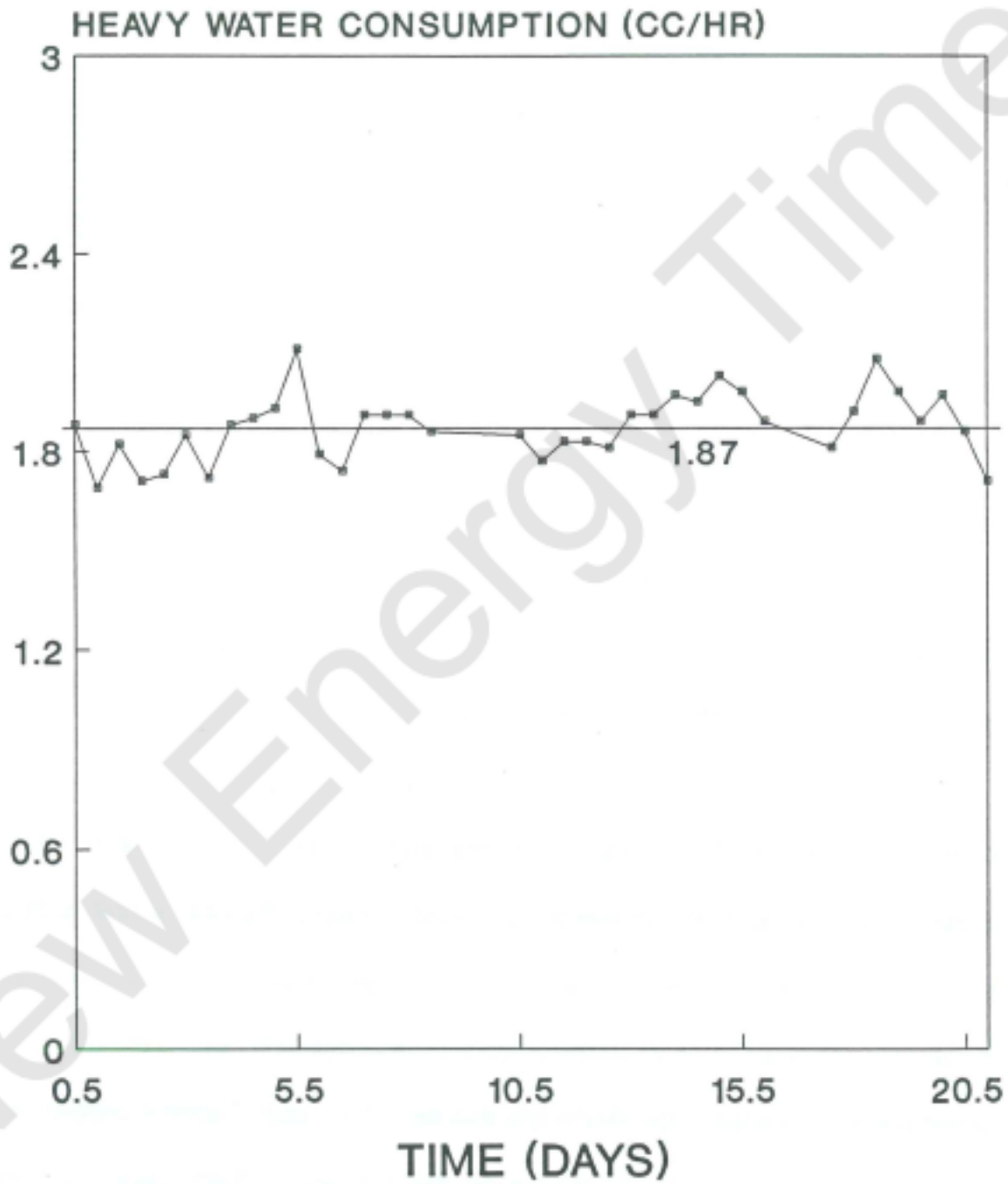
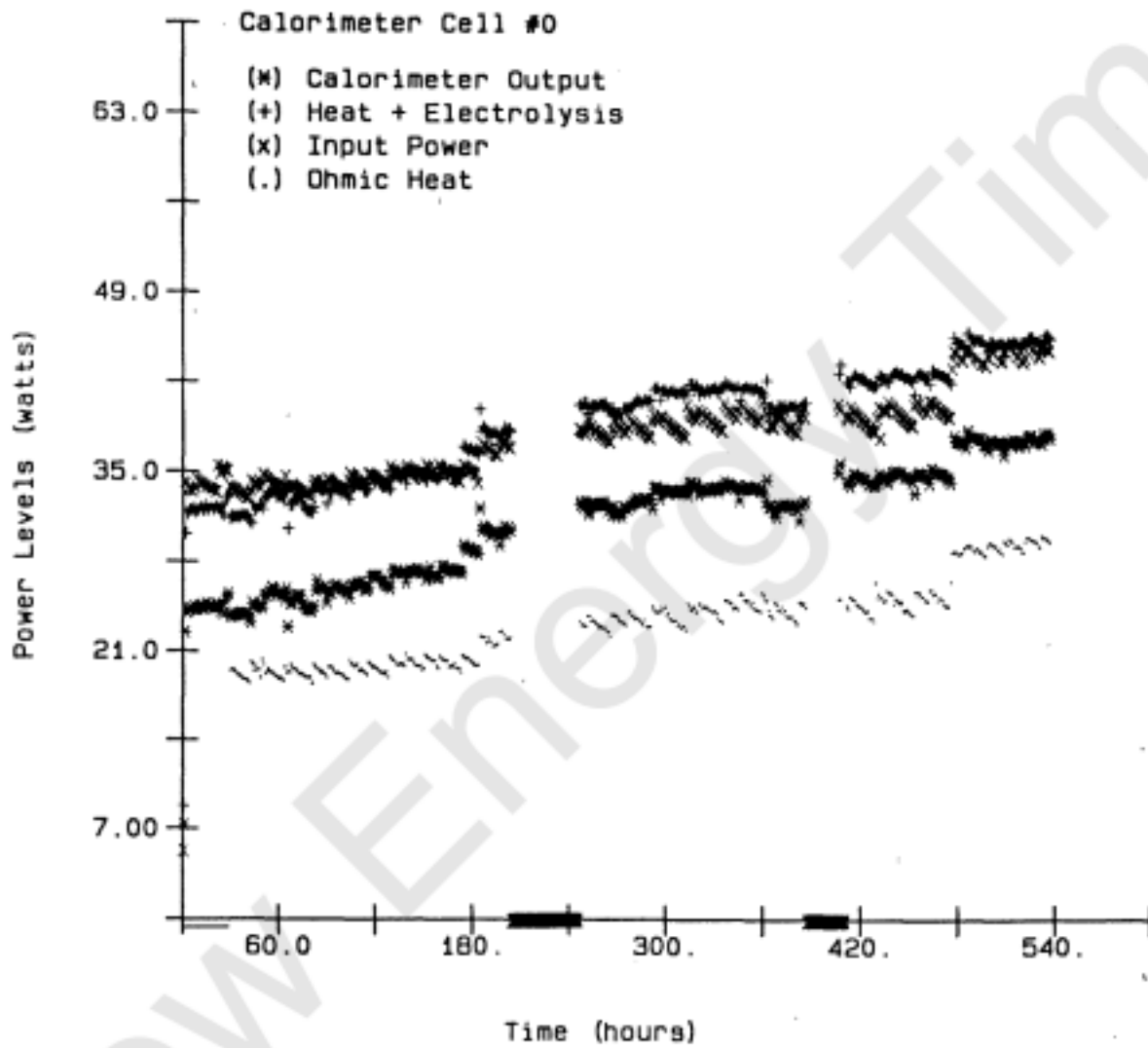Fig. 3. Heavy water consumption in cell #0 for the first 21 days of operation.

Fig. 4. The measured output parameters of cell #0.

curve, represented by the dots, is the ohmic power, $I^2_{cell} \times R_{electrolyte}$, deposited in the electrolyte. The curve represented by the asterisks is the measured calorimeter power output determined by comparing the temperature difference across the teflon with the calibration curve obtained with the electrical resistance heater. The curve represented by the x's is the electrical input power to the cell, $V_{cell} \times I_{cell}$. Finally, the curve represented by the (+) symbol is the sum of calorimeter plus the electrolysis power value of 7.77 watts. During the initial 75 hours of the experiment, cell #0 exhibited a slight negative heat balance. At a level of less than 2 watts tapering to zero at approximately 75 hours, this indicates an energy storage of approximately 270 kjoules. This far exceeds the hydride heat of formation value of approximately 3 kjoules calculated for these rods. Cell #0 remained in balance until the 180 hour mark when a positive imbalance of two watts was observed. Twelve hours after this apparent excess heat event began, the temperature of the water bath was inadvertently changed from an initial value of 18°C to 13°. The ohmic power increased at this point due to the increased electrolyte resistance at the lower temperature. The input power also increased with the increased electrolyte resistance because the cells were driven by constant current sources. The calorimeter output also increased with the lower temperature and maintained the 2 watt excess. The sawtooth behavior, which is most evident on the input power and ohmic power curves, with a period of approximately 12 hours occurred because of the changing level of liquid in the cell due to electrolysis and the periodic refilling twice a day. As the liquid level decreases, the heat transfer area changes and the electrolyte resistance decreases as the molality increases. Although the affect of these changes is not accurately known, we only use data taken at

the peaks of the sawtooth, where we know the calibration is accurate, for evaluation. The gap in the data represents a period when the cell was removed from the calorimeter socket for 30 hours. During this period, the socket was re-calibrated at the lower temperature and the cell was placed in the neutron counter. All of the parameters of the cell were monitored during this time except heat output. We arbitrarily chose to display data taken only when the cell was in the socket. The imbalance increased slightly until the 370 hour mark when the temperature of the bath was deliberately raised to 18°C. The imbalance nearly disappeared but recovered and increased over the next 120 hours to slightly over 3 watts. At approximately 480 hours the cell bath temperature was lowered to 5°C in an attempt to study the effect of temperature changes on the imbalance. The excess power disappeared at this point and repeated temperature and current cycling failed to reproduce the effect. The power balance for cell #0 for the first 25 days of operation is shown in Fig. 5. The data were averaged over a twelve hour period for this graph. We continued the experiment for a total period of 1800 hours with no recurrence of the excess heat observation. The other cells remained in accurate power balance during the entire experimental period. During the observation of heat imbalance in cell #0, cell's #0 and #1 were switched in their calorimeter sockets to verify that the apparatus was working properly. The power readings for each cell during this period were consistent with the calibrations for both cells, the measured imbalance in cell #0 remained irrespective of the calorimeter socket used.
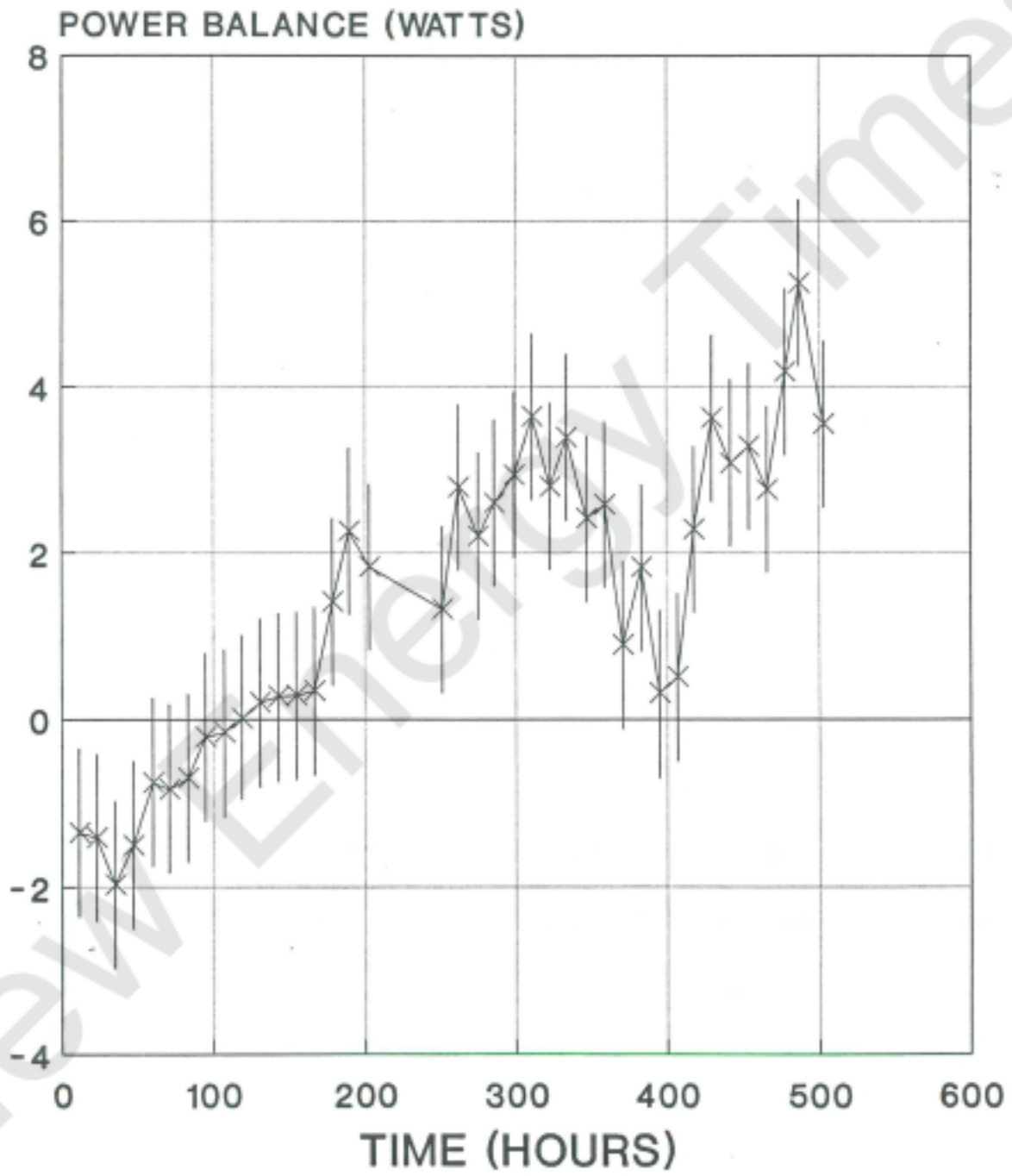
Fig. 5. Power balance plot for cell #0.

ADDITIONAL MEASUREMENTS

Shortly after the power imbalance was discovered, cell #0 was removed from the calorimetry socket and placed in a shielded neutron counter containing a pair of NE213 scintillator detectors with pulse shape discrimination. The neutron emission level of the cell was determined to be less than 1×10^{-24} neutrons/sec/d-d pair, as set by the background level of the counting system. The tritium level of the initial electrolyte fill of D_2O was measured to be 1.0×10^6 dpm/cc and increased to a level of 1.3×10^6 dpm/cc 50 hours after the beginning of the apparent excess power production. The accuracy of the tritium measurement was at best 10 per cent and because of this uncertainty we draw no conclusions from our measurement.

CONCLUSIONS

During a period of approximately 300 hours, one cell of four exhibited a positive power imbalance of 2-3 watts after a short period of negative imbalance. The mechanism responsible for this behavior has not been identified; it appears to be a transitory effect with some dependence on temperature.

REFERENCES

1. Martin Fleischmann and Stanley Pons, J. Electroanal. Chem. <u>261</u>, 301-8 (1989).

2. J. S. Bullock, IV, G. L. Powell, and D. P. Hutchinson, <u>Electrochemical Factors in Cold Fusion Experiments</u>, TM Y/DZ-490, Visuals prepared for Workshop on Cold

Fusion Phenomena, Sant Fe, New Mexico, May 23-25, 1989, Martin Marietta Energy

Systems, Inc., Oak Ridge Y-12 Plant, May 1989.