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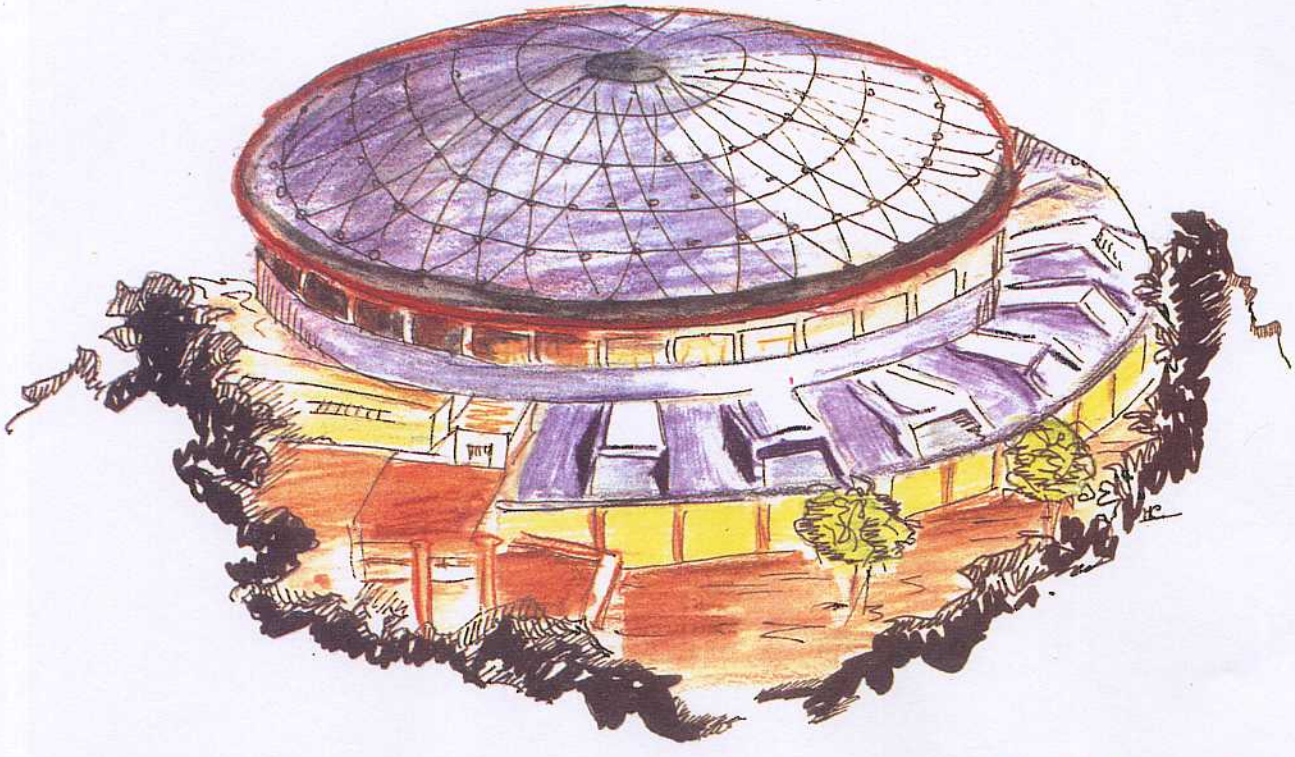

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MEASUREMENTS OF EXCESS HEAT AND TRITIUM DURING SELF-BIASED PULSED ELECTROLYSIS OF Pd-D_2O

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ABSTRACT

Following the Takahashi results about large excess heat by pulsed electrolysis, we built a gas–closed flow calorimeter to perform pulsed current electrolysis. Some blank tests, using Au plate cathode, were carried out to characterize the system. Four cold–worked Pd sheets were tested and two of them produced 7.5% and 6% of mean excess heat for many weeks. The others Pd sheets did not produce excess heat though one of them, after a deuterium re–loading, gave up to +25% of excess heat but only for few hours. Tritium analysis was carried out and some coincidence between tritium production and excess heat was found.

1. – APPARATUS

We realized an electrolytic system [Fig. 1] using a cylindric polyethylene vessel (12 cm of diameter, 7 cm height, 1 cm tickness) as an improved type of that reported by A.Takahashi [1].

We put, as cooler, a double turned copper coil (nickel coated and covered by acrylic resin) inside the vessel. A 1.2 Kw (maximum power) electrical heater was placed on the bottom of the vessel; like the cooler, it was nickel coated and covered by acrylic resin. The use of this particular insulation is required to avoid a contamination of the electrolytic solution due to the aggressivity of concentrated base(0.3M/l of LiOD or LiOH). The electrodes used were sheets (2.5 cm, 2.5 cm, 0.1 cm) as cathode and a Pt wire (100 cm long, 0.05 cm of diameter) turned around as anode. The electrodes were separated by 1 cm teflon bars and located at the center of the bottom of the vessel; a diagonal Pt wire (0.05 cm diameter), 0.3 cm far from the surface of the sheet, was used as the voltage reference electrode.

A 1 cm tick Ni rod, like inner temperature sensor, was put,very close to the electrodes. Three Pt short wires (1, 1.5 and 2.5 cm long) were put on the top of the vessel and are used for the purpose of solution level sensors.

All the materials used into the vessel were tested against unwanted poisoning of the solution.

The vessel was thermal insulated from environment by 5 cm tick polystyrene and 7 turns of alumined mylar.

The cooling system [Fig. 2] consists of a inner coil, a peristaltic pump and a water bath; the cooling liquid is ordinary water.

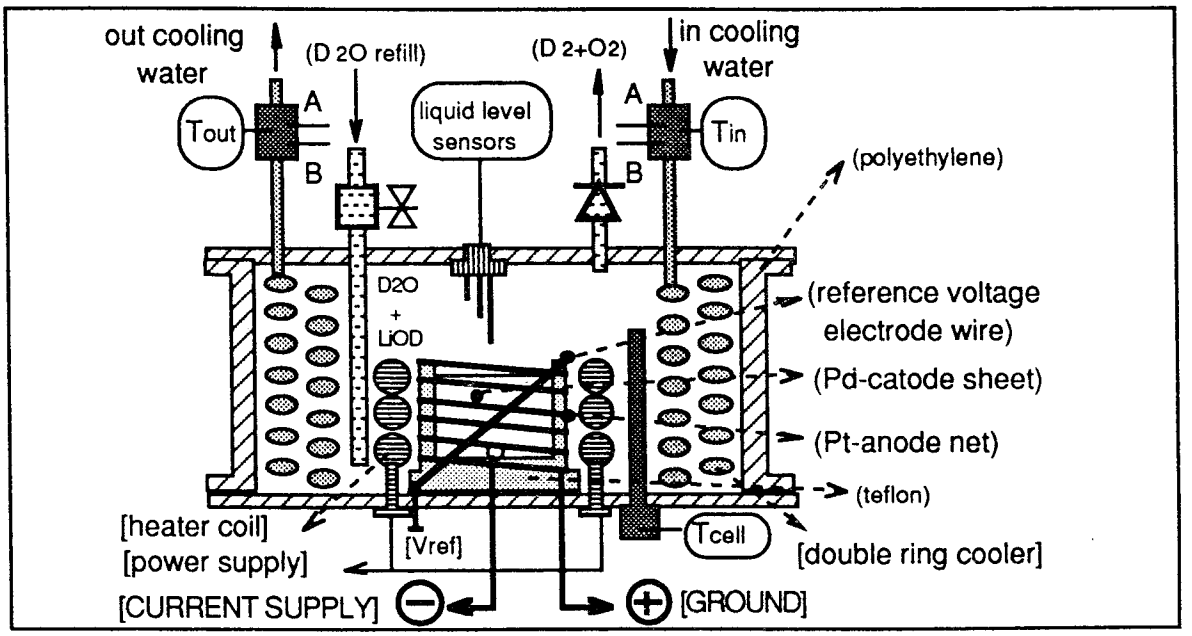

FIG. 1 – Inner vessel.

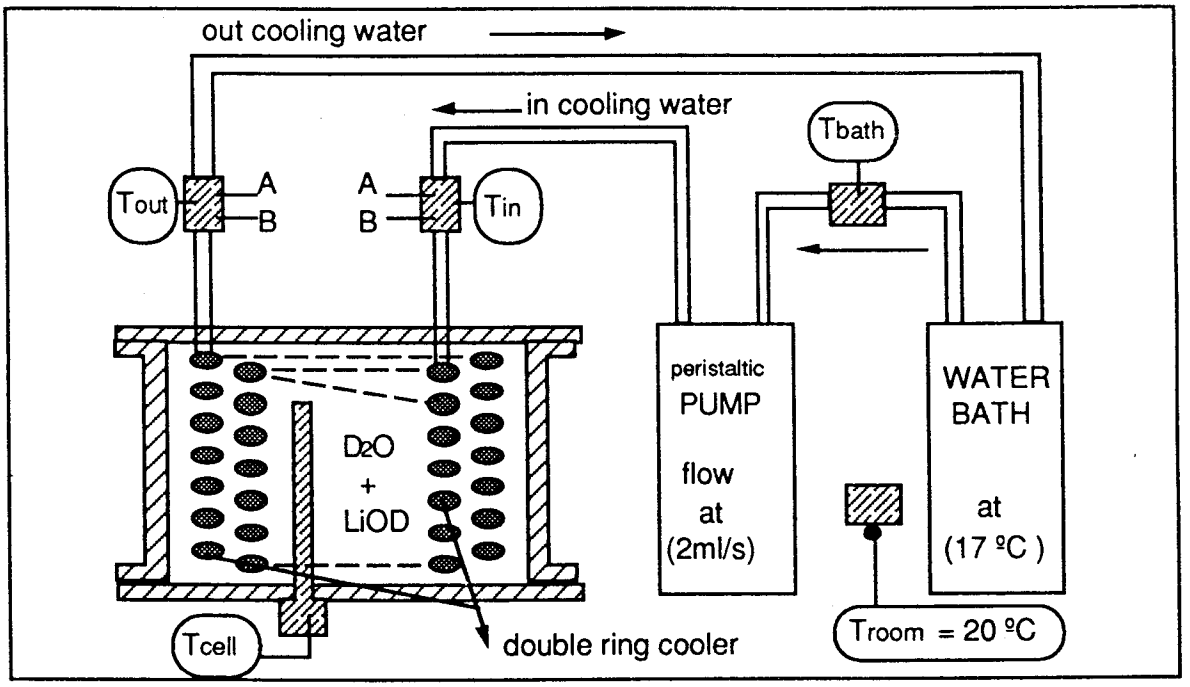

FIG. 2 – Cooling system.

The inner coil (0.5 cm of diameter and 4 m long) was overwhelmed to improve the cooling efficiency of the cooler fluid.The computer–controlled peristaltic pump was used to get a variable, constant cooling, flow ranging between 0.5 and 30 ml/s.

The water bath allows to get a 17 °C constant input temperature.

Seven temperature sensors (Si device AD590) are used and their sensitivity is 1 μA/°C. Using a 10 kΩ loading resistor in the circuit, we get, trough an operational amplifier (OP227), a value of 10 mV/°C. The most important sensors placed outside the vessel, the input and

output of the cooler, are doubled. This configuration allows to get a double independent control about the output thermal energy.

The outgoing gases from D_2O dissociation are sent into a close system as shown in Fig. 3. A bottle is used to condense the vapors from the warm solution due to the electrolysis. Two optional large volume rubber balls are used to collect the gases and vacuum/over–pressure pump is used for pressure operating tests. A recombiner (gas diffusion electrode of E–TEK, USA), working at room temperature, is placed into a bottle to recombine the D_2 and O_2 gases into D_2O. The D_2O is routinely collected both for periodic tritium analysis and measurement of dissociated water (to check against self–recombination into the electrolyte vessel). Two pressure sensors (one analogic and one other digital) are used. Two in–line low–drop pressure valves are used to avoid a gas return to the vessel from the recombiner (mainly CO_2). A teflon tube entering into the vessel is used to refill the D_2O.

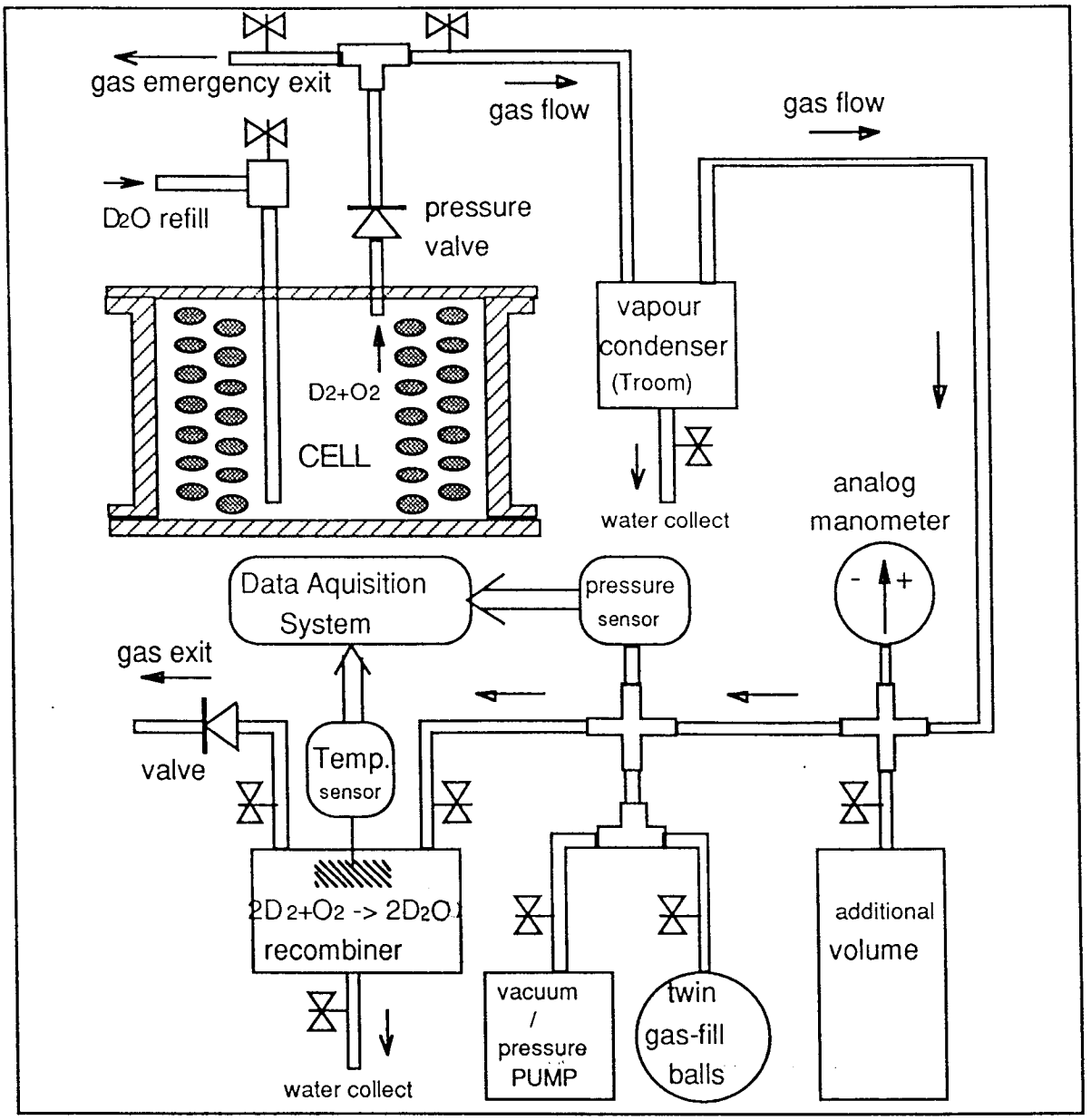

FIG. 3 – Gas system.

A specific home–made circuit [Fig. 4] was used to control the constant–current generator in order to perform a time dependent electrolysis. The typical shapes used were a 20 minutes period, 0.25 to 5.1 A saw–tooth wave and 20 to 360 minutes half period, 0.25 to 7 A square wave. The wave controller is auto or manual, time and amplitude, selectable.

Two fast recovery–time high power diodes (mod. 40HFL80S05 by IR) were inserted between the generator and the electrodes to avoid a deuterium deloading from the Pd cathode during the fast transition current edge [3]: a reverse voltage polarization can occur for short time in this condition.

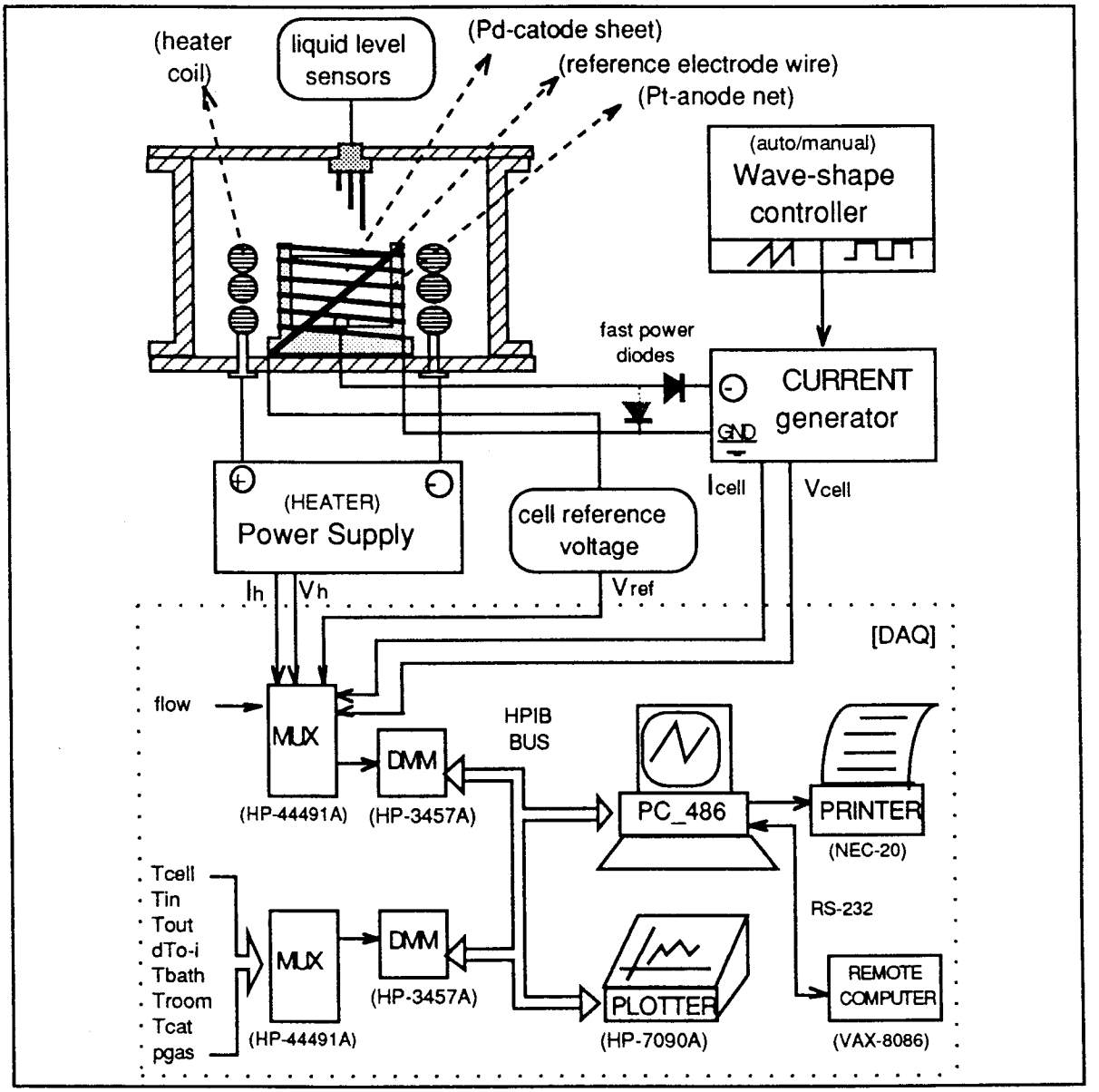

FIG. 4 – Power supply and acquisition system.

An independent voltage generator is used to supply the inner heater for calorimetric calibration.

All the electric and thermal parameters were computer acquired by a IEEE488 bus connect to two 6.5 digits high sensitivity DMM (HP–3457A) multiplexed. They are: seven temperatures

(absolute and differential inlet and outlet cooling fluid, inner vessel, water bath, recombiner and room), current and voltage of the vessel, reference cathode voltage, outgoing gas pressure and peristaltic pump flow. Three of these parameters were independently selected and on–line plotted by a high resolution color graphics plotter (HP–7090A).

A PC–486 computer was used to monitor and acquire the parameters and linked to remote computer (VAX–8086) to store and off–line analyze the data.

2. CALIBRATION AND EXPERIMENTAL PROCEDURES

We performed two different types of thermal calibration: electric calibration, using the inner heater, and electrolytic calibration during the electrolysis with an Au plate cathode. Generally the calibration were performed before and after a measurement. In Fig. 5 are shown electric calibration data ranging over 1 month performed in 4 different ways changing or the electrode (Au or Pd) or the electrolyte ($LiOH+H_2O$ or $LiOD+D_2O$).

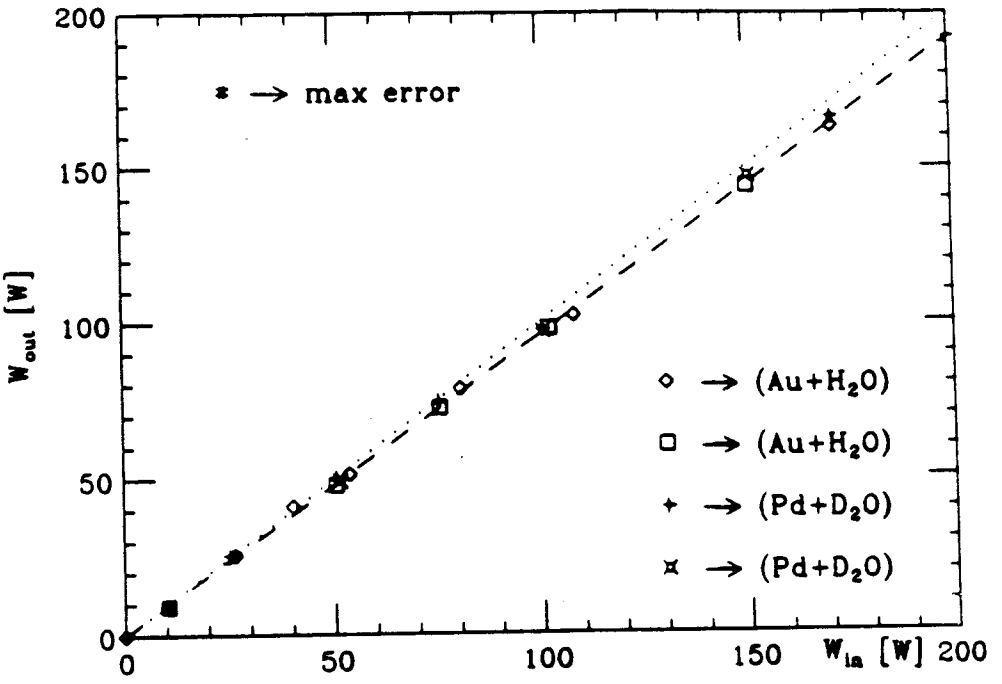

FIG. 5 – Calorimeter thermal calibration.

The data show the linearity and stability of the calorimeter up to 180 W of input power, calculated as the product of the voltage times the current at the heater, in respect to the output power (in watt) calculated as (1):

$$W_{out} = K \cdot \phi \cdot \Delta T \qquad (1)$$

where, K= 4.184 J·/(ml·K) is a constant conversion factor taking into account the specific heat of cooling fluid (light water), ϕ is the cooling fluid flow in ml/s, ΔT is the temperature difference between the output and the input of the cooling fluid. The slope difference between the ideal curve (dotted in the plot), in the case of no heat lost by dissipation, and the straight interpolation curve of the data is 4 ± 1% (because the thermal conductivity of vessel walls and water vapors). This slope difference is 5 ± 1% in case of electrolytic calibration (Au cathode and $LiOD+D_2O$ solution) and the increase is almost due to the energy loss because outgoing

gases. The sensitivity of the calorimeter, flow dependent, is 0.418 W/(ml/s) if cooling fluid is water; the resolution, dependent on thermometers sensitivity and flow stability, is estimated to be about 1.5%.

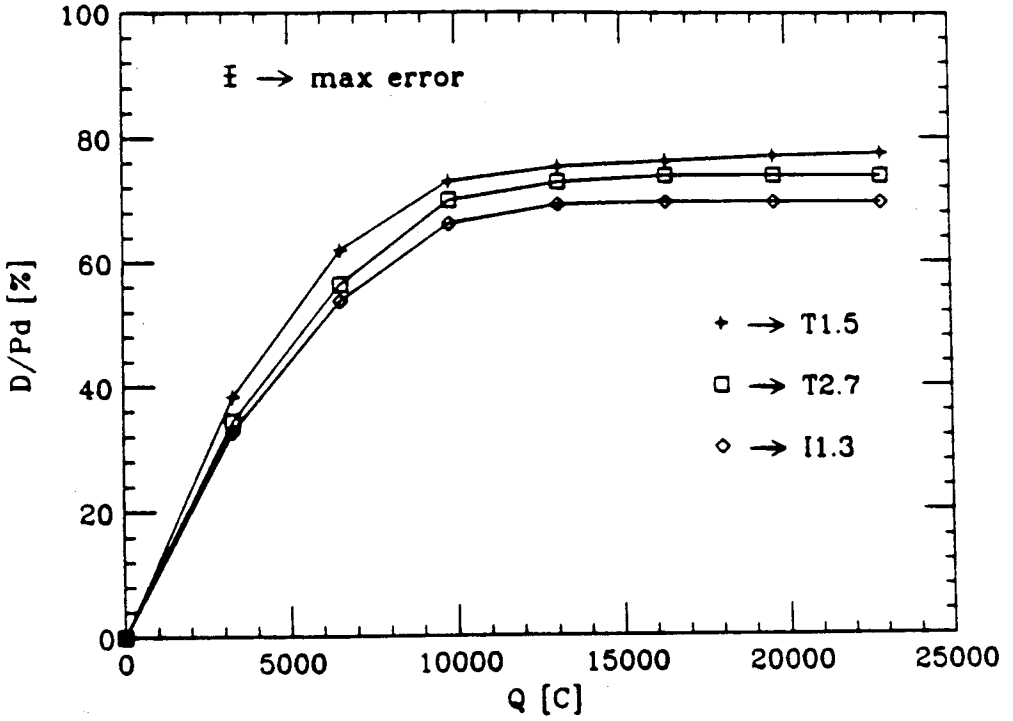

FIG. 6 – D/Pd ratio for 3 different Pd sheets.

A specific procedure was adopted to measure the D adsorbed quantity into Pd cathode. During the 6 or 7 first current saw–teeth, the recombiner was excluded and the pressure of electrolytic gases (D_2+O_2) was collected into a well known volume. From the D_2 gas missing pressure, because D adsorbed by cathode, we could calculate the charging ratio D/Pd. After the sixth current ramp the missing pressure measurement sensitivity becomes too low to estimate the D/Pd variation. After the tenth ramp we opened the recombiner to the gas system. In Fig. 6 it is shown the D/Pd ratio versus the electric charge flowed between the electrodes for three different Pd sheets: each data point in the plot corresponds to the D/Pd value cumulated during a ramp. A later D/Pd independent check, based on D_2 gas evolution during Pd discharging at the end of the experiment (with no current applied to the electrode) gave a similar results; we supposed, in this last case, that the equilibrium ratio is 0.67 at STP.

Several tests were performed to study the electrolytic processes and characterize the calorimetric system.

Blank tests were performed using a Au cathode sheet and the electrolytic solution (0.3 M) was or H_2O+LiOH or D_2O+LiOD. The excitation used, as before described, was pulsed current: ramp current from the beginning of the test (until half a day maximum) and then square wave current (several days).

The D_2O from the recombiner was periodically collected and its Tritium contents was analyzed.

A neutron detector (REM counter) was located very close to the vessel to monitoring large neutron emissions just for safety reasons.

3. RESULTS

During two months of experimentation 4 cold worked Pd sheets, by two different Japanese Firms, were tested: Tanaka Kikinzoku K.K. batch #1 (we call T1.2 and T1.5 which hardness is 155÷170 Vickers at 200g–10s) and batch #2 (T2.7) production (hardness: 145 Vickers), and IMRA Industries batch #1 (I1.3) production. Similar Pd sheets from Tanaka batch #1 and #2 were tested by E.Storm [2]. In Table I is reported the list of all the tests performed.

Table I – List of the tests performed.

TEST	DENSITY g/cm^3	DATE d/m/y	CURRENT A	ΔE/E %	TRITIUM (excess)	NOTES
HEATER	——	2/8/92 3/8/92	DC	——	——	calib
Au/Pt LiOH+H2O	——	3/8/92 4/8/92	ramp+sqr max (4A)	——	——	blank
Au/Pt LiOD+D2O	——	4/8/92 6/8/92	ramp+sqr max (4A)	——	± 3%	blank
Pd/Pt [T1.2]	≈11.8	6/8/92 25/8/92	ramp+sqr max (5A)	12% max < 7.5% >	(26%)	D/Pd >0.75
Au/Pt LiOD+D2O	——	7/9/92 12/9/92	ramp+sqr max (5A)	——	± 3%	blank
Pd/Pt [I1.3]	11.99	12/9/92 22/9/92	ramp+sqr max (7A)	< 2% (25% peak)	(18%)	D/Pd=0.69 (≈0.84)
Pd/Pt [T2.7]	11.99	23/9/92 2/10/92	ramp+sqr max (7A)	< 2%	unknown	D/Pd=0.72
Pd/Pt [T1.5]	11.75	3/10/92 24/10/92	ramp+sqr max (7A)	8% max < 6% >	(36%)	D/Pd=0.79 running

No excess heat (±2%) was ever detected during the blank runs.

No excess tritium (±3%) was detected,during the blanks, apart the enrichment due to electrolysis, computed with a value of 2 for the isotopic separation factor.

The T1.2 Pd sheet gave excess heat up to about 12% maximum (≈ 4 W of ≈ 30 W mean input power), two days after the beginning of the run [Fig. 7]. At the beginning, the current was ramped for 1 day and the excess heat occurred just some hours after the start run. During the following 5 days, with square wave current, the mean excess heat was about 7.5%. After that we retry to use ramp current, hoping to increase the excess heat by a D over–loading into the Pd, but the excess heat decreased sensitively.

After 3 days of ramp current we switched again on square wave current and the excess heat returned to a average value of 7.5%, lasting for 10 days. A long time main Laboratory black–out abruptly stopped the test. An overall excess heat of about 3 MJ were produced in 19 days. Because we did not measure at the beginning the maximum D/Pd charging value, we estimated this value (>0.75) when the plate was discharged. A total of +26% excess Tritium (+240 dpm/ml) was measured from the recombined D_2O water collected, taking into account the enrichment factor (≅2) of the tritium in the solution.

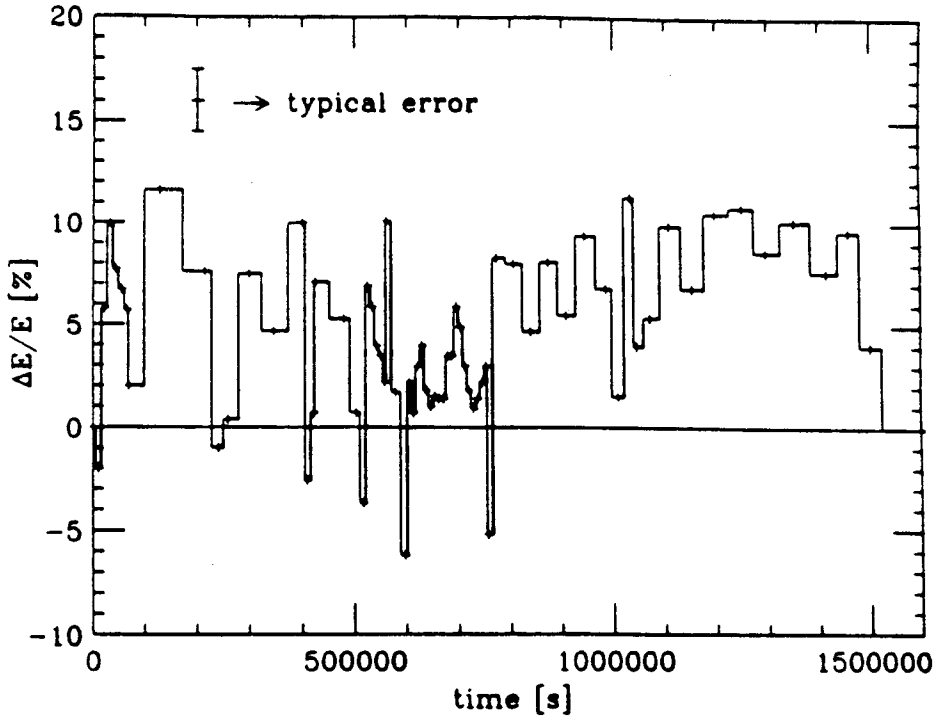

FIG. 7 – The T1.2 Pd sheet gave excess heat up to +12%.

The I1.3 Pd sheet did not produce relevant excess heat up to 7 days so we decided to stop the current supply for 12 hours letting the Pd electrode to deload the over–charged deuterium. After that we restarted the deuterium loading with some current ramps: the D/Pd reached the value of 0.84 ±0.04 starting from 0.67 (D/Pd value at equilibrium at STP); we note that the previous first charging up D/Pd value was 0.69. After this reloading, we used square current further increasing the high level from 5.1 up to 7.2 A. After this operation the excess heat reached the 25% peak value lasting just some hours. During the 2 days following no relevant excess heat appeared [Fig. 8]. The adding of borosilicate, to check if glass contamination can help the D adsorption on Pd surface, did not produced relevant effects. The overall excess Tritium produced was estimated be around +18% (+172 dpm/ml).

The T2.7 Pd sheet, operated in the same conditions of the previous sheets, produced no relevant excess heat (<2%) during 9 days of experiments.

The T1.5 Pd sheet gave the highest D/Pd value on the first charging up (D/Pd ≅0.79). After 2 days of current ramp, the current square wave was selected and the excess heat started from 4% (+2.5 W of about 60 W mean input power) increasing to about 6% in about 67 hours [Fig. 9]. After this time a peristaltic pump failure occurred, so that the current was put to low value (0.25 A) for many hours. The excess Tritium measured,until the pump failure, was +36% (+340 dpm/ml).

After the fixing of the pump, the test restarted and the Pd sheet continued to produce about 5% mean excess heat for many days. This Pd sheet is still under run.

The reference voltage, from the diagonal Pt wire in front of the cathode, was always acquired and under study. It has been observed a sort of correlation between this parameter and the deuterium adsorption into the Pd.

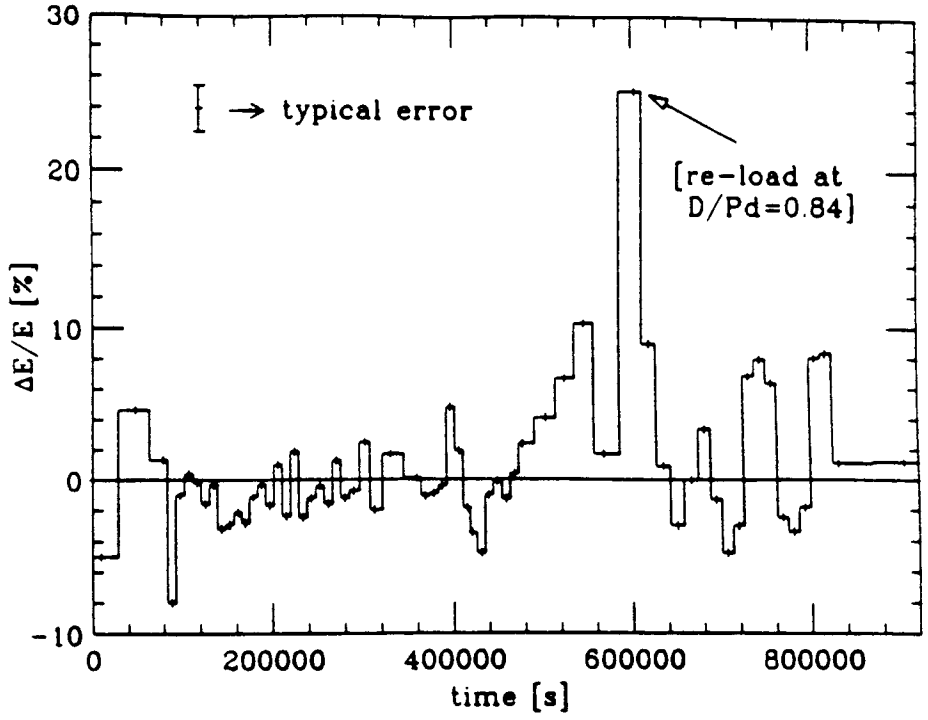

FIG. 8 – The I1.3 Pd sheet gave once excess heat of +25% for short time.

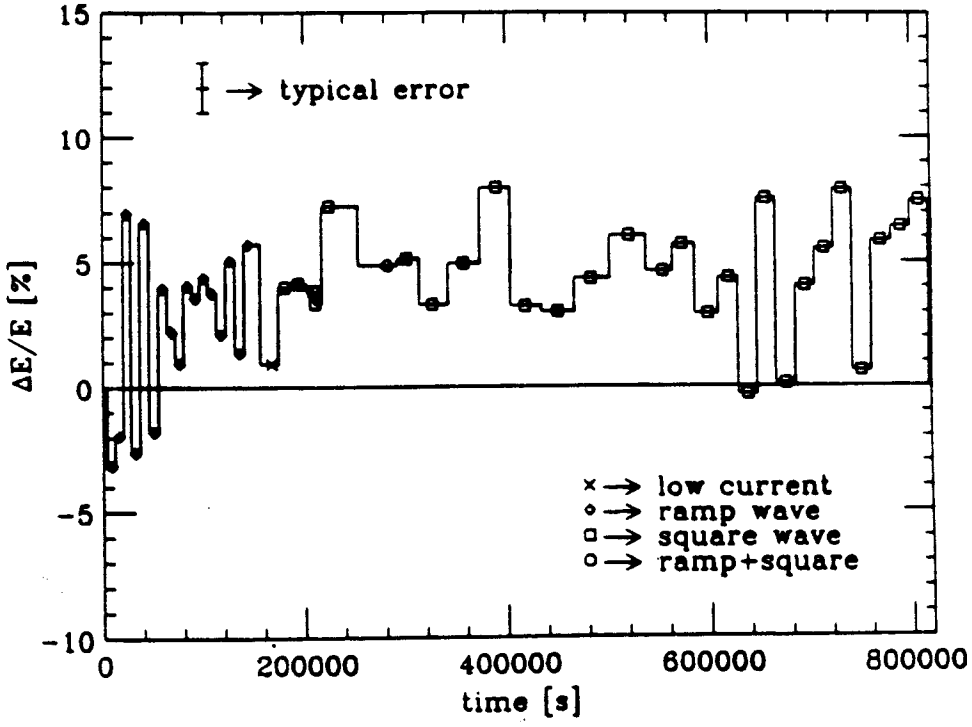

FIG. 9 – The T1.5 Pd sheet gave excess heat of about +5% for long time.

Because this parameter involves the conductivity and the temperature of solution, apart the electric charge status of Pd–Pt pile, the correlation with the D/Pd parameter is not yet completely clear.

Looking at Table I, the D/Pd seems correlated to the mass density of the Pd sheet in this way: the D/Pd ratio increases if the mass density decreases.

4. CONCLUSIONS

By the tests performed, with our cold–worked Pd sheets, we can say that a high sensitivity flow calorimetry is required to observe, undoubtedly, excess heat even at low levels (5%).

The self–biased pulsed electrolysis, with a proper circuit,seems able to reduce the long deuterium charging time to a few hours and the excess heat generally appears some hours later; the excess heat is strictly correlate to high D/Pd charging ratio (> 0.75)

Looking at our data, it seems that there is a sort of correlation between excess heat and the low mass density (lower then the 12 g/cm^3 "standard" value) occurred to two Pd sheets.

The excess tritium (although low values) seems occur when excess heat is obtained.

In conclusion, we can say that the metallurgy of the Pd electrodes plays a very important role both for the high D/Pd ratios and large excess heat; moreover, the deuterium charging methods (pulsed current) strongly help the production of excess heat.

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REFERENCES

[1] A.Takahashi et al. "Excess Heat and Nuclear Products by D_2O/Pd Electrolysis and Multibody Fusion", Submitted to Applied Electromagnetics in Materials, (March 1992).

[2] E.K.Storms. "Measurements of Excess Heat From a Type Electrolytic Cell Using Palladium Sheet." Submitted to Fusion Technology (July 1992).

[3] F.Celani et al. "RESULT OF THE 1st GENERATION, AT GRAN SASSO UNDERGROUND LABORATORY, ON NUCLEAR COLD FUSION." Conference Proceedings, SIF Bologna 1989, Vol. 24 pag. 257 (1989).