

# Mass Flow Calorimetry

Michael C. H. McKubre and Francis Tanzella  
*Materials Research Laboratory*  
*SRI International, Menlo Park, California*

## Abstract

Discussion of the Mass Flow first principles calorimeter in this paper is based primarily on the analysis and experience gained at SRI in answering the question: “is there a Fleischmann Pons heat effect (FPE)”?. Subsequently other mass flow calorimeters, or more generically heat balance calorimeters, were designed to answer this same question and some comment will be directed to the technical differences resulting from different design philosophies, specifically those designed and operated by ENEA, and Energetics Technologies.

Discussion will be undertaken of ideal and non-ideal calorimeter operation, design principles and practical implementation including long and short term accuracy and sensitivity as well as limitations of heat balance calorimeters as the vehicle chosen to study the FPE.

## Introduction

The needs of so-called “cold fusion” calorimeters are so different from those intended for use studying brief chemical reactions that, apart from basic principles, very little of value can be learned from studying that community, and little reference will be made to them here.

First a few words about the special purpose that constrains the design. The generation of mass flow or more generically heat balance calorimeters under discussion were constructed to achieve confidence and give credence to a result that was not believed. Fleischmann *et al.* [1], and others had reported results of a nuclear level heat effect resulting from the extensive electrochemical insertion of deuterium into palladium cathodes over an extended period of time by means of electrolysis of heavy water in heavily alkaline conditions. This effect has subsequently become known as the “Fleischmann Pons Effect” or FPE.

If true, this result was seen by some as a potential energy source, or at the very least a new potentially interesting physical effect. By others it was viewed as an unwelcome diversion of attention which was criticized as “irreproducible” or the result of unspecified “inaccuracies”. With regard to the second, apparently informed statements were made that “all calorimeters” were “intrinsically inaccurate”, an assertion that early pioneers of chemical thermodynamics in the early 20<sup>th</sup> and even late 19<sup>th</sup> century would have found puzzling. In this climate, however, the challenges to the second-generation FPE calorimeters were threefold:

- i. To allow reproducible demonstration of the effect – whether it be real or the consequence of (unidentified) systematic error,
- ii. To exhibit proven levels of accuracy, over sufficient periods to quantify heat generation consistent with the FPE,

- iii. The operating principal must be sufficiently simple to allow an open-minded non-specialist to visualize the full range of potential error.

## Design Principles

With these needs well in mind a group of senior physical scientists was convened at SRI<sup>1</sup> to consider the design of a simple, first-principals calorimeter with high and stable accuracy, capable of accommodating a sufficient volume and input power range without compromising the electrochemical needs, or the need to know the chemical state of the system under test. The first result of this design exercise was presented with results at ICCF2 [2] and states:

*“Our calorimeters were designed with the philosophy that in precise calorimetry, and in the search for unusual reaction products, it is desirable to have a closed system, and a knowledge at all times of the composition of the reacting system. All experiments were performed with closed and sealed electrochemical cells operating from 40 to 10,000 psi above atmospheric pressure. Axial resistance measurements were made to monitor the D/Pd or H/Pd ratio.”*

This covers the requirements of physical operating condition and the perceived needs for both calorimetric and reaction diagnostic, reasons to retain products in a closed cell and to measure the chemical (and electrochemical) state of the system under test at all times. Additional constraints were imposed by points i to iii above. The calorimeters were designed and constructed according to the following ten requirements:

1. As conceptually simple, first-principals devices based on the first law of thermodynamics<sup>2</sup>.
2. With a requirement to maintain complete control of the critical chemical and electrochemical operating parameters, including cell temperature.
3. To accommodate a large dynamic range of heat input and output anticipated to be ~100 mW – 100 W (later extended to 500 W).
4. To permit complete, on-line monitoring of all important physical, chemical, electrochemical and thermal variables.
5. With multiple measurement redundancy of variables critical to calorimetry (*e.g.* temperature).
6. So that heat was measured accurately, equally and completely, independent of its source position within the calorimeter.
7. To allow high precision (the greater of 10 mW or 0.1% of power input) and high and stable accuracy for operating times as long as 1000 hours.
8. To operate as closely as possible to the (thermal) steady state, thus simplifying calorimetric data analysis.

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<sup>1</sup> The authors are very much indebted to this group, which expanded with time, but had as its core: Jason Chao, Bindi Chexal, Steve Crouch-Baker, Jon McCarty, Tom Passell, Joe Santucci, Stuart Smedley, Robert Weaver and Sharon Wing.

<sup>2</sup> It is interesting to note that our widespread and deep trust in this law is based exactly on our confidence in calorimetric accuracy.

9. With sufficient time resolution to permit simple non steady state correction allowing source reconstruction of possible thermal transients.
10. To be operated in such a way that known sources of potential systematic error yield conservative estimates of “excess” heat.

## Heat balance calorimetry

One means of calorimetry was considered (in 1989) best able to meet the above-listed requirements. Often called mass flow calorimetry because of its emphasis on heat convected by a moving fluid mass, Heat Balance Calorimetry is accomplished by monitoring the heat gained or lost by the heat transfer fluid as follows:

$$Q_o = \delta m / \delta t C_{ps} (T_i - T_o) \quad [1]$$

where:

$Q_o$  = process heating (output) power (W)

$\delta m / \delta t$  = mass flow of heat transfer fluid (kg/s)

$C_{ps}$  = specific heat of heat transfer fluid (J/(kg K))

$T_i$  = inlet temperature of heat transfer fluid (K)

$T_o$  = outlet temperature of heat transfer fluid (K)

Heat balance calorimetry has been described as “*the ideal method of measuring heat since the heat entering and leaving the system through the heating/cooling jacket is measured from the heat transfer fluid (which has known properties). This eliminates most of the calibration problems encountered by heat flow and power compensation calorimetry*” [3].

As written, equation [1] has no calorimeter dependent calibration requirements. Given independent, fundamental calibrated references for mass and time (hence  $\delta m / \delta t$ ) and temperature (or temperature difference), and independent accurately known properties of the mass transport fluid, then the measurement of  $Q$  is absolute. This calibration independence is very important. Drifts in calorimeter “calibration constant” are the greatest cause of concern and error in FPE experiments which must last hundreds of hours before the effect is seen, and may last thousands<sup>1</sup>.

Input power to an electrochemical cell operating thermodynamically closed is simply the product of the electrochemical current and the voltage measured at the calorimetric boundary (i.e. at a point on the surface that is neither inside nor outside). To meet requirements 2 and 8

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<sup>1</sup> The effect of drift was eliminated and turned to advantage in the heat flow calorimeters designed by Fleischmann and Pons by daily, automated Joule calibration pulses. The presence of drift and rather clumsy handling of it essentially invalidated several early “negative” results as the position of the “baseline” was adjusted daily by arbitrary assertion that the “excess power” was zero.

above allowing independent control of electrolyte temperature and steady state operation it is necessary to add an input electrical Joule heater to complement the electrochemical power input. In this configuration,

$$Q_i = I_{EC} V_{EC} + I_J V_J \quad [2]$$

and we define as excess power the difference between the calorimetrically determined heating output power and the sum of power input,

$$Q_{XS} = Q_o - Q_i \quad [3]$$

Note that  $Q_{XS}$  may have either sign. Negative “excess” is possible, although this condition has never been observed in any mass flow calorimetry performed at SRI in studies of the FPE except during transient conditions as will be discussed shortly.

#### Departures from ideality:

To obtain accuracies higher than ~1%, two factors affecting calorimeter performance must be taken into account:

##### 1. Thermal efficiency

Equation [1] accounts for heat removed from the calorimeter by convection of the thermal transfer fluid. Heat may also penetrate the calorimeter boundary by conductive exchange with the ambient. Of particular concern are metallic wires and pipes. If the environment is configured in such a way that the ambient is the inlet temperature, then equation [1] can be simply rewritten to include a conductive loss term,  $k$ ,

$$Q_o = (\delta m / \delta t C_{ps} + k) (T_i - T_o) \quad [4]$$

Since  $k$  is a calorimeter specific constant that does require calibration, it is important that it be kept small to preserve first principals operation. By careful insulation, controlled geometry and selection of the fluid flow rate,  $k$  was typically less than 1% of  $\delta m / \delta t C_{ps}$  in the SRI mass flow calorimeters. Because  $k$  is defined by geometry, it is also very unlikely to change and was observed to be stable.

In high temperature operation one should expect radiative in addition to conductive transport. No such non-linear tem has been observed or required in the mass flow studies so far performed at SRI or by our close collaborators. In high temperature studies [4] performed at Energetics Technologies reflective surfaces were used to minimize radiative heat transport.

##### 2. Thermal time constant

Input power is measured effectively instantaneously while the calorimetric output thermal power responds with the thermal time constant(s) of the calorimeter. To make accurate subtraction of  $Q_o - Q_i$  in order to calculate  $Q_{XS}$  at the same instant and thus improve (instantaneous) accuracy and permit study of thermal transients, it is necessary to apply one or a series of exponential filters to  $Q_i$  so that the terms on the right side of equation [3] refer to the same time of measurement.

Although other heat transfer processes might be considered, three terms dominate the transfer of electrochemical cell heat out of the calorimeter:

- a. The conduction communication of electrochemical cell heat to the moving heat transfer fluid
- b. Convective transport of the heated fluid element to the outlet temperature sensors
- c. Convective thermal dilution of this heat due to the incoming mass flow at constant rate and constant (cooler) temperature.

Terms “a” and “c” depend exponentially on time. In all calorimeters studied at SRI the time constant for “a” and “b” were substantially less than for “c” and it was found sufficient to adopt a single level of exponential filtering with the following form.

$$\Delta Q = \sum_{\Delta t = 0}^t \Delta Q_{i,\Delta t} \left( 1 - e^{-\Delta t/\tau} \right) \quad [5]$$

where  $\Delta t$  is the time interval of measurement and  $\tau$  is the composite time constant.

In this way the output power was corrected using the sum of the exponential decay response to each stepped change in  $Q_i$  from the preceding  $t/\Delta t$  measurement intervals (6 hours) of  $P_{In}$ . At this point the response of  $P_{Out}$  has achieved >99.99% of its steady-state value for  $\tau_2 = 0.33$  h. For some data sets, particularly those in which the bath temperature was changed, corrections were also made for the effect on  $P_{Out}$  caused by the heat capacity and changing temperature of the cell contents. The mathematical form of this correction is given by equation [6].

$$\Delta P_{Out} = [ M_{Water} C_{ps,Water} + M_{Solid} C_{ps,Solid} ] \Delta \bar{T} / \Delta t \quad [6]$$

where subscripts “Water” and “Solid” refer to the liquid (*i.e.* heavy or light water) and solid components of the electrochemical cell and  $M$  is the mass of these cell components.

In practice, because  $\bar{T}$  (the average temperature of the cell and its contents) is a slow-moving function of time,  $\Delta \bar{T} / \Delta t$  can be calculated as the slope at the respective time series functions,  $\delta T / \delta t$ , at each point in the data series.

It is important to remember that the form of the non-steady-state corrections is such that, while these can significantly improve calorimetric precision, they do not affect the accuracy of total excess energy generation. The round trip integral effect of both the  $\delta Q / \delta t$  and  $\delta T / \delta t$  corrections expressed by Equations [5] and [6] is zero for the same initial and final conditions.

The consequences of the non-idealities of mass flow calorimetry expressed in equations [4] and [5] are represented graphically in Fig. 1. For an arbitrary stepped increase in input power of 1 W at time  $t=0$  the response of the output temperature sensors respond exponentially with time constant  $\tau$ . For a calorimeter with 100% thermal efficiency ( $k = 0$ ) shown by the black line in

Fig. 1, the output responds asymptotically to the input step, but to a lower value at lower thermal efficiency. The effect of “a” above is to add a second (faster) exponential response, the effect of “b” above is to add a (short) onset delay.

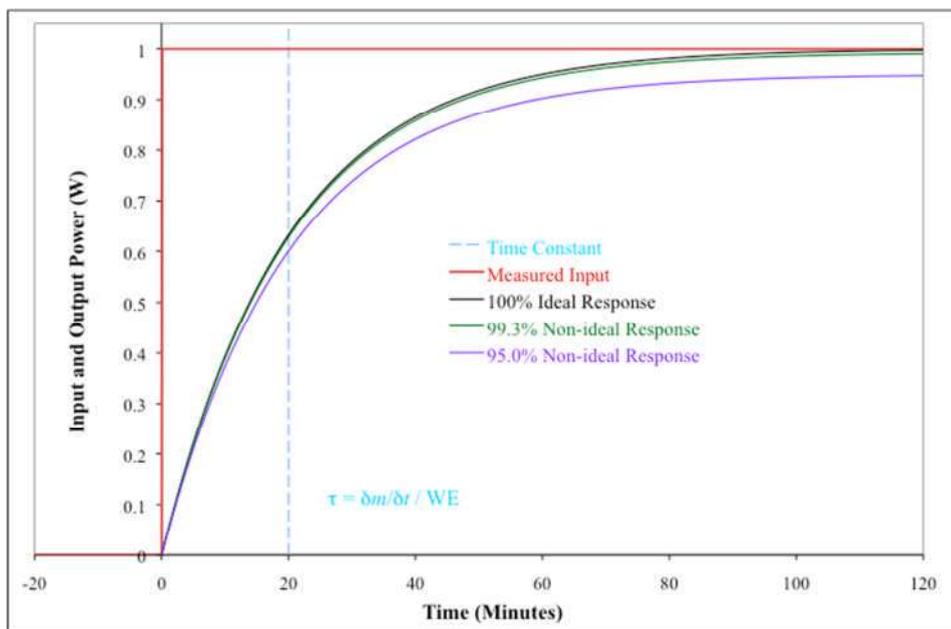


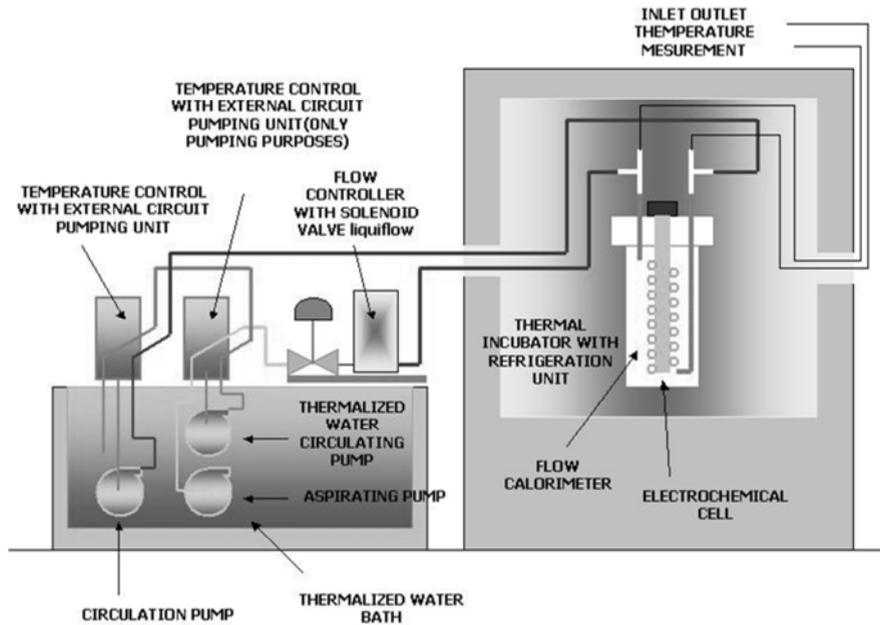
Figure 1. Non-ideal response of mass flow calorimeters

## Practical implementation

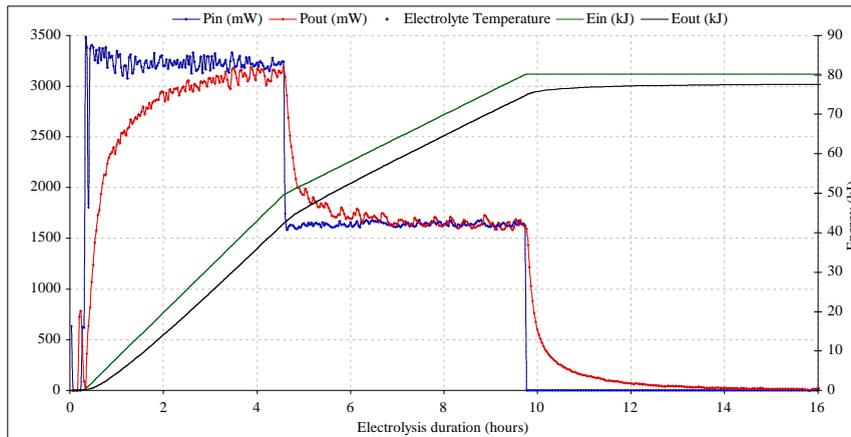
To preserve first principles operation as closely as possible as one of the major strengths of mass flow or heat balance method, we are concerned to keep conduction and radiation losses ( $k$ ) to a minimum. Several methods have been evolved in FPE calorimeters. One of the simplest methods is to incorporate a high efficiency heat exchanger within the electrolyte and heavily insulate the perimeter. This method has been used successfully by Arata [5], Violante [6] and others [7]. An important figure of merit for all configurations of mass flow calorimeters is the thermal efficiency,  $\Phi$ , which reflects the fraction of the total heat removed by convective flow.

$$\Phi = Q_{Convection} / [Q_{Convection} + Q_{Conduction} + Q_{Radiation}] \quad [7]$$

Figure 2 shows an implementation of this method at ENEA [see Ref. 8, p. 238] with the calibration of the thermal efficiency using a Pd electrode in LiOH shown in Fig. 2. The mass flow coils can be observed in section inside the electrochemical cell. For this example the attained thermal efficiency was 97.5%. While relatively low for a mass flow calorimeter, this is an impressive value for this “inside out” geometry because of the relatively small exposed surface area of the immersed heat exchanger compared with the outer surface. Another limiting constraint is the need to use insulating, or insulation covered materials for the heat exchanger to prevent chemical contamination of the electrolyte thus compromising the cathode electrochemistry.



**Figure 2. ENEA Mass Flow calorimeter with internal heat exchanger**

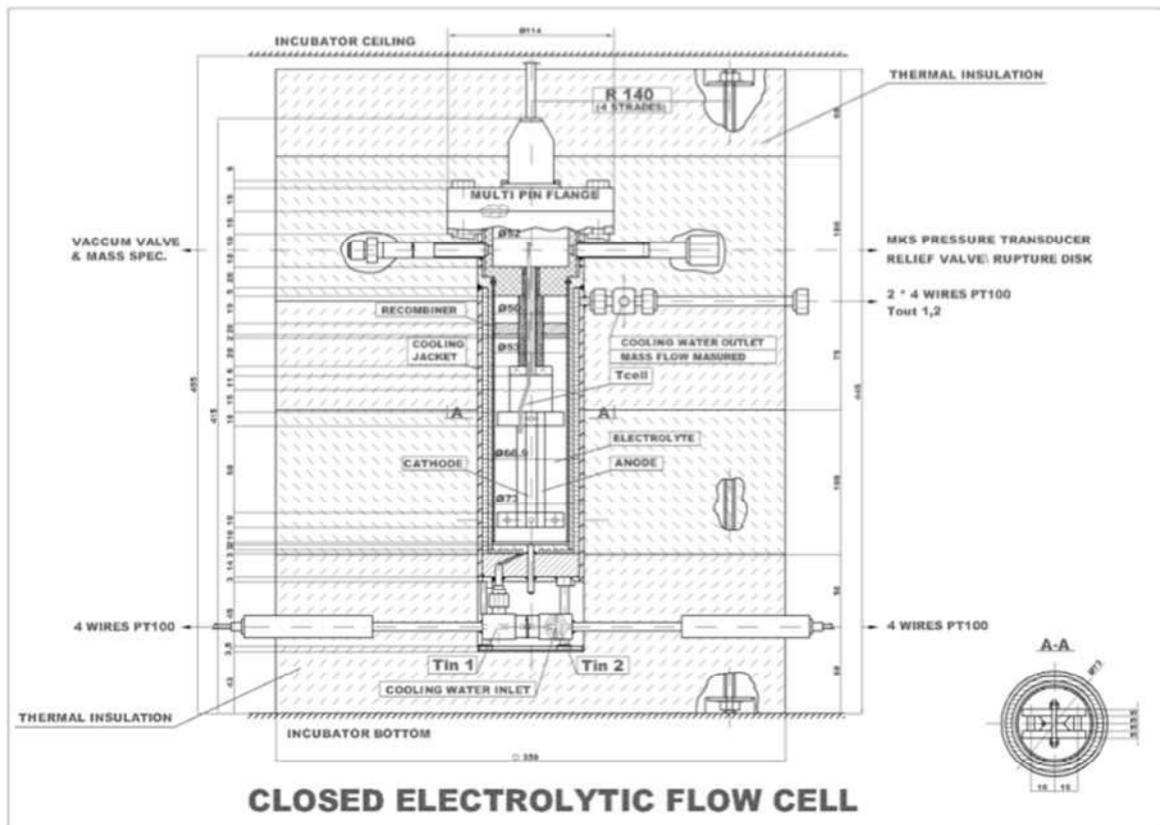


**Figure 3. Calibration of ENEA calorimeter using Pd cathode in 0.1M LiOH**

In general higher thermal efficiencies can be achieved with the inverse geometry which positions the heat exchanger to cover as much as possible of the cell external area. Particularly elegant designs have been implemented by Energetics Technologies in which the heat exchanger is a helical flow channel machined into the external surface of the cell to ensure intimate thermal contact. An early design with the heat exchanger covering the cylindrical walls in  $2\pi$  geometry with insulating end caps was used to study heat production from a glow-discharge FPE [4].

A thermally more efficient design was recently implemented by Energetics Technologies to study SuperWave<sup>®</sup> stimulated electrolytic FPE heat production in helium leak tight,

thermodynamically closed cells. In this design, shown in Fig. 4, the bottom and cylindrical sides of the cell are fitted with spiral and helical water flow channels. This design resulted from extensive engineering development efforts at Energetics Technologies, and elaborate finite element thermal modeling at ENEA. Because the top is not actively cooled, however, and due to thermal conduction out along numerous electrical power and sensor wires and gas lines, the maximum thermal efficiency so far achieved with this design is only ~95%.



**Figure 4. Energetics Technologies closed electrolytic mass flow calorimeter cell<sup>1</sup>**

To achieve values of  $\Phi$  higher than 99%, very particular attention must be paid to numerous details of design. The labyrinth calorimeter developed at SRI and shown in Fig. 5, achieved  $\Phi > 99.3\%$ . Higher values were attainable at higher mass flow rates, but with decreased sensitivities. We will examine this design more closely as a way to highlight these design details. The contained electrochemical cell, capable of operating autonomously, is shown in Fig. 6.

<sup>1</sup> The authors are indebted to S. Lesin and A. Godfrey of Energetics Technologies for permission to reproduce this Figure.

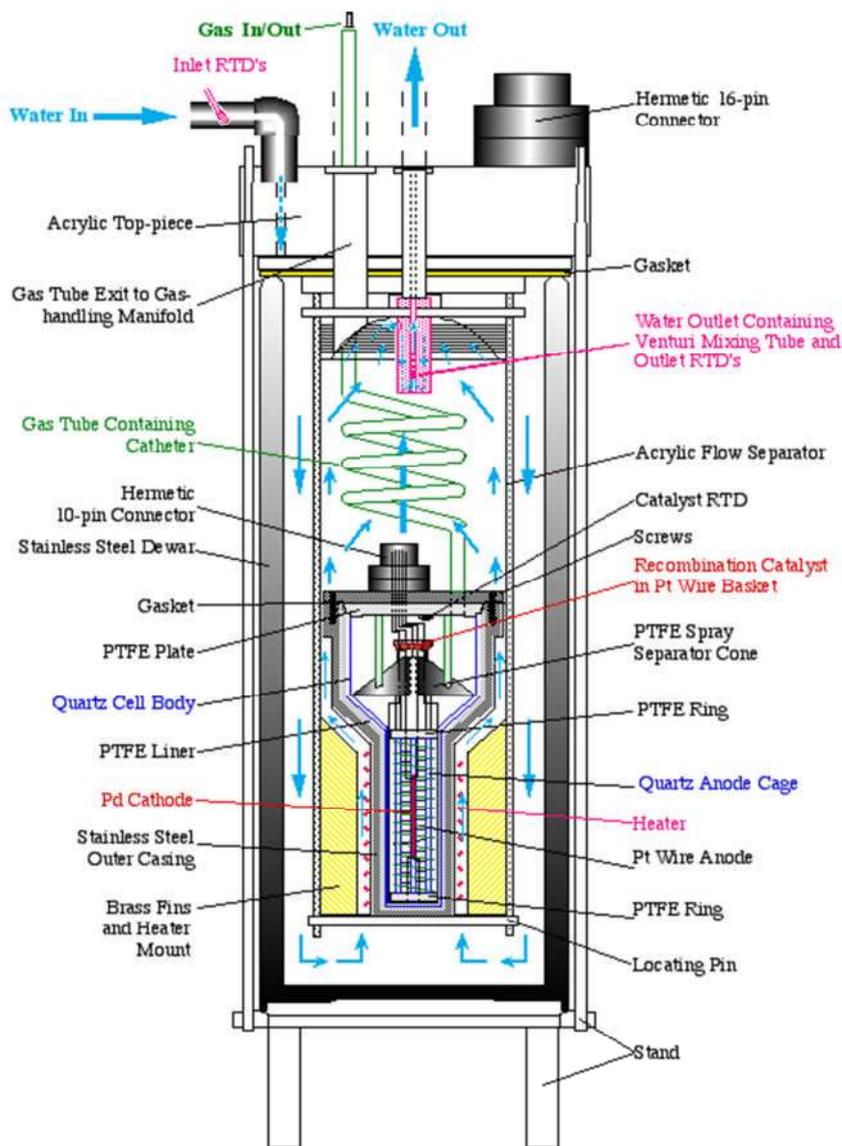
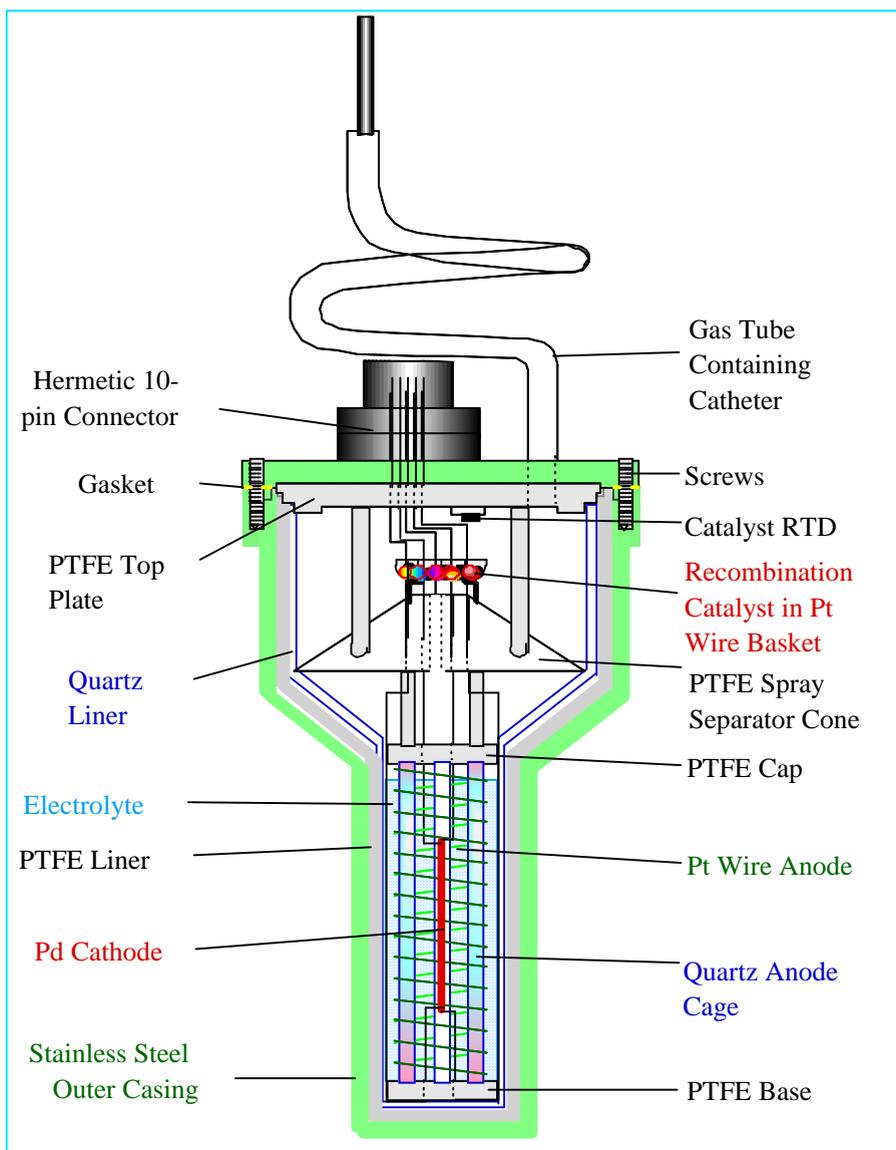


Figure 5. SRI Labyrinth Mass Flow Calorimeter circa 1992

Due to issues of irreproducible interfacial kinetics and bulk deuterium loading [see companion paper, ref. 9] experiments were started in a “farm” of 12 DoL cells sometimes intentionally identical. Only those cells that exhibited acceptable loading and interfacial dynamics were promoted to the calorimeter shown in Fig. 5. The DoL cells therefore needed to exhibit two different sets of characteristics:

- i. To be consistent with the needs of good electrochemistry and maintain scrupulous cleanliness for long periods of time in strong basic electrolytes and at the high current levels demanded of FPE experiments
- ii. To be compatible with the needs of good calorimetry and maintain hermeticity for long periods of time.



**Figure 6. SRI Degree of Loading (DoL) and Calorimeter Cell**

The first was accomplished by using a quartz (fused silica) cell body with fitting PTFE head. All components structural or otherwise inside the cell in contact with either electrolyte or vapor were manufactured of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , PTFE, Pt or Pd. Internal recombination and thus thermodynamic closure, was provided by either Pt or Pd on  $\text{Al}_2\text{O}_3$  recombination catalyst suspended above a PTFE conic section designed to prevent electrolyte splash damage and allow the condensed recombine (either  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$ ) to wash deposits back into the electrolyte. The working volume was  $\sim 30 \text{ cm}^3$ . Using this materials selection and design geometry these cells are capable of sustained operation in 1 M base at currents above 1 A for period over 1000 hours.

The hermetic design of the DoL cell allows for full immersion in the mass flow fluid so that the moving mass of calorimetry fluid (in this case air saturated water) can remove heat efficiently from each of 5 geometrically disperse heat sources:

1. The product of the electrochemical current flow and the cathode interfacial impedance and any excess heat source located at the cathode (in the case shown at the axial center of the cell)
2. The product of the current flow and the electrolyte resistance path due to and located within the electrolyte volume between cathode and anode (or anodes)
3. The product of the current flow and the anode interfacial impedance located in an axially symmetric cylindrical shell relatively close to the cell wall
4. The heat of recombination of H<sub>2</sub> and O<sub>2</sub> or D<sub>2</sub> and O<sub>2</sub> at the recombination catalyst located in the volume of the recombiner near the top of the cell
5. The product of the current in the Joule heater used for power compensation and calibration, located in an axially symmetric cylindrical shell immediately outside and intimately contacting<sup>1</sup> the cell wall.

All of these terms are significant and differently couple to the calorimeter and outside environment. In a well-stirred electrolyte as exists above relatively modest current densities, the first three terms constitute effectively a single volume source. In the steady state the recombination thermal power is equal to the electrochemical current times the thermoneutral voltage of 1.48 V for H<sub>2</sub>O or 1.23 V for D<sub>2</sub>O. The Joule heater, while axially symmetric with the electrolyte volumetric heat source, is closer and therefore temporally and thermally better coupled to the convecting mass flow fluid.

By enveloping the whole DoL cell in the flow as shown in Fig. 5, we were able to establish within better than 0.1% (1 ppt) that the measurement of heat (the output thermal power) was independent of its source within the calorimeter. This degree of position insensitivity is very difficult to achieve with the “inside out” mass flow calorimeter design of the type shown in Fig. 2, or by the use of an external heat exchanger as shown in Fig. 3.

Several other features of the calorimeter shown in Fig. 5 merit further discussion. In employing equation [6] with a single conductive loss term,  $k$ , it is necessary to ensure that the calorimeter experiences a single, stable thermal ambient environment. The calorimeter shown in Fig. 5 was submerged inside a large (~ 1 m<sup>3</sup>), water bath that was well stirred and well regulated<sup>2</sup>. This bath was placed in the center of an isolated, temperature controlled room. The mass flow fluid (water) was drawn from the bath past two inlet RTD sensors placed directly in the flow stream. The flow entered to head of the calorimeter through a flow distribution header

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<sup>1</sup> In calorimetric operation the Joule heater is held in place by a push-fit, finned brass heatsink that fills the radial space between the outside of the cell and the inside of the flow channel to ensure rapid coupling of the heat from all sources to the moving mass flow fluid.

<sup>2</sup> Temperature gradients and variability both short and long term were maintained below  $\pm 3$  mK. A Quartz Crystal reference thermometer [HP Model 2804A was maintained as a temperature standard in this bath.

and was channeled down through the annular volume between the inner wall of a 2 liter stainless steel Dewar and a thermally insulating barrier to form a flow labyrinth reversing direction at the bottom to flow past the submersed electrochemical cell. The electrical leads from the cell were dressed in the reverse direction from a hermetic connector at the top of the cell to another at the top of the calorimeter. The purpose of this arrangement is to minimize conductive heat loss radially from the cell and along the electrical leads used for electrochemical control and measurement. In the labyrinth configuration heat leaving by these paths is picked up in the incoming fluid and delivered to the outlet sensors for measurement.

The final feature of the calorimeter is the hemispherically domed insulating head that houses the outlet temperature sensors. The hemispherical shape was designed to minimize the formation of thermal “pockets” at higher or lower temperature than the average. The mass flow fluid flows through a small hole at the highest accessible point of the hemisphere to enter the outer annulus of a small flow labyrinth containing a venturi (helical) flow mixer. Turning the corner this flow enters a small axial flow channel designed to ensure good mixing at the operating mass flow rate (typically ~1 g/s).

These flow precautions were taken to ensure that the outlet temperatures measured represent an accurate average value in the fluid flow. The outlet temperature sensors were situated within the axial outflow channel, directly in contact with the outgoing fluid. Two RTD sensors were used, identical to the two at the inlet, to provide a redundant measurement of  $\Delta T$ . In some experiments two additional thermistor sensors were used at the outlet to provide a redundancy of measurement method.

An FMI QV-0SSY constant displacement pump was used to draw water from the top of the calorimeter through a standard heat exchanger to ensure constant mass flow. This flow was then pumped directly into a reservoir placed on a Setra 5000L electronic balance that was polled regularly by the data acquisition system to measure the mass flow rate as  $\Delta m/\Delta t$ . When the balance reservoir is filled a siphon automatically forms and empties the vessel rapidly<sup>1</sup>.

## Brief evaluation of errors

Excess power is calculated as the difference between the output power and the input power

$$Q_{XS} = Q_o - Q_i = (\Delta m/\Delta t C_{ps} + k) (T_i - T_o) - I_{EC} V_{EC} - I_J V_J \quad [8]$$

Temperatures were measured using 100  $\Omega$  platinum resistance temperature devices (RTD's) so that to first order,

$$T = T^\circ + (R - R^\circ) / \alpha R^\circ \quad [9]$$

where  $\alpha$  is the (known) temperature coefficient of resistance for Pt, and  $R^\circ$  is the sensor resistance at some known temperature (typically 0°C).

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<sup>1</sup> This normally disrupts only one, and at most two determinations of  $\Delta m/\Delta t$ . In general the flows were very stable but redundant mass flow measurements occasionally were used for added accuracy.

A complete error propagation model has been developed for the calorimeter shown in Fig. 5; the basic elements are reproduced below. Errors propagate from mis-measurement of each of the terms. The constants and variables needed to measure  $Q_{XS}$  and its uncertainty may be divided into three classes:

1. Measured variables:  $\Delta m$ ,  $\Delta t$ ,  $R$ ,  $I$  and  $V$ .
2. Predetermined constants:  $C_{ps}$ ,  $\alpha$  and  $R^\circ$ .
3. The calorimeter inefficiency:  $k$ .

Measurements of mass, time, resistance, current and voltage rely on the calibration accuracy of the devices being used. At SRI the instruments used were periodically calibrated to accuracies better than 1 part per thousand (<1 ppt) and typically better than 1 part in ten thousand. Measuring  $R^\circ$  with the same instrument used to measure  $R$  further increases measurement accuracy. Systematic errors in the calorimetry critical temperature difference tend to cancel since this depends on the difference of resistances measured with the same meter at almost identical times.

The heat capacity of air-saturated water and the temperature coefficient of Pt resistance are well-measured constants. It should be noted that these are not constant with temperature; for accuracies better than 1 ppt it is necessary to take account of the fact that the outlet temperature may vary over of a considerable range, affecting both  $C_{ps}$  and  $\alpha$ .

What remains is the conductive loss term or calorimeter thermal inefficiency,  $k$ . Three factors contribute to reducing the inaccuracy in this term and increase its long-term stability and thus influence on overall calorimeter accuracy.

- a. By design and selection of mass flow rate  $k$  is maintained to be a small fraction of  $\Delta m/\Delta t C_{ps}$ . Typically this constant was held to contribute ~1% or less of the output power and it can be measured easily with better than  $\pm 10\%$  accuracy thus contributing <1 ppt to the overall measurement.
- b. The method of calibration using a Joule heater pulse determines  $k$  in terms of the other predetermined constants. In this way the cumulative error is reduced and recalibration can be performed at any time (in the absence of excess power) using a Joule heater pulse.
- c. The value of  $k$  is determined by the geometry and materials properties of heat conduction pathways. With the calorimeter isolated in the constant temperature bath these are not likely to change, and were not observed to do so.

For the Labyrinth Mass Flow Calorimeter shown in Fig. 5 the maximum error in the typical operating range of input power and mass flow rates ( $Q_i = 5 - 20$  W,  $\partial m/\partial t \sim 1$  g/s) was  $\pm 0.35\%$  of  $Q_i$ . The largest source of error in practice is mis-measurement of the average temperature of the outgoing fluid stream due to flow streaming. Care must be taken to ensure good flow mixing and the avoidance of particulates in the flow stream.

## Conclusions

With some attention to detail heat balance calorimeters based on the mass flow of water are capable and robust instruments that combine the desirable features of simplicity of design and calorimetric analysis, adequate accuracy, high long-term stability and low initial materials and operating costs. By these criteria such devices are well suited to studies of the FPE and have been widely employed with considerable success [7, 11]. Mass flow calorimeters are conceptually simple, first principles devices based on the first law of thermodynamics. They are able to accommodate and operate nearly linearly over a large dynamic range of heat input and output, extending easily to 500 W while maintaining better than 1% accuracy. Designs are available to permit the measurement of heat accurately, equally and completely, independent of its source position within the calorimeter.

Several potential disadvantages and undesirable features nevertheless are implicit in the mass flow principle and subject operation to added complexity. Designs needed to maintain high accuracy, such as those shown in Figures 2, 4 and 5 are not cheap to develop or implement. Highest accuracy (closest to first principles) operation with enveloping mass flow renders the cells opaque and inaccessible, increasing the difficulty of identifying and rectifying technical issues within the cell. To achieve accuracies approaching or exceeding 0.1% it is necessary to take account of the (known) temperature variability of the heat capacity of air-saturated water and the temperature coefficient of Pt resistance.

A final point is perhaps pertinent only to FPE studies. Fleischmann and Pons exploited a positive temperature coefficient of the excess heat phenomenon [10] to produce large effects, and several authors have noted [7, 11, 12] that to initiate or stimulate the effect sometimes required a step or abrupt change in conditions. Mass flow calorimeters are by design and nature thermally sluggish. They are not capable of responding quickly to a rapid change in input conditions. The steady state method favored at SRI actually opposes thermal change by maintaining the total input power constant. To the extent that changes in thermal condition are necessary to produce or intensify the effect under test then the heat flow design of Fleischmann and Pons [1] offers clear advantage.

## Acknowledgment

As specified in "Design Principles" this paper summarizes briefly knowledge and experience accumulated by a very large number of contributors over a period of nearly 20 years. The authors would like to acknowledge and thank each of those who have contributed and recognize that in doing so the somewhat opaque and outmoded science of calorimetry may have been rendered less so. None of this change and innovation would have occurred without the stimulus provided by Martin Fleischmann and Stanley Pons to whom we offer our final and ultimate acknowledgment.

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