

A flow calorimetry study of the Ni/H System

G. Cammarota, W. Collis, A. Rizzo, C. Stremmenos

INTRODUCTION

This paper documents the continuing calorimetric study of the nickel natural hydrogen system at Department of Physical and Inorganic Chemistry at the University of Bologna, Italy. Our previous unpublished work had already verified anomalous increase in temperature of a nickel sample loaded with sub-atmospheric hydrogen first noted by Piantelli and co-workers^{1,2}. To ensure that such temperature anomalies were not the result of changes in heat transmission, it was decided to investigate the system using a flow calorimeter.

CALORIMETER

Fig 1 shows schematically the form of the water flow calorimeter used in this experiment. The central reaction cell contains the rolled nickel foil. Some ten turns of Cr-V heating wire is wound round this. Naturally the wire is electrically insulated from the nickel. The sample and heating wire is contained in a quartz dewar cylinder which is placed in a glass cylinder through which cooling water can be made to flow. The glass cylinder is enclosed in an aluminium cylinder containing expanded polyurethane as a heat insulator.

Sample temperature is monitored by a single thermocouple. Two pairs of thermocouples monitor inlet and outlet water temperatures. All thermocouples are individually calibrated to a few milli-degrees Celsius. Thermocouples are monitored by continuously by a computerized data acquisition system.

Water Flow Calorimeter for Nickel / Hydrogen System

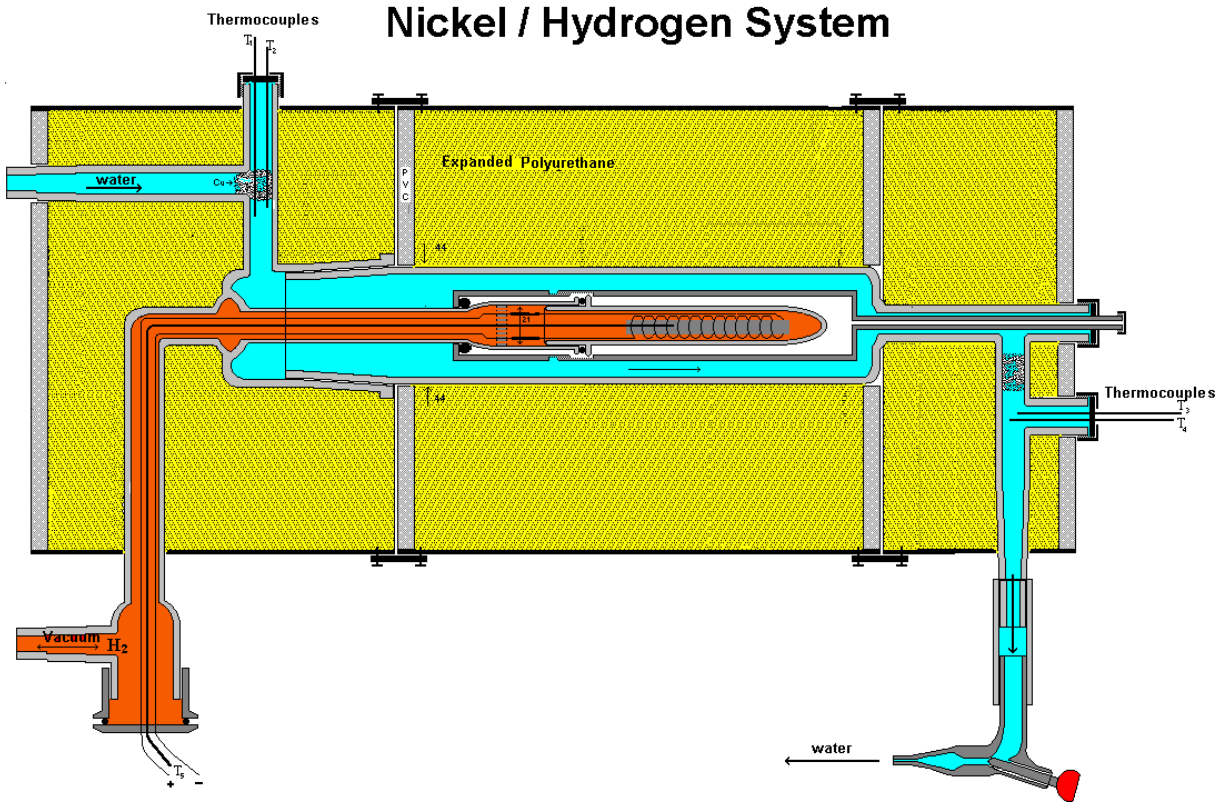
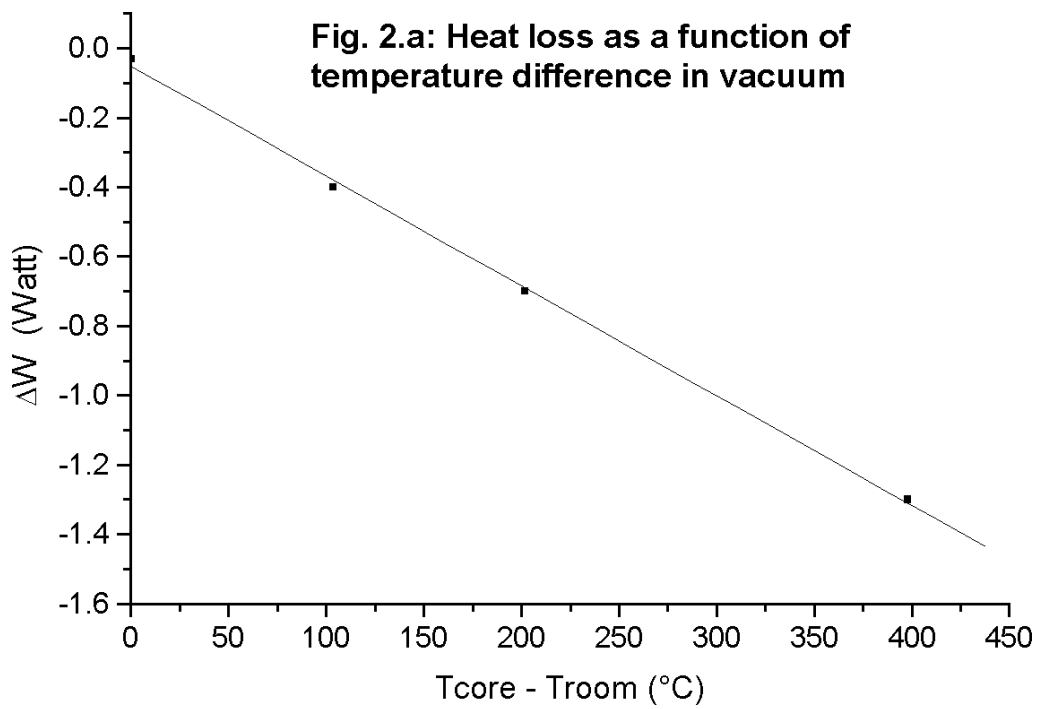


Fig. 2.a: Heat loss as a function of temperature difference in vacuum



CALORIMETER CALIBRATION

The calorimeter is calibrated by comparing heat recovered in the water with electrical heating power when a steady state is achieved. Fig 2 shows the calibration curve for heat loss as a function of the temperature difference between nickel sample (T_c) and environment (T_a). The heat losses are only a small proportion of the electrical heating input (typically 5%) and are largely independent of the state of the calorimeter core, (vacuum, Nickel + hydrogen, Nickel + vacuum).

$$Q_{\text{loss}} \text{ in Watts} = V.A - m.C_p.T$$

where Q is the calculated heat loss

V is the heater EMF in Volts

A is the heater current in Amps

m is the mass of water in g sec^{-1}

C_p is the specific heat of water in $\text{Joules } ^\circ\text{C}^{-1} \text{ g}^{-1} = 4.185$

T is the temperature difference of the cooling water

Water is forced to flow using a peristaltic pump fed from a fixed height reservoir with overflow. Typical flow rates m are $0.7 - 1 \text{ g sec}^{-1}$ and are measured using a cylinder and stop-watch. Flow rates significantly outside this range may cause dynamic flow variations. Bubbles are reduced in the water by using modest flow rates and degassing the water under a partial vacuum (980 mBar).

Typical water temperature differences T are 5-15 $^\circ\text{C}$. Naturally, measurements are made in a stationary regime of constant m & T. Water input temperature is maintained just above room temperature using a constant temperature bath (23.5 $^\circ\text{C}$) ensuring that temperature variations are small and that the calorimeter absorbs no heat from the environment.

Typically an electrical heating power of 25 Watts is required to maintain the Nickel sample at 400 $^\circ\text{C}$. In practice, the electric power supplied is slightly larger than the heating power recovered in the water due to losses from the system as shown in Fig. 2.

Figure 2.b
Heat loss as function of temperature difference
in hydrogen atmosphere

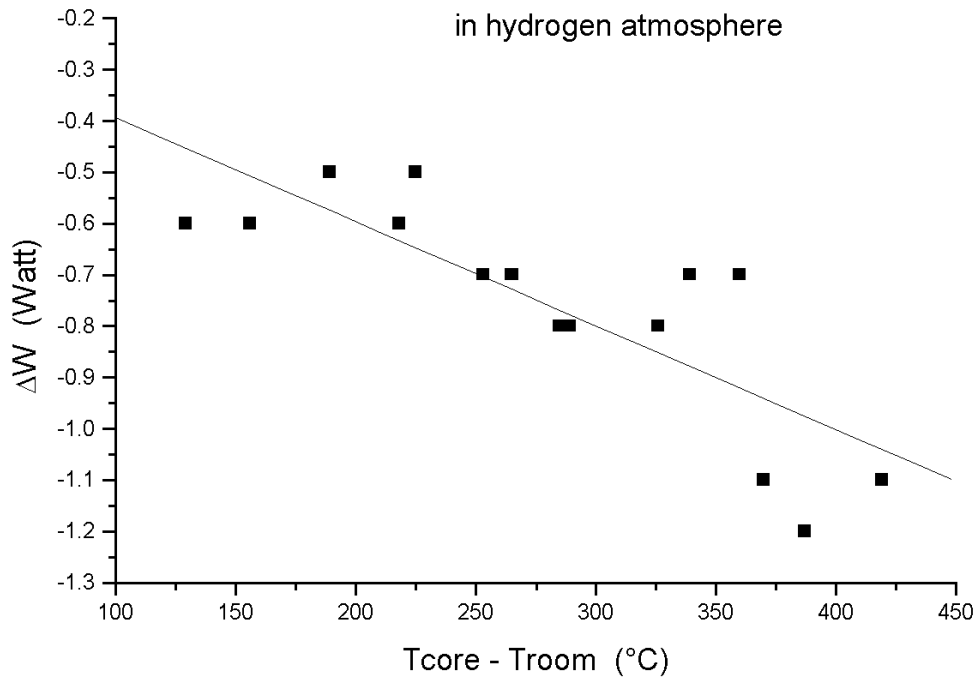
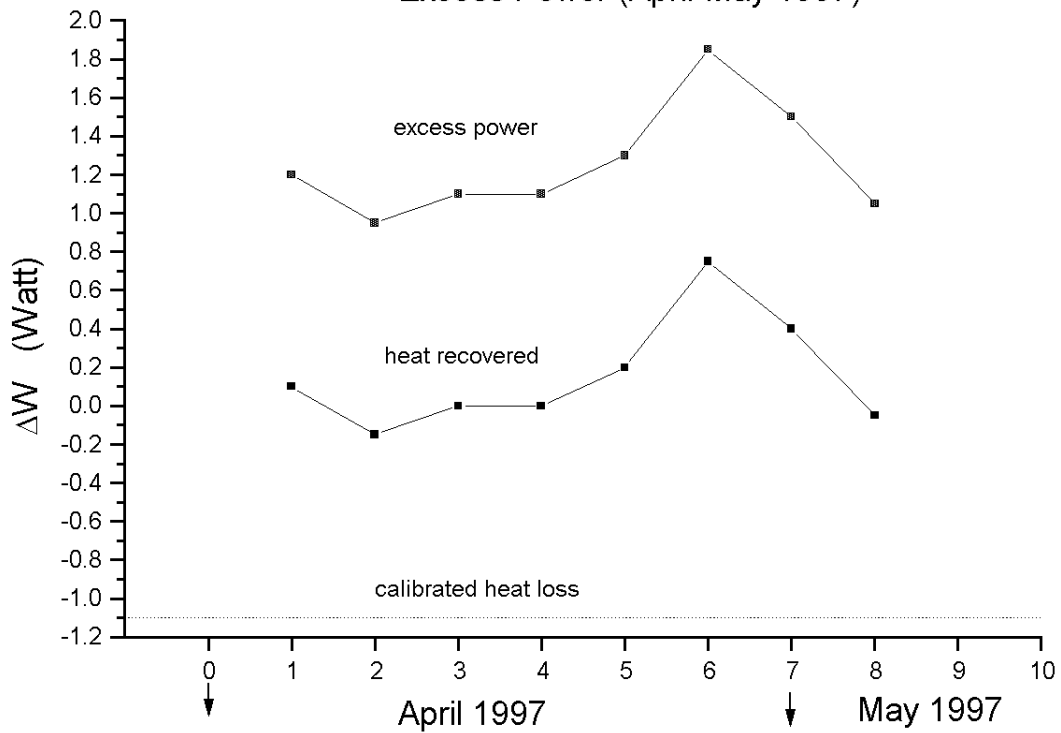


Figure 3
Excess Power (April-May 1997)



PREPARATION OF THE NICKEL SAMPLE

The nickel sample was a foil 0.1 x 50 x 33.8 mm weighing 1.51 g. Impurities, as determined by the supplier are:-

Se	75 ppm	Zr	9 ppm
Mo	30 ppm	Sn	6 ppm
Si	25 ppm	Na	2 ppm
Fe	9 ppm	Mg	0.4 ppm

The first treatment consists of immersing the nickel foil in chromous acid for 20 minutes and rinsing first with tap water, followed by distilled water. The mixture is made by adding 5g of Cr_2O_3 to 1 litre of sulphuric acid. They are secondly cleaned by ultra-sound agitation in a 50% acetone 50% trielene solvent.

An additional treatment facilitates hydrogen loading consists in the electro deposition of a thin nickel layer on the nickel foil in weakly alkaline media. The electrolyte consists of NiSO_4 (210 g/L), NiCl (60 g/L), NH_4SO_4 (50 g/L). The pH was adjusted to 8 +/- 0.1 with about 25 ml .880 g/L NH_4OH . In addition 0.5 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 1g ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, was added to ensure a more even deposition.

Electrolysis was carried out at room temperature 23 °C, 0.225 A cm^{-2} per 57 sec, without mixing. Some experimentation was required to find the optimum current density. The current was adjusted to provide a uniform rough surface to the previously shiny nickel foil.

Degassing and Loading Phase

The nickel foil is rolled up and inserted in the cell. The pressure is reduced to 10^{-6} torr and the heater wire is connected to a stabilized DC power supply (14 V, 5 A max) to bring the temperature of the nickel sample to about 620 °C for 2 days. One observes, if the calorimeter is opened, that the nickel surface remains quite shiny. Note that no hydrogen has yet been introduced.

Hydrogen gas is loaded into Nickel with difficulty as the surface hydride

layer tends to block further entry of the gas. Our technique is to use very low pressure of hydrogen initially and cycle the temperature of the sample from 150 to 400 °C.

The hydrogen gas (Praxair) of spectroscopic purity was introduced into the cell under vacuum slowly reaching about 1 mBar with the nickel sample heated to a maximum of 400 °C. The pressure declined to below 1 mBar (ie hydrogen absorption occurred). In successive temperature cycling steps we raised the pressure to 10, 50, 300mbar noting an absorption of 91mbar over 17 days. Further hydrogen was absorbed over the next weeks calculated as 1.94 mMoles equivalent to $\text{NiH}_{0.2}$.

Calorimetric Measurements

When the Nickel had absorbed hydrogen, we recovered as much power in the water than we supplied as electrical heat, and the balance make positive over the next days. Fig. 3 show the excess power measured.

Discussion

In the anomalous excess heat phase the temperature of the nickel rises by some 1.5 °C and there were small but rapid oscillations of temperature, phenomena already noted. In fact previous (non-calorimetric) experiments had produced 60 °C increases in Nickel temperature suggesting that power production can be substantially higher.

In this experiment, no attempt was made to trigger excess power nor was any magnetic field used (other than that of the heater) in contrast to other techniques^{1,2}. Nevertheless, the excess power corresponds to at least 1.2 W over a period of 35 days (3.6 MJ), which is far beyond the possibilities of any chemical reaction involving the hydrogen or nickel present.

Errors in measurement of electrical power, flow rate, temperatures cannot account for the apparent excess power. However non perfect mixing of the water could result in erroneous excess power. And in fact of the two output

thermocouples, the upstream one systematically registered a higher temperature. This is possibly due to heat conduction along the thermocouple wire. However, to be conservative, we calculated the temperatures to be the mean of the pair. Of course a hypothetical non mixing of the water would also occur during calibration and any error in the calculation of heat recovery would be compensated by a similar error in the estimate of heat loss.

ACKNOWLEDGEMENTS

We are grateful to ENECO, Inc. for financial assistance for this project.

REFERENCES

1. S. Focardi, R. Habel, and F. Piantelli, "Anomalous Heat Production in Ni-H Systems", *Il Nuovo Cimento*, vol 107A, p 103, 163 January 1994.
2. F. Piantelli, "Evidence for the production of heat and nuclear effects in the Siena experiment", presented at 4th conference on the State of Cold Fusion in Italy, held at Siena, 24-25 March 1995. Proceedings unpublished as of October 1997.
3. S. Focardi, V. Garbani, V. Montalbano, F. Piantelli and S. Veronesi, "On the Ni-H System". Conference Proceedings Vol. 64 Anomalies in Hydrogen / Deuterium Loaded Metals W. J. M. F. Collis (Ed.) SIF Bologna 1999. pp 35-47. (These Proceedings).