CNAM Electrochimie Industrielle P. Clauzon- J.F. Fauvarque- G. Lallevé

CNAM, Laboratoire de Sciences Nucléaires G. Le Buzit

#### ABSTRACT

## A boiling - water calorimeter for the study of the abnormal excess heat observed during MIZUNO-like experiments

We have reported at the ICCF12 conference (at Yokohama, Japan) the results of a study on abnormal excess heat observed during MIZUNO-like experiments (1). These experiments are plasma electrolyses of water. The electrolyses were carried out in a beaker under quite strong DC voltages (300-350 volts). The amount of electrical energy injected (input) in the system was measured by an appropriate wattmeter. The measure of vaporised water weights (output) gave the thermal energies appeared in the system. Under convenient conditions, the ratio (COP) of thermal energy to electrical energy was greater than one (abnormal excess heat) as reported by Mizuno.

However, the possible loss of tiny droplets of water, the eventual storage and destorage of thermal energy and maybe wrong indications of the wattmeter in severe conditions of current and voltage have been suggested as possible artefacts, bringing doubts on our experimental conclusions. In the new device described here after, a boiling - water calorimeter, the possible loss of electrolyte droplets and the storage and de-storage of thermal energy were measured and taken into account. Their influence is negligible. The measurement of the thermal heat given by a resistance in series with the electrolysis experiment showed us that the wattmeter gave consistent results within an accuracy of 2%, and also results obtained using two different watt meters were identical.

Our experiments have confirmed the appearance of abnormal excess heat. Energy out over energy in ratio (COP) gives us reproducible results around 1.3 at 350 volts. Thus, these results validate completely all the preceding results presented at YOKOHAMA (ICCF12). This new device seems to be suitable for more detailed studies related to the MIZUNO experiment. We present finally some ideas for a future experimental program.

(1) "Abnormal excess heat observed during MIZUNO-type experiments" by J.F. FAUVARQUE- P.P. CLAUZON- G.J-M. LALLEVE (CNAM – Paris). Paper presented at ICCF12 Conference (Yokohama, Japan) in November 2005.



Fig 1: Scheme of the boiling water calorimeter.

## Paper presentation

- 1- Introduction
- 2- Description of the calorimeter
- 3- Recommendations for reproducible tests
- 4- Results obtained
- 5- Discussion of possible artefacts
- 6- Conclusions- future experiments

#### **1- Introduction:**

In 1989, Fleischmann and Pons reported an anomalous exothermal reaction during electrolysis of heavy water at palladium cathode. Since that time numerous authors have reported anomalous heat generated during water electrolysis, either in heavy water or in light water. The MIZUNO experiment is an electrolysis experiment of light water in plasma mode. A. MIZUNO reported excess heats, and also excess hydrogen production. In order to explain this phenomenon, CIRILLO (ref.3) has presented transmutations in the cathode materials. Abnormal heat productions could be associated with the appearance of Osmium, Iridium, platinum and gold but without quantitative measurements.

Usually, experiments describing excess heat evolution failed to be reproducible by different authors. We reported that MIZUNO experiments can be easily reproduced. In our device, the cathode is made of Tungsten (as used for welding), the anode is a platined titanium grid and the electrolyte is a potassium carbonate  $K_2CO_3$  at 0.2 M in pure water.

The first experimental set up was described in ref.1. We measured the input of electrical energy and the loss of water by weighing the remaining electrolyte. The main results were:

- values of COP ( COP is the performance coefficient Power out over Power in) observed as high as 1.3. (30 % of excess water evaporated for a given input of electrical energy)
- Values of COP increased when the voltage was increasing beyond a value in the vicinity of 250 volt.
- when potassium was changed into other alkalis in the electrolyte, we could notice that the voltage at the beginning of increasing COP was smaller as atomic mass of the alkali is higher.
- replacement of the ordinary pure water in the electrolyte by heavy water did not make any meaningful change in the results.

However, the possible loss of electrolyte in tiny droplets, the eventual storage and destorage of thermal energy and maybe wrong indications of the wattmeter placed in severe conditions for the current and the voltage (plasma instability) have been suggested as possible artefacts, being able to give doubts on our experimental conclusions. This is why we were considering a new experimental set-up, the boiling-water calorimeter, in order to answer these critics. Furthermore, the excess heat was calculated from the difference between two large figures (mass of electrolyte before electrolysis minus mass of electrolyte after electrolysis). So we turned our mind toward a direct measurement of evaporated water mass by condensing it and weighing the condensed water, thus increasing the precision of the determination of excess heat.

#### 2- Boiling-water calorimeter description:

This new calorimeter scheme in Fig.1. A big beaker (5 liters) is placed on a heating plate with a magnetic stirring rod. A complementary thermal heater may be added inside the beaker in order to speed up the temperature setting at 100°C of the beaker. This beaker may be replaced by a Dewar, which will minimise the thermal losses, but then cannot allow the direct observation of the cathode running.

The beaker is insulated and a small window in the thermal insulator allows to look at the working cathode under test (active length of the cathode, behaviour and colour of the plasma). Fig.2 gives a photograph of the separated parts of the calorimeter.



Fig.2 View of the parts of the calorimeter

More detailed photos of the reactor placed inside the 51 beaker are given in Fig.3. One can see:

- the anode made of platinized titanium grid in lower part
- the tungsten cathode placed inside its silica tube
- the calibration electric heater. This 20 ohms resistance is set in a glass tube within silicon oil for a good thermal contact. The two wires for the electrical supply can be seen.





Fig.3 Detailed views of the internal reactor

Fig.4 shows the complete set up running, with the condenser. A small beaker placed on a balance give the weight of the condensed water in continuous mode if wanted. Inside the reactor, we placed a Teflon screen with multiple small holes in order to stop droplets if any.

The water inside the beaker, but outside the reactor, is boiling (100°C everywhere inside the 51 beaker). The reactor is of course also at 100°C. Any power produced inside the reactor gives immediately a steam production which is then condensed in the condenser and the water obtained falls down in the small beaker. In fact, thermal losses cannot be completely avoided. They take place in the upper part because the steam produced outside the reactor and under the beaker cover is not uniformly at 100°C. The condenser yield may be also not equal to 100%, in spite of a second condenser placed above the first one.

Due to these thermal losses (which may be avoided in an experimental advanced set-up completely immersed in 100°C water), the calibrations that we made with the internal resistance have given a ratio of power out over power in (COP) of 0.95 whatever the power in between 100 watts to 300 watts. This value looks to us satisfactory and so we run the electrolysis experiments. Of course, we do from time to time control calibrations and especially for each series of electrolysis runs.

Nota bene: we were able to see during the calibration tests that storage-unstorage (due to thermal energy inside the internal resistance) was negligible. We also observed during a long test without any power in the reactor that less than 1.1g of water was measured inside the small beaker in 5 minutes. This small leak is due to the thermal losses under the 51 beaker cover.



Fig.4 Complete set-up running

#### **3-** Recommendations for reproducible tests:

These experiments are very sensitive to experimental conditions. But if one follows the experimental recommendations hereafter, a 100% reproducibility is almost guarantied.

For a given geometrical configuration, one must optimise various characteristics:

- the titration of the electrolyte salt (here 0.2M)
- the salt nature ( $K_2CO_3$  in our case, but other alkaline salts are possible)
- the geometrical characteristics of the active part of the cathode ( diameter, length, point form..)
- the gap between the cathode and the surrounding anode
- the reactor environment must be imperatively at 100°C temperature
- during the rise in voltage, one has to stay a few minutes (5 to 10 minutes) at different levels in order to condition the cathode. One observes in general a decrease of the current intensity value when staying at a given level. One must wait the current stabilisation before increasing to the next level.

A very important point is obtaining a power level in agreement with the characteristics of the reactor and the condenser. In our case, we had to go not over 1A for good operating conditions (electrical power from 300 to 350 watts). A too large power leads to violent moves of the electrolyte which disrupt the plasma around the cathode. The abnormal heat then disappears. We must at that time stop the experiment in order to review the length of the cathode active part, or the cathode diameter, or the electrolyte salt titration, etc... The power must be appropriately adjusted...

A positive result is obtained generally when the plasma colour is orange-red, when the electrolyte boiling is quiet and the vortices avoided. As the cathode is worn little by little, the power decreases and then it is difficult to exceed 10 to 20 minutes for a run duration. It would be of interest in the future to keep constant the active part of the cathode and also the electrolyte level (continuous addition of pure water in order to maintain constant the electrolyte titration).

#### 4- Results obtained:

One example among numerous positive tests is presented here. It is a positive experiment at 350 volts followed by a calibration done with the internal resistance at 300 watts (electrolysis at 0 volt) and then a return to 350 volts electrolysis, without of course any power in the resistance...

	Duration	Water Condens	Thermal power	Electrical	Electrical	СОР	l averag.	The loss in
	min	g	W	W.h	W (*)		A	weight of the
350	0	74,5(*)	0	0	0,0	-	-	cathode is 0.806 g, that
350	1	86,7	459,5	7,28	436,8	1,05	1,25	
350	2	97,9	421,9	13,7	382,2	1,10	1,09	means at most
350	3	108,7	406,8	20,0	382,2	1,06	1,09	3688 J
350	4	119,1	391,7	25,8	349,2	1,12	1,00	considering
350	5	129,2	380,4	31,4	330,6	1,15	0,94	tungsten
350	6	138,8	361,6	36,6	313,8	1,15	0,90	oxidation
350	7	148,0	346,5	41,4	286,2	1,21	0,82	Oxidation.
350	8	157,0	339,0	45,8	268,2	1,26	0,77	(*) initial value is
350	9	165,9	335,2	50,5	280,2	1,20	0,80	not zero; that
350	10	174,7	331,5	55,5	298,2	1,11	0,85	corresponds to
								the beginning of
		226452,0		199656,0	moy.	1,14	0,93	registration.

We stop the electrolysis without any other change and we operate at about 300 watts the internal resistance :

length	Condens. water	Thermal power	Electrical energy	Electrical power	СОР
min	g	W	W.h	W (*)	
0	10,8	0		0,0	
1	18,2	278,7	5,064	303,8	0,92
2	25,4	271,2	10,1	299,8	0,90
3	32,5	267,4	15,1	300,0	0,89
4	39,7	271,2	20,1	299,4	0,91
5	46,9	271,2	25,1	300,6	0,90
		81586,0 J	90216,0 J	moy. W	0,90
		COP	0,90	300,7	

We operate again the electrolysis at 350 volts without the internal resistance:

	duration	Condens. water	Thermal power	Electrical energy	Electrical power	СОР
V	min	g	W	W.h	W (*)	
	0	9,8	0		0,0	
350	1	20,8	414,3	5,89	353,4	1,17
350	2	29,8	339,0	10,7	291,0	1,16
350	3	42,6	482,1	17,5	402,6	1,20
350	4	52,9	388,0	23,0	333,0	1,17
350	5	63,1	384,2	28,5	328,8	1,17
350	6	73,2	380,4	33,7	315,6	1,21
350	7	82,8	361,6	38,7	298,2	1,21
					moy. W	
		164980 J		139356 J	331,8	1,18

In our geometrical set up, the values for the COP obtained with an electrical resistance at 300 watts are  $0.90 \pm 0.01$ . This means that 0.10 must be added to the crude values of COP measured during plasma. The actual COP during the second part of the run is  $1.28 \pm 0.02$ , and is  $1.24 \pm 0.03$  during the first part of the run.

The results obtained in measuring the condensed water vapour are completely in accordance with the values that we presented at ICCF 12 Conference (Yokohama) by measuring the mass of evaporated water. The whole set of results of Ref 1 is validated by this recent set of results.

#### Reproducibility:

The main characteristic of our new results is their reproducibility at 100%. This achieved feature is of course one of the most important goals for our CMNS community. To illustrate this fact, during March and April 2007, about 10 tests were done and results shown in the below table . Among them, 9 tests gave positive results for the COP : COP values between 1.16 to 1.31. The negative result was completely understood . It was at first delicate to find out because due to the silica tube wrapping the tungsten cathode which was splitted in the hidden side of the window. Thus, the active length of the cathode was actually longer than we had foreseen and then the electrical power was too high and thus leading to bad COP value.

Summary table of various results obtained on March and April 2007					
Tests N°	V (Volts)	Electrical power (Watts)	СОР	INCIDENT	
1	350	215	1.29	none	
2	350 350 350	200 227 218	1,31 1,30 1.30	none	
3	300 350	261 305	1,20 1,16	none	
4	300	500	0.96	Silica tube fissured	
6	350	366	1.16	none	
7	350	319	1.17	none	
8	390	155	1.24	none	

#### **5-** Discussion of possible artefacts :

#### Tungsten combustion:

The tungsten combustion gives 842000 J/M. The mass M is 184 g. The loss of Tungsten in table 1 is 0.806 g i.e. 3688 J if its disparition is caused by combustion. The total thermal energy measured in this run is: 226452 J. Even if we supposed that all these 3688 J go into the reactor (this is not true, because part of the tungsten is found at the bottom of the reactor), that represents only 1.6 % of the thermal power.

No chemical reactions can explain the observed excess energy.

However, the persistence of a blue opaline colour of the condensed water results from the release of an tungsten aerosol with the steam. We found that the content of tungsten in the condensed water was never higher than 0.8g per 100g of condensed water. This is not a problem.

#### Electrolyte tiny droplets pollution of the condensed water :

Electrolyte contains initially 16 grams of Potassium per litre. We have verified the potassium content of numerous condensed water samples, in case of positive experiments and also negative experiments.

All the values of potassium contents were between 0.024 to 0.085 g/l. The tiny droplets pollution is not a problem.

#### Storage and unstorage :

Thermal storage and unstorage are very reduced by conception. The reactor is always maintained at 100°C and the only storage unstorage comes from the stored energy in the electrodes. The tests we made show that the power became stable in a few seconds, the power transients being very

small. The fig.5 gives you an example of what we observed with the end of a 400 electric watts experiment.



Fig. 5 Unstorage : 400 electrical watts at the experiment end.

Stabilisation was observed within 15 seconds and the extra weight of condensed water was less than 1g for a total content of 107 g.

Storage and unstorage cannot be considered as an artefact.

# Water tranfer towards the condensed water due to temperatures inhomogeneities (cover part of the 51 beaker) :

Before any energy rise in the reactor, we have observed a small water mass transfer. The largest values we have observed were 5g in 10 minutes. This transfer is very small as compared to the mass of condensed water in 10 minutes of an ordinary experiment: about 100 g in ten minutes. This point is corrected by the calibration measurement.

Here again, it is not an actual artefact.

### Reliability of the UNIGOR wattmeter :

We have shown in ref.2 the results obtained with the following test: an external ohmic heater is set in series with the electrolysis experiment in order to have the same very unstable electric current. This heater is placed in a dewar beaker with water and the weight of the evaporated water, when an electrolysis experiment is done, can be compared with the watt-hours measured by the UNIGOR wattmeter. This demonstration is not a definitive one, but the gaps between the compared measurements were never higher than 2%.

We made also a comparison of the values measured by the UNIGOR wattmeter (1 point every 1 minute) and a SIEMENS wattmeter (1 point every 10 seconds), wattmeters of different conceptions. This comparison is quite satisfactory (Fig. 6).





The summing up of all the corrections considered shows that three items can be taken into account for correcting the COP values:

- Tungsten combustion:	- 1.6% max
- Water transfer:	- 1.7% max

- Wattmeter precision:  $\pm 2\%$  max

Total: -5.3% max

If now you consider that the calibration tests give a COP between 0.90 to 0.95, the +10 to +5 % to add overcomes the negative value of 5.3% correction. Has not been considered the plasma light radiation energy escaping out of the reactor.

In conclusion, the values of COP higher than 1 (1.30 here) are really meaningful.

#### 6- Conclusions – future experiments :

The reproducibility of our positive experiments is now very close to 100%, not for saying 100%. The COP values obtained, unexplained for the moment, seem to us very important because of the high values of abnormal excess heats measured (tens or even about a hundred of watts). An explanation of this phenomenon would be a very important event...

We have seen that this phenomenon appears when the colour of the plasma around the cathode is orange, when the environment is quiet and the voltage high. In the course of future experiments which may contribute to find a possible explanation, one can look at:

- higher voltages ; the current density seems to be a decisive item . But it is important to avoid too large power for obtaining excess heat.
- it could be interesting to prospect pulsed electrical supply which allow to have in peaks higher voltages without cathodes suffering of high powers.
- A lot of parametrical experiments could be done when complementary means are available : material tests for the electrodes, other salts for the electrolytes, etc....

#### AKNOWLEDGEMENTS :

The authors want to thank very much J-L. NAUDIN of GIFNET, who has done MIZUNO-like experiments with success and has brought their attention on these experiments. They want also to thank very much Jacques DUFOUR (CNAM) and Didier NOËL (EDF Les Renardières) for fruitful discussions.

#### Litterature

**Ref**: (1) Ref. 1 Experimental study of glow discharge in light water with Tungsten electrodes by D.Y. Chung,Y. Aoki, F. Senftle and T. Mizuno ICCF11 conference in Marseille (Oct.31- Nov.5 / 2004).

**Ref : (2)** "Abnormal excess heat observed during Mizuno-type experiments" by J.F.Fauvarque - P.P. Clauzon - G. J-M. Lallevé -Service d'électrochimie Industrielle du CNAM- Paper given at Yokohama - Nov. 2005 - ICCMS12 meeting.

**Ref : (3)** Jean-Louis Naudin site : <u>http://www.jlnlabs.org</u> Experiment description : <u>http://jlnlabs.imars.com/cfr/index.htm</u>