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A Search for Neutrons and Gamma Rays Associated with Tritium Production in Deuterided Metals*

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Tritium activity has been measured in several Pd-Ni-D_2O electrolytic cells, as reported previously[1,2]. At the present time 13 separate cells have shown tritium at 10^2 to 10^6 times the background level of the D_2O used in these experiments. The appearance of the activity in the electrolyte and in the gas phase occurs over a period of hours to a a few days after remaining at or near the background level during 4-10 weeks of charging in 0.1 M LiOD, D_2O solution. The present paper deals with attempts to reproduce the tritium measurements and to establish the source, from either contamination or nuclear reaction.

The sudden appearance of tritium activity in the cells requires the tritium to be loaded in a component prior to the beginning of cell operation in a contamination model. Release is assumed to be caused by deterioration of one of the materials used in the 0.1 M LiOD solution. In an extensive set of tests, no contamination has been found in the starting materials or in normal water blanks. Results for neutron and gamma-ray correlations have proved to be negative also. The limit set on the absence of 2.5 MeV neutrons for the t/n ratio is 10^7 from that expected in the d+d reaction, and 10^3 for 14 MeV neutrons expected from the t+d secondary reaction. Similarly, Coulomb excitation gamma rays expected from the interaction of 3 MeV protons with Pd are found to be absent, which indicates that the d(d,p)t two-body reaction does not occur in the Pd electrode.

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1) K.L.Wolf,et al, Workshop on Cold Fusion, Santa Fe,N.M. 1989
2) N.J.C. Packham, et al, J. Electroanal. Chem. Oct.7,1989.

Introduction

The present paper deals with the search for the source of significant levels of tritium that have been found in Pd-Ni-D_2O electrolytic cells. Observations are given on the appearance of tritium in the cells, and two experiments are described which have attempted to correlate the tritium with neutron and gamma-ray emission. In the absence of a direct correlation with a live-time nuclear effect, a strict program of sampling and blanks must be followed in order to check for contamination. Results are given from the initial phases of such a study.

Tritium from Electrolytic Cells - Verification

Activity attributed to the beta decay of tritium was first detected in samples of electrolytes from cells at TAMU utilizing in situ liquid scintillation counting performed by the Health- Physics Department. A detector was constructed at the Cyclotron Institute for detailed measurements of the energy spectra. Figure 1 shows the results of a measurement presented as a traditional Kurie plot, in order to determine the beta endpoint energy for identification. Good agreement is obtained with the expected value of 18 keV for tritium beta decay. A comparision with a tritium standard provides agreement to the 2% level at all parts of the spectrum. Samples from four cells have been measured in this fashion, including activity from catalytic recombination of H_2 and O_2 gases evolved from a cell. An 18 keV endpoint energy from an activity carried in the gas phase leaves no doubt that tritium activity is being measured. Quantitative measurements by four outside laboratories confirm the validity of these meaurements[2], but the type of energy measurements is unknown.

The Appearance of Tritium

Table I shows a compilation of the data collected by two research groups at TAMU for 13 electrolytic cells. The background level of the tritium activity in the D_2O used is approximately 160 d/m which can be compared to the rates in Table I. Usually four times the cell volume of 15 ml has been used over the lifetime of a cell. Thus one need not consider separation factors or selective distillation in most of the samples documentated. Conservation of mass dictates the elimination of concentration mechanisms as a viable explanation. Another cell not included in Table I produced tritium at 12 times the background level, but had a titanium cathode and is not discussed here.

An activity vs time measurement was conducted in six of the 13 cells mentioned in Table I, which provides more information. Figure 2 shows the most detailed series of timed assays. After the cell was charged at a current density of 60 ma/cm^2 for four weeks, the current density was increased to 500 ma/cm^2 at the start time of Fig.2. It can be seen that the tritium activity in the electrolyte built up within a few hours. Simailarly, Fig.3 shows a plot of the tritium activity in the electrolyte vs the date of assay. A buildup of tritium occurs within a 48 hour period correlated with a period of high cell current. The constant activity levels and later decreases are interpreted as the end of production and displacement, respectively with continuuing electrolysis. Tritium activity appears during a period of high current

density or after such a period within a few days. On the basis of the six cells which have been followed with tritium assays, no significant tritium activity was detected with only low current conditions. Another significant feature involves three cells which were fitted with separate recombination catalyst cells to provide a measurement on the tritium level in the gas phase. In all cases the concentration of tritium was much higher in the recombinant D_2O compared to the electrolyte, which is opposite to that expected from separation factors. Cell C-8 in Table I produced a factor of 300 times more tritium in the gas phase, both in concentration and in integrated activity. This factor is comparable to the recombination rate measured for these cells. Cell C-8 showed the highest total amount of tritium totalling about 10^{16} atoms, but it is not the highest level observed in the electrolyte. The gas phase / electrolyte ratio of integrated amounts of tritium is quite variable. In a second larger cell C-9 with a volume of 100 ml the total activity is higher in the electrolyte. As described later, only a tritium concentration is known for the recombinant for cell D-6 with most of the remaining activity introduced into the electrolyte from the recombinant. At least an order of magnitude more tritium was produced in the gas phase than in the electrolyte from this small 15 ml cell. Many factors can be thought of which could influence the amount of tritium that exchanges with the D_2O in the electrolyte, such as the distance traveled by bubbles and the degree of saturation of gases in the electrolyte at the time of tritium emission.

Cell Design

Figure 4 provides a schematic of the rather simple design for most of the cells used in the present study. A 12-15 ml pyrex centrifuge tube is used to provide a compact design, chiefly for a large solid angle in the neutron experiments. No cooling water was used to avoid degradation of neutron spectra, thus the cells run at elevated temperatures near boiling during high current periods. The cathode consists of a 1 mm diameter Pd wire approximately 4 cm in length. The cyclindrical anode is made of Ni mesh. Cell potentials are 2.5-3 volts while charging at 50-60 ma/cm^2 and up to 15 volts at high current density, 500ma/cm^2. Black-green NiO is formed and settles to the bottom of the cell, but does not adhere to the cathode. Cells are charged for at least a month before a 10- 12 hour period of high current is applied. This procedure is repeated until a Ni-wire electrode connection fails, up to three months. Cell C-7 in Table I showed a low yield of tritium after one week of charging and a period of high current,which is the shortest production time found.

Neutron Detection

A system based on 3" X 5" NE213 liquid scintillators(Fig.5) has been used to provide a low background measurement for neutron emission. Pulse shape discrimination methods are used to reject gamma rays resulting in a background of 0.5 c/m for 5% total efficiency. An active cosmic ray shield of 1/4" plastic scintillator surrounds a passive shield of 10-12" thick parawax and the neutron detector situated within. The principal source of background is from the neutron component of the cosmic ray showers. The principal advantage of this type of detector is the measurement of the neutron energy spectrum. The system is sensitive to neutrons ranging from 1 to

50 MeV. Neutron energy spectra measured previously are indicative of a neutron energy of 2.5 MeV expected from the d(d,n)^{3}He reaction as shown in Fig.6, correspondig to cell C-D in Table I. The region above 2.5 MeV is found to be useful in detecting cosmic ray showers and thus can increase the sensitivity somewhat. The present paper uses the neutron data to establish limits due to the lack of 2.5 and 14 MeV neutrons in correlation with tritium measurements.

Gamma-Ray Detection

A 25% intrinsic germanium detector was active for six D_2O cells for the entire cell lifetimes in the study described later.[2] Passive lead shielding was used to minimize gamma-ray background contributions. The excellent resolution of a germanium detector provides an unambiguous identification, in this instance for the lower levels of the palladium isotopes in the 300-600 keV region. Figure 7 shows a sample spectrum covering the energy range from 80-3200 keV. Coulomb excitation of the Pd isotopes is expected by the 3 MeV protons from the d(d,p)t reaction, if it occurs. The overall efficiency of the detector is approximately 1%, which along with the probability of Coulomb excitation (10^{-7}) means the method is not one of the most sensitive. For the tritium production observed in cell D-6, a significant limit was set as discussed later.

Neutron-Tritium Correlations

Cell C-D listed in Table I showed two instances of neutron emission approximately 2 hours in duration each at levels of 20-60 n/min, and also showed tritium corresponding to 1.6×10^{13} atoms. The apparent branching ratio, equal to the t/n ratio, is 10^9 instead of 1:1 expected from measurements at normal fusion energies for the d + d reaction. The unknown factor here is whether or not the cell was counted for neutrons at the correct time, since cell C-D was not followed with timed assays. The next stage in the correlation was attempted with the same electrode which was melted and reformed to insure the absence of tritium, and the cell was neutron counted for 1 1/2 months. A period of neutron emission was observed but no tritium was produced above background levels.

Cell C-G was neutron counted during a period of positive tritium production as shown previously in Fig.3. The neutron count rate is plotted in Fig.8 along with the periods which were defined by the tritium assays. A small increase in the neutron rate given over 100 minute intervals shows a slight increase at the time of cell current increase, but is not regarded to be statistically significant. Over a 48 hour period a lower limit on the t/n ratio is determined to be 7×10^7. If there were a large enhancement in the t + p branch, further difficulties are encountered because of the lack of 14 MeV neutrons from the d(t,n)^{4}He secondary reaction which would be expected to occur from the 1 MeV tritons. The discrepancy here is 10^3-10^4, depending upon where the reaction takes place (surface,volume).

Tritium-Gamma Ray Correlations

The neutron measurements suggest strongly that either something quite unexpected occurs in nuclear reactions, or that we have been observing tritium contamination initially buried within the cell components. Laboratories and equipment have been checked thoroughly and it is clear that no widespread contamination is present. Samples of Pd and Ni have been checked at LANL[5] and no tritium was found.

Similarly samples of materials have been dissolved and counted in the present study, but not in the numbers necessary and not with proper sampling techniques for a model based on spot contamination. Light water blanks seem to provide an inclusive means for contamination checks, but only two light water cells were constructed in the previous studies[2], and both at the Cyclotron Institute. In the present series, 12 cells were prepared, limited by the Pd on hand, split equally between light water and heavy water electrolytes, with no other differences. The materials and methods used previously were duplicated, except for the 1mm Pd wire which was from a different batch but from the same company. Cell M-1 listed in Table I was constructed with this Pd and had shown a low level production. Table II shows the results from that study which was recently completed. All cells were charged at 80 ma for one month and then run at 600 ma for 12 hours, with no tritium activity detected above background. The procedure was repeated and again all were negative at the end of the second round of charging and high current. Cell D-6 showed a yield of approximately 5×10^{13} tritium atoms when assayed four days after the second high current period. The time profile of the activity is shown in Fig.9 with the activity concentration as a function of time in days. The recombination fraction stops at the peak because the catalyst cell (Fig.4) blew out the plunger, glass wool and catalyst beads, along with 0.5 ml of recombinant in the fume hood and into the immediate area. A wash of the catalyst beads gave 40,000 d/m of tritium activity. Approximately 3 ml of the recombinant drained back into the electrolytic cell, with only 0.2 ml remaining, which was sufficient for an assay. Thus most of the activity in the electrolyte originated from the recombinant. The rapid decrease in the activity in the electrolyte is not fully understood, but a similar effect was observed for cell C-8. It is suggested that since the closed cells operate under an appreciable positive pressure, the amount of dissolved td gas decreases as the pressure is reduced, along with the normal displacement with d_2 as the cell continues to run. During this four day period, no enhanced gamma-ray lines were observed which sets a limit for a descrepancy of a factor of 50. Due to the statistics of the matter, one D_2O cell does not prove the case one way or the other and this study will continue in the Martin group with 20 new cells.

TABLE I

TRITIUM ACTIVITY FROM PALLADIUM - NICKEL CELLS

CELL	ELECTRODE TREATMENT[a]	ELECTROLYTE[b]		ACTIVITY (d $min^{-1}ml^{-1}$)
C-A[d]	B	1		4.9×10^6
C-B	C	2		3.7×10^6
C-C	D	1		
	after charging at 0.05 amp/cm^2 for 4 weeks			64
	after 2 hours at 0.5 amp/cm^2			5290
	after 6 hours at 0.5 amp/cm^2			5.0×10^5
	after 12 hours at 0.5 amp/cm^2			7.6×10^5
C-D[c]	B	2		1.2×10^5
C-E	A	1		3.8×10^4
C-F	B	1		6.3×10^4
C-G	A	2		
after charging at 0.05 amp for 4 weeks; 0.5amp,12 hours				120
after additional charging for 1 week,				250
after 0.1 amp for 24 hours, 0.3 amp for 1 hour				1.5×10^4
C-2 (3 mm)	B	1		6.3×10^4
C-3 (3 mm)	C	1		0
C-1 (6 mm)	A	1		69
C-7	A	1		7.5×10^3
M-1	A	1		6.4×10^3
C-8	B	2	15 ml electr.	5.0×10^5
			15 ml recomb.	1.5×10^8
C-9 (3mm)	B	1	100ml electr.	6.7×10^4
			10ml recomb.	2.5×10^5
			100ml electr.	1.9×10^5
			8ml recomb.	2.4×10^5
D-6	B	1	14ml electr.	4.0×10^5
			recomb	1.3×10^6

a) electrode treatment: A, no treatment; B, vacuum anneal; C, acid etch; D, electroclean
b) solution type: 1, 0.1M LiOD; 2, 0.1 M LiOD + 0.1mM NaCN
c) cell JBA5 which has shown neutron activity, 50 X/min
d) verified by second ^3H counter at TAMU and by 5 other laboratories
All electrodes are 1mm diameter palladium except where noted.
All cell volumes are 12-15 ml except where noted
A blank count rate of 65 c/min has been subtracted before calculation of activities.

TABLE II

Cyclotron Institute 10/13/89

Reproducibility Test, Tritium Activity

6 H_2O and 6 D_2O Cells, 1mm X 4 cm Pd, Ni Mesh

CELL	d/m/ml	start	max (electr)	max (recomb)
H-1		59	62	69
H-2		30	35	45
H-3		34	45	47
H-4		30	37	27
H-5		21	15	17
H-6		37	26	41
D-1		170	190	185
D-2		165	195	180
D-3		190	220	250
D-4		165	240	190
D-5		200	290	160
D-6		160	4.01×10^5	1.26×10^6

All cells were run at 500ma/cm^2 for two 12-hour periods, separated by one month of charging. Total charging time was 2.5 months.

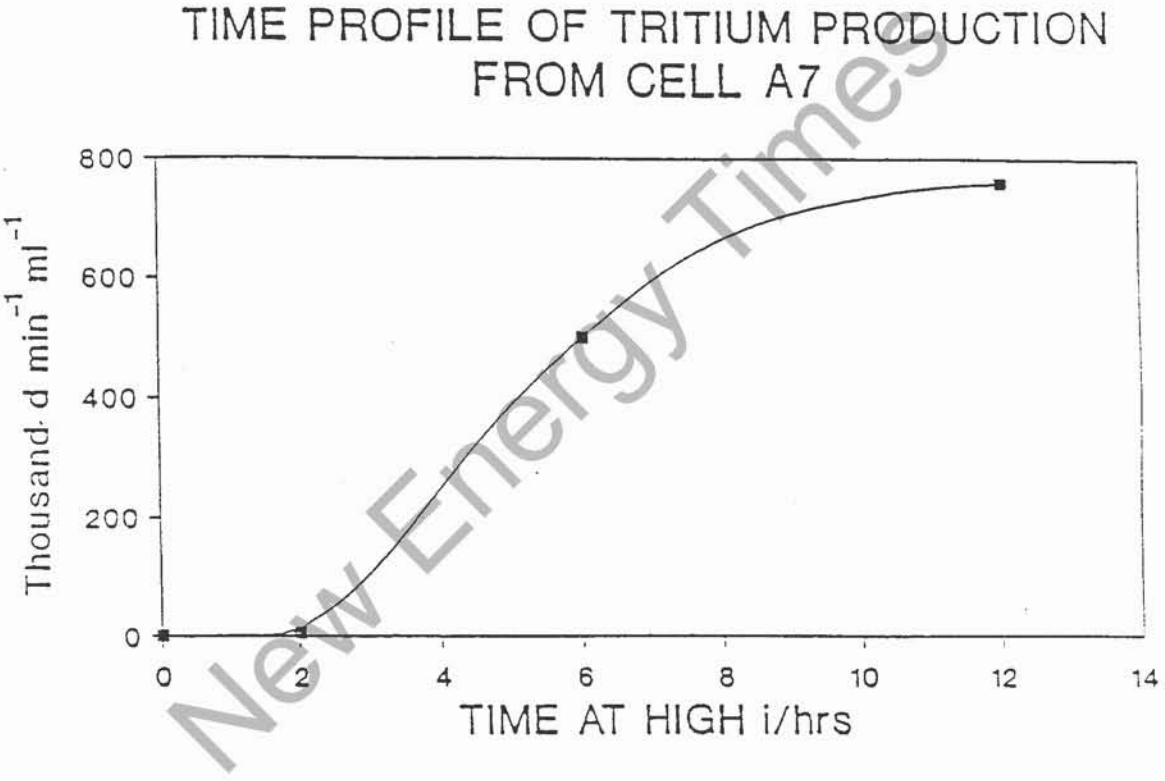

Fig. 1.

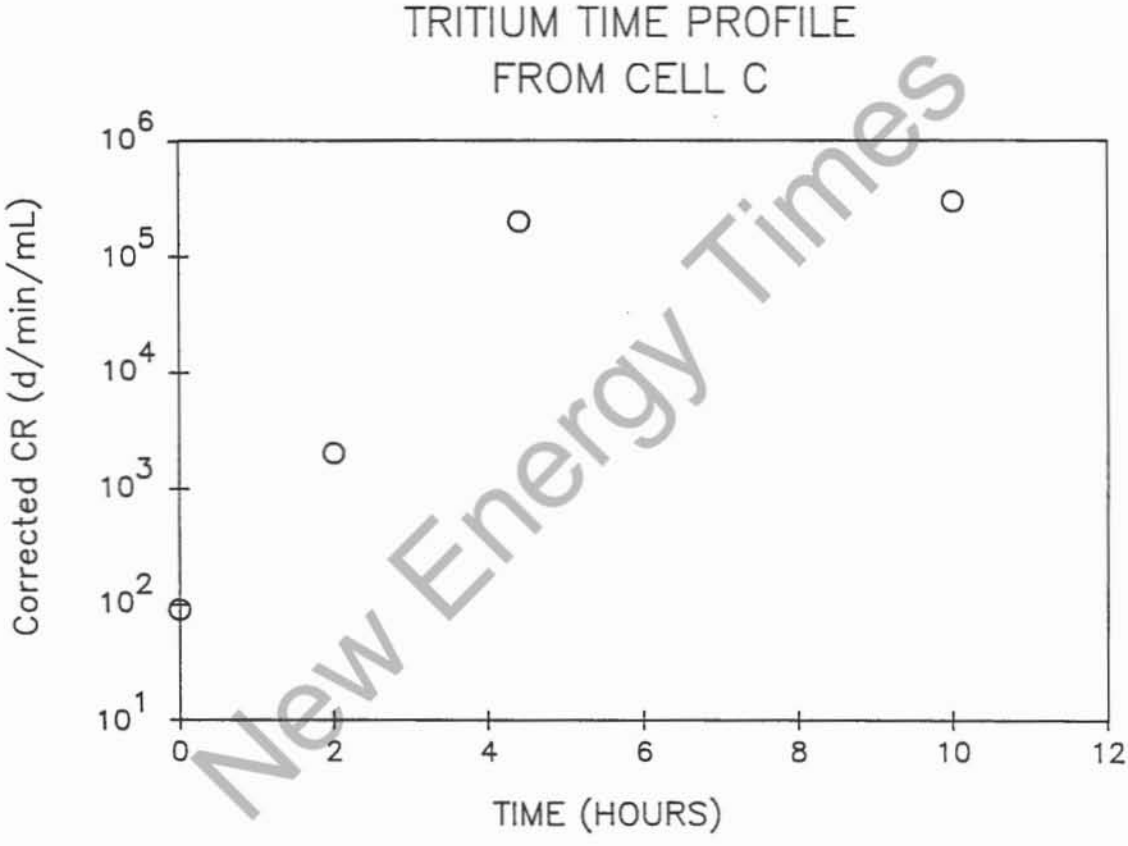

Fig. 2.

Plot of Tritium Counts vs. Date Sampled for JBXR1

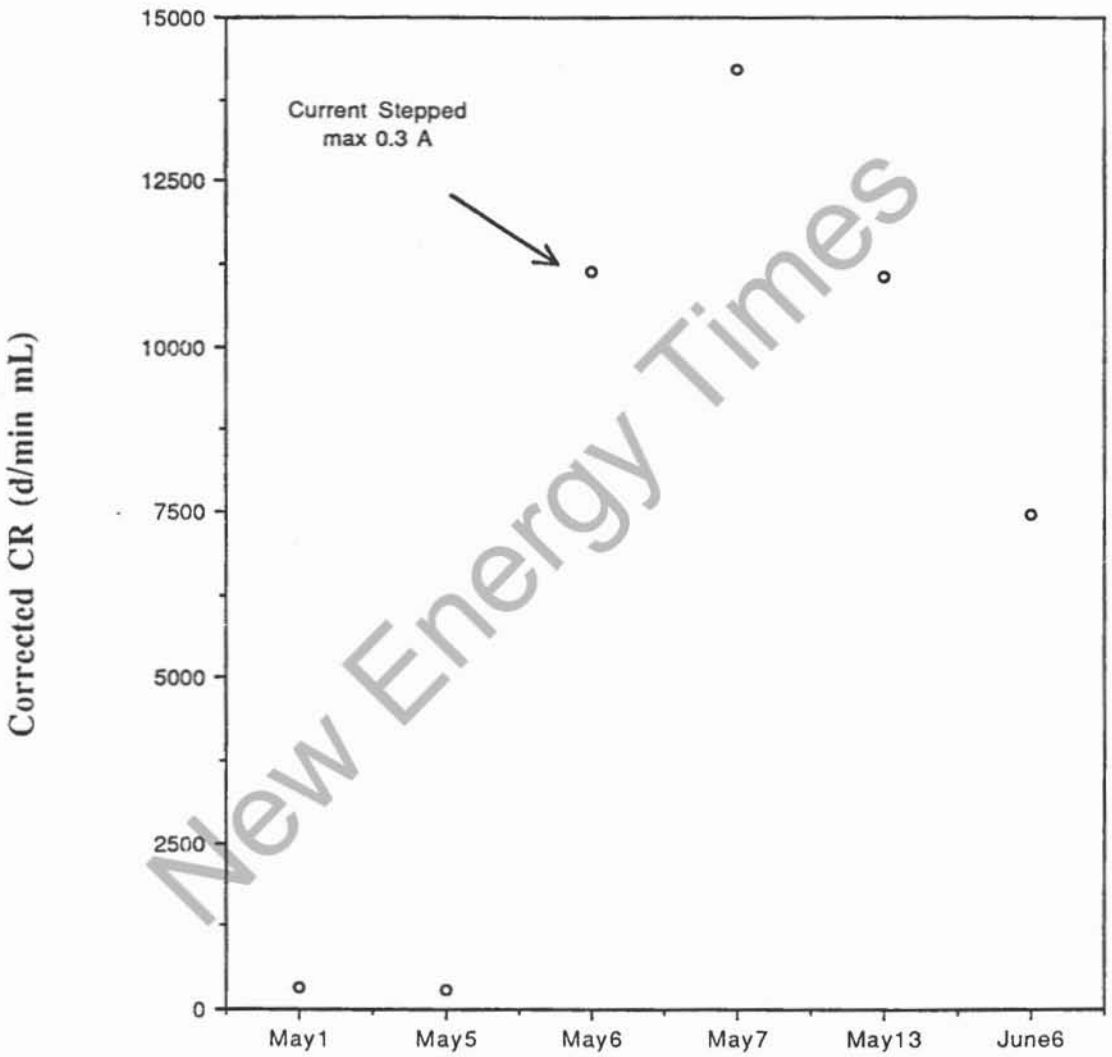

Fig. 3.

Electrochemical Cell Schematic

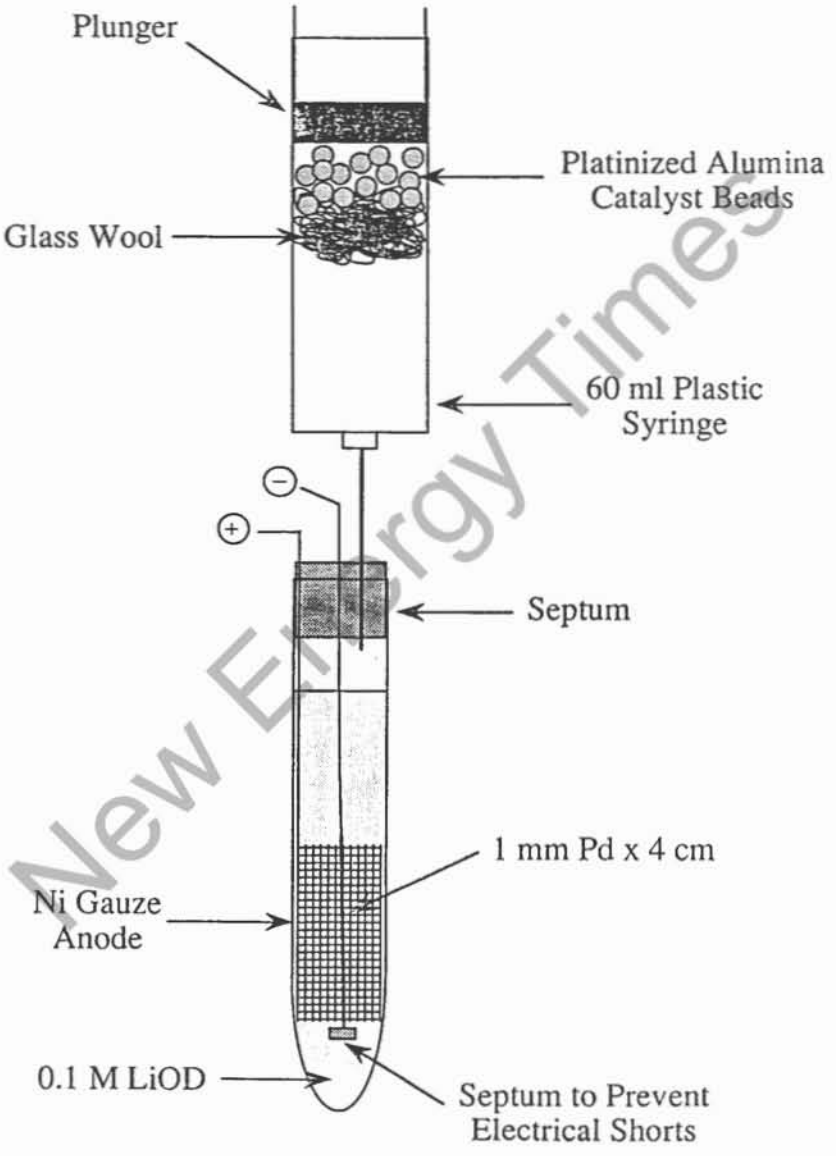

Fig. 4

Neutron Counting-
Instrument and Setup

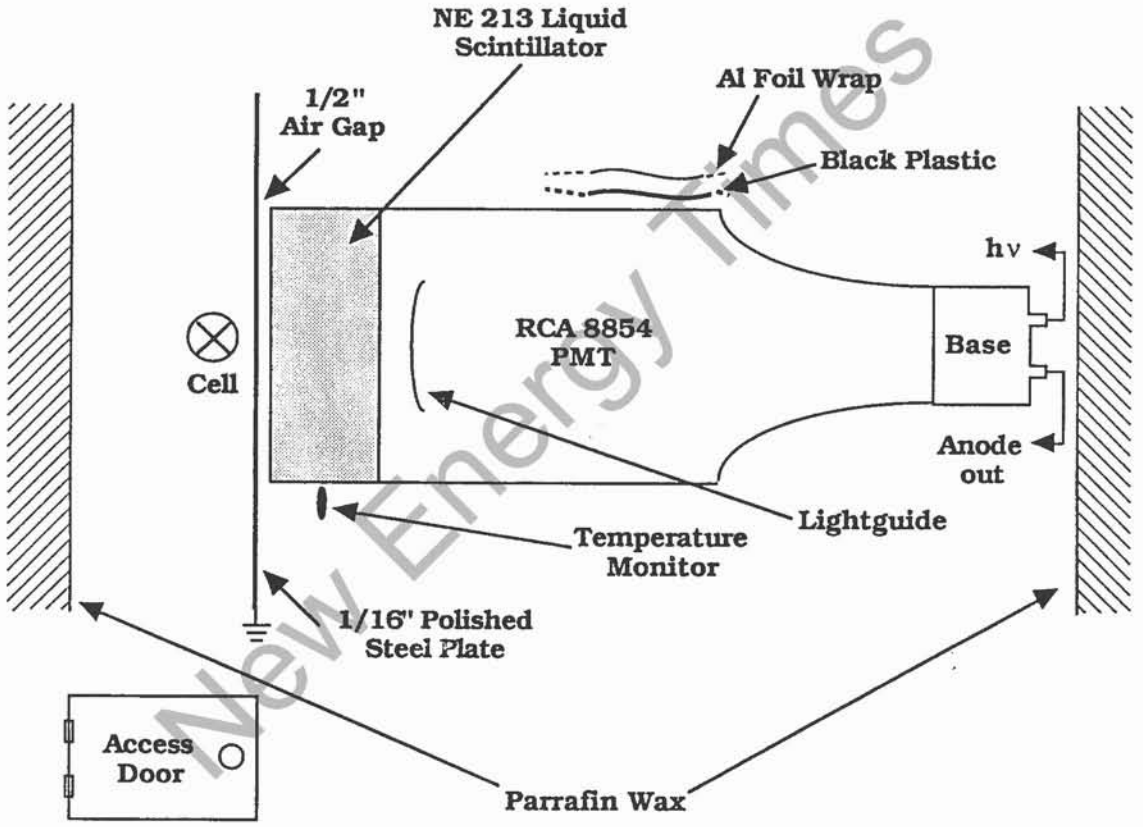

Fig. 5

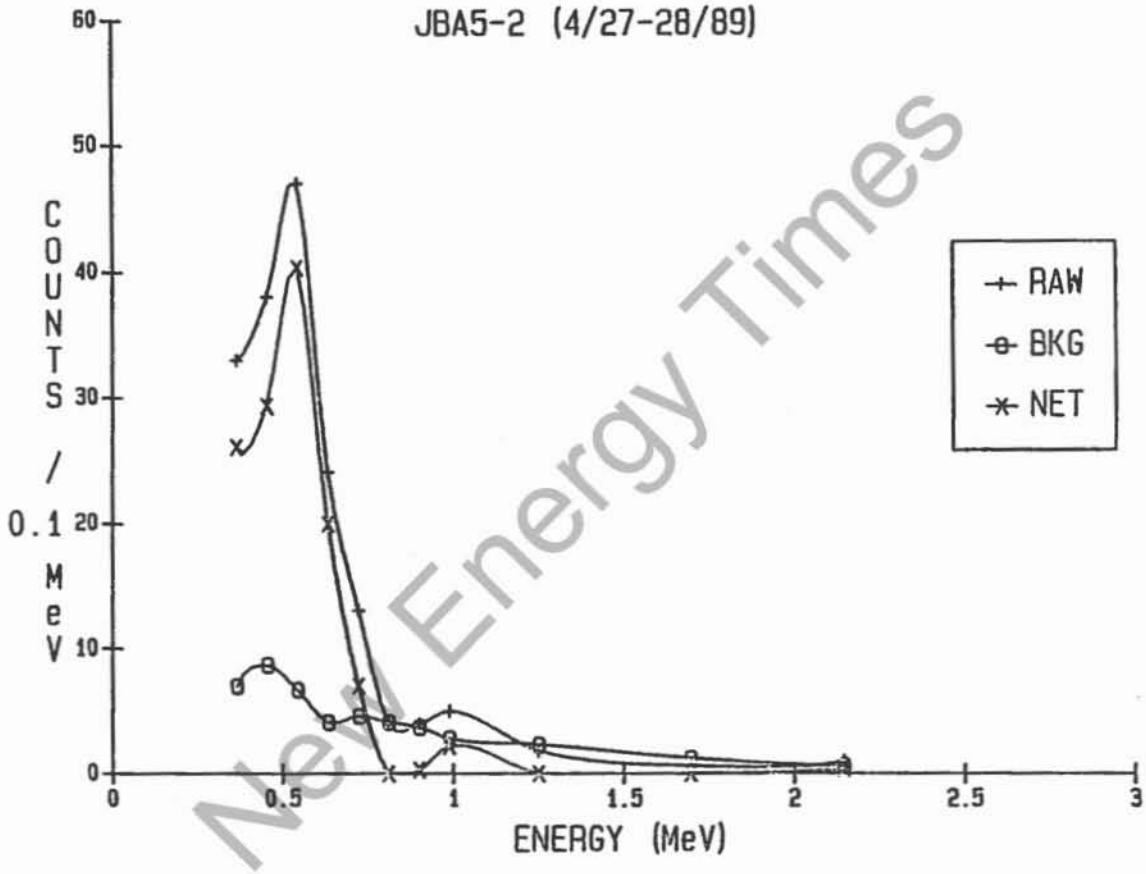

Fig. 6.

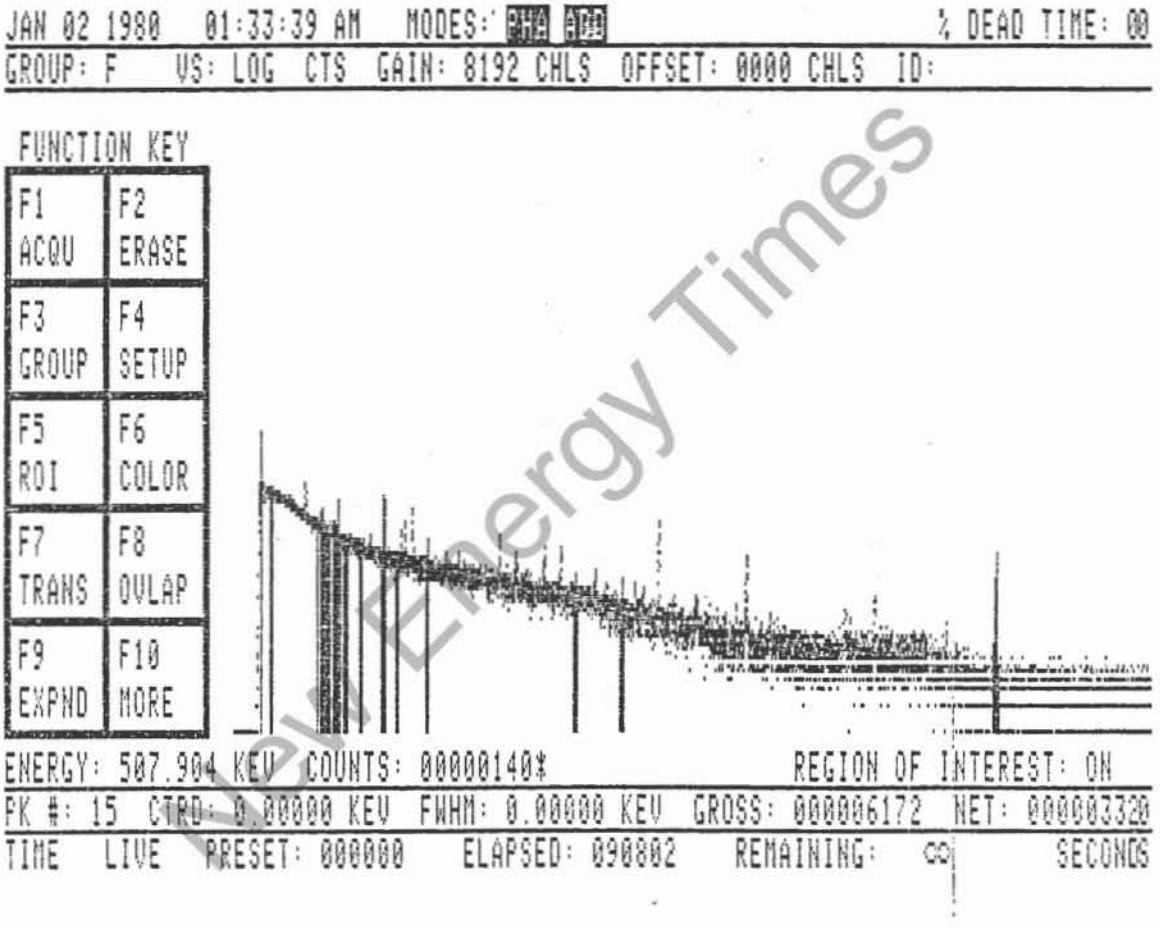

Fig. 7.

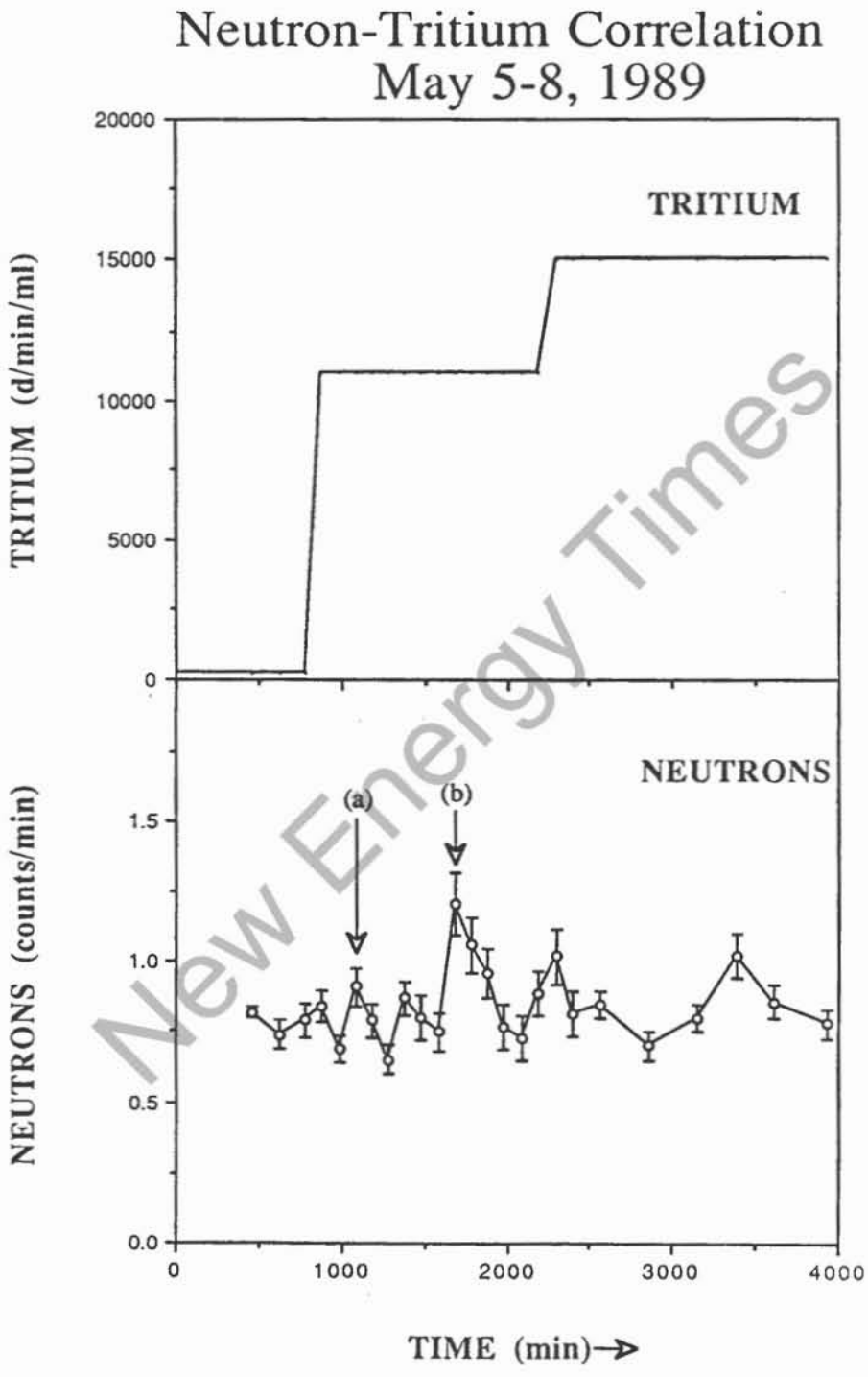

Fig. 8.

Time Profile D-6

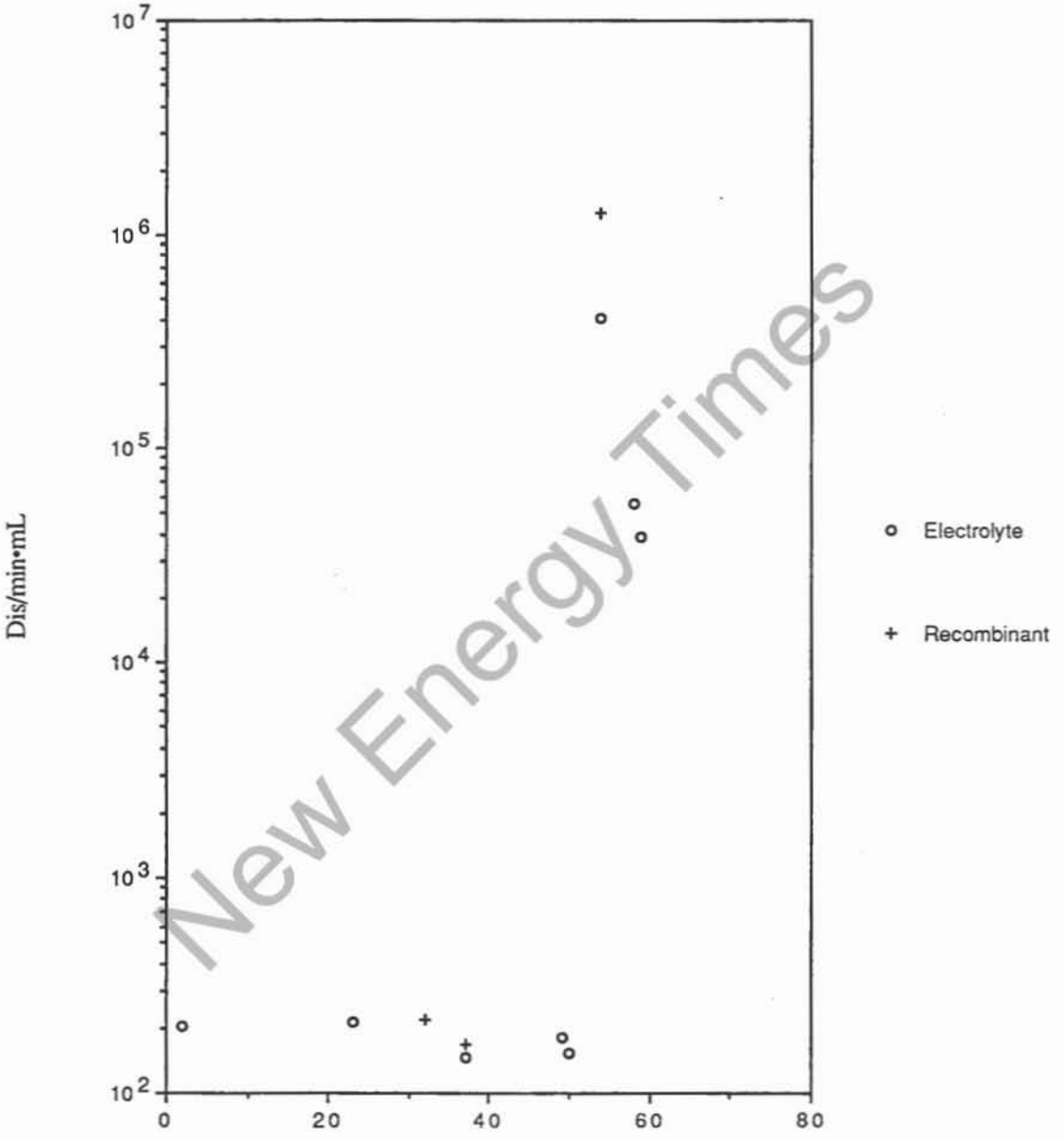

Fig. 9.

DISCUSSION (WOLF)

Hoffman: Do you have any iron impurity in your cells with nickel counterelectrodes?

Wolf: X-ray analysis shows iron, chromium as well as other metals present, which must be impurities in the nickel. Some impurities in the electrolyte are insignificant, whereas others are present in surprising amounts.

Yeager: Concerning the samples that were distilled before tritium analysis, how was the sample removed, and what is your opinion regarding distillation disturbing tritium analysis?

Wolf: Distillation had no effect in regard to tritium analysis on the cell liquid that we sampled.

Yeager: How did you verify the measurements?

Wolf: Solids were removed from the electrolyte by centrifuging and by filtering. Many measurements were made, including a very large number of blanks. After cells had operated up to periods of several months, high scintillation levels were suddenly seen. Proof that these indications were caused by tritium is given by the spectral shape and the proper beta end-point energy of approximately 18 keV. Are you concerned that chemiluminescence effects may be mistaken for tritium?

Yeager: Yes, since these may account for the abnormally large values which you have seen.

Wolf: No. We have hundreds of blank samples to show that it was not so. It is well known that chemiluminescence problems can occur in concentrated LiOH solutions. Thus, we examined blanks with different concentrations of LiOD. Even then, the chemiluminescence effect will eventually die out if the sample is left in the dark. All samples were double-counted. The first count was taken after leaving the sample for 30 minutes after preparation. The sample was then left in the dark and was recounted one or two days later. If any discrepancy between the two counts was seen, further testing would follow. We discovered no problem unless a concentrated LiOD solution was used, meaning 1 M or more. Samples in the present work were 0.1 M or pure D_2O from the recombination on a catalyst.

Yeager: I am concerned about impurities that may originate from the platinum or nickel counterelectrodes.

Wolf: There is always that danger. For example, the presence of nickel oxide might cause chemiluminescence and give false tritium readings, but it is removed from the solutions prior to counting. A reproducible beta end-point energy

corresponding to a tritium standard is strong evidence for the identification of tritium and is far stronger evidence than indirect tests such as distillation of the solution.

Appleby: What is your opinion about the effect of peroxides on the scintillation cocktail?

Wolf: Bleaches can certainly affect the results, but even they are eliminated with time. We confirmed that the two-stage counting procedure which we used would even eliminate the effect of deliberately added peroxide.

Appleby: The presence of ozone is another possibility, since it can be produced at the anode.

Yeager: Coming back to the point about distillation. A Case Western Reserve sample was distilled at Westinghouse before counting was performed.

Bockris: Los Alamos also distilled our samples, and results were the same before and after.

Wolf: Because of experiments of this type, we concluded that routine distillation was not necessary. At Case Western you would be far better off collecting an energy spectrum to make sure that you have tritium and not some other alpha, beta, or gamma activity from contamination, especially for the very low levels of activity.

Rafelski: In your gamma-ray experiments, what was the background count level?

Wolf: It is shown in our paper. I should point out that we used a high-resolution germanium detector measuring gamma rays, with a sensitivity limit of about 100 to 150 counts per day. Our effort was aimed at exceptions to the background, particularly in regard to energy levels corresponding to those in palladium isotopes.

Teller: You have not seen the energetic protons which you would expect from nuclear fusion reactions.

Wolf: Our results indicate that energetic protons are not present. In addition, we have seen no indications of 1 MeV tritons through the $t(d,^4He)n$ secondary reaction with 14 MeV neutrons. Any tritons present have a low kinetic energy, certainly less than the requirement for TD fusion.

Lewis: 100 keV or less?

Wolf: Our best estimate is 10-20 keV.

Bockris: I would like to point out that all the cells were isolated in a secure laboratory. No tritium had ever been used there before, and no assay showed tritium contamination. Very long periods of charging were required before significant amounts of tritium were seen in the cells, typically from 2-6 weeks. One significant result was that obtained with a cell including an external recombination catalyst. At least an order of magnitude more tritium activity was in the recombinant as compared to the electrolyte.

Wolf: In addition, the fact that distilled electrolyte showed the same results as electrolyte counted directly from the cells indicates that tritium had exchanged with D_2O.

Jones: Did your germanium detector show any evidence of palladium energy levels?

Wolf: We detected no palladium gamma rays with any degree of confidence. Over a 4-day period which produced tritium evolution from cell D-6, there was a discrepancy of at least a factor of 50 compared to the expected rate.

Jones: So something was visible.

Wolf: The background has some cosmic-ray induced gammas as well as the natural room background. Further analysis is required for setting limits on extremely low gamma rates.

Fleischmann: What is the energy range which you are examining?

Wolf: We measure over the range from 80 keV to 3.5 MeV, but the Coulomb excitation gammas cover the range of 300-500 keV, actually up to 555 keV. There are five lines that provide quite a characteristic signature for the palladium isotopes in terms of energies and intensities. Our limit, set by use of these Coulomb excitation gammas of a factor of 50, assumed that the tritium was produced during a 4-day period corresponding to the assay interval. If tritium production were continuous over a period of 60 days (the cell was counted over the entire lifetime), the factor of 50 is reduced somewhat, but discrepancy remains. The exact factor cannot be quoted now because we have yet to complete the detailed analysis of the spectra over the entire 60 days.

Santucci: What proton energy did your results represent?

Wolf: Assuming that the factor of 50 is correct, the proton energy would have been 3 MeV. The Coulomb excitation probability would, of course, be lower if the proton energy is reduced. A Coulex calculation is then required to estimate how much lower the proton energy must be below the predicted 3 MeV.

Jones: You seem to be telling us that there are no protons and that the triton energy is less than one MeV. What is your opinion concerning the theoretical possibility that a triton of this energy can be produced in a fusion process? Could it be via the type of process considered in the 1938 Oppenheimer-Phillips paper?

Wolf: We are not trying to theorize but simply trying to report our observations. We find no correlation of radiation with tritium production, and we have had two cycles of tritium production when the counters were in operation. This does not eliminate the possibility that tritium could build up from the tritium inside the palladium electrode, which would then be released as the lattice becomes cracked. The Coulomb excitation part of the energy is perhaps a better indication for the

lack of 3 MeV protons, because the gamma counter was in operation during the entire lifetime of the cell.

Kim: Some of the energetic protons that may be produced in the process should go into the electrolyte.

Wolf: If the protons are produced on or close to the surface, that would be correct, but that cannot represent more than a factor of 2-3, assuming isotropic emission of the protons.

Fleischmann: Statistically, some of the protons must go toward the interior of the electrode.

Wolf: We would take into account the solid angle effect.

Kim: Did you determine the Coulomb excitation cross section?

Wolf: Yes, it has been measured many years ago and again quite recently, explicitly for 3 MeV protons stopping in Pd.

Rafelski: If the expected energy is not present in the triton, it would be surprising to find it in the proton.

Appleby: Where do you suppose that the excess energy goes?

Wolf: I do not know. At present, all I can say about it is where it is not going. The tritium may be caused by contamination in one of the cell construction materials, so there may be no excess energy.

Teller: Some of your reactions do not appear to conserve energy.

Rafelski: You obtain a neutron signal at 2.5 MeV, yet you appear not to have tritions of the correct energy. Some rare nuclear reactions seem to conserve energy, whereas others seem to lose energy.

Wolf: The probability of 2.5 MeV neutron emission is quite low, and it is not necessarily correlated with tritium.

Rafelski: One might say that there are two kinds of cold fusion. In one, the probability of 2.5 MeV neutrons is strongly enhanced, i.e., no energy disappears.

Teller: Such reactions may be strongly enhanced, but they nevertheless occur at a level which is 10^{-8} times lower than that of the overall reaction, represented by the heat produced. Two unusual observations might be questionable, whereas three will be out of the question, unless there is some common cause which is different from anything which we have previously experienced. There is a common cause of these things. The Gamow tunneling probability is one problem. Apparent nonconservation of energy is another. The observations mean that something very different from previous observations is occurring, assuming that we are all not mistaken.

Fleischmann: When we first started to announce these observations, we acknowledged that it may all be a mistake. It still may be a mistake, but I believe that we are beginning to narrow down the possibilities.