MODELING THE [3]He CONCENTRATION IN A CLARKE et al. GAS SAMPLE FROM AN ARATA-STYLE CATHODE

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ABSTRACT

The time history of [3]He concentrations in gas samples collected and analyzed by Clarke et al. is modeled. A deficiency relative to expected helium suggests loss through microfractures identified by Farkas.

1. INTRODUCTION

During late 1998 and early 1999 Mckubre et al. at SRI electrochemically deposited D atoms onto an Arata-style cathode and observed 64 MJ of integrated excess heat.[1] On 1 September 1999 Oliver at PNNL punctured the cathode and collected a sample of the internal gases.[2] The sampled gases were analyzed by a mass spectrometer and found to contain 75% water vapor and 25% dry gas at a total sample pressure of 22 Torr. An attempt to measure the helium concentration within a portion of the sample showed no clear detection of either [3]He or [4]He. The collected gas was returned to SRT and then sent to Clarke at McMaster University. Clarke had developed a high sensitivity [3]He measurement system that could identify~10^4 [3]He atoms in an analyzed sample. In an exploratory analysis of a small portion of the received sample, he was surprised to find an easily measured [3]He component. The wet gas sample was also found to contain a major amount of tritium. Some of this tritium embedded itself into a portion of his system, contaminating the system and reducing its ability to quantitatively measure small amounts of [3]He. Clarke found it necessary to replace major portions of his system to regain most of his pretest [3]He detectivity. Clarke analyzed aliquots of separated condensate and dry gas taken from the sample bottle. He found that 99% of the contained tritium was in the water vapor component. He modeled the sample collection and concluded that the cathode interior had contained $1.8\pm0.3\times10^{15}$ atoms of tritium. The wet gas concentration of tritium was sufficiently high that Clarke concluded that all the observed [3]He was a decay product of the tritium component. Clarke repackaged the remaining wet gas into a new container and returned the sample to Oliver at PNNL. Oliver divided the sample into 3 relatively large portions. He measured the [3]He concentration in 2 of the portions on 18 December 1999, and in the third portion on 10 February 2000. The observed increase in [3]He concentration confirmed the presence of tritium, but the tritium concentration was somewhat less than the previous accurate Clarke-determined value. Clarke concluded that fractionation between water and dry gas had occurred during his repacking of the sample.

My interest in the Clarke et al.[2] results has focused on their failure to observe significant concentrations of [4]He, which is the primary reaction product predicted by the simplest form of many-body cold fusion reaction.[3] The helium concentrations listed in Table III of Clarke et al. show a [4]He/[3]He ratio=~0.1, whereas the [4]He/[3]He ratio found in air is >~5×10^5. My expectation was that major amounts of [4]He nuclear product would be present in the post-run gas retained in the Arata-style cathode. It seemed to me that the Clarke et al. low value of [4]He might by caused by a gas sampling problem described in their paper. The gas sampling collection process encountered a "mishap" during which 90+% of the initially released gas was pumped away ~5 minutes after puncture. It seemed that this lost fraction might have contained most of the initially present helium. The gas that was finally collected might have consisted solely of hydrogen desorbed from the Pd-black contained within the interior of the Arata-style cathode. If all the [4]He had been lost on 1 September, so too would all of the [3]He have been lost. I was therefore motivated to model the time

history of [3]He concentrations that were reported by Clarke et al. This modeling effort is presented in this paper. The modeling was made possible by additional information provided by Oliver regarding the sampling manifold configuration at PNNL, and by Clarke regarding a repackaging of the sample at McMaster University.

2. GAS SAMPLE COLLECTION

The Clarke et al. interpretation of the gas analysis data is based on a high-pressure gas-release modeling of the collection process. They assumed that the dry gas in the collected sample was partitioned in accord with the perfect gas law without fractionation within the dry gas components. It seemed to me that this modeling ignored dynamic effects that might have invalidated the dry gas composition uniformity assumed to have existed throughout the manifold system by the end of the first 5 minutes. The authors did not include desorption of hydrogen from the Pd black contained within the Arata-style cathode, and did not consider possible effects associated with a continuing flow of water vapor from

Figure 1. Gas Sampling Manifold at PNNL

evaporation liquid water as it flowed from the puncture-expansion volume into the sampling manifold. At equilibrium the Pd-black would have contained much more hydrogen that the intergranular gas. Figure 1 is a drawing of the sample collection manifold and metering system. Following puncturing, the gas released from the cathode first enters a 13.8-cc expansion volume containing the puncture device. It then passed through valve V1 into the manifold-plus-vacuum-gage-plus-sample-collection-volume, which adds an additional volume of 130 cc. Desorbing hydrogen and water outflowing through valve V1 could have inhibited the homogenizing effect of diffusion throughout the 5-minute interval before V1 was closed. Following puncturing of the cathode the pressure gage recorded no increase in manifold pressure. Because the pressure gate read zero, the operators closed V1 after a 5-minute flow time, and pumped away 90+% of the initially released gas. They then back-filled the manifold with nitrogen. Again the pressure gage failed to respond. The operators fixed a problem with the pressure gage switch, pumped away the nitrogen, closed off the manifold, opened V1 and collected their 41.6-cc test sample of cathode gas. The pressure of the gas sample as collected was 21.9 Torr at 26.5ºC. As mentioned, mass spectrometry showed the gas to be 75% water vapor and 25% dry gas, mostly hydrogen. There is no record as to how long the full collection process took. The initial expansion period is reported to be ~5 minutes, during which the pressure gage problem was recognized and a course of action adopted. My guess, based on conversation with Oliver, is that ~5 minutes additional was consumed in pumping out the manifold, back- filling with nitrogen, solving the pressure gage problem and pumping out the nitrogen; and ~5 minutes more in the final gas expansion process and in letting the pressure stabilize in the sample collection volume. The pressure in the sample volume appeared to be stable at the time the valve V2 was closed, isolating the sample volume.

In the Clarke et al. modeling of the collection process, the authors assumed an accessible intergranular volume within the Arata-style cathode of 0.6 cc. This value seems low to me since Pd-black as normally packed into the interior volume of the cathode has an initial density of the order of 1 g/cc, which is about 0.1x the density of bulk Pd. Clarke et al. calculated a pre-puncture pressure within the cell for the dry gas of ~18.8 atm. This value seems unexpectedly high to me, since the cathode was operated anodically for 2.3 months prior to the end of the experiment run. Anodic operation should have pumped away most of the available hydrogen, possibly reducing the hydrogen fraction in the Pd powder from that in equilibrium with β-Pd hydride to that in equilibrium with α-Pd hydride. The dry gas pressure in the as-collected sample was 5.4 Torr, which corresponds to a hydrogen pressure in equilibrium with α-Pd hydride. I think the ideal-gas modeling applied to the gas collection process predicts too high a pressure. In any case, a time history
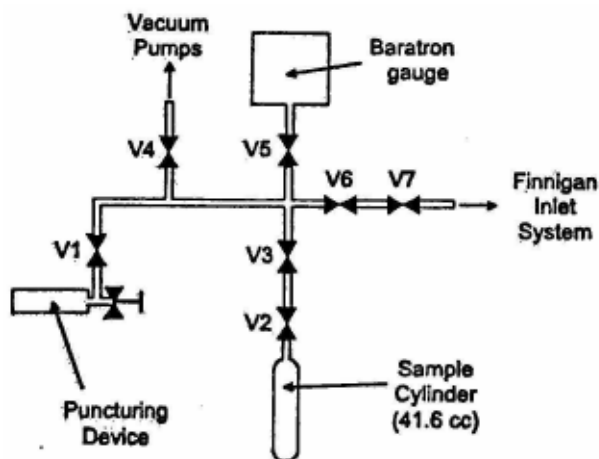
modeling of the [3]He concentration provides an independent check on the helium loss question.

3. MODELING THE [3]He HISTORY

Figure 2 shows one of my models of the time history of [3]He concentration. I have expressed the plotted values of [3]He concentration in terms of atoms [3]He/cc STP of dry gas. I have expressed concentration in terms of the dry gas rather than in terms of cc STP total (wet) gas because the water fraction was not kept constant during the time period covered. (Clarke et al. use atoms/cc STP of 3:1 wet gas as their concentration reference.) The curve shown in the Figure is drawn so as to pass through the average of the 2 PNNL data points obtained on 18 December. These data points should be the most reliable because they used relatively large aliquots of gas, which permitted the [3]He to be measured at maximum accuracy. The slope of the curve during the 1 September to 11 December interval was chosen to match Clarke's tritium measurements on condensate samples taken from aliquots of the collected wet gas. The condensate fractions were sealed in helium-impervious aluminum silicate glass ampoules and were stored for times sufficient to allow the build-up of enough [3]He to enable accurate measurement. Clarke considered these data the most reliable measures of tritium. The tritium concentration in the water was measured by observing the time rate of increase in [3]He content in these identically collected samples, which were analyzed for [3]He after various storage intervals. In drawing the Figure 2 curve the tritium concentration was treated as a selectable parameter, but one to be selected within the range of Clarke's error bars. The other parameter that was varied was the fraction of water lost during the sample repackaging on 1 December. It was assumed that the rate of [3]He increase dropped on 1 December because almost all of the tritium was contained in the water fraction,

[3]He concentration referenced to cc STP of dry gas, assuming 48% water lost 1 November (1 Sept. tritium concentration: 2.06 x 10^{14} atom/cc STP wet gas)
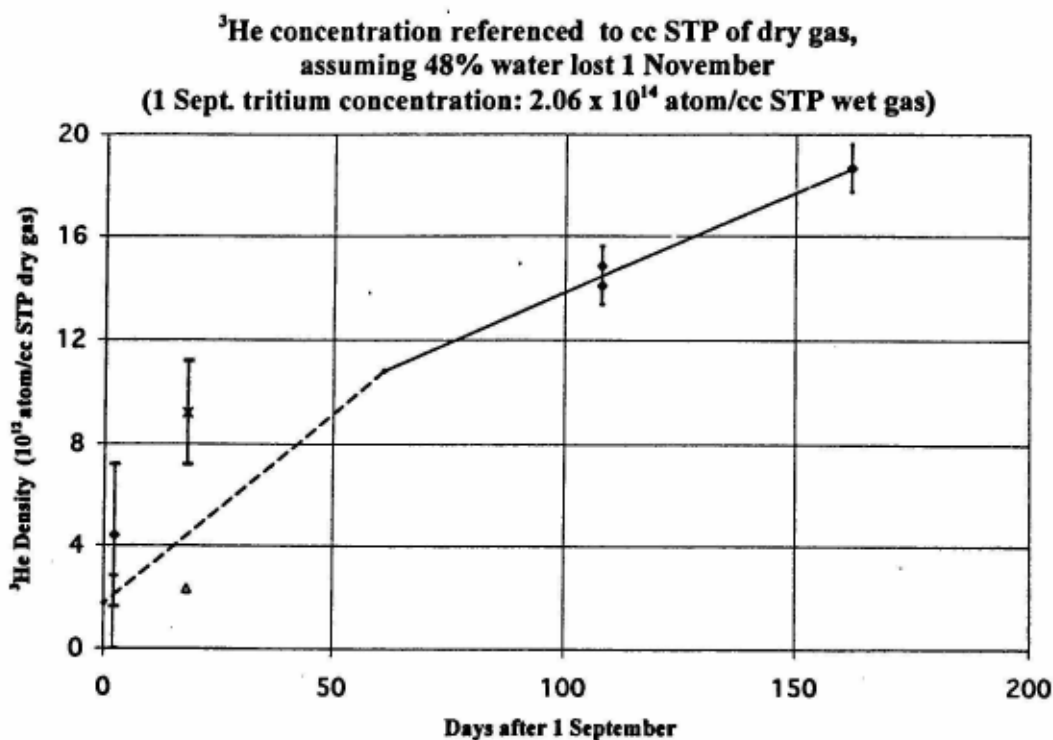
Figure 2. Model of [3]He concentrations using Clarke's preferred tritium concentration

part of which was lost. The repackaging was carried out in a system containing considerable glass. Clarke's best estimate of the water fraction lost at repackaging is 40%. The discontinuity in the rate of [3]He increase drawn in Figure 1 corresponds to a 48% loss of water. This 48% change in slope makes the curve pass through the PNNL [3]He data point of 18 February. This Figure 2 modeling supports the view that some, but not all, the [3]He was lost on 1 September.

Figure 3 shows a second modeling of the [3]He data. In the Fig. 3 modeling both the selected initial tritium concentration in the water component and the water loss fraction at repackaging differ from Clarke's preferred values. The selected initial tritium concentration is 1-"sigma" higher than Clarke's preferred value,

and the water loss fraction is 55% instead of 40%. The Figure 3. model is consistent with total [3]He loss on 1 September. However, it is to be noted that the plotted curve is outside the error limits assigned by Clarke to his initial measurement of [3]He concentration, which was the discovery measurement made on 28 September. This measurement was made on an exploratory sample that had been bled into the input manifold of the spectrometer system. The pressure of the sample was measured on a mercury manometer to be 1.5 Torr. Clarke says that the error in pressure measurement was less than the error bars assigned to the data point. The assigned error bars were based in part on uncertainty he assigned to possible water loss. If all the water fraction was lost at the start of the sample test, the measured [3]He concentration would have been recorded as the value indicated by the triangle on the plot. The curve drawn in Fig. 3 would then be consistent with the measurements. Clarke does not accept the likelihood of major water loss during the 28 September analysis.
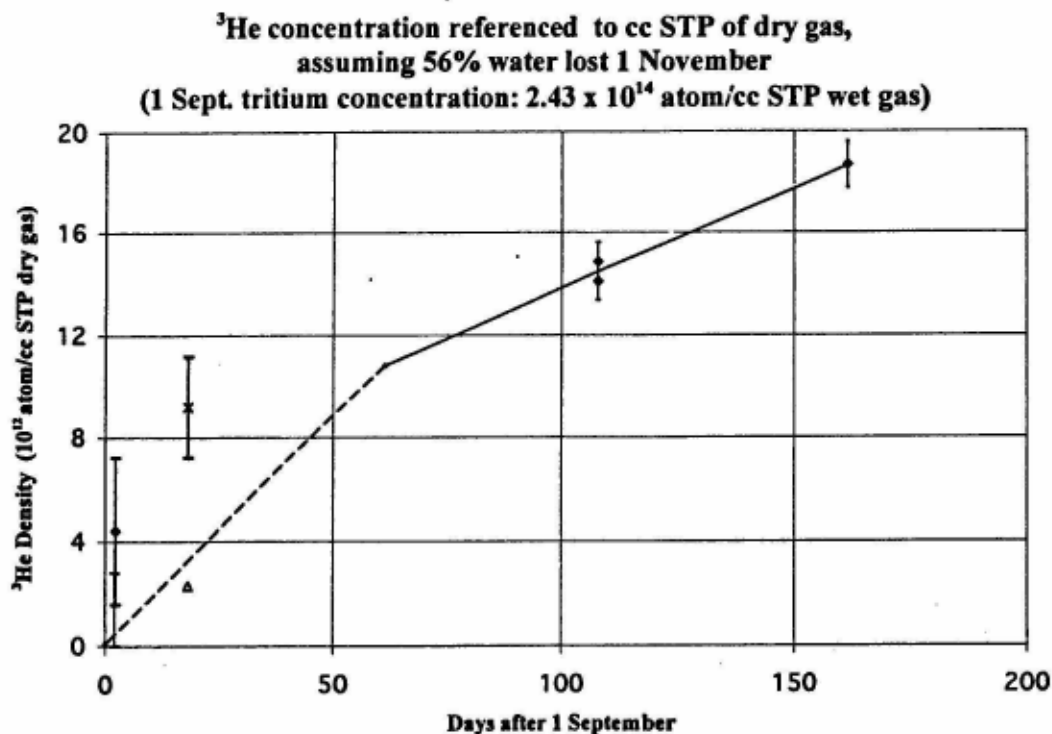

Figure 3. Model of [3]He concentrations using an upper limit Clarke tritium concentration

4. ARATA AND ZHANG EVIDENCE FOR HELIUM LOSS

The net result of my modeling is that I cannot say whether or not full [3]He loss occurred on 1 September. A similar gas collection was carried out by Arata and Zhang[4] subsequent to the work of Clarke et al., Arata and Zhang punctured a cathode that has produced about 54 MJ of integrated excess heat. They observed a Pressure rise to 30 Torr "immediately after piercing", followed by a rise to 1.1 bar 5 hours later. They made repeated measurements of the [4]He content in aliquots of the released gas accumulation over a 24-day period of time. They then pumped away the initial accumulation of [4]He and accompanying gas, heated the cathode to ~250°C for 30 minutes, analyzed the desorbed gas, and again found substantial [4]He. About 1 week later they pumped away this second sample of gas, heated the cathode to about 300 °C for 3 hours, analyzed the desorbed gas, and recorded an even larger amount of [4]He. Their integrated released [4]He was ~0.05% of that required to explain the observed integrated excess heat at 24-MeV per [4]He atom. So both studies show that the helium content in post-mortem Arata-style cathodes is less than that required to explain the integrated excess heat. This result contrasts with several studies using solid cathodes, where integrated [4]He in the electrolysis off-gases matches observed integrated excess heat.[1.5]

5. HELIUM LOSS THROUGH MICROCRACKS

The discrepancy between observed ^{4}He and that commensurate with integrated excess heat is probably due to helium leakage through the cathode containment wall. It is probably not explained by any generation of ^{4}He at, or near, the electrolyte-metal interface, as seems to occur with heat-producing solid cathodes. Clarke et al. provided evidence that the nuclear reaction region was in the interior of the cathode. They measured the ^{3}He concentration profile within the containment wall of the bottle-like cathode by analyzing 6 metal slices taken from different depths within the cathode wall. As shown in Figure 4 the ^{3}He concentration in the metal was highest near the inside surface of their bottle and lowest near the electrolyte-metal interface.
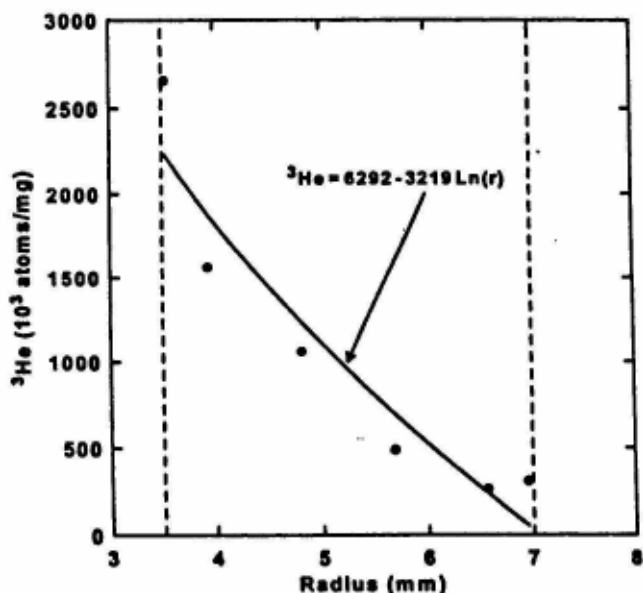

Figure 4. Concentration of ^{3}He in metal slices taken from wall of an Arata-style cathode. This Figure is Fig. 6 of Clarke et al.[2], as published in *Fus. Sci. and Technolog.* The fall-of in concentration from the interior of the cathode outwards towards the exterior metal-electrolyte interface shows that the nuclearly active region was in the internal volume of the Arata-style cell.

The trapped ^{3}He is considered to be a decay product of diffusing tritium. Hence an inside-bottle origin is indicated. Instead, the low helium values are more likely due to leakage from the interior volume as a result of a loss of structural integrity in the Pd metal of the containment bottle, produced by stresses accompanying expansion during hydriding followed by contraction during dehydriding. Pure Pd metal is not used in commercial hydrogen purification filters because of loss of integrity. To avoid this problem, commercial practice is to use Pd, Ag alloy. Gas flow through microcracks could cause a preferential loss of helium. Supporting this picture, Farkas[6] has shown that Pd hydride develops microcracks during electrolysis. Working with mixtures of H_2O and D_2O he studied differences in H/D ratio between the electrolyte, inside-the-metal gas, and evolved gas. He found that the absorption/desorption process is not microscopically reversible, which causes a change in isotopic composition. He found that the hydrogen escaping from the bulk Pd metal during electrolysis was exiting through microcracks in the form of diatomic gas, whereas the hydrogen enters the metal through electrochemical deposition of atoms onto the surface. Without this difference in process he could not model the observed difference in H/D ratio. Loss of helium via microcracks does not require that helium be able to chemically diffuse through bulk Pd metal. Since mechanical diffusion through microcracks is involved, helium could leak outward faster than accompanying hydrogen. Also, operation of Arata-style cathodes results in generation of high pressure hydrogen gas within the cathode. Direct measurements on a cathode by Arata and Zhang showed a peak pressure exceeding 600 bar.[7] Physical distortion of the cathode occurs. Experimental cells at SRI have cracked and lost their ability to contain hydrogen. As degradation develops, permeability to helium would be expected to occur before permeability to hydrogen. Interestingly, the initial mass analysis by Oliver showed a 0.6% nitrogen and 0.2% oxygen component. The presence of these gases suggests that the cathode studied by Clarke et al. had

become slightly permeable to air.

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