

Search for Evidence of Nuclear Transmutations in the CETI RIFEX Kit

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Abstract

A series of experiments has been performed with the CETI RIFEX kit. In each experiment an electrolytic cell with a cathode composed of metal-coated plastic beads was operated for two weeks. The cathode beads were then analyzed by x-ray fluorescence for evidence of nuclear transmutations. Several elements were observed to appear in the reacted beads. Analyses of the electrolyte and other components of the system in contact with the electrolyte are not conclusive but suggest to us that these elements were present in the system initially.

Introduction

RIFEX stands for Reaction In a Film Excited compleX. Clean Energy Technologies, Inc (CETI) made the RIFEX kit available in late 1996 to provide "the opportunity to examine and conduct research on CETI's Patterson Power Cell which has received several U.S. Patents and has been acclaimed as the first device to reliably demonstrate chemically assisted nuclear reactions."¹ Most of the evidence for these nuclear reactions comes from the work of Dr. George Miley at the University of Illinois.^{2,3}

The RIFEX kit consists mainly of a special electrolysis cell that is very similar to the cell described in patents⁴ by Dr. James A. Patterson of CETI. The cathode in this cell is composed of a bed of plastic beads that have been coated with a thin layer of metal. It is in this thin metal coating that the nuclear reactions are reported to occur.

During operation of the cell, 86 ml of Li_2SO_4 electrolyte is circulated slowly through the cell by an external pump. Electrolysis is conducted at a 20 mA and the electrolyte is maintained at about 70°C by an in-line heater located in the electrolyte circuit just before the cell.

A typical run lasts for two weeks. The beads are then removed from the cell and analyzed for evidence of nuclear reactions (e.g., new elements, unusual isotopic ratios).

Due to the electrolysis, many cations that are present in the electrolyte will be deposited on the cathode beads. Therefore it is important that all possible sources for these elements be ruled out before concluding that they have been created in the film by a nuclear reaction. To this end, the RIFEX kit is primarily constructed of non-metallic components.

Our primary goal in this investigation was confirmation of Dr. Miley's reports that new elements were being created in the bead coatings. With large excess power ratios being

reported by CETI for cells with similar beads, Dr. Miley's results appeared to fit perfectly with the hypothesis that nuclear reactions were occurring in the cell.

To look for these elements we employed x-ray fluorescence (XRF) which is a non-destructive elemental analysis technique that provides excellent specimen versatility. Liquids, solids, powders, beads and odd shapes can all be accommodated with relative ease. Importantly, we happen to have a great deal of experience with XRF analysis consisting of 20+ years designing, building, and supporting a wide variety of industrial XRF analyzer systems.⁵ This work involved countless application studies wherein XRF results were compared with other analytical techniques. An incredible variety of errors were encountered in these application studies, and the experience of finding and correcting them has been of great value to the present investigation.

We decided to limit our investigation to elements whose x-ray emission lines fall in a region (4-14 keV) where analytical conditions are favorable and quantification of results is relatively straightforward. This region includes 56 elements in two groups: Sc-Sr (K x-rays) and Cs-U (L x-rays). Possibly important elements missing from this region include: Li, Al, Si, Zr, Pd, Ag, & Cd. Seven of the nine elements Miley referred to as "NAA elements"² are included in these two groups. NAA stands for Neutron Activation Analysis. Miley's NAA elements are Mg, Al, V, Fe, Co, Ni, Cu, Zn, & Ag. Our analysis misses only Mg, Al, & Ag.

Over most of our analytical range, the x-rays are sufficiently energetic to penetrate through several layers of the styrene beads used in this study. This enabled us to analyze the 1 cc of beads typically involved in a run all at once and obtain a single result that represented the average composition of the beads.

XRF does not distinguish between the different isotopes of an element. It is sensitive only to total elemental concentrations. In some respects this can be considered beneficial for an initial investigation because it eliminates a complex set of variables from the analytical puzzle. If we can first confirm that new elements are indeed being created then additional studies to investigate isotopic distributions are certainly warranted.

A secondary goal in this investigation was confirmation of the excess heat measurements made by Miley and Cravens on similar beads undergoing electrolysis. This work is covered in a separate paper.⁶

Initial Preparations and Description of Apparatus

We received our RIFEX kit in December 1996 immediately after attending a training session hosted by Dr. Miley on the University of Illinois campus. The session provided basic instructions on the experiment protocol and a review of Dr. Miley's findings.

There were 3 different kinds of beads included in the kit. All of them were based on the same 1 mm diameter (nominal) polystyrene beads but the coatings were (1) 0.2 micron Pd, (2) 0.2 micron Pd and 0.2 micron Ni, and (3) 800 Angstrom (0.08 micron) Ni. The first two were made by CETI using their patented electroplating process. The third type was made in Miley's lab by sputtering Ni onto bare polystyrene beads. At the training session Miley suggested that we focus our transmutation investigation on the Ni beads because most of his results at that time had been obtained on similar beads.

The kit contained two cells. A twice-scale section view of the assembled cell is shown in Figure 1. The cell consists of a tubular body with two endplugs. Each endplug has a Pt lead wire that passes through a seal and then is crimped onto a perforated Ti plate that serves in the upper case as the anode and in the lower case as a contact for the beads which form the cathode in this cell. The bead bed sits in direct contact with the cathode endplug. On top of the bead bed are two nylon screens that prevent the beads from escaping. An O-ring sits on top of the screens to space the anode endplug away from the screens.

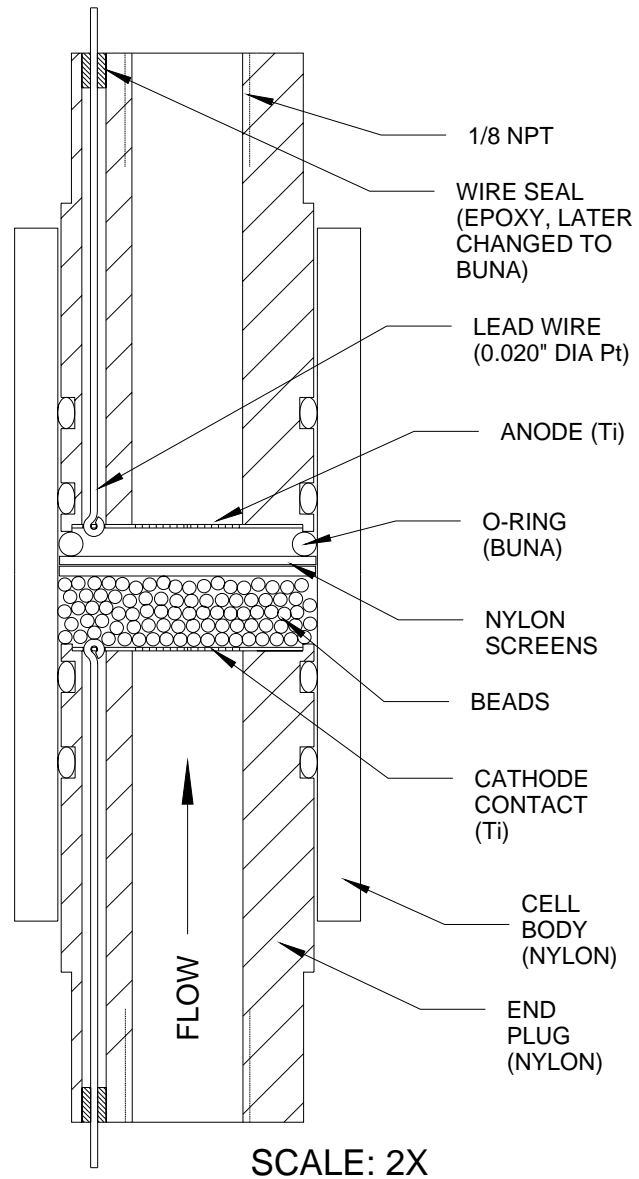


Figure 1

As shown in the drawing the endplugs are sealed to the cell body with O-rings and have a 1/8 NPT female thread that accepts a male run tee fitting. This tee fitting (not shown) provides an electrolyte passage and a port for the temperature probe.

The kit also contained an electrolyte reservoir made of acrylic plastic, additional plastic fittings, 1/4" OD Teflon tubing, a Gelman 47mm in-line polycarbonate filter holder with cellulose acetate filters, reagent grade Li_2SO_4 , a plastic stand to hold the cell and reservoir, and an insulated test chamber. Also included was a detailed written protocol for the experiment. The kit did not include the electrolyte pump, in-line electrolyte heater, electrolysis power supply, temperature sensors, meters, or data recording equipment.

Schematic of Electrolyte Circuit:

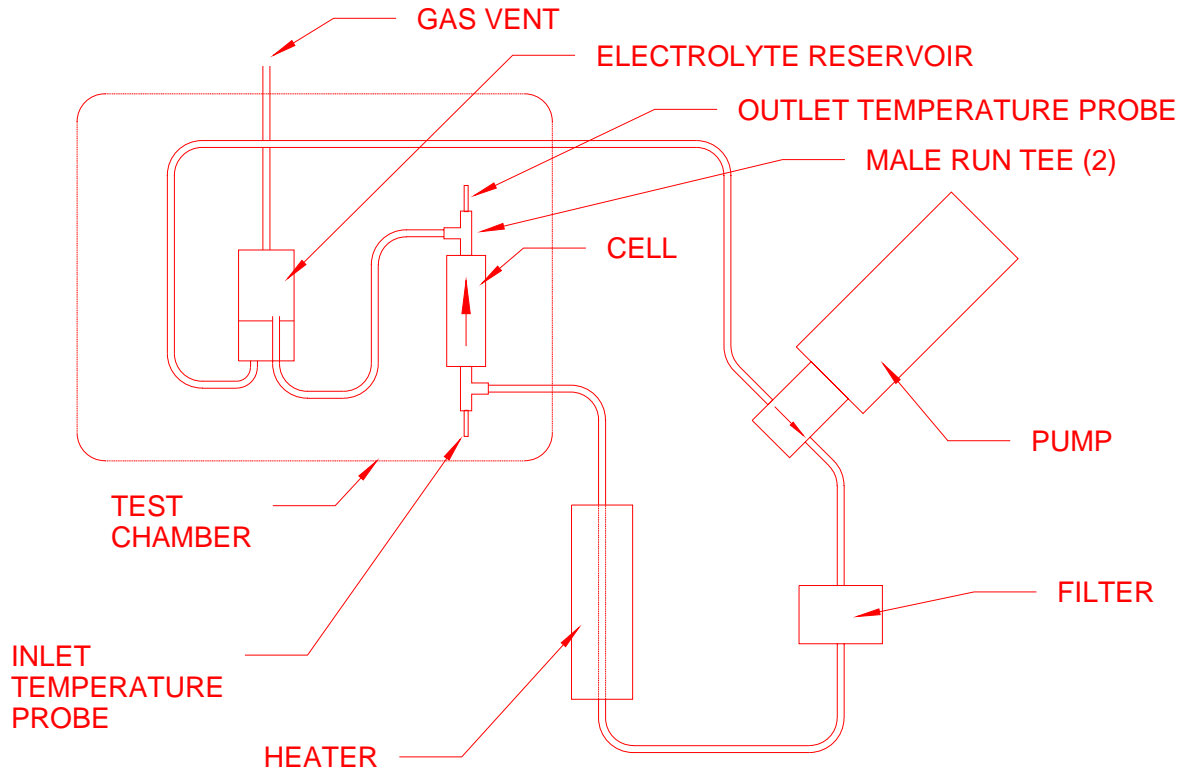


Figure 2

Electrolyte Pump: We purchased the recommended pump (model RHOCKC) and flow controller (model V200) from Fluid Metering Inc. This pump has a ceramic piston and cylinder that contact the fluid. The flow controller serves to run the pump motor at a precisely regulated, selectable speed. We constructed a stand to support the pump in one of the manufacturer's recommended orientations (45° angle downward as shown).

Electrolyte Heater: We designed and constructed our own in-line electrolyte heater. The first version of this heater was a stirred oil-bath into which a seamless coil of Teflon tubing was immersed. The aluminum bath vessel was heated with a wrap-around heating element controlled by an Omega CN76000 that sensed bath temperature via a K thermocouple immersed in the bath. This system worked very well as an in-line heater during initial qualification tests of the circulation system. However it became apparent during these tests that it would be very difficult to guarantee that traces of oil would not

contaminate the interior of the circulation system during routine handling and disassembly of the various components.

The oil-bath was abandoned and a second in-line heater was designed and constructed. Great care was taken to ensure that the electrolyte system was not contaminated with oil during the removal of the first heater. The new heater consisted simply of two rectangular Al blocks with half-round grooves on one side that were bolted together around a 19 cm long section of the Teflon tubing like a stockade clamp. A 50 W strip heater was attached to one of the Al blocks and the K thermocouple was secured to the other. The whole assembly was placed in a Styrofoam box to minimize heat losses. During operation the Omega controller maintained the Al block assembly at an empirically determined temperature of 115°C. This was sufficient to warm the electrolyte to 70°C during its 15 sec residence within the heater (the inside diameter of the Teflon tubing is 4.8 mm so, at the nominal electrolyte flow rate of 14.3 ml/min, the fluid velocity is 1.3 cm/sec).

Test Chamber: The test chamber (a modified ice chest) supplied with the RIFEX kit was designed so that the cell and reservoir had to first be placed down into the relatively tight interior of the chamber and then the tubing connections made up. This proved to be virtually impossible for our hands so a new chamber was constructed from a larger ice chest. The lid of the new ice chest was inverted and mounted on elevated supports to provide access to the underside. The cell and reservoir assembly was then installed on top of the inverted lid and all the necessary tubes and wires were led down and out through small holes drilled in the lid. This arrangement provided easy access to the cell for servicing. Inverting the unmodified lower portion of the ice chest and setting it down over the cell onto the lid easily closed the new chamber. Photographs of this experimental setup can be viewed on our web page.⁷

Power Supply: We used a Kepco Model PAT 21-1 wired for constant-current operation (regulation stability <0.1%). This supply is capable of a maximum of 1 ampere and has a ceiling of about 42 volts in constant-current mode.

Data Recording and Temperature Measurement: To monitor the runs we used a Keithley Model 2000 DVM with a 10-channel scanner card interfaced to an IBM-compatible PC running a custom data acquisition program. The following parameters were measured every 20 seconds, plotted on screen and logged to disk:

1. inlet electrolyte temperature
2. outlet electrolyte temperature
3. cell voltage
4. cell current
5. room air temperature
6. temperature of the in-line heater block.

All temperatures were measured with BetaTHERM precision 0.2°C interchangeable thermistors. These thermistors were simply connected directly to the inputs of the

Keithley, which read their resistance and reported it to the computer, which calculated the corresponding temperature using the Steinhart-Hart equation (with coefficients supplied by BetaTHERM). We have compared these thermistors to precision 0.1°C glass thermometers on numerous occasions in our lab and they always agree within 0.2°C.

Li₂SO₄: 16 g of Li₂SO₄ was supplied with the RIFEX kit. To provide sufficient material for several experiments and the necessary analytical work, we purchased an additional 50 g of the same grade (product number 20365-3) from Aldrich Chemical Co. Fortunately our Li₂SO₄ came from the same Aldrich lot (lot number 06207MF) as the material supplied with the kit. We blended all the Li₂SO₄ together thoroughly before starting the experiments.

Leaks: During qualification tests we had a number of problems with leaks in the original RIFEX kit design. The plastic pipe thread (1/8 NPT) connection between the male run tee fitting and the machined nylon cell endplugs was the biggest problem. Expansion and contraction of the plastic during cycling from ambient to 70°C always seemed to loosen that connection to the verge of leaking. Eventually, as noted later, we modified those connections to use O-ring seals. We also had problems with the wire seals that were originally made with epoxy. We eventually replaced them with custom-made elastomer seals.

Initial Analytical Investigations: Before performing any experimental runs with the RIFEX kit we performed semi-quantitative XRF analysis on several of the components.

The XRF spectrometer employed for this investigation was a Model EX-6000 manufactured by Jordan Valley Applied Research. This is a high-performance Si(Li) detector laboratory XRF system with both direct-filtered and secondary-target excitation capabilities. We were very fortunate to have free unlimited access to this instrument for this study. Detailed XRF analyses can be quite expensive at a commercial laboratory.

To perform an XRF analysis the sample must be placed in the spectrometer so that its surface is located where the x-ray beam will strike it and where the resulting scattered and fluorescent radiation will enter the detector. Powders and liquids are usually placed in special XRF cups with thin-film bottoms (typically 6 micron thick polypropylene) that allow the x-rays to enter and leave the cup without significant absorption. Large solid samples such as fittings, machined pieces, etc. must be supported over the spectrometer aperture so that at least some portion of the sample is in the correct location.

The analysis is performed by illuminating the sample surface with energetic x-rays and detecting the fluorescent and scattered x-rays that are emitted. In the EX-6000 the illuminating radiation is generated by an x-ray tube. The tube voltage is adjusted so that the radiation is sufficiently energetic to excite the desired electron shells in the selected analytes. The tube current is adjusted to provide the desired total x-ray intensity at the detector (several thousand x-rays per second). In the EX-6000, filters are available to alter the spectral distribution of the tube radiation. These are generally used to "harden" the tube spectrum, eliminating most of the lower energy radiation which, if not filtered

out, interferes directly with the x-rays of interest from the sample. The EX-6000 also has a secondary-target capability in which the tube radiation is directed at a selected pure-element target and then the K x-rays emitted by the target are directed at the sample for the analysis. This feature provides almost monochromatic excitation and yields the best detection limits for a selected range of elements because the excitation efficiency is high and the low-energy background from the x-ray tube is virtually eliminated.

The detector must have sufficient energy resolution to separate the various x-rays from the sample so that the constituents can be accurately identified and quantified. The Si(Li) detector used in the JVAR EX-6000 operates at liquid nitrogen temperatures and achieves an energy resolution of ~150 eV (FWHM for the 6 keV line from ⁵⁵Fe). This resolution is quite sufficient for most XRF analytical purposes. Note: x-ray energy is inversely related to x-ray wavelength by $E = hc/\lambda$.

The detector counts individual x-rays and together with the supporting electronics infers the energy of each detected x-ray from the pulse height. The measured energy is used to address the corresponding channel in a 2048-channel analyzer and the count therein is incremented. As the analysis proceeds, each detected x-ray increments one of these channels and thus the spectrum of x-rays from the sample is recorded.

As emission spectra go, x-ray spectra are particularly simple to interpret. For the purposes at hand the K x-ray signature of an element is a doublet (two closely-spaced lines). The lower energy line, called the K_{α} , is about 6 times more intense than the higher energy line, the K_{β} . The L x-ray signature of an element is a little more complex. There are three main groups of L lines, the L_{α} , L_{β} , and L_{γ} (in order of increasing energy). Each of these groups contains two or more lines but usually the L x-ray signature appears as a simple triplet. As emitted by typical samples the L_{α} and L_{β} are about the same intensity and the L_{γ} is about 1/6 of that intensity. The K and L series of x-ray lines overlap but within each series the lines increase monotonically in energy with increasing atomic number. This and the characteristic doublet/triplet appearance makes identification of elements by their x-ray signature easy and quite reliable. Sometimes there are overlaps which must be untangled but x-ray spectra are far simpler and less cluttered than optical emission spectra for example. A table giving the energies of the x-ray lines for all the elements can be found in the CRC Handbook of Chemistry and Physics.

In the x-ray spectrum collected during an XRF analysis, the intensity of a given element's x-rays is directly related to the concentration of that element in the sample. This fact permits easy semi-quantitative interpretation of x-ray spectra. A big peak means there is lots of that element present, a little peak means a small concentration, and no peak means that the element's concentration is below the detection limit. Detection limits vary considerably but are often in the 1-50 ppm range.

The first thing we looked at with XRF was the dark gray epoxy used to hold the electrodes into the cell endplugs. This epoxy was in direct contact with the electrolyte in the cell. The x-ray spectrum from the epoxy is shown in Figure 3. The horizontal axis is x-ray energy ranging from 0 to 40 keV. The vertical axis is the intensity of the x-rays.

The most familiar lines are the K x-ray doublet from Fe at about 6 keV. The label "Fe" appears near the top of the Fe K_{α} and the smaller Fe K_{β} immediately to the right is not labeled. To the left of the Fe peaks are those of Ca and Ti (small). To the right of the Fe peaks we see the K x-ray signature of Sr (again the K_{β} is not labeled). Further to the right we come to a mess of lines and a big hump that comprise the scattered radiation from the x-ray tube, which has a Rh anode. The tube emits a spectral continuum (bremsstrahlung) with the Rh lines superimposed. These x-rays scatter both elastically (no energy loss) and inelastically (with some energy loss) from the sample which splits each Rh line into two. At the far right we see the K x-ray signature of Ba (excited by the high-energy tail of the bremsstrahlung). Both the K_{α} and K_{β} are labeled and, at these high energies, you can see the K_{β} resolved into the $K_{\beta 1}$ and $K_{\beta 2}$. The "VFS: 4000" label tells how many counts it takes to reach full vertical scale.

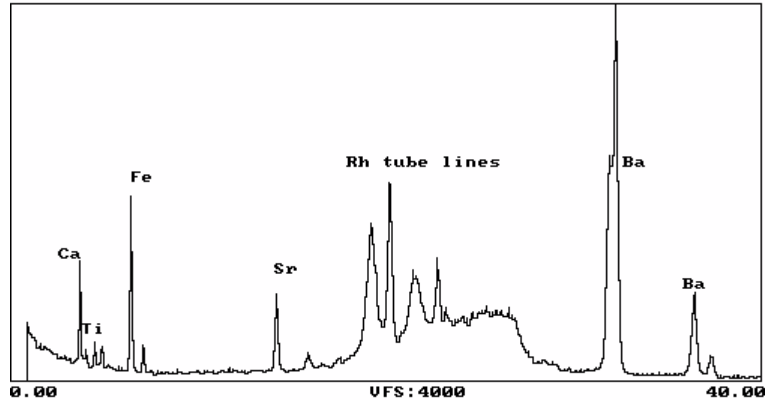


Figure 3

We contacted CETI about the epoxy and learned that it is a type known as J-B WELD. We contacted the J-B WELD Company and they provided the following concentrations for the inorganic constituents of J-B WELD epoxy:

- | | |
|------------------------|-------------------------|
| 35-40% CaCO_3 | 17-20% BaSO_4 |
| 1-3% TiO_2 | 1-3% magnesium silicate |
| 8-10% Fe (iron powder) | 1-3% SiO_2 |

Comparing these concentrations to the peak heights in Figure 3 we can see that the XRF sensitivity varies significantly from element to element. For example, the Ca peak is smaller than the Fe peak yet the elemental Ca concentration is about equal to the Fe concentration. This is due to Fe being more efficiently excited than Ca in this analysis and Fe x-rays being less heavily absorbed in the sample matrix than Ca x-rays. Consider the Sr peak. Sr is so efficiently excited in this analysis that the Sr concentration is probably less than 1% of the Ca concentration. In fact, it is likely that the Sr is simply a trace constituent of the CaCO_3 filler material. Despite these difficulties, the x-ray spectrum provides a quick easy way to examine the elemental content of a wide variety of materials.

We discussed the epoxy as a potential source of contamination with CETI and then decided to proceed on the first run using these endplugs because the epoxy prevented disassembly of the endplugs and no other endplugs were immediately available.

Next we disassembled the FMI pump head and used XRF to look at the ceramic piston (3/16" diameter, 1" long); one of the few components in the electrolyte circulation system that was not plastic. As indicated in Figure 4, we observed only low levels of Fe and Zr in this ceramic. Because of the size and shape of the piston it could not be presented properly to the spectrometer. We could therefore only estimate the concentrations of these elements: a few tenths of a percent Fe and a few hundredths of a percent Zr (again the analysis is much more sensitive to Zr than to Fe).

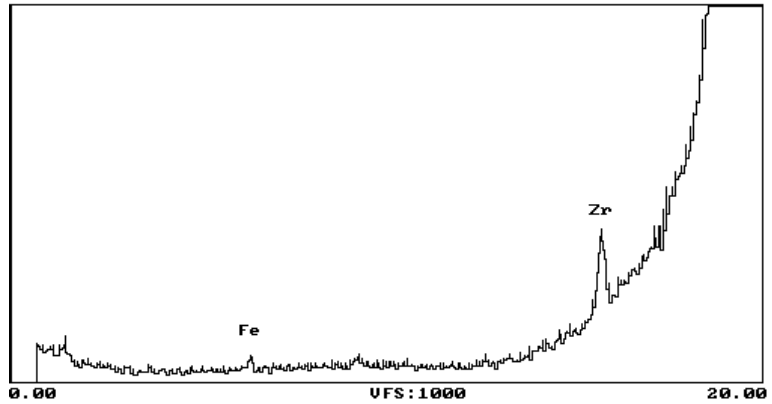


Figure 4

We also looked at the fresh Ni beads before starting the run. In Figure 5, you can see the expected prominent Ni peak (both the K_{α} and K_{β} lines are visible and labeled) and a small Fe peak which indicates that the Fe/Ni ratio of the fresh coating is about 0.1. We discussed this result with Mike Williams who made these beads in Miley's lab and he could provide no explanation for the source of this Fe. He said the sputtering target was very pure Ni with only 20 ppm Fe in it. He further related that the Auger specialist at the University of Illinois said there was no sign of Fe peaks in the surface surveys performed on similar beads during Miley's investigations. Interestingly, the NAA results on fresh Ni beads presented by Miley² in Table 4a show an Fe/Ni ratio of 0.12, essentially the same as we observed.

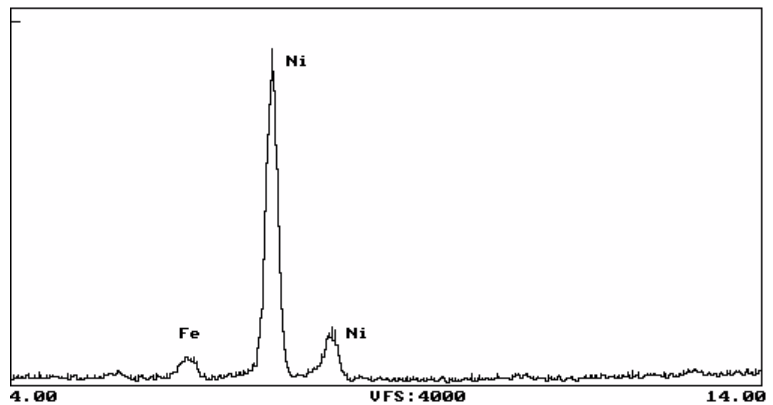


Figure 5

We resolved this mystery by examining the uncoated beads supplied with the RIFEX kit. The spectra in Figure 6 show the uncoated beads in solid gray and the Ni beads as a solid black line. Note that the Fe peaks overlap perfectly

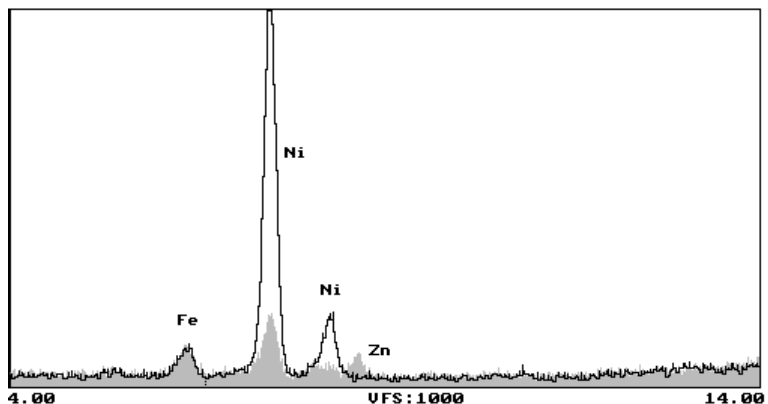


Figure 6

indicating that the Fe content of both beads is the same. The Fe is not in the coating but in the bead. XRF (and NAA) can see right through these thin Ni coatings but Auger electron spectroscopy cannot. Interestingly, the uncoated beads also have a noticeable Ni peak and a low-intensity Zn peak that does not appear in the Ni coated beads, which were unsulfonated. The uncoated beads had been sulfonated by CETI. Perhaps the Ni and Zn were picked up in that process.

Run 1

We started preparations for Run 1 by washing all components of the cell with Alconox detergent and rinsing with DI water (we used DI water for all our RIFEX procedures and will refer to it simply as water from here on). Wearing undusted latex finger cots (used for all cell assembly procedures hereafter) and following the steps in the protocol we assembled the cell with a 1 cc charge of the Ni-coated beads. First the cathode endplug was inserted halfway into the cylindrical cell body. This assembly was held upright and the beads poured into the cell body and settled into a close-packed flat-topped bed by flooding them with water and tapping the side of the cell. The water was drained from the cell and two discs of nylon screen (a 200 micron mesh followed by a 500 micron mesh) were placed on top of the bead bed. Next an O-ring that fits snugly inside the cell body was pushed down into contact with the nylon screens. Finally the anode endplug was inserted into the cell body without twisting until it contacted the O-ring.

The cell assembly was placed between two plastic compression plates that engage shoulders on the protruding endplugs. Four bolts connect the two compression plates and were tightened until a 15-30 pound compressive force was achieved. This force is transmitted by the endplugs directly to the cell contents.

After assembling the cell and installing it in the electrolyte circuit, we cleaned the circuit by circulating a 5% NH_4OH solution for 30 minutes. We rinsed the circuit with DI water until the pH of the water exiting the system was below 7.1.

We emptied the electrolyte circuit as well as possible, leaving perhaps 5ml of water behind, and filled the reservoir with 86 ml of 0.5M Li_2SO_4 solution. This solution was circulated at 14.3 ml/min for the remainder of the run.

We started the run at about 1400 hours on 23JAN97 by applying a constant current of 0.020 amps to the cell. This current was maintained for the remainder of the run. The electrolyte heater was off at this time and the electrolyte temperature was about 25°C.

After a 3 hour loading period during which the cell voltage rose from 3.9 volts to about 4.5 volts, the electrolyte heater was turned on. After two more hours, the electrolyte temperature stabilized at about 70°C. This temperature was maintained for the remainder of the run. The elevated electrolyte temperature lowered the cell voltage to about 4.0 volts.

Throughout the run we added DI water to the reservoir periodically to make up for electrolysis and evaporative losses. The former was only about 0.2 ml/day but the latter was 5-10 ml/day. These additions were very carefully made with a clean plastic syringe and a length of small-bore Teflon tubing leading into the reservoir.

On 27JAN97 a gradual seepage was observed at the 1/8 NPT connection to the bottom endplug.

On 31JAN97 a small wet spot was observed under the cell. The loss of Li_2SO_4 was negligible.

On 1FEB97 the leak had increased to the point where action was required. We interrupted the electrolysis power and quickly drained the cell, disconnected the lower electrolyte line, tightened the lower tee fitting one full turn, reconnected the line, resumed circulation and restored electrolysis power within 13 minutes of interrupting it.

For some reason this procedure made the cell voltage jump to about 5.2 volts. After consultation with CETI, we tightened the axial clamp bolts one full turn but that did not change the voltage. It remained at about 5.2 volts for the remainder of the run.

On 9FEB97 we ended the run. Total duration under electrolysis power at 70°C was about 400 hours. We drained the circuit and collected the used electrolyte. Upon disassembly of the cell we discovered that the beads were significantly altered in appearance. Virtually all of the original metallic sheen was gone. Some of the beads looked totally clear, most were a light brown color. Most of the other components in contact with the electrolyte including the nylon screens, the anode, and the plastic fittings throughout the electrolyte circuit were noticeably brown in color.

We recovered the beads, washed them in water thoroughly and dried them gently. With clean, dry, reacted beads in hand we proceeded directly to the XRF spectrometer and collected the spectrum shown in Figure 7.

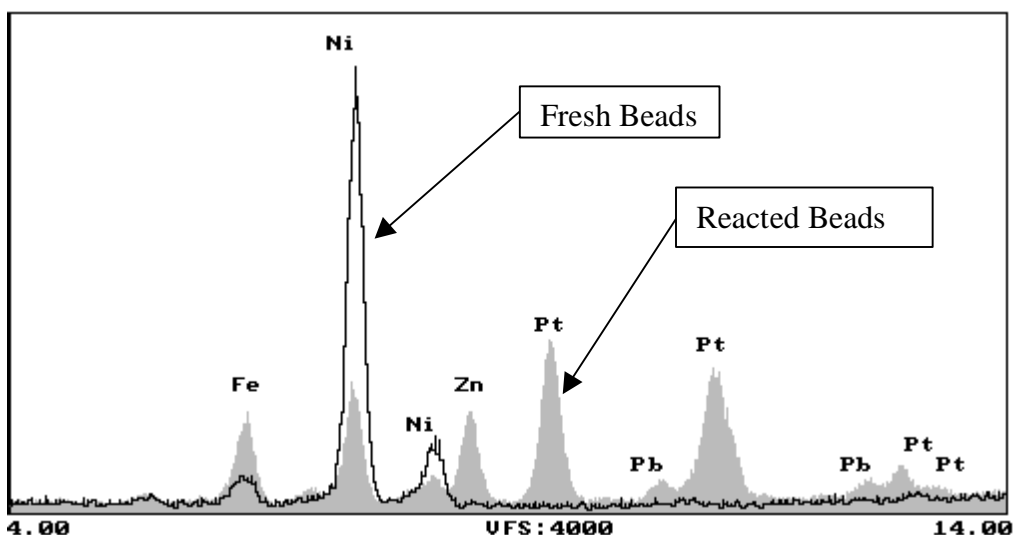


Figure 7

The reacted bead spectrum is solid gray and the fresh bead spectrum is overlaid as a black line for comparison. The horizontal scale is 4-14 keV. Examining these spectra we see first that the reacted beads have significantly more Fe and less Ni than the fresh beads. Also, the reacted beads have high levels of Zn & Pt (note the characteristic L x-ray signature of Pt) and a lower level of Pb, none of which were noticeable in the fresh beads. For all practical purposes, no other elements in this region were detected. Roughly, the "visual" detection limit for these elements is 30 ppm or 0.01 microgram/bead, which is equivalent to about 15 micrograms in the entire 1cc bead bed. This is the concentration required to make a noticeable peak in the spectrum. For reference the Ni concentration in the fresh beads is about 1700 ppm or 0.6 micrograms/bead. We will quantify these results in detail later but for this semi-quantitative discussion you can assume that the XRF sensitivity for all the elements in this region is the same.

Notable elements absent from our reacted bead spectrum include Cr and Cu. Miley reported⁸ finding 1840 ppm Cu in similar reacted beads. Such a concentration in our beads would have produced a very large peak higher than the Ni peak in the fresh beads. He also reported 1126 ppm Cr, which would have produced a half-scale peak in our spectrum above. Miley did report finding Fe, Zn, & Pb in his early work² and later he reported³ finding Pt in the reacted beads.

Actually, we were heartened by these findings. At least we had found some new elements in our beads and some of the same ones that Miley reported.

We next set out to examine the various components of the electrolyte circuit for possible sources of the new elements in our reacted beads: Fe, Zn, Pt, & Pb.

There was an obvious potential source for the Pt. Each endplug had a Pt lead wire running in through a wire seal and leading up to the Ti electrodes where it was crimped through a pair of closely spaced holes in the electrode. It did not seem likely that such a small exposed area of Pt could be responsible for the large Pt peaks observed in the reacted bead but we resolved to eliminate the Pt from the cell anyway.

We noticed that many of the plastic fittings in the circuit were rather brown in color after the run. In particular, the little nylon inserts that keep the Teflon tubing from collapsing in the compression fittings were quite brown in color. We examined these brown parts with XRF and observed a significant Pt signal and nothing else. Apparently the Pt was circulating throughout the system and depositing on these fittings as well as the beads.

The lot analysis supplied by Aldrich Chemical Co for the Li_2SO_4 included only one of our elements of interest: Zn. They listed its concentration as 4 ppm. A rough estimate of the Zn concentration we observed in the reacted beads indicated that the entire bead bed contained about 100 micrograms of Zn. At 4 ppm Zn, the 86ml of 0.5M Li_2SO_4 electrolyte used in the experiment would contain only 19 micrograms of Zn. Clearly there was additional Zn coming from another source.

The male run tees used to connect to the cell were white and opaque compared to the rather translucent fittings used elsewhere in the circuit. We therefore suspected that these fittings contained some kind of filler material. One of these fittings was presented to the XRF spectrometer and we found measurable levels of Al, Si, Ca, Ti, Fe, & Zn (we adjusted the spectrometer to look at lighter elements for this analysis). A rough estimate of the concentrations of these elements was obtained via standardless fundamental parameters:⁹ 3100 ppm Al, 14200 ppm Si, 360 ppm S, 10800 ppm Ca, 3600 ppm Ti, 170 ppm Fe, 90 ppm Zn, & 110 ppm Sr. We cut open one of the used fittings and flattened it out so the interior surface, which had been exposed to the circulating electrolyte, could be presented to the XRF analyzer. We did the same for a new fitting and compared the two surfaces. There were no striking differences in the two spectra but, due to the high x-ray transmission of polypropylene, a depletion of the fillers in the surface of the used sample might not cause a noticeable reduction in the peak heights. Still it seemed unlikely that the low concentrations of Fe and Zn in these fittings could be the cause of the Fe and Zn observed in the reacted beads.

We looked at the polycarbonate body of the filter holder. It was very clean.

The filter holder had a black plastic support grate in it. We examined this grate via XRF and observed only very low levels (few ppm) of S and Fe.

We looked at the used Ti anode and found it to be pretty clean. There were no Zn, Fe, or Pb peaks visible.

We looked at the nylon cell body and the nylon part of the endplugs. They were both very clean.

We looked at the Teflon tubing used in the electrolyte circuit. It was very clean.

We finally got around to looking at the buna spacer O-ring that was inside the cell...what a strong Zn signal! The spectra in Figure 8 show the comparison between the O-ring (solid gray) and the fresh Ni beads (black line) under the same XRF excitation conditions. We spoke to Dennis Coz of the Akron Rubber Development Group and he informed us that many rubber formulations including buna

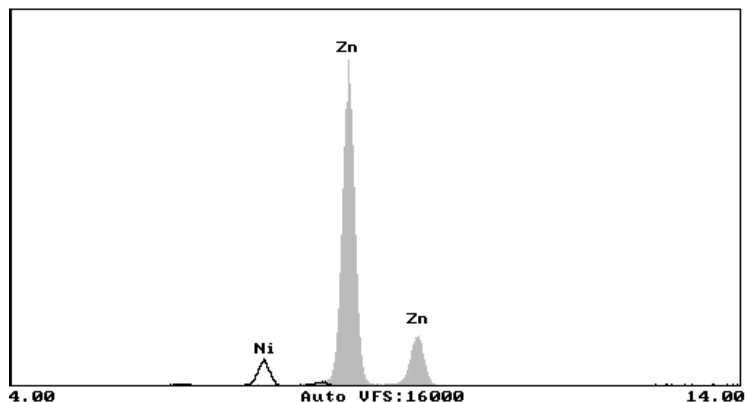


Figure 8

have 2-5 pph (parts per hundred) of ZnO to help activate the curing process. He further informed us that Viton rubber would probably be free of Zn.

This discovery stimulated us to examine the orange silicone O-ring in the filter holder. As might be expected from the color, we observed a small Fe peak in its spectrum, probably less than 1% Fe.

Armed with potential explanations for the Pt, Zn & Fe (but not the Pb) we set out to perform Run 2.

Run 2

In response to our concerns about the JB-WELD epoxy, CETI provided a new cell with a new endplug design that contained no epoxy at all. The new Ti electrode was a neatly machined disc that fit into a shallow recess in the face of the endplug.

We were determined to eliminate the Pt lead wires for Run 2. Having some skill at TIG welding we proposed to CETI that we change the lead wires from Pt to Ti and weld them to the electrodes to create an all-Ti design. CETI approved of this plan¹⁰ so we ordered some Ti wire and began to practice the extremely delicate process of fusing a 0.5 mm diameter Ti wire to a 0.25mm thick Ti sheet. We rapidly discovered that our welding machine was much too coarse for the job. At its minimum current setting (about 10 amps) the Ti sheet melted away at an uncontrollable rate. Through the cooperation of the local Miller representative, we located a Miller Synchronwave 350 that can go down to 2 amperes of welding current. We made arrangements to borrow some time on the 350 from its owner and, with a bit of luck, managed to make two very satisfactory welds. We had the all-Ti electrode assemblies.

We also replaced nearly every O-ring in the electrolyte circuit with a Viton O-ring. We had to purchase several sizes of Viton O-rings for this purpose. Using standardless fundamental parameters again we found the following elemental concentrations (in ppm) in them.

Table 1: XRF Analysis of Viton O-rings

Size	Ba	Sr	Ca
15 mm x 2 mm	7000	170	1500
-010	2400	57	7600
-115	1100	45	7300
-003	6000	200	16000

Clearly these O-rings were made from different Viton formulations but at least none of them had any Zn.

Somehow we forgot to replace the orange silicone O-ring in the filter holder.

We replaced the white male run tee fittings and all the fittings and inserts that were colored brown from the first run with new translucent polypropylene fittings that looked very clean on XRF. We modified the new male run tee fittings to provide an O-ring seal, which eliminated leakage in the pipe threads.

Using a fresh 1 cc charge of Ni beads and our all-Ti electrode assemblies we assembled the cell exactly as before. We installed the assembled cell in the circuit and performed the same cleaning and flushing procedure as before, strictly following the RIFEX protocol.

We filled the reservoir with 86 ml of fresh 0.5M Li_2SO_4 solution (same batch used in Run 1) and started circulation at 14.3 ml/min.

With the system at ambient temperature we applied the 20 mA electrolysis power and observed the cell voltage. It started at 9 volts and climbed in seconds to 20 volts! It was still climbing when we decided to turn off the power a few minutes later. In disbelief we connected a voltmeter across the cell to check our data acquisition system. When we restored power the voltmeter confirmed a cell voltage of 20 volts and climbing! To make sure the problem wasn't due to a pocket of air in the cell, we briefly circulated the electrolyte at 80 ml/min. The voltage continued to climb past 25 volts. We shut down everything. It was becoming apparent that something was dreadfully wrong with this cell, and it probably involved the all-Ti electrodes.

We set up a simple experiment on the bench with two Ti wires dipped down into a small beaker full of 0.5M Li_2SO_4 solution. When we connected our constant current supply to this test cell, we observed the same behavior. At first the voltage was relatively low and we got the usual bubbling at each electrode. However, in less than a minute, the voltage climbed up to the power supply's limit (42 volts) and the bubbling essentially stopped. We inserted an ammeter in the circuit and discovered that the cell had become non-conductive. Even at 42 volts only a couple of milliamps were flowing through the cell.

We made only one change in this little experiment and the answer to our quandary became apparent. We replaced the Ti anode wire with a Pt wire of similar dimensions and the voltage immediately fell to about 4 volts and stayed there while both electrodes bubbled furiously.

Conclusion: Ti does not work as an anode. As it turns out, *bare* Ti does not work as an anode. John Healy of Heraeus Englehard Electrochemistry Corp. informed us that Ti is commonly used as an anode in industrial electrolytic processes but it is always coated with a precious metal oxide such as iridium oxide or ruthenium oxide. Actually he said that the coating is the real anode. The Ti just serves as a corrosion-resistant electrically-conductive support for the coating. When we described our problem to him he said that bare Ti would rapidly form an oxide coating under anodic conditions and would become completely insulated from the electrolyte under almost all conditions (the only exception being strong fluorine-based electrolytes which would dissolve the titanium oxide). This behavior is apparently what makes Ti the material of choice for the racks that hold aluminum parts during anodizing.

It was now clear to us that the Ti disc was an inactive part of the original anode. All the electrolysis current was apparently being conducted to the electrolyte through the small exposed surface of the Pt lead wire.

We related all this to CETI and, frankly, the information was not well received. They maintained that bare Ti would function properly as an anode in the RIFEX cell and instructed us to return to the original anode design. Reluctantly, we complied.

We disassembled the cell, taking care to collect all the beads. To our surprise we discovered that the Ni coatings were totally gone. We had only exposed these beads to a few milliamps of electrolysis current for less than 5 minutes during our discovery of the Ti anode problem. After that they sat in the cell immersed in Li_2SO_4 solution for a few days while we investigated the anode problem. We shipped the damaged beads back to CETI and they replaced them with new ones.

We removed the welded Ti wire from the Ti anode disc and crimped a Pt lead wire through the holes provided just like the original anode was constructed. This time however, the holes were considerably closer to the outside edge of the Ti sheet than before.

Using a fresh 1 cc charge of Ni beads, the new anode assembly, and the all-Ti cathode assembly we assembled the cell exactly as before. We installed the assembled cell in the circuit and performed the same cleaning and flushing procedure as before.

We filled the reservoir with 86 ml of fresh 0.5M Li_2SO_4 solution (same batch used in Run 1) and started circulation at 14.3 ml/min.

With the system at ambient temperature we applied the 20 mA electrolysis power and observed the cell voltage. It started at 5 volts and climbed steadily over a few minutes to about 7 volts. Something was still wrong! It occurred to us that the new location of the Pt lead wire, closer to the outside of the disc, was probably somewhat underneath the spacer O-ring in the cell. Further, when the axial clamping force was applied to the cell it was likely that the O-ring would flatten and cover even more of the small loop of Pt wire.

Anxious to get Run 2 underway and convinced that we understood the problem we threw caution to the winds and took matters into our own hands. We drained the cell and carefully removed the anode endplug without disturbing the O-ring, nylon screens, and bead bed. We uncrimped the Pt wire from the Ti disc and pulled about 2cm of it through the hole in the disc. Fortunately there was sufficient excess outside the cell to allow this and our elastomer wire seal also permitted this sliding to occur. We then fashioned this length into a circular loop about 0.6cm in diameter, bent the wire sharply where it came through the disc, and arranged the loop to lie flat and centered against the Ti disc. Thus we had fashioned a simple Pt anode of substantial area.

We carefully reassembled the cell and restored circulation of the electrolyte at 14.3 ml/min. With the system at ambient temperature we again applied the 20 mA electrolysis

The level of Zn in the Run 2 beads is about half of that in the Run 1 beads. This reduction fits with the removal of the buna O-rings but we were apparently still getting Zn from another source.

Figure 10 compares the Run 2 beads (solid gray) to the fresh Ni beads (black line):

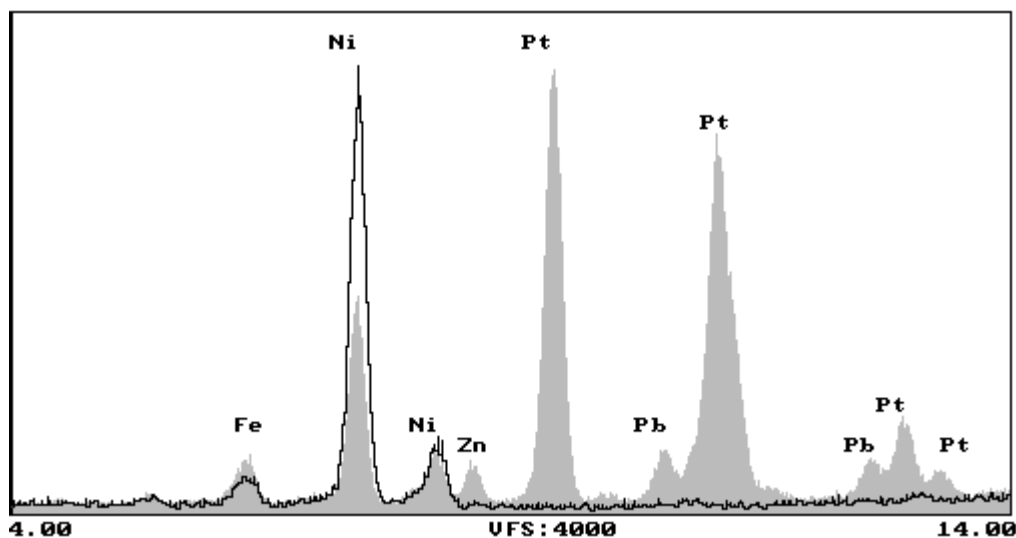


Figure 10

As you can see, the Fe peak in the Run 2 beads is only slightly higher than the Fe peak in the fresh beads. Possibly the Fe is coming from a specific source that was being depleted from run to run. In comparing these two spectra there is an apparent anomaly in the Ni K_{α}/K_{β} ratio. This is caused by a minor Pt L x-ray called the L_1 (Ell-ell) which falls right on top of the Ni K_{β} , making it look anomalously large in the Run 2 bead spectrum.

It was difficult to draw any firm conclusions from Run 2. We saw the same elements that Run 1 produced but in different amounts. As mentioned above, the beads looked quite different so it was apparent that the reaction had proceeded differently in Run 2. This alone could be responsible for most of the concentration differences. Perhaps the reason for these differences was simply the fact that Run 2 lasted only 315 hours whereas Run 1 had lasted 400 hours.

We decided to move on to Run 3. Again we were determined to eliminate Pt from the cell but, this time, we did not have CETI's support. In fact, they had cautioned during the Ti anode discussions that changing the anode in the cell might alter the reactions we were investigating significantly. We were naturally concerned about this possibility but decided that we had to take the risk.

Run 3

We purchased some Pd wire and fabricated a Pd anode very similar to the Pt loop anode used in Run 2. We selected Pd because it is chemically similar to Pt and its x-ray lines are very distinct from those of Pt.

Using a fresh 1 cc charge of Ni beads and the new Pd anode assembly we assembled the cell exactly as before. We installed the assembled cell in the circuit and performed the same cleaning and flushing procedure as before, strictly following the RIFEX protocol.

We filled the reservoir with 86 ml of fresh 0.5M Li_2SO_4 solution (new batch) and started circulation at 14.3 ml/min.

With the system at ambient temperature we applied the 20 mA electrolysis power and observed the cell voltage. It started at 2.92 volts and climbed steadily over the next hour to 3.2 volts. It appeared that Pd was working properly as an anode.

At 1800 hours on 2APR97 we enabled the electrolyte heater (right after the one-hour loading period).

As before we added 5-10 ml of water every day during the run to make up for evaporative and electrolysis losses.

We ended the run at 2200 hours on 16APR97. Total duration under electrolysis power at 70°C was about 314 hours. We drained the circuit and collected the used electrolyte. Upon disassembly of the cell we discovered that the beads were very similar in appearance to the Run 2 beads. Some of them were clear and had apparently lost their coatings but most of them retained a metallic appearance.

We recovered the beads, washed them in water thoroughly, dried them gently, and proceeded to the XRF spectrometer and collected the spectrum shown in Figure 11.

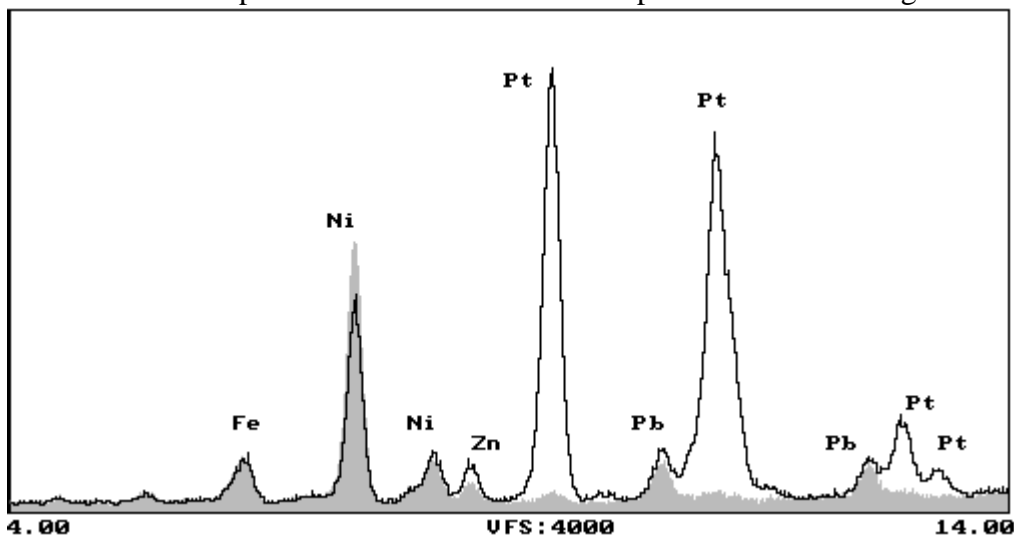


Figure 11

The Run 3 beads are shown in solid gray. The Run 2 beads are shown as a black line for comparison. The most obvious difference is the dramatic reduction in Pt content. Eliminating the Pt from the cell had virtually eliminated the Pt from the reacted beads. The small level of Pt that does show up in the Run 3 beads is likely to be from Pt that was deposited throughout the electrolyte circuit during the earlier runs when Pt was presumably present at high levels in the electrolyte. These Pt deposits could have been dissolved and transported to the beads in Run 3.

Note that the Zn content of the Run 3 beads is somewhat lower than that of the Run 2 beads. We speculate that this reduction is due to a gradual purging of Zn from the electrolyte circuit since Run 1 when Zn levels were high due to the buna O-rings.

Figure 12 shows a different portion of the x-ray spectrum where the K x-rays of Pd lie.

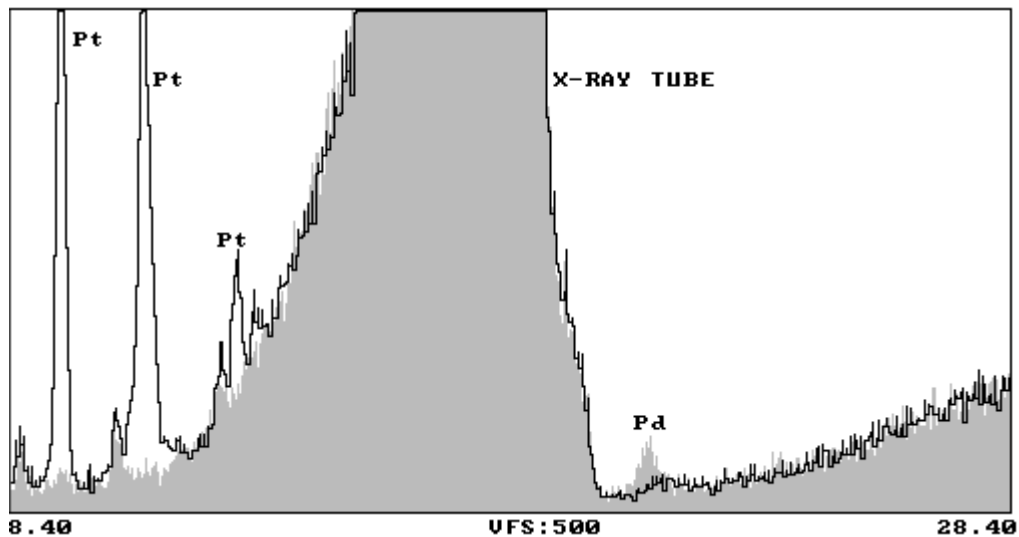


Figure 12

The Run 3 beads are shown in solid gray. The Run 2 beads are shown as a black line for comparison. The huge peak in the center is radiation emitted by the x-ray tube. Note the Pd x-ray peak in the Run 3 beads. The sensitivity for Pd is not very good under these conditions. It could easily be the case that this little peak represents as much or more Pd as the Pt found in the Run 2 beads.

This comparison essentially proves that some of the anode material was deposited on the beads in both cases. This should not be surprising even for relatively inert metals such as Pt. The electrolysis action exposes the anode metal to atomic oxygen, which is very reactive. Although resistant to oxidation, Pt and Pd are not absolutely immune. Once dissolved, the electrolysis action tends to plate the anode metal onto the cathode.

Figure 13 compares the Run 3 beads (solid gray) to fresh Ni beads (black line).

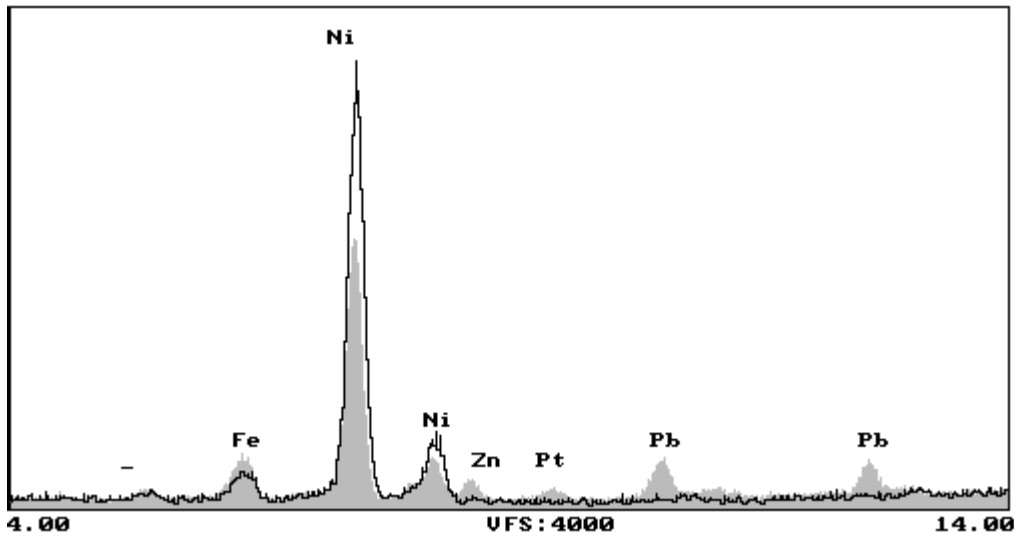


Figure 13

Despite CETI's cautions we were satisfied that the Pt was coming from the Pt lead wires used in the earlier runs. We found it impossible to entertain the hypothesis that Pt was being produced by transmutation in the cell only when Pt lead wires were used.

We had also greatly reduced the Zn by eliminating the buna O-rings. The remaining anomalies were the Pb, the remaining Zn, and the slight increase in Fe content. The reduction in Ni content is not surprising as some of the reacted beads are clear and have obviously lost their coatings.

Quantification of XRF results

The traditional method of quantifying XRF results is to calibrate the spectrometer's response with known standards. In a case like this where the sample form is unusual (relatively large metal-coated plastic beads) it is very important to have a known standard that is similar in form to the unknown samples. The obvious candidate for this known standard was the fresh Ni beads. Unfortunately, we discovered that there is considerable uncertainty in their Ni content.

The beads were identified as "Microspheres - 800 Angstroms Ni" in the RIFEX kit. Miley told us, however, that these beads were essentially identical to the ones he had used in his research. In both of his papers^{2,3} he gives the Ni coating thickness as 650 Å.

Unfortunately, the RIFEX Ni beads have never been analyzed by NAA but Miley was able to give us NAA results for the 4 previous batches of similar beads. The results are shown in Table 2 below:

Table 2: Miley's NAA Ni results on beads similar to the RIFEX beads

Batch #	ppm Ni
n60	1821
60	1729.5
60(4)	1635
76	1784

Since the RIFEX beads were produced by the same process as these four batches we elected to average these concentrations and assign the tentative value of 1743 ppm Ni to the RIFEX beads.

To convert this bulk concentration value into a Ni coating thickness we needed to know the average diameter of the beads. We measured 100 beads with Brown & Sharpe dial calipers (accurate to 0.02 mm) and found the size distribution depicted in Figure 14.

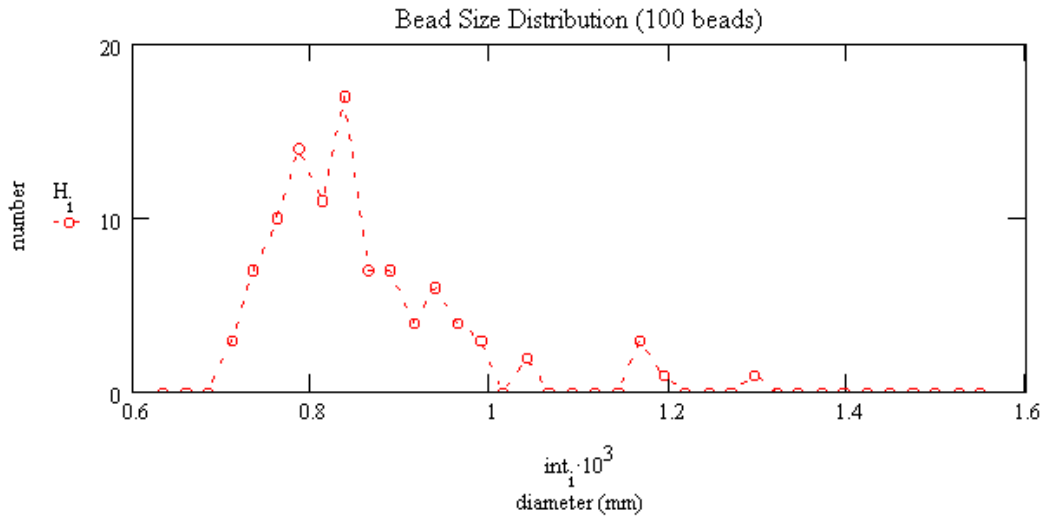


Figure 14

The mean diameter (for surface area and volume calculations) was found to be 0.863 mm (Miley gives² the bead diameter as 1.06 mm). Assuming the specific gravity of the beads was 1.05 (polystyrene), we calculated the average mass of a bead to be 353 micrograms (Miley gives² 609 micrograms). If our average bead wa 1743 ppm Ni, the mass of Ni present would be 0.615 micrograms. If that much Ni was spread uniformly over the surface of a 0.863 mm diameter sphere, the thickness would be only 296 Å.

This uncertainty (296-800 Å) in the Ni coating thickness prevented us from using the fresh Ni beads as a calibration standard. We therefore resorted to a standardless fundamental parameters⁹ (SFP) calibration for these beads. We made the assumption that the bead matrix was styrene and we corrected for the fact that 1 cc of beads in an 18mm sample cup did not constitute an infinitely thick sample for the x-rays. Fortunately we had available some pure Ni balls about the same size as the RIFEX beads and these were used to establish the sensitivity of the XRF spectrometer to Ni and to automatically correct for any geometry effects from the relatively large spherical shapes. The result of

this calibration (details available upon request¹¹) was an XRF analysis of 1594 ppm Ni. This was reasonably close (only 9% low) to the average value of Miley's NAA Ni results. Based upon a general confidence in NAA results derived from previous experiences and a past history of modest successes with SFP, we decided to simply accept our SFP calibration results for all the elements of interest. The results are presented in Tables 3 and 4.

Table 3: XRF Results (ppm)

Sample ID	Fe	Ni	Zn	Pt	Pb
Fresh	196 ±14	1594 ±20	1 ±3	2 ±4	2 ±2
Run1	623 ±20	430 ±11	184 ±6	539 ±11	31 ±4
Run 2	377 ±16	755 ±14	67 ±4	1438 ±17	72 ±5
Run 3	337 ±16	958 ±15	37 ±3	36 ±5	68 ±4

Table 4: XRF Results (total micrograms in bead bed)

Sample ID	Fe	Ni	Zn	Pt	Pb
Fresh	130 ±9	1062 ±13	1 ±2	1 ±2	1 ±2
Run1	415 ±13	286 ±7	122 ±4	359 ±8	20 ±2
Run 2	251 ±11	503 ±9	45 ±3	958 ±11	48 ±3
Run 3	225 ±10	638 ±10	25 ±2	24 ±3	46 ±3

The values in Table 4 were calculated from those in Table 3 using a bead bed weight of 0.67 g (measured on fresh beads). The analytical conditions used for these analyses were 40 kV anode voltage, 4 mA emission current, Mo secondary target, and a 400 second measurement time.

The stated error limits are 2-sigma counting statistics and represent only the calculated statistical precision of these measurements. The accuracy is likely to be much worse. Past experiences with SFP calibrations have produced results that are almost always within ±50% of the actual value and usually within ±20%.

Tentative Conclusions

Patterns in the XRF results suggest that the electrolyte circuit can become contaminated with an element during one run and then deliver that element to the beads in subsequent runs. Look at the Zn concentrations, for example. In Run 1, the system was probably contaminated with Zn from the buna O-rings and 122 micrograms of Zn were collected on the beads. In Run 2, with the buna O-rings removed, we got 45 micrograms of Zn and then in Run 3 we got 25 micrograms of Zn, as if the Zn was slowly being purged from the circuit.

Also consider the Pt results. In Run 1 and Run 2 the system was probably contaminated with Pt from the Pt anode. In Run 3, with the Pt removed from the system we see a much

smaller but still measurable quantity of Pt in the reacted beads, almost certainly due to Pt contamination of the circuit.

With this perspective we decided to focus our attention on the remaining anomalies in the results from Run 3, i.e. where did the Fe, Zn, and Pb come from?

Analysis of the Electrolyte

We decided to have the fresh Li_2SO_4 analyzed for Fe, Zn and Pb. We sent samples of our well-blended Li_2SO_4 stock to Galbraith Laboratories¹² and General Engineering Laboratories.¹³ The results are presented in Table 5.

Table 5: Laboratory analysis of the Li_2SO_4 (in ppm)

Lab	Fe	Zn	Pb
Galbraith	<0.9	9	5
General Engineering	2.9	51	9
Aldrich lot analysis	-	4	-

The agreement among these results is, in our experience, fairly typical of such low-level analyses with the exception of the General Engineering Zn result. We asked them to repeat the Zn analysis on a fresh split of the Li_2SO_4 and their second result was 31 ppm Zn...not a lot better. A possible cause for their apparent error is the unusual sample matrix (i.e. pure Li_2SO_4).

Using these results we calculated the mass of each element present in the RIFEX electrolyte circuit (i.e. the mass of each element in 86 ml of a 0.5M solution of this Li_2SO_4). The results, along with the increase in mass observed for each of these elements in the Run 3 reacted beads are presented in Table 6.

Table 6: Total micrograms of element in fresh electrolyte and observed increase in element in the reacted beads

	Fe	Zn	Pb
Galbraith	<4	43	24
General Engineering	14	147*	43
Aldrich lot analysis	-	19	-
Run 3 reacted beads	95	24	45

* based upon their second analysis

Except for the Fe it was now apparent that the Li_2SO_4 contained sufficient quantities of these elements to explain their appearance in the reacted beads. There was only one thing left to do: analyze the used electrolyte to see if it had been depleted of these elements.

We slowly evaporated (at 70°C) some of the Run 3 electrolyte to dryness and sent a measured sample to Galbraith Labs for analysis. We corrected the results they got for the fact that the used Li_2SO_4 was actually $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ whereas the new Li_2SO_4 was

anhydrous. The corrected results are presented in Table 7 along with their original results on the new Li_2SO_4 for comparison.

Table 7: Galbraith Labs Analysis of New and Used Li_2SO_4 (in ppm)

Sample	Fe	Zn	Pb
New Li_2SO_4	<0.9	9	5
Li_2SO_4 from Run 3	1.4	6	<1

Both Pb and Zn had indeed been depleted. In the case of Zn, the observed depletion would provide 14 micrograms to deposit on the beads, somewhat less than the 24 micrograms found in the Run 3 beads. In the case of Pb, the observed depletion would provide 19-24 micrograms, again somewhat less than the 45 micrograms of Pb found in the Run 3 beads.

Interestingly the Fe content of the electrolyte appeared to increase slightly due to usage as if there was still a source of Fe in the system.

Discussion

Despite a large investment in time and money, this study is not exhaustive. We performed only three runs with our RIFEX kit. We followed the protocol provided by CETI to the best of our ability but difficulties with the apparatus forced us to make a few changes on each run. As a result each of the three runs behaved noticeably differently.

The Ni coating on the beads was heavily attacked in each of our runs (see Table 4). In contrast, Miley's run with similar beads (his run #8) appears to have produced Ni. Table 4a in reference 2 indicates that his beads doubled in Ni content during the run. We cannot explain this difference. Primarily interested in new elements on the beads, we made no effort to track the Ni lost from our beads.

We employed only elemental analysis (not isotopic analysis) in our study and we limited our investigation to a few prominent elements that appeared in the reacted beads. The laboratories we employed for analysis of the electrolyte were expensive and incredibly slow. We were disappointed, but not surprised, by the lack of agreement between these laboratories on the same samples.

The small volume of material produced by these runs significantly limits the depth to which the analytical investigation may be carried. For example, it took almost all of the electrolyte from Run 3 just to obtain the few laboratory analyses presented above.

We did obtain results from our investigation. However, we can only speculate as to their significance.

Speculation

We are convinced by the dramatic reduction in Pt in Run 3 (which used a Pd anode) that the Pt observed in the Run 1 and Run 2 beads came from the Pt anodes used in those runs. We spoke to several electrochemists about this issue and the general consensus was that Pt does indeed oxidize under anodic conditions but more slowly than any other metal.

For Pb and Zn, the analyses of the new and used electrolyte strongly suggest to us that the appearance of these elements in the reacted beads is due to a simple electrodeposition process. The observed depletion of these two elements falls about a factor of 2 short of matching their concentration in the reacted beads but this difference is not likely to be significant. In the case of Zn, the data in Table 4 indicates that we could still be collecting Zn that was introduced into the circuit in Run 1. If only 10 of the 24 micrograms of Zn found in the Run 3 beads came from residual Zn in the circuit, the electrolyte depletion would explain the balance. In the case of Pb, perhaps Galbraith's analysis of the new Li_2SO_4 was low by a factor of 2. General Engineering Labs reported almost twice as much Pb in the new Li_2SO_4 as Galbraith. Finally we must consider the possibility of errors in our XRF results.

The Fe content of the reacted beads is a bit more mysterious. All the electrolyte analyses agree that it is not coming from the Li_2SO_4 . The iron powder in the JB-WELD epoxy clearly contaminated the system during Run 1 but the data in Table 4 suggests that the Fe content of the reacted beads would level off at about 200 ppm if more runs were performed. Since the uncoated beads contain 130 ppm Fe, this leaves about 70 ppm (47 micrograms in the bead bed) of Fe that somehow appears in the reacted beads. Possible identified sources for this iron include residual Fe deposited in the circuit during Run 1, the red silicone O-ring in the filter holder, and the ceramic piston and cylinder in the electrolyte pump.

We believe that these elements appear in the reacted beads as a result of electrodeposition of cations in the electrolyte that were either present initially or were dissolved from various sources in the electrolyte circuit. However, our quantification of these elements and their potential sources does not balance precisely. In our opinion the possible explanations for this discrepancy in quantification should be prioritized as follows:

1. Errors in the laboratory analysis of the fresh and used electrolyte
2. Errors in the XRF analysis of the reacted beads
3. Residual contamination of the electrolyte circuit from Run 1
4. Known sources of contamination within the electrolyte circuit (in the case of Fe)
5. As yet unidentified sources of contamination within the electrolyte circuit
6. Creation of these elements by nuclear transmutations in the cell

We do not lightly place nuclear transmutations last in this list. At the outset of this study, we were encouraged by reports of large excess heat from cells with similar beads. Indeed, Miley reported³ observing low levels of excess heat (~0.5 watt) from beads

virtually identical to those in the RIFEX kit. The existence of a strong excess heat phenomenon, exceeding all possible stored chemical energy limits, essentially demanded that nuclear reactions were involved.

One must consider the possibility that the excess heat measurements were in error.

If there were no excess heat, essentially all incentive to search for evidence of nuclear reactions would disappear. Further, we would no longer be tempted to interpret relatively minor discrepancies in the analysis of the cell components as such evidence.

Our own calorimetric measurements on the beads in the RIFEX kit⁶ show no evidence of excess heat. This is at odds with Dr. Miley's experimental results³ but consistent with the possibility that there are no nuclear reactions occurring in the RIFEX kit.

Acknowledgements

We would like to thank Dr. George Miley and Mike Williams of the University of Illinois for discussions. We are also indebted to Dr. Dennis Cravens and Maria Okuniewski of CETI for their patience and guidance with the RIFEX protocol.

We would like to thank Dr. Peter F. Berry of TN Technologies, Inc., Round Rock TX, for his invaluable assistance with the standardless fundamental parameters XRF calibration. We would also like to thank Rick Comtois and Dr. Robert Tisdale of Jordan Valley Applied Research, Inc. Austin TX, for making the EX-6000 XRF system available for this study.

Finally, we gratefully acknowledge partial support of this work by the Fetzer Institute, Kalamazoo, MI.

Epilogue

SIMS Analysis of the Run 3 Beads

After reviewing a draft of our report, Dr. Miley offered to perform SIMS (Secondary Ion Mass Spectroscopy) analysis on the Run 3 beads. We submitted the entire lot (~1 cm³) to him for analysis and encouraged him to measure several spots on several beads to obtain a representative result.

Miley's SIMS lab performed 4 separate analyses on the Run 3 beads and averaged the results¹⁴.

Figure E1 shows a comparison between the elemental concentrations found in our Run 3 beads (solid black circles) and those found in 7 of the runs that Miley has included in his reports^{2,3} (various symbols according to the legend). The graph is a plot of production rate vs mass number.

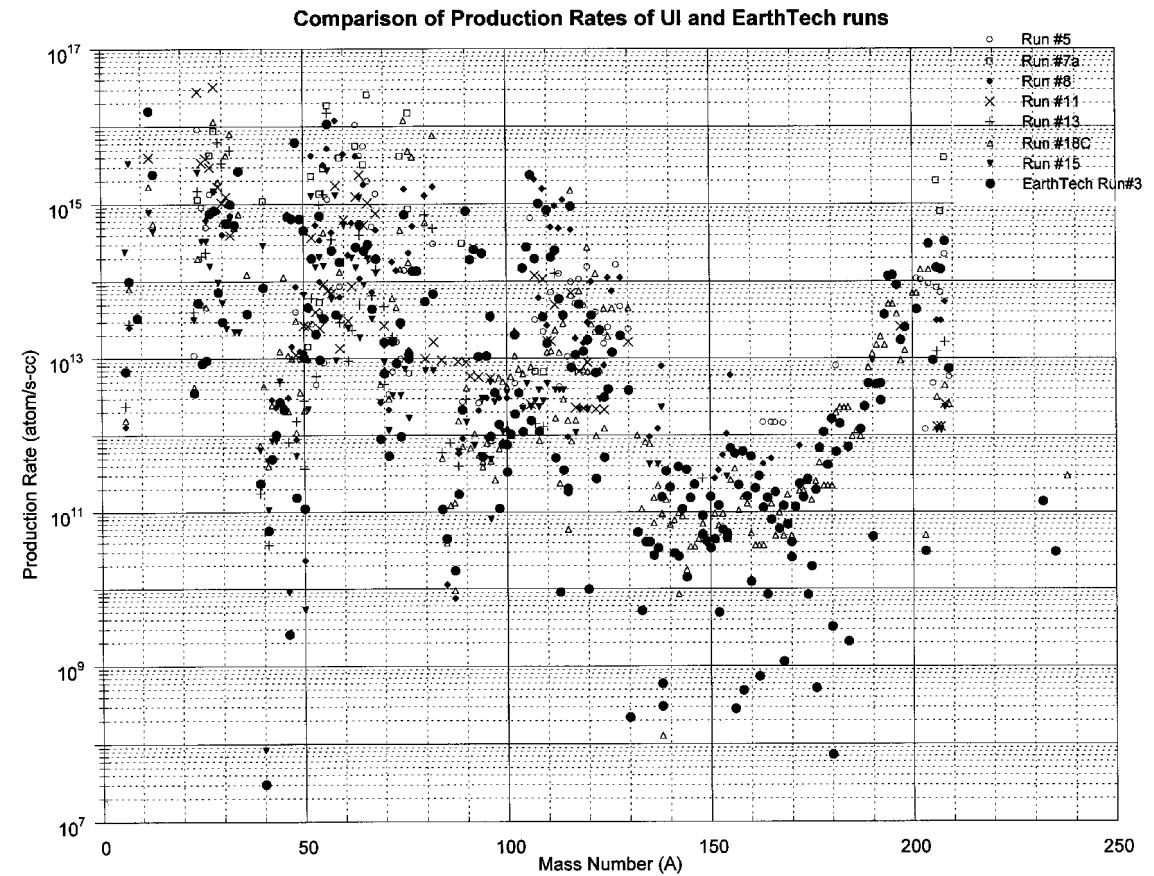


Figure E1

It is immediately apparent that there is a substantial similarity between these results. The SIMS detected scores of elements in our Run 3 beads at levels similar to those found in Miley's runs!

To evaluate the SIMS results properly, we need to quantify the relationship between production rate and weight concentration in the reacted beads. The production rate is stated in atoms/sec per cubic centimeter of coating and can be calculated as follows:

$$R = \frac{C \cdot m \cdot N_A}{A \cdot V \cdot t}$$

where

R = production rate

C = change in weight concentration of an element in the reacted beads

m = mass of a bead

N_A = Avogadro's number

A = atomic weight of the element

V = volume of the bead coating

t = duration of the run (~300 hours)

In applying this relationship we are faced with an unresolved factor-of-two uncertainty. Miley's standard bead is 1.05 mm in diameter, weighs 606 micrograms, and has a 650Å thick coating. Our measurements of the actual RIFEX beads indicate a 0.86 mm diameter, a weight of 353 micrograms, and a 296Å coating. Fortunately, a factor-of-two uncertainty is not very important here. We are considering a range of production rates that covers 10 orders of magnitude from 10^7 to 10^{17} atoms/sec-cc.

Of primary interest is the production rate that corresponds to the minimum detectable amount of an element in the reacted beads. Using our XRF methods, the detection limit approaches 10 ppm under favorable conditions. Taking the element V for example, 10 ppm in the reacted beads (assuming the fresh beads contained no V) corresponds to a production rate of about 4×10^{14} atoms/sec-cc. This is quite a large value, near the top of the observed SIMS production rates.

Does this mean that XRF is relatively insensitive? For comparison let's look at the various methods employed to analyze the electrolyte. In our case we submitted the dry Li_2SO_4 to the laboratory so they could control the sample preparation as needed to achieve the best possible detection limit. Galbraith Labs balked at our request to achieve 0.1 ppm accuracy in the analysis of Fe, Zn & Pb in Li_2SO_4 . They estimated an accuracy of 0.5 ppm and they reported the results rounded to the nearest ppm. It is therefore reasonable to assume that their detection limit is about 1 ppm for such elements in Li_2SO_4 . Our RIFEX runs used 4.5 g of Li_2SO_4 . At a concentration of 1 ppm, there would be 4.5 micrograms of that element in the fresh electrolyte. If all of that element were deposited on the beads during the run, the resulting concentration in the reacted beads would be 7 ppm...very close to the XRF detection limit.

What about direct analysis of the electrolyte? Here is an ICP-MS analysis performed by CETI on a 0.5M solution of the RIFEX Li_2SO_4 (data received via email from Maria Okuniewski on 12MAR97):

Element	Mass	Concentration ($\mu\text{g/L}$)
Mg	25	<1000
Ca	44	<5000
Ti	49	617
V	51	<250
Cr	52	<150
Mn	55	<10
Fe	57	<1250
Co	59	<50
Ni	60	<20
Ni	62	<150
Cu	63	<400
Cu	65	<400
Zn	68	<500
Ge	73	<100
Se	82	<250
Zr	90	188.9
Zr	91	182.2
Nb	93	<100
Mo	97	<50
Ru	101	<100
Pd	102	105.2
Pd	104	<100
Pd	105	<100
Ag	107	<10
Ag	109	<10
Cd	114	<150
Sn	117	<50
Sn	118	<50
Sn	119	<50
Sn	120	<50
Yb	171	<100
Yb	172	<100
Yb	173	<100
Hf	177	<100
Hf	178	<100
Hf	179	<100

A report of "<50" tells us that the detection limit is 50 $\mu\text{g/L}$. There are a few elements with detection limits better than 50 $\mu\text{g/L}$ and many that are worse. Taking 50 $\mu\text{g/L}$ as a typical detection limit, we can convert that into a total of 4.3 micrograms in the 86 ml of electrolyte used in our RIFEX runs. If all of that were deposited on the beads the resulting concentration would be about 6 ppm, again close to the XRF detection limit of 10 ppm.

So all these analytical methods, except SIMS, have roughly equivalent detection limits. Using the production rate formula we can plot a line on the SIMS data from our Run 3 beads that represents the approximate detection limit of the other analytical methods. (The line has been labeled "1 ppm" because it represents that concentration in the dry Li_2SO_4).

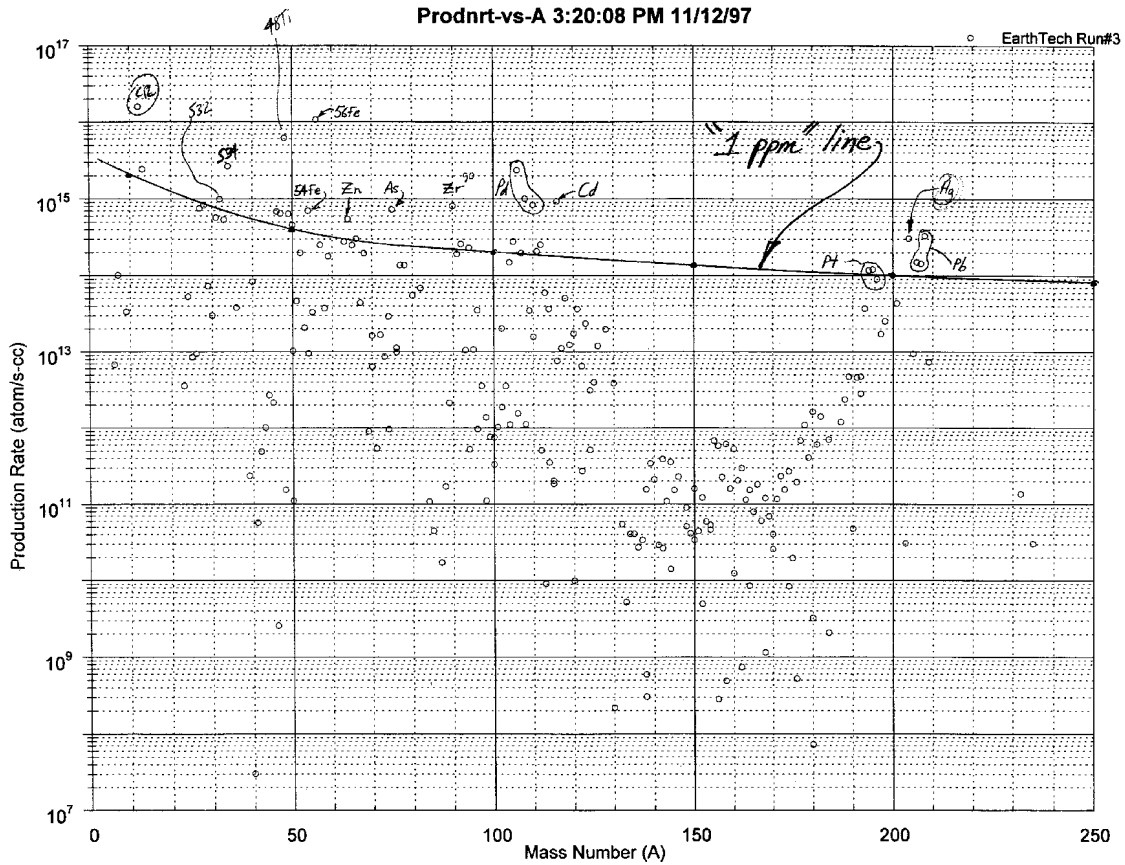


Figure E2

Most of the SIMS results are below the line! SIMS is a very sensitive analytical technique but, in this case, the effective sensitivity is greatly enhanced. The SIMS directly analyzes the thin bead coating upon which contaminants from the entire volume of electrolyte tend to be deposited by the electrolysis. In essence, the RIFEX experiment serves as a preconcentration step for SIMS analysis of trace elements in the electrolyte. This realization has an enormous impact on the matter at hand:

Every SIMS element that sits below the 1 ppm line could possibly be coming from an undetectable trace contaminant in the electrolyte.

For the purposes at hand, we will therefore ignore all of the SIMS results that are below the 1 ppm line. We simply do not have the means to prove that those elements were not present in the electrolyte at the start of the run. Even if we employed analytical methods

with 10x better sensitivity only a handful of additional elements would be included. The majority of the SIMS results are several orders of magnitude below the 1 ppm line.

What about the elements that are above the 1 ppm line? Several of them (Fe, Zn, Pb, Pt, & Pd) were detected in our analytical work and have been traced to identifiable sources within the RIFEX circuit. Some of them (C, S, Zr, & Cd) are not in our XRF analytical range. The remainder (Ti, As, & Hg) warrant some discussion. The total SIMS Ti result is equivalent to 213 ppm Ti in the Run 3 beads. Our XRF results showed little or no Ti and our detection limit for Ti is probably ~30 ppm. We cannot resolve this Ti discrepancy. Regarding As, the SIMS may well be correct. The SIMS result works out to 28 ppm As. Such an As peak could be hiding beneath the Pb L_{α} peak from the 68 ppm Pb; it's a classic XRF interference.

The Hg is an interesting case. The point labeled Hg in Figure E2 is ^{204}Hg . There were only 2 counts in that channel in the SIMS raw data...and there were zero counts in the channels for ^{196}Hg , ^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg , & ^{202}Hg which comprise the other 70% of the naturally occurring Hg isotopes. Should we conclude that the run produced a small amount of ^{204}Hg and none of the other Hg isotopes?...or should we suspect that noise or some other instrumental error is responsible for those 2 counts?

Discussion

As far as we are concerned, Miley's SIMS analysis of our Run 3 beads does not change the conclusions and speculations presented earlier in the main report.

In our opinion further investigation into the possibility of nuclear reactions in the RIFEX kit should be contingent upon confirmation of the excess heat phenomenon. At this time, we have concluded our search for excess heat in the RIFEX kit with negative results⁶. However, we stand ready to test new beads for excess heat if/when they become available. If we can confirm the excess heat phenomenon, we will eagerly reopen our search for evidence of nuclear reactions.

¹ RIFEX kit sales brochure, Clean Energy Technologies, Inc. 1996

² Miley, George H. & James A. Patterson. 1996a. Nuclear transmutations in thin-film nickel coatings undergoing electrolysis. Second International Conference in Low-Energy Nuclear Reaction. Texas A&M, College Station, Texas. (September 13-14).

³ Miley, George H., G. Narne, M. J. Williams, J. A. Patterson, J. Nix, D. Cravens, and H. Hora. 1996b. Quantitative observation of transmutation products occurring in thin-film coated microspheres during electrolysis. Proceedings of the ICCF-6. Hokkaido Japan. (October 14-17).

⁴ U.S. Patent 5,372,688, James A. Patterson, Inventor, "System For Electrolysis of Liquid Electrolyte"

⁵ Scott Little was General Manager of ASOMA Instruments, Inc. Austin TX from 1979 to 1990 and Manager of Analytical Instrument Development at TN Technologies, Inc, Round Rock, TX from 1990 to 1993.

⁶ Little, Scott & H. E. Puthoff, "Calorimetric Study of Pd/Ni Beads from the CETI RIFEX Kit". Available upon request. Contact little@eden.com.

⁷ <http://www.eden.com/~little/rifex1.jpg> and <http://www.eden.com/~little/rifex2.jpg>

⁸ Table 4a of ref 2

⁹ Standardless fundamental parameters is an XRF calibration method wherein the analyte concentrations are calculated from the measured x-ray line intensities and the known values of fluorescent yields, photoelectric cross sections, mass attenuation coefficients, and densities of the elements observed in the sample. Usually some approximations must be made for the light elements in the sample that cannot practically be measured via XRF (e.g. $Z < 11$).

¹⁰ Telephone conversation with Dr. Patterson on 18FEB97

¹¹ A Mathcad 6.0 worksheet containing the calculations behind our XRF results is available upon request. Contact little@eden.com.

¹² Galbraith Laboratories, Inc. 2323 Sycamore Drive, Knoxville TN 37950-1610

¹³ General Engineering Laboratories, 2040 Savage Road, Charleston SC 29417

¹⁴ Raw SIMS data available upon request from EarthTech. Contact little@eden.com