ANALYZING NUCLEAR ASH FROM THE ELECTROCATALYTIC REDUCTION OF RADIOACTIVITY IN URANIUM AND THORIUM

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Abstract

A proprietary electrolytic system for the reduction of radioactivity in uranium and thorium was evaluated from June through December 1996. An exhaustive analysis of reaction materials taken before, during and after the experiments was carried out. These tests involved trace metals analysis via Neutron Activation Analysis (NAA), Energy Dispersive Atomic X-ray (EDAX) analysis and Inductively Coupled Plasma Mass Spectroscopy (ICP/MS). Additional tests involved high resolution mass spectroscopy of evolved gasses and reaction products, allowing isotopic differentiation, and high resolution gamma spectroscopy. Neutrons were searched for via ^{235}U fission fragments and n-γ reactions.

The results of over 10 series of runs were ambiguous. However, the definitive test: operating a system in a low background cave with high resolution gamma spectroscopy, failed to show any radioactive reduction of the system as a whole. Regardless of these results, the testing protocols developed define the standard and rigor by which any proposed catalytically reduced radioactive system must be subjected. It is crucial that statistically significant results be obtained, including the statistical uniformity of the matrix composition, as otherwise comparisons will be impossible and the conclusions drawn will be erroneous.

1. Introduction

J. Bochris [BOCK92], T. Claytor [CLAY90], J. Jorne [JORN94], G. Miley [MILE96], and others have presented low energy nuclear effects occurring in solid lattices. Some of these experiments have reported elemental transmutation as well. All of these systems have either metal hydrides, deuterides, or proton conductors in common. JWK International Corporation and its team sought to apply low energy elemental transmutation observed in hydrided materials to radioactive materials, and undertook an evaluation of a proprietary system developed to electrocatalytically reduce actinide radioactivity using a model uranium/thorium system in a solid catalyst.

2. Catalytic System Operation

We employed a proprietary 0.25 gram matrix slightly impregnated with ^{235}U depleted uranium and thorium. Uranium and thorium were chosen as test elements because they are both radioactive and form metal hydrides. The latter condition is hypothesized as necessary for the proposed effect at room temperature by electrolytically forming uranium and thorium hydrides in the presence of lithium sulfate in the electrolyte. The matrix is formulated in several proprietary steps resulting in dispersed uranium and thorium oxides. These oxides are very stable, and should resist chemical attack in the cell.

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3. Instrumentation

Instrumentation was employed to assess the matrix and system prior, during and after an experimental run. The goal of this instrumentation was to establish:

- evidence of radioactive reduction
- evidence of nuclear transmutation

This was accomplished by monitoring radiation and trace materials.

3.1 Radiation Measurements

Geiger Counters are sensitive to X-rays, beta particles, gamma rays and alpha particles. With the exception of the gamma rays, the others are easily attenuated by the water and the plastic components used in the system. Consequently, we observe gamma lines using liquid nitrogen cooled Ge detectors in a low background Pb shielded cave.

^{235}U makes a sensitive *in situ* neutron diagnostic, because of its high fission cross section to < 0.5 ev and > 1 MeV neutrons. Similarly, the lithium sulfate in the water electrolyte and the polycarbonate housings make good detectors for neutron capture, gamma (n-γ) reactions.

Only one naturally occurring isotope of uranium, ^{235}U, with a half life of 7.04×10^8 years, has detectable gamma lines: 185.7 and 143.8 KeV. It should be noted that the 185.7 KeV line is easily confused with the ^{226}Ra 186.1 KeV line. However, ^{238}U, with a 4.47×10^9 year half life, decays to:

$$^{238}U \; -> \; ^{234}Th + \alpha + \gamma \; -> \; ^{234m}Pa + \gamma + \beta \; -> \; ^{234}U \; + \beta$$
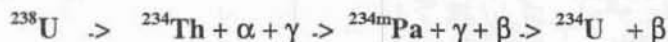
Consequently, we observed two > 1 MeV γ lines of ^{234m}Pa, and two > 90 KeV lines from ^{234}Th. ^{234m}Pa has a half life 1.17 minutes. Naturally occurring thorium, which is 100% ^{232}Th with a 1.4×10^{10} year half-life, decays as:

$$^{232}Th \; -> ^{228}Ra + \alpha \; -> \; ^{228}Ac + \gamma + \beta \; -> \; ^{228}Th + \beta$$

We observed over ten gamma lines from ^{228}Ac ranging in energy from 270 KeV to over 1 MeV. If the daughter products of U and Th are not in secular equilibrium with their parents, then they would not provide an accurate measure of the parent's presence. Because of the relatively long half-lives of two of the daughters: 5.7 years for ^{228}Ra and 24 days for ^{234}Th, we are concerned about the time required to re-establish secular equilibrium. However, we are most concerned about breaking the ^{232}Th decay chain since ^{228}Ra may form an insoluble precipitate, $RaSO_4$. **This is of particular concern in all electrolysis studies using both Th and Li_2SO_4.**

Alpha and beta particles were counted with a scintillator in vacuum. Using the Feather Analysis technique, calibrated sheets of aluminum and lead were utilized to provide a known attenuation to beta particles and X-rays [OVER60]. This was used as an ancillary monitor of sample radioactivity.

One indication of elemental transmutation would be evidence of a K-capture of an electron or the X-ray emission which occurs when an electron fills a new shell formed during transmutation. Since we were not calibrated to detect photons below 90 KeV, and were not sensitive below 40 KeV, we were unable to observe these X-rays.

3.2 Trace Material Analysis

If nuclear processes are occurring, then a *nuclear ash* must result. Since the overall radioactivity may be reduced by the process, then the nuclear ash must be stable. Several different instruments were employed to monitor trace materials, including:

- Neutron Activation Analysis
- Inductively Coupled Plasma Mass Spectroscopy
- Energy Dispersive Atomic X-ray Analysis

Neutron activation analysis (NAA) requires subjecting a sample to an intense neutron flux for several minutes followed by successive counting periods where gamma ray emissions are recorded. Not all elements can be activated by this mechanism, but for those that can be, NAA provides an exquisitely sensitive technique accurate to parts per billion or better for some isotopes. NAA can also be used to give isotopic data. However, care must be taken, where assumptions of isotopic natural abundance are made, as well as where there is a variable abundance, such as with lead. Unfortunately, ^{235}U present in the samples also fission during NAA and its', and ^{238}U, fission products complicate the elemental analysis. Neutron Activation Analysis was performed in three different facilities.

Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) compliments NAA. A sample is heated to several thousand degrees Celsius and injected into a mass spectrometer. The technique is typically sensitive to parts per billion. Unfortunately, three orders of magnitude in sensitivity is lost because of the small sample sizes employed. This results in a sensitivity of about 2-5 parts per million. Although this is sufficient for many of the candidate transmutation materials, it is insensitive at this level to the rare earths that are also candidate transmutation products. The argon isotope ^{40}Ar, which is used as the feed gas in the instrument, interferes with the calcium isotope ^{40}Ca, and compromises the sensitivity for this isotope.

In addition, sample preparation compromises this technique. Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) requires that a sample be dissolved in a liquid for injection. Very corrosive acids are chosen such as perchloric acid. Unfortunately, another candidate transmutation element, silicon, does not dissolve in perchloric acid, so "wet" preparation is very important. The ICP/MS samples run were dissolved in perchloric acid.

A high resolution ICP/MS can be tuned to count specific ions with a particular mass. This can be used to accurately determine the isotopic abundance of various elements. Unfortunately, isotopes with the same mass, such as the nickel isotope ^{64}Ni and the zinc isotope ^{64}Zn are indistinguishable even with the highest resolution mass spectrometer. These isotopes require a chemical separation prior to the ICP/MS analysis.

Energy Dispersive Atomic X-ray (EDAX) analysis provides a surface elemental scan by looking at secondary X-rays from a Scanning Electron Microscope (SEM) electron beam as it is directed across a sample. This technique is sensitive to parts per thousand. However, this low resolution is useful since an element must be in high concentration to be observed by this technique.

4. Results of Experiments with Uranium and Thorium

Samples were taken from runs including used and unused U and Th impregnated matrix, and used and unused high purity 1 molar Li_2SO_4. The tubing, plastic housings and filter paper were also analyzed. The possible effects observed included reductions in radioactivity and elemental transmutation, however these were inconclusive because of inhomogeneous samples and statistically incomplete sampling.

Most significantly, real-time gamma monitoring of a closed system resulted in **no reduction** in gamma lines from ^{235}U, or the ^{238}U decay chain or the ^{232}Th decay chain. The non-operating experiment was housed sufficiently long in the gamma detector to trap radon

gas in a closed system and showed an **increase** in ^{212}Pb and ^{208}Tl activity, both of which are expected in the ^{232}Th decay chain and are radon decay products.

High resolution mass spectroscopy of the evolved gasses during experiments at the University of Rochester (UR) and NRL showed **no isotopic** or gas production anomalies. Curiously, the UR experiment, which was gas sampled, indicated radioactive reduction by matrix measurements, whereas the NRL gas sampled experiment showed no reduction during the real time gamma counting experiment.

U and Th were found to *apparently* decrease by 50%-90%, as measured in the same sample before and after an experimental run, by alpha, beta and gamma counting. Very little U and no Th was on the filter paper or in the electrolyte, as measured by gamma counting and neutron activation of the electrolyte. However, it was difficult to accurately weigh the matrix after a run because of Li_2SO_4 coatings and the possibility of washing away the matrix while rinsing off the Li_2SO_4. It is suspected that matrix fines became distributed throughout the system, thereby resulting in an "apparent" reduction.

ICP/MS showed an apparent increase in elemental Ba(+104x), Ca, Ni(+18.5x), Mg, Zn(+10x), Al, Pb (+15x) and decreases in U and Th. However, the material was not uniform, rendering before and after run comparisons statistically impossible. Further testing is also required to rule out contamination from handling and other sources. Various "inert" components, such as o-rings, have been shown to be contamination sources, especially barium [LITT98]. It is worth noting that due to the short time scales of the experiments, typically 4 hours, and the low current densities, less than 0.2 amps, an insignificant electrolytically induced contamination concentration should occur [BOCK96].

U and Th have a neutron excess. ^{238}U has a ratio of 146:92 or 1.6:1, neutrons to protons. ^{232}Th has a ratio of 142:90, also 1.6:1. Any transmutation of these elements must account for these surplus neutrons. ICP/MS data of possible transmuted Mg, Ni, Cu, Zn and Ba showed no change in their naturally occurring isotopic abundances within the statistical error of the measurement. Indeed, there were 1-2 percent changes between the used and unused samples, as well as natural abundances, but these were all within the error bars. The inability to distinguish between ^{64}Ni and ^{64}Zn leaves open the possibility that the heavy nickel isotope ^{64}Ni may be in higher abundance and the light zinc isotope ^{64}Zn in lower abundance, or *vice versa*. Similarly, ^{67}Zn can not be reported because it overlaps with doubly charged ^{134}Ba^{++} in the mass spectrometer.

ICP/MS is accurate enough to correctly identify three uranium isotopes: ^{234}U, ^{235}U, and ^{238}U in the samples. Since we used depleted ^{235}U uranium, ICP/MS showed the samples contained 0.2% ^{235}U, vs. a natural abundance of 0.7% ^{235}U, which is consistent with commercially available uranium.

EDAX analysis showed the initial matrix to consist of S, U, Cu, and Th. After a run there was a qualitative reduction in the U and Th line heights, along with the additional presence of Mg, Al, Si, Sb, Cr, Fe, Ni, Cu, Os, and Pt. Os may be confused with a Cu peak. S was in the original matrix, and in the Li_2SO_4 added to the electrolyte. There were trace amounts of Cr, Fe, Ni and Pt in the system, primarily in the electrical feed wires and Ti electrodes. Similarly, Al and Si were present in the alumina pump head used prior to the adoption of a contact-less peristaltic pump. However, Ti was notably absent, despite the Ti electrodes presenting the largest surface area for contact. This may be indicative of an oxide forming on the Ti, thereby sealing it from contact with the electrolyte, as well as reducing its electrical conductivity. It was suggested that under these conditions the Pt feed wire provides the majority of the surface area for electrolysis, and hence, an active source of contamination [LITT98].

It should also be noted that the U nucleus binding energy provides on the order of 200 MeV/nucleus fission. Although these experiments were run without calorimetry, there was no perceptible temperature increase (>5° C) associated with liberating this energy. Thorium fission would also result in similar excess energy.

5. Statistical Sampling

The major flaw in this study was the inability to establish a normal distribution for the radioactive matrix so as to allow random sampling to give statistically meaningful results of both radioactive and trace materials before and after experiments. A significant effort will be required in the future to determine the statistical distribution of the matrix components, since ICP/MS and NAA are destructive, and comparisons require a normal distribution. Similarly, the small sample size, coupled with the secular dis-equilibrium of the U and Th daughter decay products, gave rise to poor gamma counting statistics.

6. Conclusion

These were the first exhaustive measurements of possible radioactive reduction attempting to account for mass, neutron and radiation balances. Although 50-90% apparent reductions in U and Th were indicated by a variety of analytic techniques comparing the matrix before and after an experiment, its inhomogeneous nature coupled with possible losses through handling, make statistically significant comparisons impossible. It is likely that fines with a high surface to volume ratio, and consequently increased U and Th uptake during matrix fabrication, were mechanically redistributed through the system, thereby accounting for observed radioactive reductions. Morrison [MORR98] suggested tagging future experiments with strong gamma emitters like ^{137}Cs or ^{131}I to track material transport. However, the tag's chemistry will differ from that of U and Th, or their decay daughters.

There were **no isotope shifts** from natural abundance within experimental error for Mg, Ni, Cu, Zn, Ba, or U. There was **no evidence of >100 KeV** radiation, indicating neither radioactive fission products nor neutrons observed by n-γ reactions. **No anomalous gases or isotopes** were seen during two runs. Both the **neutron surplus** and the **unseen excess binding energy** present major experimental and theoretical difficulties for the proposed system. Similarly, the observed lack of radioactive reduction in a system undergoing real time gamma analysis challenges claims of radioactive reduction.

These experimental protocols, monitoring energy, mass, neutron and radiation balances in a statistically significant way, are required of all systems purporting to reduce radioactivity using hitherto unknown physical processes.

7. References

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