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Preliminary Results with "Cincinnati Group Cell" on Thorium "Transmutation" under 50 Hz AC Excitation

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Abstract

We give the procedure and the results of experiments performed with a standard "Cincinnati Group Cell", aimed to observe possible "transmutation" of Th in other elements via an AC electrolytic process. Three techniques have been used to avoid bias due to spurious effects: α -radiometry, ICP/MS and ICP/optical, looking at difference between initial and final solution and between blank (no Th) and black (with Th) processed solutions. We found deficit of Th after process and new elements produced. The results are still not conclusive on transmutation and we discuss arguments in favour and against the transmutation hypothesis. We clarify the critical points of the measurement techniques, adding some suggestions to improve the reliability of results in future measurements.

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PROCEDURE AND MEASUREMENTS

We performed, at the CISE Nuclear Laboratory, from February 1998, four experiments with the so called "Cincinnati Group Cell" (CG), consisting of Zr–Zr electrodes cell using the 50 Hz AC line found in Italy. The aim was to verify possible "transmutation" phenomena claimed on tests performed elsewhere⁽¹⁾. We followed as far as possible the protocol suggested in *Infinite Energy Vol.3 No.13–14 (1997)*, trying to reproduce the voltage vs time plot, apart from the frequency (50 Hz instead of 60 Hz). We used for the four experiments the same cell "standard LENT–1 type" with the addition of a mechanical line to insert a manometer and a safety valve by a stainless steel tube screwed in the cylindrical Zr vessel and vertically (radially) oriented upward (Fig. 1).

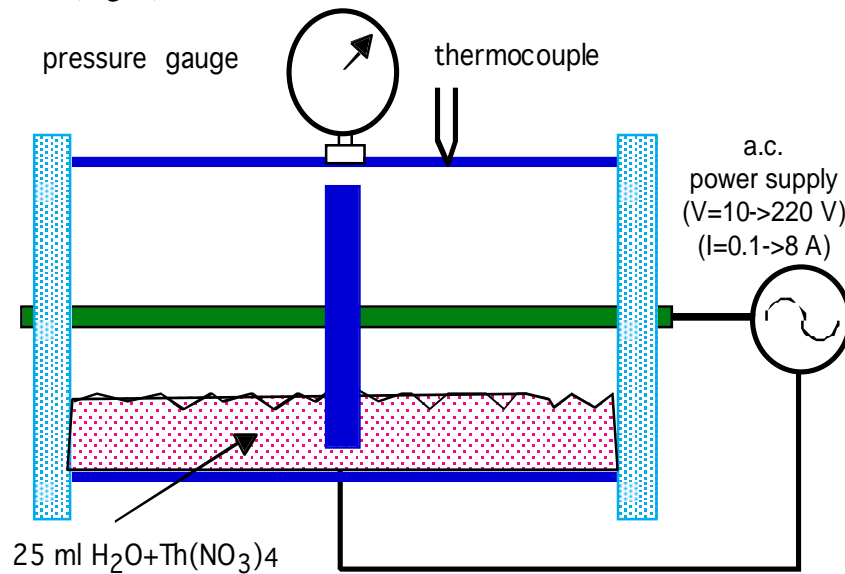


Fig. 1 – The Cincinnati Cell": inner cell and disk are Zr.

The test was performed under aspiration chamber with some mechanical protection in a radiochemical laboratory. The cell was vented with a steady air flux concentrated on the upper part of the cylindrical vessel (kept with axis horizontal). The temperature was monitored by a thermocouple (electrically insulated) in contact with the bottom part and thermally insulated from the ambient.

The first two experiments were "blank" control runs that were mainly aimed to understand the intrinsic peculiarity of this type of AC electrolysis.

In experiment #1, we used a solution 80 mM of NaNO₃ in deionized water (25 ml). We followed as close as possible the I–V–T (current–voltage–temperature) protocol developed by CG. We experienced abrupt temperature and pressure increases which broke the safety valve. Before the experiment, we analysed a Zr disk (inner electrode) at SEM, confirming the purity of Zr. After the experiment we analysed the material inside the cell (ICP/MS); nothing "strange" was observed: only Zr, Hf (a common impurity of Zr) and Na. The cell was then mechanically cleaned by removing ≈0.1 mm of the surface to closely restore the "virgin cell" condition before this experiment.

Experiment #2 was similar to #1 except that the electrolyte was a 20 mM solution of HCl in deionized water and we modified the I–V–T protocol to avoid a large pressure build-up, i.e. starting electrolysis from as low as 10 V (not 50 V minimum according to CG protocol): we waited to increase the voltage further until the current "naturally" decreased. Using this method,

we reached voltage as high as 220 V instead of maximum 177 V specified in the CG procedure. Maximum current was 2.4 A; maximum temperature was $<100\text{ }^{\circ}\text{C}$ and the pressure was ≈ 1 bar. The processing time was ≈ 35 minutes (see Fig. 2). After the final cooling we extracted the suspension using a syringe; we performed washing first with 25 ml, 20 mM HCl and then with 10 ml of deionized water. After dismounting, all the part of the cell have been washed with the solution previously collected, adding to it also the gel of Zr hydroxide adhering to the inner and outer electrode. SEM analysis of a fraction of particulate showed the presence of Zr, O, Cl. ICP/MS analysis showed: Zr, Hf, Cl.

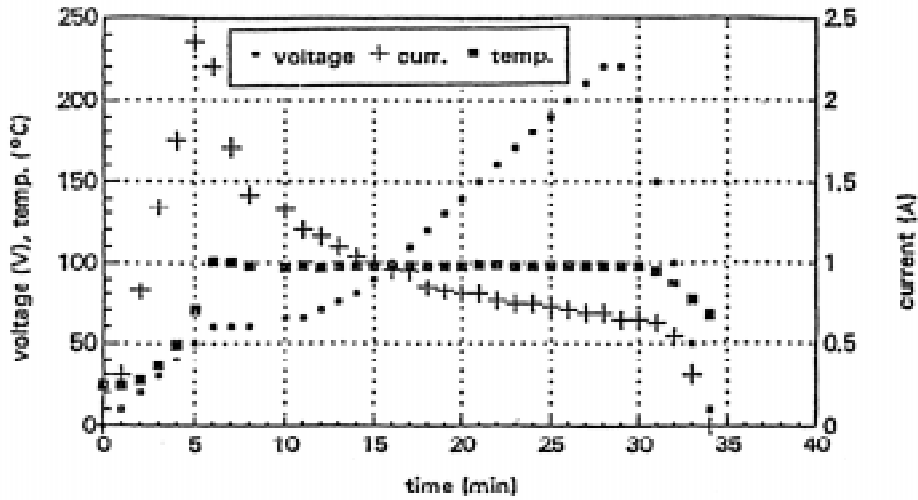


Fig. 2 – Experiment #2: 2nd blank run (following the 1st blank run).

Experiment #3 was made using 25 ml of electrolyte taken from 100 ml of a solution 20 mM HCl in deionized water containing 1 g of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$. This Th salt was taken from a CISE stock with radioactive ^{232}Th chain in equilibrium. Radiometric intensities showed an activity ratio $^{230}\text{Th}/^{232}\text{Th} \approx 12.5$, showing that the starting ore contained a lot of ^{234}U in equilibrium with ^{230}Th . The traces of ^{230}Th was therefore quite large for α -radiometry, although very small in atomic percentage.

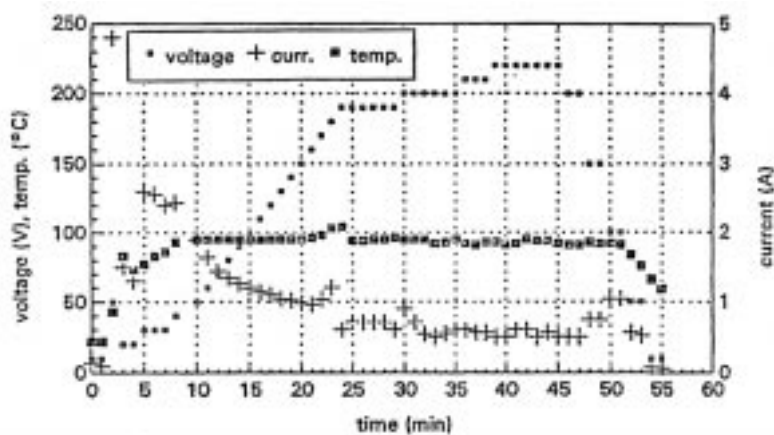


Fig. 3 – Experiment #3: 1st black run: V–I–T vs time.

The experiment was run for 55 minutes with $I_{\text{max}}=2.6\text{ A}$, $V_{\text{max}}=220\text{ V}$, $P_{\text{max}}= 30\text{ psi}$ (Fig. 3). At the end (after cooling and dismounting the cell), washings first with 20 mM HCl and later with mixed $\text{HNO}_3 + \text{HCl}$ were performed, collecting $\approx 48.7\text{ g}$ of gel present on

various part of the cell. From weight loss, it is estimated in ≈ 0.245 g the total quantity of Zr removed by the process and washing corrosion. SEM analysis of a fraction of the particulate showed presence of Zr, Th, O, Cl, probably in form of oxychlorides and oxyhydrates of Zr and Th.

Qualitative analysis ICP/MS revealed B, Cs, Hg, Na, Al, V, Cr, Ni, Zn, Pb and Mn. A chemical balance indicated that $\approx 18\%$ of the original Th was missing and a radiometric balance ($\alpha+\beta$) showed a $\approx 12\%$ Th deficit.

The ($\alpha+\beta$) measurements by scintillation counting were made after two weeks, a time sufficient to recovery the equilibrium in the radioactivity chain of ^{232}Th , so counteracting possible distortions of this equilibrium due to the chemical process. The analysis of α -spectra on samples of the processed and unprocessed solution (good resolution technique: thin deposited samples in front of silicon solid-state detector) did not show any difference in the ratio $^{232}\text{Th}/^{228}\text{Th}$ between two solutions (this is true also for the ratio $^{232}\text{Th}/^{230}\text{Th}$).

The contribution of the particulate phase to the mass balance was particularly high ($>60\%$ both chemically and radiometrically); this contribution may have been underestimated in experiments made elsewhere.

Experiment #4 was made after removing possible residuals of the exp.#3: the cell was exposed for 2 minutes to a solution HNO_3 (6.5 M) + HF (1.25 M), removing 0.55 g of material (mainly Zr ≈ 0.025 mm) including the residual oxides of the previous test. We used 25 ml of the same solution as exp.#3, following the protocol in Fig. 4, with a maximum current of 4.8 A and a maximum pressure of 190 psi. The cooling air flux was kept "low" both in the first 40 minutes period and in the last 10 minutes period, intensified between 40 and 45 minutes. At the end, after cooling, the over-pressure disappeared.

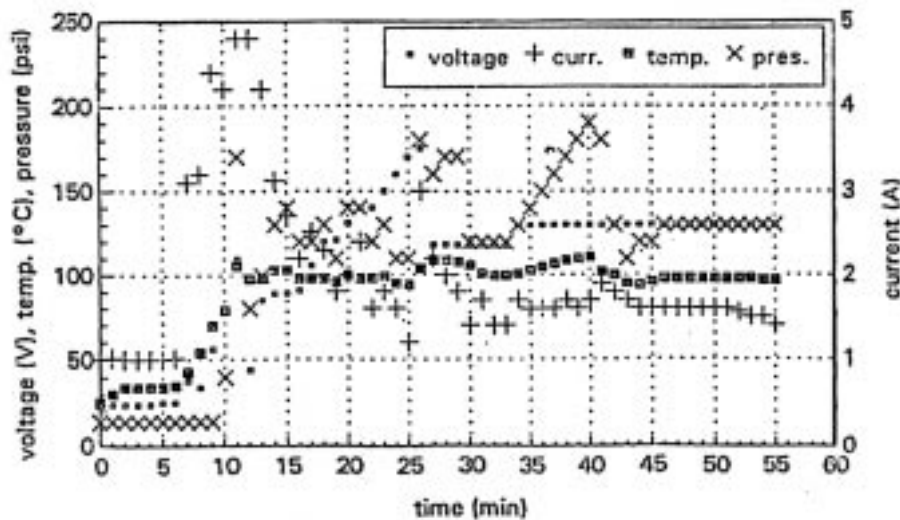


Fig. 4 – Experiment #4: 2nd black run: V-I-T-p vs time.

After extraction of the suspension and washing with H_2O (25 ml), a first chemical treatment was made with 25 ml of nitric-fluoridric solution and repeated water washing. Since other solid phase remained into the cell, a second treatment for 2 minutes with the same acid solution was performed to perfectly polish the cell. From weight loss, the quantity of Zr totally removed by the electrolysis and washing procedure was estimated to be ≈ 1.370 g. The chemical balance of Th and the elements seen in significant quantities after processing are

quoted (in mg) in Table 1.

Table 1 – Quantity of elements present in the final solution, corresponding to the 250 mg of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (or 102 mg of Th) in the initial solution. The figures for each element are indicated as (mg)/(25 ml of original solution)

Th	78 (deficit $\approx 24\%$)
$^{10}\text{B} + ^{11}\text{B}$	3.2
Cu	1.0 \div 1.5
^{133}Cs	0.2
Hg	0.15

The elements in Table 1 were not present in the blank solution and so we can suppose they are formed during the process. The measured Th deficit should not be due to the massive losses during manipulation needed for solubilization. However, these conclusions should be taken with some caution, since internal standards (like ^{229}Th or other chemical elements like potassium) have not been used. Isotopic ratios for B and Hg are the natural ones. *For Cu the isotopic ratio is very significantly different from the natural one.* Cs has only one stable isotope.

All the four elements have been quantified accurately also at the low concentration in Tab. 1: it is difficult to ascribe their presence to cross-contamination. The analysis have been made both with ICP/MS and ICP/optical. As consequence some masses (apparently Sc, Ti, Ag, Sn) have been recognised as instrumental effects or due to the formation of molecular ions ZrO, HfO or simply double charged Zr.

Traces of other elements have been observed: Na, Al, V, Cr, Ni, Zn, Pb, Mn. These elements, although seen by the instrumentation, could be due to contamination by reagents or to the material present in the cell; they have not been analysed quantitatively until now.

The radiometric tests ($\alpha + \beta$ by scintillation) gave a Th deficit of $\approx 14\%$ (recall the presence of ^{230}Th with an activity of ≈ 12.6 times that of ^{232}Th when comparing the radiometric balance with the chemical balance).

The α -spectrometry gave, as in exp.#3, no differences in Th isotopic ratios between unprocessed and processed solutions.

DISCUSSION AND CONCLUSION

From our experimental results we can deduce arguments both in favour and against the reality of transmutation of thorium in other elements in the course of our a.c. electrolytic process.

The argument in favour are essentially:

- The mass balance of Th, both chemical and radiometric, is well below 100% (not however with deficit of $\approx 50\%$ or larger claimed in other experiments).
- Detection of various elements in significant quantities not detected in blank run (B, Cu, Cs, Hg).
- Detection of traces of various elements not seen in blank run.
- Isotopic ratio for Cu different from natural one.

The arguments against are essentially:

- The high contribution to mass balance of the particulate phase, very difficult to be completely collected and solubilized, which can give systematic errors not studied by

repeating the test. Recall that the ratio: [Zr stripped by electrodes in the process]/[total deficit of Th] is ≈ 70 in mass terms and ≈ 150 in atomic term, at least.

- The hard solubility of the particulate phase may imply introduction of impurities by concentrated reagents, so explaining traces of various elements found. Note that the hard chemical process on the particulate phase has not been exactly the same for the blank run and for the black run.
- The relatively abundant elements B, Hg have natural isotopic ratios (but not the Cu; Cs has only one stable isotope).
- In the mass region of Cu many peaks are present in ICP/MS measurements.
- Th isotopic ratios are roughly equal for processed and unprocessed solution. However, due to the not very large Th mass deficit, this is not a very sensitive index.

The global output is in our opinion that these preliminary measurements are not still conclusive for the transmutation issue.

We cannot anyway discard the arguments in favour of transmutations and, in view of the importance of potential applications, we suggest that this type of experiment should be repeated with still better attention to the critical points of the technique involved. In particular:

- We maintain the importance of using α -radiometric technique together with ICP/MS and ICP/optical technique.
- It is important to do the same chemical treatment for blank (no Th) and black runs and, as far as it is possible, the same voltage–time protocol and cooling system.
- To improve discrimination between effects and artefacts, it may be very useful to follow this procedure (we already tested it):
 - i) perform first on a processed blank (without Th) quantitative measurement of the dominant elements (mainly Zr, Cl and those present in reagents) seen with the double technique ICP/MS and ICP/optical;
 - ii) prepare a new blank solution containing in the same quantities the dominant elements;
 - iii) perform on this new (unprocessed) blank a complete elements analysis of the solution with the same techniques. In this way it is possible to correct for "matrix" effects (essentially interference effects due to dominant elements) the lower signals from ICP methods.
- Since it seems that the frequency of current may have some relevance (50 Hz may work worse than 60 Hz) we suggest the use of a frequency doubler (100÷120 Hz) in the hope of reducing the ratio [mass of particulate]/[mass deficit of Th].
- In our opinion, the γ -radiometry may have some usefulness both on–line and after the process but it cannot give clear information since γ -rays are due to the other elements in the radioactivity chain of ^{232}Th which can have a very different electrochemical (and perhaps transmutation) history in the process.
- For the α -radiometry it should be useful to start with a Th salt having lower content of ^{230}Th than our one. It depends essentially on the ratio U/Th in the original ore.

Acknowledgements

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Reference

[1] Letters by R.R.Liversage – Infinite Energy 3, No 13–14 (1997). pag. 20.