ORNL/TM-2014/211

Californium Recovery from Palladium Wire

Jonathan D. Burns

August 2014

**Approved for public release;
distribution is unlimited.**

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

DOCUMENT AVAILABILITY

Reports produced after January 1, 1996, are generally available free via US Department of Energy (DOE) SciTech Connect.

Website http://www.osti.gov/scitech/

Reports produced before January 1, 1996, may be purchased by members of the public from the following source:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone 703-605-6000 (1-800-553-6847)
TDD 703-487-4639
Fax 703-605-6900
E-mail info@ntis.gov
Website http://www.ntis.gov/help/ordermethods.aspx

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange representatives, and International Nuclear Information System representatives from the following source:

Office of Scientific and Technical Information
PO Box 62
Oak Ridge, TN 37831
Telephone 865-576-8401
Fax 865-576-5728
E-mail reports@osti.gov
Website http://www.osti.gov/contact.html

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-2014/211

Nuclear Security and Isotope Technology

CALIFORNIUM RECOVERY FROM PALLADIUM WIRE

Jonathan D. Burns

Date Published: August 2014

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6283
managed by
UT-BATTELLE, LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

Page

LIST OF FIGURES

Figure **Page**

LIST OF TABLES

Table **Page**

ABSTRACT

The recovery of ^{252}Cf from palladium-^{252}Cf cermet wires was investigated to determine the feasibility of implementing it into the cermet wire production operation at Oak Ridge National Laboratory's Radiochemical Engineering Development Center. The dissolution of Pd wire in 8 *M* HNO_3 and trace amounts of HCl was studied at both ambient and elevated temperatures. These studies showed that it took days to dissolve the wire at ambient temperature and only 2 hours at 60°C. Adjusting the ratio of the volume of solvent to the mass of the wire segment showed little change in the kinetics of dissolution, which ranged from 0.176 mL/mg down to 0.019 mL/mg. A successful chromatographic separation of ^{153}Gd, a surrogate for ^{252}Cf, from Pd was demonstrated using AG 50x8 cation exchange resin with a bed volume of 0.5 mL and an internal diameter of 0.8 cm.

1. INTRODUCTION

The production of palladium-^{252}Cf cermet wires was first developed at Savannah River National Laboratory in the 1960s by Mosley et al.[1] One of the reasons Pd was selected is because it is well known to be soluble in oxidizing acids. This characteristic was acknowledged early on to be advantageous if ^{252}Cf recovery was ever warranted. While ^{252}Cf recovery from Pd wire had not been forgotten, its use and the exact practice of the method had been shelved for the last several decades. However, interest in the dissolution of Pd wire recently increased because of several problems encountered during the fabrication of Pd-Cf wires routinely produced at the Radiochemical Engineering Development Center (REDC) located at Oak Ridge National Laboratory. During the processing of the last two ^{252}Cf campaigns, Campaign 74 and Campaign 75, many issues became apparent, several of which manifested themselves in the back end of the process. For instance, at the end of the melting operation, the Pd-Cf cermet was found to have a very rough surface in some cases, with cavities of various sizes that were assumed to come from a volatile species "popping out" of the surface. In addition, splintering or fracturing was observed during the rolling of a melt into a wire (Fig. 1).

Fig. 1. Surface imperfections of Pd-Cf melt (right) and splintering of a rolled wire (left).

These undesirable characteristics can result in the material being unsuitable for shipment, as it does not meet quality standards. However, a usable quantity of ^{252}Cf may be trapped within the Pd-Cf cermet. Currently, there is no process in place to recover ^{252}Cf from the Pd-Cf cermet. Several experiments were designed to identify a method for recovering Cf from Pd wire. It was decided that the best approach to achieve complete recovery of the ^{252}Cf would be to dissolve the Pd wire and perform a separation of the Pd-Cf solution.

2. EXPERIMENTAL

2.1 REAGENTS

Palladium metal wire (99.99%, Pd wire) was purchased from Refining Systems Inc., and was obtained from the same lot used in californium wire fabrication in Building 7930. Nitric acid (69–70% ACS Grade, HNO_3) was purchased from BDH, Inc., and hydrochloric acid (ACS plus, HCl) was purchased from

Fisher Scientific, Inc. The ^{153}Gd was taken from stock on hand at the REDC. The BioRad® AG 50x8 with a particle size of 90–150 µm was purchased from Bio-Rad Laboratories, Inc. Distilled deionized (ddi) H_2O was obtained from a Millipore Milli-Q® Academic Ultrapure Water Purification System with a Quantum® EX Ultrapure Organex Cartridge filter operated at 18.2 MΩ·cm at 25°C.

2.2 PALLADIUM WIRE DISSOLUTION

The generic dissolution was carried out as follows. A small piece of Pd wire was cut, weighed, and placed in a 20 mL glass scintillation vial. A stoichiometric amount of concentrated HCl, assuming the formation of $[PdCl_4]^{2-}$, was added directly to the wire section. Next, a predetermined amount of 8 *M* HNO_3 (10 mL, 5 mL, or 1 mL) was added to the scintillation vial. Dissolution studies were conducted at room temperature and at elevated temperatures. For the samples that were heated, the scintillation vial was placed on a hot plate that was preheated so that the solution would warm to 60°C. In all cases, 100 µL samples were periodically taken to track the progress of the dissolution.

2.3 COLUMN PREPARATION

A column was packed with AG 50x8 cation exchange resin with a bed volume (BV) of 0.5 mL and an internal diameter (ID) of 0.8 cm. The resin was wetted in ddi H_2O and packed in a plastic, disposable column with a polymer frit at the bottom. The column was then conditioned with at least 3 BV of 8 *M* HNO_3 and then relaxed with at least 2 BV of ddi H_2O. Quartz wool was then placed at the top of the resin bed to hold the resin in place and to prevent disruption of the resin when the solution was added.

2.4 SOLUTION ANALYSIS

The Pd concentrations were determined by inductively coupled plasma–mass spectrometry analyses performed by Materials and Chemistry Laboratory, Inc. The ^{153}Gd was determined by gamma spectroscopy using a Genie 2000 gamma spectroscopy system. The gamma-ray detector was a 50 cm^3 intrinsic Ge detector with a resolution of 1.0 keV at 123 keV and 1.8 keV at 1332 keV. Analysis was performed using a PC-based multichannel analyzer windowed on ^{153}Gd (97 keV and 103 keV).

3. RESULTS AND DISCUSSION

3.1 PALLADIUM WIRE DISSOLUTION AT AMBIENT TEMPERATURE

The first step was to determine the rate at which the Pd wire dissolves at room temperature. For this, 53.8 mg of the Pd wire was contacted with 170.8 µL of concentrated HCl and 10 mL of 8 *M* HNO_3, where HNO_3 is the oxidizing agent and the HCl provides Cl^- as a complexing agent. The small amount of Cl^- was used to help push the dissolution to completion by tying up the Pd ion in a chloride complex, most likely as $[PdCl_4]^{2-}$ (see equations below).

(a) $\mathrm{Pd}_S^0 + 2\mathrm{HNO}_3 \rightleftharpoons \mathrm{Pd}_{aq}^{2+} + 2\mathrm{NO}_2 + 2\mathrm{OH}^-$

(b) $\mathrm{Pd}^{2+} + 4\mathrm{Cl}^- \rightleftharpoons [\mathrm{PdCl}_4]^{2-}$

Upon addition of the concentrated HCl directly to the Pd wire, there was no visible reaction; however, upon addition of the 8 *M* HNO_3 the wire began to dissolve. As the wire dissolved, a dark brown-red color appeared in close proximity to the wire, and upon swirling and mixing, the solution turned a yellow tint. This continued, with the solution turning darker as the wire continued to dissolve (Fig. 2). The wire was left to dissolve over a weekend, and by Monday the solution was very dark brown-red color with a slight dark spot where the wire had been. Upon swirling the solution, the spot disappeared. A few minutes after swirling, a fine dust settled in the bottom of the vial. The concentration of Pd in solution was determined after 160 min and after 2.5 days to be 0.630 mg/mL and 4.48 mg/mL, respectively. The final concentration of Pd in solution only represents *ca.* 84.7% of the mass of Pd. This, combined with the visible solids in the vial, indicates that the dissolution was not complete or that some of the Pd precipitated back out after dissolution. In either case, the very fine nature of the solid should still rapidly facilitate the recovery of any Cf imbedded in the wire.

For the purposes of this study, no attempt was made to identify the solid, as it was outside the scope of this project; however, a couple of likely possibilities are offered here. First, the Pd wire could have only partially dissolved, leaving the remainder as undissolved metal. The other possibility is that the Pd wire fully dissolved, with a portion precipitating back out of solution, as the metal or as an oxide or hydroxide. In either case, adding more Cl^- to the solution should help drive and keep the Pd^{2+} as an aqueous complex. To reiterate what was stated previously, regardless of the exact scenario, any Cf present should be recovered quantitatively.

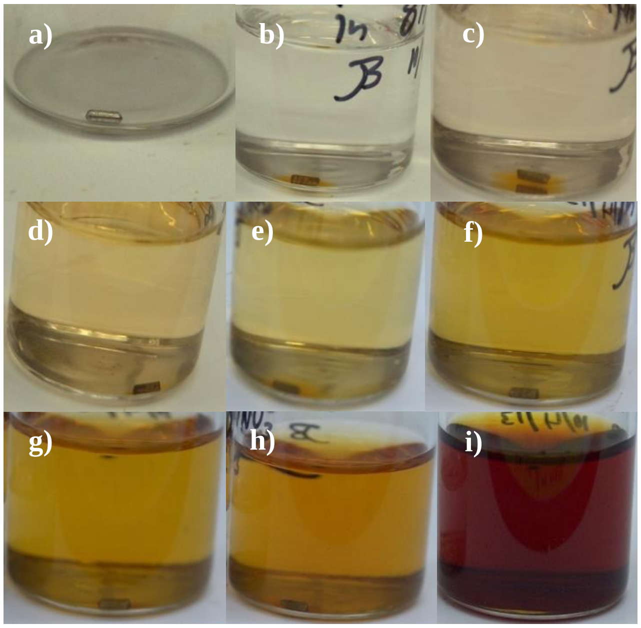

Fig. 2. The Pd wire (a) before addition of any solvent; the dissolution of Pd wire at ambient temperature (b) immediately after, (c) 4 minutes, (d) 15 minutes, (e) 30 minutes, (f) 60 minutes, (g) 100 minutes , (h) 153 minutes, and (i) 2.5 days after addition of 8 *M* HNO_3.

3.2 PALLADIUM WIRE DISSOLUTION AT 60°C

The recovery of ^{252}Cf from the Pd wires will take place in the hot cell in Building 7930, which has restrictions on the types and duration of chemical processing. In order to make this recovery process practical under the current operating restrictions in Building 7930, the Pd wire will need to be completely dissolved within the standard 8 hr work shift and cannot be left unattended overnight, let alone left over the weekend. To improve the kinetics of the dissolution, the temperature was increased from ambient to 60°C. The previously described dissolution method (Section 3.1) was used to contact 56.8 mg of Pd wire with 194.2 μL of concentrated HCl and 10 mL of 8 *M* HNO_3. The solution was then placed on a hot plate, which had been heated to 60°C using a digital thermometer and a beaker of water. Upon placing the vial on the hot plate, the brown color around the wire began to move up in the solution (Fig. 3). The wire dissolved much faster at the elevated temperature, and after 2 hr there was only a slight dust left on the bottom of the vial. The vial was then heated for an additional hour. The concentration of Pd in solution was determined to be 4.61 mg/mL at both the 2 and 3 hr time intervals. This result indicates it will take no more than 2 hr for the wire to dissolve at 60°C; however, much like the ambient tests, the final Pd concentration only represented *ca.* 82.8% of the mass of Pd.

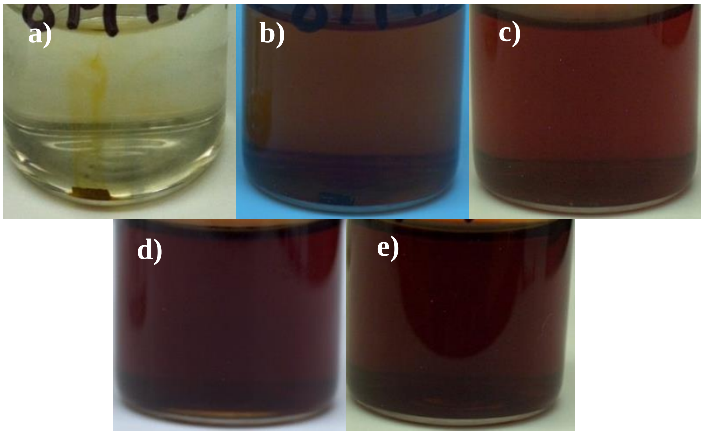

Fig. 3. The dissolution of Pd wire at 60°C (a) immediately, (b) 0.5 hr, (c) 1 hr, (d) 2 hr, and (e) 3 hr after the addition of 8 *M* HNO_3 and placing the vial on the hot plate.

3.3 PALLADIUM WIRE DISSOLUTION IN SMALLER VOLUMES

To increase the practicality of the dissolution, an investigation was carried out to determine if the ratio of the volume of acid to mass of the Pd wire could be reduced while keeping the temperature at 60°C. First, 61.0 mg was contacted with 209.2 µL of concentrated HCl and 5 mL of 8 *M* HNO_3, and second, 51.7 mg was contacted with 177.4 µL of concentrated HCl and 1 mL of 8 *M* HNO_3. The behavior of the dissolution in both was similar to previous results (Fig. 4), and after 3 hr there was only a small amount of dust on the bottom of each vial. The concentration of Pd in solution was determined to be 9.23 mg/mL and 34.7 mg/mL in the 5 mL and 1 mL dissolutions, respectively. Following the previous results, neither showed complete dissolution of the Pd, with only *ca.* 78.8% of the total mass of Pd observed in the 5 mL dissolution and *ca*. 79.0% in the 1 mL dissolution.

The reduction in the ratio of the volume of acid to the mass of wire is more advantageous when observed relative to the full-scale process. The average Pd-Cf wire is about 5 g, so the bench-top process would have to be scaled up by a factor of 100 to match actual hot cell conditions. This means that a 5 g wire could be dissolved in 100 mL of 8 *M* HNO_3, rather than 1 L. As discussed in the next section, the solution will need to be diluted in preparation for the ion exchange process, to keep the volume-to-mass ratio as low as possible to reduce waste, increase ease of handling downstream, and assist in recovery efficiency.

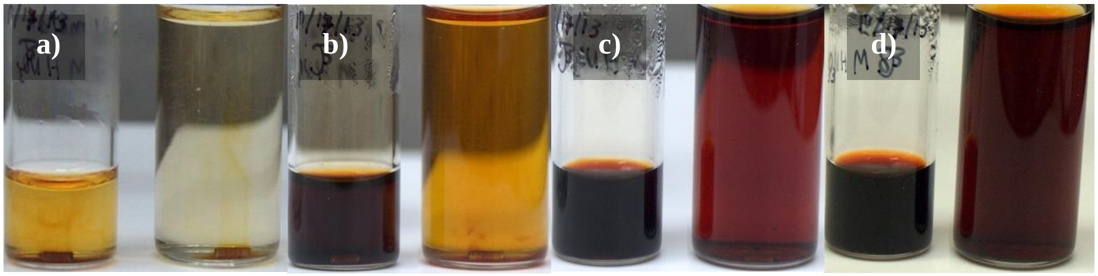

Fig. 4. The dissolution of Pd wire at 60°C in 1 mL (left) and 5 mL (right) of solution (a) immediately, (b) 30 min, (c) 60 min, and (d) 180 min after addition of 8 *M* HNO_3 to the vial on the hot plate.

3.4 DILUTION OF PALLADIUM SOLUTION

To separate the Cf from the Pd the acidity of the solution must be reduced to around 1 *M* total acid in order to load the Cf^{3+} onto a cation exchange resin. An investigation was carried out to determine if the solution could be diluted without Pd precipitation. Samples of 50 µL were taken from the Pd dissolution at room temperature and diluted into 1 mL of ddi H_2O, 0.1 *M* HCl, and 0.1 *M* HNO_3, and the results are shown in Fig. 5. No precipitation was observed in any of the dilutions, but in all three cases, the solution turned a light yellow color. This yellow color is indicative of the tetrachloropalladium(II) specie $[PdCl_4]^{2-}$ (Fig. 6). It should be mentioned that there is also a potential for a Pd nitrate anionic complex to form as well; however, it is believed that the major species is $[PdCl_4]^{2-}$ due to the yellow color of the solution. The formation of this anionic species is desirable, as it increases the driving force for the separation.

Fig. 5. The dilution of 50 µL of 4.48 mg/mL Pd 8 M HNO_3 into 1 mL of (left) ddi H_2O, (middle) 0.1 *M* HCl, and (right) 0.1 *M* HNO_3.

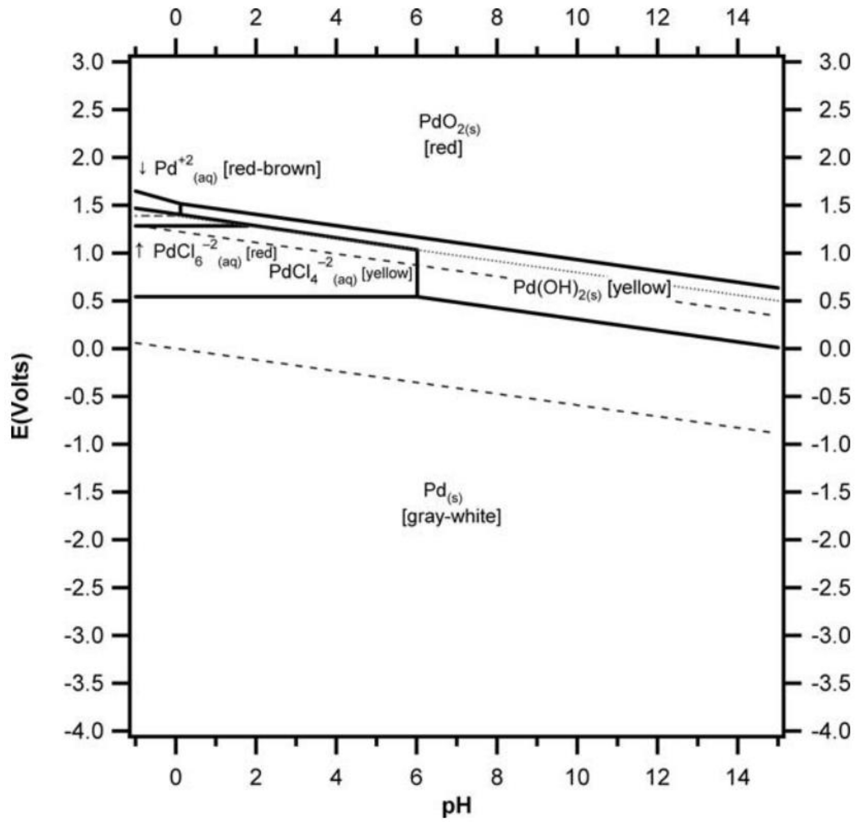

Fig. 6. Pourbaix diagram for Pd/Cl species. Adapted from Schweitzer and Pesterield[2]

3.5 SEPARATION OF PALLADIUM AND GADOLINIUM

A separation method was devised to separate Pd from Cf using the cation exchange resin AG 50x8. In low acidity, the Cf^{3+} will be retained by the resin, while the $[PdCl_4]^{2-}$ will pass through the column. To test this approach, ^{153}Gd was used as a surrogate for Cf because of their similar ion size and effective nuclear charge.[3] The Pd dilution in ddi H_2O was used for the feed solution, and it was spiked with 1.4 µCi of ^{153}Gd. The final acidity of this feed solution was *ca.* 1.22 *M*. The feed solution was passed through the column (Fig. 7), and a large amount of the Pd, along with the yellow color, was retained by the quartz wool used to keep the column bed packed. The column was then washed with 0.1 *M* HNO_3, and the rest of the Pd and color came off in the first column volume of the wash (Fig. 8). The column was then stripped with 8 *M* HNO_3, and the ^{153}Gd was removed from the column. A final water wash of the column was performed to relax the resin back to its initial state (Fig. 8).

Fig. 7. Separation of Pd and Gd using an AG 50x8 cation exchange column, with a BV = 0.5 and ID = 0.8 cm.

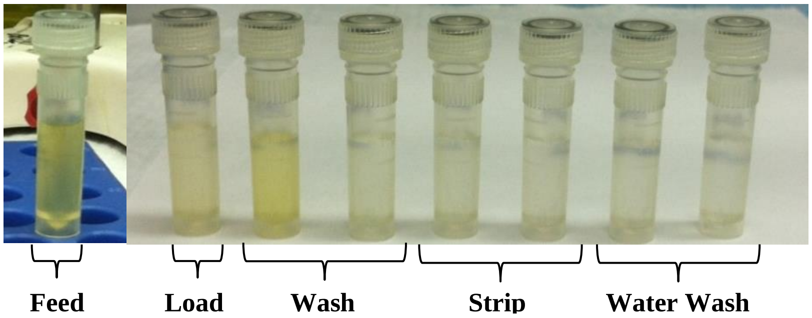

Fig. 8. The feed (left) and fractions collected (right) from the Pd/Gd separation.

The results of the column separation are presented in Table 1. This system shows great potential for separating Pd from Gd. It must be noted that this was just a first attempt and that the separation has not been optimized. Better separation might be accomplished by increasing the amount of wash solution or increasing the acidity of the wash from 0.1 *M* up to 0.5 *M* HNO_3.

Table 1. Results of the separation of palladium from gadolinium

ID	Eluent (HNO_3)	Volume (mL)	Column volume	^{153}Gd (%)	Pd (%)
Load	1.22 M	1.15	2.3	0	31.2
Wash 1	0.1 M	1	4.3	0	63.2
Wash2	0.1 M	1	6.3	0	0.9
Strip 1	8 M	1	8.3	14	4.4
Strip 2	8 M	1	10.3	72.9	0.2
WW1	H_2O	1	12.3	13.1	0
WW2	H_2O	1	14.3	0	0

4. CONCLUSION

The recovery of ^{252}Cf from Pd-^{252}Cf cermet wires by dissolution and ion exchange has been investigated and found to be a relatively simple process. The Pd wire segments can be dissolved in 8 *M* HNO_3 with trace amounts of HCl in less than 2 hr at 60°C. The ratio of the volume of solvent to the mass of the wire was in a range in which the average 5 g cermet wire can be dissolved in 100 mL of mixed acid. During the separation process that follows, this dilution results in a manageable volume of 800 mL. The separation of ^{153}Gd, a surrogate for ^{252}Cf, and Pd was performed using AG 50x8 cation exchange column, where the Gd was retained by the column and the Pd passed through as $[PdCl_4]^{2-}$. At the end of this separation, the Gd and, by extrapolation, Cf will be in the same environment as at the beginning of the cermet wire production, making this a very useful recycle process to incorporate into the current production process.

5. ACKNOWLEDGMENTS

This research is supported by the Isotope Program, Office of Nuclear Physics of the US Department of Energy.

6. REFERENCES

1. W. C. Mosley, P. K. Smith, and P. E. McBeath, “Neutron Sources of Palladium ^{252}Cf Oxide Cermet Wire. Applications of Californium-252,” *Proceedings of the American Nuclear Society National Topical Meeting*, Austin, Texas, September 11–13, 1972, 1975.

2. G. K. Schweitzer and L. L. Pesterfield, pp. 327–329 in The Aqueous Chemistry of the Elements Oxford University Press, New York, 2010.

3. E. Mauerhofer, K. Zhernosekoc, and F. Rosch, *Radiochim. Acta* **91**, 473–477 (2003).