CONF-

LA-UR--90-2566

DE90 015059

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

Received by OSTI

AUG 0 6 1990

TITLE Automated Homogeneous Oxalate Precipitation of Pu(III)

AUTHOR(S) S.L. Yarbro, S.B. Schreiber, S.L. Dunn, C.W. Mills

SUBMITTED TO 50th Anniversary of the Discovery of the Transuranium Elements
200th ACS Meeting, Washington D.C., 1990

DISCLAIMER

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.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

MASTER

[illegible]

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITE

Automated Homogeneous Oxalate Precipitation of Pu(III)

Stephen L. Yarbro*, Stephen B. Schreiber, Sharon L. Dunn and
Clifford W. Mills

Los Alamos National Laboratory, P.O. Box 1663 MS E501, Los Alamos, NM 87545
Phone no. (505) 667-2333, FAX (505) 665-1780

ABSTRACT

Homogeneous oxalate precipitation using diethyl oxalate was compared to precipitating Pu(III) oxalate with solid oxalic acid. The diethyl oxalate technique at 75° C is better because it gives 50% less plutonium in the filtrate with a reasonable filtering time. Also, the procedure for the homogeneous precipitation is easier to automate because the liquid diethyl oxalate is simpler to introduce into the precipitator than solid oxalic acid. It also provides flexibility because the hydrolysis rate and therefore the precipitation rate can be controlled by varying the temperature.

Introduction

At the Los Alamos National Laboratory Plutonium Facility, ion exchange is used to recover plutonium from a variety of scrap materials. During this procedure, the impure plutonium solution is passed through a bed of ion exchange resin and the plutonium is preferentially absorbed. After the resin bed is washed to remove residual impurities, the plutonium is eluted with dilute acid and a reductant. Since the sorbed Pu(IV) is reduced to weakly held Pu(III), the plutonium can be recovered from the eluate by precipitation with solid oxalic acid. Solid oxalic acid is used instead of liquid oxalic acid because it produces less filtrate volume for recovery. However, the solid oxalic powder is difficult to introduce into the precipitator especially in the glovebox. Also, it is difficult to measure the large amounts necessary to remove the plutonium from large volumes of eluate. Often, there is excess oxalate ion present, causing high plutonium losses to the filtrate and foaming in the following evaporation step. The current precipitation procedure is also labor intensive and results in higher than necessary operator radiation exposures. At Los Alamos, the Advanced Testing Line for Actinide Separations (ATLAS) is being installed to conduct engineering and chemistry research on all phases of plutonium processing. Consequently, an engineering evaluation was begun to streamline this unit operation for eventual operation in the ATLAS facility.

Process Chemistry

Diethyl oxalate will hydrolyze to form oxalate ion according to the following reaction:

$$C_2O_4(C_2H_5)_2 + 2H_2O \longrightarrow H_2C_2O_4 + 2C_2H_5OH \qquad (1)$$

The hydrolysis rate is accelerated by heat and therefore easily controlled. Also, the rate is catalyzed by acid and can be represented by the following first-order equation [1]:

$$dC/dt = k[C_2O_4(C_2H_5)_2] \qquad (2)$$

$$k = Ae^{-E/RT} \quad A = f([H^+]) \qquad (3)$$

Because of the chemistry involved, we suspected that the homogeneous precipitation using diethyl oxalate would have several advantages over the conventional method. First, commercially available diethyl oxalate is reasonably concentrated (~7.3 M) and would not produce much more filtrate than solid oxalic acid. Second, being a liquid it would be easier to introduce into the precipitator than a powder. Third, the reaction rate can be controlled by altering the temperature. Therefore, the precipitation can be performed automatically with a simple temperature control system reducing operator effort. Finally, based on past experience, the oxalate cake produced with the homogeneous precipitation technique should be easier to filter with less Pu in the filtrate than achieveable with solid oxalic acid.

Therefore, a study was begun to examine two aspects of the diethyl oxalate procedure. First, the effect of acid concentration and temperature on the hydrolysis rate were studied. Then, the actual performance on plutonium solutions was measured.

Experimental Details

To measure the effect of temperature and acid concentration on the hydrolysis rate, a stoppered 250 ml erlenmeyer flask was used. The solution was stirred with a magnetic stirrer to ensure that it was well mixed. A constant temperature water bath was used to control the solution temperature. The flask was closed to prevent evaporation and possible concentration of the solution. Samples were removed periodically and titrated with a standardized 0.1 N $KMnO_4$ solution for oxalate concentration according to the procedure outlined in [2]. All reagents used were reagent grade "Baker Analyzed" from J.T. Baker. Table 1 shows the different combinations of acid and temperature used in first portion of this study.

Table 1

Parameters for Determining the Hydroysis Rate of Diethyl Oxalate

RUN	[HNO_3 M]	Temperature °C
1	0.5	50
2	0.5	70
3	1.0	50
4	1.0	70

Each run had 5 mls of 7.3 M diethyl oxalate combined with 95 mls of acid at the selected concentration. The flask was placed in the water bath after it had reached the appropriate temperature and the first sample was taken five minutes later.

For the second portion of the study, a stock solution of 21.4 gPu/L, 0.6 M HNO_3 was prepared. The solution was obtained by dissolving plutonium oxide that was purified by ion exchange to less than 100 ppm of each individual impurity. The concentrated solution was then diluted to the desired plutonium and acid concentrations. Tared thirty milliliter medium frit Gooch crucibles were used to filter the plutonium oxalate slurries. Filteration factors were calculated by first measuring the filtration time for 100 ml of distilled water through the frit and then measuring the filtration time for the plutonium oxalate slurry. The slurry filtration time was divided by the water filtration time to provide a filtration factor for comparison [3]. Each Pu(III) precipitation was done with five grams of Pu in 250 ml of solution. The precipitation equipment was simple and consisted of a beaker placed on a stirrer/hot plate. The temperature was monitored with a thermometer. The plutonium valence was adjusted by digesting the solution for 30 mins. at 50°C or higher with a 1:1 mole ratio of ascorbic acid to plutonium. After the solution had reached the appropriate temperature, the diethyl oxalate was added and digested for 90 mins. Enough diethyl oxalate was added to provide a 0.1 M excess of oxalate after the precipitation was complete. After filtration, a sample was removed for plutonium analysis by radiochemistry. The experimental conditions used in the plutonium portion of the study are shown in Table 2.

Table 2

Parameters for the Homogeneous Pu(III) Precipitation

RUN	Precipitant	Temperature°C
5	solid oxalic	25
6	liquid	58
7	liquid	73

Results

The raw data from Runs 1-4 is plotted in Figure 1.

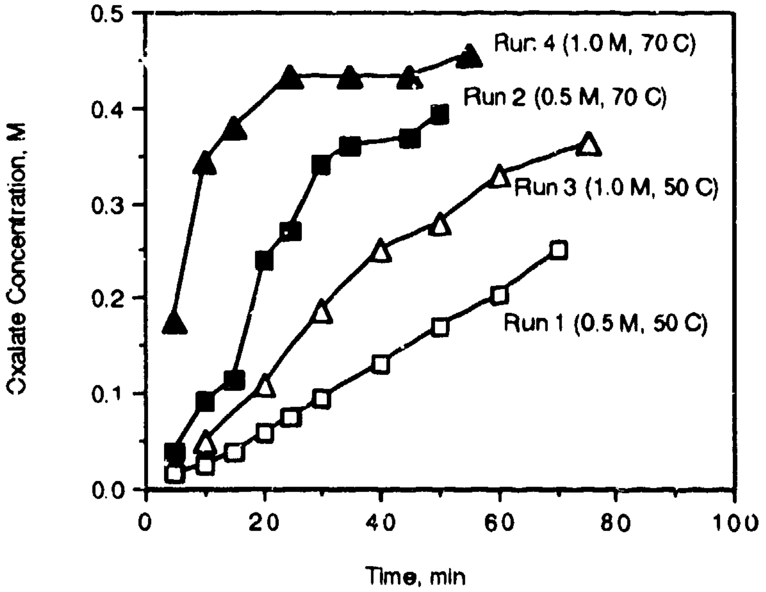

Figure 1. Effect of [HNO_3] and Temperature on the Hydrolysis Rate of Diethyl Oxalate

It is apparent from the plots that both temperature and acid concentration have a significant effect on the hydrolysis. From [1] and [4], the data was plotted as $\ln(C/C_o)$ vs.time assuming a first order reaction. The data was used to derive an equation for the reaction rate constant corrected as a function of acid and temperature for use in later design work. The plot for all four runs is shown in Figure 2.

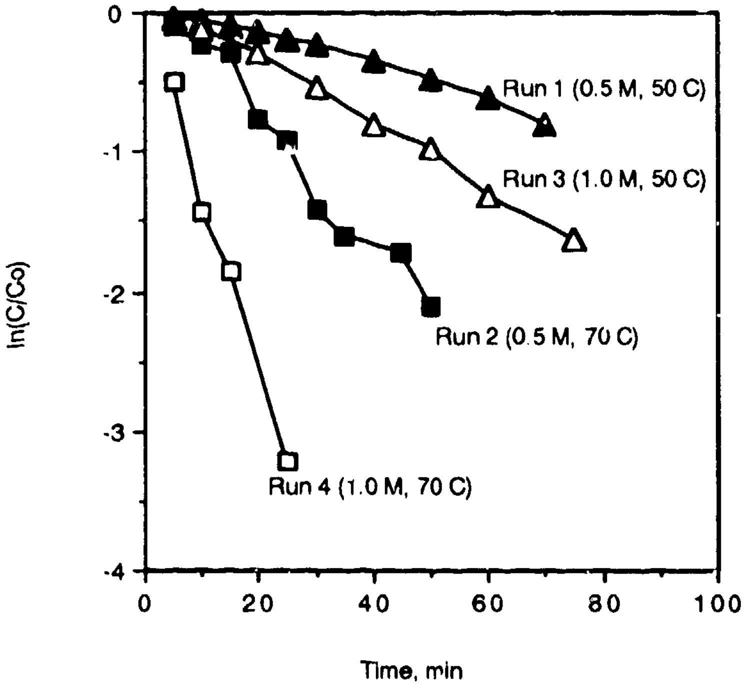

Figure 2. Reaction Rate Data for Diethyl Oxalate Hydrolysis

The slight curvature of the lines is thought to be due to the partial titration of the alcohol generated from the hydrolysis reaction. From the data, the derived equation for the reaction rate constant is

$$k([H^+],T) = \{11.6[H^+] + 11.9\}e^{-15,451/RT} \qquad (3)$$

with R = 1.987 cal/g-mole and T in degrees Kelvin.

The experimental results from the Pu(III) oxalate precipitations are summarized in Table 3.

Table 3

Results of Pu(III) Oxalate Precipitation Runs

RUN	Precipitant	Temp°C	Filtrate [Pu]	Filtration Factor
5	solid oxalic	25	25.8 mg/L	1.010
6	liquid	58	288.0 mg/L	1.158
7	liquid	73	13.3 mg/L	0.937

From the results, it appears that there is an optimum hydrolysis rate for precipitation. Since a slurry should not filter faster than water, filtration factors cannot be less than one as indicated in Table 3. Unfortunately, there were slight perturbations in the available plant vacuum that could not be controlled. Therefore, the data really show that the oxalate slurry formed in Run 7 was coarse, large particles and filtered as well as water. The oxalate slurry formed using solid oxalic acid was a decent coarse precipitate and filtered well with filtrate losses somewhat higher than the minimum solubility reported in [5]. The solubility data for the region of interest has been replotted in Figure 3 from [5] with the plutonium filtrate concentrations added for clarity.

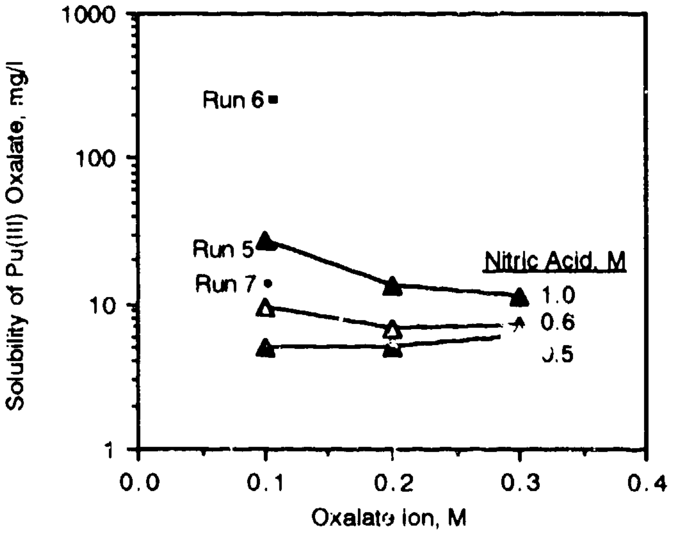

Figure 3. Plutonium Concentrations in Oxalate Solutions (Reproduced with permission from [5])

The slurry produced in Run 7 filtered well with the plutonium losses in the filtrate close to the minimum obtainable. They were also only half of the plutonium concentrations achieved with a carefully controlled precipitation with solid oxalic acid. Therefore, it appears that the homogeneous precipitation offers some advantages for plant operation and would reduce the plutonium going to waste treatment operations by 50%.

Conclusions

It appears that a homogeneous oxalate precipitation of Pu(III) from ion exchange eluates using diethyl oxalate is feasible and offers advantages over the current method. For example, the current solid oxalic acid method is difficult to operate remotely because of the difficulty involved with introducing the powder into the precipitator. With diethyl oxalate, the liquid can be easily vacuumed transferred into the vessel and a simple heating system can be used to perform the precipitation. Then, the actual labor required is reduced to filtering and handling the oxalate cake. However, one area remains to be examined before the process can be introduced into the plant. The behavior of the ethyl alcohol produced and its potential fire hazard will have to be thouroughly examined. Also, the behavior of the alcohol in boiling nitric acid solutions encountered in the evaporator will be studied. If these questions can be addressed, then the process will potentially reduce the plutonium going to waste treatment by 50% and reduce operator time and exposures.

References

1. Ritchie, M. *Chemical Kinetics in Homogeneous Systems*, New York, NY, John Wiley & Sons, Inc., 1966
2. Vogel, A.I., *A Text-book of Quanitative Analysis Including Elementary Instrumental Analysis*, New York, NY, John Wiley & Sons, Inc., 1951
3. Burney, G.A., Dukes, E.K., *Precipitation of Neptunium Oxalate*, DP-594, E.I. Du Pont de Nemours & Co., Savannah River Laboratory, July 1961
4. Hill, C.G., *An Introduction to Chemical Engineering Kinetics and Reactor Design*, New York, NY, John Wiley & Sons, Inc., 1977
5. Burney, G.A., Porter, J.A., *Solubilities of Pu(III), Am(III) and Cm(III) Oxalates*, Inorg. Nucl. Chem. Letters, Vol.3, pp.79-85, 1967