CENTRAL RESEARCH
DOCUMENT COLLECTION

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

OAK RIDGE NATIONAL LABORATORY LIBRARIES

3 4456 0549929 8

ORNL - TM - 1558

COPY NO. -

DATE - June 22, 1966

INVESTIGATION OF DENITRATION OF HIGH-NITRATE PLUTONIA SOLS BY BAKING

M. H. Lloyd and Eugene J. Kosiancic*

ABSTRACT

The denitration of high-nitrate plutonium (IV) polymer sols by baking to produce low nitrate plutonia sols was investigated. A plutonia sol with a nitrate to plutonium ratio as low as 0.4 was obtained, and extrapolation of the data indicate that lower ratios should be obtained by further baking. Two temperatures were investigated and in both cases a linear plot of the data was obtained by assuming the reaction was second order with respect to residual nitrate concentration. Experimental rate constants were determined from the plots. Additional data are required to determine if the rate remains constant when baking to lower nitrate values.

*On assignment with the Chemical Technology Division, Oak Ridge National Laboratory from Babcock and Wilcox, Chemistry Division, Nuclear Development Center, Lynchburg, Virginia.

NOTICE This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

CONTENTS

Page

Abstract 1

Introduction 4

Denitration of High-Nitrate Plutonium (IV) Polymer Sols by Baking 4

Experimental. 4

Discussion of Results 7

Conclusion. 8

References 18

OAK RIDGE NATIONAL LABORATORY LIBRARIES

3 4456 0549929 8

INTRODUCTION

The interest in plutonium as a nuclear fuel material led to the development of a plutonia sol gel process at Oak Ridge National Laboratory.[1,2] Plutonia sols are useful for making either dense plutonia or for mixing with thoria or urania sols to produce dense homogeneous oxide mixtures. For either application, a plutonia sol with a low nitrate content is required for optimum results. The present ORNL process for making plutonia sols involves formation of a high-nitrate sol (NO_3^- to Pu mole ratio from 1 to 2.5) from a plutonium (IV) precipitate, which is then denitrated by baking the sol (Fig. 1).

The purpose of this work was to better define the variables in the baking procedure and to establish nitrate removal rates as a function of temperature.

DENITRATION OF HIGH-NITRATE PLUTONIUM (IV) POLYMER SOLS BY BAKING

Experimental

The general ORNL procedure (Fig. 1) was employed in preparing the high-nitrate sols. The plutonium (IV) nitrate stock solution was titrated with a standard 0.1 M sodium hydroxide solution to determine the number of equivalents of hydroxide required to precipitate the plutonium. The ammonium hydroxide strike solution was then prepared, based upon the determined equivalence and an arbitrarily set excess of 100%. A reverse-strike procedure was used, in which the stock plutonium nitrate solution was added, with vigorous stirring, to one

ORNL DWG. 66-3861

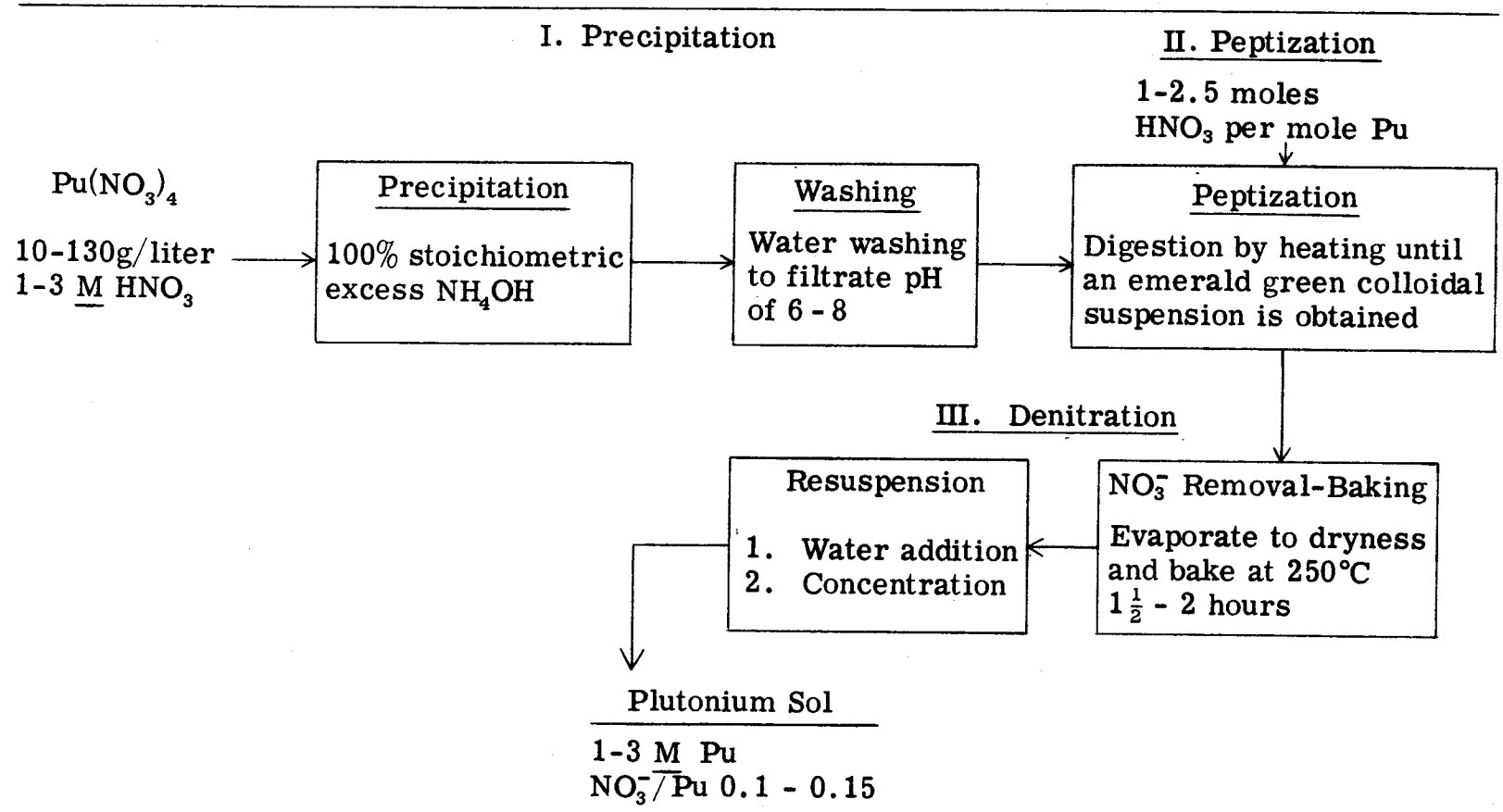

Fig. 1. Plutonia Sol-Gel Process

liter of an ammonium hydroxide solution at room temperature. The rate of addition was 6 ml/min. After the precipitate was filtered, five washings with 500 ml of distilled water for each washing were required to reduce the filtrate pH below 7. The washed precipitate was peptized in one liter of water by heating to 50°C and adding enough nitric acid to give an NO_3:Pu mole ratio of 2.5. The high-nitrate sol was then evaporated to dryness and the resulting solids were used as a starting material for the baking procedure. After the solids were baked for a period of time, 25 to 50 ml of distilled water were added to reform the sol, and a small sample of the resulting colloidal solution was removed for analysis. The procedure of baking, resolling, and sampling was repeated until a low nitrate to plutonium mole ratio was obtained.

It was assumed that the milliequivalents of nitrate present in each sol sample was equal to the milliequivalents of base required to titrate the sample to pH 9. This gave an approximate nitrate concentration. Selected samples were also submitted for a Kjeldahl nitrate analysis. An experimentally determined specific activity for the plutonium being used in the experiments was used to calculate plutonium content from gross alpha counts.

An estimate of particle size in the plutonium sols was determined by a millipore filter analysis. Four samples of each sol were prepared in a uniform manner. Three of the samples were passed through filters with pore sizes of 100, 500, and 1000 A respectively. The fourth sample was used as a reference. The procedure is given below:

(a) Twenty-five lambda of a sol (50 lambda for sample EK-S-12) was mixed with 2 ml water in a 25-ml beaker.

(b) The diluted sol was filtered through a millipore filter in a pressure apparatus with 40 psi on the system. The filter was subsequently washed three times with 2-ml portions of distilled water. The filtrate and washings were collected in a 10 ml volumetric flask and diluted to 10-ml.

(c) Aliquots of the sol were filtered through the remaining filter sizes and a reference solution was made by diluting an aliquot to 10 ml. The gross alpha counts of each solution were then compared to the reference.

Results

Since analytical samples were removed throughout the baking period, plots of nitrate concentration versus time would require correction for nitrate removal, especially since the loss of nitrate from sampling was in some instances greater than that from baking. A more convenient approach was to use the NO_3^-:Pu mole ratio, since this value is independent of sampling losses. This required an assumption that the denitration was not dependent on the amount of plutonium present. Since a linear relationship was obtained with this assumption, it appears to be valid. Data for denitration at 120°C and 205°C are given in Tables 1 through 4. The information in Tables 1 and 3 was obtained from Kjeldahl nitrate analysis and gross alpha counting. The data in Tables 2 and 4 are based upon sodium hydroxide titration for nitrate analysis and material balance calculations for plutonium content. Similar curves were obtained from both sets of data at the same temperature when the NO_3^- to Pu mole ratio was plotted as a function of time. The curves for 120°C and 205°C are shown in Figs. 2 and 3, respectively. A linear relationship between nitrate content and time was found when the Pu to NO_3^- mole ratio was plotted against the time of baking. This relationship suggests a second-order dependence on nitrate content. Figures 4 and 5 show the linear relationship obtained when the data are plotted in this fashion. The slope of these straight lines should be the experimental rate constants for the reaction. The slope obtained at 120°C was 3.12×10^{-4} mole Pu per mole $NO_3^- \cdot$ min by titration data. At 205°C, the slope was 1.22×10^{-2} mole Pu per mole $NO_3^- \cdot$ min, for the data obtained by Kjeldahl analysis and gross alpha counting. From the two values, an estimate of the activation energy for the reaction can be calculated as shown below:

$$\log \frac{k_1}{k_2} = \frac{E\,(\text{activation})}{2.303\ R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where k_1 = rate constant at $T_1 = 3.12 \times 10^{-4} \dfrac{\text{mole Pu}}{\text{mole } NO_3^- \times \text{min}}$

k_2 = rate constant at $T_2 = 1.22 \times 10^{-2} \dfrac{\text{mole Pu}}{\text{mole } NO_3^- \times \text{min}}$

$T_1 = 393°K$

$T_2 = 478°K$

$R = 1.987 \dfrac{\text{cal}}{\text{mole} \times °K}$

The calculated value for E, the activation energy for the denitration reaction, is 24.4 kcal per mole.

In Table 5, the results of filtration experiments are given. The results indicate that very little, if any, growth in particle size occurred during the 16-hour baking-repeptizing process at 120°C. It appears that little growth occurs when the nitrate content remains approximately constant.

Conclusion

The rate of denitration at 120°C is too slow to be practical for a routine process, while denitration at 205°C is more realistic, but still is time consuming. More data are required to better establish the temperature relationship, to determine if the rate remains constant when baking to lower nitrate values, and to determine if the decomposition rate changes for different NO_3^- to Pu mole ratios at the same denitration temperature. Further work is also needed to determine if the baking time or decomposition rate is reproducible for a specific NO_3^- to Pu mole ratio at a specific temperature. If not, other process parameters need to be established and controlled before this approach can be used for routine denitration of plutonia sols.

Table 1. Denitration of Plutonium (IV) Sol at 120° ±5°C

Baking Time (Min.)	Sample[a]	Gross Alpha counts $min^{-1} ml^{-1}$	NO_3^- mg/ml	Pu[b] mg/ml	Pu g	Pu Moles	NO_3^- g	NO_3^- Moles	NO_3^-/Pu (Mole ratio)
0	EK-S-3	22.22×10^{10}	c	268	6.70	0.0280	---	---	---
600	EK-S-12	1.71×10^{10}	68.8	206	5.16	0.0216	1.72	0.0277	1.28
960	EK-S-18	1.07×10^{10}	38.4	129	3.23	0.0135	0.96	0.0155	1.15

[a]Same sample used for data in Tables 1 and 2.

[b]The specific activity used for calculation was experimentally determined to be 8.28×10^7 counts min^{-1} mg^{-1}.

[c]Sample lost in analysis, no value available.

Table 2. Denitration of Plutonia (IV) Sol at 120° ±5°C

Baking Time (min)	Sample[a]	NO_3^- Moles[b]	Pu Moles[c]	Mole Ratio $\frac{NO_3^-}{Pu}$	Mole Ratio $\frac{Pu}{NO_3^-}$
0	Starting sol	0.108	0.045	2.40	0.417
60	EK-S-3	0.0735	0.0280	2.62	0.382
120	EK-S-4	0.067	0.0258	2.60	0.385
380	EK-S-5	0.0593	0.0237	2.50	0.4
240	EK-S-6	0.0505	0.0218	2.32	0.431
300	EK-S-7	0.0465	0.0201	2.31	0.433
360	EK-S-8	0.0416	0.0185	2.25	0.444
420	EK-S-9	0.0357	0.0170	2.10	0.476
480	EK-S-10	0.0313	0.0156	2.01	0.498
540	EK-S-11	0.0269	0.0143	1.88	0.532
600	EK-S-12	0.025	0.0132	1.89	0.529
660	EK-S-13	0.0225	0.0121	1.86	0.538
720	EK-S-14	0.022	0.0111	1.98	0.505
780	EK-S-15	0.0164	0.0102	1.61	0.621
840	EK-S-16	0.0162	0.0094	1.72	0.581
900	EK-S-17	0.0162	0.0086	1.88	0.532
960	EK-S-18	0.0124	0.0079	1.57	0.637

[a]Twenty-five ml of water was used to dissolve the baked solids, and 2-ml samples were taken for analysis except for EK-S-3 in which a 1.5-ml sample was taken.

[b]Determined by sodium hydroxide titration.

[c]Calculated on basis of amount of plutonium at the start of the experiment and corrected for the amount removed in analytical samples.

Table 3. Denitration of Plutonium (IV) Sol at 205° ±5°C

Baking Time (Min)	Sample	Gross Alpha Counts $min^{-1} ml^{-1}$	NO_3^- mg/ml	Total[a] Vol. ml	Pu[b] conc. mg/ml	Pu g	Pu Moles	NO_3^- g	NO_3^- Moles	Mole Ratio NO_3^-/Pu	Mole Ratio Pu/NO_3^-
0	EK-2-S-1	1.09×10^9	9.54	--	13.2	--	--	--	--	2.80	.35
15	EK-2-S-2	3.27×10^{10}	1.14	25	395	9.87	0.0413	2.85	0.0460	(1.11)	.898
30	EK-2-S-3	1.57×10^{10}	97.4	50	190	9.48	0.0397	4.87	0.0785	1.98	.505
45	EK-2-S-4	1.55×10^{10}	60.9	50	187	9.36	0.0392	3.04	0.0491	1.25	.797
60	EK-2-S-5	1.38×10^{10}	35.8	50	167	8.33	0.0349	1.79	0.0289	0.82	1.21
90	EK-2-S-6	1.37×10^{10}	28.9	50	165	8.27	0.0346	1.44	0.0233	0.673	1.48
120	EK-2-S-7	1.28×10^{10}	22.3	50	155	7.73	0.0323	1.11	0.0180	0.556	1.80
150	EK-2-S-8	1.15×10^{10}	20.4	50	139	6.94	0.0290	1.02	0.0164	0.566	1.77

[a]Volume of water used to disperse the baked solids. Four-(4) ml samples were taken for analysis except for EK-2-S-2 in which a 2-ml sample was taken. Analysis of EK-2-S-1 was performed on the original sol solution.

[b]The specific activity used for calculations was determined experimentally to be 8.28×10^7 counts $min^{-1} mg^{-1}$.

Table 4. Denitration of Plutonium (IV) Sol at 205° ±5°C

Baking Time (Min)	Sample[a]	Pu / Moles[b]	NO_3^- / Moles[c]	Mole Ratio NO_3^- / Pu	Mole Ratio Pu / NO_3^-
0	EK-2-S-1	0.0480	0.1080	2.25	0.444
15	EK-2-S-2	0.0480	0.0645	1.34	0.746
30	EK-2-S-3	0.0440	0.0530	1.20	0.833
45	EK-2-S-4	0.0405	0.0415	1.02	0.930
60	EK-2-S-5	0.0370	0.0320	0.865	1.156
90	EK-2-S-6	0.0342	0.0225	0.658	1.520
120	EK-2-S-7	0.0315	0.0165	0.524	1.908
150	EK-2-S-8	0.0290	0.0115	0.397	2.519

[a]Same sample used for data in Table 1 and 2.

[b]Calculated on basis of the amount of plutonium at the start of the experiment, corrected for the amount removed in sampling.

[c]Determined by a sodium hydroxide titration.

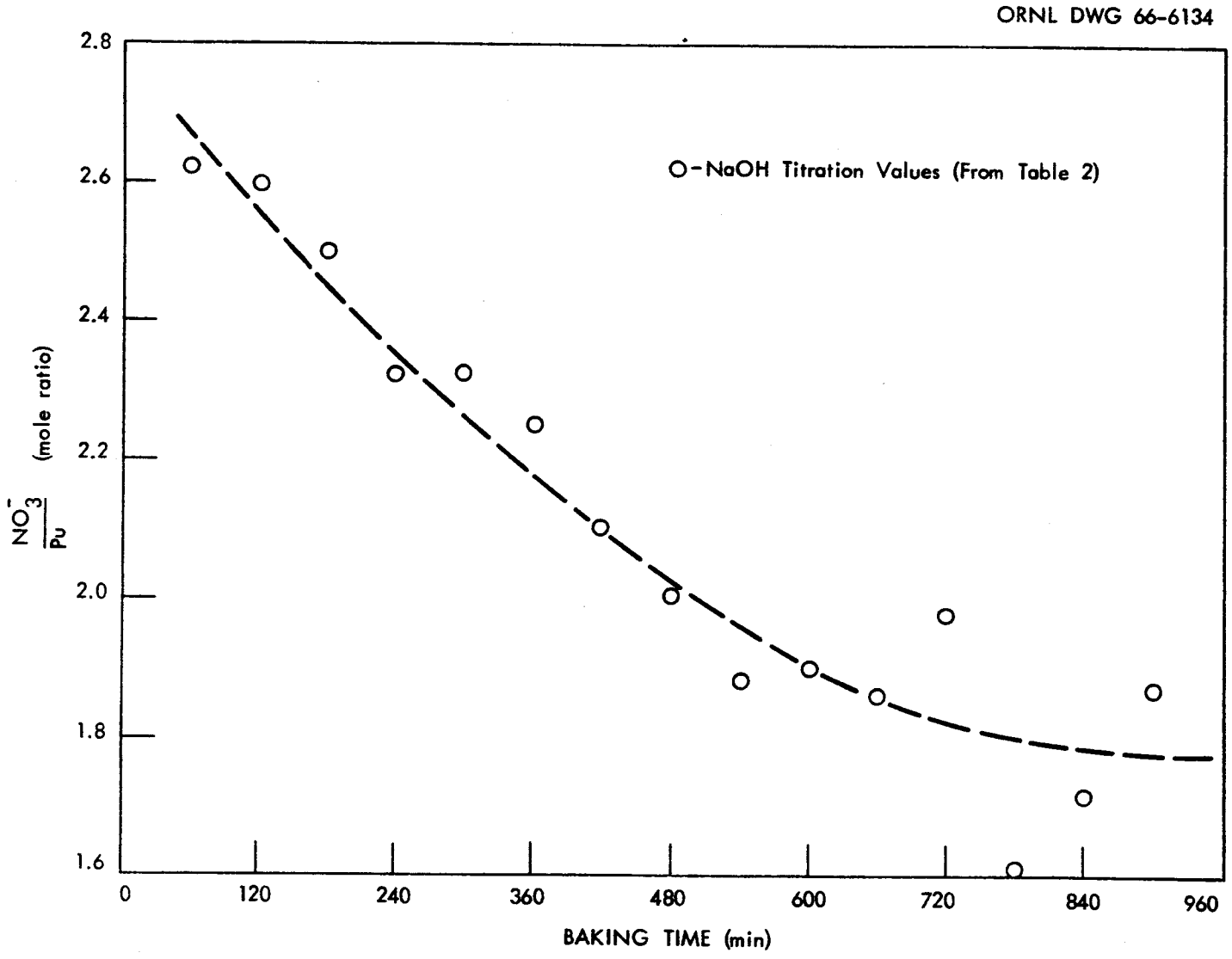

Fig. 2. Denitration of Plutonia (IV) Sol at 120° ± 5°C.

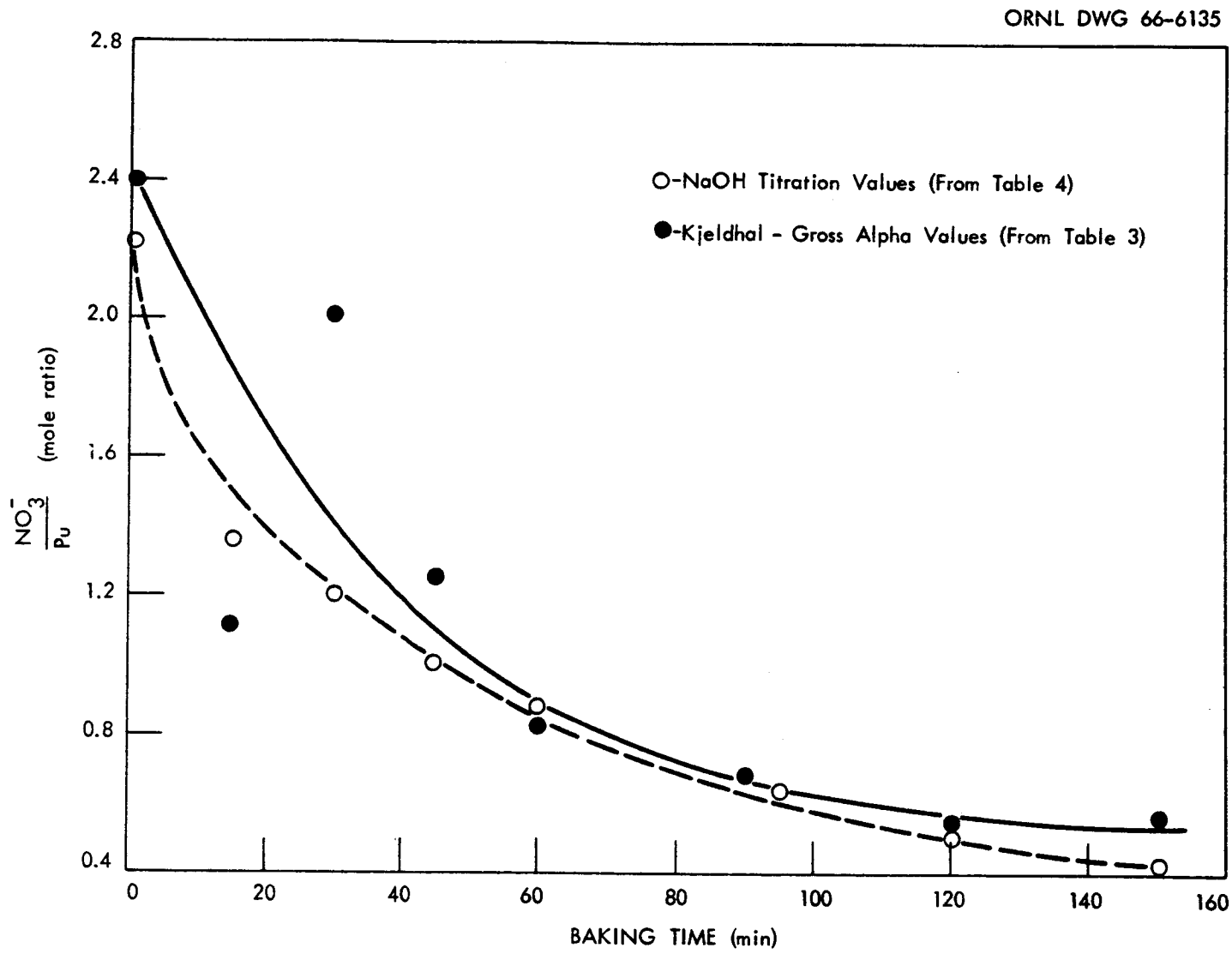

Fig. 3. Denitration of Plutonia (IV) Sol at 205° ± 5°C.

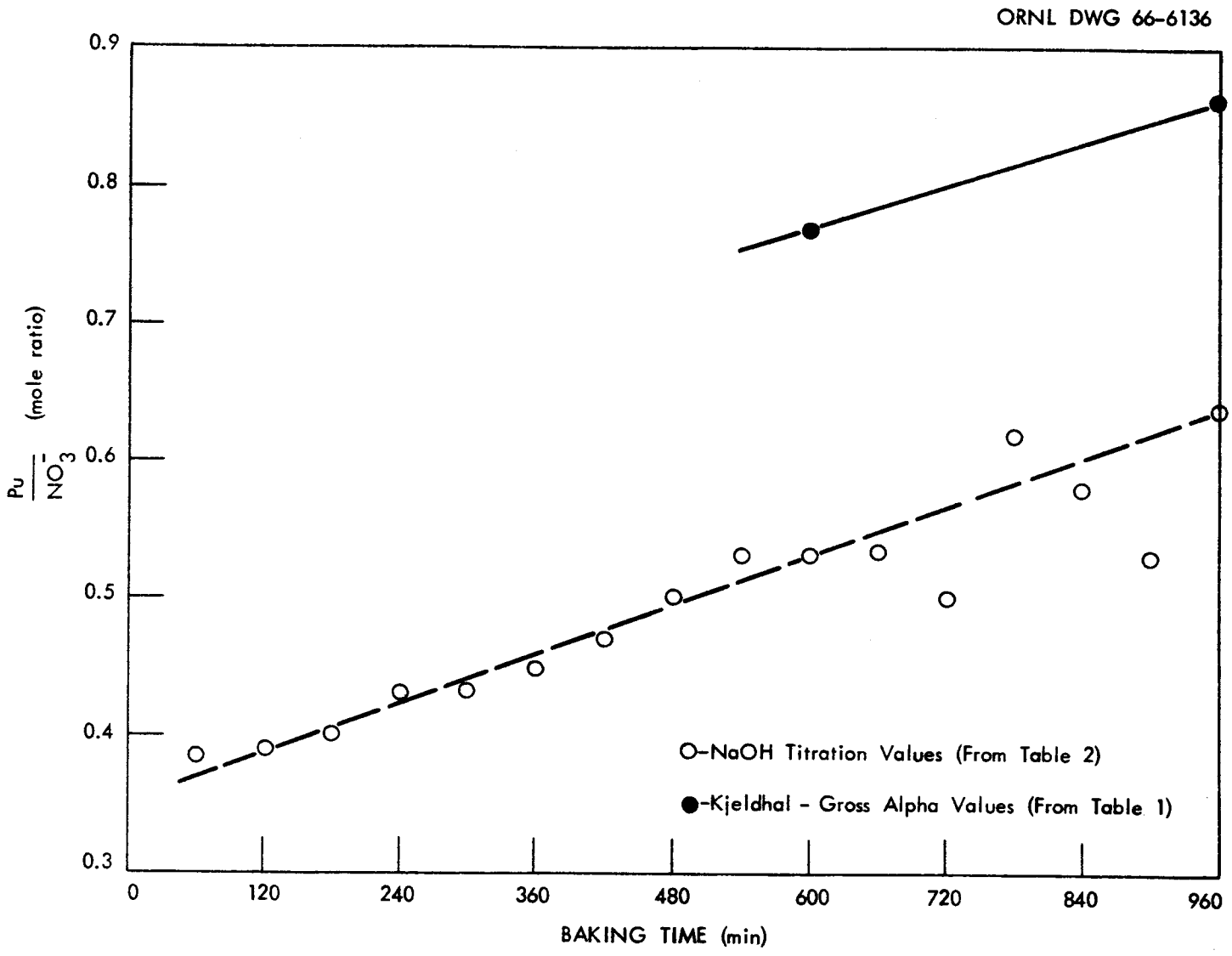

Fig. 4. Denitration of Plutonia (IV) Sol at 120° ± 5°C.

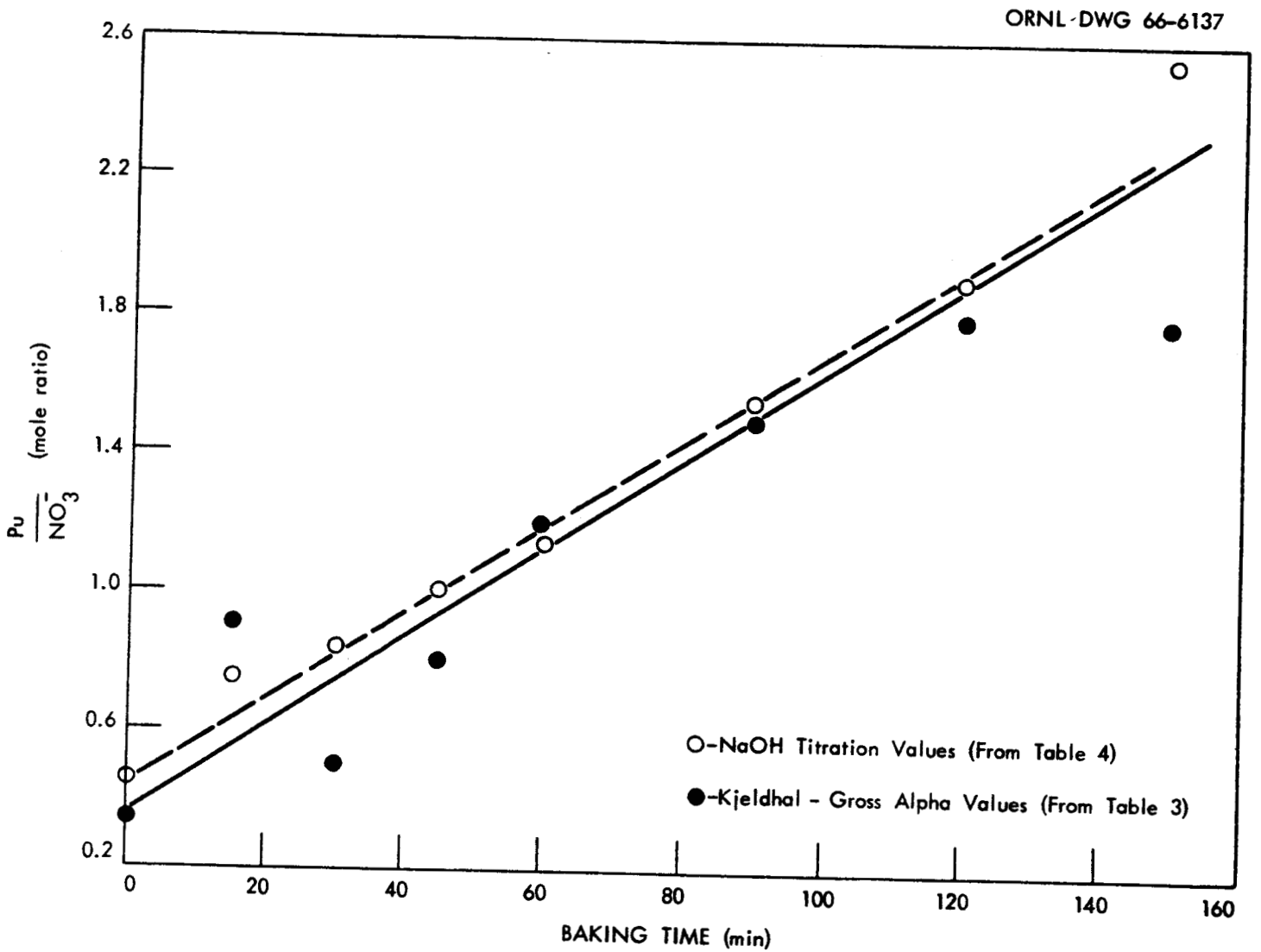

Fig. 5. Denitration of Plutonia (IV) Sol at 205° ± 5°C.

Table 5. Particle Size Distribution of Plutonia Sol Baked at 120° ±5°C

Sample[a]	Baking Time (Min)	Filter Size A	Gross alpha Counts $min^{-1} ml^{-1}$	% Passing[b] through Filter
EK-S-3	60	Control	5.3×10^7	---
		1000	4.4×10^7	83
		500	5.2×10^7	98
		100	4.8×10^7	90
EK-S-12	600	Control	5.6×10^7	---
		1000	5.6×10^7	100
		500	5.7×10^7	100
		100	5.2×10^7	93
EK-S-18	960	Control	2.62×10^7	---
		1000	2.43×10^7	93
		500	2.20×10^7	84
		100	1.95×10^7	74

[a]See Table 2 for sample history.

[b]Determined by comparing the gross alpha of each solution passed through the filter with its corresponding control solution.

REFERENCES

1. D. E. Ferguson et al., Chemical Techonology Division Annual Progress Report, May 31, 1965, ORNL-3830, pp. 144-48.
2. P. A. Haas, W. D. Bond, M. H. Lloyd, and J. P. McBride, "Sol-Gel Process Development and Microsphere Preparation" presented at the Second International Thorium Fuel Cycle Symposium held in Gatlinburg, Tennessee, May 3-6, 1966. To be published in proceedings.

INTERNAL DISTRIBUTION

1. R. D. Baybarz
2. R. E. Biggers
3. R. E. Blanco
4. W. D. Bond
5. R. E. Brooksbank
6. K. B. Brown
7. S. R. Buxton
8. J. M. Chandler
9. S. D. Clinton
10. F. L. Culler
11. D. E. Ferguson
12. L. M. Ferris
13. T. A. Gens
14. H. E. Goeller
15. P. A. Haas
16. R. G. Haire
17. C. J. Hardy
18. C. C. Haws, Jr.
19. A. R. Irvine
20-21. F. G. Kitts
22. A. T. Kleinsteuber
23. N. A. Krohn
24-25. R. E. Leuze
26-27. M. H. Lloyd
28. J. P. McBride
29. K. H. McCorkle
30. A. B. Meservey
31. J. G. Moore
32. L. E. Morse
33. K. J. Notz
34. J. R. Parrott
35. W. L. Pattison
36. J. J. Perona
37. J. T. Roberts
38. A. D. Ryon
39. J. W. Snider
40. J. W. Ullmann
41. W. E. Unger
42. M. E. Whatley
43-44. R. G Wymer
45-46. Central Research Library
47. Document Reference Section
48-50. Laboratory Records
51. Laboratory Records, RC
52. ORNL Patent Office

EXTERNAL DISTRIBUTION

53. R. W. Barber, AEC, Wash.
54. C. B. Deering, AEC, ORO
55-59. E. J. Kosiancic, B&W, Lynchburg, Va.
60. W. H. McVey, AEC, Wash.
61. Research and Development Div., ORO
62-76. DTIE