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A STUDY OF THE POLYMERIZATION, DEPOLYMERIZATION, AND PRECIPITATION OF TETRAVALENT PLUTONIUM AS FUNCTIONS OF TEMPERATURE AND ACIDITY BY SPECTROPHOTOMETRIC METHODS: PRELIMINARY REPORT

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A STUDY* OF THE POLYMERIZATION, DEPOLYMERIZATION, AND PRECIPITATION OF TETRAVALENT PLUTONIUM AS FUNCTIONS OF TEMPERATURE AND ACIDITY BY SPECTROPHOTOMETRIC METHODS: PRELIMINARY REPORT**

D. A. Costanzo R. E. Biggers

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D. A. Costanzo R. E. Biggers

Abstract

Absorption spectrophotometric studies of some problems relevant to plutonium solution chemistry were undertaken. The objectives of these studies were: to determine the kinetics of the polymerization of tetravalent plutonium; to determine the kinetics of the depolymerization of polymeric plutonium(IV); and, to determine the properties of plutonium(IV) polymer under representative solution conditions of acidity, temperature, and ion concentrations encountered in fuel processing.

The polymerization of tetravalent plutonium was studied as a function of the plutonium concentration, (1-8 mg Pu/ml), nitric acid concentration, (0.03-0.3 M), and temperature (25° - 95°). Under these conditions, disproportionation and nitrate oxidation of the tetravalent plutonium occurred and were also studied. From these studies it is clearly indicated that colloidal polymer formation is favored by an increase in the plutonium concentration and temperature, or by a decrease in the acidity. Temperature had a pronounced effect on the rate and extent of polymer formation at any particular acidity.

For solutions containing initially Pu^{3+} and PuO_2^{2+} (resulting from the rapid disproportionation of Pu^{4+} at low acidity) the removal of Pu^{4+} from solution by polymerization of Pu^{4+} was observed to cause the reversal of the disproportionation reaction. This effect is more pronounced, the lower the acidity. The effects of $UO_2(NO_3)_2$, $Al(NO_3)_3$, $NaNO_3$, and F^- upon the kinetics of polymer formation in acidic nitrate media were also determined at low acidities and elevated temperatures. In the presence of high concentrations of the nitrate salts the colloidal plutonium(IV) polymer was observed to precipitate.

The precipitation of "aged" colloidal Pu(IV) polymer by nitrate-containing electrolytes, e.g., HNO_3, $Al(NO_3)_3$, $NaNO_3$, and $LiNO_3$, was studied at 25°C. The Pu(IV) polymer was "aged" by refluxing for 24 hours at the boiling temperature. The amount of "aged" polymer precipitated reached a maximum at 2-3 M nitrate, and decreased thereafter with an increase in nitrate concentration. Precipitation did not occur above a nitrate concentration of 4 M.

The kinetics of the depolymerization of freshly prepared Pu(IV) polymer to ionic plutonium were determined at several acidities between 1 to 10 M HNO_3 as a function of temperature. The depolymerization reaction kinetics at fixed acidity were observed to be first order,

depending only upon the concentration of plutonium present as polymer. The rate of depolymerization of "aged" Pu(IV) polymer was determined in 5 M HNO_3 as a function of temperature. The HNO_3 concentration was maintained above 4 M to prevent the precipitation of the polymer. The effects of fluoride, of sulfate, and of fluoride in the presence of a 4:1 mole ratio excess of aluminum on the depolymerization kinetics was also studied.

These studies show that polymer formation and precipitation can be prevented by the proper control of solution conditions, and that polymer, once formed, can be depolymerized.

Introduction

The recovery of plutonium from irradiated nuclear fuels by aqueous processing methods normally involves dissolution of the fuel in nitric acid followed by solvent extraction or ion exchange purification of tetravalent plutonium from the acidic nitrate medium. Hydrolysis and subsequent polymerization of the tetravalent plutonium could cause difficulty because polymeric plutonium is neither extracted by usual solvents, nor sorbed on ion-exchange resins. In addition, the increased formation of polymeric colloidal plutonium at elevated temperatures by water dilution, or by contacting the solutions with steam, can cause the colloidal polymer to precipitate, if the temperature exceeds the precipitation temperature for any given solution. These phenomena could result in serious criticality problems, plugged lines, and loss of plutonium to waste process streams. In addition, the solutions and precipitates would require drastic treatment before becoming suitable for further processing. Difficulties of this nature at ORNL have been discussed recently.(11)

For these and other reasons the formation of polymeric species in plutonium solutions has been a subject of occasional study(4-10) since Kraus (1,2,3) first studied it in the mid-forties. It was established in these early studies that of the valence states of plutonium the tetravalent state is the one which can polymerize, and that the solution acidity is the most important variable. In a solution less acidic than about 0.3 M H^+ at room temperature and 1.26 M H^+ at the boiling point, it has been reported that polymerization can occur.(9) As the plutonium concentration increases, the tendency to polymerize increases. It was further established that the polymerization was a nearly irreversible phenomena at room temperature, but that on long exposure to high acidities, polymerization could be reversed in a nearly first order reaction, dependent only on the plutonium concentration at fixed acidity. Fluorides and sulfates were qualitatively shown to speed depolymerization, and electrolytes were shown to precipitate the colloidal polymer. It was also established that the polymer is not a well defined chemical species, but appears to be composed of polymer aggregates which show a very wide distribution of molecular weights.(10) Due to the lack of sufficiently detailed information concerning the formation and properties of polymeric plutonium under conditions of importance in power reactor fuel processing, this study was undertaken in an attempt to provide data relevant to some of the existing problems.

In this study the goal was to obtain kinetic data for the polymerization and depolymerization of tetravalent plutonium under representative fuel processing conditions of acidity, temperature, anion concentrations, and several other parameters. In addition, information on the precipitation of polymer and absorption spectra were obtained.

Some aspects of the work are summarized in the sections that follow. It should be understood that the results reported herein are preliminary. A discussion of the hazards and experimental procedure evaluation for these studies has been previously published.(12) A detailed report of all aspects of the work will be published when the analysis of all of the data is completed. The forthcoming report will also contain a critical review of all the known literature relevant to this problem.

I. Cary Model 14-PM Spectrophotometer and Glove Box Facility for High Level Alpha Materials

A Cary Model 14-PM spectrophotometer was used in this study to obtain spectral data. In order to carry out kinetic studies an automatic programmer system was installed, by means of which it was possible to automatically control the spectrophotometer and run spectra at preset time intervals over multiples of 24 hours arranged programs.

In order to employ the spectrophotometer for measurements on solution containing plutonium, which emit high levels of alpha particle radiation, a glove box was designed and constructed to contain the plutonium and the end compartments of the spectrophotometer. A photograph of the spectrophotometer and its attached glove box is shown in Fig. 1. The glove box provides for complete containment of activity in case of accidental breakage or leakage of the sample cell. The glove box is constructed entirely of lucite with interconnecting edges screwed and cemented together. The left side is a lucite template cut to provide an absolute containment seal, via a neoprene gasket, to the end of the spectrophotometer.

One 12-inch and one 8-inch port are provided for the transfer of absorption cells and other necessary equipment. Two glove ports, located at the level of the sample-reference compartment entries at the top of the glove box, are provided for the manipulations necessary for obtaining spectral measurements. Four pairs of glove ports, located at the base of the box, are provided for servicing and adjustment of the end compartments of the spectrophotometer. These ports are so located that all enclosed parts of the spectrophotometer are accessible.

Thirty air-tight, sealed adapters and fittings mounted into the back panel supply the necessary services required, e.g., thermostatted and cooling water, thermocouples, air, electricity, etc.

In order to obtain spectral data at elevated temperatures the absorption cells in the spectrophotometer could be independently heated up to about 100°C by means of miniaturized circulating water baths contained within the glove box. Specially constructed jacketed absorption cells of various optical path lengths were employed in this work.

To minimize contamination to the spectrophotometer, a conventional alpha glove box (not shown in Fig. 1) was attached to the 8-inch port at the upper right by means of a flexible polyethylene tube. All necessary sample preparation, cell filling, emptying, cleaning, and other necessary operations are performed in the glove box attached to the spectrophotometer glove box.

All transfers of materials and equipment are made by the sealed polyethylene tube technique. Complete containment was maintained at all times. A more detailed discussion of the experimental techniques and facilities used has been presented elsewhere.(12)

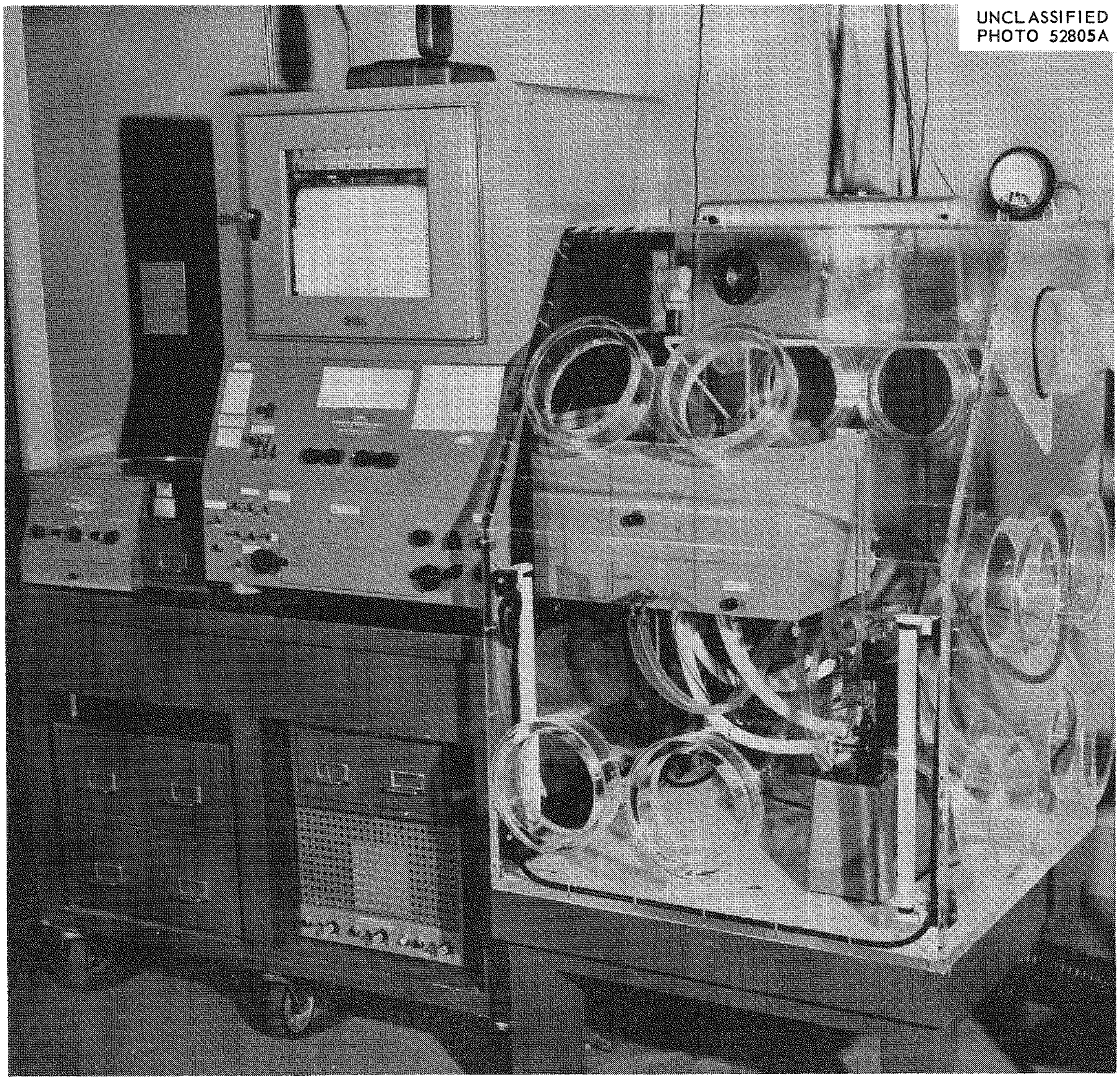

Fig. 1. Cary Model 14-PM Spectrophotometer and Glove Box Facility for High Level Alpha Materials.

II. Reactions of Quadrivalent Plutonium in Acidic Aqueous Solutions

Studies of the polymerization and depolymerization of Pu(IV) are complicated by the fact that disproportionation and nitrate oxidation of the plutonium may occur simultaneously with the polymerization and depolymerization. As shown in the following equations, the polymerization, disproportionation, and nitrate oxidation reactions are acid dependent. The mechanisms for (1) and (3) are not known at the present time.

(1) Polymerization:

$$y\,Pu^{4+} + (x + 2y)\,H_2O \longrightarrow \underset{\text{Polymer}}{(PuO_2)_y \cdot x\,H_2O} + 4yH^+$$

(2) Disproportionation:

Consists of:

$$\text{(a)}\quad Pu^{4+} + Pu^{4+} + 2H_2O \rightleftharpoons Pu^{3+} + PuO_2^{+} + 4H^+$$

$$\text{(b)}\quad PuO_2^{+} + Pu^{4+} \rightleftharpoons Pu^{3+} + PuO_2^{2+}$$

Net Reaction:

$$3Pu^{4+} + 2H_2O \rightleftharpoons 2Pu^{3+} + PuO_2^{2+} + 4H^+$$

(3) Nitrate Oxidation:

$$3\,Pu^{4+} + 2H_2O + 2NO_3^- \rightleftharpoons 3PuO_2^{2+} + 2NO + 4H^+$$

The rate and extent of the respective reactions depend both on solution acidity and on the temperature. Thus, in order to use the spectrophotometric method to study plutonium polymer solutions that contain the ionic species Pu^{3+}, Pu^{4+} and PuO_2^{2+} it is necessary to obtain standard absorption spectral data for the respective valence states and of the polymer under conditions which duplicate the experimentally studied conditions of acidity, temperature, and anion concentration.

Digital computing techniques developed at ORNL make possible the analysis of the complex absorption spectra of solutions that contain the various plutonium ions, as well as the polymerized Pu(IV). Thus, it is possible to establish the concentrations of the various species present and to make other necessary types of analyses of the data. Conventional computational methods of analysis used to analyze spectrophotometric data from multicomponent systems cannot be used because the majority of the absorption spectra obtained in the present work are those of dynamic, reacting systems. A method of analysis applicable to dynamic systems is under development at ORNL,(14) and will be published soon.

III. Absorption Spectra of Pu(III, IV, and VI) in 1 M HNO_3 at 25°C.

Standard absorption spectral data for trivalent, tetravalent, and hexavalent plutonium were obtained at acidities ranging from 0.5 to 7.5 M and at temperatures between 25 and 95°C. Spectra have also been obtained in other relevant media.

In order to illustrate the nature of the complex spectra and the sharpness of the absorption peaks of analytical importance, the absorption spectra of trivalent, tetravalent and hexavalent plutonium in 1 M HNO_3 at 25°C are shown in Fig. 2. The absorption peaks employed in this study are the major peaks occurring at approximately 4760 Å for Pu^{4+}, 6000 Å for Pu^{3+}, and 8300 Å for PuO_2^{2+}. However, several wavelengths for each ionic species,as well as polymeric species,are utilized in the digital computation methods employed.

The spectral characteristics of the individual ionic species do not differ markedly with an increase in nitric acid concentration or with an increase in nitrate ion concentration. However, small but significant differences in magnitude and position of the peaks do exist due to nitrate complex formation.

IV. Effect of Temperature on the Molar Absorptivity of Pu(VI) in 1 M HNO_3

The magnitudes of the absorption peaks of the respective valence states decrease markedly with an increase in temperature from 25 to 95°C. This factor, in addition to wavelength shifts, must be considered in an analysis of the spectral data. The effect of temperature on the molar absorptivity of the Pu^{4+} peak occurring at 8304 Å in 1 M HNO_3 at several concentrations of plutonium is shown in Fig. 3. At a given concentration of plutonium, the absorptivity of the peak occurring at 8304 Å decreases in a linear manner with an increase in temperature. At a given temperature, if the instrumental spectral slit width is too

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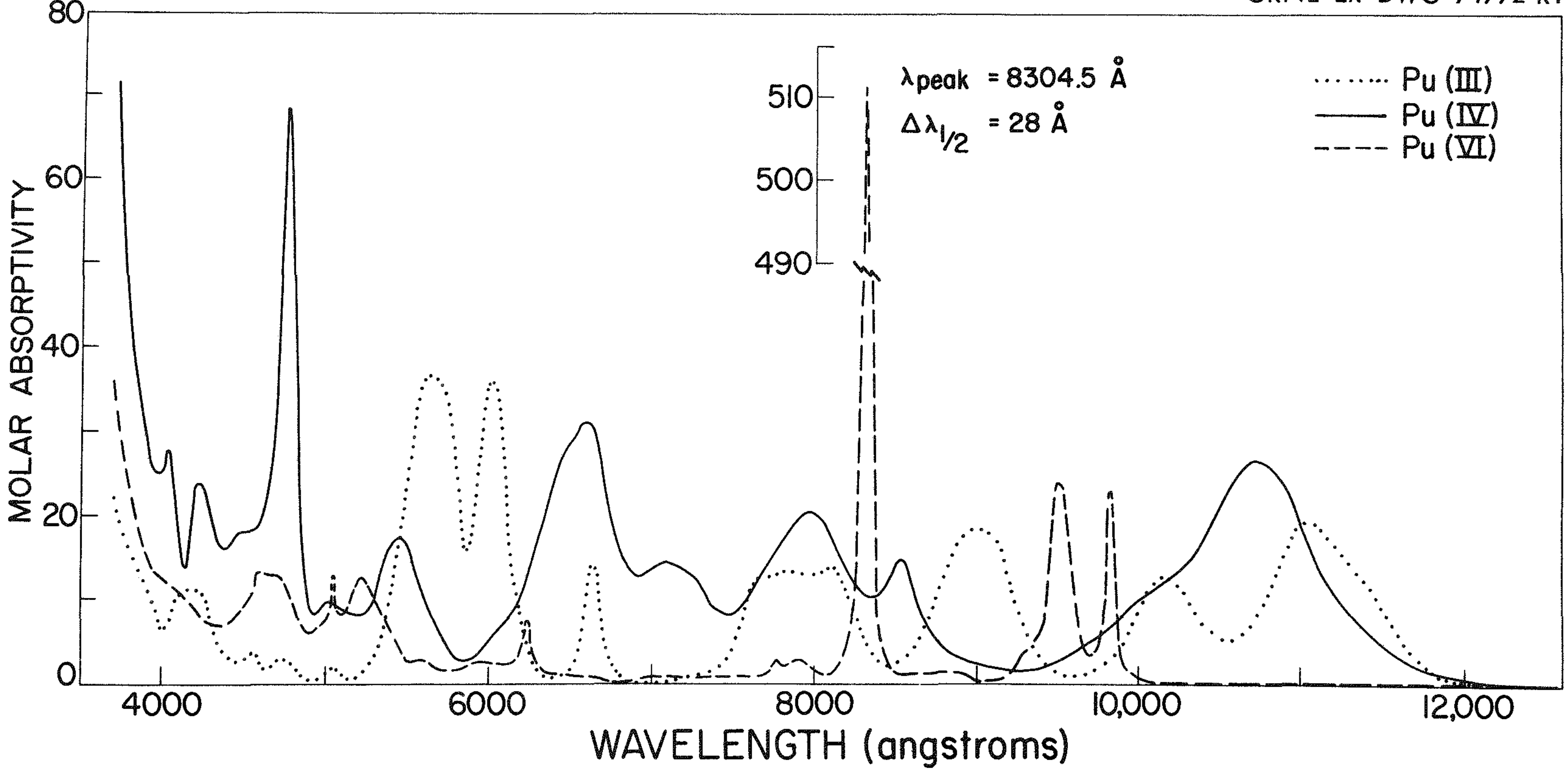

Fig. 2. Absorption Spectra of Pu(III, IV, and VI) in 1 M HNO_3 at 25°C.

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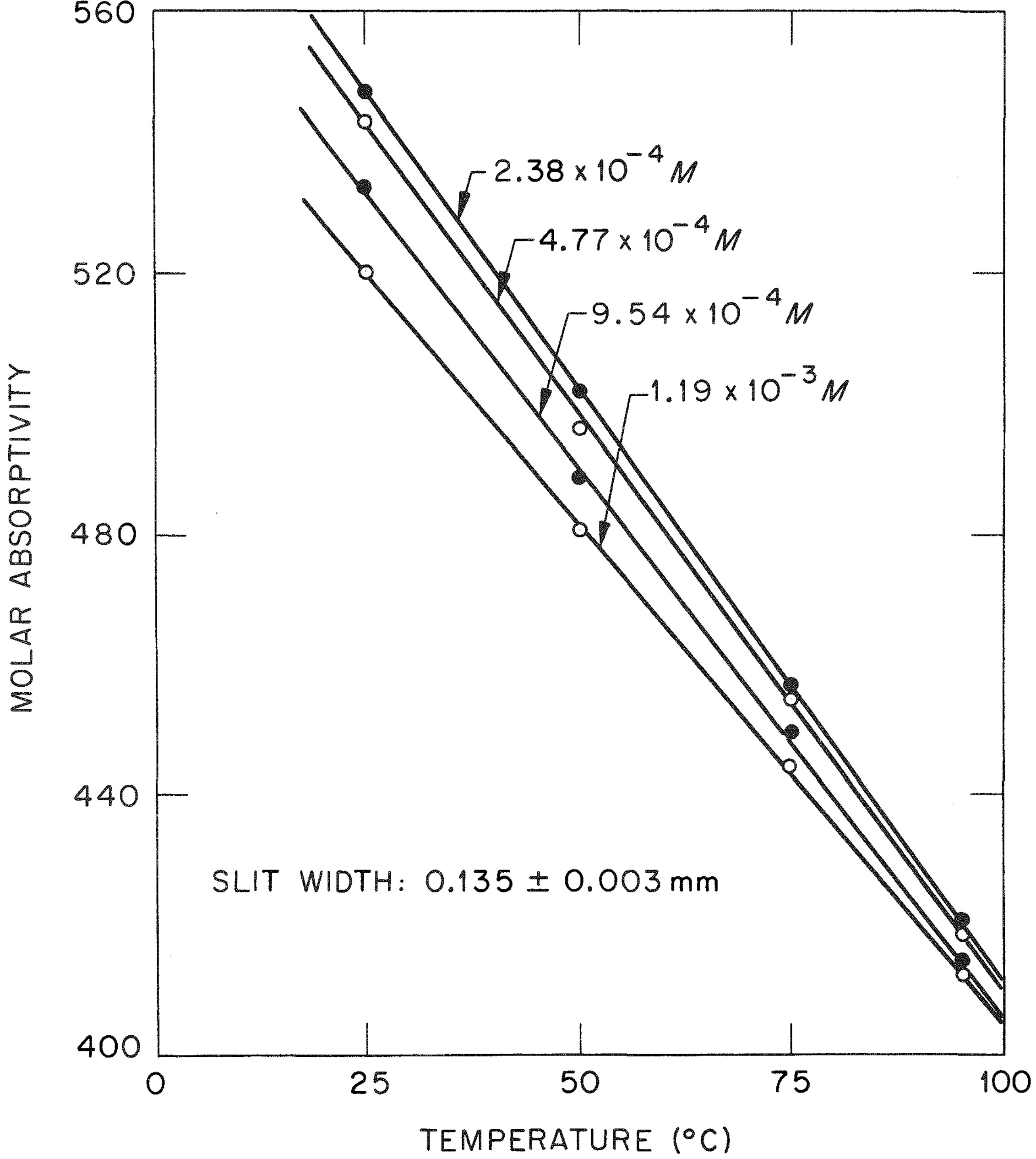

Fig. 3. Effect of Temperature on the Molar Absorptivity of Pu(VI) in 1 M HNO_3.

wide, Beer's law will not be obeyed because of the extreme sharpness of the peak. In order to resolve the PuO_2^{2+} peak under automatic recording conditions, the value of the slit width must be somewhat smaller than that indicated on Fig. 3 in order to yield a spectral slit width of the order of 2.8 A.

For the PuO_2^{2+} peak the temperature coefficient of the molar absorptivity varies from 1.53 liters/mole-cm./°C. at 1.9×10^{-3} $\underline{M}$ Pu to 1.70 liters/mole-cm./°C. at 2.38×10^{-4} $\underline{M}$ Pu.

V. Absorption Spectra of Polymerized Pu(IV) in 0.2 $\underline{M}$ HNO_3 at 25°C -- Effect of Ageing at Room Temperature and at the Boiling Point

The absorption spectra of the emerald-green colloidal plutonium polymer solutions are different from the spectra of all the ionic species of plutonium. Most striking in the polymer spectrum is the absence of the peak for the ionic tetravalent state which occurs at approximately 4760 Å. Also, the molar absorptivity at 4000 Å is approximately 100 for the polymeric Pu(IV) versus approximately 25 for ionic Pu^{4+}. The molar absorptivity of polymer at 4000 Å was the principal value used in the analysis of the spectral data.

Solutions of polymeric plutonium do not necessarily exhibit a constant absorptivity at a given wavelength for the reason that polymeric plutonium is not a well defined chemical species. The differences in absorptivity arise from the method and temperature of preparation, and from ageing. However, for a given polymer preparation, Beer's law is obeyed.

The effect of ageing on the absorption spectrum of "fresh" polymer is shown in Fig. 4. Fresh polymer was prepared by the dilution with water of a concentrated plutonium solution containing 220 g Pu^{4+}/liter in 3 $\underline{M}$ HNO_3 to 2.20 g Pu^{4+}/liter. Polymer was also prepared by the precipitation of Pu(IV) hydroxide, followed by dissolution in nitric acid and acidity adjustment with ammonium hydroxide and water. The fresh polymer solutions were sparged with nitric oxide gas to convert any PuO_2^{2+} formed by disproportionation back to Pu^{4+}. The polymer was separated from ionic species by ion exchange, and from any precipitated polymer by centrifugation to approximately 5000 G for 15 minutes.

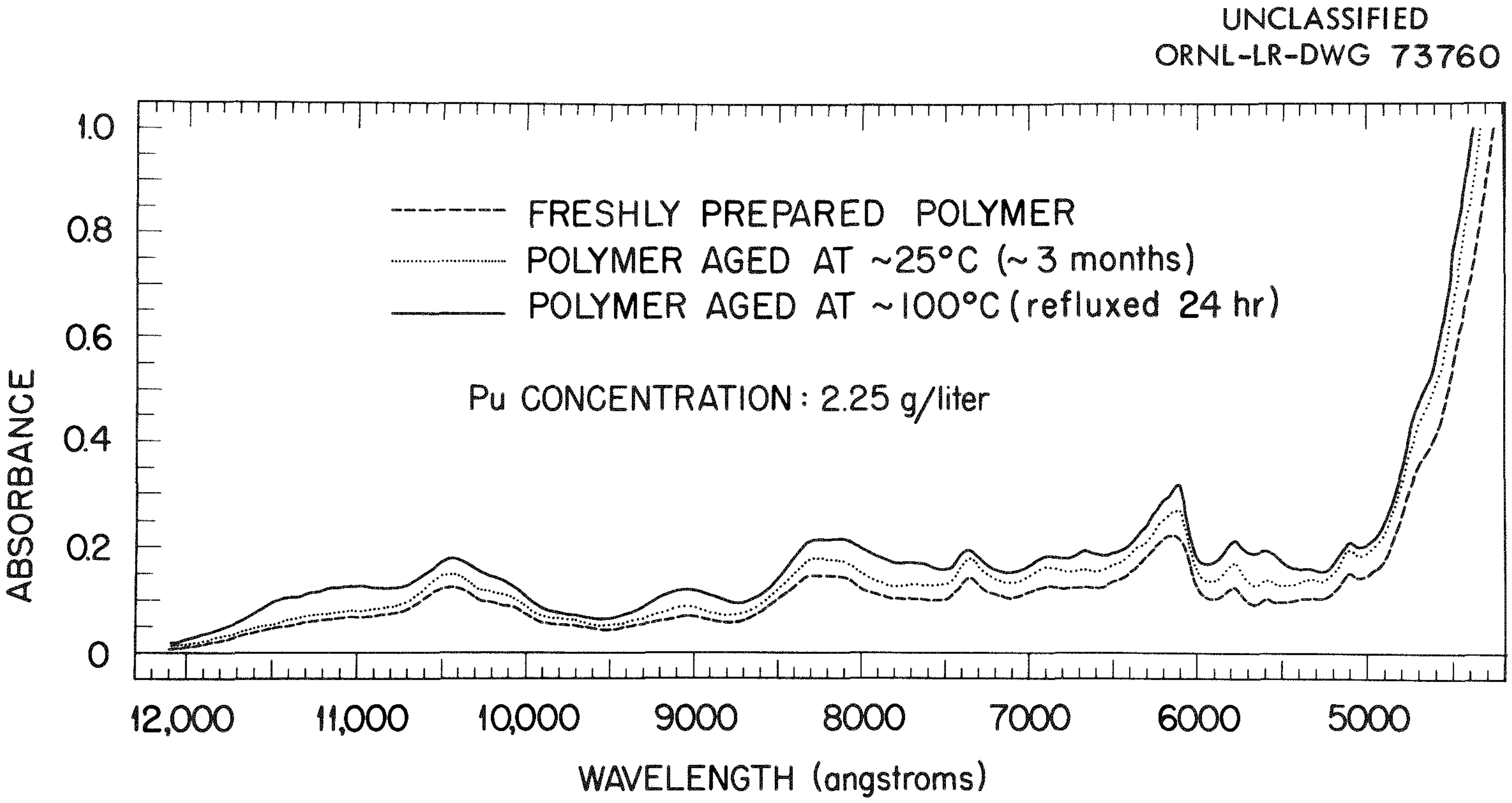

Fig. 4. Absorption Spectra of Polymerized Pu(IV) in 0.2 M HNO_3 at 25°C – Effect of Ageing at Room Temperature and at the Boiling Point.

The polymer was aged both by standing for several months at room temperature, and by refluxing for 24 hours at the boiling temperature. During refluxing, the solution was sparged with nitric oxide gas to convert PuO_2^{2+} present in solution back to Pu^{4+}, which in turn polymerizes at this acidity and temperature. Ionic Pu^{4+} resulting from the depolymerization of the fresh polymer at the elevated temperature and converted to PuO_2^{2+} by nitrate oxidation, is reduced to Pu^{4+} by nitric oxide by reversal of the reaction in equation (3).

It was found to be possible to determine ionic plutonium in the presence of polymer by coulometric analysis because polymer is not electrolytically reducible at the controlled potentials employed in the method.(13) The total plutonium concentration was determined after converting the polymer to the ionic state by heating to fumes of SO_3 with H_2SO_4-HF solution. Polymer concentration was determined by difference. This method serves as an independent check on the spectrophotometric method of analysis for polymer.

VI. Effect of Acidity on the Rate of Polymerization of Pu(IV) in Nitric Acid at 25°C.

The effect of acidity upon the rate of the polymerization of Pu(IV) at 25°C in nitric acid for solutions containing 2.20 g/l of plutonium is shown in Fig. 5. Solutions were prepared by diluting a stock solution containing 220 g/l Pu(IV) in 3.0 $\underline{M}$ HNO_3 with dilute nitric acid to give the desired final solution acidity. As indicated, the rate of the polymerization is much more rapid at the lower acidities.

In 0.15 $\underline{M}$ HNO_3, a small amount of polymer appeared to be present at the time of solution preparation and did not appear to increase with time. It is believed that the presence of this polymer was due in part to the initial dilution of the concentrated plutonium stock solution with acid more dilute than 0.1 $\underline{M}$, rather than to formation as a result of the final solution acidity. Due to the irreversibility of the polymerization reaction in that solution, the polymer did not revert back to the ionic species. The rapid disproportionation of Pu^{4+} is indicated by the nearly stoichiometric amounts of Pu^{3+} and PuO_2^{2+} present.

At 0.075 $\underline{M}$ HNO_3, a large amount of polymer appears immediately upon preparation of the solution. The rate of disproportionation of ionic

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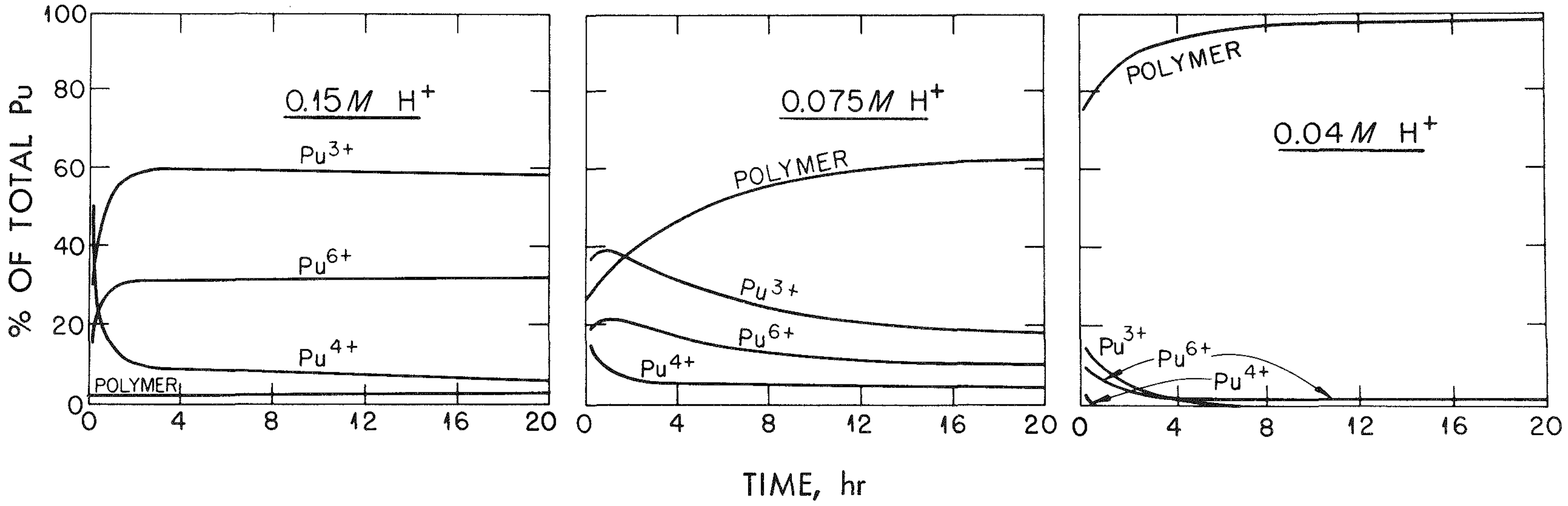

Fig. 5. Effect of Acidity on the Rate of Polymerization of Pu(IV) in Nitric Acid at 25°C.

Pu^{4+} is also very rapid at this acid concentration. Most interesting is the fact that the PuO_2^{2+} and Pu^{3+} reproportionate to form ionic Pu^{4+}. This Pu^{4+} then immediately polymerized as indicated in Fig. 5 by the increase with time of the amount of polymer present. The transient ionic state was not directly observed. The stability of the polymer at low acidities serves as a driving force to reverse the disproportionation reaction.

At 0.04 M HNO_3, the rate of disproportionation and polymerization is very rapid. No evidence of Pu^{4+} was found after 10 minutes. The rate of the reproportionation is also rapid and resulted in the complete disappearance of Pu^{3+} after approximately 6 hours. Some PuO_2^{2+} remained at the end of that time, perhaps due to the nitrate oxidation of Pu^{4+}. Thus, as the acidity of a solution is decreased there are two reaction paths available for polymerization: direct polymerization of the ionic Pu^{4+}, and indirect, i.e., polymerization of the Pu^{4+} resulting from the reproportionation of Pu^{3+} and PuO_2^{2+} that are formed as the acidity is decreased.

VII. Effect of Temperature on the Rate of Polymerization of Pu(IV) in 0.075 M HNO_3

The effect of temperature on the rate of polymerization of Pu(IV) in 0.075 M HNO_3 at 25°, 50° and 75°C for solutions containing 2.20 g/l of Pu is shown in Fig. 6. The solutions were prepared by dilution of a concentrated solution of ionic Pu^{4+} with dilute acid at room temperature. Five minutes was required for sample preparation, cell filling, and transfer of the sample cell into the spectrophotometer. The solutions were heated for five minutes or until a desired equilbration temperature was obtained and then the first spectrum was obtained. Consequently, the initial concentrations of plutonium species during the first few minutes after mixing are not shown because they would not necessarily represent those concentrations which would have been present if it were possible to simultaneously prepare the solutions and equilibrate them at an elevated temperature.

The results show that the rate of polymer formation increases very rapidly with an increase in the temperature. The initial amounts of Pu^{3+} and PuO_2^{2+} shown result from the disproportionation of Pu^{4+} during

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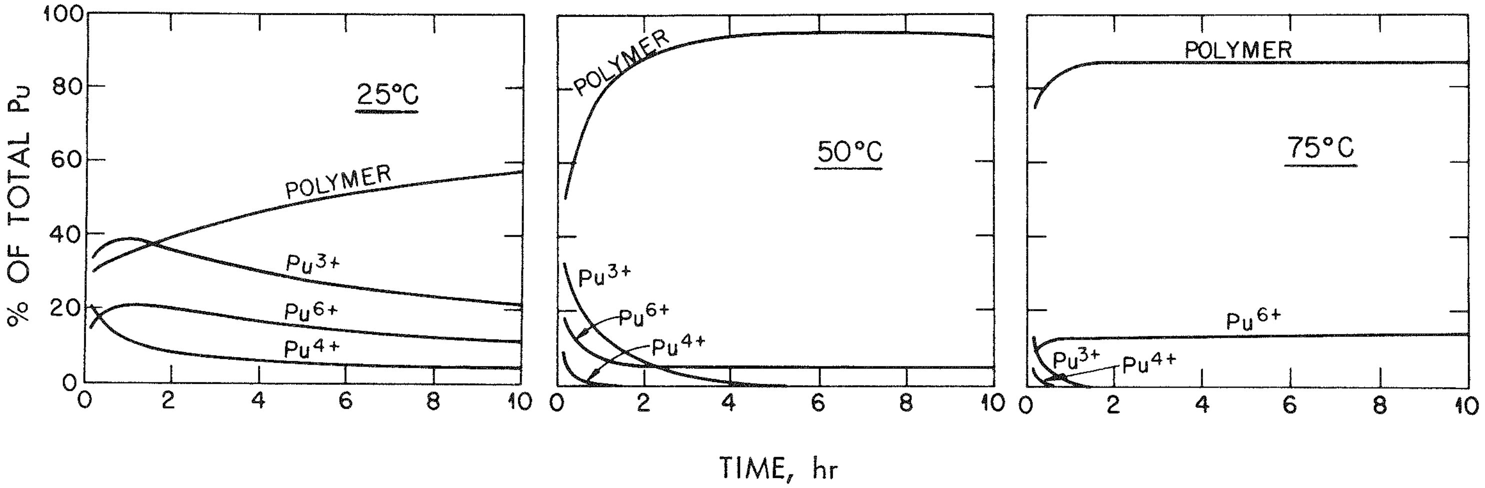

Fig. 6. Effect of Temperature on the Rate of Polymerization of Pu(IV) in 0.075 M HNO_3.

the time interval between solution preparation and the start of the first spectral measurement. At the three temperatures, 25°, 50°, and 75°C, the reproportionation of the Pu^{3+} and PuO_2^{2+} to form polymer is quite apparent, the rate increasing very rapidly with temperature. At 75°C the Pu^{3+} concentration has decreased to zero by the end of two hours, due perhaps, not only to the reproportionation reaction, but also as a result of nitrate oxidation. The increase in the amount of PuO_2^{2+} present at that time at which Pu^{3+} has disappeared, at 75°C as compared to 50°C is almost certainly due to the increase in the rate of nitrate oxidation of Pu^{4+} at the higher temperature.

VIII. Precipitation of Aged Pu(IV) Polymer by Electrolytes at 25°C

It was observed in the polymer formation studies that at low acidity and elevated temperature—the optimum conditions for polymer formation—the plutonium polymer precipitated when high concentrations of $UO_2(NO_3)$, $Al(NO_3)$, or $NaNO_3$ were present.

The effect of nitrate salts and nitric acid upon the precipitation of aged polymer at 25°C is shown in Fig. 7. The solutions were prepared by dilution of an aged polymer stock solution with equivalent volumes of reagents to give the indicated concentrations. The aged polymer stock solution contained 3.24 mg Pu/ml as polymer in 0.3 M HNO_3 and was aged by refluxing 24 hours at the boiling temperature, simulating polymer formation at elevated temperature (cf. Section V).

It should be noted that these curves were made from data obtained by coulometric(13) and alpha analysis of the supernate soon after the addition of the indicated acidified salts or acid to a more concentrated polymer stock solution followed by centrifugation at 5000 G for 5 minutes. During the short period of time necessary to prepare the sample, precipitate the polymer, and centrifuge, depolymerization did not occur to any significant extent. In earlier work Kraus(1,15) has shown that 0.15 equivalents of any of the anions, IO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, PO_4^{2-}, or $Fe(CN)_6^{2-}$ per mole of Pu, present as polymer, is sufficient for essentially complete precipitation of the colloidal polymer, irrespective of the valence of the anion. This may be contrasted with the usual

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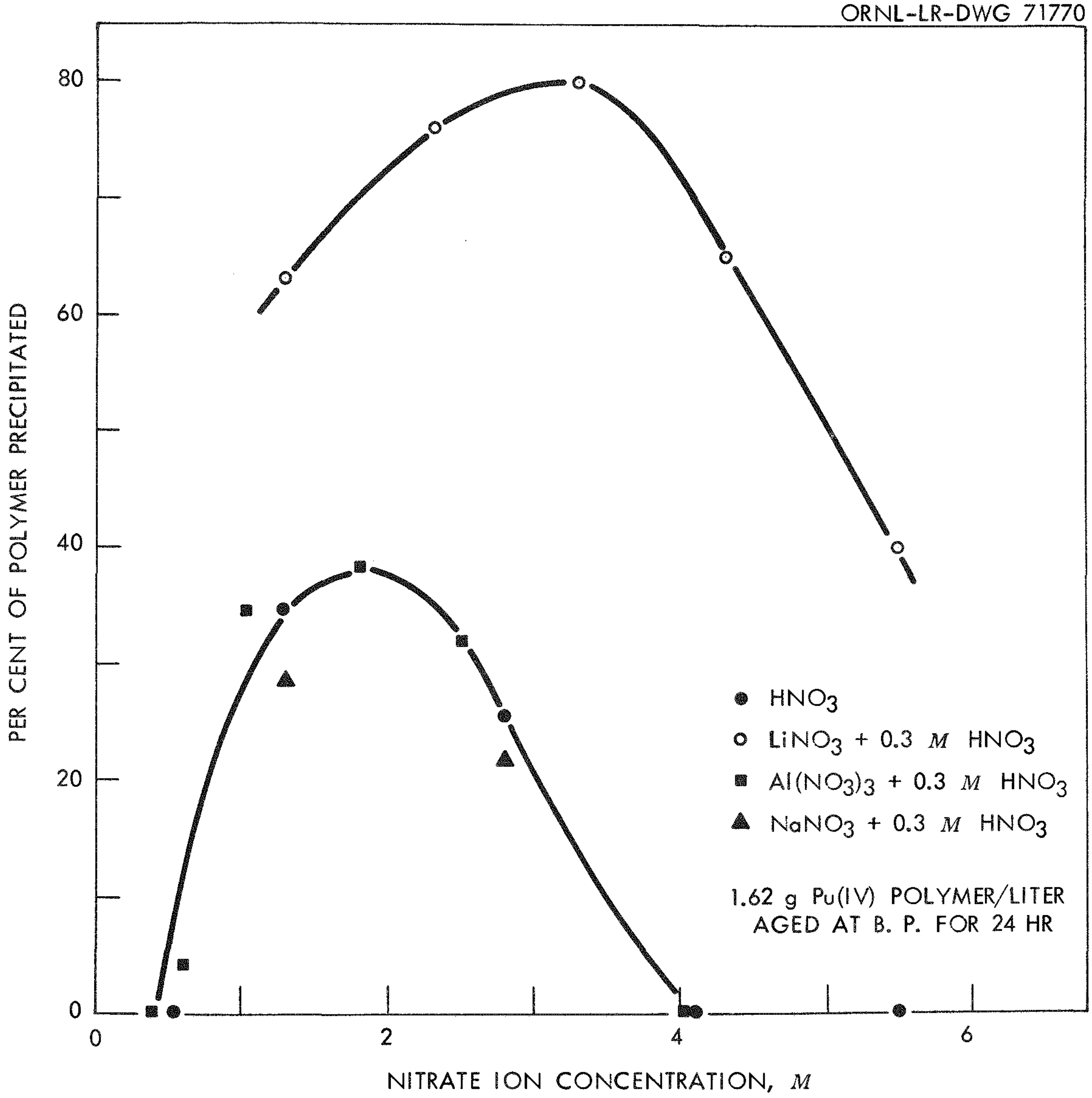

Fig. 7. Precipitation of Aged Pu(IV) Polymer by Electrolytes at 25°C.

behavior of colloids, where a triply charged anion is 500 to 1000 times as effective a precipitant as a monovalent anion. This effect is also to be contrasted with the data shown in Fig. 7. In these nitrate media (HNO_3, $Al(NO_3)$, $NaNO_3$), a 60-fold excess of nitrate ion is required to just initiate precipitation. The amount of aged polymer precipitated from the solutions containing 1.62 g Pu/liter reached a maximum at about 2 M nitrate ion concentration and decreased with further increase in nitrate ion concentration.

It is apparent that in most cases of process importance, if polymer is formed, it should not precipitate if the total nitrate ion concentration in the HNO_3-$Al(NO_3)_3$-$UO_2(NO_3)_2$ system is held above 4 M.

The striking difference in behavior of $LiNO_3$ as compared to the other nitrate salts is not readily apparent at this time. This anamolous behavior may be due in part to the greater mean activity coefficient of $LiNO_3$, as compared to the others, to ionic hydration phenomena peculiar to the lithium ion, or perhaps the polymer may act as an inorganic ion exchange medium and selectively absorb lithium ion.

IX. Conversion of Freshly Prepared Polymeric Pu(IV) to Ionic Pu in Nitric Acid at 25°C

The depolymerization, or conversion, of freshly made polymer to ionic plutonium in nitric acid at several acidities at 25°C is shown in Fig. 8. The curves were obtained from spectrophotometric analysis of solutions prepared by the addition of nitric acid to a more concentrated stock solution of "fresh" polymer to give the indicated acidities. Precipitation of the "fresh" polymer did not occur at any concentration of nitric acid up to 15 M. This is probably due to the relatively low molecular weight of the "fresh" polymer, as compared to "aged" polymer, and differences in charge and structure.

As expected, the rate of depolymerization increases rapidly with an increase in the nitric acid concentration. Depolymerization proceeds as a first order reaction, dependent only on the plutonium polymer concentration at fixed acidities. The times given in Fig. 8 are the times required for 50% of the polymer to be converted to ionic plutonium.

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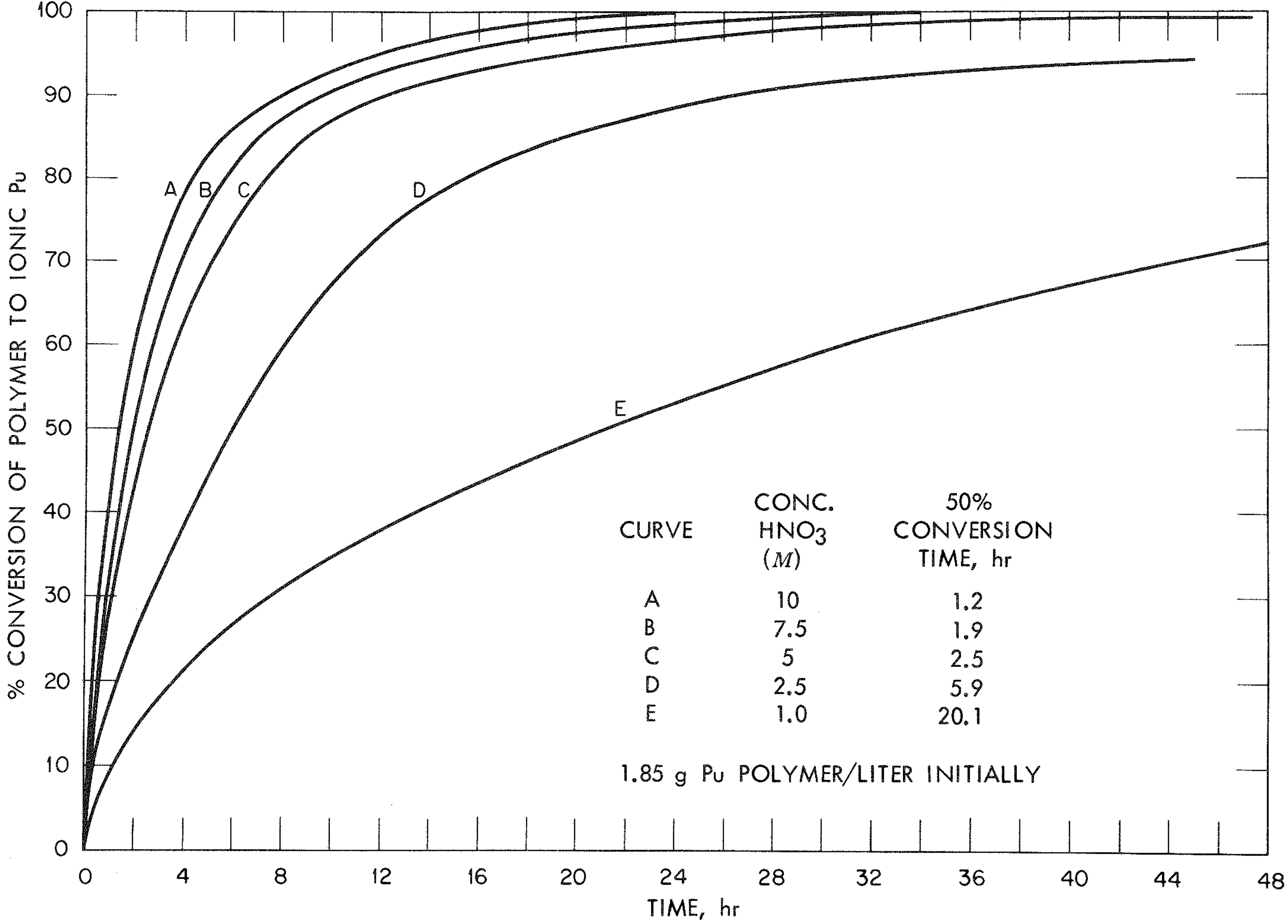

Fig. 8. Conversion of Freshly Prepared Polymeric Pu(IV) to Ionic Pu in Nitric Acid at 25°C.

X. Conversion of Aged Polymeric Pu(IV) to Ionic Pu with 5 M HNO_3 and Various Complexing Agents

The depolymerization, or conversion, of aged polymer to ionic plutonium in 5 M HNO_3 at normal and elevated temperature, and also in 5 M HNO_3 with the addition of various complexing agents is shown in Fig. 9. The time, in hours, shown to the right of the mid-point of each curve, represents the time required to convert 50% of the polymer to ionic plutonium.

In all these experiments the nitric acid concentration was maintained at 5 M to prevent precipitation of the aged polymer.

The effect of ageing on the rate of depolymerization time is indicated by a comparison of curve F (Fig. 9) with curve C (Fig. 8). The 50% conversion time for aged polymer in 5 M HNO_3 at 25°C is 320 hours, versus 20 hours for fresh polymer under identical conditions.

The remarkable effect of temperature on the rate of depolymerization of aged polymer is indicated by the comparison of the 50% conversion times of curves B at 95°C and curve F at 25°C. At 95°C the required time is 0.56 hours versus 320 hours at 25°C, which represents a 6000-fold increase in rate for a 70°C increase in temperature.

The effect of complexing agents (i.e., fluoride and sulfate) on the rate is indicated by curves A, C, D, and E. As one might expect, the rate of depolymerization in the presence of fluoride is far greater than in the presence of sulfate, as is indicated by the 50% conversion time of 3.2 hours for 0.001 M F^-, versus 18 hours for 0.1 M SO_4^{2-} (curves C and E). If one were to compare fluoride ion with sulfate ion at equal concentration, the difference in rate would be further emphasized, i.e., 0.001 M sulfate would have a negligible effect.

The effect of 0.001 M F^- ion on the rate of depolymerization is shown by a comparison of the rate curves C and F, which show a 100-fold decrease (from 320 to 3.2 hours) of the 50% conversion time with fluoride present. If the fluoride ion concentration is increased to 0.05 M F^- the conversion to the ionic state is complete within less than 5 minutes (not shown in Fig. 9).

The difference in the rate as indicated by curves C and D for 0.001 M F^- shows the effect of complexing of the fluoride by aluminum.

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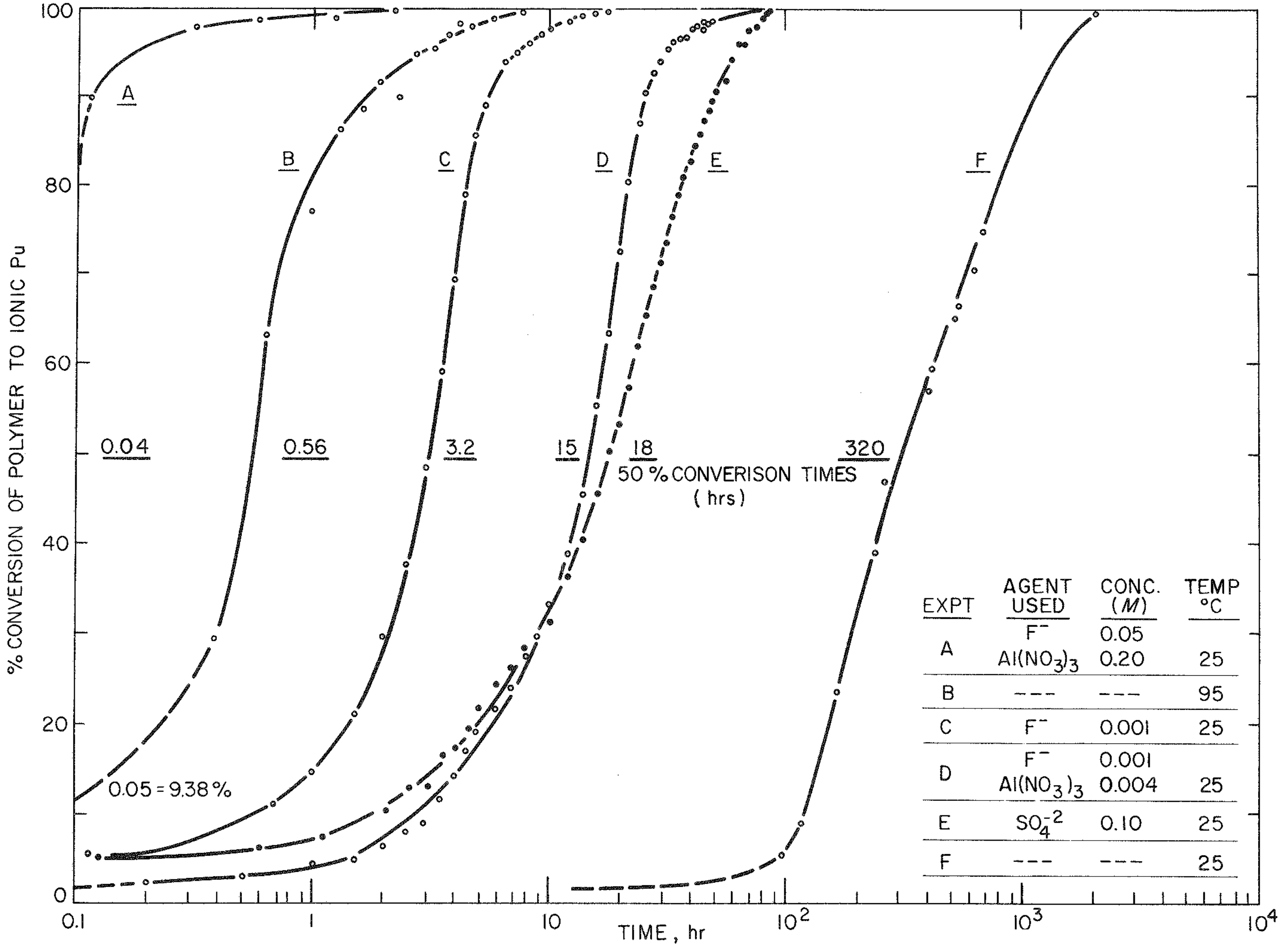

EXPT	AGENT USED	CONC. (*M*)	TEMP °C
A	F^- $Al(NO_3)_3$	0.05 0.20	25
B	---	---	95
C	F^-	0.001	25
D	F^- $Al(NO_3)_3$	0.001 0.004	25
E	SO_4^{-2}	0.10	25
F	---	---	25

Fig. 9. Conversion of Aged Polymeric Pu(IV) to Ionic Pu with 5 M HNO_3 and Various Complexing Agents.

The presence of aluminum is desirable under processing condition to minimize corrosion of process equipment by fluoride. Curves A and D show the effect of fluoride ion concentration on the rate when aluminum is present in a 4:1 mole ratio of Al to F^-. Complexing of the fluoride by aluminum decreases the rate of depolymerization by a factor of about 5. For a fifty-fold increase in the concentration of fluoride (and aluminum), approximately a 400-fold increase in rate is indicated by the 50% conversion times. The maximum difference in rate obtained in this study is indicated by the difference between curves A and F, which show an 8,000-fold increase in the rate of depolymerization of the polymer.

Although the presence of fluoride in 5 M HNO_3 results in a tremendous increase in the rate of depolymerization, the presence of fluoride does not prevent the polymerization of ionic quadrivalent plutonium at low acidities. For a solution containing 2.2 mg Pu/ml initially present as Pu^{4+} and 0.04 M HNO_3 - 0.2 M $Al(NO_3)_2$ - 0.05 M NaF, the extent of polymerization of Pu^{4+} is comparable to that of a solution of similar acidity and aluminum nitrate concentration containing no fluoride.

The results of this study clearly show that polymer formation can be prevented by the proper control of process solution conditions, and that polymer, once formed, can be depolymerized.

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