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Plutonium(IV) and Thorium(IV) Hydrous Polymer Chemistry

G. L. Johnson
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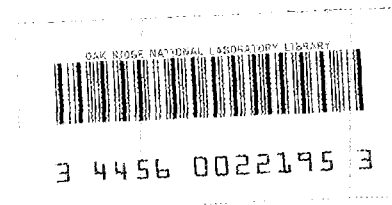
CHEMISTRY DIVISION

PLUTONIUM(IV) AND THORIUM(IV) HYDROUS POLYMER CHEMISTRY

G. L. Johnson and L. M. Toth

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PLUTONIUM(IV) AND THORIUM(IV) HYDROUS POLYMER CHEMISTRY

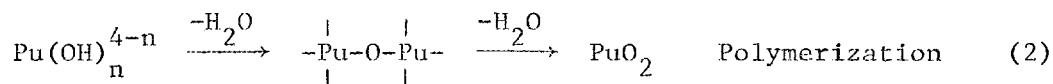
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ABSTRACT

The recent attention given to Pu(IV) polymers has warranted a review of plutonium and thorium hydrolysis chemistry with respect to the various experimental approaches and insights gained therein. Differing terminologies used in the experimental procedures have often confused the understanding of the chemical processes which occur between the first hydrolysis reaction of the tetravalent actinide and its final dehydration to form the crystalline oxide. This report focuses on the polymer aging reaction which is defined here in terms of A. W. Thomas' ol to oxo conversion reaction and involves simply the conversion of hydroxyl-bridged polymer links to oxygen-bridged linkages. Thorium(IV) hydrolytic reactions are included because they are analogous in many respects to those of Pu(IV) and offer a simpler chemical system for experimental study. Future work using spectroscopic techniques should significantly improve the description of this aging phenomenon.

1. INTRODUCTION

During the past thirty-five years considerable attention has been focused on Pu(IV) polymer chemistry because of its interference in nuclear fuel ion-exchange and extraction schemes. The polymerization of Pu(IV) ordinarily follows so closely after its hydrolysis that the two reactions are experimentally difficult to separate. Conceptually, however, the reactions can be treated separately and written as:



where, by elimination of water, the hydrolyzed form of the tetravalent ion forms cross-linked groups of Pu atoms, polymeric colloids, precipitates, and ultimately, crystalline PuO_2 . Were it not for their part in the nuclear fuel cycle, the reactions depicted above probably would not have received much attention because the detailed mechanisms involved are most difficult to study under controlled conditions — even with modern instrumentation.

Research on Pu(IV) hydrous polymers has proceeded along several approaches.¹ Initially the Pu(IV) hydrolysis and polymerization reactions were examined but the rapid irreversible polymerization of the hydrolysis products prevented the identification of any products beyond the mono-hydroxy species. Ultracentrifugation and light scattering experiments were subsequently used to describe the extent of polymerization which was found to vary from 10 - 10^8 molecular units. However, the difficulty of conducting experiments on Pu(IV) ultimately led most of the early researchers to hydrolysis studies on other metal cations that produced simple aggregates of only a few monomer units in length.

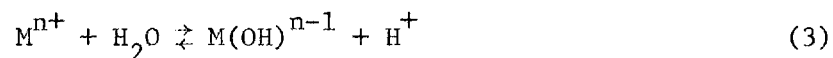
During the past 10-15 years, the recurring problem of inextractable plutonium polymer in fuel reprocessing solutions and waste effluents has encouraged further efforts toward control of the polymer chemistry. These efforts have focused heavily on (1) the prevention of polymer formation, (2) the determination of kinetic parameters which permit operation without the polymer reaction² and (3) the reversal of the polymerization reaction once it had occurred.³ Within this period there has developed a tendency to interpret current data in terms of models that neglect many of the earlier fundamental concepts. Realizing that such a pitfall is encouraged by the limited number of open literature publications on the plutonium polymerization subject, it was clear that a review of some earlier concepts would be very helpful in the development of further discussions and research efforts. This report is not intended to be an all-inclusive review of actinide hydrolysis and polymerization phenomena; but instead it is intended to present the current data in the perspective of some classical models. It will conclude by

showing that a single unifying model which is consistent with all the experimental data can be given for the polymerization reaction. Nevertheless, there are aspects of this model which require further work. Because differences in terminology often obscure the comparison of the many kinds of data, we shall endeavor to describe these data with reference to the actual chemical processes taking place. Therefore, our reference point shall be the reactions themselves with emphasis on the chemical (as opposed to the physical) phenomena. Thorium is included in the discussion because it is analogous to plutonium in many aspects of its polymer chemistry. The greater ease of handling thorium compounds and its much simpler chemistry makes it an attractive starting point from which to begin.

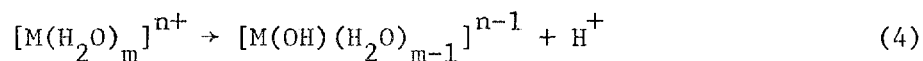
2. BASIC CONCEPTS^{4,5}

2.1 Hydrolysis

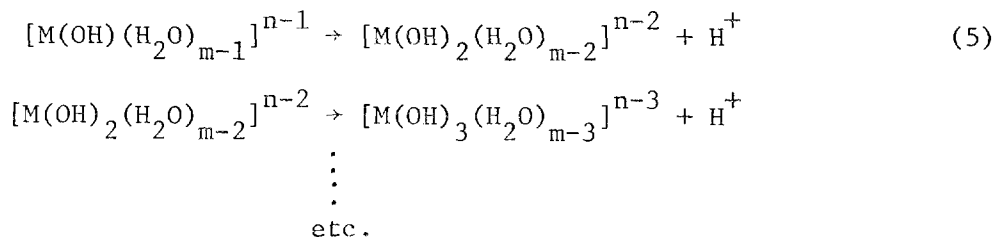
Nearly all metal cations undergo hydrolysis when their salts are dissolved in water. This is represented simply by:



Not shown in this equation are the waters of solvation about the metal cation, which are assumed to decrease in number according to the extent of hydrolysis. A more complete representation of the above process that includes the solvating water is considered important to the current discussion because it is this water which is involved in the hydrolysis and polymerization reactions. Including the water, Eq. 3 becomes:

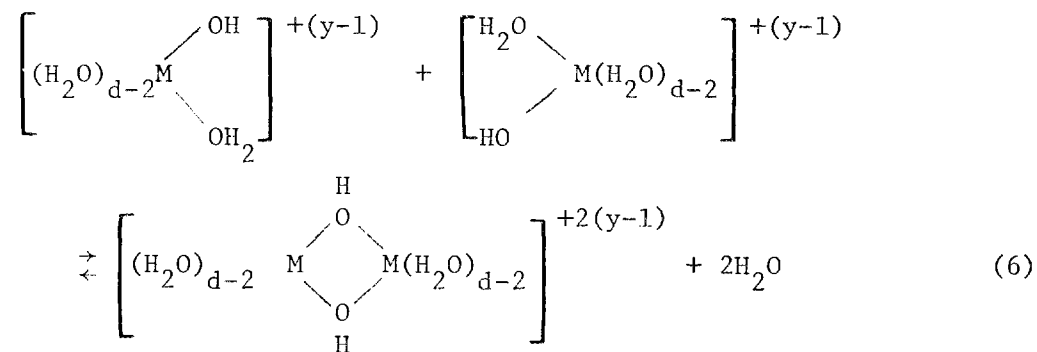


Subsequent steps may also occur in the hydrolysis and are indicated as:



These reactions, in effect, involve nothing more than the conversion of H_2O ligands to OH^- . But, as will be evident later, other chemical reactions and/or attainment of solubility limits compete with the simple hydrolysis scheme given above and complicate the chemistry of the system.

One such alternate route prior to complete hydrolysis is the aggregation of two or more hydrolyzed species as depicted in the following simplified equation:



In reactions such as this, a solvating water molecule about one cationic species is replaced by a hydroxyl group already attached to another. The hydroxyl ion is thus shared by the two metal atoms forming a polynuclear hydroxyl-bridged aggregate. In the example of Eq. 6, two hydroxyls are being shared after the elimination of two waters to form a cyclic dinuclear species. By a continuation of the above process it is possible that high molecular weight polynuclear chains, sheets, and even three-dimensional structures can form.

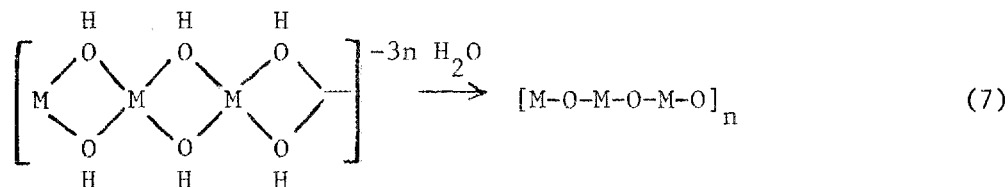
Some examples of metallic ions that undergo aggregation reactions in aqueous solution are given in Table 1.

Table 1. Metallic ions undergoing cationic aggregation processes in aqueous solution^{4,5}

Oxidation state	Metallic ions
II	Ni, Hg, Co, Be, Cu, Sn, Pb, Mn, Mg, Cd, Zn
III	Al, Cr, In, Ga, Sc, La, Co, Rh, Fe, Bi
IV	Zr, Hf, Th, U, Pu, Ru, Np, Ti, V (as in VO^{+2}), Ce
V	Pa, Pu (as in PuO_2^+), Np (as in NpO_2^+)
VI	U (as in UO_2^{+2}), Np (as in NpO_2^{+2}), Pu (as in PuO_2^{+2})

Not all the metals listed in Table 1 yield high molecular weight species in solution. Some form only dinuclear or trinuclear complexes. For example, Ce^{4+} , Fe^{3+} , and V^{4+} form only dinuclear species upon hydrolysis; Be^{2+} forms a trimer; Bi^{3+} , at high pH, forms polymers with 5-6 units; but Th^{4+} and Pu^{4+} form polymers with molecular weights of at least 4000.

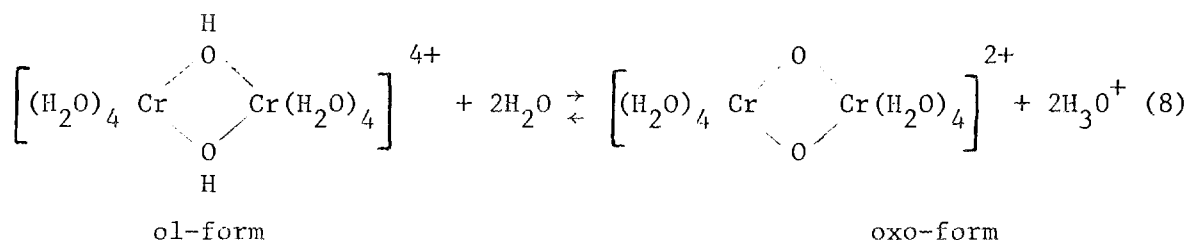
A. W. Thomas was one of the first to interpret these polymerization phenomena consistently⁶ as a result of his work on the metallic ions such as Al^{3+} , Th^{4+} , and Zr^{4+} . He coined the term "olation" for the formation of such "diol" (dihydroxy) bridges as shown in Eq. 6 and he identified the polymer thus bridged by hydroxyl groups as the "ol" form. Under appropriate conditions (generally those of high temperature, prolonged aging, and/or high pH) he observed irreversible elimination of more water accompanied by the formation of oxygen bridges between the metal atoms. For example:



Thomas suggested^{5,6} the term "oxolation" for the reaction and he identified the resultant product as the "oxo" form of the hydrolyzed species. Pokras⁶

alludes to some "doubtful points in the oxolation argument"; but, for our purposes, the concept of hydroxyl- to oxygen-bridging conversion appears to be the most plausible characterization of the polymer aging process and shall be used as the reference model throughout this report.

Another means of obtaining the oxo species is by the loss of a proton from every hydroxyl group.⁵ This mechanism has been suggested to account for the observation that solutions of basic chromium salts become more acidic and the salts less soluble when solutions are heated. This reaction can be represented by:



Although the reaction is indicated as reversible, the back reaction is very slow. In general, ol-compounds are more readily depolymerized by protons than oxo-compounds in support of the "oxo" = "aged" equivalence. The solid manifestation of the aged polymer is a material which is more difficult to dissolve and has a sharper diffraction pattern with characteristics of the crystalline oxide. Olation and oxolation phenomena have been shown or are suspected to exist in solutions of the metallic cations listed in Table 1.

2.2 Sol-Gel Phenomena

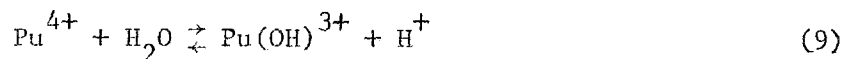
As the hydrolysis and aggregation (polymerization) reactions of Eqs. 4-8 proceed, the aggregates increase in size and rapidly reach colloidal dimensions (a size that is rather arbitrarily given as 10-1000 Å).⁷ Dispersed in solution, these colloidal polymers are referred to as sols whereas the precipitates, which result from flocculation of the dispersed aggregates, are identified as gels. The dispersal of a polymer, once precipitated, is known as peptization and is often accomplished by acid "dissolution" of the gel. Under certain conditions sols of some cation

aggregates, notably Th^{4+} and Pu^{4+} , can remain stable for years¹ and exhibit many properties identical to those of true solutions. Particularly useful in this regard is the stability of Pu^{4+} polymer sols which permit concentration determinations through the measurement of visible-UV spectra and the application of Beer's Law.

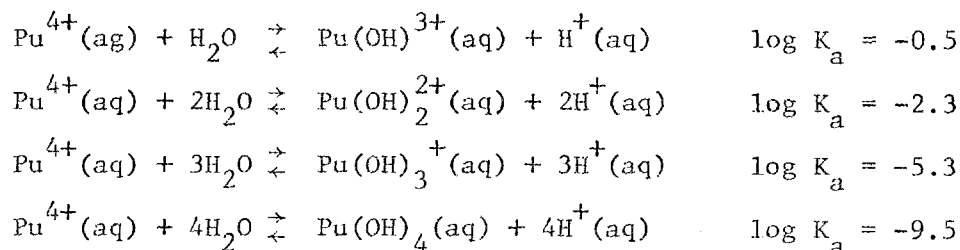
Various experimental techniques have been useful in the study of cation aggregates formed by hydrolysis. These have been reviewed by Gimblett⁵ and more recently by Baes & Mesmer.⁴ The procedures include potentiometry, visible-UV spectroscopy, ultra-centrifugation, x-ray and electron diffraction, light-scattering, and microscopy. Some specific examples will be cited later in this report as they apply to Pu(IV) and Th(IV) polymers.

3. Pu(IV) HYDROLYSIS AND POLYMERIZATION

The hydrolytic behavior of Pu(IV) is consistent with the general description given in the preceding pages. At acidities greater than about 0.1 N, Pu(IV) exists as a simple tetravalent cation coordinated to water and, under suitable conditions, to available anions such as Cl^- or NO_3^- .^{2,8} The first hydrolysis constant for the reaction



has been measured in aqueous perchlorate solutions by Rabideau,⁹ and Kraus and Nelson.¹⁰ Values of $\log K_{\text{conc}}$ have been found by these authors to range from -1.27 to -1.73 at 25°C in 2 M perchlorate solutions (LiClO_4 and NaClO_4). In 1973, Metivier¹¹ obtained evidence for the existence of the hydrolytic species: $\text{Pu}(\text{OH})_2^{2+}$, $\text{Pu}(\text{OH})_3^+$ and $\text{Pu}(\text{OH})_4$. Baes and Mesmer⁴ have estimated the following $\log K_a$ values assuming no polymer formation occurs:



Invariably, however, the polymerization of Pu(IV) follows the first hydrolysis reaction as the acidity of the aqueous solution is decreased to 0.1 N and below. The formation of Pu(IV) polymer is dependent on the Pu(IV) concentration, the acidity of the medium, the presence of other complexing ions and the temperature. Depolymerization of Pu(IV) polymer is often very slow and becomes even slower for polymers formed at elevated temperatures (i.e., polymers that have been aged). The aged polymers are more difficult to depolymerize because of more extensive cross-linking and probably also because of a modification of the bridging structure from hydroxyl- to oxygen-bridged groups. Costanzo and Biggers³ have reported that in 5 N HNO_3 at 25°C, polymers that had been aged for several months at room temperature or for 24 hr at 100°C had a depolymerization half-time of 320 hr compared to only 20 hr for freshly prepared polymers under otherwise identical conditions. Depolymerization of even the aged polymers becomes rapid at elevated temperatures; e.g. the half-time is 0.56 hr at 95°C. More recently, Bell, Friedman and Toth^{12,13} have reported similar findings for the photodepolymerization rates of fresh and aged polymers dispersed in $HClO_4$ solutions.

The polymer has a small positive charge which enables it to be almost completely precipitated by equivalent quantities of ions such as nitrate iodate, sulfate, oxalate, phosphate and ferricyanide; and experimental results^{14,15} have demonstrated that the average charge per monomer unit is +0.15 to +0.40. Polymers precipitated from chloride solutions yield no additional chloride ion on depolymerization which suggests that the polymer network is held together by hydroxyl and oxygen bridges with the exclusion of chloride ions. Polymer molecular weights of 4×10^3 to 10^{10} have been reported¹ by various investigators. Apparently the variation is due to the method of polymer preparation.

It has been stated in some instances¹ that the rapid precipitation of Pu(IV) by the addition of strong base results in monomeric Pu(IV) species whereas Pu(IV) first polymerized, then precipitated and redissolved gives a solution composed entirely of polymeric Pu(IV). However, using the model proposed by Thomas, an alternative interpretation is that the

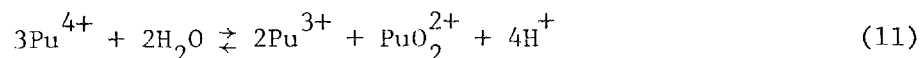
rapidly precipitated form is actually a hydroxy-bridged polymer which readily dissociates back to monomeric species if redissolved in solutions of appropriate acidity while the solutions from which Pu(IV) is first polymerized and then precipitated contain substantial oxygen bridging in the polymer network.

In other studies, Haire, Lloyd, Beasley, and Milligan¹⁶ have shown through electron microscopy and diffraction measurements that the freshly precipitated Pu(IV) polymers consisted of small amorphous particles. After sufficient aging in an aqueous medium, the amorphous material became essentially crystalline with diffraction patterns corresponding to the cubic PuO₂ (oxygen-bridged) fluorite structure. The authors found no indication of a definite crystalline hydroxide such as Pu(OH)₄. This is not altogether surprising since the hydroxyl-bridged polymer, which could possibly have a Pu(OH)₄ stoichiometry, probably occurs only as an amorphous material and any attempts to crystallize it merely results in aging, loss of water, and the formation of the more stable PuO₂ structure. (It seems reasonable to expect a crystalline modification of Pu(OH)₄ might be possible at low, <20°C, temperatures). As a result of their measurements, Lloyd et al describe the Pu(IV) polymer as consisting of primary discrete crystalline particles (25Å size) which aggregate into larger particles as polymerization progresses. Their model aptly describes diffraction and microscopic data but does not touch on the chemical bonding in the particles. Even though it presents a unique view of the Pu(IV) polymer, it is still consistent with the Thomas model which predicts the chemical changes that must be occurring concurrently with the physical aggregation of primary particles since the fresh amorphous particles most probably would contain monomer units held together by extensive hydroxyl bridging while the aged crystalline particles would contain a predominant number of oxygen-bridged units.

One aspect of the chemistry of the various plutonium(IV) hydroxides and the oxide that has been ignored by many researchers is the ability of these materials to absorb carbon dioxide. In an infrared study by Toth and Friedman¹⁷ of plutonium(IV) polymer, the polymer was found to absorb

CO₂ from the air with the resulting formation of carbonate-ion functional groups in the polymer structure. The atom ratio of Pu/C in an atmosphere-equilibrated polymer gel was estimated to be about 3. In another study of the adsorption of CO₂ on uranium and plutonium oxides,¹⁸ it was observed that for UO_{2.04} a very fast adsorption occurred in less than a tenth of a second followed by a slow adsorption lasting in excess of 16 hours. Similar results were observed for PuO₂ but an analytical study was not possible. The CO₂ fractional coverage for PuO₂ increased from 0.18 to 0.46 at 30°C as the CO₂ pressure was increased from 15 to 300 torr. The coverage for both oxides, UO₂ and PuO₂, decreased for temperatures from 60 to 100°C. From these experiments, it is conceivable that atmospheric CO₂ may be an important factor in the chemistry of these systems and is worthy of further investigation. It could possibly provide a reaction mechanism which would give some insight into reactive sites in the polymer network.

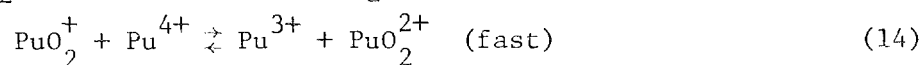
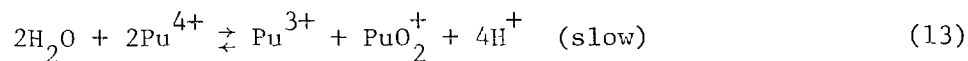
The subject of Pu(IV) hydrolysis and polymerization cannot be left without recognizing a competing reaction that occurs when base is added to strongly acidic solutions of Pu(IV) -- the disproportionation of Pu(IV):



The disproportionation equilibrium constant,

$$K = \frac{[\text{Pu}^{3+}]^2 [\text{PuO}_2^{2+}] [\text{H}^+]^4}{[\text{Pu}^{4+}]^3}, \quad (12)$$

in HCl solutions of unit ionic strength at 25°C is 1.9×10^{-3} . For similar conditions but using HClO₄, K is reported to be 8.9×10^{-3} . Although the net reaction for Pu(IV), disproportionation can be represented as indicated above, Connick¹⁹ has shown that the overall reaction consists of two separate steps:



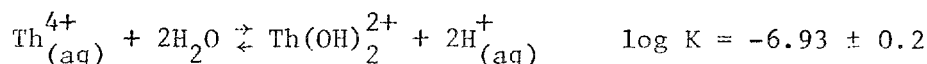
The oxidation potentials of the plutonium(III-IV), (IV-V), and (V-VI) couples are so close that all of these states and their hydrolysis products may coexist over a fairly wide set of conditions. The net effect of the disproportionation equilibrium in relation to hydrolysis and polymerization is to complicate the hydrolysis kinetics of Pu(IV)²⁰ and to retard the hydrolytic reactions by the acid produced in the reaction represented by Eq. 11.

4. Th(IV) HYDROLYSIS AND POLYMERIZATION

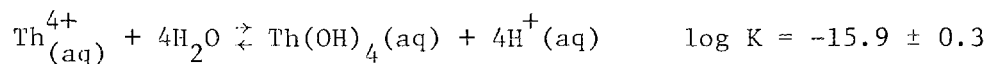
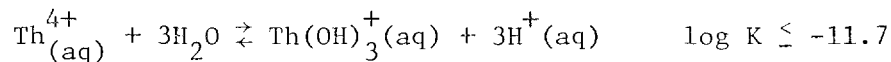
Th⁴⁺ ion is the largest tetravalent cation (ionic radius of about 1.0 Å in comparison to Pu⁴⁺ and U⁴⁺ which have 0.90 and 0.93 Å radii, respectively²¹) and, therefore, the most resistant to hydrolysis. It forms stable complexes with fluoride ion and with oxygen-donor ligands. Important insoluble compounds are those with fluoride, iodate, oxalate, phosphate, and oxide.⁴

Hydrolysis becomes detectable in solutions of "ordinary" concentrations between pH 2 and 3. The hydroxyl number, \bar{n} , i.e. the number of hydroxides per Th(IV), depends upon the thorium concentration and, in perchlorate solution, can reach values of 2.5 near pH 4 before "irreversible" hydrolysis in solution or precipitation of hydrous ThO₂ occurs. The maximum hydroxyl number that can be attained reversibly is considerably lower in chloride solutions and lower still in nitrate solutions.

Even at the lowest values of \bar{n} and Th(IV) concentrations, mononuclear species have been clearly identified only in perchlorate solutions. The first two hydrolysis constants for mononuclear species in 1 M NaClO₄ are:^{22,23}



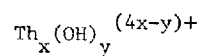
Baes and Mesmer⁴ estimate log K values for the formation of the next two hydrolysis products to be as follows:



Polymeric hydrolysis products of Th(IV) have been studied intensively with the dimer, $\text{Th}_2(\text{OH})_2^{6+}$, and a hexamer, either $\text{Th}_6(\text{OH})_{14}^{10+}$ or $\text{Th}_6(\text{OH})_{15}^{9+}$ being proposed in nearly all the studies. It is clear that additional polynuclear species are formed, but there is little agreement about the identity of these additional products. Table 2 summarizes the rather extensive list of Th(IV) hydrolysis products that have been proposed and/or identified.

Hentz and Johnson,²⁴ in a study of the polynuclear hydrolysis products of Th^{4+} in 1 M ClO_4^- solutions, found an increase in the weight-average degree of polymerization with increasing \bar{n} that showed no evidence of leveling off at $\bar{n} \approx 2.5$. The average charge per monomer unit was found to be less than $4-\bar{n}$. This indicates that ClO_4^- ion is included in the polymeric species. Johansson²⁵ found discrete dimeric complexes, $\text{Th}_2(\text{OH})_2(\text{NO}_3)_6(\text{H}_2\text{O})_6$, in the crystal structure of the basic nitrate, $\text{Th}(\text{OH})(\text{NO}_3)_3(\text{H}_2\text{O})_4$. The two thorium atoms, at a distance of 3.94 Å, are joined by two OH bridges. Each thorium atom is coordinated also by three bidentate nitrate groups and three water molecules for a total coordination number of 11. From x-ray scattering measurements of 2 M $\text{Th}(\text{NO}_3)_4$ aqueous solutions, Johansson²⁶ concluded that when Th^{4+} is hydrolyzed: (1) polynuclear hydrolysis products are formed in which the shortest distance between thorium atoms is 3.94 Å; and the thorium atoms are most probably joined together by double hydroxide bridges; (2) The average number of thorium atoms nearest a given thorium atom increases from approximately 1 at $\bar{n} = 0.7$ to approximately 3 at $\bar{n} = 2.4$; the experimental data indicates that the average degree of polymerization does not exceed 5 or 6 up to $\bar{n} = 2.4$; (3) Even though it is necessary to assume more than one important polynuclear species besides the dimer, identification of the other species was not possible; (4) The number of oxygen atoms around each thorium atom

Table 2. Proposed hydrolysis products of Th⁴⁺



Medium	Maximum Th(IV) conc. $\frac{M}{l}$	Maximum \bar{n}	x,y																	Reference
			1,1	1,2	2,1	2,2	2,3	2,4	2,5	3,1	3,3	3,5	3,6	4,8	4,12	6,14	6,15	10,25		
1M (Na)ClO ₄	0.016	2.5	(X)	X		X												(other polynuclear species)	22	
1m (Na)ClO ₄	0.02	2.3	X	X		X							X or X				X		23	
1M (Na)ClO ₄	0.5	2.0			X			X			X		(X)		X				27	
3M (Na)Cl	0.1	1.7				X	X		(X)	(X)	X				X			(X)	28	
3M (K)NO ₃	0.13	0.47		(X)		X	X										X		29	
3M (Li)NO ₃	0.12	0.42				X				(X)	X								29	
3M (Mg)(NO ₃) ₂	0.12	0.52				X					X						X		29	
4M (Na)NO ₃	0.5	1.5				X							X		X				27	

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decreased from 11 to approximately 9.5 with increasing \bar{n} ; bidentate nitrate groups were included in the coordination. Johansson drew similar conclusions about perchlorate and chloride solutions. Concerning the structure of the polymers, Johansson found tetrahedral tetramers to be consistent with the data; and there was no evidence for either long chains of the type $[\text{Th}(\text{OH})_2]_n$ or hexamers with a regular octahedral structure.

Lundgren³⁰ has reported that thorium hydroxide, $\text{Th}(\text{OH})_4$, is easily prepared by precipitation with an excess of aqueous ammonia or sodium hydroxide. Its structure consists of a long chain built up of zig-zag rows of Th(IV) ions situated on alternate sides of a double row of hydroxide ions.³⁰ Thorium dioxide, ThO_2 , is obtained by ignition of the oxo acid salts or of the hydroxide. Both ThO_2 and polymeric $\text{Th}(\text{OH})_4$ can be peptized with dilute HNO_3 to form sols. Both sols contain some nitrate ion [0.08 mole NO_3^- /mole Th for the sol prepared from ThO_2 and 0.3 mole NO_3^- /mole Th for the sol prepared from polymeric $\text{Th}(\text{OH})_4$.] This adsorbed NO_3^- can be reversibly displaced from the sol by CO_2 .

5. CONCLUSIONS

Although differing in degree, the hydrolytic behavior of Pu(IV) and Th(IV) is quite similar. Plutonium begins to hydrolyze at pH values near 1 whereas Th(IV) does not hydrolyze until pH values are between 2 and 3. Although Th(IV) also forms polymeric hydroxyl and oxygen-bridged species, the extent of polymerization is not as great as in the plutonium case; consequently, more low molecular weight hydroxyl species have been characterized for Th(IV) than for Pu(IV). Figure 1 summarizes the hydrolytic behavior of these ions and reviews the regions where the terms introduced in this report are defined. Also shown in the figure are the regions touched by the various experimental approaches and finally the fuel reprocessing problem area which still requires further attention.

In this report we have sought to present all of the terminology and methodology used in previous investigations of actinide hydrolytic reactions and to stress that although these studies have been directed at the

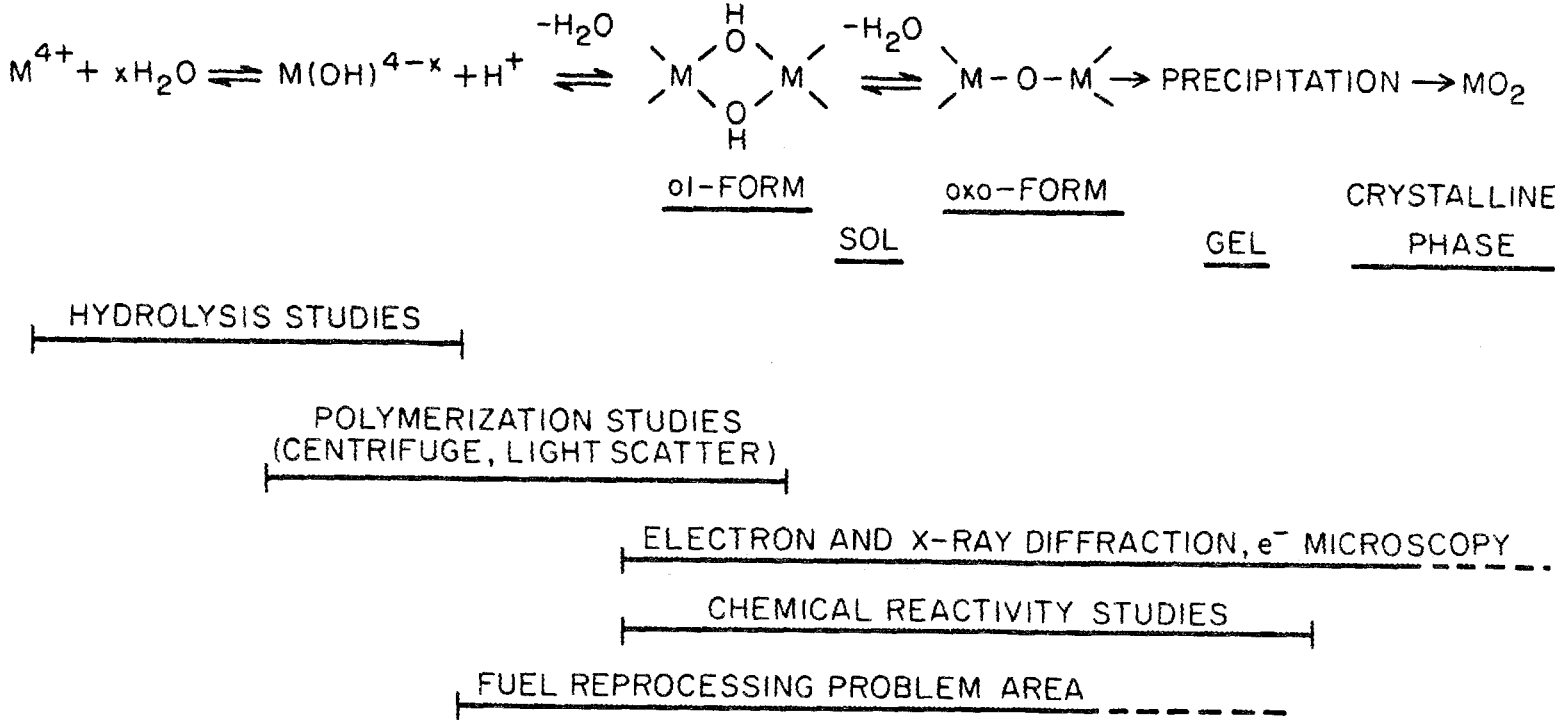


Figure 1. Hydrolysis and Polymerization of Tetravalent Actinides.

same overall process, they have often been focused on certain discrete steps. Because of the focus, discontinuities in our understanding of the general process and a failure to appreciate the need of further research can easily arise. Although the simple hydrolysis reactions have been fairly well characterized, details on the polymerization, depolymerization and aging processes have not. Polymer aging, though commonly recognized as meaning increased polymer stability and greater crystallinity, still remains somewhat of a mystery when viewed from a chemical bonding aspect. It is remarkable that the almost obsolete "ol - oxo" model of Thomas is consistent with so many of the experimental observations made to date. To our knowledge, there are no exceptions that would suggest this model to be inadequate; and as a consequence, we propose that the ol-oxo model be used to describe the aging phenomena. It is our belief that the usage of structural methods such as IR and Raman spectroscopy could elucidate the chemical aspects of polymer aging, but in the meantime, such models will remain essential to our understanding of the polymer chemistry.

6. ACKNOWLEDGEMENTS

The authors wish to thank J. T. Bell for his many helpful comments and interest in this work.

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