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SOL-GEL PREPARATION OF LANTHANIDE OXIDE MICROSPHERES AND CHARACTERIZATION OF SOLS AND GELS OF LANTHANIDE HYDROXIDES, THORIA, URANIA, AND PLUTONIA

CFSTI PRICES

C. J. Hardy*

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*Guest scientist from the Chemistry Division, Atomic Energy Research Establishment, Harwell, England; terminal report for period March, 1965 to July, 1966.

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SOL-GEL PREPARATION OF LANTHANIDE OXIDE MICROSPHERES AND CHARACTERIZATION OF SOLS AND GELS OF LANTHANIDE HYDROXIDES, THORIA, URANIA, AND PLUTONIA

C. J. Hardy

ABSTRACT

Laboratory methods have been developed to produce microspheres of lanthanide oxides with a controlled size (50-500 microns diameter), high density (up to 98% of theoretical crystal density), low surface area (0.01-0.1 m^2/g), and good crushing strength, by using sols and gels of the hydroxides as intermediates. Lanthanide oxides in this form are useful as neutron absorbers in reactor control rods, as burnable poisons in fuel elements, and as high-intensity β-γ sources in numerous applications. The knowledge gained is being applied to the preparation of oxides of americium and curium for incorporation in targets in the High Flux Isotope Reactor.

UV, visible, IR, and Raman spectra of sols and gels of lanthanide hydroxides, thoria, urania, and thoria-UO_3 mixtures, were measured to (a) determine the nature of the bonding between the components, e.g., nitrate and lanthanide ions, (b) obtain rapid analyses for nitrate and lanthanide ions, and (c) determine the size of the colloidal particles by turbidity and light-scattering measurements (both methods gave results in good agreement for thoria sols containing particles of 200 A diameter, but appreciably larger than the crystallite size measured by x-ray line-broadening; the difference may be due to aggregation or to poly-dispersity). Preliminary measurements of the turbidities of plutonia sols were made, and difficulties were experienced in interpreting the results; the particles in one sol appeared to have a diameter of about 640 A and a molecular weight of 9×10^8.

Sols and gels of lanthanide hydroxides and urania were examined by electron microscopy and electron diffraction to determine the size, shape, and crystallinity of the colloidal particles at the various stages in the processes to make microspheres of oxides. Freshly precipitated U^{4+} hydroxide contained amorphous particles of 20 to 30 A diameter, which when aged for days at 25°C or hours at 60°C, changed into primary cubic crystals of UO_2 with sides 10 to 20 A which were combined into loose aggregates of up to 800 A diameter. Lanthanide hydroxides were also in the form of amorphous particles of 30 to 60 A diameter when freshly precipitated. These changed into crystalline sheets up to several hundred angstroms wide when aged in the mother liquor, or into rods, tubes, or rolled sheets up to several thousand angstroms long when thoroughly washed and aged in water. Randomly arranged bundles of these rod-shaped crystals were present in microspheres of the lanthanide hydroxide gels. Electron micrographs of replicas of etched polished surfaces of the dense oxides obtained by heating the gels to 1450°C showed grains of width 5 to 10 μ containing oriented crystalline units of width 0.2 to 0.5 μ. The oriented units were probably polycrystalline because x-ray line-broadening measurements indicated a crystallite size of 500 to 700 A.

1. INTRODUCTION

Methods for the production of sols and gels of the lanthanide elements, and for the characterization of these, and also of sols and gels of thoria, urania and plutonia, have been examined over a period of 18 months in collaboration with members of the Chemical Technology Division.

Sols and gels of the lanthanide hydroxides were examined firstly with a view to developing a method for preparing microspheres of dense oxides for various applications, e.g., for incorporation in cermets in reactor control rods, and secondly to obtain knowledge which would help in the preparation of microspheres of oxides of americium and curium for incorporation in targets in the High Flux Isotope Reactor at Oak Ridge. Preliminary results were reported in internal memoranda and the methods and results were outlined in papers presented at symposia at Berkeley[1] and Denver[2] in June, 1966. Details of the work will be given in an ORNL report in course of preparation[3], hence only a summary of the work is given in section 2 of this report.

Electron microscopy and electron diffraction patterns have been used to determine the size, shape, and crystallinity of the colloidal particles at various stages in the preparation of sols and gels of the lanthanide hydroxides (section 2) and also of UO_2 (section 3). The details of the work on UO_2 are given in ORNL-3963[4], and therefore only a summary of the results is given in section 3.

UV, visible, IR, and Raman spectra of sols and gels of lanthanide hydroxides, thoria, urania, and thoria-UO_3, have been measured to (a) rapidly analyse the concentration of nitrate and lanthanide ions in sols and gels, (b) determine the nature of the bonding between the components, e.g., nitrate and metal ions, and UO_3 adsorbed on particles in ThO_2-UO_3 sols, and (c) determine the size of the colloidal particles by turbidity and light-scattering methods. Preliminary measurements have also been made on PuO_2 sols, and these have shown up some problems in interpreting the data. The spectroscopic work is described in detail in section 4 of this memorandum.

2. PREPARATION OF LANTHANIDE OXIDE MICROSPHERES BY SOL-GEL METHODS

This program was carried out in collaboration with S. R. Buxton and M. H. Lloyd to obtain, on a laboratory scale, microspheres of lanthanide oxides with a density close to the theoretical crystal density, and with a high crushing strength. In addition, the sols and gels used as intermediates were characterized by chemical analysis, electron microscopy, and spectrophotometry. Details of the work will be given in an ORNL report in course of preparation[3].

The main method of preparation of the sols of lanthanide hydroxides was as follows:

(a) the hydroxide was precipitated by adding a 0.2 M lanthanide nitrate solution to a 20-fold excess of 8 M NH_4OH stirred in a beaker at 25°C;

(b) the precipitate was centrifuged and washed with CO_2-free distilled water five to six times, with intermediate centrifugation and decantation of the wash liquors; a volume of about 200 ml of water per g of metal was used and the pH of the wash liquor decreased from 11 to 9.1-9.4.

(c) the damp paste was shaken for a few minutes, during which time it liquefied to form a fairly viscous sol containing about 0.4-0.5 M metal and a residual nitrate concentration of about 0.04 M (for Eu and the heavier lanthanides) to 0.1 M (for the lower lanthanides). The sols were heated for 1 to 2 hr at 80°C, during which time the initially amorphous colloidal particles were converted to crystalline particles (see electron microscopy results later), the pH decreased to 5-6.5, and the viscosity decreased to less than 2 cp. The sols were then concentrated to 2.5-3 M metal in a rotary vacuum evaporator.

Microspheres of gel were prepared by injecting droplets of the sols into a long-chain alcohol in a tapered column in which an upflow of the alcohol fluidized the droplets[5]. The alcohol (generally 2-ethyl-1-hexanol) dehydrated the sol spheres, and glassy gel spheres were formed of controlled size in the range 30- to 900-μ diameter. The spheres were filtered out from the solvent after a period of 30 min to 1 hr, washed with methanol, and dried. They were free-flowing at this stage. One problem which was encountered in the column was a tendency for the microspheres to agglomerate. This could be prevented only by the addition of small amounts of surface-active agents, e.g., 0.2 vol/vol % Amine O (Geigy) and 0.05% Span 80 (Atlas).

The gel microspheres were converted to oxide microspheres by (a) drying them at 100° to 125°C for several hours in vacuum, (b) heating them at about 100°C per hr to 500°C in vacuum and holding them at that temperature for about 3 hr to decompose residual nitrate, (c) heating them at about 100°C per hr to a temperature between 1000 and 1500°C in air and holding them at that temperature for about 3 hr to obtain a high density product. The shrinkage of microspheres of europium hydroxide gel initially 560 μ diameter (prepared from a 3 M sol) on heating them to 1450°C by the above method was by a factor of 1.69 on the diameter, or 5 on the volume, most of which shrinkage occurred in the temperature range 900° to 1450°C. Densities of the order of 95 to 98% of the theoretical crystal density were obtained routinely, with surface areas of 0.01 to 0.1 m^2/g and crystallite sizes (by x-ray line-broadening) of the order of 300 A (Pr_6O_{11} at 1000°C) to 750 A (Eu_2O_3 at 1450°C). Polished cross-sections showed negligible porosity if the spheres were prepared from concentrated (2-3 M) sols, but some closed porosity if prepared from dilute (0.5 M) sols. Crushing strengths of single microspheres (averages for 10 to 30 spheres) ranged from 200 g for 120 μ diameter to 1.5-2.5 kg for 450 μ diameter. Crushing strengths of europium oxide microspheres heated to 1450°C to obtain the monoclinic form (from the cubic form at 1000°C) were not as high as those of other lanthanide oxides which did not have a change of crystal form in this temperature range.

Spectroscopy in the ultraviolet, visible and infrared regions was used

(a) for the rapid analysis of the concentrations of the metal ion and nitrate ion in the sols (see also section 4.1),

(b) to study the form of bonding of the components of the sols and gels, e.g., residual nitrate was shown to be coordinated to the metal (see also section 4.6), and

(c) to calculate the size of the aggregates of colloidal particles, e.g., for a praseodymium hydroxide sol, molecular weights of 2×10^7 to 10^8, and particle diameters of 200 to 400 A were found.

Electron microscopy and electron diffraction measurements showed that the initial precipitates of lanthanide hydroxides consisted of amorphous particles of 30 to 60 A diameter which crystallized slowly (1 hr to several days at 25°C depending upon the particular lanthanide element) into rod-shaped particles which aggregated into bundles of the order of 1000 to 5000 A long and 100 to 500 A wide. The shape and size of the crystalline particles depended upon the conditions of aging of the sols. Sheets up to several hundred angstroms wide were observed when the particles were aged in the mother liquor (e.g., 8 $\underline{M}$ NH_4OH - 0.2 $\underline{M}$ nitrate ion), and rods, tubes or rolled sheets up to several thousand angstroms long when the precipitated hydroxide was thoroughly washed and aged in water at pH 6 to 9. The aggregates of crystalline trihydroxide particles were randomly oriented in the gel spheres prepared by the standard method, but were converted during the calcination procedure into small oriented crystallites of the oxides. Electron micrographs of replicas of etched polished surfaces of the dense oxides (1450°C) showed grains of width 5-10 μ containing oriented units of width 0.2-0.5 μ. The oriented units were probably polycrystalline because x-ray line-broadening measurements indicated a crystallite size of 500-700 A.

Potential uses of lanthanide oxide microspheres are suggested in industry in general and in the atomic energy industry in particular, e.g., incorporation of europium oxide in cermets in reactor control rods. The method is also applicable to the preparation of sols, gels, and oxides of the trivalent transplutonium elements, of which americium and curium are of interest for incorporation in targets in the High Flux Isotope Reactor at Oak Ridge to produce trans-curium isotopes in the National Heavy Element Research Program.

3. EXAMINATION OF HYDROUS UO_2 PRECIPITATES AND SOLS BY ELECTRON MICROSCOPY, ELECTRON DIFFRACTION, AND SPECTROPHOTOMETRY

Microspheres of UO_2 for use in nuclear fuel are prepared by a sol-gel method[5] in which uranous hydroxide is precipitated from uranous nitrate or uranous nitrate-formate solution, the precipitate is washed to the point of incipient peptization, and finally, the filter-cake is heated at 60°C to form a sol. Electron micrographs and selected-area electron diffraction patterns were obtained of the precipitates and sols at various stages in the process, and the size and crystallinity of the colloidal particles was determined. Details of the work are given in ORNL-3963[4].

The studies showed that the initial precipitates consisted of irregularly shaped aggregates of particles of hydrous uranium dioxide of 15 to 25 A diameter. The initially diffuse lines in the electron diffraction patterns became sharper with increased aging at 25°C. Sols prepared by heating the filtered and washed precipitates at 60°C consisted of cubic UO_2 crystals with sides 10 to 20 A long. The presence of 0.4 mole of formate per mole of uranium in the sols gave more uniform dispersion on the electron microscope grids, but did not appreciably affect the size or the lattice spacing of the primary crystallites.

The turbidities or apparent absorption spectra of the diluted sols were measured from 8000 to 3000 A. The optical density varied inversely with the 1.2 to 1.4th power of the wavelength from 8000 to 4000 A, and with the fourth power of the wavelength at less than 4000 A. The maximum diameter of the scattering particles calculated (for details see section 4.3) from the turbidity at 4000 A was about 800 A, which agrees with the size of aggregates observed on the electron micrographs.

A model is proposed[4] for the physical and chemical constitution of the sol particles in the presence of formate, in which formate ions bridge pairs of uranium atoms on the surface of primary cubic crystallites of 10.9 A edge length; these crystallites are then considered to form aggregates of up to 800 A diameter.

Measurements were also made of the turbidities of two uranium sols prepared by different methods by L. E. Morse and the apparent sizes of the particles were calculated. Sol A was prepared by the standard method[5] from a uranous nitrate-formate solution, was a black color, and contained about 2 M U^{4+}, a nitrate/U mole ratio of 0.05, and a formate/U ratio of 0.5. Sol B was prepared by precipitation of uranous hydroxide with hexamethylenetetramine, was a blue-black color, and contained about 2 M U^{4+}. The apparent absorption of these sols (diluted to a concentration of 6×10^{-3} M U and measured in 1-mm cells in a Cary Model 14 spectrophotometer) varied inversely with the 4th power of the wavelength from 3250 to 4000 A, indicating ideal scattering behavior. The absorption varied inversely with the 1.3rd power of the wavelength for Sol A and the 1.8th power for Sol B from 5000 to 8500 A and weak absorption peaks were observed at 6710 and about 8500 A. The previous work had shown that the particles in sols prepared by the standard method consisted of UO_2 crystals, hence the monomer molecular weight and refractive index of UO_2 were used to calculate the following apparent particle molecular weights and diameters from the absorbances at 4000 A:

Sol	Molecular Weight	Diameter, A
A	1.9×10^9	710
B	3.3×10^9	860

The results were very similar for the two sols and no obvious explanation could be seen for the marked bluish color of the sol B prepared with hexamethylenetetramine.

4. SPECTROSCOPY OF SOL-GEL MATERIALS

4.1 Analysis of the Concentration of Nitrate and Lanthanide Ions

The amounts of metal ion and nitrate in sols, gels, and microspheres of lanthanide hydroxide were measured simply and rapidly by dissolving 50 to 100 mg of solid sample, or 1 to 2 ml of sol, in 3 to 5 ml of dilute perchloric acid, adjusting the perchloric acid concentration to about 1 M, and measuring the spectrum in a 1-cm cell versus water in the region 2800 to 6500 A.

The wavelengths and molar absorptivities of the various bands (determined on solutions prepared by dissolving weighed amounts of freshly calcined oxides in perchloric acid) for a series of lanthanides will be reported separately[3]. Typical results were:

Ion	Band Maximum, A	Molar Absorptivity
Pr^{3+}	4440	10.1
Eu^{3+}	3935	2.42
NO_3^-	3000	7.3

The following formula was used to correct the observed optical density (OD) for the nitrate ion at 3000 A for the contribution from the UV band of Eu^{3+} (no correction was needed for Pr^{3+}):

Corrected OD(NO_3^-) = Observed OD(3000 A) - 0.157 x OD(3935 A)

in which the observed OD's are corrected for background absorption. When only the ratio of NO_3^-/metal was required, an accurately measured weight or volume of sample was not needed. The presence of droplets of an organic drying solvent or of an amine used for denitration gave a cloudy solution, and these impurities had to be removed by washing the solution twice with an equal volume of benzene, followed by removal of traces of benzene by blowing air through the solution for 15 min.

4.2 Reflectance Spectra of Microspheres

The measurement of reflectance spectra in the visible region was examined as a potential method for the determination of the mole ratio of nitrate to metal, and of the relative amounts of different metals in microspheres of lanthanide hydroxide gels or oxides directly, without the need to employ any chemical treatment. Microspheres containing Nd^{3+}, Pr^{3+}, and NO_3^- ions were selected because of the numerous intense and sharp absorption peaks of these metal ions in the 3000 to 10,000 A region. Samples of about 100 mg of 100 to 200 μ diameter microspheres of mixed Nd/Pr-oxides/hydroxides both before and after firing at 1100°C were examined (with the assistance of J. P. Young) in a Cary Model 14 Spectrophotometer fitted with a reflectance attachment. The absorption spectrum of the unfired microspheres dissolved in 1 M perchloric acid was also measured. The fired microspheres were black and gave only a continuous reflection spectrum from 2500 to 7500 A; this will not be discussed further.

The mole ratio of the Nd^{3+} to Pr^{3+} based on the absorption spectrum of the solution and published extinction coefficients of the peaks at 5220, 5756 A(Nd) and 4442, 4818 A(Pr) was 1.77, equivalent to 64 mole % Nd; the mole ratio of NO_3^- to (Nd + Pr) was 0.020. All of the peaks in the reflection spectrum were shifted to the red with respect to the absorption spectrum of the solution, the mean shifts being 56 ± 7 A for Pr, and 36 ± 12 A for Nd. Multiple bands were resolved to a higher degree in the reflection spectrum, e.g., 5 peaks plus a shoulder in the region 5000 to 5400 A for the absorption spectrum of the solution, corresponding to 8 peaks plus a shoulder in the reflection spectrum. Shifts of this order and splitting of bands have been reported previously[6] for praseodymium complexes, e.g., $Pr(OH)_3$ compared with the aquo ion.

The relative intensities of the peaks, expressed as optical density for the reflection peak ÷ optical density for the absorption peak (1-cm cell), varied from 0.7 for the Nd^{3+} peak at 7454 A to 3.0 for the Pr^{3+} peak at 5943 A, and no correlation with wavelength or element was apparent. This unexpectedly large variation of relative intensity at different wavelengths made the measurement of reflectance spectra unsuitable for the direct analysis of the mole ratios of NO_3^- to metal, or of the mole ratios of different metals, without more extensive measurements and careful calibration. The variation was probably due mainly to the different degrees of resolution of the multiple bands in absorption and reflection.

4.3 Turbidity and Light-Scattering Measurements on Sols of ThO_2

The molecular weight and shape of sol particles can be calculated from measurements of the scattering of light by the sol. The two principal methods are based on the measurement of the light scattered at 90° (or some other angle) to the incident beam, or of the decrease in the intensity transmitted along the axis of the beam. The latter method is experimentally more simple and has been examined for thoria sols (prior to its application to less well-defined sols of lanthanide hydroxides and plutonium polymer) and the results for one sol compared with results from light scattering measurements at 90°.

The conditions which must be satisfied for the application of simple mathematical expressions to the calculation of molecular weight are: (a) the sol particles should have a diameter less than $\lambda/20$, where λ is the wavelength of the incident light, (b) the particles should be isotropic, (c) the decrease in light-intensity should be due solely to scattering and not to absorption, (d) the turbidity (τ), which is proportional to the optical density, should be related linearly to the concentration of the sol particles, (e) the term $\tau\lambda^4$ should be constant with λ (non-constancy of this term may indicate absorption), and (f) a plot of log τ versus log λ should be linear with a slope of -4 (slopes less than -4 require a more complicated mathematical treatment).

Three thoria sols were examined in detail, Sol A (supplied by K. H. McCorkle, Code No. 6S-11-SDC) of concentration 3.42 M ThO_2, and Sol B, prepared by dissolving solid gel (supplied by K. H. McCorkle, Code No. OX 700) in CO_2-free water to a concentration of 0.2 M ThO_2, aged 1 day at 25°C, and Sol C, as Sol B but aged in a sealed tube at 25°C for 5 weeks. These sols were diluted with water to concentrations from 0.34 M to 0.034 M ThO_2 and kept in sealed tubes to reduce contamination by CO_2. Their turbidities were measured in 1-cm cells from 3000 to 10,000 A in a Cary Model 14 spectrophotometer (with the assistance of J. T. Bell and D. O. Campbell). Refractive indexes of the sols were measured with a Zeiss Immersion-Refractometer and white light and a constant value of 0.0200 ± 0.005 liter $mole^{-1}$ was obtained over the range 0.85 to 0.034 M ThO_2 at 25°C. The turbidity was also measured for Sol B from measurements of the light scattered at 90° in a Brice-Phoenix scattering photometer (J. S. Johnson, Chemistry Division) at wavelengths of 4360 A and 5460 A.

Conditions (a) and (b) were thought to be satisfied by these sols because electron microscopy and x-ray line-broadening measurements indicated particles of approximately spherical symmetry with crystallite sizes of 70 A for Sol A and 142 A for Sol B. The variation of τ with sol concentration was linear only up to about 0.1 M ThO_2, above which τ was appreciably lower than expected (i.e., 20 to 40% low at 0.34 M ThO_2, dependent on λ), hence, condition (d) was obeyed only at low concentration. Conditions (e) and (f) were satisfied as shown by mean values of $\tau\lambda^4$ of $(2.312 \pm 0.021) \times 10^{-18}$ from 4000 to 7000 A for the 0.342 M ThO_2 sol A, and $(7.25 \pm 0.18) \times 10^{-18}$ for the 0.0855 M ThO_2 sol A; the exponents of the plots of log τ versus log λ were between -3.96 and -4.14.

The basic equations used to calculate the weight-average particle molecular weight (M) and radius (r) were taken from the work of B. D. Chun[7], (for further details, see G. Oster[8],):

$$M = \frac{3\tau N \lambda^4 c}{32\pi^3 n_o^2 (n - n_o)^2} = \frac{1.026 \times 10^{21} \tau \lambda^4 c}{(n - n_o)^2}$$

in which τ is equal to 2.303 times the optical density in a 1-cm cell, λ is the wavelength in cm, c is the concentration of the sol in g/cc, N is

Avogadro's number, and n_o and n are the refractive indexes of the solvent and the sol at wavelength λ;

$$r^6 = \frac{3\,\tau\,\lambda^{*4}\,M\,(m^2+2)^2}{128\,\pi^5\,Nc(m^2-1)^2} = \frac{1.107 \times 10^{-28}\,\tau\,\lambda^4\,M}{c}$$

in which $\lambda^* = \lambda/n_o$, and $m = n_{solute}/n_{sol} = 2.200/n_{sol}$ for ThO_2.

Two methods were used to correct M for the nonlinearity of τ with c, (a) M (and r) was calculated for the transmittance results at $\lambda = 4000$, 5000, and 6000 A for each value of c and extrapolated graphically to $c = 0$, (b) c/τ was plotted against c for both transmittance and 90° light scattering results; the intercept on the c/τ axis at $c = 0$ was estimated and the value of M was then calculated from the equation $Hc/\tau = 1/M + 2\,Bc$, in which H and B are both constants. Both methods of calculation gave identical results for the transmittance data. The transmittance method of measurement and the 90° light-scattering method both gave identical results for Sol B.

Sol	Method	Mean Apparent M	r, A	X-ray Crystallite Size, A
A	Transmittance	$6.7 \pm 0.5 \times 10^7$	117 ± 2	70 ± 7
B	Transmittance and Light Scattering at 90°	$5.6 \pm 0.5 \times 10^7$	110 ± 6	142 ± 10
C	Transmittance	$4.8 \pm 0.3 \times 10^7$	106 ± 4	142 ± 10

The errors in M and r were estimated from the scatter of the points in the extrapolations to $c = 0$.

The particle radius of 110 A for Sol B was appreciably higher than the value from the x-ray line-broadening method. The "crystallite" size of 142 A given by the latter method can be interpreted as the length of the edge of a cube, in which case the radius of the sphere of equivalent volume is 88 A (20% lower than 106 A, or 1.75 times lower on a volume basis). However, the value of 117 A for Sol A corresponded to a volume 20 times larger than that of the x-ray "crystallite" (cube edge value, 70 A; radius of equivalent sphere, 43 A). These results can be interpreted as indicating that the particle size which is effective in scattering light is due to an aggregate of a number of basic crystallites. However, the x-ray line-broadening measurements were made on solid gels or on concentrated sols, and it is possible that some aggregation of the basic crystallites may have occurred on diluting the concentrated Sol A with water, or on dissolving the gel to prepare Sols B and C in water. Another explanation is that there is a small proportion of large particles in the sols which leads to a high value of the weight-average molecular weight, but which does not significantly raise the average crystallite size as measured by the x-ray line-broadening method. An example of this effect is shown by assuming 1 weight % of particles of 150 A radius in the presence of 99% of 43 A radius (i.e., conditions that might apply to Sol A); substitution in the equations indicates that 98% of the turbidity would arise from the 1% of 150 A particles, and the apparent radius would be 128 A. This hypothesis could be tested by passing the sols through millipore filters of known pore size, e.g., 100 A, determining the proportion retained, and examining the filtrate by light-scattering and electron microscopy.

The conclusion that dilute thoria sols consisted of agglomerates or flocs of the basic single crystallites was also reached by McCorkle[9] from studies of the viscosity, electron microscopy, absorption spectra, and adsorption of nitrate ions by ThO_2 sols. In particular, McCorkle also observed that the apparent radius calculated from light scattering (transmittance measurements) was always significantly larger than that calculated from x-ray line-broadening measurements.

4.4 Visible and Infrared Absorption Spectra of Sols of ThO_2-UO_3

Absorption spectra in the visible and infrared regions have been measured for sols containing ThO_2 and UO_3 in order to gain a better understanding of (a) the mode of bonding of the residual nitrate and the metal atoms, (b) the reasons for the limited uptake of UO_3 by a pre-formed ThO_2 sol, and (c) the reddish color of the product obtained by mixing yellow UO_3 with colorless ThO_2 or by denitrating a mixed thorium nitrate-uranyl nitrate solution with an amine.

The preliminary results described below indicated that part of the nitrate in the sols was present as nitrate ions and part as coordinated nitrate groups. In dried gel all of the nitrate was in the coordinated form. The absorbance of the "red" sols in the visible-UV region varied with a high (e.g., -5th to -20th) power of the wavelength, and this can be explained on the basis of a strong absorption peak (ϵ, 6×10^3) due to a uranium or uranium-thorium complex species at about 2500 A with a relatively large half-width of 2000 A.

4.4.1 Visible and Near Infrared Spectra of Sols of ThO_2-UO_3

Spectra were measured from 12,000 A to 2200 A in a Cary Model 14 spectrophotometer for sols of ThO_2-UO_3 prepared in two ways:

(a) by addition of hydrated UO_3 to a pre-formed ThO_2 sol and digesting the mixture for several days. The resulting reddish-orange sol (K. H. McCorkle, Code No. 6S-11-SDC) contained 1.6 M ThO_2, 0.17 M UO_2^{2+}, and 0.17 M nitrate, had a thoria crystallite size of about 70 A, and was markedly thixotropic with a setting time of about 30 min.

(b) by denitration of a solution of thorium and uranyl nitrates by amine extraction (R. H. Rainey, Code No. M65-59C). The transparent reddish-yellow sol contained 0.11 M ThO_2, 0.0107 M UO_2^{2+}, 0.046 M nitrate, and had a crystallite size of approximately 25 A.

Spectra of these sols in 1-mm cells and of diluted sols (10 X with water) in 1-mm and 10-mm cells are given in Fig. 1, together with a spectrum of 1.6 M ThO_2 sol with no uranium present. The sol prepared by the first method (a) gave a smooth curve (C) from 3600 to 6000 A (no significant absorption from 6000 to 12,000 A) with a weak peak at about 4500 A. The absorption or turbidity varied with the -5.8th power of the wavelength below 5500 A, and with the -4th power above 5500 A. The absorption-turbidity curve appears to be made up of at least three components (1) a curve due to scattering of light by the approximately 70 A diam ThO_2 particles, (2) a weak absorption peak at about 4500 A (ϵ approximately 2, based on U concentration), and (3) a strong absorption peak with λ_{max} less than 3500 A. The last two peaks appear to be connected with the layer of U(VI) species adsorbed on the particles because thoria sols without uranium do not show these peaks.

The spectra of the sol prepared by the second method (b) was measured to 2200 A (Curve C). Comparison of the Curve A (undiluted sol), Curve B,

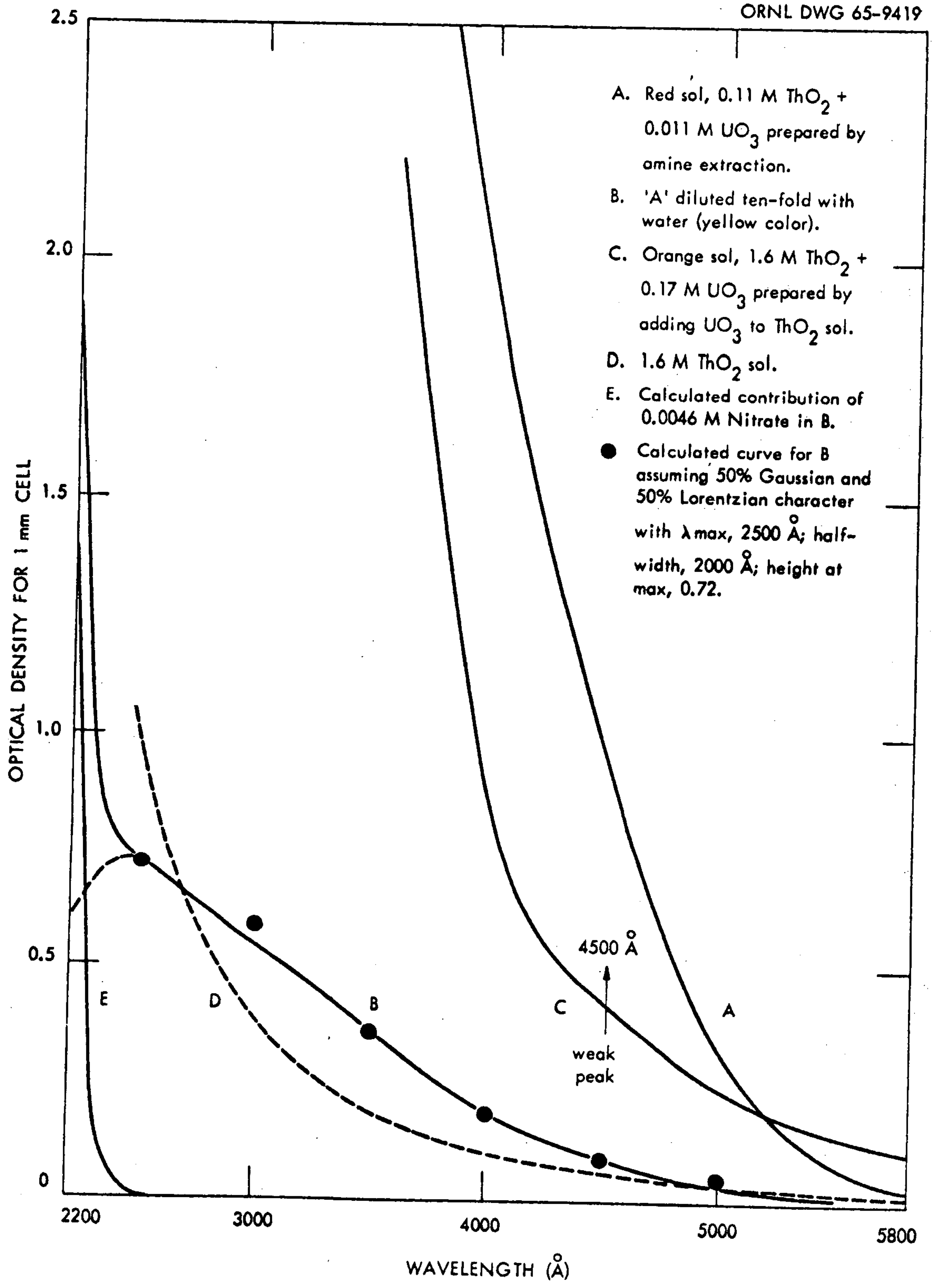

Fig. 1. Absorption Spectra of ThO_2 - UO_3 Sols.

and other data for 1-cm cells shows that the absorption is proportional to ThO_2 concentration and to path length within experimental error over the range 3800 to 6000 A. No significant absorption was found from 7000 to 12,000 A. Plots of log absorption versus log wavelength had slopes varying from -20 at 5000 to 6000 A, to -4.6 at 3500 to 4000 A, whereas a curve arising from pure scattering has a constant slope of -4. The absorption Curve B is made up of at least two major components (the contribution due to light scattered by approximately 25 A diameter ThO_2-UO_3 particles is negligible), (1) a very strong ($\epsilon = 9 \times 10^3$ at 1936 A) peak for nitrate ion (Curve E) and (2) a strong peak ($\epsilon \sim 6 \times 10^3$ at 2500 A) for a uranium or uranium-thorium complex species. The shape of the curve for (2) from 2500 to 5000 A can be fitted approximately by assuming that it has 50% Gaussian-50% Lorentzian character with λ_{max} 2500 A and a peak width of 2000 A at half maximum absorption.

4.4.2 Infrared Spectra of Sols of ThO_2-UO_3

The spectra of the ThO_2-UO_3 sol prepared by the first method described above, and the materials (ThO_2 sol, UO_3 powder) from which it was made, were measured from 2 to 15 microns in a Perkin-Elmer Infracord spectrometer fitted with a NaCl prism. The measurement of spectra with this instrument was made difficult by the evaporation of water from the thin films of the sols which were held between silver chloride plates, as a result of which the sols quickly set to gels. This behavior was turned to advantage by measuring selected absorption peaks as a function of time, but only qualitative results could be obtained in this way.

The results showed that part of the residual nitrate was present in the sols as "free" nitrate ion (strong absorption at 7.2 μ), and part as nitrate groups coordinated to thorium or uranium atoms on the surface or inside the particles (absorption peaks at 6.7, 7.8 and 9.75 μ, similar to those found with solid thorium nitrate hydrate, see section 4.5). In the dried gels of ThO_2 and ThO_2-UO_3 substantially all of the nitrate appeared to be in the coordinated form. The ThO_2-UO_3 sol and gel gave a strong band at 10.9 μ, which was probably due to a stretching vibration of the uranyl group. Sharp, strong bands for water were observed at 2.85 and 6.2 μ.

The UO_3 powder starting material gave four broad bands in the 10 to 14 μ region, which were probably due to U-O stretching vibrations or to deformation bands of OH groups. When the powder was aged in water, the band at 10.5 μ intensified at the expense of the other bands. This band was assigned to a characteristic stretching vibration of the uranyl group, and it corresponded approximately to the broad band at 10.9 μ found in the ThO_2-UO_3 sol, the difference (30 to 40 cm^{-1}) reflecting some considerable change in the bonding environment of the uranium atom.

Any future study of these, or similar sols and gels should be done with a spectrometer with higher sensitivity and resolution, and with the sols and gels in sealed cells to prevent evaporation. It might then be possible to identify the structure of the adsorbed uranium species by correlation of the spectra with those reported for a series of UO_3 hydrates and ammonium diuranate by A. M. Deane at Harwell.[10]

4.5 Raman Spectra of ThO_2 Sols and Thorium Nitrate (with the assistance of O. L. Keller and G. Begun)

Infrared spectra of sols of ThO_2 containing nitrate and UO_3 were measured (section 4.4) in order to obtain a better understanding of the mode of bonding of these species to the ThO_2 surface. However, the presence of water prevented good resolution of the stretching vibrations at 6 to 10 μ of the relatively small amount of nitrate. Raman spectra were therefore measured on a Cary Model 81 instrument for concentrated sols of 2 to 4 M ThO_2, because water was not expected to interfere in this technique.

The strong Raman-active band at 9.5 μ (1050 cm^{-1}) arising from the NO stretching vibration of the NO_3 group was observed in sols of 1.6 M ThO_2 (0.16 M NO_3) and 3.8 M ThO_2 (0.8 M NO_3). The symmetric and antisymmetric NO_2 stretching vibrations at 6 to 8 μ could not be seen even at the highest sensitivity in standard 7 mm diam, 50 ml capacity, tubular glass cells, and observation of these bands is essential for the interpretation of the mode of bonding. Tubular glass cells of special geometry with central light pipes of (a) solid glass rod, (b) hollow parallel glass tube, and (c) hollow conical glass tube, were also tried in an attempt to extract the Raman scattered light more efficiently, but without success. It was concluded that the weakness of the Raman effect counterbalanced the advantage of the lack of interference by water and that the measurement of infrared spectra of sols would be of more value, especially if a more sensitive instrument were used than the Perkin-Elmer Infracord referred to in section 4.4.

However, a satisfactory Raman spectrum of crystalline thorium nitrate pentahydrate was obtained for the first time using a special 5-ml cell with a conical annular light-pipe designed by O. L. Keller. The main bands in the spectrum were at different frequencies to those in infrared spectra reported by J. S. Cho and M. E. Wadsworth[11], J. R. Ferraro[12], and C. C. Addison and B. M. Gatehouse[13]. The main differences were in the degree of separation of the ν_4 and ν_1 bands (Table 1).

Table 1. Comparison of Infrared and Raman Spectra of Hydrated Thorium Nitrate

I.R.	I.R.	I.R.		Raman	Assignment
Cho and Wadsworth (KBr disc)	Addison & Gatehouse (mull)	Ferraro (KBr disc)	Ferraro (mull)	Hardy (pure solid)	
1505, s	1520, vs	1510, vs, b	1502, vs, b	1546, m	ν_4 (NO_2 antisymm. st)
1487, s	1506, sh			1498, m	
1315, m	1323, s	1326, sh	1322, m	1288, w	ν_1 (NO_2 symm. st)
1285, s	1292, vs	1306, vs	1295, vs	1223, w	
1030, vs	1036, sh	1023, m	1035, sh	1037, vs	ν_2 (NO st)
1023, s	1030, vs		1030, m		
805, sh	811, m	796, w	814, w	805, vw	ν_6 out-of-plane rocking
798, s	805, m		808, w		
748, sh	756, m	745, w	750, m	746, s	ν_3/ν_5 NO_2 bend
738, s	744, m			711, w	

Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; st, stretching; b, broad)

A considerable amount of information could be obtained by measuring Raman spectra of solid gels of ThO_2 containing nitrate and UO_3, as well as infrared spectra. The advantages of the Raman method are the lack of interference by water and the absence of reactive window materials or mulling agents. The objects of future work should first be to obtain spectra of better quality, and then the interpretation of them in terms of the mode of bonding of the nitrate and uranium to the ThO_2 matrix and surface.

4.6 Infrared Spectra of Various Sol-Gel Materials

Infrared spectra were measured on a Perkin-Elmer Infracord spectrometer in the range 2.5 to 15 μ for the qualitative analysis of impurities. Samples of solid lanthanide hydroxide gels and lanthanide oxides were pressed into pellets with potassium bromide or were ground up as mulls with Nujol, and sols and gels were also held as thin films between silver chloride plates. Organic matter, e.g., residual tetramethylammonium ions, or long-chain alcohols used to dry the sols, was detected in some batches of microspheres by the C-H stretching vibrations in the 3 and 7 μ regions. The absorption of CO_2 by a sol or gel was also detected by the C-O stretching vibrations at 6.7, 7.1 and 11.3 μ, except that there was interference in the 7 μ region when a large amount of nitrate was present.

The residual nitrate showed up clearly in the microspheres of lanthanide hydroxide gels as strong bands at 6.7 and 7.3 μ and a weaker band at 9.4 μ (the 7.3 μ band in KBr discs was due to nitrate ions produced by reaction of the sample with the KBr to give KNO_3). The bands were similar to those found in solid lanthanide nitrate hydrates (i.e., they were characteristic of nitrate groups coordinated to the metal ions, and not characteristic of nitrate ions). In sols the nitrate bands were broader and subject to interference from the strong band of water at 6.1 μ. Calcined oxides showed a featureless spectrum from 2.5 to 15 μ; observation at higher wavelengths may be useful in the future in that it may show up the metal-oxygen stretching bands.

Infrared spectra were also measured of hydrated nitrates and carbonates of praseodymium, neodymium, and europium heated to various temperatures up to 900°C, to assist in the interpretation of the mode of decomposition of small amounts of these materials present in lanthanide hydroxide gels during calcination to oxides. The spectra showed that the nitrates were decomposed during the presoaking step at 500°C (prior to heating the gel spheres to 1000 to 1500°C to convert them to dense oxide), but that the carbonates were only fully decomposed after they had been heated for several hours at 900°C. Details of the spectra, and suggested intermediates in the decomposition, will be discussed in an ORNL report on the preparation of lanthanide oxide microspheres[3].

4.7 Visible and Ultraviolet Spectra of Sols of PuO_2

Preliminary measurements were made of the absorption spectra of plutonium sols to study the feasibility of determining sizes of the colloidal particles by a simple spectrophotometric method as was used for UO_2 and ThO_2 sols (sections 3 and 4.3 respectively).

Three sols were examined and these were prepared as follows:

Sol A (Code No. X1) was prepared by the standard method[14] by M. H. Lloyd by precipitation of Pu(IV) hydroxide with ammonium hydroxide, washing the precipitate thoroughly, baking it to reduce the amount of residual nitrate, and addition of a 0.1 mole ratio of nitric acid to Pu(IV) to stabilize the sol; the final plutonium concentration was about 250 g/liter. The nitrate to plutonium mole ratio was about 0.3, and the sol was diluted with water to 10 and 1 g Pu/liter.

Sol B (Code No. 138-6) was prepared by M. H. Lloyd in a similar way to Sol A and contained 277 g Pu/liter and a nitrate to plutonium mole ratio of 0.33; the sol had been aged for about 4 months during which time the particles sedimented to the bottom of the container and the mixture was shaken to resuspend the particles before dilution with water or with 10^{-2} $\underline{M}$ HNO_3 to give sols containing 3 to 11 g Pu/liter.

Sol C (Code No. D-17-DIR-2) was prepared by R. G. Haire by precipitation from an aged and heated Pu(IV) polymer solution, and had a plutonium concentration of 405 g/liter, and a nitrate to plutonium mole ratio of about 0.2. This sol was an almost transparent green color, whereas sols A and B had a milky yellow-green color. The sol was diluted to 1 to 20 g Pu/liter, with 5×10^{-3} $\underline{M}$ HNO_3.

The absorption spectra of the sols were measured over the range 2500 to 10,000 A in 1-mm or 1-cm cells in a Cary Model 14 spectrophotometer. A series of broad absorption peaks were observed superimposed on a background absorption which increased as the wavelength decreased. The absorption peaks were at similar wavelengths to those reported for plutonium polymer in dilute acid or alkaline solution[15,16] (Table 2).

Table 2. Comparison of the Wavelengths (mμ) of Absorption Peaks for Sol C and Plutonium Polymer Solution

Sol C	508	531	575	608	688	732	812
Polymer (Kraus[15])	510		579	618			817
Polymer (Ockenden[16])	510		580	615	690	740	825

The background absorption (at low concentrations of plutonium at which the polymer peaks were of low intensity) was similar to that shown by sols of ThO_2, UO_2, and lanthanide hydroxides. The absorbance of this background absorption corrected for the cell blanks and for the plutonium polymer peaks is given as a function of wavelength and plutonium concentration in Table 3. Plots of log background absorption versus log wavelength did not give straight lines of slope -4 as expected for ideal

Table 3. Measurements of the Apparent Absorbance of Sols of PuO_2

Sol	Pu conc.	Apparent Absorbance[*] of Sol at Wavelength, A									Slope[††] of Plot
Letter	g/l	2500	3000	3500	4000	4500	5000	6000	7000	8000	Log τ vs Log λ
A[†]	1.0	0.826	0.346	0.168	0.076	0.020	0.002	--	--	--	5.1
	10.0	--	--	1.655	0.791	0.235	0.073	0.045	0.041	0.030	10.7
B	2.8	--	--	--	--	--	0.909	0.453	0.298	0.195	3.34
	5.5[x]	--	--	--	--	--	1.869	0.883	0.553	0.360	3.45
	5.5	--	--	--	--	--	1.381	0.683	0.438	0.280	3.45
	11.1	--	--	--	--	--	3.07	1.443	1.003	0.585	3.55
C[**]	1.0	--	--	1.17	0.465	0.122	0.064	0.052	0.046	0.040	0.70
	2.0	--	--	--	0.910	0.231	0.102	0.079	0.070	0.056	1.09
	14.2	--	--	--	--	1.52	0.539	0.348	0.285	0.220	1.90
	20.0	--	--	--	--	--	0.779	0.513	0.421	0.320	1.91

[*] Apparent absorbance is the absorbance corrected for cell blank and for plutonium polymer peaks.

[†] Absorbances for Sol A are given for a 1-mm cell, all others for a 1-cm cell.

[x] Diluted with 10^{-2} $\underline{M}$ HNO_3, others with water (except Sol C, see below).

[**] All diluted with 5×10^{-3} $\underline{M}$ HNO_3.

[††] All slopes negative.

scattering by small spherical particles and observed for ThO_2 Sols (section 4.3). The slopes varied from -11 for Sol A to -0.7 for Sol C (see Table 3) depending upon the wavelength and on the plutonium concentration. Plots of absorbance versus plutonium concentration were approximately linear for these sols, which indicated that multiple scattering of light by the particles was not a significant factor.

Meaningful values of the particle molecular weight and radius can only be calculated from the simple equations (section 4) if the slope of the log absorbance-log wavelength plots is approximately -4. Only the data for Sol B approach this value, and a particle molecular weight and radius have therefore only been calculated for this sol.

In the calculation it was assumed that

(a) the sol particles consisted of PuO_2 (this is supported by x-ray evidence that the crystallites show a pattern similar to that of crystalline PuO_2 - unpublished work by R. G. Haire and M. H. Lloyd),

(b) the refractive index increment for the sols was the same as for ThO_2 sols (0.074 cm^3/g), and the refractive index of pure PuO_2 was the same as for pure ThO_2 (2.20).

The results for Sol B based on absorbances measured at 6000 A were

$$\text{Molecular Weight} = 9.3 \times 10^8, \text{ Radius} = 320 \text{ A.}$$

This molecular weight is probably of the correct order of magnitude although it assumes a monodisperse sol with spherical particles, neither of which assumptions may be correct. This value can be compared with values in the literature for molecular weights of plutonium polymer, viz.

	minimum	maximum
Ockenden and Welch[16]	4×10^3 (diffusion method)	10^{10} (α-track counting)
Kraus[15]	4×10^5 (diffusion method)	2×10^7 (ultracentrifuge method)

In conclusion, one could say that these preliminary results only serve to indicate the complexity of the system. The three sols examined all gave a spectrum qualitatively similar to the spectrum of plutonium polymer, but they gave widely different exponents for the plot of log absorbance versus log wavelength. Part of this variation of slope may be due to the difficulty in correcting the observed total absorption for the contribution of the plutonium polymer absorption peaks, particularly at the higher plutonium concentrations. The absorption data for the milky yellow-green aged Sol B gave a reasonable particle molecular weight and radius, but the data for the transparent green Sol C are particularly difficult to interpret. The low slopes of the log-log plot imply a relatively large size of particle according to the theories of light-scattering by spherical particles, but this conflicts with

(a) the transparent appearance (which is usually characteristic of a small particle size for a substance with such a high refractive index), and

(b) preliminary results by R. G. Haire on the pressure filtration of the sol through a 1000 A millipore filter, which showed that the bulk of the plutonium passed through, whereas relatively little of Sol B passed through under similar conditions.

A careful comparison of measurements of turbidity, light scattering at low angles, x-ray diffraction, and electron microscopy is desirable on a number of plutonium sols. It may then be possible to obtain accurate data on the size, shape, and crystallinity of the colloidal particles, and to use the turbidity measurements in a spectrophotometer for the rapid routine measurement of particle size. This could then lead to the goal of controlling these properties in future processes.

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