PREPARATION AND PROPERTIES OF NITRATE-DEFICIENT GADOLINIUM NITRATE SOLUTIONS+

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Abstract - Gadolinium nitrate solutions (~0.001M) were made nitrate-deficient by contact with hydroxyl-form anion exchange resin. These metastable solutions aged with a decrease in pH and in the amount of soluble gadolinium. Gamma irradiation with ^{60}Co increased the rate of aging. Nitrate deficiency was qualitatively detected and quantitatively determined. At ~23°C, the solubility product constant, K_{sp}, of gadolinium hydroxide in an aged and irradiated solution in H_2O was $10^{-26.8}$; for an aged solution in D_2O, K_{sp} was $10^{-26.6}$.

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DISCLAIMER

INTRODUCTION

Because of the high neutron absorption cross sections of some gadolinium isotopes, gadolinium salts in solution are used to control nuclear reactivity in aqueous systems. At the Savannah River Plant, gadolinium nitrate at 0.001M in the reactor D_2O coolant-moderator provides a supplementary mode of reactor shutdown [1].

The solution of gadolinium nitrate must be stable with respect to loss of dissolved gadolinium through precipitation or through deposition on reactor components. Gadolinium hydroxide can precipitate from metastable solutions that contain less than the stoichiometric amount of nitrate (nitrate-deficient solutions).

Hydrolysis of gadolinium salt solutions and the solubility of gadolinium hydroxide have been described [2]. However, reported work has been primarily concerned with solutions of the stoichiometric salts in H_2O. The present studies concern the preparation and analysis of nitrate-deficient solutions, the effect of time and gamma radiation on their stability, and the determination of the solubility of gadolinium hydroxide in H_2O and D_2O.

EXPERIMENTAL

Preparation of nitrate-deficient solutions. 0.001M gadolinium nitrate solutions were prepared by dissolving $Gd(NO_3)_3 \cdot 5H_2O$ (Alfa Products) in deionized water. Nitrate was selectively removed from the solution by contact with the anion exchange resin Amberlite® IRA-400(OH^-) (Rohm and Haas Co), which was thoroughly

washed with water before use. The nitrate-deficient solutions were prepared either by adding small amounts of resin to the solution (batch method) or by passing the solution through a column of the resin (column method).

Auxiliary procedures. Gadolinium was determined by titration with standard ethylenediaminetetraacetic acid (EDTA), using xylenol orange indicator and hexamethylenetetramine hydrochloride buffer [3].

Nitrate was determined by ion chromatography [4], by nitrate-selective electrode using the standard addition/dilution technique [5], or by ion exchange. In the ion exchange method, a known volume of solution was passed slowly through a column of the cation resin Amberlite® IR-120(H^+), and the column was subsequently thoroughly rinsed with water. The H^+ content of the combined effluent and washings, which represents the total nitrate content of the nitrate-deficient solution, was determined by titration with NaOH.

"Soluble" and "insoluble" gadolinium species in the solution were separated by filtration through a Millipore® (Millipore Corporation) filter of 0.45-micron pore size.

The pH and pD were determined in the conventional manner with a pH meter and a combination pH glass electrode. Commercial buffers in H_2O were used to standardize the system for pH measurements. An acetate buffer of pD 5.23 [6] and a phosphate buffer of pD 7.43 [7] were used to standardize the D_2O system.

Turbidity was measured nephelometrically with a Hach Laboratory Turbidimeter, Model 2100A (Hach Chemical Company), with liquid turbidity standards furnished with the instrument.

Conductivity was measured at ambient temperature (~23°C) with an Electromark® Analyzer, Model 4403 (Markson Science, Inc.).

Solutions were irradiated with a ^{60}Co source at a dose rate of 3.5×10^5 rad/hour to a total dose of 7.0×10^6 rad at ~ 37°C. The air-saturated solutions were contained in borosilicate glass bottles with ground-glass stoppers.

Qualitative identification of nitrate deficiency. Solutions with pH > 7 were obviously nitrate-deficient. The following test was useful for identifying nitrate-deficiency in solutions with pH < 7.

To 5-mL sample, 100 µL of 10% KF was added. A pH increase to above pH 7 indicated the solution was nitrate-deficient.

Quantitative determination of nitrate deficiency. Gadolinium content was first determined by EDTA titration. Then this equivalent amount of Na_2H_2EDTA solution was added to a second 5-mL sample. If the measured pH was greater than 7, the solution was titrated to pH 7 with standard 0.01M HCl; if the pH was less than 7, titration was with standard 0.01M NaOH. The % nitrate deficiency was calculated as follows:

$$\text{for pH} > 7: \quad \frac{(2 \times \text{mmoles Gd}) + (\text{mmoles HCl})}{(3 \times \text{mmoles Gd})} \times 100$$

$$\text{for pH} < 7: \quad \frac{(2 \times \text{mmoles Gd}) - (\text{mmoles NaOH})}{(3 \times \text{mmoles Gd})} \times 100$$

RESULTS AND DISCUSSION

Preparation of solutions. Nitrate-deficient solutions were produced by selective removal of nitrate from 0.001M gadolinium nitrate solutions by Amberlite® IRA-400(OH^-). A variety of soluble gadolinium hydroxo complexes will be present in these solutions, depending on the degree of nitrate depletion. The action of the resin is illustrated by the reaction:

$$Gd(NO_3)_3 + nResOH \rightarrow Gd(OH)_n^{(3-n)+} + (3-n)NO_3^- + nResNO_3$$

In the batch preparation method, the degree of nitrate depletion could be controlled by the amount of resin added. In the column preparation method, the composition of the effluent was less predictable.

The column effluents had a pH > 9, but were not visibly turbid. More than 80% of the gadolinium passed through the column, presumably as soluble hydroxo complexes. The mole ratio of Gd/NO_3 in the effluent was several times greater than that in the influent. Both the gadolinium and nitrate that remained on the resin columns were retained in the upper part of the column.

Properties of nitrate-deficient solutions. The pH of the solutions varied with the degree of nitrate depletion and with age. Fig. 1 shows the decrease in pH and the change in conductivity for a typical solution prepared by the column method and aged at room temperature. The pH of the initial solution was high, but decreased rapidly during the first few days; a steady

value was reached within two to three weeks. Conductivity, determined on a separate portion of that solution, decreased rapidly for about a week, then increased, to reach a steady value of ∿10 μmho/cm. The mechanism that caused the conductivity rise after several aging days was not investigated, but the conductivity increase probably reflects formation of gadolinium species of higher mobility and/or release of free nitrate as the solution and precipitate age.

The conductivity was roughly proportional to the soluble gadolinium concentration rather than to total gadolinium (Fig. 2). These conductivities were measured on aged solutions with different degrees of nitrate depletion. The solutions were prepared by the batch method from 0.001M gadolinium nitrate solutions in H_2O and D_2O. They were not visibly turbid, and they contained about 0.001M total gadolinium.

The slope of the line in Fig. 2 provides an estimate of the average equivalent conductance of the "soluble"* gadolinium species: ∿ 122 mho-cm^2 in H_2O and 102 mho-cm^2 in D_2O. These values are close to the equivalent conductances of stoichiometric 0.001M $Gd(NO_3)_3$ [8].

Effect of gamma radiation. Table 1 shows the effect of the gamma irradiation on nitrate-deficient solutions of different ages and degrees of nitrate depletion. Turbidity changes were slight, but turbidity generally increased with irradiation.

*"Soluble" gadolinium is defined as that not filtered out by a 0.45-micron Millipore® filter.

Conductivity changes were variable, reflecting the age of the solution when irradiated, as illustrated in Fig. 1. The decrease in pH and the increase in the fraction of insoluble gadolinium in the irradiated solutions, as compared with the unirradiated solutions, was interpreted to mean that irradiation enhanced the rate of aging of the solution.

The effect of irradiation on aging behavior is illustrated in Fig. 3. The pH is shown as a function of time for two portions of the same solution, one portion of which was irradiated. The solution was freshly prepared before the irradiation. The pH of the irradiated solution decreased sharply and then continued to decrease much more rapidly than that of the unirradiated solution. This increase in the rate of aging is probably due to coagulation of the charged colloidal gadolinium species by the ionizing radiation. This phenomenon has been observed in other colloidal systems [9].

Determination of solubility product constants. The concentration of soluble gadolinium [Gd] and the measured pH or pD were used to calculate solubility product constants, K_{sp}, defined by:

$$K_{sp} = [Gd]\ [OH]^3$$

The hydroxide concentration [OH] is derived from the measured pH (and [OD] from pD) through the respective ionization constants of H_2O [10] and D_2O [11]. Thus, at 25°C, the solubility product constants can be calculated from the following:

in H_2O: $pK_{sp} = - \log [Gd] + 3(pH - 14.00)$

in D_2O, $pK_{sp} = -\log [Gd] + 3(pD - 14.87)$

Because of the effect of aging, an exact K_{sp} is difficult to establish. As the solution ages, the colloidal particles agglomerate and become less soluble, which is reflected by a decrease in pH and a corresponding increase in pK_{sp}. For freshly precipitated $Gd(OH)_3$, the pK_{sp} is 21.7 [12]. For $Gd(OH)_3$ aged 200 days, the pK_{sp} is 26.88 [13].

Table 2 shows a set of solutions in H_2O in which the average pK_{sp} was 25.5, after 7 days of aging. Three solutions that were irradiated (and hence more aged) produced an average pK_{sp} of 26.8, in essential agreement with the published value for $Gd(OH)_3$ that was aged 200 days.

Table 2 also shows a set of 7-day-old solutions in D_2O had an average pK_{sp} of 26.6. Extrapolation from the H_2O data indicates the pK_{sp} in D_2O after prolonged aging would be $\sim$ 27.9.

Analysis of nitrate-deficient solutions. The solutions are regarded as containing the hypothetical gadolinium compound $Gd(OH)_n(NO_3)_{3-n}$. The degree of nitrate deficiency is determined from the amount of hydroxide released when the gadolinium is complexed. Hydroxide is qualitatively detected by pH measurement or quantitatively determined by acid titration.

In the qualitative procedure, excess fluoride is added, which complexes gadolinium as the fluoride and releases hydroxyl ions:

$$Gd(OH)_n(NO_3)_{3-n} + \text{excess } F^- \rightarrow GdF_3 + KNO_3 + n\ OH^-$$

If the pH increases above the neutral point, nitrate deficiency is indicated. In theory, for quantitative determination, the OH^- released after fluoride addition can be titrated with standard acid. In practice, the end point is diffuse because of the buffering action of the fluoride, and more satisfactory results are obtained with the EDTA procedure described below.

For quantitative determination, addition of an equivalent amount of Na_2H_2EDTA for gadolinium complexation releases two hydrogen ions from the EDTA as well as the OH^- from the gadolinium species:

$$Gd(OH)_n(NO_3)_{3-n} + Na_2H_2EDTA \rightarrow$$

$$GdEDTA^- + (n-3)NO_3^- + 2Na^+ + nOH^- + 2H^+$$

The net $[H^+]$ or $[OH^-]$ is determined by titration with standard base or acid.

Table 3 shows the results when these procedures were used to analyze a set of gadolinium nitrate solutions with different degrees of nitrate depletion. The first three solutions were untreated gadolinium nitrate.

The qualitative test identified nitrate deficiency in these solutions with pH < 7, by the increase in pH above the neutral point of 7. The quantitative results indicate that the untreated $Gd(NO_3)_3$ solutions may have been slightly nitrate-rich. Nitrate deficiency values follow the same sequence as the pH change of the qualitative test for all the samples.

The last column provides a comparison with nitrate deficiencies determined from independent nitrate determinations by ion-selective electrode, ion chromatography, and ion exchange procedures. The good agreement confirms the reliability of the determination by EDTA.

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Table 1. Irradiation of Nitrate-Deficient Solutions

Solution	Mode of Preparation	Age When Irradiated	Turbidity, NTU[a]	Conductivity μmho/cm	pH	Gadolinium Total, 10^{-4} M	Gadolinium Fraction "Insoluble"[b]	Nitrate, 10^{-4} M
1	column	2 days	2.5	10.5	9.17	8.9	0.18	[c]
1[d]			9.7	39.4	6.55	8.9	0.86	[c]
2	column	7 days	14.5	4.7	9.22	7.0	0.75	4.7
2[d]			15.0	9.5	6.70	7.0	0.95	[c]
3	batch	1 day	1.9	147	7.41	6.2	0.13	13
3[d]			1.9	156	6.23	6.2	0.25	[c]
4	column	6 hours	0.67	14.7	9.6	8.6	0.03	4.4
4[d]			0.95	5.8	8.6	8.6	0.25	[c]

[a] *NTU = Nephelometric Turbidity Units*

[b] Removed by filtration through 0.45-micron filter

[c] Not determined

[d] Irradiated to gamma dose of 7 megarads

Table 2. Solubility product constants of $Gd(OH)_3$ and $Gd(OD)_3$ at 25°C

Solvent	pH or pD	Gd, 10^{-4}M Soluble	Gd, 10^{-4}M Total	pK_{sp}	Comments
H_2O	6.53	8.25	9.68	25.49	Batch ion exchange, 7 days old
	6.59	6.35	9.68	25.42	(not irradiated)
	6.68	4.37	9.68	25.31	
	6.68	3.85	9.68	25.37	
	6.68	3.08	9.68	25.47	
	6.83	1.51	9.68	25.33	
	7.09	0.380	9.68	25.15	
			Average =	25.46	
	6.55	1.27	8.86	26.25	Column ion exchange,
	6.70	0.319	6.95	27.40	(irradiated)
	6.23	4.93	6.18	26.62	
			Average =	26.76	
D_2O	6.94	8.31	9.45	26.87	Batch ion exchange, 7 days old
	7.04	6.66	9.45	26.67	(not irradiated)
	7.10	5.47	9.45	26.57	
	7.12	3.85	9.45	26.66	
	7.24	2.66	9.45	26.47	
			Average =	26.65	

Table 3. Nitrate Deficiency

Solution	Total Gd^{3+} 10^{-4} M	Qualitative Procedure A, pH change	% Nitrate Deficiency By EDTA Procedure	% Nitrate Deficiency From NO_3^- Determinations
$Gd(NO_3)_3$	9.50	5.6 to 7.0	-3	--
	9.60	5.6 to 7.0	-5	--
	9.83	5.6 to 7.0	-4	-2[a]
Nitrate Deficient Solutions	7.56	6.1 to 8.7	9.5	16[a]
	6.40	6.2 to 9.3	31	32[b,c]
	6.93	7.3 to 10.3	76	--
	6.80	8.8 to 10.5	82	--
	8.09	8.5 to 10.6	87	86[c]

[a] Ion selective electrode

[b] Ion chromatograph

[c] Cation exchange

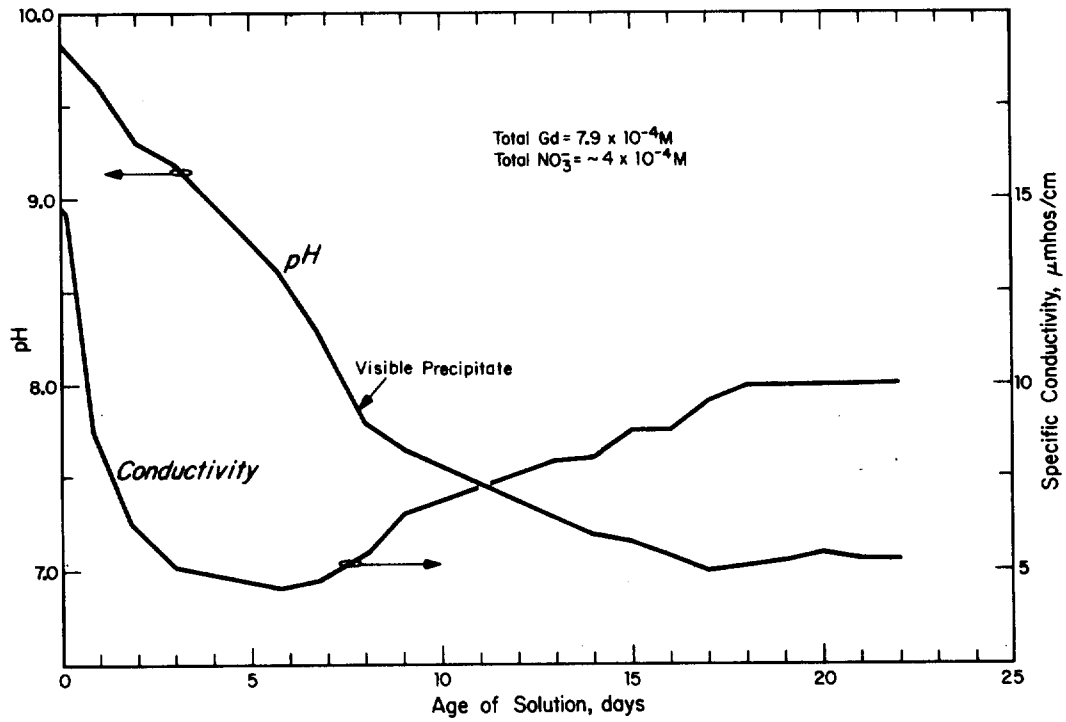

Fig. 1. pH and conductivity during aging of nitrate-deficient gadolinium nitrate solution at 25°C

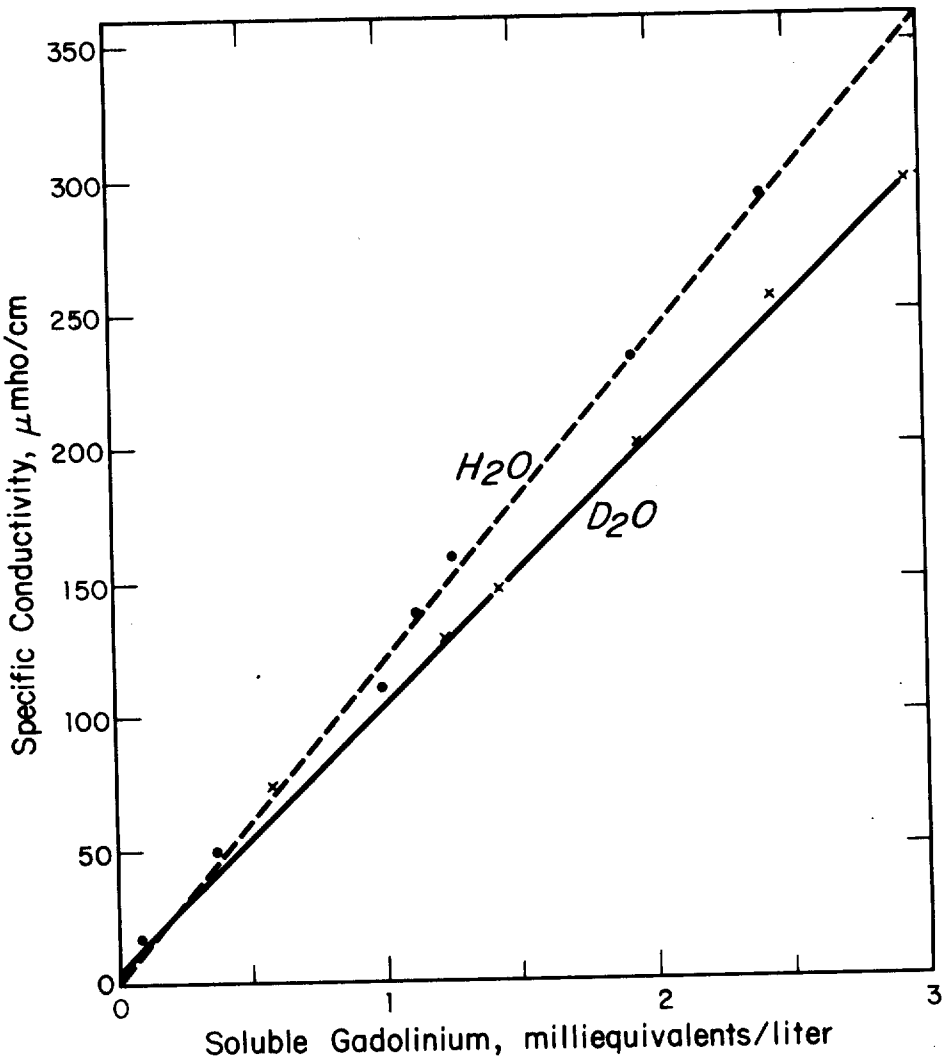

Fig. 2. Conductivity and soluble gadolinium in aged nitrate-deficient gadolinium nitrate solutions in H_2O and D_2O at 25°C

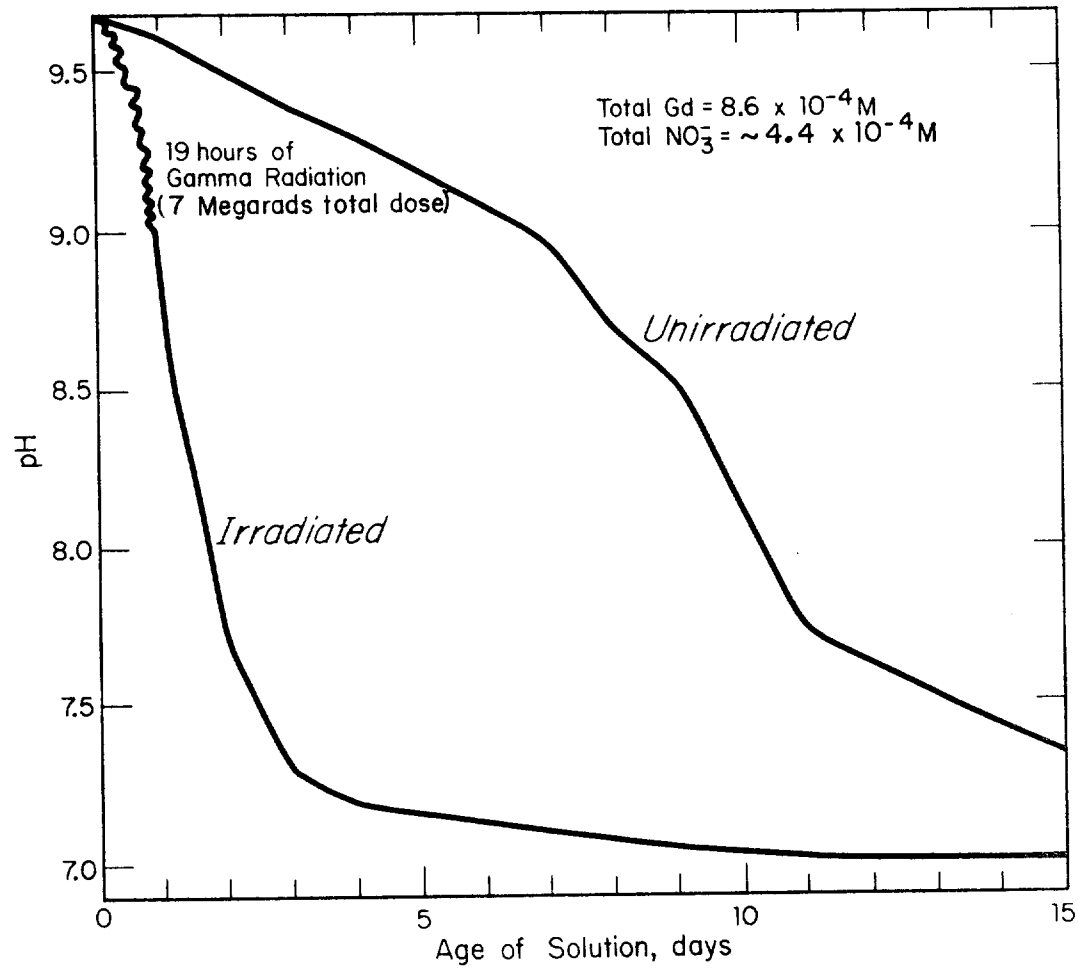

Fig. 3. Effect of gamma irradiation on aging of nitrate-deficient gadolinium nitrate solution at 25°C