OAK RIDGE NATIONAL LABORATORY

OPERATED BY MARTIN MARIETTA ENERGY SYSTEMS, INC.

POST OFFICE BOX X OAK RIDGE, TENNESSEE 37831

April 11, 1985

Dr. J. W. Bradbury Geotechnical Branch Office of Nuclear Material Safety and Safeguards U.S. Nuclear Regulatory Commission Room 623-SS Washington, D.C. 20555

WM Record File B-0290 ORNL	WM Project <u>10, 11, 16</u> Docket No PDR_
Distribution:	LPDR B, N.S.
Return to WM, 623-SS)	23

Dear John:

Enclosed is the progress report for the month of April 1985 for B0290, "Laboratory Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters, Experimental Strategies, Laboratory Techniques and Procedures," and LR-290-10, "Recommendations on Geochemical Modeling of Radionuclide Solubility/Speciation."

Sincerely, Jusan

Susan K. Whatley, Manager Repository Licensing Analysis and Support Chemical Technology Division

SKW:bek

Enclosure

cc:	Office of the Director, NMSS Division Director, NMSS Divis M. R. Knapp, Chief, Geotechnik R. J. Starmer, Geotechnical D. J. Brooks, Geotechnical B Branch Chief, Waste Management	(Attn: Program Support Bra sion of Waste Management (2 ical Branch Branch ranch nt Branch, RES	nch))	
	G. F. Birchard, Waste Manager	ment Branch, RES		¥
	W. D. Arnold	A. D. Kelmers	85	IM DO
	J. T. Bell	D. C. Kocher	A	200
	J. G. Blencoe	A. P. Malinauskas	² D	2ê
	A. G. Croff	R. E. Meyer	E E	E
	N. H. Cutshall	F. G. Seeley	01	200
	L. M. Ferris	R. G. Wymer	A	É É
	J. R. Hightower	SKW File (2)	<u>هب</u>	RO
	G. K. Jacobs		00	

)324 8504 IRES EXIO

MONTHLY PROGRESS REPORT FOR MARCH 1985

PROJECT TITLE: Laboratory Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters, Experimental Strategies, Laboratory Techniques, and Procedures

PROJECT MANAGER: S. K. Whatley

TASK LEADER: A. D. Kelmers

SCIENTIFIC STAFF: W. D. Arnold, J. G. Blencoe, G. K. Jacobs, R. E. Meyer, and F. G. Seeley

ACTIVITY NUMBER: ORNL #41 37 54 92 6 (FIN No. B0290) NRC #50 19 03 1

PROGRESS HIGHLIGHTS:

Technetium Studies:

Last month, we reported results for anoxic redox condition sorption tests for pertechnetate and Cohassett basalt which were designed to measure the effect of basalt particle size or surface area on the sorption of technetium. In those tests, Cohassett basalt was crushed and screened into a range of particle-size fractions under anoxic conditions, but the sized basalt had then been stored for several months in the anoxic box before we used it. The tests were batch contact experiments for 50 days at 60°C, and the initial concentration of pertechnetate was 10^{-8} mol/L. Those tests showed no clear correlation between particle size and technetium sorption ratio. This was unexpected since we had previously shown a strong correlation between particle size and sorption ratio for sorption of neptunium(V). The neptunium sorption ratios increased from 4.7 to 275 L/kg as the basalt particle size decreased from <210/>105 to <37 µm.

We repeated the pertechnetate tests, with the exception that the contact time was shortened to 14 days and new samples of Cohassett basalt used in the tests were freshly ground and sized under anoxic conditions. There was essentially no difference between the previous and current sorption ratios for the three larger particle-size fractions: <210/>105, <105/>74, and $\langle 74/\rangle 44$ µm. For the fine fractions ($\langle 44/\rangle 37$ and $\langle 37$ µm), however, the sorption ratios were about a factor of four larger than in the previous experiments. Sorption ratios ranged from about 15 to 23 L/kg for the three larger particle-size fractions and from about 82 to 103 L/kg for the two small particle-size fractions. Thus, there appears to be a modest effect of the basalt particle-size fraction employed in the tests on technetium sorption. But it also appears that the ability of basalt to reduce and sorb technetium is extremely sensitive to the presence of even traces of oxygen since basalt stored in the anoxic condition box was less active. This extreme sensitivity to oxygen does not appear to exist in the parallel work with neptunium.

Neptunium Studies:

6

Techniques are being developed to prepare neptunium-containing groundwater solutions with the neptunium in a single, defined valence. No sorption tests were done this month since the sample of 235 Np needed for that work still has not been received from ANL.

Uranium Studies:

We previously reported that sodium boltwoodite precipitated from uranium(VI)traced synthetic groundwaters GR-2 and GR-4 at 60°C under both oxic and anoxic conditions in 30-day tests. In parallel tests this month with uranium-free GR-2 and GR-4, no precipitate of any kind formed after 30 days at 60°C. Thus, sodium boltwoodite formation is not dependent upon coprecipitation of other insoluble phases.

Material Acquisition:

Four gallons of J-13 well water were received from the NNWSI.

Material Characterization:

To prepare the first tuff sample for sorption/solubility experiments, approximately 2.4 kg of Topopah Spring tuff from the Busted Butte outcrop was crushed and ground so that 100% passed a 240- μ m screen. The particlesize distribution was determined. Thin section and x-ray diffraction analyses are in progress. Analysis of the J-13 groundwater was completed; the results were in good agreement with J-13 analyses published by NNWSI.

Preliminary examination of thin sections indicates that lithic fragments, "reaction rims," and groundmass material may be significantly different in the Topopah Spring outcrop and core specimens. A comparison of the mineralogies and textures of the outcrop and core specimens will be discussed in future reports.

Samples of synthetic J-13 groundwater were prepared, and initial experiments were conducted to determine methods of controlling pH by regulating the partial pressure of CO_2 . In preliminary experiments, a five percent CO_2 -air mixture maintained the pH at about 6.5. Thus, to maintain the pH at the desired value of 7.0, a somewhat smaller percentage of CO_2 will be required.

Geochemical Calculations:

Geochemical modeling activities emphasized evaluation of the radionuclide solubility/speciation calculations of Ogard and Kerrisk (LA-10188-MS) for the Yucca Mountain site. Preliminary results confirmed the obvious: calculated solubilites were sensitive to the boundary conditions and thermodynamic data utilized in the calculations. Some sensitivity calculations for uranium are planned to help guide various experimental strategies for the evaluation of the NNWSI sorption information for Yucca Mountain.

General Aspects:

The recent paper by Rai and Ryon [Inorg. Chem. 24, 247-251 (1985)] is a classic documentation of the uncertainties in some commonly used thermodynamic values for actinides. The authors show that no evidence exists for neptunium(IV) anionic species such as $Np(OH)_5$ or neptunium(IV)-carbonate complexes, although such species are included in all thermodynamic data bases used in geochemical modeling. They also repeat previous criticisms of the obviously incorrect value for the formation constant for $PuCO_3^{2+}$ which is also included in data bases. The authors conclude: "The values of actinide carbonate complexes reported in the literature are grossly in error." A copy of the paper and a letter report (LR-290-10) by G. K. Jacobs are attached.

MEETINGS AND TRIPS:

None

REPORTS AND PUBLICATIONS:

The draft annual report for FY 1984 was forwarded to the NRC Project Manager for comment and review in February; it will be revised and issued after receipt of the Manager's review.

The draft quarterly progress report for the first quarter of FY 1985 has been compiled and will be forwarded to the NRC Project Manager soon for review and comment.

The draft quarterly progress report for the second quarter of FY 1985 is being compiled.

PROBLEM AREAS:

None

COST/BUDGET REPORT:

Expenditures were \$43.5K for the month of March and \$264.2K for the fiscal year to date. A detailed cost/budget report will be sent under separate cover.



LETTER REPORT

TITLE:Recommendations on Geochemical Modeling of
Radionuclide Solubility/SpeciationAUTHOR:Gary K. JacobsPROJECT TITLE:Laboratory Evaluation of DOE Radionuclide Solubility
Data and Selected Retardation Parameters,
Experimental Strategies, Laboratory Techniques, and
ProceduresPROJECT MANAGER:Susan K. WhatleyACTIVITY NUMBER:ORNL #41 37 54 92 6 (FIN No. B0290)
NRC #50 19 03 1

It has become increasingly apparent that predicting the maximum concentration of radionuclides in groundwaters based solely on thermodynamic principles is not justifiable with respect to both regulatory attitudes and technical concerns. For example, the NRC Technical Position on the determination of radionuclide solubilities, which is consistent with the recommendations-from our recent conference on geochemical modeling, clearly states that "...by themselves, computer calculations are insufficient to establish the nature and significance of radionuclide solubility/speciation under repository conditions." (see attachment 1, NRC, 1984).

Of items A - D discussed in Attachment 1, the limitations associated with the thermodynamic data are probably the most serious at this time. It is clear that for many of the important radionuclides (e.g., U, Pu, Np, Am, Tc,) reliable solubilities cannot be calculated. For example, Rai and Ryan (1985) discuss that there is no evidence for the existence of the aqueous species $U(OH)_5^-$, $PuCO_3^{2+}$, $Np(OH)_5^-$, and $Np(CO_3)_n^{4-2n}$. Yet, these are the species predicted to predominate solution concentrations in many computer calculations. In addition, uranium-bearing solids, for which there are no thermodynamic data available, are known to precipitate in experiments (including some of our own), thereby making predicted solubilities of uranium inherently inconsistent with some experimental data. Even sensitivity calculations can be misleading if an inappropriate thermodynamic data base is used with a geochemical model. For example, if a complex which may form under repository conditions has not been identified in laboratory studies and has no data available (either actual or estimated) for the thermodynamic calculations, sensitivity calculations will be meaningless. It is essential that all potentially important complexes and solids be identified through scoping experiments, and the thermodynamic data for them be obtained or estimated in order to properly perform sensitivity calculations.

To be consistent with the Technical Position of the NRC and the recommendations from our conference, I suggest that we discontinue attempting to model radionuclide solubility/speciation. Until a well-documented, internally-consistent, and verified data base is available, calculations such as this will only contribute to the proliferation of confusing, suspect, and, in some cases, totally incorrect results and conclusions. Laboratory efforts must be initiated to obtain the important thermodynamic parameters for the key radionuclides before calculations such as this will be meaningful. This recommendation includes discontinuing the type of comparative calculations of the DOE projects such as was accomplished for the Early et al. (1982) BWIP report (Kelmers et al., 1984). I believe that the NRC Technical Position and supporting literature provides sufficient justification for simply stating that studies such as Early's are interesting, but not relevant for the licensing of a repository. Any further effort to evaluate studies similar to Early's does not seem justified at this time. For some radionuclides [e.g., U(VI), Pb], the available data may be sufficient to perform some interpretations of laboratory experiments and/or sensitivity calculations. However, the limitations associated with studies such as this need to be carefully documented.

This is not meant to imply that we should discontinue all geochemical modeling activities. On the contrary, I recommend that we increase the use of geochemical models in the areas where they are most useful and have been shown to be reliable. The interpretive, rather than predictive, applications need to be emphasized. Some potential areas for the increased application include evaluating geochemical conditions, groundwater chemistry, rock/water interactions at elevated temperature, and natural analogs. I strongly urge that activities in these areas be emphasized over the highly uncertain modeling of radionuclide solubility/speciation. For the next year, increased emphasis on natural analogs may be most appropriate in conjunction with our planning of the conference on natural analogs.

References

Early, T. O., D. R. Drewes, G. K. Jacobs, and R. C. Routson, 1982, Geochemical Controls on Radionuclide Releases from a Nuclear Waste Repository in Basalt: Estimated Solubilities for Selected Elements, RHO-BW-ST-39 P, Rockwell Hanford Operations, Richland, Washington.

Kelmers, A. D., J. H. Kessler, W. D. Arnold, R. E. Meyer, N. H. Cutshall, G. K. Jacobs, S. Y. Lee, and R. J. Clark, 1984, <u>Progress</u> in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Projects: Report for January <u>- March 1984</u>, NUREG/CR-3851, Vol. 2, ORNL/TM-9191/V2, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

NRC, 1984, Determination of Radionuclide Solubility in Groundwater for Assessment of High-Level Waste Isolation, U.S. Nuclear Regulatory Commission Technical Position, November 1984.

Rai, D. and J. L. Ryan, 1985, "Neptunium(IV) Hydrous Oxide Solubility under Reducing Conditions and Carbonate Conditions," <u>Inorg. Chem.</u>, v. 24, p. 247-251. preconditioned (saturated) filters can be used. If incomplete filtration is suspected, finer filters or more rigorous centrifugation should be used.

ý,

· · ·

Most solubility experiments study the chemistry of only one radionuclide, in contrast to the repository system which will have numerous radionuclides. Solubilities obtained in studies of one radionuclide may be much greater than those in systems containing numerous radionuclides. For example, when there is a limiting amount of complexing ligand, the concentration of a single radionuclide would be greater than that if two or more radionuclides were present which competed for the ligand. Solubility studies using multiple radionuclides can be used to address this uncertainty.

4.5 Geochemical Modeling and Solubility/Speciation Calculations

Solubility and speciation of radionuclides in various synthetic and natural groundwaters can be calculated using computer codes. However, the results of these calculations may have limited validity for the following reasons:

A. <u>Equilibrium assumed.</u> Calculations of radionuclide solubility/ speciation are based on the assumptions that both homogeneous (one-phase, groundwater) equilibrium and heterogeneous (multiphase, groundwater and solids) equilibrium are achieved. However, it is unrealistic to expect that reaction rates will be so rapid that both homogeneous and heterogeneous equilibria will continuously prevail under conditions of varying temperature, mineralogy, pH, and redox potential. Furthermore, the radionuclide solubilities are calculated in equilibrium with most stable solid phase(s) which can result in nonconservative concentrations.

B. <u>Incomplete mass transfer.</u> Generally, solubility/speciation computer codes that are presently available (e.g., PHREEQE, EQ3/6) do not permit a proper accounting for <u>all</u> of the potential chemical effects in mass transfer processes, such as ion-exchange and chemisorption.

C. <u>Data base limitations.</u> It is well known that the data bases for radionuclides in solubility/speciation computer codes are incomplete and also contain data of questionable validity. Numerous radionuclide complexes can form in groundwaters, but independent evidence that proves the existence of particular species is almost nonexistent. It is, therefore, likely that some complexes inferred to exist in significant concentrations under certain conditions may, in fact, not exist at all. Furthermore, it is likely that there are some important radionuclide complexes which have yet to be identified. Corresponding omissions also probably exist in the list of radionuclide-bearing solids that can form as a result of reactions between groundwaters and coexisting solid materials. Finally, the uncertainty (limits of error) of thermodynamic data, such as log K and ΔH_f values for speciation reactions can be large.

D. <u>Experimental validation required</u>. As a result of the above considerations and the complexity of the repository system, any solubility/speciation calculations will require experimental validation before their results can be employed in repository performance assessments.

Thus, by themselves, the results of computer calculations are insufficient to establish the nature and significance of radionuclide solubility/speciation under repository conditions. However, geochemical models are useful for characterizing geochemical conditions (e.g., groundwater chemistry, redox, pH controls and thermal stability), and for interpreting experimental data. These calculations could be used to guide experimental determinations and should only assume a supplementary and/or supporting role in the determination of solubility/speciation values unless they can be shown to be fully consistent with a substantial body of independent (experimental data) information.

15

Volume 20

Number 3

January 30, 1985



C Copyright 1985 by the American Chemical Society

Articles

Contribution from the Pacific Northwest Laboratory, Richland, Washington 99352

Neptunium(IV) Hydrous Oxide Solubility under Reducing and Carbonate Conditions

DHANPAT RAI* and JACK L. RYAN

Received March 20, 1984

Solubility of Np(IV) hydrous oxide was approached from the oversaturation direction in the presence of reducing agents (Na₂S₂O₄, metallic Fe, metallic Zn) with and without 0.01 M total carbonate and in the range pH 6-14.2. In all of the above solutions in this range contacting Np(IV) hydrous oxide, Np concentrations were at or below the detection limit for Np (~10^{-4.3} M). No evidence was found for any amphoteric behavior of Np(IV). Although it was not possible to determine absolute hydrolysis constant or carbonate complexation constant values for Np(IV) from these experiments, the results do set an upper limit of log $\beta_5^* < -24.7$ for Np⁴⁺ + 5H₂O = Np(OH)₃⁻ + 5H⁺ and of log β_n (Np⁴⁺ + nCO₃²⁺ = Np(CO₃)_n⁽⁻²ⁿ⁾ <22.5, <27.9, <33.2, <38.5, and <41.6 for $\beta_1 - \beta_2$, respectively. The results provide no evidence for such reactions, but if they are assumed to occur, these upper limits are many orders of magnitude lower than previously reported.

Introduction

Under reducing conditions such as those that might be present at some of the proposed radioactive waste disposal sites, actinides, especially uranium and neptunium, will be present in the tetravalent state. Therefore, solubility data for tetravalent actinide compounds are needed to determine the potential hazards of disposing of actinide-containing wastes in geologic repositories. Predictions about the solubility of different actinide compounds have recently been reported by several authors.¹⁻⁷ These predictions, for the most part, are based on thermodynamic data that are selected from unreliable and questionable experimental values and/or are in most cases estimated on the basis of techniques of uncertain validity. For example, the second, third, and fourth U(IV) hydrolysis constants have been estimated by assuming linear arithmetic progression among the logarithms of the equilibrium constants⁸ from questionable experimental data⁹ for the fifth hydrolysis constant. These data in turn have been applied to other actinides as well. However, Ryan and Rai¹⁰ conducted careful experiments but found no evidence for the existence of the fifth U(IV) hydrolysis species, thereby casting serious doubt on the accuracy of values of the second, third, and fourth hydrolysis constants as well.

- (1) Allard, B.; Kipatsi, H. K.; Liljenzin, J. O. J. Inorg. Nucl. Chem. 1980, 12, 1015
- Lemire, R. J.; Tremaine, P. R. J. Chem. Eng. Data 1980, 25, 361.
 Rai, D.; Serne, R. J. J. Environ. Qual. 1977, 6, 89.
 Ogard, A. E.: Duffy, C. J. Nucl. Chem. Waste Manage. 1981, 2, 169.
- Allard, B. "Actinides in Perspective"; Edelstein, N., Ed.; Pergamon (5)
- Press: Oxford, 1982, pp 553-580. Rai, D.; Serne, R. J. Solid Phases and Solution Species of Different (6) Elements in Geologic Environments", Report PNL-2651; Pacific Northwest Laboratory: Richland, WA, 1978.
- Langmuir, D. Geochem. Cosmochim. Acta 1978, 42, 547.
 Baes, C. F.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976.
- (9) Gayer, K. M.; Leider, H. Can. J. Chem. 1957, 35, 5.
- (10) Ryan. J. L.; Rai, D. Polyhedron 1983, 2, 947.

Moskvin and Gelman¹¹ studied Pu(IV) carbonate complexes in concentrated (0.36-3.6 M) carbonate solution, concluded that only the PuCO₃²⁴ complex was present, and reported its formation constant value as $\beta_1 = K_1 = 9.1 \times 10^{46}$ on the basis of the solubility of Pu(IV) hydrous oxide as a function of carbonate concentration at pH 11.5. As was pointed out several years ago by one of the present authors to another¹² who was reviewing the entire field of plutonium chemistry, this value is much too high to be believable. Despite this and apparently because the Moskvin and Gelman¹¹ value was the only available experimental value until recently, several authors^{2,13,14} who reviewed actinide thermodynamic data in the past have chosen to include this value (or a somewhat revised value based on the Moskvin and Gelman¹¹ data) in their calculations without critical comment as to its validity. This value for the Pu(IV) carbonate complex has been assumed to apply to other tetravalent actinides as well. Recently, Kim et al.15 reported values for all of the formation constants of the Pu(IV) carbonate complexes PuCO₃²⁺ through Pu(CO₃)₅⁶⁻. Their value of $\beta_1 = 1.3 \times 10^{47}$ is slightly higher than even the Moskvin and Gelman¹¹ value. There are a variety of reasons for completely rejecting such carbonate formation constant values; four are discussed briefly. First, the formation constant for complexes between hard-acid metals and hard-base ligands having a constant ligand atom (in this case oxygen) can be semiquantitatively related to ligand basicity (as measured by acid association constant) and metal ion charge density. On this basis and by comparison of

- (11) Moskvin, A. I.; Gelman, A. D. Russ. J. Inorg. Chem. (Engl. Transl.) 1958, J, 1898.
- Cleveland, J. M. "The Chemistry of Plutonium"; Gordon and Breach:
- (12) New York, 1970; p 120.
 (13) Keller, C. "The Chemistry of the Transuranium Elements"; Verlag Chemie GmbH: Weinheim, Germany, 1971; pp 198-199, 415.
 (14) Phillips, S. L. "Hydrolysis and Formation Constants at 25 °C", Report
- LBL-14313; Lawrence Berkeley Laboratory: Berkeley, CA, 1982.
- (15) Kim, J. I.; Lierse, C. H.; Baumgartner, F. ACS Symp. Ser. 1983, No. 216. 318.

0020-1669/85/1324-0247\$01.50/0 © 1985 American Chemical Society

248 Inorganic Chemistry, Vol -4 No. 3, 1985

formation constants of a variety of ox jonor complexes such as carboxylates etc. of tetravalent actinities and other metal ions of similar charge density, a reasonable value for the formation constant of $PuCO_3^{2+}$ of about 10^{12} with an upper limit of about 10¹⁵ is reached. Second, the formation constant, β_1 , of the Pu(IV) ethylenediaminetetracetic acid (EDTA)¹³ complex is about 10²⁶. EDTA has virtually the same basicity as carbonate, the first and second acid association constants are nearly identical for EDTA and carbonate, ¹⁶ and EDTA is hexadentate whereas CO_3^{2-} is at most a "short-bite" bidentate. On the basis of the well-known chelate effect,¹⁷ it can be expected that at least β_2 , and most likely β_1 ($\beta_1 = K_1 K_2 K_1$) and possibly β_4 for carbonate, should be smaller than β_1 for EDTA. (The only reason that β_1 for EDTA could conceivably be smaller than β_1 for carbonate would be because two of the EDTA donor atoms are nitrogen instead of oxygen.) On the basis of a reasonable decreasing progression in K_1, K_2, K_3 , etc., this would also indicate a likely value of no more than about 10^{12} for β_1 for Pu(IV) carbonate. Third, formation of PuCO₃²⁺ at high pH can be expressed as

 $PuO_2 \cdot xH_2O + CO_2 + 2H^+ = PuCO_1^{2+} + (x + 1)H_2O$ (1)

It can be seen from the pH dependence of this reaction, if the PuCO₁²⁺ species had a sufficiently large formation constant to allow an even measurable concentration of such an ion in the solutions studied by Moskvin and Gelman,¹¹ namely pH 11.5 and 0.36-3.6 M CO32 solutions having equilibrium CO2 pressures less than that of air, it would be the principal species present in strong acid solutions (such as >1 M HClO₄) in equilibrium with the CO₂ content of air. Because such carbonate complexes are not observed, the conclusions of Moskvin and Gelman¹¹ and Kim et al.¹⁵ are most certainly incorrect. Equations similar to eq 1 can be extended to higher carbonate complexes (and to other metals with highly insoluble hydroxides or hydrous oxides) to show that only anionic complexes can contribute to any appreciable extent to solubility in carbonate or bicarbonate solutions. Since, in the case of tetravalent actinides, anionic complexes involve at least three carbonates, solubilities can be expected to drop rapidly with decrease in carbonate concentration below those known to occur in >1 M carbonate-bicarbonate solutions. Fourth, the measured Pu(IV) concentration¹⁸ in equilibrium with Pu(IV) hydrous oxide at pH 8 in equilibrium with air is definitely $<10^{-10}$ M, whereas the value predicted from the results of Kim et al.¹⁵ or Moskvin and Gelman,¹¹ using the hydrous oxide solubility product of Rai,¹⁹ is approximately 4×10^8 M.

The Np(IV)-ammonium carbonate system has been studied²⁰ by a solubility method at pH values of 8.6-8.8 and up to 2.2 M $(NH_4)_2CO_3$. It was concluded that the single species Np- $(OH)_4CO_3^{2-}$ was formed with a formation constant from the Np⁴⁺ ion of 1.20×10^{53} . Unfortunately, the method used to calculate this constant was completely erroneous. Errors included subtraction of a large constant value from all the measured solubilities in order to make this fit a first-power carbonate dependence, assumption that total carbonate plus bicarbonate is entirely carbonate at pH values where bicarbonate predominates and the carbonate to bicarbonate ratio is pH dependent, and provision of no evidence that the assumed "Np(OH)4-xH2O" was the equilibrium solid phase in these Np(IV)-saturated concentrated ammonium carbonate solutions, whereas three different ammonium tetravalent actinide (An) carbonate salts, (NH₄)₂An(CO₃)₃·xH₂O, $(NH_4)_4An(CO_3)_4 xH_2O$, and $(NH_4)_6An(CO_3)_5 xH_2O$, have been reported²¹ to have been isolated from ammonium carbonate solutions. Correction of the first two of these errors indicates that

- (16) Sillen, L. G.; Martell, A. E. "Stability Constants of Metal-Ion Complexes" The Chemical Society: London, 1964.
- Cotton, F. A.; Wilkinson, G. W. "Advanced Inorganic Chemistry", 3rd (17) ed.; Wiley Interscience: New York, 1972; pp 451, 650-652. (18) Rai, D.; Serne, R. J.; Moore, D. A. Soil. Sci. Soc. Am. J. 1980, 44, 490.
- (19) Rai, D. Radiochim. Acta 1984, 35, 97.
- (20) Moskvin, A. I. Soviet Radiochem. (Engl. Transl.) 1971, 13, 694.
 (21) Brown, D. "Comprehensive Inorganic Chemistry"; Bailar, J. C., Emeléus, H. J., Nyholm, R., Trotman-Dickensen, A. F., Eds.; Pergamon Press: New York, 1973; Vol. 5, pp 280-282.

the reported solutilit, Jually show somewhat less than a half-power dependence on carbonate. In addition, the single absorption spectrum presented²⁰ would appear to indicate an appreciable fraction of Np(VI), or an impurity with a similar absorption spectrum. If, as assumed,²⁰ Np(IV) hydrous oxide is the solid phase and Np(OH)₄CO₃²⁻ is the solution species, the Np(IV) solubility in these strong carbonate solutions would be pH independent above about 11.5 where carbonate dominates but would decrease markedly below this pH as carbonate converts to bicarbonate. This is the opposite of what was found for Pu(IV) by the same author,¹¹ and also his Pu(IV) solubilities¹¹ were much less at pH 11.5 than were the Np(IV) solubilities²⁰ at pH 8.6-8.8 for the same range of total carbonate levels. We have also observed a greater solubility of U(IV) in bicarbonate than in carbonate solutions. On these bases, the conclusions of ref 20 appear to be without merit.

Although our recent experimental results (unpublished results of Rai, Swanson, and Ryan; estimates from Strickert and Rai²²) put the logarithm of the solubility product of Np(IV) hydrous oxide at about -53.5, the data for (1) Np(IV) hydrolysis constants, (2) redox boundary between Np(IV) and Np(V), and (3) Np(IV) carbonate complexes are not available. These data are needed to determine Np concentrations in equilibrium with Np(IV) compounds under waste disposal site pH, E_{h} , and carbonate concentrations. Therefore, this study was undertaken to determine the solubility of Np(IV) hydrous oxide under reducing conditions, a range in pH values, and carbonate concentration as high as might be expected under waste site conditions.

Experimental Section

Reagents. Neptunium-237 was purified by anion exchange in nitric acid,²³ was essentially free (<34 ppm ²³⁹Pu and ~2 ppm ²⁴⁰Pu) of other α -emitting elements or isotopes, and contained <100 ppm other metallic impurities. The anion-exchange product was thermally evaporated to incipient denitration, with conversion to Np(VI). The residue was diluted about 10-fold with 12 M HCl and was again taken to incipient solidification, and this step was repeated five or six more times to thoroughly remove nitrates. The final solution was taken up in 6 M HCl. H_2O_2 (30%) was added to the solution to the point of precipitation of large amounts of Np(IV) peroxide, but thermal decomposition of the H₂O₂ produced about 15% reoxidation to Np(V) with the remainder Np(IV). The solution was then reduced to a mixture of Np(IV) and Np(III) in the cathode compartment of a partitioned electrolytic cell using a Ptgauze cathode and graphite anode. The Np(III) reverted rapidly to Np(IV) in the presence of air. Np(IV) remained stable in the 1.35 M Np-6 M HCl stock solution.

Deionized water was deaerated by boiling and thorough sparging at room temperature with an inert gas (>99.99% N2 or Ar with only a few parts per million oxygen). Two different NaOH stock solutions (10.5 and 1.93 M) were prepared in an inert atmosphere from a new bottle of reagent grade pellets of NaOH. The 10.5 M NaOH solution was found to contain 0.0152 M carbonate¹⁰ and was treated with a 7.5% excess of BaCl₂ to reduce carbonate through BaCO₃ precipitation. This solution was kept in a closed container in an inert atmosphere for several weeks before use. The 1.93 M NaOH solution, freshly prepared at the time of the experiments, was used only in experiments involving the effects of carbonate on the solubility of Np(IV) hydrous oxide.

Because the precise $E_{\rm b}$ boundary, as a function of pH, between Np-(IV) and Np(V) is not known and because appropriate redox agents to study this boundary have also not been tested, several redox agents were tested for their efficiency in maintaining Np in the reduced state. These redox agents included Na₂S₂O₄, Fe, Ni, Pb, and Zn. Na₂S₂O₄ was obtained from Sigma Chemical, and an alkaline 1 M stock solution was prepared under N2 immediately before use. Iron (powder, 325 mesh), Ni (powder, grade 1), and Pb (powder, 200 mesh) were from Alfa Products, and Zn (dust) was from the Scientific Supply Co.

General Procedures. All experiments were conducted in a glovebox with a prepurified N_2 (99.99% with a few ppm oxygen) atmosphere. Basic solutions of 0.05 M Na2S2O4 in glass centrifuge tubes were spiked with 0.03 mL of Np(IV) stock solution containing approximately 10 mg of Np, taking care that the solutions never became acidic. Solution

Ryan, J. L. "Concentration and Final Purification of Neptunium by Anion Exchange" Report HW-59193 REV: Hanford Laboratories: Richland, WA, 1959.

⁽²²⁾ Strickert, R. G.; Rai, D.; Fulton, D. W. ACS Symp. Ser. 1984, No. 246, 135.

Neptunium(IV) Hydrous Oxida Solubility

• -

Table I.	Equilibrium Constants and	A Reduction
Potential	s for Different Redox Agents	

reaction	log K	<i>E</i> *, V
$2SO_3^{2-} + 2H_2O + 2e^- = S_2O_4^{2-} + 4OH^-$	-37.86	-1.12
Fe²+ + 2e² ≠ Fe	-13.82	-0.409
Zn²+ + 2e' ₹ Zn	-25.79	-0.763
Pb ²⁺ + 2e ⁻ ≠ Pb	-4.25	-0.126
Ni ²⁺ + 2e ⁻ ≠Ni	-7.77	-0.23

volumes were adjusted to 40 mL, and pH values were adjusted to cover a range of pH 8-12.5 with perchloric acid or the carbonate-free NaOH stock solution. A 40-mL portion of 0.105, 0.42, 0.63, 0.84, 1.05, 1.55, and 2.10 M NaOH (carbonate free) containing 0.05 M Na₂S₂O₄ was also each spiked with 0.03 mL of Np(IV) stock solution. The precipitation of Np(IV) hydrous oxide and neutralization of excess acid consumed only 0.004 M, which is about 4% of the lowest hydroxide concentration used. Samples were sealed immediately after preparation and shaken until analyzed.

For experiments using metal reductants, 0.03-mL portions of Np(IV) stock solution were added to glass centrifuge tubes containing 40 mL of deaerated deionized water and 0.1 g of Fe, Ni, Pb, or Zn powders. The pH values of these suspensions were adjusted to cover a range of 2.5-8.5, and they were equilibrated as discussed above.

For the carbonate studies, samples containing 0.05 M Na₂S₂O₆ or 2.5 mg of Fe/mL and 0.01 M NaHCO₃ were adjusted to a range in pH values with HCl or freshly prepared NaOH stock solution (1.93 M) and were equilibrated as discussed above.

Measurements. Redox potentials were measured with a platinum electrode calibrated against quinhydrone buffers. The pH was measured to within 0.025 unit with a combination-glass electrode calibrated against pH buffers covering the range of pH values in the experiments.

Because of the inadequacy of centrifugation alone,¹⁸ Amicon type F-25 Centriflo membrane cones (Amicon Corp., Lexington, MA) with effective 25 000 molecular weight cutoffs and approximately 18-Å pore sizes were used to effectively separate solids from solutions. Pretreatment steps, as suggested by Rai,¹⁹ consisted of (1) washing and equilibrating the filters with deionized waters adjusted to the pH values of the given samples to avoid precipitation or dissolution of the solid phase due to change in the pH during filtration, and (2) passing a small aliquot of the sample through the filters (this filtrate was discarded) to saturate any possible adsorption sites on the filters and filtration containers.

Oxidation state analyses of the Np stock solution were by spectrophotometry and of dilute Np solutions were by solvent extraction techniques. Neptunium(IV) concentrations were determined from 0.5 M TTA in xylene extractions from nearly equal volumes of filtered solutions containing ~ 1 M HCl from which only monomeric Np(IV) extracts.²⁴ The total and solvent-extracted Np concentrations were determined by liquid scintillation α counting using Packard Insta-Gel and a Beckman (Model LS-9800) counter. The minimum detectable counts and thus the detection limits were determined by eq 2 from Curie.²⁵ where T is the counting time in minutes and R_0 is the background rate (background divided by counting time in minutes).

minimum detectable count rate = $2.71/T + 4.65(R_B/T)^{1/2}$ (2)

Results and Discussion

The thermodynamic equilibrium constants and standard equilibrium potentials of redox agents ($Na_2S_2O_4$, Zn, Fe, Ni, and Pb in order of increasing potential) used in this study are shown in Table I. Because these redox agents (1) are not redox buffers, (2) have not been previously tested as to whether they are kinetically active and appropriate for the Np system, and (3) have not been previously tested for their pH range of applicability, the measured redox values may not have any meaning in the thermodynamic sense. The intention in this study was to maintain low redox potential, not necessarily a fixed potential, where higher oxidation states of Np are not the dominant species in solution or at least are below our measurement detection limit. Under oxidizing conditions comparable to air, Np(V) is the dominant solution oxidation state and the solubility will decrease by a factor



Figure 1. Redox potentials, measured with a platinum electrode, of Np(IV) hydrous oxide suspensions containing different redox agents after about 8 days of equilibration.

of 10 with each unit decrease in pe (negative logarithm of the electron activity) as noted in eq 3. The solubility in terms of

$$NpO_2 H_2 O = NpO_2^+ + xH_2 O + e^-$$
 (3)

Np(IV) is independent of pe as shown in eq 4. As pe decreases

$$NpO_2 xH_2 O = Np^{4+} + 4OH^{-} + (x - 2)H_2 O$$
 (4)

(more reducing) further, the dominant solution oxidation state will become Np(III) whose concentration increases by a factor of 10 per unit decrease in PE as shown in eq 5. From the

$$NpO_{2}xH_{2}O + e^{-} = Np^{3+} + 4OH^{-} + (x - 2)H_{2}O$$
 (5)

logarithm of the solubility product of NpO2-xH2O of -53.5 (unpublished data of Rai, Swanson, and Ryan) and accepted Np(III)-Np(IV) and Np(IV)-Np(V) redox potentials, it is easily shown that above pH 3 in the absence of hydrolysis Np(IV) would never be the dominant solution oxidation state at any value of pc. At all pH values, the minimum solubilities of $NpO_2 xH_2O$ as a function of pe will occur when the concentration of Np(IV) species is at a maximum relative to Np(III) and Np(V) species. Where this occurs will depend on all the hydrolysis constants for the three oxidation states. In any case, regardless of pe, the measured solubility will be an upper limit for Np(IV) because its concentration is pe independent. The measured redox potentials of many of the equilibration solutions containing various reducing agents are shown in Figure 1. The values show that $Na_2S_2O_4$, Fe, and Zn in general maintained redox potentials close to the boundary at which water is reduced to produce H₂. Lead and nickel did not maintain such low potentials, and measured solubilities in these solutions were well above the detection limig $(10^{-4.4}-10^{-7.5} \text{ M})$. Oxidation state analyses of these solutions by TTA extraction indicated that essentially all the Np was in oxidized form, either Np(V) or Np(VI), in all samples. No further attempt was made to interpret these results.

The Np concentrations in the presence of $Na_2S_2O_4$ are reported in Table II. The results indicate that Np concentrations at pH values >7.7 are below are near the detection limit of Np ($10^{-8.3}$ M). Although the original samples were adjusted to obtain a large range (pH 8-14.2) and separation in pH among samples, the pH values of those initially at or below pH 11.0 dropped and were found to be between pH 6.99 and 7.11. Since oxidation of $S_2O_4^{2-}$ consumes hydroxide (Table I), it is felt that this pH decrease in the initially low hydroxide samples is due to oxidation by residual O_2 present in the solutions or from the glovebox atmosphere. The further disproportionation of $S_2O_4^{2-}$ under acidic conditions producing a variety of products such as sulfur and thiosulfate is known to be rapid,¹⁷ and this also lowers pH. Thus, the reducing power of $S_2O_4^{2-}$ would be affected. The samples with pH values of <7.2 on an average contained Np 1.5 orders of magnitude higher than the detection limit (10^{-8.3} M). Despite our low measured potentials, we believe this is a result of ineffectiveness of $S_2 O_4^{2-}$ at the lower pH values either because of the complexing ability of its disproportionation products or because of the effect

⁽²⁴⁾ Poskanzer, A. M.; Foreman, B. M. J. Inorg. Nucl. Chem. 1961, 16, 323.

⁽²⁵⁾ Curie, L. A. Anal. Chem. 1968, 40, 586.

⁽²⁶⁾ Weast, W. J. "Handbook of Chemistry and Physics": The Chemical

Rubber Co.: Cleveland, OH, 1972. (27) Hamer, W. J.; Wu, Y. C. J. Phys. Chem. Ref. Data 1972. 1, 1047.

Table II. Measured Np(IV) Hydro 12-Day Contact Time in 0.05 M Na₂S₂ Different pH Values with NaOH Jubilities at a 9- to ations Adjusted to

ifferent pH V	alues with NaOH		· · · · · · · · · · · · · · · · · · ·
no.	pHª	PE	log [Np, M]
600	6.99	-6.69	-6.46
601	7.05	-6.63	-6.98
602	7.12	-6.63	-6.67
603	6.95	-6.57	-6.47
604	7.11	-6.66	-6.81
605	7.10	-6.69	-6.89
606	7.71	-6.71	-8.02
607	11.24	-6.84	<-8.29
608	12.36	-6.79	<-8.29
609	12.46	-6.66	<-8.29
610	12.91	-6.59	<-8.29
611	13.19	ND	<-8.29
612	13.46	ND	<-8.29
613	13.63	ND	<-8.29
614	13.75	ND	<-8.29
61.5	13.85	ND	-8.26
616	14.03	ND	-8.06
617	14.18	-8.16	-7.92

⁶ The starting pH values of sample no. 600-607 were adjusted to 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, and 11.5, respectively. Samples no. 610-617 contained 0.015, 0.21, 0.42, 0.63, 0.84, 1.05, 1.55, and 2.10 M NaOH, respectively. The pH values of these samples were calculated from the NaOH concentrations and mcan ionic activities reported by Hamer and Wu.²⁷ ^b ND = not determined.



Figure 2. Measured apparent solubilities of Np(IV) hydrous oxide in different redox agents (detection limit for Np $\sim 10^{-4.3}-10^{-4.4}$ M). Solid lines represent predicted solubilities from currently available thermodynamic data with log $K_{sp} = -53.5$ from unpublished data of Rai, Swanson, and Ryan and the values of hydrolysis constants (Np⁴⁺ + $nH_2O = Np(OH)_a^{4-n} + nH^+$) of Np(OH)₄⁰ (log $\beta_4^{*} = 9.9$) and of Np(OH)₅⁻ (log $\beta_5^{*} = -17$) from Allard et al.¹

on its reducing ability. This conclusion is supported by the solubility results using iron or zinc as reductants, where in the range pH 6-7.5 all samples were found to be below the detection limit of $10^{-8.3}$ M Np. Because of the pH dependence of the dithionite-sulfite couple (Table I), both iron and zinc should be stronger reducing agents than dithionite in this pH region and the oxidation products, Fe(II) and Zn(II), should be adequately soluble to not add a complication in their use.

The solubilities, using $Na_2S_2O_4$ in the higher pH region and Fe and Zn in the lower pH region, plotted in Figure 2 show that under reducing condition and pH values >6 the Np concentrations in solutions contacting Np(IV) hydrous oxide (approached from oversaturation direction) are near or below the detection limit for Np of 10^{-8.3} M. The experimental results are compared in Figure 2 with values based on thermodynamic predictions using the logarithm of the solubility product value of -53.5 (unpublished data of Rai, Swanson, and Ryan) for eq 4 and the estimated hydrolysis constant data reported by Allard et al.¹ The experi-



Figure 3. Measured solubility of Np(IV) hydrous oxide in the presence of 0.01 M total carbonate and Fe and Na₂S₂O₄ as reductants (detection limit for Np ~10^{-4.2}-10^{-4.4} M). Using log $K_{up} = -53.5$ for Np(IV) hydrous oxide from unpublished data of Rai, Swanson, and Ryan and (1) assuming values of log β_1 for Pu(IV) carbonate complex¹³ apply to Np, the calculated activity of NpCO₃²⁺ is represented by the solid lind and (2) assuming log β_1 of Np(IV) carbonate to be lower than log β_1 of Pu(IV) carbonate by the same ratio that the logarithm of the association constant, log (1/K_{up}), of Np(IV) hydrous oxide is lower than that of Pu(IV) hydrous oxide, the calculated activity of NpCO₃²⁺ is given by the dashed line. The activities of higher carbonate complexes, and thus the total Np(IV) hydrous oxide solubility, would be several orders of magnitude higher than that of NpCO₃²⁺ on the basis of the published¹⁵ values of $\beta_2 - \beta_5$.

mental results show no evidence for amphoteric behavior of Np(IV) and thus the existence of Np(OH)₅⁻, consistent with our earlier results on U(IV),¹⁰ which is in sharp contrast to predictions based on estimated thermodynamic data. If it is assumed that the Np(OH)₅⁻ species exists at all, the log β_5^* value of the fifth hydrolysis constant (eq 6) must be <-24.7 as compared with -17

$$Np^{4+} + 5H_2O \implies Np(OH)_5^- + 5H^+$$
 (6)

estimated by Allard et al.¹ Because the reported values of the second, third, and fourth hydrolysis constants were estimated by interpolation between the first and fifth constants, they must also be considered incorrect even if the interpolation method⁴ is considered valid.

The effect of 0.01 M total carbonate on the Np(IV) hydrous oxide solubility in the appropriate pH range and in the presence of Na₂S₂O₄ and Fe as reductants was studied (Figure 3). The results show that the Np concentrations are near or below the detection limit, as is the case in the absence of carbonate, indicating no measureable effect of 0.01 M total carbonate on the solubility of Np(IV) hydrous oxide. The thermodynamic data for Pu(IV) carbonate complexes reported by Kim et al.¹⁵ if assumed to apply to the adjacent actinide Np, indicates that Np(IV) hydrous oxide should have been very soluble. Although we cannot calculate from our data the value for the Np carbonate complexes, our experimental results show that the values for the carbonate complexes reported by Kim et al.¹⁵ are very much in error. On the basis of our data, the values for log β_1 through log β_5 (eq 7) must be <22.5,

$$Np^{4+} + nCO_3^{2-} = Np(CO_3)_n^{4-2n}$$
 (7)

<27.9, <33.2, <38.5, and <41.6, respectively: whereas, the corresponding log β_1 through log β_5 for Pu(IV) carbonate complexes reported by Kim et al.¹⁵ are 47.1, 55.0, 57.9, 59.6, and 62.4, respectively. These calculations show that the log β_n values reported in the literature are >18 orders of magnitude too high. The actual values for the carbonate complexes are expected to be several orders of magnitude lower than the limits calculated from our data.

Although it is not possible to determine either absolute hydrolysis constant or carbonate complexation constant values for Np(IV) from these results, several significant conclusions can be drawn: (1) Solubility of Np(IV) h, /oxide under reducing conditions can be used to set upper limits on solubility-controlled concentrations of Np, and these concentrations are below the maximum permissible concentrations in uncontrolled discharge.28 (2) Most carbonate ground waters (<0.01 M total carbonate) will not significantly increase the Np(IV) hydrous oxide solubility

(28) "Standards for Protection Against Radiation", Report 10 CFR 20; U.S. Nuclear Regulatory Commission: Washington, DC, 1979.

above the maximum sible concentrations. (3) Contrary to predictions based on mermodynamic data reported in the literature, no evidence was found for amphoteric behavior of Np(IV). (4) The values of tetravalent actinide carbonate complexes reported in the literature are grossly in error.

Acknowledgment. This research was conducted for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. We thank Margaret McCulloch for analytical assistance.

Registry No. Np, 7439-99-8; NpO2, 12035-79-9; Na2S2O4, 7775-14-6.

Contribution from the Chemistry Departments, Ben-Gurion University of the Negev, and Nuclear Research Centre Negev, Beer-Sheva, Israel

Stabilization of the Monovalent Nickel Complex with 1,4,8,11-Tetraazacyclotetradecane in Aqueous Solutions by N- and C-Methylation. An Electrochemical and Pulse **Radiolysis Study**

NUSRALLAH JUBRAN,¹⁴ GREGORY GINZBURG,^{14,b} HAIM COHEN,⁴¹ YAACOV KORESH,¹⁶ and DAN MEYERSTEIN*144

Received August 11, 1983

The divalent nickel complexes with 1,4,8,11-tetraazacyclotetradecane (L1), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L₂), meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L₃), and 1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11tetraazacyclotetradecane (L_e) were reduced by reactions with e_{sc}^{-} and CO₂⁻ and by electrochemical reactions in aqueous solutions. The redox potentials of the NiL_i²⁺/NiL_i⁺ couples are -1.58, -1.15, -1.42, and -0.98 V vs. SCE for i = 1, 2, 3, and 4, respectively. The UV absorption bands of NiL_i⁺ are attributed to CTTS transitions. The kinetics of reduction of Co(NH₃)₆⁺, Ru(NH₃)₆⁺. O2, and N2O by NiL,* are reported and discussed. The self-exchange rates of reaction between NiL,* and NiL,2* were calculated by using the Marcus cross relation. The EPR spectra of NiL2⁺ and NiL4⁺ are reported. The complexation of NiL1⁺ by OH⁻ was studied. The results are discussed in detail. NiL₁⁺ and NiL₄⁺ are suggested as new, powerful, easily attainable singleelectron-reducing agents that can be used over a wide pH range in aqueous solutions.

Introduction

¢

We have recently observed that the reduction of the planar isomer of (C-meso-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11tetraazacyclotetradecane)nickel(II), NiL42+, yields the corresponding monovalent complex, which is surprisingly stable in aqueous solutions.² The kinetic stability of NiL₄⁺ in comparison to that of NiL₃⁺, L₃ = C-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, was attributed to two main factors; (a) The ligand loss reaction

$$NiL^{+} + 2H_{3}O^{+}_{aa} \rightarrow Ni^{+}_{aa} + LH_{2}^{2+}$$
(1)

is hindered or at least considerably slowed down by N-methylation. (b) The two-electron reduction of water

$$NiL^+ + 2H^+ \rightarrow NiL^{3+} + H_2$$
 (2)

is endothermic for $L = L_4$ whereas it is exothermic for $L = L_3$.³ The differences in the redox potentials of NiL_4^{2+} and NiL_3^{2+} were attributed to the more hydrophobic nature of NiL₄²⁺ in comparison with that of NiL_3^{2+} and/or to the fact that the nickel-nitrogen bond length is larger in NiL₄^{2+.2}

Due to the interest in the effect of macrocyclic ligands on the redox properties of transition-metal complexes in general and nickel complexes specifically,449 we decided to extend these studies.

- (1) (a) Ben-Gurion University of the Negev. (b) Deceased, Aug 5th 1981. (c) Nuclear Research Centre Negev.
- (2) Jubran, N.; Ginzburg, G.; Cohen, H.; Meyerstein, D. J. Chem. Soc., Chem. Commun. 1982, 517.
- (3) E^o for the couple NiL₃(H₂O)₂³⁺/NiL₃²⁺ was estimated as E^o = 0.93 V vs. SCE.⁴ As NiL₃(H₂O)₂³⁺ has a pK_s at 3.7.⁵ E^o is even lower in neutral solutions. We were unable to oxidize NiL₄²⁺ even by Br₂⁻².² Furthermore, the data in this work suggest that E^{*}_{NiLa²⁺/NiLa²⁺} >
- E^o_{NiL,j²/NiL,j²⁺}.
 (4) Zeigerson, E.; Ginzburg, G.; Kirsehenbaum, L. J.; Meyerstein, D. J. Electroanal Chem. Interfacial Electrochem. 1981, 127, 113.
- Cohen, H.; Kirschenbaum, L. J.; Zeigerson, E.; Jaacobi, M.; Fuchs, E.; Ginzburg, G.; Meyerstein, D. Inorg. Chem. 1979, 18, 2763.
 Lovecchio, F. V.; Gore, E. S.; Busch, D. H. J. Am. Chem. Soc. 1974.
- 96. 3109.

In this report we analyze the effect of nitrogen and carbon methylation of (1.4,8,11-tetraazacyclotetradecane)nickel(11), NiL,²⁺, on the redox couple NiL²⁺/NiL⁺ by comparing the chemical properties of NiL₁⁺, NiL₂⁺, NiL₃⁺, and NiL₄⁺ (L₂ = 1,4,8,11tetramethyl-1,4,8,11-tetraazacyclotetradecane). In addition to the electrochemical properties and specific rates of redox reactions studied by pulse radiolysis also the visible spectra of NiL²⁺ and pK values for the reaction

$$NiL^{2+} + OH^{-} = NiL(OH)^{+}$$
(3)

are reported. The last two properties are used as indicators for the ligand field strength and for steric hindrance along the z axis in the four complexes studied.

Experimental Section

Materials. The complexes NiL₁(ClO₄)₂ and NiL₃(ClO₄)₂ were prepared from the free ligands and Ni(CH₃CO₂)₂ as earlier described.⁹ $NiL_2(ClO_4)_2$ and $NiL_4(ClO_4)_2$ were prepared by N-methylation of $NiL_1(ClO_4)_2$ and $NiL_3(ClO_4)_2$, respectively, with use of the method described by Barefield et al.,¹⁰ i.e. deprotonation by solid KOH and methylation by CH_3I in Me₂SO. The IR spectra of $NiL_2(ClO_4)_2$ and NiL4(ClO4)2 in KBr pellets showed no bands due to N-H stretching, and the proton NMR spectra of these complexes were identical with those reported in the literature.10

All other materials were of AR grade and were used without further treatment. All solutions were prepared with use of heat-distilled water that was then passed through a Millipore setup, the final resistance being >10 MΩ.

Electrochemical Measurements. A three-electrode cell was used. Working electrodes were a dropping mercury electrode (DME) for polarograms, the Metrohm E 410 hanging-mercury-drop electrode

- Haines, R. I.; McAuley, A. Coord. Chem. Rev. 1981, 39, 77. Zeigerson, E.; Bar, I.; Bernstein, J.; Kirschenbaum, L. J.; Meyerstein, (9)
- D. Inorg. Chem. 1982, 21, 73. Wagner, F.; Barefield, E. K. Inorg. Chem. 1976, 15, 408. Wagner, F.; Morella, M. T.; d'Annello, M. J.; Wang, A. H. J.; Barefield, E. K. J. (10) Am. Chem. Soc. 1974, 96, 2625.

⁽⁷⁾ Busch, D. H.; Pillsbury, D. G.; Lovecchio, F. V.; Tait, A. M.; Hung, Y.; Jackels, S.; Rakowski, M. C.; Schammel, W. P.; Martin, L. Y. ACS Symp. Ser. 1977, No. 38, 32.

NOO				
NNG FORM -426A (2-79)	U.S. NUÇLE	AR REGULATORY COMMISSION	1. REPORT NUMBER (If any)	Obtain in advance from Division of Technical
NCRM 3201			ORNL/NRC/LTR-85/15	Information and Document Control
PUBLICA	TIONS RELEASE FOR	UNCLASSIFIED	2. DISTRIBUTION CATEGORY NO.	Insert appropriate numb
· WRC CONT	RACTOR AND CONSU (Please Type or Prin	LTANT REPORTS	(If env) NA	from the NRC Distributi Cotogory List (see WUREG-0550)
3. TITLE ANCO SUBTITLE	(State in full as shown on docume)	nți	· · · · · · · · · · · · · · · · · · ·	
Laboratory Eval Parameters, Exp	luation of DOE Radi perimental Strategi	onuclide Solubility I es, Laboratory Techni	Data and Selected Reta Lques, and Procedures.	rdation
4. AUTHORSS (If more than th	hree, name first author followed by "	end others")		
S. K. Whatley				•
S. NAME OF CONTRACTO	R	MAILING ADDRESS (Number en	d street, city, state and zip code)	TELEPHONE NO.
S. K. Whatley	nal Tabaratary	'P. O. Box X		
6 DATE MANNISCHIPT	A NEC BOORAN SPONSOR	Uak Kidge, IN 3783		624-6135
COMPLETEED		FECHNICAL MUNITUR	A STATE OF A	TELEPHONE NO.
March 1985	J. W. Bradbury			427-4571
8. CONTRACT DATA				
8. CONTRACT OR FIN M	NUMBER (Do not list DOE contract	number B0290		
b. IF CONTRACTOR IS	AUTHORIZED TO PRINT, PLE	ASE PROVIDE THE FOLLOWING I	FORMATION	
	Number of Copies Printed	Estimated Composition Cost	Estimated Printing Cost	
	•	•	l	
B. TYPE OF DOCUMENT	(Check appropriate box)	·····	· · · · · · · · · · · · · · · · · · ·	
A. TECHNICAL REPOR	3T	•		
(1) FUPHMAL (2) INTTERIM	x		•••••••••••••••••••••••••••••••	
b. CONFERENCE PAPE	ER			
(1) TTTLE OF CONF	ERENCE PAPER:	······································		
191 PLATEIRS AF AA				
IZI SARTEIS/ UF CO	NFERENCE:			
(3) LOCATION OF	ONFERENCE:			·····
(3) LOCATION OF CO	NFERENCE: CONFERENCE: e of item, e.g., thesis, speech, journa	el article, guide, etc.)		
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate typ) 10. SPECIAL_DISTRIBUTIO	INFERENCE: CONFERENCE: le of item, e.g., thesis, speech, journu DN (Send all sopies to the Distribution	el article, guide, etc.) n Services Branch, Division el Technical In	formation and Document Control.) (Specify a	peciel instructions such es
(3) LOCATION OF CO (3) LOCATION OF CO c. OTHER (Indicate hyp- 10. SPECIAL DISTRIBUTIO	NFERENCE: CONFERENCE: e of item, e.g., thesis, speech, journu NN /Send off sopies to the Distribution "Make evailable only as specifica distribution. Continue instruction	el article, guide, etc.) n Services Branch, Division of Technical In Ily approved by program office," er "Send s on reverse er separate sheet il necessan	formation and Documant Cantrol.) (Specify s to attached addressees." Submit addressec r.)	 pecial instructions such as I mailing labels for special
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate type)	NFERENCE: CONFERENCE: e of item, e.g., thesis, speech, journi ON (Send all sopies to the Distribution "Make available only as specifica distribution. Continue instruction.	el article, guide, etc.) n Services Branch, Division el Technical In Ily approved ±y program offica." er "Send s en reverse er separate sheet il necessarj	formation and Documant Control.) (Spacify s to attached addressees." Submit addressed r.)	peciel instructions such as I meiling labels for speciel
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate type)	INFERENCE: CONFERENCE: e of item, e.g., thesis, speech, journi ON /Send all copies to the Distribution "Make available only as specifica distribution. Continue instruction.	el article, guide, etc.) n Services Branch, Division el Technical In Ily approved by program offica." er "Send s on reverse er separate sheet il necessarj	formation and Documant Cantrol.) (Specify s to attached addressees." Submit addressed r.)	pecial instructions such as I mailing labels for special
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate type) 10. SPECIAL DISTRIBUTIO	NFERENCE: CONFERENCE: e of item, e.g., thesis, speech, journi ON /Send off sopies to the Distribution "Make available only as specifics distribution. Continue instruction only as specifical.	el article, guide, etc.] n Services Branch, Division of Technical In lly approved by program office." er "Send s on reverse or separate sheet if necessary Ly approved by NRC Pr	formation and Documant Control.) (Spacify s to attached addressees." Sutmit addressed .) ogram Office.	 pecial instructions such as I mailing labels for special
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate type) 10. SPECIAL DISTRIBUTIO Make available (NFERENCE: CONFERENCE: e of item, e.g. thesis, speech, journa ON (Send ell copies to the Distribution "Make available only as specifica distribution. Continue instruction only as specifical:	el erticle, guide, etc.] n Services Brench, Division el Technicel In Ily approved by program office, " er "Send s en reverse er seperate sheet il necessar 1y approved by NRC Pr	formation and Documant Control.) (Specify a to attached addressees." Sutmit addressed .) ogram Office.	peciel instructions such as I meiling lebels for speciel
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate type) 10. SPECIAL DISTRIBUTIO Make available (NFERENCE: CONFERENCE: e of item, e.g. thesis, speech, journe "Make evailable only as specifica distribution. Continue instruction only as specifical:	el anicle, guide, etc.] n Services Branch, Division el Technical Im Ily approved by program office." er "Send s en reverze er separate sheet il necessar ly approved by NRC Pr	formation and Document Centrol J (Specify s to attached addressees." Sutmit addresse .J Ogram Office.	pecial instructions such as I mailing labels for special
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate typ 10. SPECIAL DISTRIBUTIO Make available (NFERENCE: CONFERENCE: e of item, e.g., thesis, speech, journa ON /Send off sopies to the Distribution "Make available only as specifics distribution. Continue instruction only as specifical:	el anticle, guide, etc.] n Services Branch, Division of Technical In lly approved by program office." er "Send s on reverse er separate sheet il necessar Ly approved by NRC Pr	formetion and Document Centrol J (Specify a to attoched eddressees." Sutmit addressee J Ogram Office.	pecial instructions such as I mailing labels for special
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate typ 10. SPECIAL_DISTRIBUTIO Make available (NFERENCE: CONFERENCE: e of item, e.g. thesis, speech, journa NN (Send ell sopies to the Distribution "Make available only as specifica distribution. Continue instruction only as specifical:	el erticle, guide, etc.] n Services Brench, Division el Technicel In ily approved by program offica." er "Send s en reverse er seperate sheet il necessar 1y approved by NRC Pr	formation and Documant Cantrol.) (Specify a to attached addressess." Sutmit addressed (.) Ogram Office.	pecial instructions such as I mailing labels for special
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate typ 10. SPECIAL_DISTRIBUTIO Make available (NFERENCE: CONFERENCE: e of item, e.g., thesis, speech, journa ON (Send ell sopies to the Distribution "Make available only as specifica distribution. Continue instruction only as specifical:	el anicle, guide, etc.] n Services Branch, Division el Technical Im lly approved by program office." er "Send s en reverze er separate sheet il necessar ly approved by NRC Pr	formation and Document Centrol J (Specify s to attached addressees." Sutmit addressed .J ogram Office.	pecial instructions such as I mailing latels for special
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate typ)	NFERENCE: CONFERENCE: e of item, e.g., thesis, speech, journa "Make available only as specifics distribution. Continue instruction only as specifical:	el anicle, guide, etc.] n Services Branch, Division of Technical In lly approved by program office." er "Send s on reverse er separate sheet il necessar Ly approved by NRC Pr	formation and Documant Cantrol J (Spacify a to attached addressess." Sutmit addresses J Ogram Office.	peciel instructions such as I meiling labels for speciel
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate typ 10. SPECIAL_DISTRIBUTIO Make available (INFERENCE: CONFERENCE: e of item, e.g. thesis, speech, journa NN (Send ell sopies to the Distribution "Make available only as specifica distribution. Continue instruction only as specifical:	el article, guide, etc.] n Services Branch, Division el Technical In lly approved by program office," er "Send s on reverse er separate sheet il necessar ly approved by NRC Pr	formation and Documant Control.) (Spacify s to attached addressees." Sutmit addressed .) ogram Office.	pecial instructions such as I mailing labels for specia
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate typ 10. SPECIAL_DISTRIBUTIO Make available (NFERENCE: CONFERENCE: e of item, e.g., thesis, speech, journal ON (Send ell copies to the Distribution "Make evailable only as specifica distribution. Continue instruction only as specifical:	el erticle, guide, etc.] n Services Brench, Division el Technicel In lly approved by program office." er "Send s en reverse er seperate sheet il necessar ly approved by NRC Pr	formation and Document Centrol J (Specify s to attached addressees." Sutmit addressed .J Ogram Office.	pecial instructions such as I mailing labels for special
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate typ 10. SPECIAL DISTRIBUTIO Make available (INFERENCE: CONFERENCE: e of item, e.g., thesis, speech, journa Nh /Send off sopies to the Distribution "Make available only as specifice distribution. Continue instruction only as specifical:	el anicle, guide, etc.] n Services Branch, Division el Technical In lly approved ty program office." er "Send s on reverse er separate sheet il necessar Ly approved by NRC Pr	formetion and Document Centrol J (Specify a to attached addressees." Sutmit addressed J Ogram Office.	peciel instructions such as I meiling latels for speciel
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate typ 10. SPECIAL DISTRIBUTIO Make available (Make available (INFERENCE: CONFERENCE: e of item, e.g. thesis, speech, journal N (Send ell copies to the Distribution "Make available only as specifica distribution. Continue instruction only as specifical: (If eppliceble)	el anicle, guide, etc.] n Services Branch, Division el Technical In lly approved ty program office." er "Send s on reverse er separate sheet il necessar ly approved by NRC Pr 12. SUBMITTED BY	formetion and Document Centrol J (Specify a to attoched eddressees." Sutmit eddressed .J Ogram Office.	pecial instructions such as I mailing latels for special
(3) LOCATION OF ((3) LOCATION OF (c. OTHEER (Indicate typ 10. SPECIAL_DISTRIBUTIO Make available (Make available (1. PATENT TLEARANCE Forward to compare the signe with the rested document TO: Accorportate Patent C	INFERENCE: CONFERENCE: e of item, e.g. thesis, speech, journi "Make available only as specifica distribution. Continue instruction. Only as specifical: (If eppliceble) od NRC Form 426A together ts for review. Coursel	el enticle, guide, etc.) n Services Branch, Division el Technicel In lity approved by program office." er "Send s on reverse or separate sheet il necessary ly approved by NRC Pr <u>12. SUBMITTED BY</u> •. NAME OF AUTHORIZED CON W. N. Drewery, La	formation and Documant Control.) (Specify a to attached eddressees." Sut mit eddressee .) ogram Office.	peciel instructions such as I meiling latels for speciel TTOR (Type or print)
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate hyp 10. SPECIAL DISTRIBUTIO Make available (Make available (11. PATENT CLEARANCE Forward monsted document TO: Appropriate Patent (INFERENCE: CONFERENCE: The of item, e.g., thesis, speech, journal Make evailable only as specifica distribution. Continue instruction. Only as specifical: (If epplicable) If applicable) MARC Form 426A together ts for review. Counsel FE NOT BEOLUBED	el enticle, guide, etc.) n Services Brench, Division el Technicel In ily approved by program office." er "Send s en reverse er separate sheet il necessary ly approved by NRC Pr 12. SUBMITTED BY a. NAME OF AUTHORIZED CON W. N. Drewery, La b. OFFICIAL'S ORGANIZATION	formation and Documant Cantrol J (Specify a to attached addressees." Sutmit addressed J ogram Office.	peciel instructions such as I meiling lebels for speciel TTOR (Type or print)
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate hyp 10. SPECIAL_DISTRIBUTIC Make available Make available Make available forward == Distributic Forward =	INFERENCE: CONFERENCE: of item, e.g., thesis, speech, journal "Make available only as specifica distribution. Continue instruction only as specifical: (If eppliceble) d NRC Form 426A together ts for review. Counsel CE NOT REQUIRED CE GRANTED	el anicle, guide, etc.) In Services Branch, Division of Technical Im Ily approved by program office." er "Send s on reverse or separate sheet if necessary Ly approved by NRC Pr 12. SUBMITTED BY a. NAME OF AUTHORIZED CON W. N. Drewery, La b. OFFICIAL'S ORGANIZATION	formation and Documant Control J (Specify a to attached addressees." Sutmit addressee J ogram Office. TRACTOR OFFICIAL OR NRC MONI HOTATOTY Records Super	peciel instructions such as I meiling labels for speciel TTOR (Type or print) TTOR (Type or print)
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate hyp 10. SPECIAL: DISTRIBUTIC Make available Make available 1. PATENT CLEARANCE Forward :=Dmplated, signe with the meased document TO: App. ropriate Patent C a. PATENT CLEARANCE b. PATENT CLEARANCE c. PATENT CLEARANCE	INFERENCE: CONFERENCE: e of item, e.g. thesis, speech, journal "Make available only as specifica distribution. Continue instruction. only as specifical: (If eppliceble) id NRC Form 426A together ts for review. Counsel CE NOT REQUIRED CE GRANTED CE DENIED	el enicle, guide, etc.) In Services Branch, Division el Technical In Ily approved by program office," er "Send s on reverse er separate sheet il necessary ly approved by NRC Pr 12. SUBMITTED BY a. NAME OF AUTHORIZED CON W. N. Drewery, La b. OFFICIAL'S ORGANIZATION Oak Ridge National	formation and Documant Control J (Specify a to attached addressees." Submit addressee J ogram Office. ITRACTOR OFFICIAL OR NRC MONT boratory Records Super AL UNIT 1 Labaratory	peciel instructions such as I meiling labels for speciel ITOR (Type or print) TVIBOT
(3) LOCATION OF ((3) LOCATION OF (c. OTHER (Indicate hyp) 10. SPECIAL: DISTRIBUTIC Make available Make available 1. PATENT CLEARANCE Forward :=Dompleted, signed with the rested document TO: App. roppriate Patent C a. PATENT CLEARANCE b. PATENT CLEARANCE c. PATENT CLEARANCE L. PATENT CLEARANCE C. PATENT CLEARANCE D. PATENT CLEARANCE C. PATENT CLEARANCE	INFERENCE: CONFERENCE: e of item, e.g. thesis, speech, journal Make available only as specifica distribution. Continue instruction. only as specifical: (If eppliceble) id NRC Form 426A together ts for review. Counsel CE NOT REQUIRED CE GRANTED CE DENIED SNATURE DATE	el enicle, guide, etc.) In Services Branch, Division el Technical Im Ily approved by program office, " er "Send s on reverse er separate sheet il necessary ly approved by NRC Pr 12. SUBMITTED BY a. NAME OF AUTHORIZED CON W. N. Drewery, La b. OFFICIAL'S ORGANIZATION Oak Ridge National c. SIGNATURE (Authorized contract	formation and Document Control J (Specify a to attached eddressees." Submit eddressee J ogram Office. ITRACTOR OFFICIAL OR NRC MONI boratory Records Super AL UNIT 1 Labaratory or efficiel or NRC Monikor	pecial instructions such as I mailing latels for special ITOR (Type or print) TVIBOT