

April 11, 1985

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

WM-RES
WM Record File
B0287
ORNL HZ

WM Project 10,11,16
Docket No. _____
PDR
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Joan-Ticket
CZ

Dear Dave:

Enclosed is the progress report for the month of ^{MARCH} April 1985 for B0287, "Technical Assistance in Geochemistry," and LR-290-10. As discussed, the technical reviews of "Geochemical Sensitivity Analysis, I. Radioelement Speciation," by M. D. Siegel, K. L. Erickson, and D. A. Vopicka, and "Analysis of Data from Batch Sorption Experiments When Radionuclides Undergo Chemical Speciation Reactions," by K. L. Erickson, should be completed by April 18, 1985.

Bob Myers has begun to review the literature on americium and anticipates having a first draft of the topical report by July 1985. At the present time, I have not assigned anyone to start work on the topical report on plutonium. I will discuss this with you in the near future.

Sincerely,

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

SKW: bek

Enclosure

cc: Office of the Director, NMSS (Attn: Program Support Branch)
Division Director, NMSS Division of Waste Management (2)
M. R. Knapp, Chief, Geotechnical Branch
R. J. Starmer, Geochemistry Section, Geotechnical Branch
Branch Chief, Waste Management Branch, RES

W. D. Arnold
J. T. Bell
J. G. Blencoe
N. H. Cutshall
L. M. Ferris
J. R. Hightower
G. K. Jacobs

A. D. Kelmers
D. C. Kocher
A. P. Malinauskas
R. E. Meyer
F. G. Seeley
R. G. Wymer
SKW File (2)

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B-0287 PDR

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MONTHLY PROGRESS REPORT FOR MARCH 1985

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: S. K. Whatley

ACTIVITY NUMBER: ORNL #41 37 54 92 4 (FIN No. B0287)/NRC #50 19 03 01

TECHNICAL HIGHLIGHTS

Task 1 - BWIP Geochemical Technical Assistance

No activity.

Task 2 - NNWSI Geochemical Technical Assistance

The report Theoretical and Experimental Determination of Matrix Diffusion and Related Solute Transport Properties of Fractured Tuffs from the Nevada Test Site, LA-9741-MS, 1982, by G. R. Walter, was reviewed in conjunction with the update of the topical report on matrix diffusion. This report is a key NNWSI report on matrix diffusion in tuffaceous rocks from the NTS. It appears to be the only report published to date that deals with both experimental and theoretical aspects of matrix diffusion in NTS tuffs.

The principal objectives of the research were to: (1) measure the most important physical and chemical parameters that control matrix diffusion in fractured tuff; (2) identify and evaluate non-reactive solutes (groundwater tracers) for use in both field and laboratory tests of matrix diffusion in tuff; and (3) develop a detailed mathematical model of solute diffusion from fractures to a rock matrix. Because the physical properties of rocks have such a profound influence on matrix diffusion of solutes, Walter performed various laboratory experiments to determine the following matrix properties of his tuff samples: (1) porosity, (2) pore-size distribution, (3) effective diffusion coefficients, and (4) bulk resistivity at varying frequencies. Additionally, preliminary experiments were conducted to evaluate the membrane properties of the tuffs and to determine the importance of osmotic transport processes.

The experimental and SEM data that Walter obtained on the tortuosity and constrictivity of pore space in NTS tuffs are particularly noteworthy because they are the only data of that kind that have been published. (By contrast, there are copious data available on the porosities of NTS tuffs.) The principal shortcoming of the work is that the theory presented in the report is not applied to any "real" matrix diffusion problems (e.g., predicting the nature and extent of matrix diffusion of a conservative solute in a representative elementary volume of NTS tuff), so it has not yet been demonstrated that the theory can be used in practical applications. However, the report

states that refinements of the theory are proceeding, and efforts are underway to develop a computer code that will permit the theory to be tested.

The report Preliminary Evaluation of Hydrologic Properties of Cores of Unsaturated Tuff, Test Well USW H-1, Yucca Mountain, Nevada, USGS Water-Resources Investigations Report 84-4193, 1984, by E. P. Weeks and W. E. Wilson was also reviewed. The report presents new and (apparently) high-quality hydrologic data that can be used to ascertain the nature of groundwater movement in the unsaturated zone beneath Yucca Mountain. This report was cited repeatedly by DOE (1984) as a source of data that lends support to the DOE "matrix flow" hydrologic model for the unsaturated zone at Yucca Mountain. However, the hydrologic data presented in the report apply only to unfractured tuff.

Various comments on the more significant data/conclusions presented in the report are:

1. Ambient moisture tension in the unfractured tuffs was found to range from 1 to 2 bars, but the authors do not explain how their data on moisture tension are related to the matric ("suction") potentials of the tuffaceous rocks. It would be useful to know whether the data on moisture tension are consistent with the DOE (1984) assertion that unsaturated, porous, tuffaceous rocks beneath Yucca Mountain have matric potentials that range from -5 to -20 bars.
2. On page 2 the report states "In unsaturated zones that are hundreds of meters thick, the large near-surface fluctuations in soil-moisture tension that result from episodic infiltration events followed by evapotranspiration become totally dampened at depth, and deep percolation becomes nearly constant with time." This very significant conclusion that does not appear in the abstract of the report is important because it forms the basis for estimating an average vertical groundwater flux in the unsaturated zone using information on hydraulic-head gradient and effective hydraulic conductivity.
3. From their data, Weeks and Wilson estimate that vertical flux of groundwater through the unsaturated, porous, tuffaceous rocks beneath Yucca Mountain ranges from 0.003 to 0.2 mm/yr. This estimate suggests that, in the unsaturated, porous, and unfractured tuffaceous rocks beneath Yucca Mountain, groundwater movement is extremely slow.

The Weeks and Wilson data, which applies strictly to unfractured tuffaceous rocks, does not appear to preclude (or even contradict) the suggestion that groundwater movement in the unsaturated, porous, tuffaceous rocks beneath Yucca Mountain may occur principally by fracture flow. The Weeks and Wilson data can be cited as evidence supporting slow movement of groundwater in the unsaturated zone beneath Yucca Mountain if it is assumed a priori that groundwater flow occurs predominately by matrix

flow, but it is not appropriate to use these data as evidence to support a "matrix flow" hydrologic model vis-a-vis a "fracture flow" model because the Weeks and Wilson data indicate nothing about the likelihood of fracture flow of groundwater in the unsaturated zone at Yucca Mountain.

Reference: DOE, 1984, Draft Environmental Assessment, Yucca Mountain Site, Nevada Research and Development Area, Nevada, DOE/RW-0012.

Task 3 - Salt Geochemical Technical Assistance

No activity this month. At present the technical staff is not working on brine migration. As discussed in October 1984, we have insufficient resources to undertake the tasks requested in your letter of September 27, 1984, without curtailing activities in other areas.

Task 4 - Short-Term Geochemical Technical Assistance

A recent paper by Rai and Ryon [Inorg. Chem. 24, 247-251 (1985)] was reviewed by G. K. Jacobs in support of the NRC FIN No. B0290 project. This paper 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 $\text{Np}(\text{OH})_5^-$ 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.

Task 5 - Project Management

We have begun our preliminary planning for the conference on natural analogs. We are tentatively scheduling the conference for April 1986. This avoids conflicts with the AGS and ANS spring meetings. We have put together a preliminary outline for the conference and will be getting input from Doug Brookins (subcontractor from University of New Mexico) shortly. This conference will be modeled after the geochemical modeling workshop held last spring. We plan to have an introductory session to address regulatory criteria, a general discussion of the usefulness of natural analogs, and a discussion on the logic/philosophy of reasoning by analogy. There will be three main sessions relating to natural analogs for: (1) engineered barriers, (2) geochemical conditions and radionuclide migration, and (3) geochemical model validation. As more details are developed, we will forward the information to the NRC project manager for review.

MEETINGS AND TRIPS: None

REPORTS AND PUBLICATIONS: None

PROBLEM AREAS: None

COST/BUDGET REPORT:

Expenditures were \$25.0K for March 1985 and \$185.4K for FY 1985. A detailed cost/budget report will be sent under separate cover.

LETTER REPORT

TITLE: Recommendations on Geochemical Modeling of
Radionuclide Solubility/Speciation

AUTHOR: Gary K. Jacobs

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

PROJECT MANAGER: Susan K. Whatley

ACTIVITY 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, Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Projects: Report for January - March 1984, 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," Inorg. Chem., 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.

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

C. Data base limitations. 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. Experimental validation required. 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.

Articles

Contribution from the Pacific Northwest Laboratory,
Richland, Washington 99352

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

DHANPAT RAI* and JACK L. RYAN

Received March 20, 1984

Solubility of Np(IV) hydrrous oxide was approached from the oversaturation direction in the presence of reducing agents ($\text{Na}_2\text{S}_2\text{O}_4$, 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) hydrrous oxide, Np concentrations were at or below the detection limit for Np ($\sim 10^{-8.3}$ 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 $\log \beta_3^* < -24.7$ for $\text{Np}^{4+} + 5\text{H}_2\text{O} \rightleftharpoons \text{Np}(\text{OH})_5^- + 5\text{H}^+$ and of $\log \beta_n$ ($\text{Np}^{4+} + n\text{CO}_3^{2-} \rightleftharpoons \text{Np}(\text{CO}_3)_n^{4-2n}$) $< 22.5, < 27.9, < 33.2, < 38.5,$ and < 41.6 for β_1 – β_5 , 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

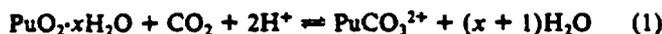
Under reducing conditions such as those that might be present at some of the proposed radioactive waste disposal sites, actinides, especially uranium and neptunium, will be present in the tetravalent state. Therefore, solubility data for tetravalent actinide compounds are needed to determine the potential 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.

Moskvin and Gelman¹¹ studied Pu(IV) carbonate complexes in concentrated (0.36–3.6 M) carbonate solution, concluded that only the PuCO_3^{2+} 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) hydrrous 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 PuCO_3^{2+} through $\text{Pu}(\text{CO}_3)_5^{6-}$. 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

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

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- (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.

formation constants of a variety of oxygen donor complexes such as carboxylates etc. of tetravalent actinides 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 10^{15} is reached. Second, the formation constant, β_1 , of the Pu(IV) ethylenediaminetetraacetic acid (EDTA)¹³ complex is about 10^{26} . 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_3 ($\beta_3 = K_1K_2K_3$) 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_3 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 PuCO_3^{2+} at high pH can be expressed as



It can be seen from the pH dependence of this reaction, if the PuCO_3^{2+} species had a sufficiently large formation constant to allow an even measurable concentration of such an ion in the solutions studied by Moskvina and Gelman,¹¹ namely pH 11.5 and 0.36–3.6 M CO_3^{2-} solutions having equilibrium CO_2 pressures less than that of air, it would be the principal species present in strong acid solutions (such as >1 M HClO_4) in equilibrium with the CO_2 content of air. Because such carbonate complexes are not observed, the conclusions of Moskvina 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 Moskvina 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 $(\text{NH}_4)_2\text{CO}_3$. It was concluded that the single species $\text{Np}(\text{OH})_4\text{CO}_3^{2-}$ was formed with a formation constant from the Np^{4+} ion of 1.20×10^{23} . 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 " $\text{Np}(\text{OH})_4 \cdot x\text{H}_2\text{O}$ " was the equilibrium solid phase in these Np(IV)-saturated concentrated ammonium carbonate solutions, whereas three different ammonium tetravalent actinide (An) carbonate salts, $(\text{NH}_4)_2\text{An}(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$, $(\text{NH}_4)_4\text{An}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$, and $(\text{NH}_4)_6\text{An}(\text{CO}_3) \cdot x\text{H}_2\text{O}$, have been reported²¹ to have been isolated from ammonium carbonate solutions. Correction of the first two of these errors indicates that

the reported solubilities actually 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 $\text{Np}(\text{OH})_4\text{CO}_3^{2-}$ 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 ^{239}Pu and ~ 2 ppm ^{240}Pu) of other α -emitting elements or isotopes, and contained <100 ppm other metallic impurities. The anion-exchange product was thermally evaporated to incipient denaturation, 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 H_2O_2 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 Pt-gauze 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 ($>99.99\%$ N_2 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 BaCl_2 to reduce carbonate through BaCO_3 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_h 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 $\text{Na}_2\text{S}_2\text{O}_4$, Fe, Ni, Pb, and Zn. $\text{Na}_2\text{S}_2\text{O}_4$ was obtained from Sigma Chemical, and an alkaline 1 M stock solution was prepared under N_2 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 $\text{Na}_2\text{S}_2\text{O}_4$ 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

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Table I. Equilibrium Constants and Standard Reduction Potentials for Different Redox Agents

reaction	log K	E°, V
$2\text{SO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{S}_2\text{O}_4^{2-} + 4\text{OH}^-$	-37.86	-1.12
$\text{Fe}^{3+} + 2\text{e}^- \rightleftharpoons \text{Fe}$	-13.82	-0.409
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-25.79	-0.763
$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$	-4.25	-0.126
$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}$	-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 $\text{Na}_2\text{S}_2\text{O}_4$ 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 $\text{Na}_2\text{S}_2\text{O}_4$ or 2.5 mg of Fe/mL and 0.01 M NaHCO_3 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 25000 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_B is the background rate (background divided by counting time in minutes).

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

Results and Discussion

The thermodynamic equilibrium constants and standard equilibrium potentials of redox agents ($\text{Na}_2\text{S}_2\text{O}_4$, 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

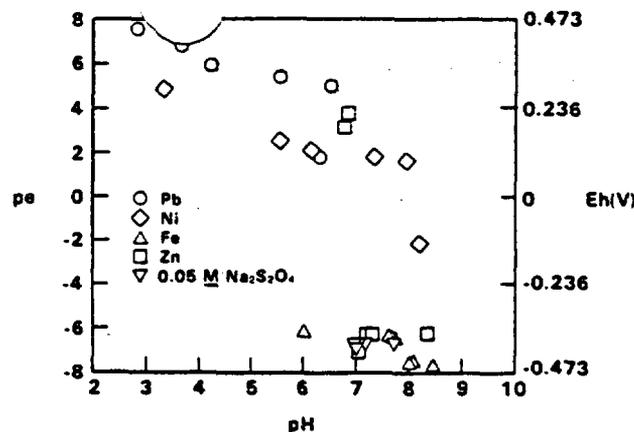
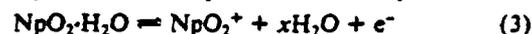


Figure 1. Redox potentials, measured with a platinum electrode, of Np(IV) hydrous oxide suspensions containing different redox agents after about 8 days of equilibration.

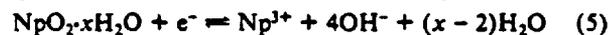
of 10 with each unit decrease in p_e (negative logarithm of the electron activity) as noted in eq 3. The solubility in terms of



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



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



logarithm of the solubility product of $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ 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 p_e . At all pH values, the minimum solubilities of $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ as a function of p_e 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 p_e , the measured solubility will be an upper limit for Np(IV) because its concentration is p_e independent. The measured redox potentials of many of the equilibration solutions containing various reducing agents are shown in Figure 1. The values show that $\text{Na}_2\text{S}_2\text{O}_4$, Fe, and Zn in general maintained redox potentials close to the boundary at which water is reduced to produce H_2 . Lead and nickel did not maintain such low potentials, and measured solubilities in these solutions were well above the detection limit ($10^{-4.4}$ – $10^{-7.3}$ 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 $\text{Na}_2\text{S}_2\text{O}_4$ are reported in Table II. The results indicate that Np concentrations at pH values >7.7 are below or 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 $\text{S}_2\text{O}_4^{2-}$ 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 $\text{S}_2\text{O}_4^{2-}$ 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 $\text{S}_2\text{O}_4^{2-}$ 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 $\text{S}_2\text{O}_4^{2-}$ at the lower pH values either because of the complexing ability of its disproportionation products or because of the effect

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Table II. Measured Np(IV) Hydroxide Solubilities at a 9- to 12-Day Contact Time in 0.05 M $\text{Na}_2\text{S}_2\text{O}_4$ Solutions Adjusted to Different pH Values with NaOH

no.	pH ^a	PE ^b	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
615	13.85	ND	-8.26
616	14.03	ND	-8.06
617	14.18	-8.16	-7.92

^a The starting pH values of sample no. 600-607 were adjusted to 8.0, 8.5, 9.0, 9.5, 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 mean ionic activities reported by Hamer and Wu.²⁷ ^b ND = not determined.

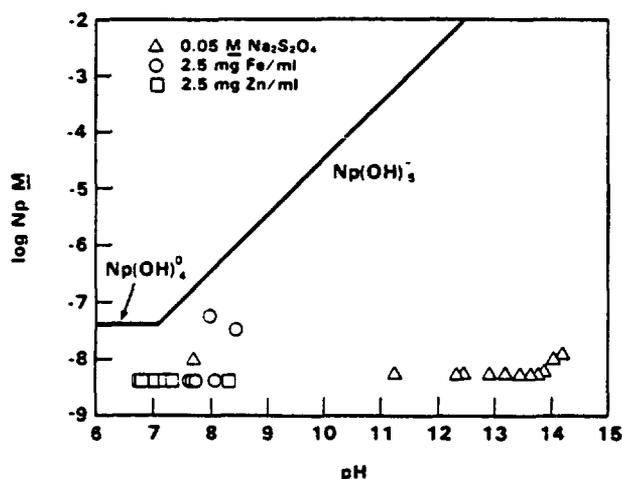


Figure 2. Measured apparent solubilities of Np(IV) hydroxide in different redox agents (detection limit for Np $\sim 10^{-8.3}$ - $10^{-8.4}$ M). Solid lines represent predicted solubilities from currently available thermodynamic data with $\log K_{sp} = -53.5$ from unpublished data of Rai, Swanson, and Ryan and the values of hydrolysis constants ($\text{Np}^{4+} + n\text{H}_2\text{O} \rightleftharpoons \text{Np}(\text{OH})_n^{4-n} + n\text{H}^+$) of $\text{Np}(\text{OH})_4^0$ ($\log \beta_4^0 = 9.9$) and of $\text{Np}(\text{OH})_5^-$ ($\log \beta_5^- = -17$) 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 $\text{Na}_2\text{S}_2\text{O}_4$ 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) hydroxide (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-

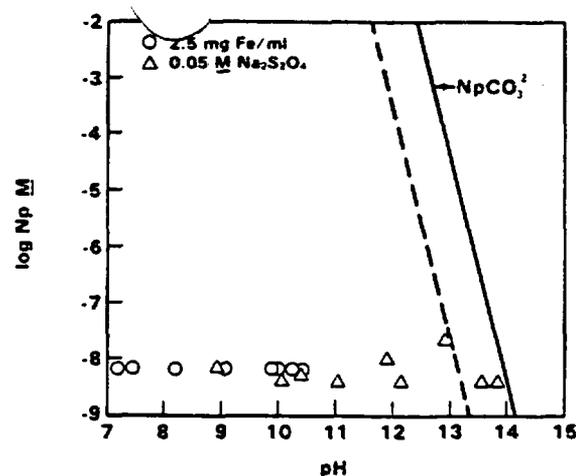


Figure 3. Measured solubility of Np(IV) hydroxide in the presence of 0.01 M total carbonate and Fe and $\text{Na}_2\text{S}_2\text{O}_4$ as reductants (detection limit for Np $\sim 10^{-8.2}$ - $10^{-8.4}$ M). Using $\log K_{sp} = -53.5$ for Np(IV) hydroxide from unpublished data of Rai, Swanson, and Ryan and (1) assuming values of $\log \beta_1$ for Pu(IV) carbonate complex¹⁵ apply to Np, the calculated activity of NpCO_3^{2+} is represented by the solid line and (2) assuming $\log \beta_1$ of Np(IV) carbonate to be lower than $\log \beta_1$ of Pu(IV) carbonate by the same ratio that the logarithm of the association constant, $\log (1/K_{sp})$, of Np(IV) hydroxide is lower than that of Pu(IV) hydroxide, the calculated activity of NpCO_3^{2+} is given by the dashed line. The activities of higher carbonate complexes, and thus the total Np(IV) hydroxide solubility, would be several orders of magnitude higher than that of NpCO_3^{2+} on the basis of the published¹⁵ values of β_2 - β_5 .

mental results show no evidence for amphoteric behavior of Np(IV) and thus the existence of $\text{Np}(\text{OH})_5^-$, 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 $\text{Np}(\text{OH})_5^-$ species exists at all, the $\log \beta_5^-$ value of the fifth hydrolysis constant (eq 6) must be <-24.7 as compared with -17



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 method⁸ is considered valid.

The effect of 0.01 M total carbonate on the Np(IV) hydroxide solubility in the appropriate pH range and in the presence of $\text{Na}_2\text{S}_2\text{O}_4$ 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 measurable effect of 0.01 M total carbonate on the solubility of Np(IV) hydroxide. 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) hydroxide 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 $\log \beta_1$ through $\log \beta_5$ (eq 7) must be <22.5 ,



<27.9 , <33.2 , <38.5 , and <41.6 , respectively; whereas, the corresponding $\log \beta_1$ through $\log \beta_5$ 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 $\log \beta_n$ 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) hydroxide 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

above the maximum permissible concentrations. (3) Contrary to predictions based on thermodynamic 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.

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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

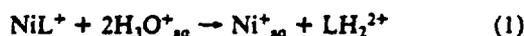
NUSRALLAH JUBRAN,^{1a} GREGORY GINZBURG,^{1a,b} HAIM COHEN,^{1a,c} YAACOV KORESH,^{1c} and DAN MEYERSTEIN^{1a,c}

Received August 11, 1983

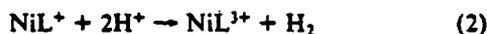
The divalent nickel complexes with 1,4,8,11-tetraazacyclotetradecane (L₁), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L₂), *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L₃), and 1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane (L₄) were reduced by reactions with e_{aq}⁻ 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)₆³⁺, Ru(NH₃)₆³⁺, O₂, and N₂O by NiL_i⁺ are reported and discussed. The self-exchange rates of reaction between NiL_i⁺ and NiL_i²⁺ were calculated by using the Marcus cross relation. The EPR spectra of NiL₃²⁺ and NiL₄²⁺ are reported. The complexation of NiL_i²⁺ by OH⁻ was studied. The results are discussed in detail. NiL₂⁺ and NiL₄⁺ are suggested as new, powerful, easily attainable single-electron-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-1,4,8,11-tetraazacyclotetradecane)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



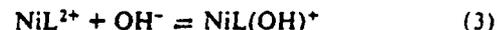
is hindered or at least considerably slowed down by N-methylation. (b) The two-electron reduction of water



is endothermic for L = L₄ whereas it is exothermic for L = L₃.³ The differences in the redox potentials of NiL₄²⁺ and NiL₃²⁺ were attributed to the more hydrophobic nature of NiL₄²⁺ in comparison with that of NiL₃²⁺ and/or to the fact that the nickel-nitrogen bond length is larger in NiL₄²⁺.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,⁴⁻⁹ we decided to extend these studies.

In this report we analyze the effect of nitrogen and carbon methylation of (1,4,8,11-tetraazacyclotetradecane)nickel(II), NiL_i²⁺, on the redox couple NiL_i²⁺/NiL_i⁺ by comparing the chemical properties of NiL₁⁺, NiL₂⁺, NiL₃⁺, and NiL₄⁺ (L₂ = 1,4,8,11-tetramethyl-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 NiL_i²⁺ and p*K* values for the reaction



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 NiL₂(ClO₄)₂ were prepared from the free ligands and Ni(CH₃CO₂)₂ as earlier described.⁹ NiL₃(ClO₄)₂ and NiL₄(ClO₄)₂ were prepared by N-methylation of NiL₁(ClO₄)₂ and NiL₂(ClO₄)₂, respectively, with use of the method described by Barefield et al.,¹⁰ i.e. deprotonation by solid KOH and methylation by CH₃I in Me₂SO. The IR spectra of NiL₂(ClO₄)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

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