地球化学データベースの開発研究（Ⅱ）

－概要－

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地球化学データベースの開発研究（II）

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要旨

　本研究は、高レベル放射性廃棄物地層処分システムの性能評価における評価の信頼性を高めるために、処分環境下で生起すると想定される種々の現象の適切なモデル化を進めるとともに、使用するデータの信頼性を向上させることを目的とし、実施したものである。得られた成果は下記の通りである。

1) 地球化学データ・モデルの品質保証
   第二次取りまとめ報告書を支援するための地球化学データベース（最新の熱力学データベース）ならびに解析，プログラムに関する技術資料を作成した。
2) 原位置データを基にした地下水分類、水質支配的反応
   第二次取りまとめ報告書で採用されている地下水分類を支援するため、原位置データに基づく解析を行い、3種類の地下水を分類した。
3) Se及びPbの熱力学データに関する研究
   これまでの試験結果を踏まえ、より現実的なSe溶解度制限固相の設定のための実験データ取得を目的として実施した。実験環境における硫酸還元菌の確認を実施したところ、硫酸還元菌の存在は確認されなかった。
4) 放射性元素の地球化学データ取得計画に関する検討
   第二次取りまとめ報告書に基づき、重要元素・課題の摘出を行い、放射化学研究施設（QUALITY）における試験計画を立案した。
5) 緩衝材の長期安定性に関する地球化学的研究
   文献調査を実施するとともに、熱力学的及び速度論的モデルを構築するために必要な実験計画を立案した。
6) 処分サイト選定プロセスにおける技術的指標の検討
   サイト選定に関する海外でのガイドラインならびにナチュラルアナログの観点から調査を行い、地球化学に関するサイト選定の技術指標を整理した。

Development Study on the Geological Database(II)

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ABSTRCT

This study has been carried out in order to increase the reliability of the performance assessment of geological isolation systems for high level wastes. We have been investigating a proper modeling of various phenomena, which would occur in the disposal environment and improving the reliability of geochemical data used in the performance assessment. The results are summarized as follows:

1) Quality assurance for geochemical data and modeling

   We have compiled technical report, geochemical database (newest thermodynamic database), and calculation, conversion program for geochemical analysis, which supporting the second progress report.

2) Study on groundwater categorization and dominant reaction based on site data

   We have carried out HCA/PCA analysis based on observed deep groundwater to support groundwater categorization of the second progress report. We concluded 3-type model groundwater categorized by analysis.

3) Experimental study on thermodynamic data of Se and Pd

   It is confirmed that sulfate reduction bacteria do not exist in our experimental environment.

4) Planning on data acquisition for geochemical data of radioactive elements

   Firstly we have pick up key radioactive elements and future studies based on the second progress report. Then we have draw up R&D plan for QUALITY.

5) Geochemical study on the long-term stability of backfill material

   An extensive literature review was carried out about the effect of Iron on Bentonite stability. Experimental conditions are researched to develop thermodynamic and kinetic modeling.

6) Study on the technical geochemistry guideline of site selection for disposal

   We have researched on the recommendation of sites for HLW(guideline of site selection) in foreign country and site selection from a view point of natural analogue. And we have summarized geochemistry technical guideline for site selection.

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1. はじめに

高レベル放射性廃棄物地層処分システムの性能評価において，評価の信頼性を高めるためには，処分環境下で生起すると想定される種々の現象の適切なモデル化を進めるとともに，使用するデータの信頼性を向上させることが重要となる。

このような背景により，本研究では昨年度までの成果を踏まえ，下記の項目を実施した。

1）地球化学データ・モデルの品質保証
2）原位置データを基にした地下水分類，水質の支配的反応
3）Se および Pd の熱力学データに関する実験的研究
4）放射性元素の地球化学データ取得計画に関する検討
5）緩衝材の長期安定性に関する地球化学的研究
6）処分サイト選定プロセスにおける技術的指標の検討

２．地球化学データ・モデルの品質保証

　地球化学データ・モデルの品質を保証するためには，重要な品質特性として定義されている追跡可能性，再現性，科学的防御性の観点から，これらの特性を配慮しつつドキュメントとしてまとめることが不可欠となる。本研究では，昨年度までに整備してきた地球化学元素対象とした鉱物・水溶性化学種の熱力学データや解析作業，熱力学データベース変換プログラムの作成作業に係わるドキュメントを作成した。

　本章では，以下に示す 8 件のドキュメントを作成した。各ドキュメントの内容は次ページ以降に示す。

（１）　Critical Evaluation of Thermodynamic and Kinetic Data for Non-Radioactive Minerals, Gases and Aqueous Species

（２）　Thermodynamic Database for Geochemical Calculations

（３）　Kinetic Data for Geochemical Calculations

（４）　Models of Cement-Water Interaction and a Compilation of Associated Thermodynamic Data

（５）　5 Geostatistical Analysis of Groundwater Chemistry in Japan: Evaluation of the Base Case Groundwater Set

（６）　Comments on PNC's Thermodynamic Data Evaluation Procedures and Recommended Revisions to PNC-TDB.H3.0

（７）　熱力学データベース変換プログラム

（８）　緩衝材中での空隙水化学のシナリオ

2.1 Critical Evaluation of Thermodynamic and Kinetic Data for Non-Radioactive Minerals, Gases and Aqueous Species

Summary

This first report on the project "Critical Evaluation of Thermodynamic and Kinetic Data for Non-Radioactive Minerals, Gases and Aqueous Species" summarizes work completed to date on the following three tasks:

TASK-1: Thermodynamic data for primary minerals, aqueous species, and gases,

TASK-2: Rate laws and associated kinetic data for minerals and aqueous species, and

TASK-3: Thermodynamic and kinetic data for major and important minerals in hyperalkaline environments associated with cementitious near-field components.

The main emphasis of the work completed during this first reporting period is to recommend high-quality thermodynamic data for minerals, gases and aqueous species. The thermodynamic basis supporting these data is also documented, as are statistical/mathematical methods used to define criteria for data selection and rejection. A recommended course of action is proposed for final selection of these data prior to their "freezing" for use in Heisei-12. Preliminary results on Tasks 2 and 3 are also briefly described.

Recent progress in consolidating thermodynamic data appropriate for geologic systems has stressed the development of compilations that fulfill two basic conditions:

- selected values are based on evaluations involving thermophysical, thermochemical, volumetric and phase-equilibrium data, and thus are not constrained solely by calorimetric data, and

- the procedures employed in the evaluations are documented,

The first of these conditions is based on the realization that enthalpies of formation have not in general been determined calorimetrically with the accuracy necessary to reproduce phase-equilibrium data More recently it has also been recognized that solubility data should be

included in these evaluations to the extent possible because data retrieved solely from calorimetric and phase-equilibrium experiments are often inconsistent with experimental solubility behavior at lower temperatures and pressures. This is particularly important for the present investigation where mineral-solution equilibria at groundwater temperatures and pressures are of primary interest.

The second condition is necessary for two reasons. First, data-analysis procedures may lead to recommended values of thermodynamic properties that are in conflict with accepted values. To resolve these conflicts, it is essential to understand the thermodynamic framework and assumptions supporting the procedures, as well as the statistical/mathematical basis for selecting, and rejecting, experimental observations. Second, it is highly desirable that a user should be able to update and refine the database as results of new experimental or field studies become available. This also requires familiarity with the details of thermodynamic relations supporting the database.

Three groups of investigators have compiled several databases over the past 21 years that fulfill these basic conditions. These databases are referred to in the following as "first tier" to emphasize their current pre-eminence as sources of high-quality thermodynamic data. The first-tier databases have to varying degrees grown out of older data compilations, many of which also contain high-quality data. These are referred to below as second-tier sources.

The first-tier databases have all been developed by professors and students in Earth Sciences departments of the:

- University of California, Berkeley,

- University of British Columbia, and

- University of Cambridge.

It is thus appropriate to consider each database as the result of a group effort, which continues to the present day through investigations of former students now working at their own university or other institution. Analyses and databases originating from the University of California, Berkeley, the University of British Columbia, and the University of Cambridge are referred to as those from the "Berkeley" group, "British Columbia" group, and "Cambridge" group, respectively. Second-tier data of primary importance are based on calorimetric data generated by the U.S. Geological Survey. These data to varying degrees are used as "reference" values in the first tier data sets to constrain data from phase-equilibrium studies.

The first-tier databases include data for minerals the greatly exceed the number of minerals slated for consideration in the first year of this project. All these data are evaluated, however, because the databases are all internally consistent and are thus best considered as a whole. All the minerals recommended for consideration in this project <u>are</u> included in one or more of the first-tier databases, with two exceptions: goethite and anhydrite. It is recommended that evaluation of these two minerals should be deferred to the second year of the project.

First-tier databases generated by the Cambridge, British Columbia and Berkeley groups are all recommended as the best available. These databases are internally consistent, and the accuracy of the data has been verified by extensive comparisons with the results of high temperature/ pressure phase-equilibrium studies. The most recent published databases among these groups are probably best regarded as "works in progress". Periodic revisions and expansions of all these databases are expected in the future.

Of these three, the Berkeley-group databases, and the associated SUPCRT92 software, are further recommended as the most <u>relevant</u> with respect to the nature of problems PNC must consider. These databases and software include thermodynamic properties of minerals, gases and aqueous species, all of which are needed to evaluate mineral-water equilibria at the relatively low temperatures and pressures of interest to PNC. It is important to emphasize that the important process of evaluating the accuracy of these data by simultaneous evaluation of calorimetric, phase-equilibrium, and solubility data has only recently been seriously attempted. It is expected these efforts will continue because the SUPCRT92 software is now widely available and is actively being used by many international groups. Progress may be slow, however, because such evaluations are extremely complex and labor intensive.

Second-tier databases are not recommended for one or both of the following reasons.

1) These databases are derived primarily or entirely from calorimetric data. This is disadvantageous because calorimetric measurements have been shown to be insufficiently accurate for reliable determination of enthalpies of formation. It is important to note that some of these data provide the foundation for the first-tier databases, and in this sense the first-tier databases represent improved extensions of the calorimetry-based databases. It is recommended generally that selection of high-quality thermodynamic data should be based on simultaneous evaluation of calorimetric, phase-equilibrium, and solubility data, whenever possible.

2) These databases are uncritical compilations for which the internal consistency among reported parameters is highly questionable. Such compilations include databases supporting many popular geochemical software packages, including EQ3/6 (dataO.com), PHREEQE, and MINTEQA2[3]. Many such compilations also suffer from inadequate documentation, and little or no evidence is given that the accuracy of the data has been verified by direct comparison with experimental results.

Discussion of the above recommendations is urgently needed, and a consensus should be reached soon in order to implement calculations necessary to achieve the project's objectives. Assuming the recommendations are adopted, the following strategy is suggested for final selection of thermodynamic data prior to Heisei-12:

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[2]. An internally consistent database, dataO. sup, based on SUPCRT92 is available for use in EQ3/6, however.

1. Thermodynamic data for minerals in SUPCRT92 do not compare well in some cases with data reported in the later British Columbia and Cambridge databases. A large number of these discrepancies have been resolved in published revisions. It is recommended that these revised data should be incorporated into the project's version of SUPCRT92. Similar revisions and new data planned for aqueous species should also be incorporated as soon as they are available (early 1997).

2. It should be acknowledged that thermodynamic data needed by PNC for some minerals and aqueous species might not be included in the current, or revised, version of SUPCRT92. It is recommended that a second-level version of the database in SUPCRT92 should therefore be developed, which includes the core database plus supplemental data obtained from other sources on the standard-state Gibbs free energy and enthalpy of formation, and third-law entropies of the needed minerals and/or aqueous species. Application of the second-level database must be undertaken with the understanding that the database is no longer internally consistent. Moreover, extrapolations of the data to temperatures other than 25°C will not be possible unless Maier-Kelly coefficients for minerals and gases, and equation-of-state parameters for aqueous species are available. Recognizing these limitations in the second-level version of SUPCRT92, equilibrium constants, enthalpy of reaction, and other data can nevertheless be calculated for additional mineral-water equilibria, as needed by J

JNC. It is recommended that these additional minerals, gases and aqueous species should be identified as soon as possible.

3. Revisions to SUPCRT92 and generation of a second-level version of this software will need to be completed several months prior to the time that PNC's thermodynamic database is officially frozen, to enable final calculation of thermodynamic data supporting other geochemical codes such as PHREEQE. It is recommended that corresponding "freezing times" for the revisions and second-level versions should be identified as soon as possible.

4. The following approach is proposed for dealing with discrepant values in PNC's core thermodynamic database relative those in SUPCRT92. Over the short term (1 to 5 years), carefully document these discrepancies and acknowledge that their significance is uncertain because absolute uncertainties in the SUPCRT92 database are unknown. Over the longer term, a course of action should be undertaken to establish consistency between the two databases, either by rigorously evaluating the absolute uncertainties for key species in SUPCRT92, or by incorporating core data into this database.

2.2 Thermodynamic Database for Geochemical Calculations

Summary

The Japanese repository concept for permanent disposal of high-level nuclear wastes is based on an integrated system of natural and engineered barriers to radionuclide migration. A crystalline or sedimentary host rock (into which the wastes will be emplaced at depths of 1000m, or 500m, respectively) will function as the natural barrier. Engineered barriers will include a bentonite buffer, steel canister and vitrified-glass waste form. The natural and engineered barriers will act in concert, such that the wastes are isolated from the geosphere for long periods of time (e.g., 1000 years), and subsequent releases of radionuclides to the biosphere are below levels that would pose an unacceptable risk to the public's health.

The Japan Nuclear Cycle Development Institute (JNC) is carrying out an applied R&D program to evaluate the feasibility of this concept[1]. The program is broad in scope, and includes field studies of various geological environments (Tono, Kamaishi and Mobara sites), laboratory investigations of chemical and transport phenomena (ENTRY and QUALITY facilities), and modeling-based assessments of repository performance (PNC, 1992). A number of these studies deal specifically with geochemical and chemical engineering issues, including:

- the stability of engineered barriers in the disposal environment over time scales of thousands to millions of years,

- the solubility, aqueous-speciation and sorption behavior of radioelements and non-radioactive elements, and

- general and site-specific geochemical processes controlling groundwater evolution.

These issues can be resolved with the aid of thermodynamic models, which are routinely used by JNC and others to interpret the results of experimental and field studies (Sasamoro and Yui, 1998; Iwatsuki and Yoshida, 1998; Sasamoto and Yui, 1997; Oda et al., 1996; Sasaki et al., 1995), to predict the long-term chemical evolution of natural and engineered-barrier systems (Yui and Shibata, 1998; Yui and Sasamoto; 1997; PNC, 1992), and to evaluate associated impacts on repository performance (Yui and Shibutani, 1998; Yui and Sasamoro, 1998; PNC, 1992, Yui et al., 1992).

Thermodynamic models require basic thermodynamic data over an appropriate range of temperatures and pressures. It is essential that the basic data are reliable, because, as stated by Silva

et al. (1995), .".. *the quality of the models cannot be better than the quality of the data they are based on*". Although the validity of this statement is beyond dispute, it is useful to clarify what the terms "reliable" and "quality" mean in the context of thermodynamic databases.

1- JNC was established in 1998, and is responsible for many of the repository R&D functions formerly assigned to the Power Reactor and Nuclear Fuel Development Corporation (PNC).

Here we adopt a pragmatic definition of both terms that is consistent with concepts underlying recent advances in the development and management of thermodynamic databases (Helgeson et al., 1978; Berman, 1988, Holland and Powell, 1990; Engi, 1992; Grenthe et al., 1992; Silva et al., 1995; Gottschalk, 1997). Thus, a database is considered reliable (or to be of high quality) if the following conditions are met, or are approximated as closely as possible:

- *internal consistency* - internal consistency is established among all the data, and is maintained as the database is updated and revised (the concept of internal consistency is discussed further in Section 3),

- *experimental basis* - selected values of thermodynamic parameters are based on evaluations of all available types of relevant experimental (and field) studies, not just on subsets of preferred experimental technique, or over arbitrary ranges of temperature and pressure,

- *documentation* - all procedures in the evaluations are documented, and

- *verification of accuracy* - the accuracy of data retrieved from the evaluations is verified by comparison of calculated thermodynamic quantities with their experimental counterparts.

Unfortunately, most published compilations of thermodynamic data are not internally consistent, have not been evaluated on the basis of all (or even most) available types of experimental and field studies, and are poorly documented with respect to data sources and reasons for data selection or rejection (Engi, 1992; Nordstrom and Munoz, 1985; - important exceptions are summarized in Section 3, however). For this reason, PNC[1] commissioned a two-year project beginning in 1996 to develop a thermodynamic database that adheres as closely as possible to the conditions stated above.

The project was limited in scope to data for minerals, gases and aqueous species characteristic of geologic systems, and some engineered barriers (e.g., bentonite "clays" and corrosion products of the steel canister). The project was also intended to complement, and to be consistent with, similar efforts carried out by PNC to obtain reliable thermodynamic data for actinide and fission-product elements (Yui et al., 1992).

The results of the project are summarized in this report, where two new databases, SPRONS.JNC and PHREEQE.JNC, are described, and where the basic philosophy and associated procedures used to generate them are documented. The report is organized as follows. General comments addressing the objectives of this study in relation to JNC's overall R&D program are summarized in Section 2. A survey of existing, reliable thermodynamic databases appropriate for geologic systems is summarized in Section 3. The results of the survey are used to define a general modeling-based strategy for database development and management. The model, SUPCRT[2] (Johnson et al., 1991) is consistent with SPRONS.JNC, and is briefly described in Section 4. The SPRONS.JNC and PHREEQE.JNC databases are described in Section 5, and listings of these databases are provided in Appendices A and B, respectively. The accuracy of these databases is assessed in Section 6 by comparison of experimental and calculated equilibrium constants for selected heterogeneous reactions (mineral and gas solubilities, Appendix C) and aqueous-speciation reactions (Appendix D).

2-SUPCRT is an abbreviation of "supercritical"; SPRONS stands for Sequential-access (ASCII) file of PROperties of Natural Substances

2.3 Kinetic Data for Geochemical Calculations

Summary

Kinetic data, including rate constants, reaction orders and activation energies, are compiled for 34 hydrolysis reactions involving feldspars, sheet silicates, zeolites, oxides, pyroxenes and amphiboles, and for similar reactions involving calcite and pyrite. The data are compatible with a rate law consistent with surface reaction control and transition-state theory, which is incorporated in the geochemical software packages EQ3/6 and GWB. Kinetic data for the reactions noted above are strictly compatible with the transition-state rate law only under far-from-equilibrium conditions. It is possible that the data are conceptually consistent with this rate law under both far-from-equilibrium and near-to-equilibrium conditions, but this should be confirmed whenever possible through analysis of original experimental results.

Due to limitations in the availability of kinetic data for mineral-water reactions, and in order to simplify evaluations of geochemical models of groundwater evolution, it is convenient to assume local-equilibrium in such models whenever possible. To assess whether this assumption is reasonable, a modeling approach accounting for coupled fluid flow and water-rock interaction is described that can be used to estimate spatial and temporal scales of local equilibrium. The approach is demonstrated for conditions involving groundwater flow in fractures at JNC's Kamaishi *in-situ* tests site, and is also used to estimate the travel time necessary for oxidizing surface waters ˜ to migrate to the level of a HLW repository in crystalline rock.

The question of whether local equilibrium is a reasonable assumption must be addressed using an appropriate modeling approach. To be appropriate for conditions at the Kamaishi site using the modeling approach noted above, the fracture fill must closely approximate a porous medium, groundwater flow must be purely advective and diffusion of solutes across the fracture-host rock boundary must not occur. Moreover, the mineralogical and physical properties of the fracture must be homogeneous over a characteristic length that is greater than or equal to the equilibration length.

If these conditions are met, calculations suggest local equilibrium would be a valid assumption in groundwater evolution models applied to the Kamaishi site if:

- it applies to reactions involving calcite, stilbite (assuming its dissolution! precipitation behavior is similar to that of heulandite), laumontite, albite and prehnite, but not quartz;

- Darcy flow velocities are relatively low *(e.g.,* less than about 0.1 m/yr), and

- it is based on the assumption that equilibrium corresponds to an uncertainty in the saturation index of 0.0±0.4.

If, however, actual reaction rates in the field are lower than expected, possibly because reactive surface areas are overestimated, the modeling approach may be inappropriate because it is probably unrealistic to assume that fracture mineralogy is homogeneous over fracture lengths exceeding a few meters or tens of meters.

An analytical model of redox-front migration behavior based on the stationary-state approximation, and JNC's conceptual model of a natural events scenario involving the migration of oxidizing surface waters in fractures, suggests that oxidizing solutions could travel from the surface to the depth of a repository in crystalline rock within 400 to 50,000 years. These estimates are relatively short compared with time periods considered in safety assessments of repository performance, which suggests that time-dependent variations in the redox environment of both the near field and geosphere may need to be accounted for in these assessments. The flow velocities and concentrations of reducing minerals assumed in JNC's conceptual model may be overly conservative, however,

2.4 Models of Cement-Water Interaction and a Compilation of Associated Thermodynamic Data

Summary

Modelling approaches that have been proposed for cement-water systems are reviewed in this report, and relevant supporting thermodynamic data are compiled. The thermodynamic data include standard molal thermodynamic properties of minerals and related compounds comprising cements, and equilibrium constants for associated hydrolysis reactions. Similar data for minerals that are stable in hyperalkaline geologic environments (e.g., zeolites) are also included because these minerals could be formed as hyperalkaline fluids emanating from cementitious materials in a repository for ILW/TRU wastes interact with the surrounding host rock. Standard molal properties (*i.e.*, standard molal Gibbs free energies and enthalpies of formation and standard molal entropies), and/or equilibrium constants for associated hydrolysis reactions, are included for:

- cement minerals and related compounds (Reardon, 1992; Glasser *et al.*, 1999),
- calcium-silicate hydrate minerals (Sarkar *etal.*, 1982), and
- zeolites (calorimetric and estimated values from various sources).

All these data are accepted at face value, and it is therefore cautioned that the data, considered as a whole, may not be internally consistent. It is also important to note that the accuracy of these data have not been evaluated in the present study.

Several models appropriate for cement-water systems have been proposed in recent years. Most are similar in the sense that they represent empirical fits to laboratory data for the CSH gel-water system, and are therefore not thermodynamically defensible. An alternative modeling approach based on thermodynamic principles of solid-solution behavior appropriate for CSH gel has recently been proposed, however. It is reviewed in the present study, and evaluated in relation to experimental results obtained by JNC on cement-water interactions.

The solid-solution model is based upon a thermodynamically- and structurally-justifiable description of CSH gel in terms of a non-ideal solid-solution of portlandite and calcium silicate end-member components. Miscibility gap and solubility data for the two end-members have been employed using the computer code "MBSSAS" to investigate solubility behavior for the solid-solution. A Lippmann phase diagram constructed using MBSSAS was used to input data to PHREEQC to calculate fluid compositional data in equilibrium with the gel solid-solution. A comparison of fluid compositions calculated with the gel solid-solution model with those available in the literature for the CSH

gel-water system show good agreement.

The CSH gel solid-solution model was then used to simulate the results of JNC leaching tests using the PHREEQC software. Due to inadequacies of the PHREEQC code, it was necessary to input the CSH gel solid-solution as discrete "portlandite" and "calcium silicate" end-members with variable solubility products in accordance with the Lippmann phase diagram. CSH gel solid-solution alone was considered to simulate the behavior of OPC.

The CSH gel solid-solution model provided a reasonable fit to the JNC OPC leachate data, but there were discrepancies with the experimental data for fluid leachate volumes between 10,000 and 30,000 ml. An alternative modeling approach (Berner, 1992) provided a better overall fit to the JNC data than the solid-solution model.

Re-evaluation of the CSH gel model with respect to possible variations in end-member miscibility and solubility behavior, together with a better representation of the overall cement system (inclusion of phases other than CSH gel) is anticipated to produce a better fit of modelled and experimental data. Further development of the both the CSH gel solid-solution model and cement-leaching simulation software (PHREEQC) is recommended to improve JNCs capability to predict the evolution of cement pore fluid composition with time.

2.5 Geostatistical Analysis of Groundwater Chemistry in Japan: Evaluation of the Base Case Groundwater Set

1.1 Purpose and Objectives

The chemical composition of ambient groundwater for a geological, high level radioactive waste repository is of crucial significance to issues such as radioelement solubility limits, sorption, corrosion of the overpack, behavior of compacted clay buffers, and many other factors involved in repository safety assessment. At this time, there are no candidate repository sites established in Japan for the geological disposal of high-level radioactive waste, and only generic rock formations are under consideration. It is important that a small, but representative set of groundwater types be identified so that defensible models and data for generic repository performance assessment can be established.

Over 15,000 separate analyses of Japanese groundwaters have been compiled into a data set for the purpose of evaluating the range of geochemical conditions for waste repositories in Japan. This purpose of this report is to demonstrate the use of a multivariate statistical analysis technique, principal component analysis (PCA), to derive a set of statistically based, representative groundwater categories from the multiple chemical components and temperature that characterize the deep Japanese groundwater analyses. PCA also can be used to guide the selection of groundwaters that could be used in scenario analyses of future geological events in Japan.

Chapter 2 provides a brief summary of the analytical methods used. The groundwater database used in the analyses is discussed in Chapter 3. Results are presented in Chapter 4 for two groundwater data sets: the Base Case and the Non-Quaternary Case. Conclusions are presented in Chapter 5 and references in Chapter 6. Appendices A and C contain the graphical representations of results and Appendices B and D contain the tabular presentation of results for the Base and Non-Quaternary Cases respectively.

1.2 Background

Binary plots of chemical variables (χ_i *vs.* χ_j) have been used by JNC to evaluate the deep Japanese groundwater data set. Such plots can provide useful visual correlations and trends. However, they are limited in defining bounding or representative groundwater compositions for two reasons. First, changes of groundwater chemistry evolve through multi-dimensional chemical space; i.e., there are simultaneous co-variations in the concentrations of all cations and anions related to complex rock-water interactions. Binary chemical plots provide only a possibly misleading, two-dimensional projection of these much more convoluted multi-dimensional trends. Second, specific groundwater samples that define bounding values in one binary plot are not necessarily the

same samples that define bounding values for some other binary plot. For example, it is not generally defensible to simply combine the minimum values for Na^+ and Cl^- from one binary plot with the minimum values for Ca^{++} and HCO_3^- from another binary plot, and then assume that they define the representative composition of dilute groundwater. This approach is only defensible if the samples representing the minima for all components from the two plots are the same.

Other commonly used diagrammatic techniques for the classification and interpretation of hydrochemical data, such as Piper diagrams [1] and Schoeller diagrams [2], also suffer from various drawbacks. For example, Piper diagrams use percentages of ions rather than actual concentrations while Schoeller diagrams are only suitable for a small number of samples.

Multivariate data analysis techniques, such as factor analysis have been shown to be more effective in graphically presenting and interpreting hydrochemical data. This is particularly true when there are large numbers of samples and/or large numbers of variables per sample to be evaluated [3,4,5]. Principal component analysis (PCA) is a multivariate statistical analysis technique fundamentally similar to factor analysis. It has been used by SKB at the Aspö Hard Rock Laboratory site in Sweden to identify end-member groundwater compositions and to describe the composition of waters in the tunnels in terms of percent mixtures of the different end members [6]. It also has been used by the Nirex to evaluate groundwater compositions and flow at Sellafield in the United Kingdom [7]. A more advanced version of PCA is applied in this study to analyze deep groundwaters from across Japan for the purpose of establishing representative groundwaters to support generic repository studies.

2.6 Comments on PNC's Thermodynamic Data Evaluation Procedures and Recommended Revisions to PNC-TDB.H3.0

Summary

The Power Reactor and Nuclear Fuel Development Corporation (PNC) is evaluating the reliability of its reference thermodynamic database, PNCTDB.H3.0 (Yui et al., 1992). Such evaluations are needed periodically to account for new experimental data published in the scientific literature, and new interpretations of older datasets. If the results of such studies conflict with accepted values in the reference database, then the reasons for the discrepancies must be resolved, and the database revised if necessary. This is a complex and rime-consuming task, but one that is critically important for PNC because reliable and up-to-date thermodynamic data are needed soon to carry out geochemical and performance assessment evaluations that will be discussed in the H-12 report.

PNC-GIS staff have evaluated data for many important mineral-water equilibria (equilibrium constants and reaction enthalpies), and associated thermodynamic properties (ΔG°_f, ΔH°_f, S°, and c°_p) for individual minerals, gases and aqueous species. Preliminary results are documented in the following draft PNC Technical Reports[1]:

TR-1:   Thermodynamic Data of Silica Minerals,

TR-2:   Thermodynamic Data of Feldspar for PNC Thermodynamic Database,

TR-3:   Revised Thermodynamic Data of Kaolinite,

TR-4:   Progress Report on Thermodynamic Database Development Project - Phyllosilicare Group (Smectite),

TR-5:   Thermodynamic Data for Muscovite,

TR-6:   Pyrite,

TR-7:   Investigation of the Thermodynamic Data of Goethite,

TR-8:   Calcite and Dolomite,

TR-9:   Thermodynamic Data of Siderite and of Related Aqueous Species, and

TR-10:   Revised Thermodynamic Data of Gypsum and Anhydrite.

Each report considers the relevance of the selected mineral for PNC's site characterization/performance assessment investigations, and provides a summary of relevant thermodynamic data (including data in PNCTDB.H3.0). These data are converted if necessary {e.g., standard Gibbs energies of formation are calculated from equilibrium constants using "core" thermodynamic data for aqueous species from Silva et al. (1995)}, and compared. Reliable data are

identified based on this comparison, and revisions

[1]- Report numbers, (TR-No.), are arbitrarily assigned for later reference. An additional report by M. Mihara titled "The Developments of Thermodynamic Model of C-S-H Gel" is discussed separately in a letter report by D. Savage. to the reference database, if any, are recommended.

A similar evaluation of thermodynamic data for minerals, gases, and aqueous species has also recently been carried out for PNC by QuantiSci (Arthur et al., 1996). This study supports PNC's internal evaluations by recommending general guidelines and procedures necessary to establish accuracy and internal consistency in thermodynamic databases. The study also evaluates criteria for the selection of reliable data through analyses of results from multiple experimental and/or field studies, and recommends such data for most of the minerals, gases and aqueous species considered in PNC TRs 1-10.

The purpose of the present report is to compare the database evaluation procedures adopted by PNC with those recommended by QuantiSci, and to compare "reliable" data recommended by both groups. General remarks on the evaluation approaches adopted by PNC are summarized in the following section. Specific comments on individual reports are included in these remarks.

2.7 熱力学データベース変換プログラム

概要

高レベル放射性廃棄物地層処分システムの性能評価では，モデル地下水，間隙水組成，放射性元素の溶解度などの設定において機能の応じて，種々の地球化学コードやツールが利用されている。モデル地下水の設定においては，米国 USGS（地質調査所）にて開発された PHREEQE コードにより，深部地下水組成（pH，Eh，イオン濃度）を設定している。また，深部地下水組成の設定に当たっては活量・活量線図や Eh-pH 線図を作成し，原位置で取得された情報との照合を行いつつモデル化を行っている。本線図を効率的に作成するツールとしては，米国イリノイ大学で開発された Geochemist's Work Bench を使用している。また，人工バリア構成要素として採用されている緩衝材ベントナイトに地下水が侵入した場合の間隙水組成（pH，Eh，イオン濃度）の設定では，米国 USGS（地質調査所）で開発された PHREEQC コードが使用されている。PHREEQC は，PHREEQE コードの欠点を改善させ，かつ機能拡張を行い C 言語にて記述されたプログラムである。溶解度の設定については，前記 PHREEQE コードを使用し，ガラス固化体から溶け出す放射性元素の平衡濃度を算出している。

さらに，室内実験ならびに原位置試験データ解析を現実的な観点から実施する場合には，米国 LLNL で開発された EQ3/6（平衡論，速度論モデル）などが使用されることがある。

前記の地球化学解析コード（PHREEQE，PHREEQC，EQ3/6）や地球化学パラメータ分析ツール（Geochemist's Work Bench）は，計算を実施する上で熱力学データベース(ライブラリー；文字と数字で定義されたデータ群)が入力情報の１つとして使われている。また，解析結果は，登録されている化学種，鉱物の数や熱力学データの値に大きく依存している。従って，異なる解析コードを利用する場合においても，共通の熱力学データベースを使用することが，品質保証（解析条件の一貫性，整合性）の観点から肝要となる。ただし，熱力学データベースは解析コードによって異なるフォームで作成されているため，解析作業の効率性，解析条件の一貫性，整合性の観点から熱力学データベース変換プログラムの整備を行っておく必要がある。

本作業では，サイクル機構殿において広く利用されている PHREEQE コードの熱力学データベースを標準データベースとして，以下に示すように Geochemists Work Bench（以後 GWB と呼ぶ）用の熱力学データベースに変換するプログラムの作成ならびに PHREEQC 用の熱力学データベースに変換するプログラムの開発を行った。

    (1) PHREEQE/GWB 熱力学データベース変換プログラムの作成

    (2) PHREEQE/PHREEQC 熱力学データベース変換プログラムの作成

2.8 緩衝材中での空隙水化学のシナリオ解析

概要

　わが国の高レベル放射性廃棄物処分（HLW）ならびにTRU核種を含む放射性廃棄物処分（TRU）では，緩衝材として圧縮成形ベントナイトが採用されている。緩衝材中の化学組成は，溶解度や収着などの核種移行特性を決定することから，緩衝材の性能を評価する上で重要な役割を持つ。処分環境下において緩衝材中の化学組成を直接分析することは，困難であることから，これまでに種々のモデルによるアプローチが実施されている。一般的に，わが国のHLW，TRU廃棄物処分の性能評価においては，緩衝材中の化学組成が時間・空間領域において一定であるとの仮定の基に，簡易的なモデルにより予測されている。しかし，実現象として緩衝材中の化学組成は，時間・空間領域において変遷するため，本研究では，地球化学，物質移行連成解析コード（TRACE）を開発した。また，本研究では，検証（他のコードとの比較）ならびに確証（実験との比較）解析を行い，開発したコードの正確性，信頼性を確認した。

Abstract

A coupled reactive-transport model, TRACE, was developed and is used to simulate temporal and spatial variations in the chemistry of buffer porewater that could result from dissolution of soluble impurities, and by corrosion of the carbon steel overpack. The results using preliminary dataset indicate that soluble impurities disperse accompanying pH increase along with time and the effects of soluble impurities on porewater chemistry last for at least one hundred years. Incorporation of Fe, released from the overpack by corrosion, into smectite clays in the buffer may indirectly minimize increases in porewater pH generated by other ion-exchange reactions and calcite dissolution, but this depends on whether $Fe(OH)_2$, rather than magnetite, is assumed to be a stable corrosion product.

3. 原位置データを基にした地水分類，水質の支配的反応

　第 2 次取りまとめにおける地下水形成の考え方および地下水形成モデルの妥当性を示すためには，信頼性のある原位置データをもとに，地球化学的な検討を行う必要がある。本研究では，信頼性のある原位置地下水データ（東濃，釜石，茂原）をもとに．地下水分類や水質の支配的反応を検討し，ドキュメントを作成した。さらに地下水の Eh（酸化還元電位）に関しては，性能評価上での Eh の重要性，Eh を支配する反応，Eh を熱力学的・速度論的に検討する上で重要となる地球化学的情報（同位体，微生物など），Eh を熱力学的に検討することの妥当性について整理しドキュメントとしてまとめた。

　本章では，以下に示す 4 件のドキュメントを作成した。各ドキュメントの内容は，次ページ以降に示す。

(1) Review comments on geochemical models of groundwater evolution: Tono in-situ test site.

(2) Review comments on geochemical models of groundwater evolution: Kamaishi in-situ test site.

(3) Review comments on geochemical models of groundwater evolution: Mobara in-situ test site

(4) Oxidation-Reduction reaction: Overview and implications for repository studies.

3.1 Review Comments on Geochemical Models of Groundwater Evolution: Tono In-Situ Test Site

Summary

Field studies are being carried out by PNC to characterize the hydrogeologic and geochemical properties of several types of geologic systems in Japan. The objectives of the field studies include *characterization* of actual subsurface geochemical conditions in potential repository host rocks, and *testing* of equilibrium-based geochemical models of groundwater chemistry and evolution in relation to the actual behavior of real groundwater systems.

A draft PNC report (Sasamoto and Yui, 1998) describes the results of such testing for conditions at one of the Tono In-Situ Test Site. The modeling approach and results discussed in this report are reviewed with regard to the following questions:

- is the proposed model *adequately constrained* by site data?

- are modeling results and conclusions *consistent* with the site data?, and

- are modifications needed to improve the modeling approach?

It is concluded that the study by Sasamoto and Yui (1998) significantly advances and improves upon PNC's past efforts in the area of groundwater evolution modeling. This is primarily because a broader range of geochemical tools, including evaluation of thermodynamic stability relations among minerals and groundwaters at temperatures appropriate for the Tono site, and reaction-path simulations of possible irreversible processes controlling the evolution of Tono groundwaters are considered. Model constraints are also more closely based on the site's mineralogy and hydrochemistry.

Recommendations to further strengthen and improve the Tono study, which is still in progress, include:

- If available, all relevant data on the hydrochemistry of sedimentary host rocks at Tono should be evaluated during development and testing of the conceptual model of water-rock interactions.

- More detailed information on the actual mineralogy of the Tono site is needed, including the actual mineralogy of "plagioclase", "clay" and "zeolite".

- The uncertain reliability of thermodynamic data for some clay minerals and zeolites

should be acknowledged. This effect of this uncertainty on model predictions should also be discussed, at least qualitatively.

- Interpretations should be undertaken with caution regarding the effects of dissolved constituents, and temperature, on mineral-stability relations.

3.2 Review Comments on Geochemical Models of Groundwater Evolution: Kamaishi In-Situ Test Site

Summary

Field studies are being carried out by PNC to characterize the hydrogeologic and geochemical properties of several types of geologic systems in Japan. The objectives of the field studies include *characterization* of actual subsurface geochemical conditions in potential repository host rocks, and *testing* of equilibrium-based geochemical models of groundwater chemistry and evolution in relation to the actual behavior of real groundwater systems.

A draft PNC report (Sasamoto and Yui, 1997) describes the results of such testing for conditions at one of these sites, known as the Kamaishi In-Situ Tests Site. The modeling approach and results discussed in this report are reviewed with regard to the following questions:

- is the proposed model *adequately constrained* by site data

- are modeling results and conclusions *consistent* with the site data?, and

- are modifications needed to improve the modeling approach?

It is concluded that the study by Sasamoto and Yui (1997) is of very high technical quality overall, and that PNC generally is carrying out a sophisticated and comprehensive study of geochemical controls on the chemistry and chemical evolution of groundwater systems. Recommendations to strengthen and improve the Kamaishi study include:

- The exact nature of equilibrium in models of groundwater chemistry and evolution must be clearly defined, and should include the concepts of local, partial and metastable equilibrium. Including, or excluding, minerals for consideration in a model on the basis of assumed partial or metastable equilibrium behavior should be supported by referencing relevant laboratory and field studies.

- Stable isotope and tritium data suggest that groundwaters flow relatively rapidly through the Kamaishi site, and that an open-system model for this site may therefore be more appropriate than the closed-system model evaluated by Sasamoto and Yui (1997).

- PNC should consider all the groundwaters sampled at the Kamaishi site —not just the

older groundwaters sampled in the KH-1 borehole. Although it may reasonable to assume the older groundwaters are the most likely to have attained equilibrium, the younger groundwaters sampled in drifts and other boreholes may also provide valuable clues about irreversible processes during early stages of groundwater evolution.

- PNC should strengthen the assumption that oxidizing conditions in most Kamaishi groundwaters can be traced to difficulties in measuring reliable redox potentials. The results of various international studies, in which this has been convincingly demonstrated in both the laboratory and field, should therefore be discussed.

- Variations in the compositions of groundwaters among samples from individual fractures intersecting the E.L. 550, E.L. 250m and KD-89 drifts should be evaluated to support the (implicit) assumption that samples obtained from the KH-1 borehole are representative of solutions in the Kurahashi granodiorite.

- PNC studies (Osawa et al., 1995), which suggest that Kamaishi groundwaters flow preferentially in fractures, or fractures and adjacent altered-rock zones, should be acknowledged. The possibility that groundwaters flow only in fractures, for example, would suggest that only fracture minerals will affect groundwater evolution. Secondary effects, such as diffusional mixing of solutions in fractures and altered zones may also need to be considered, however.

- More detailed information on the actual mineralogy of the Kamaishi site is needed, including the compositions of plagioclase, sericite, chlorite, biotite, calcite and epidote, and the identities of minerals that may occur in trace amounts (e.g., clays, kaolinite, chalcedony).

- Minerals considered to be heterogeneous equilibrium constraints should be selected from among minerals actually present at Kamaishi. Minerals of igneous or hydrothermal origin should be considered with caution because they are probably unstable at low temperatures. Models indicating that groundwater compositions are supersaturated with respect to Kamaishi minerals should also be revised such that these "metastable" phases are assumed to equilibrate, if precipitation at low temperatures is reasonable.

- A lack of highly reliable thermodynamic data should not deter choices of equilibrium minerals. Reasonable estimates of the necessary data will greatly improve credibility in

the model, provided the uncertain reliability of the data is acknowledged and documented.

- PNC's approach in using a reference groundwater composition as the only criterion by which the validity of equilibrium-based models is tested should be reconsidered. It is recommended that PNC should instead consider the range in groundwater compositions actually measured at Kamaishi. PNC should then evaluate whether alternative models of groundwater evolution are equally valid, given this range.

It is also recommended that a more systematic approach toward developing and testing equilibrium-based groundwater evolution models should be adopted. The approach should include the following steps.

1. obtain detailed information on the mineralogy of the site and chemistry of site groundwaters,

2. calculate the saturation index of minerals for which it is reasonable to assume that site groundwaters are in contact,

3. develop a preliminary reaction-path model of groundwater evolution at the site, using the results of Step 2 to guide initial selection of possible equilibrium phases,

4. evaluate model results for consistency with field observations,

5. if results are inconsistent with site data, modify the reaction-path model by revising one assumption concerning whether a mineral *observed at the site* should be considered stable, unstable or metastable.

6. iterate steps 4 and 5 until an optimal model is obtained that is consistent with site mineralogy and which best explains observed groundwater compositions.

7. evaluate of the validity of the equilibrium approach by comparing results of the optimized model with site data.

These steps emphasize the iterative use of reaction-path models to raise questions concerning the validity of assumptions in an evolving conceptual model of the system. To carry this procedure out successfully, the modeler must rely on expert judgment to answer these questions.

3.3 Review Comments on Geochemical Models of Groundwater Evolution: Mobara In-Situ Test Site

Summary

Field studies are being carried out by JNC to characterize the hydrogeologic and geochemical properties of several types of geologic systems in Japan. The objectives of the field studies include *characterization* of actual subsurface geochemical conditions in potential repository host rocks, and *testing* of equilibrium-based geochemical models of groundwater chemistry and evolution in relation to the actual behavior of real groundwater systems.

Sasamoto and Yui (1999) summarize the results of JNC's geochemical investigation at the Mobara test site. In contrast to similar investigations carried out by JNC elsewhere, the Mobara study focuses primarily on characterization of subsurface geochemical conditions, with less emphasis on testing of geochemical models. Interpretation of subsurface geochemical conditions at Mobara is complicated because these solutions contain high concentrations of dissolved gases, and because the hydrostatic pressure at depths where the groundwater flows into wellbores (approximately 1000 meters from the surface) is relatively high (roughly 100 bars). Much of the work summarized by Sasamoto and Yui (1999) is therefore devoted to development and application of a geochemical modeling approach to evaluate the effects of degassing on the chemistry of Mobara groundwaters (referred to as back-titration models), and thus to characterize the chemistry of these solutions at *in-situ* pressures and temperatures in the subsurface. The "corrected" groundwater compositions are then used to test whether JNC's SRLP and SRHP saline-type groundwater evolution models (Yui and Sasamoto, 1999) are reasonable.

In the present review of the report by Sasamoto and Yui (1999) it is concluded that the concepts underlying the back-titration modeling approach are sound, and that the models are reasonably well constrained by field data. Supplementary use of "degassing models", which are essentially the reverse of back-titration models, may provide some additional insight into processes that could possibly occur in the wellbore and reservoir (e.g., concurrent degassing and precipitation of carbonate minerals). Constraints adopted in the back-titration models on redox conditions should be clarified, and the effects of other gases [e.g., $H_2S(g)$] on these conditions may need to be considered.

The main conclusion of the report – that JNC's SRLP and SRHP groundwaters are reasonable because the composition of the corrected Mobara groundwater "falls between" the compositions of these two end-members — should be defended more clearly. It is questionable, for example, why the compositions of the SRLP and SRHP groundwaters necessarily bound all possible types of saline waters in Japan.

3.4 Oxidation-Reduction Reactions: Overview and Implications for Repository Studies

Summary

The purpose of this report is to provide a survey and review on oxidation-reduction ("redox") reactions, with particular emphasis on implications for disposal of high-level waste (HLW) in deep geological formations. As an overview, the focus is on basic principles, problems, and proposed research related specifically to the assessment of redox for a HLW repository in Japan. For a more comprehensive treatment of redox and the myriad associated issues, the reader is directed to the cited textbooks used as primary references in this report.

Low redox conditions in deep geological formations is a key assumption in the "Second Progress Report on Research and Development for the Geological Disposal of HLW in Japan" (hereafter called "H12"). The release behavior of multi-valent radioelements, (e.g., Tc, Se, U, Pu, Np), as well as daughter radioelements of these radioelements, from a deep geological repository are sensitively related to redox conditions. Furthermore, the performance of certain barrier materials, such as overpack and buffer, may be impacted by redox conditions. Given this importance, this report summarizes some key topics for future technical studies.

4. ＳｅおよびＰｄの熱力学データに関する実験的研究

平成8年度および平成9年度の試験でSe溶解度に関する種々のデータを取得してきた。本年度は，これらの成果をふまえた試験を行う。平成9年度試験において Se 溶解度は，見かけ上 Se(hexagonal)固相に支配されている結果を得た。同条件での解析結果によると実測された液相 Se 濃度では，未飽和となってしまう結果を得た。一方，固相を FeSe2 と仮定すると液相 Se 濃度は，過飽和であることが解析された。この実測値と解析値の差は，液相と固相が平衡でなく，長期的には，平衡となり，より低い溶解度の FeSe2 固相の生成が期待される。そこで，本研究では，平成8年度および平成9年度の試験の結果を踏まえて，上記の現象の確認を行い，より現実的な Se 溶解度制限固相設定のために実験データを取得することを目的とする。成果の概要を以下に示す。

①試験系中の硫酸還元菌の存在について，半定量的に求めてみた結果，供試水中には，存在しないことが確認された。これによって，試験系の反応は，化学反応であり，微生物による寄与がないことが確認された。

②液相 Se 濃度は，10^{-8}mol/l レベルになるとともに，経時変化に従い減少傾向を示した。試料によっては，ICP-MS の検出限界値以下となった。

③固相は，FeSe2，FeSe，Se が確認され，浸漬期間とともに Fe-Se 鉱物が顕著になった。

＊従って，平衡状態は，確認できなかったものの，溶解度の高い Se 固相からより溶解度の低い Fe-Se 固相の変遷が確認されたことにより，性能評価上で有利な知見を得ることができた。

5. 放射性元素の地球化学データ取得計画に関する検討

第2次取りまとめの性能評価において，緊急性ならびに不足しているデータを対象として，現在建設が行われている放射化学研究施設（QUALITY）などにおいて，信頼性の高い放射性元素の地球化学データを取得するための試験計画を検討するものである。

試験計画書の作成にあたっては，今後，処分事業を実施する上で必要となる事項を摘出し，試験目的を明確にした。以下に，必要性の項目を示す。

■ 深部環境下での核種移行特性データを補充しておく必要がある。

■ 第2次取りまとめの安全裕度を明確にしておく必要がある。

■ 今後，国で策定する安全評価基準で使用されるデータならびに支援するデータ取得が必要となる。

対象元素の選定においては，下記の方針に基づきスクリーニングを行った。

■ 安全評価の結果（HLW：人工バリア）において重要な元素を考慮する。下記の元素は，地層処分研究開発第2次取りまとめ第一ドラフト「ガラス固化体1本あたりの緩衝材外側からの核種移行率」に基づき摘出したものである。

・ 処分後～十万年：Cs，Se，Ra，Tc，Sn，Th，Pb，Zr

・ 1万年～千万年：Tc，Sn，Th，Zr，U，Np，

■ 安全評価の結果（HLW：天然バリア）において重要な元素を考慮する。下記の元素は，地層処分研究開発第2次取りまとめ第一ドラフト「1次元平行平板モデルの重ね合わせによるガラス固化体1本あたりの核種移行率：処分場下流端面から100m地点」に基づき摘出したものである。

・ 処分後～十万年：Cs，Se，Tc，Sn，Pb

・ 1万年～千万年：Cs，Tc，Sn，Zr，Np

■ 安全評価の結果（TRU：天然バリア）：I，Se，C

■ 安全評価（地球化学）において，十分な確認がされていない事項（評価において仮定が設定されている場合）

・ Ra の溶解度は Ca との共沈を想定している（公開文献引用）。

・ Se の溶解度制限固相は，環境条件依存性が明確となっていない。

・ 各元素の分配係数に対して人工バリアと天然バリアの整合性確認が必要である。

上記安全評価（人工・天然バリア）の情報に基づき，上位5元素を重要元素とした場合，Cs，Se，Ra，Tc，Sn，Th，Zr，U，Pb，Np の12元素が抽出される。また，安全評価（地球化学）に係わる情報からも，前記10元素は含まれている。従って，本提案では，現実的な環境条件・安全評価に寄与させることを目的とし，上記の10元素に着目することを前提条件とした。研究計画書を表－1～3に示す。

Table-1   Procedure for acquisition(R&D) plan of geochemical data)

1.Title: **Long-term Performance of Waste Forms Containing C-14 and I-129**
2.Objective High-solubility, low-sorbing anionic radionuclides, such as C-14 and I-129, are calculated to migrate relatively rapidly through buffer and far-field rock.   Thus, restricting the rate of mobilization of these species from waste forms presents the greatest possibility for reducing their overall release rate from geological repositories.
3.Experimental Procedure There are two basic types of waste forms that can be envisioned for encapsulating C and I.   The first type is a waste form that is unstable under geological repository conditions, but releases these radionuclides at a low rate.   The second type is a waste form that is stable under expected geological repository conditions, hence the release rate of I and C will be limited by the thermodynamic solubility of this stable waste form. Cements, glasses and certain crystalline matrices are members of the first type, unstable under repository conditions.   The removal of C and I from such waste forms may be controlled by different mechanisms, such as congruent matrix dissolution, selective (incongruent) leaching, or diffusive ion-exchange.   It will be vital therefore to (1) determine the short-term and long-term mechanisms controlling radionuclide release rates, and (2) then determine what these release rates are as a function of expected geochemical conditions.   Note that certain geochemical parameters, such as salinity and pH may vary over long-time scales. Stable crystalline matrices are somewhat easier to evaluate using conventional solubility tests.   Note that it will be important to bracket such solubility measurements from both over-saturated and under-saturated conditions.   Also note that solubilities are also affected by geochemical parameters such as salinity and pH that may change over long times.
4.Reducing Agent Standard practice for achieving reducing test solutions should be used, such as iron filings as used for solubility tests (Rai and coworkers, PNNL).
5.Preparation method of material Crushing, sieving, and ultrasonic surface-cleaning of waste-form samples will probably be necessary to advance the degree of waste-form reaction in the laboratory to time scales more appropriate to

repository disposal. In addition, it will be necessary to establish the homogeneity and atomic configuration of C and I in the original waste-form matrix. EXAFS/XANES may be a useful technique, although detection limits may be a limiting factor.

6.Analysing

It will be vital to combine advanced solution chemical techniques with advanced analytical techniques for solids analysis. Bulk solids analyses, such as x-ray diffraction, are probably inadequate for the purpose of these tests. Surface analytical techniques, such as electron microprobe, TEM, STEM, PIXIE, SIMS, EELS and others should be considered to fully and unambiguously determine release mechanisms and rates of such waste forms.

7.Data Evaluation Method

Release rates as a function of key solution parameters must be established for different waste forms. It will be necessary to measure a number of solution species, not only dissolved I and C, to evaluate the release mechanisms of waste forms. Major chemical components that comprise the waste forms (Al, Si, Ca, Na, B) will have to be measured and compared against the concentration of radioelements and other minor components. Determining whether any secondary phases form, and whether they incorporate I and C, will be necessary to establishing the long-term isolation capabilities of I and C waste forms.

8.Schedule

To be determined.

Table-2   Procedure for acquisition(R&D) plan of geochemical data)

1.Title: **Determination of Conversion Factors between Batch-derived and Diffusion-derived Kds**
2.Objective   : It would be extremely useful to convert the large number of "batch-derived" Kd data to Kd values appropriate to intact materials (buffer, rock).   Three key parameters are connected in the following equation: $$De = Da(\varepsilon + \rho Kd)$$ Where De is the effective diffusion coefficient for the intact material, Da is the apparent diffusion coefficient, ε is the porosity and ρ is the density.   This can be rearranged to show: $$(De - \varepsilon Da)/ \rho Da = Kd \ (intact) \ = \ f \cdot Kd \ (batch)$$ where f is an empirical conversion factor relating the true "intact" Kd to the measured "batch" Kd. If all of the terms on the left-hand side of this equation can be measured for intact material, the "intact" Kd value can be determined and compared to "batch" Kd values.   By employing this approach for a number of radioelements, a consistent set of conversion factors for cations and anions can be established to allow conversion of other "batch" Kd values to "intact" Kd values.
3.Experimental Procedure De can be measured in intact materials in a number of ways, including diffusion tests with assumedly non-sorbing, conservative tracers (HTO) or by electrical conductivity measurements. Appropriate current carrier solutions would have to be used for different materials (e.g., KCl solution for Na-bentonite systems, NaCl solution for rocks). Da measurements can be made by a number of diffusion techniques that are well established at JNC. It would be important, however, to make these systematic De and Da measurements on intact samples at different (1) densities (especially for buffer material that may change density over time because of buffer erosion), (b) ionic strength of solutions to simulate different FRHP and SRHP waters, and (c) different radioelement concentrations so as to evaluate if there are any non-linear sorption effects that will require development of an isotherm.
4.Reducing Agent

Reducing conditions will be important for redox sensitive radioelements such as Se, Tc, U, Np, and Pu. Pre-conditioning waters with finely-divided iron filings is an approach that has worked well in radioelement solubility tests (Rai and coworkers at PNNL). Hydrazine is another reducing agent, but may present issues with respect to ion-complexing.

5.Preparation method of material

Buffer samples must be specially prepared with proper mixtures of materials and compaction to specific densities. The same sample should be used for both De and Da measurements, to assure maximum comparability of measurements.

6.Analysing

Standard Da techniques developed by JNC would be used. In addition, electrical conductivity measurements techniques have been reported in the literature (Conca and coworkers; Neretneiks and coworkers).

7.Data Evaluation Method

Measurement and interpretation of Da is difficult because it can be affected by factors such as duration of the test, non-linear sorption behavior, and curve fitting of results.

Measurement of De and Da as a function of compaction density can be useful in determining whether surface sorption or ion exchange is the dominant mechanism for sorption for each radioelement.

8.Schedule

To be determined.

Table-3 Procedure for acquisition(R&D) plan of geochemical data)

1.Title: **Determining the Chemical Buffering Properties of Bentonite-based Buffer**

2.Objective

The buffer, composed of swelling bentonite and sand-size additive, may impose long-term control ("buffering") on the chemical conditions of the repository near field and EBS. In particular, if such buffering can be confirmed, *site-selection acceptance crit*eria for groundwater pH, salinity, and Eh may be more permissive

3.Experimental Procedure

There are three important aspects of chemical buffering that can be experimentally determined:

• buffer index (the value that the buffer seeks to impose for a chemical parameter),
• buffer capacity (the amount of buffer agents present in the material), and
• buffer kinetics (the rate at which the buffer acts to achieve the buffer index).

Buffer index can be readily measured for major and minor chemical components and as a function of pH; measurement of index values as a function of Eh and trace chemical components are more difficult, are subject to detection limits and may be highly uncertain. In particular, many redox buffer pairs (e.g., $HS-/SO_4^{2-}$) are extremely slow at temperatures < 100°C.   However, reversible redox buffering by smectite clay (the principle clay in bentonite) has been show to display a reversible redox buffering capacity (Fe^{2+}/Fe^{3+} in octahedral sites) in the presence of hydrogen gas mixtures.

Titration, such as standard acid/base titration, can be employed to establish buffering capacity. The difficulty is in controlling the rate of titration with respect to buffering reaction kinetics. If titration solution is added faster than the buffering rate, a false measurement of buffer capacity may be made. Lastly, there will be a need to make measurements of buffering on intact/ compacted buffer samples. Because of the low permeability of such compacted material, the ingress of unreacted water and the egress (collection) of reacted, buffered water is a major issue. Vacuum (suction), squeezing, and centrifugation techniques have been applied in attempts to extract pristine pore waters from clay sediments; the centrifugation technique, in particular, has a high likelihood of both controlling the rate of "flow" of water into and out of clay samples, but also allowing extraction without mechanical crushing of clay particles that may release bound, inter-layer water that typically is not mobile under repository conditions.

If continuous water "flow" through samples can be established, then on-line spectrophotometric techniques or *in situ* chemical sensors can be employed to record changes in chemical parameters as

a function of time. In this way, buffering kinetics can be established.

4.Reducing Agent

Reducing conditions will be important for redox sensitive elements. Pre-conditioning waters with finely-divided iron fillings is an approach that has worked well in solubility tests (Rai and coworkers at PNNL), but the long-term stability of this poising of Eh is questionable because the dissolved concentration of redox-buffering species is low. Hydrazine is another reducing agent, but may present issues with respect to ion-complexing.

5.Preparation method of material

Buffer samples must be specially prepared with proper mixtures of materials and compaction to specific densities. There may be a need to either ultrasonically clean uncompacted buffer material or to "flush" the compacted system with initial water to remove ultra-small particles that are anomalously reactive because of their high surface area to mass ratio.

6.Analysing

A continuous flow flow-through reactor system is envisioned; this may require centrifugation for highly compacted buffer samples. Continuous measurement of egressing solution for major chemical components and pH measurement is anticipated. Eh probes may be used but sluggish response at low temperature is a potential concern. Addition of reactive redox pairs, such as envisioned for GEOFRONTS, could be added to the ingressing solution and spectrophotometric studies of the concentration of the dissolved redox pairs could be made in samples taken from the egressing solution.

7.Data Evaluation Method

Buffer index values and buffer capacity are relatively easy to measure, although the capacity for buffering should attempt to exhaust the buffer from both directions (e.g., conduct both acid and base titrations to examine pH buffering). Buffer kinetics is more problematical, especially for changing redox conditions. Use of reactive dissolved gases (oxygen or hydrogen) under pressure might be successful, as shown in previous redox studies of Fe^{2+}/Fe^{3+} in octahedral sites in smectite.

8.Schedule

To be determined.

6. 緩衝材の長期安定性に関する地球科学的研究

　現段階での高レベル放射性廃棄物地層処分システムにおける人工バリア設計では，金属材料から構成されるオーバーパックとスメクタイトを主成分とする緩衝材が接触して設置されている。そのため，処分の評価に必要な期間における，ベントナイトと金属材料との相互作用が課題となる。本研究では，オーバーパック候補材料として考えられている炭素鋼を考慮し，鉄とスメクタイトの相互作用に関する実験を行うとともに，その結果を熱力学的に検討し，さらに性能評価の観点から考察した。これらの検討結果を段階的にドキュメントとしてまとめた。

　本章では，以下に示す 3 件のドキュメントを作成した。各ドキュメントの内容は，次ページ以降に示す。
(1)　第 2 次報告
(2)　第 3 次報告
(3)　第 4 次報告

6.1 第 2 次報告

Summary

Work carried out for the project 'The Effect of Iron on Bentonite Stability' for the three months January 1999 to March 1999 is described. The following tasks have been pursued.

Characterisation of Kunipia-F

Kunipia-F has been characterised using electron probe microanalysis, XRD, SEM, TEM and cation exchange methods.

Analytical data obtained using electron probe microanalysis are not of high quality but structural formulae calculations show that ratios of oxide percent totals are consistent with reported chemical analyses of Kunipia-F.

Qualitative and quantitative analysis of Kunipia-F using XRD have been carried out. The quantitative data indicates that montmorillonite is the predominant phase present in Kunipia-F. Glycolation suggests that the montmorillonite in samples Kunipia-F 1 and Kunipia-F 2 contains less than 10 % illite interlayering. In order to determine whether or not beidellite is present, a Greene-Kelly test is required.

SEM investigations showed that almost all the Kunipia-F material has a 'cornflake' morphology with aggregates approaching 400 μm in diameter. Aggregate-forming particles are seen to be as small as 1 μm or less. Some tubular silicates observed may be zeolites.

SAED patterns of the montmorillonite obtained using transmission electron microscopy indicate that the material is composed of thin crystallites which are disordered about the c-axis. A few traces of graphite were found.

The $Cu(EDA)_2^{2+}$ technique has been used in some preliminary CEC determinations. This technique will be refined for further measurements of cation exchange capacity.

6.2 第3次報告

Summary

Work carried out for the project "The Effect of Iron on Bentonite Stability" for the period April – September 1999 is described. The following tasks have been pursued.

Characterisation of Kunipia-F

Fourier Transform-Infrared (FT-IR) analysis of Kunipia-F has been carried out in preference to Greene-Kelly tests as originally planned. In conjunction with the XRD and mineral formula data given in the Second Progress Report, the FT-IR data seems to indicate that Kunipia-F is composed primarily of sodium-montmorillonite.

Two sets of cation exchange capacity experiments have been carried out. Both were conducted in duplicate so that four determinations were obtained in total. For Experiment 1, suspensions were subjected to twelve hours of agitation. An agitation period of thirty minutes was used in Experiment 2. Significantly lower CEC values were obtained for Experiment 2. Initially, this may have been interpreted as the shorter agitation period producing incomplete cation exchange. However, data quality considerations indicate that the difference may be due in some part, to the analytical data possessing a component of analytical bias.

It is envisaged that CEC values will be obtained for batch reactor run products. If this is the case, further CEC determinations will be carried out, along with leachable cation determinations. In conjunction with very rigorous data quality control, these will enable the optimum agitation period to be determined.

A series of preliminary acid-base titrations have been conducted, to determine optimum experimental parameters (mainly relating to titration software). Further titrations will be required to determine hydrolysis constants and for adsorption site-density calculations.

Experiments

Fe(II) adsorption experiments have not been conducted as originally planned. Loss of iron (or

magnesium) from the aqueous phase of a mineral suspension may be due to precipitation of discrete iron mineral particles or adsorption of aqueous iron complexes to mineral surfaces. It is possible that aqueous Fe(II) complexes will be adsorbed to montmorillonite particles and then undergo transformation to iron compound precipitates. Without detailed spectroscopic analysis, it would not be clear as to which process was in operation. Spectroscopic analysis of Kunipia-F is problematic in that Kunipia-F possesses much structural iron. This is likely to interfere with adsorbed iron, in many spectroscopic techniques (such as Mossbauer analysis). Techniques such as EXAFS (X-Ray Absorption Fine Structure Spectroscopy) may be able to give more useful data, but gaining access to this equipment is difficult and expensive. Therefore, it seems as if adsorption studies are not feasible at present. This issue will be discussed with JNC in early October.

Batch reactor experiments have been designed and the construction of the test rig is nearly complete. The equipment will be tested and batch reactor experiments will soon be underway (late October/ early November).

Modelling

The literature concerned with the derivation of thermodynamic data for smectite / sheet silicates has been reviewed and is briefly outlined. A whole series of logarithmic activity diagrams have been constructed and a selection of representative diagrams is given. The implications these have for mineral stability in a HLW-EBS are discussed. The diagrams indicate that with a groundwater composition pertaining to high log a $[Fe^{2+}/(H^+)^2]$ values, nontronite is stable under expected repository conditions (relatively anoxic). Iron rich chlorites such as daphnite may also be stable. It is possible that montmorillonite may be altered to these phases, if the kinetics are favourable.

Improved thermodynamic modelling in conjunction with batch reactor experiments will resolve many of the unresolved issues relating to the effect of iron on bentonite stability. This will allow the development of models of bentonite alteration in bentonite-steel HLW-EBS systems.

6.3 第4次報告

Summary

The Japanese engineered bather design for HLW disposal envisages the use of a massive steel overpack around the waste canister and a substantial amount of a sodium-bentonite clay between the canister/overpack and the disposal tunnel walls. Similarly, an EBS design for TRU disposal would also involve substantial amounts of both steel canister materials and bentonite. Although the potential conversion of smectite to non-swelling illite in the repository environment has received considerable attention in the radioactive waste literature, the conversion of smectite to non-swelling iron sheet silicates has received little or none.

Iron dissolved from steel canisters during corrosion processes may react with the montmorillonite component of the bentonite to form an iron-rich clay such as nontronite, or de-stabilise the clay to form non-swelling sheet silicates such as chamosite. Iron and montmorillonite are present in a HLW EBS in roughly equimolar proportions, so that if any reaction takes place, there is scope for it to take place at a large scale. Natural system evidence shows that chloritisation reactions can take place at temperatures as low as 40°C. Quantitative models of bentonite alteration require relevant input data concerning the types, magnitudes, and rates of these reactions.

The objectives of this project (over 3 years) are to:

- Identify the types and amounts of solid products from experiments reacting montmorillonite clay with varying amounts of Fe^{2+} for different times and different temperatures.
- Evaluate the experimental data to derive rates and mechanisms of the alteration of montmorillonite to Fe sheet silicates,
- Investigate the thermodynamic stability of montmorillonite with regard to various Fe sheet silicates.
- Conduct experiments with compacted bentonite and iron to investigate impacts upon swelling behaviour.
- Assess the impact of bentonite alteration by Fe-bearing solutions upon EBS design.

In this report, work carried out for the period April – December 1999 is described. The following tasks have been pursued.

Characterisation of Kunipla-F

The bulk composition of Kunipia-F starting material was presented in the Second and Third Progress Reports of this project. XRD analyses indicate that Kunipia-F consists predominantly of di-octahedral smectite.

The end member composition of this smectite was determined by considering the FT-IR spectra of the material and its mineral formula. These techniques indicate that Kunipia-F is composed predominantly of sodium-montmorillonite.

Cation exchange capacity and acid — base titrations have been carried out on Kunipia-F. The results of these characterisation techniques are summarised in this report. It has been found that the cation exchange capacity (CEC) of Kunipia-F is approximately 122 meq/100g, as determined by the $Cu(EDA)_2^{2+}$ method.

Experiments

Batch reactor experiments have been designed. The experimental apparatus for these experiments has been designed, built and tested. The experimental apparatus consists eighteen titanium vessels and a batch reactor rig which consists of a large aluminium tray within which there are three aluminium heating blocks, these can be heated independently. Each block can accommodate six titanium vessels.

Batch reactor experiments are underway at 80, 150 and 250°C for run durations of 1, 3 and 6 months. One gram of Kunipia-F was placed in each vessel along with 50 ml of either 0.1 or 0.2 M $FeCl_2$ solution, which had been degassed with argon. The vessels were sealed under an N_2 atmosphere. The experimental parameters are summarised in the table below.

Modelling

Literature concerned with the derivation of thermodynamic data for smectite/sheet silicates has been reviewed and is outlined. A series of logarithmic activity diagrams has been constructed and a selection of representative diagrams is presented here.

These diagrams indicate that with a groundwater composition pertaining to high $Fe^{2+}/(H^+)^2$ activity ratios, nontronite is stable under expected repository conditions (relatively anoxic). Iron rich chlorites such as daphnite may also be stable. It is possible that montmorillonite may be altered to these phases, if kinetics are favourable. However, the logarithmic activity diagrams presented here must be interpreted with caution. Further considerations are required on the determination of thermodynamic data for smectite.

Improved thermodynamic modelling in conjunction with batch reactor experiments will resolve many of the unresolved issues relating to the effect of iron on bentonite stability. This will allow the development of models of bentonite alteration in a bentonite-steel HLW-EBS.

7. 処分サイト選定プロセスにおける技術的指標の検討

処分場の候補地・予定地選定に際しては，社会的要因に加え，技術的要因（例えば，地層の安定性，地下水組成，核種移行挙動パラメータなど）が処分場選定の指標として重要である。例えば，米国の高レベル放射性廃棄物処分場の予定地であるユッカマウンテンにおいても，複数のサイトからの絞り込みにおいては，技術的要因に基づき決められた事例がある。本研究では，処分場のサイト選定に係わる技術的要因に関して，以下に示す2つのアプローチにより地球化学の観点で検討し，サイト選定プロセスにおける技術的指標を整理した。

第一のアプローチとしては，米国において，処分場のサイト選定や安全基準の策定にあたり考慮されている技術的指標を調査・整理した。また，性能評価の観点で地球化学パラメータに着目した場合のサイト選定の考え方，技術的指標として挙げられている概略数値なども調査，整理する。本調査・整理については，諸外国の情報を過不足なく収集することが可能と考えられる QuantiSci 社（米国・英国）に調査を依頼した。本アプローチによる調査は，以後，米国および欧州の技術的指標と呼ぶこととする。

第二のアプローチとしては，ウラン・トリウム鉱床等における希土類元素の地球化学的挙動および鉱物－水反応などに係わる既存の研究事例をもとに，処分サイトに求められる地球化学的条件（特に長期的な核種移行挙動に着目した場合）について整理した。本調査・整理については，ナチュラルアナログの観点から地球化学の分野において，酸化還元現象の専門家である米国 GeoSolution（大本博士）に調査を依頼した。本アプローチによる調査は，以後，長期的な核種移行挙動に着目した技術的指標と呼ぶこととする。

以下に主な調査結果の概要・詳細結果を示す。

諸外国の事例に基づくサイト選定の技術的指標の調査では，HLW，TRU 廃棄物処分事業ならびに研究開発を実施している国の中から，ベルギー，フィンランド，フランス，ドイツ，スペイン，スウェーデン，スイス，イギリス，アメリカの9ヶ国を対象として，サイト選定に係わる一般的なガイドラインの調査・地球化学的な技術指標について整理した。

■ サイト選定において地球化学環境条件に係わる技術指標を考慮しない国：ドイツ，スペイン，英国，ベルギー，フィンランドは，地球化学環境に係わる技術指標を考慮していない。

■ サイト選定において地球化学環境条件に係わる技術指標を考慮する国：スイス，スウェーデン，フランス，米国は，地球化学環境に係わる技術指標を考慮している。

■ 地球化学のための技術指標：技術的指標として，詳細な数値は記載されていない。
　主な技術指標を以下に示す。
　　・　地下水組成（Eh，pH，炭酸濃度，イオン強度，有機物）
　　・　深部地下での地球化学プロセス（岩石の溶解）
　　・　詳細数値は安全解析により設定

　ナチュラルアナログに基づくサイト選定の技術的指標に関する主な調査結果を以下に示す。

■ 処分場の地下水組成として，酸化還元電位は，概ね100(mV)以下，pHは放射性元素の溶解度最小化の観点から中性領域(6〜8)が望ましい。
■ 還元剤として，岩石中では黄鉄鉱を含有していることが望ましい。
■ 核種の吸着材として，$FeOOH$(ゲーサイト)が（存在する条件，生成される条件が）望ましい。
■ 溶解度低減の観点から，炭酸塩(錯体生成強度が高い)が生成される条件は好ましくない。有機物を含む地層は炭酸塩を生成する可能性があり，還元剤として有機物を期待するのは好ましくない。有機物を含有している堆積盆などは注意すべきである。
■ 海水系の地質環境については，今後の課題であるが，一般的には，イオン強度が高くなり，溶解度の増加に寄与することから注意すべき点である。
■ 黄鉄鉱の酸化反応は，黄鉄鉱の表面電子との速い反応に続いて，水との遅い反応が支配的になる。

7.1 米国および欧州の技術的指標

(1) 米国の情報

Geochemical issues related to the selection of a site for the geologic disposal of high-level radioactive waste (HLW) are reviewed in this report. The basis for the review is the multi-year site-selection process followed by the United States prior to the selection of the Yucca Mountain site as the candidate site for the HLW repository by the U.S. Congress in 1987. Specifically, the review considers only the strengths and limitations of the geochemical aspects of the following site selection issues:

- the decision process and methodologies for assessing the suitability of the site for repository development for site selection (Chapter 2),
- technical qualifying and disqualifying criteria considered in the decision process (Chapters 3 and 4), and
- methodologies for evaluating the effects of site characterization activities and repository construction and operations on site performance (Chapter 5),

In addition, the applicability of the process or a modified form of the process to site selection studies in Japan is assessed (Chapter 6). References cited are provided in Chapter 7. Copies of the reviewed regulations are provided in the Appendices.

(2) 欧州の情報

1) ベルギー：No real site selection has taken place in Belgium and the identification of Mol as a possible site relates to the location of the Mol-Dessel nuclear research site there. As far as the authors are aware, there are no published criteria for site selection in Belgium.

2) フィンランド：Finnish site selection (like other aspects of its radioactive waste disposal programme) is very like that carried out by Sweden. However, greater emphasis has been placed upon rock structure and topography and relatively little upon geochemistry. There is a general recognition that different sites in Finland are unlikely to have very different geochemical conditions at depths greater than 100 m. Selection criteria are very pragmatic and not prescriptive in placing quantitative measures on the selection or rejection of a specific site.

3) フランス : Site selection in France has been built around geological and hydrogeological factors with a relatively minor role for geochemical factors.

4) ドイツ : Geochemical criteria have played essentially no part in the selection of sites suitable for the deep disposal of radioactve wastes in Germany. The role of geochemistry has focused almost solely on establishing whether the minerals present in the evaporite formations selected for disposal are stable from a thermal and chemical perspective.

5) スペイン : Geochemical criteria have had a very minor role in the selection of sites for radioactive waste disposal in Spain.

6) スウェーデン : A summary of the technical and geoscientific factors affecting site selection in Sweden are summarised in Table <summary>. Table <summary> Summary of important repository siting factors (technical and geoscientific only). From SKB (1992).

Siting Factor	Comment
Long-term stable environment	The repository should be situated in parts of the rock that do not comprise weak zones of fractured rock in which significant future fault movements could be triggered. The rock volumes used for the repository should not contain economic minerals or similar, since these could lead to future intrusion which might disturb the safety barriers. The groundwater at the selected depth should have long-term stable chemically reducing conditions.
Safety	The rock shall comprise an extra safety barrier through its capacity to absorb and retain any released radionuclides. This capacity is dependent upon groundwater conditions (flows, flow paths), groundwater chemistry and retardation mechanisms along the flow paths. These conditions can be allowed for by taking into account factors such as hydraulic gradient, distance between proposed repository site and discharge area, presence of water-bearing fracture zones and vein minerals, and presence of saline groundwater.
Feasibility of construction	The feasibility of construction at a particular site is determined by the location and nature of fracture zones, the presence of rock types with a tendency for collapse or to be water-bearing, size and orientation of rock stresses and mechanical properties of the bedrock.
Predictability	It is an advanatge if a site is easy to interpret, i.e. permits a high certainty in prediction of bedrock conditions between investigated parts of a site. Predictability is dependent upon degree of exposure and bedrock conditions.

7) スイス：Nagra's HLW disposal concept has very limited requirements for the performance of the geological barrier and much greater emphasis is placed upon the behaviour of the engineered barriers. There is little specification of the requirements with regard to geochemistry, and any requirements are purely secondary to those regarding physical protection of the engineered barriers. Conclusions from the Kristallin-1 safety assessment (Nagra, 1994) were that the key geological characterisitics of any potential site were as follows:

- an average specific groundwater flow in the range 10^{-11} to 10^{-13} m s^{-1} (corresponding to a hydraulic conductivity in the range 10^{-9} to 10^{-11} m s^{-1} for a hydraulic gradient of 1 %);

- a groundwater of near-neutral pH, chemically reducing, with moderate salinity, thus ensuring minimal alteration of bentonite, low solubilities and good sorption of radionuclides and an adequate canister lifetime;

- an overburden thickness of 400 m would protect the engineered barriers from near-surface geological and climatic changes.

8) 英国：Geochemical criteria have not featured at all in published guidelines or rationale for the selection of sites for the geological disposal of radioactive wastes in the UK. Instead, sites have been identified from hydrogeological or geological criteria alone.

7.2 ナチュラルアナログに基づくサイト選定の技術的指標 ／長期的な核種移行挙動に着目した技術的指標

当社(GeoSolutions International, Ltd.)の代表である大本　洋は東北大学に在職中、平成7年度より3ケ年にわたり動力炉核燃料開発事業団（現：燃料サイクル開発機構：以下JNCと省略）からの委託研究として「地層中における還元性物質の速度論的研究」を行ってきた。その研究は、「地下における放射性物質の移行は地下水の酸化還元状態に大きく支配される」、したがって「処分場を還元的環境に保つことにより放射性物質の拡散を遅延することができる」との仮説を、種々な室内実験を通し、また天然の地下水おびウラン鉱床における地球化学的研究を通し、検証することを目的とした。これらの研究は平成10年4月よりGeoSolutions International, Ltd.によって継承され、「処分選定プロセスにおける技術的指標に関する研究」の研究題目の下に、本年度においては、次の 3 つの研究目的の達成を目指した。

(1) 天然におけるウラン、トリウム等のアクチノイド元素の地球化学的挙動、地下水の地球化学的性質、および鉱物－水反応に関わる既存の研究事例をもとに、高レベル廃棄物処分での核種遅延現象に好ましい地球科学的条件を整理する。

(2) 仮に高レベル廃棄物処分において理想的でない地球化学的環境においても、人工バリアの合理化で核種拡散の遅延が可能となるか、その場合、どのような点を考慮すべきかを整理する。

(3) 上記調査、検討に基づき、地球化学的観点から、我が国における地層処サイト選定に当たって注意すべき点を整理する。

上記の目的を達成するために、次の事柄について研究を行った。

(1) 黄鉄鉱および有機物と溶存酸素の反応速度
(2) 地下水の地球化学的性質およびウラン、トリウムおよび希土類元素の挙動
(3) 天然ウラン鉱床におけるウラン、トリウムおよび希土類元素挙動の歴史

本報告書においては、第一章に本研究の地球化学的背景、第二章に黄鉄鉱および有機物と溶存酸素の反応速度の研究結果、第三章に地表水の希土類元素の地球化学についての研究結果、第四章に天然ウラン鉱床におけるウラン、トリウムおよび希土類元素挙動の歴史についての研究結果をまとめ、第五章において全体の研究目的に対する知見をまとめる。

8. おわりに

本研究では，前年度の成果受けて，下記の項目を実施した。

1) 球化学データ・モデルの品質保証
2) 位置データを基にした地下水分類，水質の支配的反応
3) e および Pd の熱力学データに関する実験的研究
4) 射性元素の地球化学データ取得計画に関する検討
5) 緩衝材の長期安定性に関する地球化学的研究
6) サイト選定プロセスにおける技術的指標の検討

1) 地球化学データ・モデルの品質保証

地球化学データの信頼性に関して，昨年度までに整備してきた熱力学データの追跡可能性，再現性，科学的防御性を確保することを目的として，全ての熱力学データの出典元となる文献を収集し，熱力学データの選定根拠をまとめた。また，反応速度定数を用いた地下水変遷解析を実施した。更に，上記の検討結果をドキュメントとしてまとめるとともに，昨年度までに実施した以下の検討成果をドキュメントとしてまとめた。

- セメント系鉱物の熱力学データの整備
- わが国の地下水水質データを用いた統計的解析および分類
- 緩衝材中での空隙水化学のシナリオ解析
- 熱力学データベース変換プログラム（PHREEQE-PHREEQC，PHREEQE-GWB）

2) 原位置データを基にした地下水分類，水質の支配的反応

信頼性の高い原位置地下水データ（東濃，釜石，茂原）に基づき，地下水分類や水質の支配的反応について検討し，その成果をドキュメントとしてまとめた。また，Eh に係わる解説書をドキュメントとしてまとめた。

3) Se および Pd の熱力学データに関する実験的研究

これまでの試験結果を踏まえ，より現実的な Se 溶解度制限固相の設定のための実験データ取得を実施した。実験環境における硫酸還元菌の確認を実施したところ，硫酸還元菌は見られなかった。

4) 放射性元素の地球化学データ取得計画に関する検討

第 2 次取りまとめ報告書に基づき，重要元素・課題の摘出を行ない，放射化学研究

施設（QUALITY）における試験計画を立案した。

5）緩衝材の長期安定性に関する地球化学的研究

　緩衝材の長期安定性に関する地球化学的知見を蓄積し，性能評価の信頼性を高めるため，鉄とスメクタイトの相互作用に関する実験的研究を実施した。本研究では，文献調査を実施するとともに，熱力学的及び速度論的モデルを構築するために必要な実験計画を立案した。この計画書に基づき，鉄とスメクタイトの相互作用に関する実験的研究を実施し，スメクタイトの変質可能性，変質生成物および変質速度に関する知見を得た。

6）処分サイト選定プロセスにおける技術的指標の検討

　サイト選定に関する米国，欧州のガイドラインならびにナチュラルアナログの観点から調査研究を行ない，地球化学に関するサイト選定の技術指標を整理した。

9．謝辞