

JNC TN7420 2000-003

**Laboratory Work in Support to
CRR Phase 1 Experiments at GTS**

July 2000

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Japan Nuclear Cycle Development Institute**

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July 2000

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PREFACE

Colloid-facilitated transport of radionuclides has been noted in repository performance assessments as a potential mechanism for increasing releases from a repository but does still remain very much an open question. One of the problems facing the performance assessment is that information on colloid properties and their chemical/transport behaviour in a repository relevant environment is not sufficient and it is therefore difficult to fully define the likely significance of the process. An *in situ* study, complemented by supporting laboratory and modelling programmes, on the coupling of solubility-limited retardation of radionuclides and colloid transport processes in a repository host rock would be a significant step in answering the debate on the relevance of colloid-facilitated transport of radionuclides.

This report documents the results of JNC's laboratory experiment and modelling effort with respect to above-mentioned important issues, carried out within the first phase (1998 – March 2000) of the Colloid and Radionuclide Retardation (CRR) experiment in the GTS (Grimsel Test Site) Phase V (1997 – 2002). The CRR is a multidisciplinary study aimed at significantly improving understanding of the *in situ* retardation of colloid-associated, safety relevant radionuclides in a fractured crystalline rock, which is split into the first phase of detailed lead-in laboratory experiments with associated modelling work and the following phase of *in situ* experiments. The whole project has been operated by Nagra (Nationale Genossenschaft für die Lagerung radioaktiver Abfälle, Switzerland) in partnership with Andra (Agence nationale pour la gestion des déchets radioactifs, France), Enresa (Empresa Nacional de Residuos Radioactivos, Spain), FZK/INE (Forschungszentrum Karlsruhe Institut für Nukleare Entsorgungstechnik under BMBF, Germany), SNL (Sandia National Laboratories under USDOE, USA) and JNC (Japan Nuclear Cycle Development Institute, Japan).

JNC has to date contributed to three tasks of the CRR Phase 1: (i) Prediction of solubility and speciation of radionuclides in FEBEX water (Task 1a), providing information necessary for defining the suitable solution, to be injected, with a radionuclide cocktail, (ii) Prediction of near-field colloid stability (Task 1b), theoretically estimating the stability of bentonite colloids and (iii) Stability of bentonite colloids (Task 2b), experimentally defining the stability of bentonite colloids under GTS-simulated conditions. The results contained herein have been incorporated, with those from other partners, in a series of internal CRR task reports and will be in a Nagra technical report. These have been specifically utilised in defining every detail of the following *in situ* experiments and are applicable to any similar study on colloid-facilitated transport of radionuclides in rocks.

まえがき

地層処分システムの性能評価において、コロイドによる放射性核種の移行の促進は核種移行率を増加させる重要なメカニズムとして考えられている。しかしながら、現在までに、処分場において想定される地質環境中におけるコロイドの特性、化学的挙動や移行挙動などが十分に把握されておらず、コロイドが放射性核種の移行に与える影響の把握については未だに重要な研究課題として残されている。したがって、室内試験およびモデル解析によりサポートされた原位置試験研究を実施し、放射性核種の遅延とコロイドの移行プロセスを総合的に把握することが必要である。このような原位置試験研究の実施により、最終的にはコロイドによる放射性核種の移行／遅延を評価することが可能になると期待される。

グリムゼル原位置試験場 (GTS、スイス) において、現在展開中のグリムゼル原位置試験・フェーズ5 (1997年～2002年) では、結晶質岩中の透水性割れ目における、コロイドによる放射性核種の移行／遅延を評価するための総合的な試験研究、「コロイドと放射性核種の遅延評価プロジェクト (CRR)」を実施している。このプロジェクトは、スイス放射性廃棄物処分協同組合 (Nagra) が中心となり、フランス放射性廃棄物管理機関 (Andra)、スペイン放射性廃棄物管理公社 (Enresa)、カールスルーエ研究センター／核廃棄物技術研究所 (FZK/INE、ただし代表機関はドイツ連邦教育科学研究技術省 (BMBF))、サンディア国立研究所 (SNL、ただし代表機関は米国エネルギー省 (USDOE))、ならびにサイクル機構の6機関により進められている。また、CRR プロジェクトは、室内試験とモデル解析を主体としたフェーズ1 (1998年～2000年3月) および原位置試験を実施するフェーズ2 (2000年4月～2002年) に二分され、現在 (2000年7月)、フェーズ1における成果の取りまとめ、およびフェーズ2における原位置試験の準備などを行っている。

サイクル機構は、CRR フェーズ1において、①FEBEX ベントナイト空隙水中における放射性核種の溶解度と化学種の推定 (タスク1a)、②ニアフィールドにおけるコロイドの安定度の推定 (タスク1b)、③ベントナイトコロイドの安定度 (タスク2b) の三つのタスクを分担した。タスク1aは、フェーズ2の原位置試験において、注入するカクテル溶液の仕様 (液性や放射性核種の濃度など) を決定するために必要な情報を提供するものであり、タスク1bおよびタスク2bは、グリムゼル原位置試験場の地質環境条件下における FEBEX ベントナイトコロイドの安定度を、それぞれ理論解析および室内試験により評価するものである。これらの室内試験およびモデル解析の結果は、フェーズ2の原位置試験の詳細を決定するために用いられるほか、コロイドと放射性核種の移行／遅延に関する同様の試験研究においても活用できると考えられる。なお、サイクル機構の試験・解析結果は、他の参加機関において得られた結果とともに、タスクごとの内部報告書に取りまとめられ、最終的な成果は Nagra 技術報告書として公開されることとなっている。

本報告書は、CRR フェーズ1においてサイクル機構が実施した、室内試験およびモデル解析の実施内容と結果について取りまとめたものである。

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1 PREDICTION OF SOLUBILITY AND SPECIATION OF RADIONUCLIDES IN FEBEX WATER

GTS-PHASE V: CRR PROJECT TASK 1A, MAY 1999

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1.1 Introduction

The relevance of the planned *in situ* experiment using radionuclides and colloids to the deep geological disposal of HLW depends on the accurate definition of the experimental system. The selection of radionuclides should result from a compromise between relevance for performance assessment, feasibility in conducting the *in situ* experiment and foreseen radionuclide/colloid transport behaviour under the experimental conditions. The specific properties of the solution to be injected *in situ* should also be considered for reliably predicting the most probable evolution of the experimental system.

As discussed at the previous GTS-CRR technical meetings, for example [1], a major source, the FEBEX water equilibrated with the FEBEX bentonite, is to be used for the planned *in situ* experiment. It is required that the injection solution be stable and the concentration of radionuclide in the solution be high so that the radionuclide could be detected even after the system evolves. To provide information necessary for defining the suitable injection solution, solubility and speciation calculations were made and here the methodology and results of the calculations are presented.

1.2 Prediction Methodology

Code and Thermodynamic Database

The calculations were performed with the PHREEQE code [2] and JNC's thermodynamic database (JNC-TDB) developed for the Second Progress Report on Research and Development for the Geological Disposal of HLW (H-12 Report). Details of the database were described in JNC's technical report [3]. For americium, neptunium and plutonium, thermodynamic data given in Appendix-2 in the report [3] were adopted for the calculations.

FEBEX Water Composition

The chemical composition of FEBEX water [4] (data sheets distributed by QuantiSci on 19th January 1999) was used in the calculations. Two types of water, specifically oxidising water and reducing water, were taken into account, Eh values of which were specified as 458mV and -189mV respectively. Table 1 shows the chemical composition of the FEBEX water, which was used in the calculations.

Solubility-limiting Phase

In the calculations, americium, neptunium, plutonium, radium, selenium, technetium, thorium and uranium were considered. In the selection of solubility-limiting solid phase corresponding to each radionuclide listed, its thermodynamic stability and information provided by solubility experiments carried out previously in JNC were taken into account.

Table 1 Chemical composition of the FEBEX water

pH		7.38
Temperature	[°C]	21.2
Eh (oxidising)	[mV]	458
Eh (reducing)	[mV]	-189
Na ⁺	[M]	9.13 x 10 ⁻²
K ⁺	[M]	3.85 x 10 ⁻⁴
Mg ²⁺	[M]	1.60 x 10 ⁻²
Ca ²⁺	[M]	1.27 x 10 ⁻²
Si ²⁺	[M]	8.56 x 10 ⁻⁵
Mn ²⁺	[M]	1.37 x 10 ⁻⁵
Ni ²⁺	[M]	5.45 x 10 ⁻⁶
Cu ²⁺	[M]	2.36 x 10 ⁻⁶
Zn ²⁺	[M]	2.44 x 10 ⁻⁵
Mo ²⁺	[M]	3.86 x 10 ⁻⁶
Al	[M]	4.45 x 10 ⁻⁶
Fe total	[M]	1.61 x 10 ⁻⁶
Cl ⁻	[M]	1.13 x 10 ⁻¹
Br ⁻	[M]	1.14 x 10 ⁻⁴
NO ₃ ⁻	[M]	1.47 x 10 ⁻³
HCO ₃ ⁻	[M]	2.17 x 10 ⁻³
SO ₄ ²⁻	[M]	1.31 x 10 ⁻²
PO ₄ ³⁻	[M]	<1.1 x 10 ⁻⁵
H ₂ SiO ₃	[M]	-

Calculations

The calculations were conducted, at 25°C, for two types of waters, considering only one element by run. One selected solubility-limiting solid phase is assumed to be at equilibrium with the FEBEX water. For silica and phosphate, 15ppm [Si(OH)₄] and 1ppm [PO₄³⁻] (equal to detection limit) were given without calculating their equilibration with chalcedony and hydroxylapatite respectively. The equilibrium calculations with pyrite were not conducted either.

In the case of americium, AmPO₄(am) is more stable than AmOHCO₃ and would give lower solubility. However, AmPO₄(am) was not selected as the solubility-limiting phase because the concentration of PO₄³⁻ in the FEBEX water was uncertain. In the oxidising FEBEX water, NaNpO₂CO₃(cr) may control solubility and it leads lower concentration of neptunium. In the calculation for uranium under the reducing condition, only U(IV) thermodynamic data was used to avoid the appearance of U(VI) species that is unlikely present under reducing conditions.

1.3 Results and Discussion

The mineral saturation indices for the FEBEX water are given in Table 2 and the solubilities for selected solid phases and the dominant species in the FEBEX water are given in Table 3.

Table 2 Saturation indices for the FEBEX water

Mineral	Saturation Index	
	Oxidising condition (Eh=458mV)	Reducing condition (Eh=-189mV)
aragonite	0.0778	0.0780
calcite	0.2224	0.2226
chalcedony	-0.2938	-0.2938
dolomite	0.6816	0.6819
Fe(OH) ₃	2.1384	-5.3275
gibbsite	1.2604	1.2604
hydroxylapatite	2.7639	2.7643
kaolinite	3.4150	3.4150
quartz	-0.0038	-0.0038
strontianite	-1.2185	-1.2172

Table 3 Solubilities of selected solid phases in the FEBEX water

Radionuclide	Redox condition	Solubility-limiting solid phase	Solubility [M]	Dominant species (%)
Am	Oxidising	AmOHCO ₃	3.65 x 10 ⁻⁷	AmCO ₃ ⁺ (61) AmOH ²⁺ (14) AmSO ₄ ⁺ (11)
	Reducing	AmOHCO ₃	3.64 x 10 ⁻⁷	AmCO ₃ ⁺ (61) AmOH ²⁺ (14) AmSO ₄ ⁺ (11)
Np	Oxidising	NpO ₂ OH	5.25 x 10 ⁻⁴	NpO ₂ ⁺ (95)
	Reducing	NpO ₂ (am)	3.25 x 10 ⁻⁹	Np(OH) ₄ (aq) (92)
Pu	Oxidising	PuO ₂ (am)	2.04 x 10 ⁻¹⁰	Pu(OH) ₂ (CO ₃) ₂ ²⁻ (53) Pu(OH) ₄ (aq) (46)
	Reducing	PuO ₂ (am)	1.51 x 10 ⁻⁸	PuCO ₃ ⁺ (60) PuOH ²⁺ (14) PuSO ₄ ⁺ (11)
Ra	Oxidising	RaSO ₄	4.74 x 10 ⁻⁸	Ra ²⁺ (100)
	Reducing	RaSO ₄	4.76 x 10 ⁻⁸	Ra ²⁺ (100)
Se	Oxidising	Se(cr)	5.64 x 10 ⁻³	HSeO ₃ ⁻ (95)
	Reducing	Se(cr)	2.60 x 10 ⁻⁹	HSe ⁻ (100)
Tc	Oxidising	TcO ₂ •2H ₂ O	—	—
	Reducing	TcO ₂ •2H ₂ O	3.18 x 10 ⁻⁸	TcO(OH) ₂ (aq) (85)
Th	Oxidising	ThO ₂ (am)	5.19 x 10 ⁻⁷	Th(OH) ₃ CO ₃ ⁻ (100)
	Reducing	ThO ₂ (am)	5.19 x 10 ⁻⁷	Th(OH) ₃ CO ₃ ⁻ (100)
U	Oxidising	UO ₃ •2H ₂ O (schoepite)	1.77 x 10 ⁻⁴	UO ₂ (CO ₃) ₃ ⁴⁻ (31) UO ₂ (CO ₃) ₂ ²⁻ (27) (UO ₂) ₂ CO ₃ (OH) ₃ (20)
	Reducing	UO ₂ (am)	1.84 x 10 ⁻⁹	U(OH) ₄ (aq) (94)

Each of the minerals except $\text{Fe}(\text{OH})_3$ (ferrihydrite) gives very similar saturation indices under the oxidising and reducing conditions (Table 2). Under both conditions, some minerals (*eg* dolomite, kaolinite) yielding calculated saturation indices greater than 0 are likely to precipitate from the FEBEX water. However, the slight under-saturation of chalcedony and the super-saturation of hydroxylapatite are consequences of the calculations assuming low silica and high phosphate concentrations respectively.

Since neptunium, plutonium, selenium and uranium are redox sensitive elements, the solubilities of selected solid phases under the oxidising condition are 5 to 6 orders of magnitude higher (for plutonium; 2 orders of magnitude lower) than those under the reducing condition. The Grimsel groundwater is highly reducing (-200mV?) and, if higher concentrations of radionuclides are used in the injection solution under oxidising conditions, precipitation of some solid phases is most likely to occur due to the change of water chemistry (*ie* redox conditions). It might occur even under different reducing conditions.

References

- [1] Alexander, W.R. and Frieg, B., 1998: Minutes of Meeting: GTS-CRR Project Meeting 3 (Karlsruhe, 29-30th October 1998). Nagra AN 98-325 (GTS-CRR 98-03).
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2 PREDICTION OF NEAR-FIELD COLLOID STABILITY

GTS PHASE V: CRR PROJECT TASK 1B, SEPTEMBER 1999

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2.1 Introduction

Bentonite colloids are generated through physical erosion of compacted bentonite at the EBS / host rock interface and may be present in groundwater in the geosphere. Sorption of radionuclides onto colloids' surface occurs, where the concentration of colloids in the groundwater is sufficiently high, and may also modify radionuclide transport behaviour. In order to evaluate the effect of colloids on radionuclide transport, it is important to estimate the stability of bentonite colloids.

Since the stability of bentonite colloids depends especially on the ionic strength of groundwater, a range of ionic strength to maintain the colloid stability has been estimated by theoretical calculations. The predictions are to be compared with experimental results (*ie* Task 2b: Stability of Bentonite Colloids) [1] for the better understanding of the stability of bentonite colloids. Here, the theory applied to the calculations and the estimated stability of bentonite colloids are presented and then the limitation of the applications is discussed.

2.2 Prediction Procedure

Physical Model

In order to estimate a range of ionic strength maintaining the colloid stability, the DLVO (Derjaguin, Landau, Verwey, Overbeek) theory was applied to the calculations by reason of its effectiveness and convenience [2]. The DLVO theory considers van der Waals attraction and diffuse double-layer repulsion as the sole operative factors. It calculates the interaction energy (as a function of interparticle distance) as the reversible isothermal work required to bring two particles from distance ∞ to distance d . Bentonite colloids assuming to have parallel plate geometries and the same surface potential, the repulsive interaction energy V_R and the van der Waals attraction energy V_A are given, based upon a classical theory, by the following equations:

$$V_R = \frac{64nkT}{\kappa} \gamma^2 \exp(-2kd) \quad \dots\dots\dots (1)$$

$$\kappa = \sqrt{\frac{8\pi n z^2 e^2}{\epsilon kT}}$$

$$\gamma = \frac{\exp\left(\frac{ze\Psi_0}{2kT}\right) - 1}{\exp\left(\frac{ze\Psi_0}{2kT}\right) + 1}$$

$$V_A = -\frac{A}{48\pi} \left[\frac{1}{d^2} + \frac{1}{(d+\delta)^2} - \frac{2}{\left(d+\frac{\delta}{2}\right)^2} \right] \quad \dots\dots\dots (2)$$

- where
- n : local ion concentration in number of ions
 - k : Boltzmann constant
 - T : absolute temperature
 - d : half-distance between the plates
 - z : valence of ion
 - e : elementary charge
 - ϵ : dielectrical constant of a medium
 - Ψ_0 : surface potential
 - A : Hamaker constant
 - δ : thickness of the unit layer.

Colloid stability can be estimated by calculating the total energy of interaction between two plates (W). It is given by summing up repulsive and attractive energies:

$$W_t = V_R + V_A \quad \dots\dots\dots (3)$$

A series of equations shown above are basic formulae used for the calculations of the interaction energies.

In the calculations, however, the effect of edge area of clay particles on the interaction of parallel plates association was not taken into account for the sake of simplicity. Platelike clay particles, in fact, have two crystallographically different surfaces (*ie* "face" and "edge" as mentioned below), each of which carries a different electrical double layer [2], and thus clay particle association is too complicated to model.

Parameters

The following values were used in the calculations mentioned above:

- Ionic strength (corresponding to symbol "*n*" in Equation (1))

$1 \times 10^{-1}, 1 \times 10^{-2}, 1 \times 10^{-3}$ (M)

- Valence of ion ("*z*" in Equation (1))

1 : A single symmetrical electrolyte was assumed in the calculations.

- Surface potential (" ψ_0 " in Equation (1))

-40mV : Zeta potential was used as the surface potential in the calculations for convenience' sake. Zeta potential of FEBEX colloids was measured by the electrophoresis method in the Task 2b experiments ($\psi_0 \approx -30$ to -40mV).

- Hamaker constant ("*A*" in Equation (2))

$1 \times 10^{-10}, 1 \times 10^{-11}, 1 \times 10^{-12}$ (erg)

- Thickness of the unit layer (" δ " in Equation (2))

10, 100 (Å)

Model Cases

The total energy of interaction was calculated for conditions with various ionic strengths (*n* = 1×10^{-1} M, 1×10^{-2} M and 1×10^{-3} M) in the following cases:

Table 1 Model cases for the prediction of colloid stability

Model Cases	<i>z</i>	ψ_0 (mV)	<i>A</i> (erg)	δ (Å)
1	1	-40	1×10^{-12}	10
2	1	-40	1×10^{-11}	10
3	1	-40	1×10^{-10}	10
4	1	-40	1×10^{-12}	100

2.3 Results and Discussion

The results of the Case 1 calculations were shown in Figure 1. Since Hamaker constants (A) for most colloids range from approximately 10^{-13} to 10^{-12} erg, the Case 1 is considered to be more realistic than the other cases. In this case, bentonite colloids are likely to be stable even if the ionic strength of colloid solution is quite high ($I = 1 \times 10^{-1}$ M).

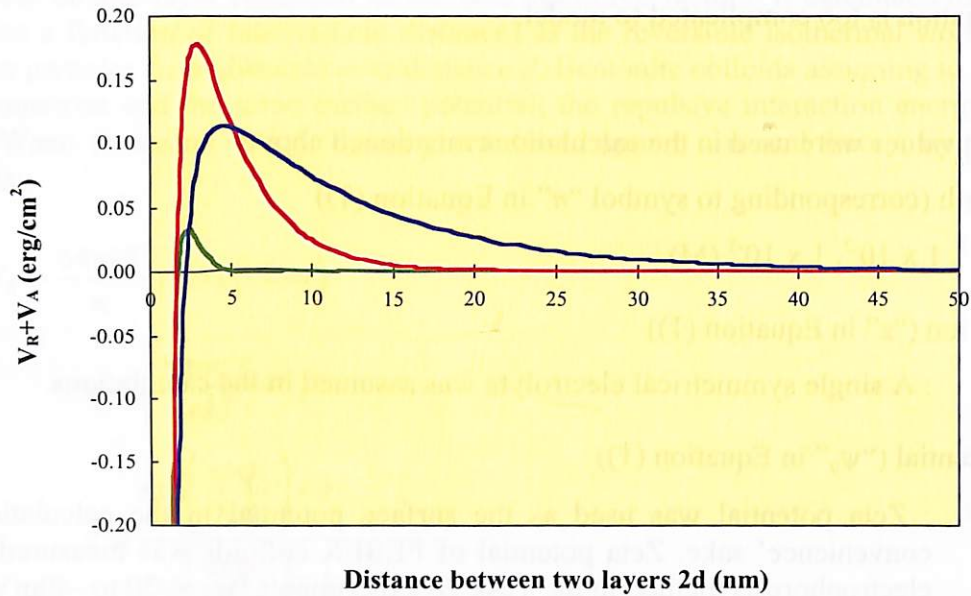


Figure 1 Potential curves estimated by the DLVO theory (Case 1)

Case 1: $\psi_0 = -40\text{mV}$, $A = 1 \times 10^{-12}$ erg, $\delta = 10\text{\AA}$
 — : $I = 1 \times 10^{-1}$ M, — : $I = 1 \times 10^{-2}$ M, — : $I = 1 \times 10^{-3}$ M

Experimental results defining the stability of the FEBEX colloids (*ie* Task 2b: Stability of Bentonite Colloids), however, demonstrated that colloid particles are expected to be flocculated in the solution where the ionic strength of the solution is higher than 1×10^{-2} M [1]. Hence it can be seen that there is a disagreement between model prediction and experiment.

At larger Hamaker constants ($A = 1 \times 10^{-11}$ erg and 1×10^{-10} erg corresponding the Cases 2 and 3, respectively) given, in contrast, colloid particles tend to be unstable and flocculated in the solution with increasing ionic strength. In these cases, the predictions are consistent with the experimental results on the stability of the FEBEX colloids. Note that, however, given conditions are not realistic.

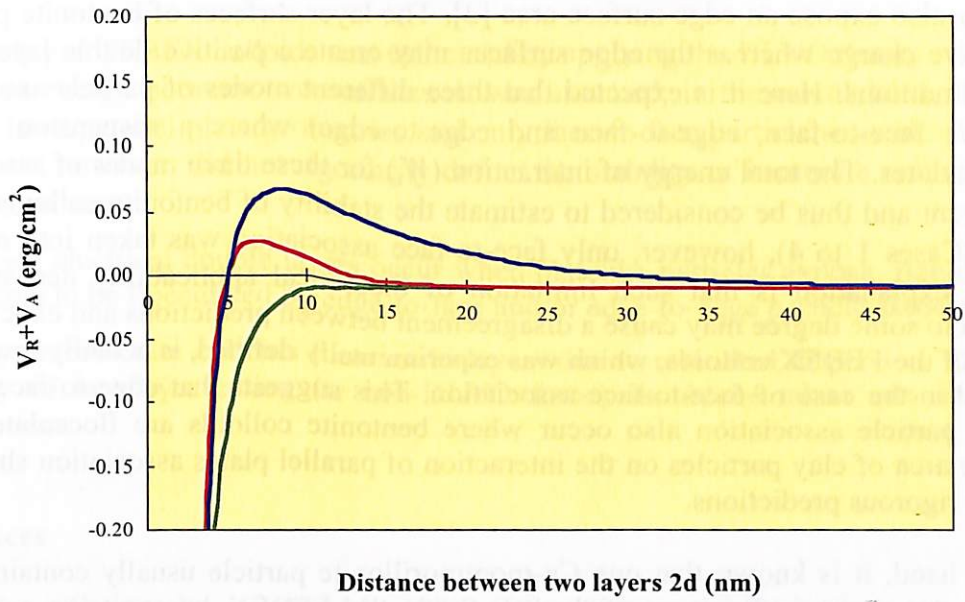


Figure 2 Potential curves estimated by the DLVO theory (Case 2)

Case 2: $\psi_0 = -40\text{mV}$, $A = 1 \times 10^{-11}$ erg, $\delta = 10\text{\AA}$
 — : $I = 1 \times 10^{-1}$ M, — : $I = 1 \times 10^{-2}$ M, — : $I = 1 \times 10^{-3}$ M

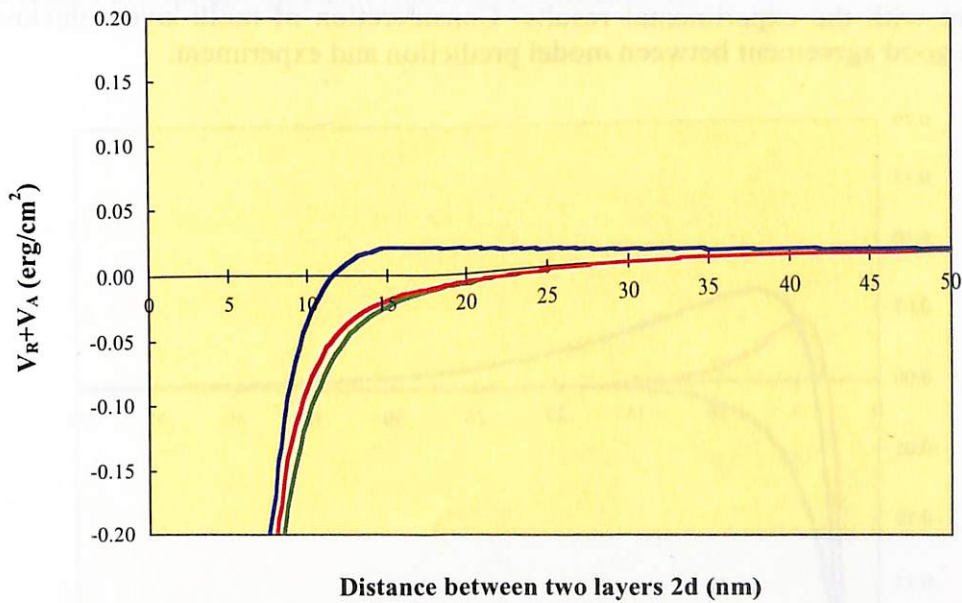


Figure 3 Potential curves estimated by the DLVO theory (Case 3)

Case 3: $\psi_0 = -40\text{mV}$, $A = 1 \times 10^{-10}$ erg, $\delta = 10\text{\AA}$
 — : $I = 1 \times 10^{-1}$ M, — : $I = 1 \times 10^{-2}$ M, — : $I = 1 \times 10^{-3}$ M

It is known that flat layer surfaces are not the only exposing surface area of platelike clay particles; they also expose an edge surface area [2]. The layer surfaces of bentonite particles carry a negative charge whereas the edge surfaces may create a positive double layer under appropriate conditions. Here it is expected that three different modes of particle association may occur (*ie* face-to-face, edge-to-face and edge-to-edge) where a suspension of clay particles flocculates. The total energy of interaction (W) for these three modes of association may be different and thus be considered to estimate the stability of bentonite colloids. In the calculations (Cases 1 to 4), however, only face-to-face association was taken into account. One possible explanation is that such limitation of theoretical applicability derived from simplification to some degree may cause a disagreement between predictions and experiments. The stability of the FEBEX colloids, which was experimentally defined, is actually lower than that estimated in the case of face-to-face association. This suggests that edge-to-face and/or edge-to-edge particle association also occur where bentonite colloids are flocculated. The effect of edge area of clay particles on the interaction of parallel plates association should be considered in rigorous predictions.

On the other hand, it is known that one Ca-montmorillonite particle usually contains more layers than a Na-montmorillonite particle [2]. Since the FEBEX bentonite is composed mainly of Ca-montmorillonite (smectite), all layers can not freely disperse (*ie* dispersion is restricted by the hydration energy). The Case 4 is then considering a larger layer thickness ($\delta = 100 \text{ \AA}$); bentonite colloids are expected to be flocculated where the ionic strength of the solution is higher than $1 \times 10^{-2} \text{ M}$ (Figure 4). Compared with the Case 1 ($\delta = 10 \text{ \AA}$; Figure 1), bentonite colloids tend to be unstable and be flocculated at a larger layer thickness, which is also consistent with the experimental results. Consideration of multi-layers thickness may lead to such a good agreement between model prediction and experiment.

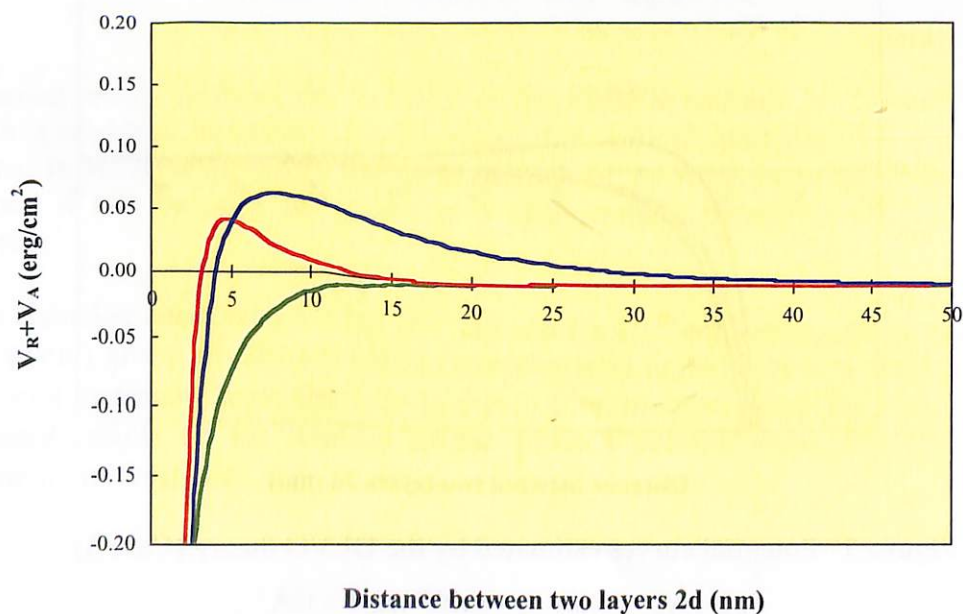


Figure 4 Potential curves estimated by the DLVO theory (Case 4)

Case 4: $\psi_0 = -40\text{mV}$, $A = 1 \times 10^{-12} \text{ erg}$, $\delta = 100 \text{ \AA}$
 — : $I = 1 \times 10^{-1} \text{ M}$, — : $I = 1 \times 10^{-2} \text{ M}$, — : $I = 1 \times 10^{-3} \text{ M}$

2.4 Conclusions

The stability of FEBEX colloids was estimated by applying the DLVO theory considering the interaction energy between two surfaces. It was assumed, in the calculations, that bentonite colloids have parallel plate geometries and only face-to-face particle association occurs. The predictions, however, did not rigorously define the stability of bentonite colloids due to the following reasons:

- Different electrical double layers occur when platelike particles expose. Bentonite colloids are likely to be flocculated by edge-to-face and/or edge-to-edge particle association.
- Ca-montmorillonite colloids form multi-layers due to restricted dispersion. The hydration energy of interlayer cation (*ie* non-DLVO force) should be taken into account in the predictions.

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3 STABILITY OF BENTONITE COLLOIDS

GTS PHASE V: CRR PROJECT TASK 2B, OCTOBER 1999

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3.1 Introduction

Bentonite colloids are generated through physical erosion of compacted bentonite at the EBS / host rock interface and may be present in groundwater in the geosphere. Sorption of radionuclides onto colloids' surface occurs, where the concentration of colloids in the groundwater is sufficiently high, and may also modify radionuclide transport behaviour. In order to evaluate the effect of colloids on radionuclide transport, it is important to understand the stability of bentonite colloids.

Since colloid stability depends especially on the chemistry of groundwater, the stability of bentonite colloids has been defined by a series of batch experiments under various chemical conditions. The artificial Grimsel groundwater (AGGW), imitating the *in situ* Grimsel groundwater (GGW), was also used for the experiment. JNC sets two different cases for these experiments: the reference case with the FEBEX bentonite and the JNC case with the Kunigel VI bentonite [1]. The experimental results in both cases are to be compared for the better understanding of the stability of bentonite colloids. Here, the experimental details and some results obtained to date in the reference case are discussed, which are also compared with the JNC case experiments that have been already completed in JNC's programme.

3.2 Experimental Procedure

0.5g crushed FEBEX bentonite were contacted with distilled water, a NaClO₄ solution or the AGGW at a solution/solid ratio (500 ml/g), which proved to be suitable for the generation of colloid in previous experiments. The NaClO₄ solutions were prepared appropriately at three ionic strength values, 1 x 10⁻³ M, 1 x 10⁻² M and 1 x 10⁻¹ M (Table 1). The AGGW was carefully prepared by adding designated reagents into distilled water [2]. The experimental solutions were then stirred for 24 hours, thereby generating FEBEX colloids in the suspension solution. For the NaClO₄ solution, the pH value of each solution was adjusted at three pH values, 6, 8 and 9, following addition of HCl or NaOH. The batch experiment with the AGGW was performed under N₂ atmosphere (0.1ppm O₂ in a glove box) and the others were carried out under aerobic conditions.

The upper layer of the experimental solution (*ie* FEBEX colloid solution) was collected after it had been kept for 2 weeks under static conditions. Si, Al and Mg concentrations of the upper layer solution were determined by ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy). The particle size distribution and zeta potential of the FEBEX colloids in the solution were measured by the laser diffraction method and the electrophoresis method, respectively. In addition, Si, Al and Mg concentrations of filtrate were also determined after the ultrafiltration (MWCO 10,000) of the experimental solution. The concentration of the FEBEX colloids was calculated on the basis of both analytical data. The procedure and conditions for the experiments can be summarised in Figure 1 and Table 1, respectively. Table 2 shows the chemical composition of the AGGW prepared as described above.

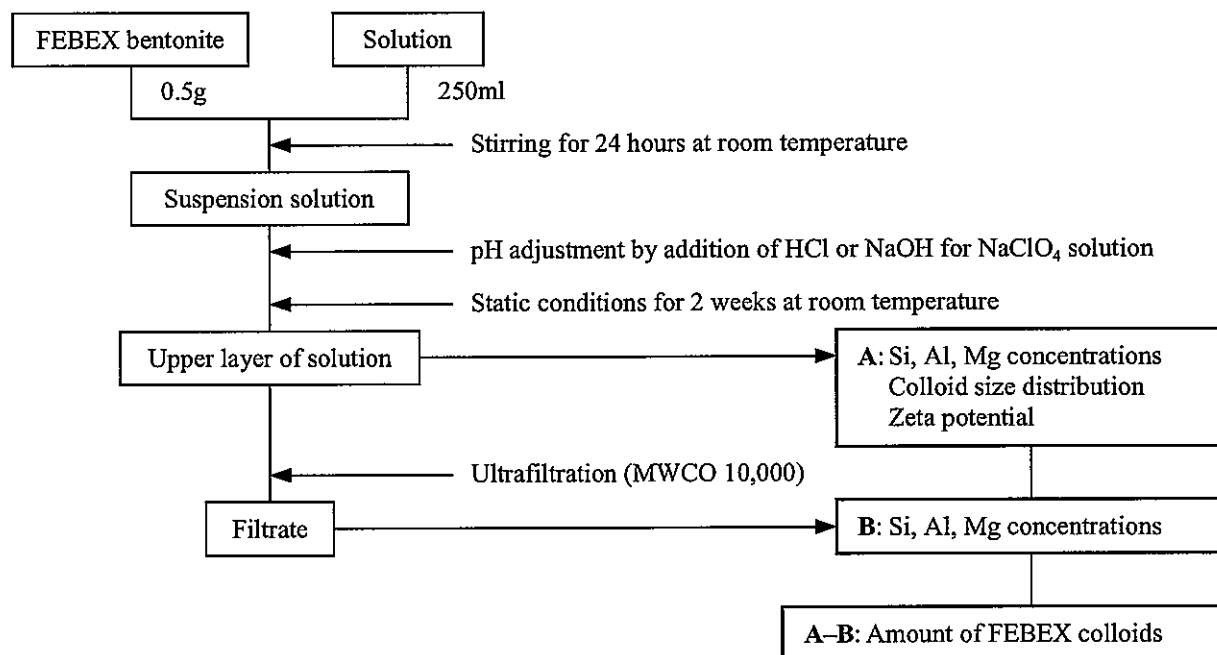


Figure 1 Experimental procedure

Table 1 Experimental conditions

Solution	pH (addition of HCl or NaOH)			
	Not added	6	8	9
Distilled water	yes	no	no	no
1x10 ⁻³ [M] NaClO ₄ sol.	no	yes	yes	yes
1x10 ⁻² [M] NaClO ₄ sol.	no	yes	yes	yes
1x10 ⁻¹ [M] NaClO ₄ sol.	no	yes	yes	yes
AGGW	yes	no	no	no

Table 2 Chemical composition of AGGW (analytical data)

		AGGW prepared by JNC	<i>In situ</i> Grimsel groundwater (GGW)*
pH		9.4	9.6
Ionic strength	[M]	0.0011	0.0012
Na ⁺	[M]	7.4 x 10 ⁻⁴	6.9 x 10 ⁻⁴
K ⁺	[M]	5.0 x 10 ⁻⁶	5.0 x 10 ⁻⁶
Mg ²⁺	[M]	7.5 x 10 ⁻⁷	6.2 x 10 ⁻⁷
Ca ²⁺	[M]	1.2 x 10 ⁻⁴	1.4 x 10 ⁻⁴
Si ²⁺	[M]	1.8 x 10 ⁻⁶	2.0 x 10 ⁻⁶
PO ₄ ³⁻	[M]	4.3 x 10 ⁻⁷	–
SO ₄ ²⁻	[M]	5.7 x 10 ⁻⁵	6.1 x 10 ⁻⁵
F ⁻	[M]	3.4 x 10 ⁻⁴	3.6 x 10 ⁻⁴
Cl ⁻	[M]	1.5 x 10 ⁻⁴	1.6 x 10 ⁻⁴
HCO ₃ ⁻	[M]	1.9 x 10 ⁻⁴	2.9 x 10 ⁻⁴
Si	[M]	2.0 x 10 ⁻⁴	2.5 x 10 ⁻⁴

* GGW data after Nagra NTB91-04 [3]

3.3 Results and Discussion

The concentrations and physical properties of the FEBEX colloids experimentally determined under various chemical conditions are shown in Table 3 and Figure 2.

Table 3 Characterisation of FEBEX colloids under various chemical conditions

Experimental solution			Colloid concentration [mg/l]	Size distribution of colloid particle* [μ m]	Zeta potential** [mV]
conc. [M]	type	pH			
Distilled water			121	0.1 – 1.1	-36
1×10^{-3}	NaClO ₄	6	129	0.3 – 2.1	-31
1×10^{-3}	NaClO ₄	8	144	0.2 – 1.4	-34
1×10^{-3}	NaClO ₄	9	140	0.2 – 1.1	-32
1×10^{-2}	NaClO ₄	6	about 1	n.d.	n.d.
1×10^{-2}	NaClO ₄	8	about 1	n.d.	n.d.
1×10^{-2}	NaClO ₄	9	about 1	n.d.	n.d.
1×10^{-1}	NaClO ₄	6	about 1	n.d.	n.d.
1×10^{-1}	NaClO ₄	8	about 1	n.d.	n.d.
1×10^{-1}	NaClO ₄	9	about 1	n.d.	n.d.
AGGW			41	0.3 – 1.4	-31

* Determined by the laser diffraction method.

** Determined by the electrophoresis method (grating rotation type).

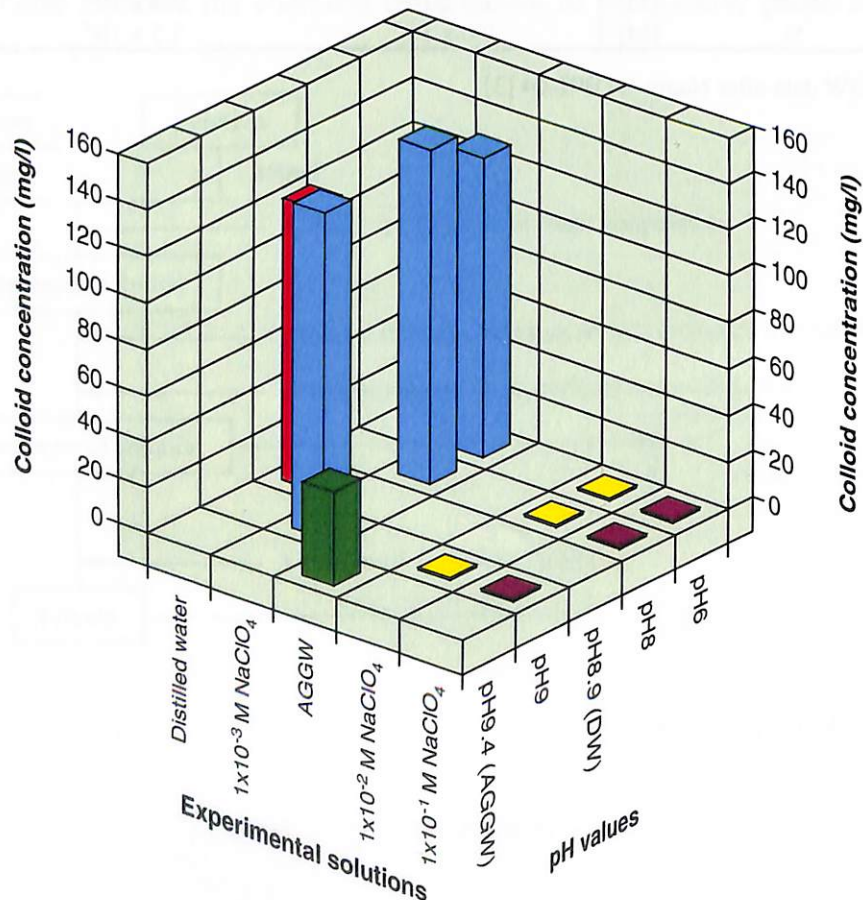


Figure 2 Concentration of FEBEX colloids under various chemical conditions

At low ionic strength (*ie* distilled water and 1×10^{-3} M NaClO₄ solution used for the experiments), the FEBEX colloids were heavily suspended in the experimental solution even after it had been kept static for 2 weeks, indicating that a large amount of colloids was generated. The concentrations of the FEBEX colloids in these solutions are higher than 100 mg/l. On the other hand, a quite lesser amount of colloids was identified in the experimental solution at relatively high ionic strength (*ie* 1×10^{-2} M and 1×10^{-1} M NaClO₄ solutions). Since Si, Al and Mg concentrations of the solution are very low, which are closed to the value of detection limit of ICP-AES, some difficulty were encountered on the quantification of the FEBEX colloids. In such a case, the size distribution and zeta potential of colloid particles were not able to be measured. The FEBEX colloids are, however, considered to be negatively charged under all the experimental conditions.

The FEBEX colloids were also suspended sufficiently in the AGGW after 2 weeks' duration. The amount of colloids generated in the AGGW was 41 mg/l, which was, however, less than that of colloids generated in distilled water or the 1×10^{-3} M NaClO₄ solution. This might be due to the slight difference in ionic strength between the experimental solutions. The stability of the FEBEX colloids does, as expected, depend on the chemical conditions of solution (*eg* groundwater). As the FEBEX colloids are, in fact, stable in the AGGW, the colloids are expected to be stable under the GW conditions.

The experimental results mentioned above are compared with those on the characterisation of the Kunigel V1 colloids, which have been made in JNC's previous programme and are shown in Table 4 and Figure 3. The concentration of the Kunigel V1 colloids depends on the ionic strength of the experimental solution, which is similar to the stability behaviour of the FEBEX colloids as described above. Bentonite colloid particles are thus stable in a solution where the ionic strength of the solution is lower than 1×10^{-2} M whereas bentonite colloids are expected to be flocculated in a solution at higher ionic strength and consequently the amount of bentonite colloids decreases in the solution.

Table 4 Characterisation of Kunigel V1 colloids under various chemical conditions

Experimental solution			Colloid concentration [mg/l]	Size distribution of colloid particle* [µm]	Zeta potential** [mV]
conc. [M]	type	pH			
Distilled water		6	314	0.22 – 5	-41
Distilled water		9	376	0.10 – 0.49	-53
1×10^{-3}	NaCl	9	326	0.12 – 0.55	-54
3×10^{-3}	NaCl	9	298	0.14 – 0.69	-66
7×10^{-3}	NaCl	9	112	0.17 – 0.87	-76
6×10^{-1}	NaCl	8	46	nd	-37

* Determined by the photon correlation and laser diffraction methods.

** Determined by the electrophoresis method (laser Doppler type).

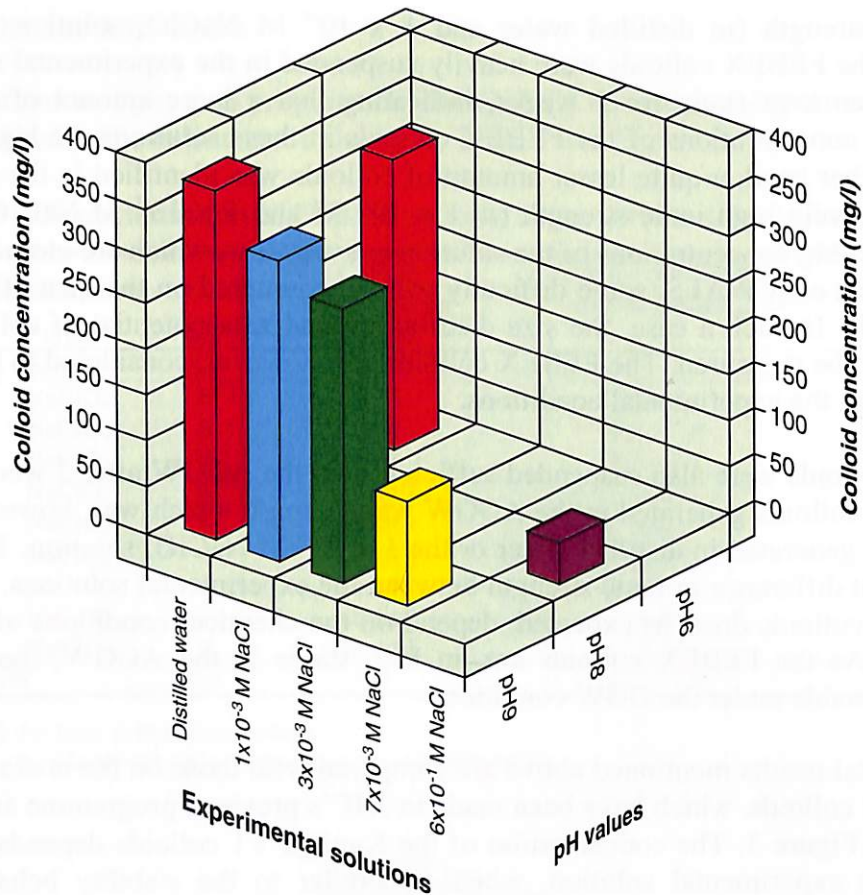


Figure 3 Concentration of Kunigel V1 colloids under various chemical conditions

Certain differences in colloid properties are, however, recognised between the both cases; the concentration of FEBEX colloids drops considerably where ionic strength is higher than 1×10^{-2} M whereas that of Kunigel V1 colloids gradually decreases with increasing ionic strength. One possible explanation is that mineralogy of both bentonites is different. The FEBEX bentonite is composed mainly of smectite (Ca-montmorillonite) whereas the Kunigel V1 bentonite contains not only smectite (Na-montmorillonite) but also a large amount of chalcedony and quartz (about 40 wt%). Only Si was detected in a higher ionic strength solution that was prepared with the Kunigel V1 bentonite, not the FEBEX bentonite, suggesting that only silica colloids were generated in the solution but montmorillonite colloids did not survive at all. The presence of chalcedony and quartz in the Kunigel V1 bentonite might enable silica colloids to be generated even under unsuitable chemical conditions. Silica colloids are normally suspended in groundwater in a fractured crystalline rock. This information may be of use in the estimation of the stability of near-field colloids (bentonite colloids coexisting with silica colloids, in some cases) in a granite-groundwater system, for example, at the GTS.

3.4 Conclusions

The stability of FEBEX colloids was defined by a series of batch experiments under various chemical conditions. The FEBEX colloids, negatively charged, are suspended in a lower ionic strength solution whereas a quite lesser amount of colloids is generated in a higher ionic strength solution as the colloids tend to be flocculated. The FEBEX colloids are stable in a solution where the ionic strength of the solution is lower than 1×10^{-2} M. The AGGW prepared has ionic strength of about 1.1×10^{-3} M (*ie* lower than 1×10^{-2} M), which is similar in chemistry to the GGW. Since the FEBEX colloids are actually generated and suspended in the AGGW, the colloids are expected to be stable under the GGW conditions. In addition, the results of both the reference case and the JNC case experiments suggest that the difference in bentonite mineralogy may affect the generation and properties of near-field colloids. In particular, the coexistence of silica colloids may dominate the stability of near-field colloids.

References

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