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Review of colloids in the geosphere and their treatment in performance assessments

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Executive Summary

Colloidal particles (that is particles in the size range 1-1000 nm) have the potential to enhance the migration of radioactive species away from a geological disposal facility (GDF) owing to their potential for transporting sorbed radionuclides. For colloids to play a significant role, they must be present, stable in the groundwater both chemically (with respect to dissolution) and colloidally (with respect to aggregation and sedimentation processes), and mobile over significant distances through the groundwater system. There must also be a significant association of radioelements with colloids. Colloid-facilitated radionuclide transport (CFRT) is potentially important for radioelements of low solubility that will also sorb strongly to mineral surfaces (such as thorium, americium or plutonium (as plutonium(III) or (IV)) whose retardation through the geosphere may be reduced by association with mobile colloids.

The need to evaluate the potential impact of colloids on the performance of an underground repository is recognised in national waste disposal programmes world-wide. Consequently many national programmes have undertaken research into colloids; this includes work undertaken in the UK. The objective of this report is to review critically the international literature and summarise current understanding concerning the key aspects of colloid behaviour in the geosphere and to make recommendations for future research.

No decision has yet been made concerning the site geology for a UK GDF. Therefore, this review considers potential colloid behaviour in a range of lithologies and their treatment in performance assessments carried out internationally for a range of disposal concepts in different host rock types. In the case of fractured rocks or permeable sedimentary rocks, colloids may potentially be advected with groundwater flow through the flowing porosity. In low-permeability sedimentary rocks, however, where transport is predominantly diffusion controlled, the rock itself is expected to provide an effective barrier to colloid migration and CFRT is not anticipated to be an issue, provided that there is no significant groundwater flow in fractures. Therefore the bulk of this review has focused on colloid behaviour in fractured rock and permeable sedimentary rock, where the potential role of colloids remains an open question.

For a GDF located in a geological environment comprising fractured and/or permeable sedimentary rock, characterisation of groundwater colloid (and natural organic) populations will be necessary to demonstrate understanding of the possible contribution of colloids to radiological risk. Therefore, this review has considered the current state of development of methods for effective sampling of groundwater to obtain samples suitable for colloid analysis, free from artefacts, and the strengths and limitations of available colloid analysis techniques. A number of recommendations are made concerning the approach to colloid characterisation as part of a future site investigation.

The review is relevant to all geological disposal concepts for higher activity wastes. A brief overview of current understanding of near-field colloids potentially arising from facilities for vitrified high level waste, spent fuel and intermediate level wastes that may migrate into and through the geosphere is included in this report. Experimental methods and modelling approaches to studying and interpreting colloid stability, transport and CFRT behaviour under a range of conditions and over a range of length scales are also discussed. Current understanding of radionuclide-colloid interactions and, in particular, the reversibility of such interactions has been reviewed.

This study has focused on the behaviour of inorganic colloids in the geosphere which are expected to be the predominant colloid types in deep groundwaters in fractured and permeable porous rock where concentrations of natural organic species are expected to be low. Detailed discussion of the behaviour of natural organic materials has been beyond the scope of this report, although the interactions of organic material with inorganic colloids have been included where these are potentially important to the behaviour of inorganic colloids. It should be noted,

however, that natural organic (predominantly humic) materials are chemically persistent and mobile in the geosphere and may potentially be more significant than inorganic colloids in facilitating radionuclide transport in deep groundwaters if there is a source of fossil organic material.

The current understanding of the potential impact of inorganic colloids on the safety of a GDF is that at the levels of mobile colloids measured in deep groundwaters (< 1mg dm^{-3}), assuming cautious values for sorption distribution coefficients onto colloids and cautiously assuming that colloids are mobile and advected with groundwater flow, without retardation, the impact of colloids will be negligible if radionuclide sorption onto colloids can be treated as reversible.

The principal uncertainty concerning the potential impact of geosphere colloids is the reversibility of radionuclide-colloid interactions. Geosphere colloids may have an impact on risk if some radionuclide-colloid associations are irreversibile. In this case, their potential impact depends on the amounts of radionuclides irreversibly associated with colloids, the mobility of those colloids in groundwater (e.g. are they removed or retarded by filtration or attachment to the rock) and the finite lifetime of such colloids as a distinct entity.

A key topic for further research identified in other national programmes concerns release of colloids from the bentonite buffer used in many HLW/SF disposal concepts. Not only may released colloids act as carriers for radionuclides released from waste packages but also there is the potential for long-term erosion of the buffer that might eventually compromise its key safety-related features. To date, there is limited data concerning colloid release rates from bentonite in contact with flowing groundwater and no clear assessment has been made concerning the potential significance of the process.

The key recommendations of this review, which are appropriate for a GDF located in a geological environment comprising fractured and/or permeable sedimentary rock, are summarised as follows:

- Characterisation of groundwater colloid (along with natural organic) populations will be necessary to demonstrate understanding of the possible contribution of geosphere colloids to radiological risk. Such colloid characterisation studies need to be properly integrated into the design of a site characterisation programme from an early stage.

- In preparation for future site characterisation studies, NDA RWMD should work with other waste management organisations internationally to develop standardised groundwater colloid sampling protocols to enable collection of representative groundwater samples for colloid analysis.

- In addition, NDA RWMD should consider investing in the development and application of improved colloid analysis techniques, in particular in the use of *in situ* techniques for colloid separation.

- The priority for future research is to address the current limited understanding of the reversibility of radionuclide-colloid interactions. A combination of a more detailed review of radioelement-mineral interactions and a sensitivity analysis of key parameters in assessment-type calculations is suggested as an initial step. The results of these activities would help to design a focused experimental programme.

- NDA RWMD should consider collaborating with international studies concerned with colloid release from a bentonite buffer, if its use is adopted in UK disposal concepts.

- NDA RWMD should keep a watching brief on the outcome of colloid studies on other national and international programmes. This would enable NDA RWMD to optimise its research activities cost-effectively and maintain a consistency of approach internationally.

Contents

Abbreviations

ADE	Advection-dispersion equation
ADZ	Alkaline disturbed zone
AECL	Atomic Energy of Canada Limited
AF4	Asymmetric flow field flow fractionation
AFM	Atomic force microscopy
ARAP	Alligator Rivers Natural Analogue Project
BFS	Blast furnace slag
BSE-SEM	Backscattering electron scanning electron microscopy
CCC	Critical coagulation concentration
CFCT	Colloid-facilitated contaminant transport
CFM	Colloid Formation and Migration (experiment in Grimsel URL)
CFRT	Colloid-facilitated radionuclide transport
CoRWM	Committee on Radioactive Waste Management
CPC	Critical particle concentration (for plugging of porous media)
CRR	Colloid and Radionuclide Retardation (experiment in Grimsel URL)
CSC	Critical salt concentration (for particle release)
CSH	Calcium silicate hydrate
CT	Colloid transport
CTRW	Continuous time random walk (model)
DBL	Diffusion boundary layer
DGT	Diffusion gradients in thin films
DLVO	Derjaguin, Landau, Verwey and Overbeek
EBS	Engineered barrier system
EDL	Electrical double layer
EDX (EDAX)	Energy dispersive X-ray analysis
ELT	Equilibrium leach test
ESCA	Electron spectroscopy for chemical analysis

ESEM	Environmental scanning electron microscopy
EXAFS (XAFS)	Extended X-ray absorption fine structure (spectroscopy)
FFFF	Flow field flow fractionation
F-P	Fokker-Plank (equation)
GDF	Geological disposal facility
GTS	Grimsel Test Site
HLW	High-level (radioactive) waste
HFSC	High fused silica content (cement)
HPF	Hyperalkaline Plume in Fracture Rock (experiment in Grimsel URL)
ICP-AES (ICP-OES)	Inductively coupled plasma-atomic (optical) emission spectroscopy
ICP-MS	Inductively coupled plasma-mass spectrometry
ILW	Intermediate-level (radioactive) waste
LIBD	Laser-induced breakdown detection
LLW	Low-level (radioactive) waste
LPAS	Laser photo-acoustic spectroscopy
LSC	Long-term Cement Studies (experimenta at Grimsel URL)
KBS-3	Swedish repository concept for spent fuel disposal
MRWS	Managing Radioactive Waste Safely
NDA	Nuclear Decommissioning Authority
NF-Pro	Near-field Processes (a European VIth framework research project)
NMR	Nuclear magnetic resonance
NOM	Natural organic matter
NRVB	Nirex Reference Vault Backfill
NTS	Nevada Test Site
OPC	Ordinary Portland cement
PA	Performance assessment
PCS	Photon correlation spectroscopy
PGRC	Phased Geological Repository Concept

PLM	Permeation liquid membrane (method)
PZC	Point of zero charge
RBS	Rutherford backscattering spectroscopy
REE	Rare earth element
RMD	Rock matrix diffusion
RWMD	Radioactive Waste Management Directorate (of NDA)
SEM	Scanning electron microscopy
SF	Spent (nuclear) fuel
SKB	Swedish Nuclear Fuel and Waste Management Company
SKI	Swedish Nuclear Power Inspectorate
SPC	Single particle counting
STEM	Scanning-tunnelling electron microscopy
TEM	Transmission electron microscopy
TOCSIN	A type of total organic carbon analyser
TRLFS	Time-resolved laser fluorescence spectroscopy
TSPA	Total System Performance Assessment
TSPA-LA	Total System Performance Assessment-License Application
URL	Underground research laboratory
USD	Uranium-series disequilibrium
USNRC	United States Nuclear Regulatory Commission
XRD	X-ray diffraction

1 Introduction

1.1 Background

As part of its Managing Radioactive Waste Safely (MRWS) programme, UK Government issued a White Paper in June 2008 setting out a framework for implementing geological disposal of the UK's higher activity radioactive waste [1]. It is currently intended that all UK higher-activity wastes will be disposed of in a single facility, providing that this facility can be developed to provide suitable, safe containment for the waste inventory.

Geological disposal facilities (GDFs) for the long-term isolation of higher level radioactive wastes are in various stages of development in a number of countries (see Alexander and McKinley [2] for an overview). These facilities utilise a combination of engineered and natural barriers to form a multi-barrier containment system for the disposed radioactivity. A range of generic geological disposal concepts, being studied and developed in the UK and internationally, could provide safe and secure geological disposal of higher activity wastes for potentially suitable UK geological settings [3].Typically a different range of disposal concepts needs to be considered in relation to each different geological setting.

Previously a subset of internationally available geological disposal concepts was used to demonstrate the general viability of geological disposal of radioactive wastes in the UK [4]. In addition, some specific disposal concepts have been worked up in more detail to support the development of waste package specifications and the assessment of the disposability of waste packages that would be produced as a result of proposals put forward by waste owners [5]. These are:

- disposal of solid intermediate-level (ILW) and certain long-lived low-level (LLW) radioactive wastes in excavated vaults which will be backfilled with a cementitious material (previously referred to as the Nirex phased geological repository concept (PGRC) [4, 6); and

- disposal of vitrified high-level wastes (HLW) and spent nuclear fuel (SF) in holes drilled in bedrock surrounded with a bentonite buffer [7], based on the 'KBS-3' concept developed in Sweden [8].

The multi-barrier containment provided by a cement-based ILW/LLW repository is illustrated in Figure 1.1. In this case, physical containment of radioelements would be achieved by immobilisation and packaging of wastes (mostly) in stainless steel containers. Emplacement of the waste packages in vaults excavated deep underground within a suitable geological environment would achieve geological isolation. Chemical conditioning would be provided by backfilling the vaults with a cementitious material (Nirex Reference Vault Backfill, NRVB) after all the waste had been emplaced in the repository. The backfill provides alkaline conditions, an environment in which most radionuclides are highly insoluble, and contributes to the sorption capacity; these characteristics form an important part of a chemical barrier to radioelement migration. Geological containment would be achieved through final sealing and closure of the repository at a time determined by future generations. Once the repository has been sealed, the prevailing chemical and physical environment will evolve in response to a range of both internal and external factors. It is expected that saturated reducing alkaline conditions will prevail for much of a repository's lifetime [9].

In the KBS-3 concept [8] (Figure 1.2), SF is encapsulated in copper canisters strengthened with a cast iron insert. The copper canisters are surrounded by a compacted bentonite clay buffer and deposited in vertical holes drilled along a series of access tunnels at a depth of approximately 500m in saturated hard rock. The tunnels and rock caverns would be backfilled with a mixture of bentonite and crushed rock. Under suitable geological conditions, the corrosion of copper is extremely slow and the copper canister is expected to maintain its integrity, despite corrosion, for an extremely long time, thereby isolating the waste. The function of the buffer material is to protect the waste container from small movements in the rock and to provide a physical and chemical barrier to the outward migration of radionuclides and the inward movement of groundwater. The bentonite absorbs water, which results in swelling; this makes it very difficult for groundwater to penetrate the clay layer to reach the canister. In addition, the clay has a significant sorption capacity for many of the radioelements that ultimately may be released from the canister, which can provide significant retardation of the transport of radionuclides into the surrounding rock.

The UK disposal concept envisages the disposal of vitrified HLW in addition to SF [7]. HLW is produced in the UK, in liquid form, from the reprocessing of SF. HLW is converted into a more stable form by immobilising it in glass (vitrification) in stainless steel canisters. Pairs of these canisters would be overpacked in a copper[1] canister for disposal.

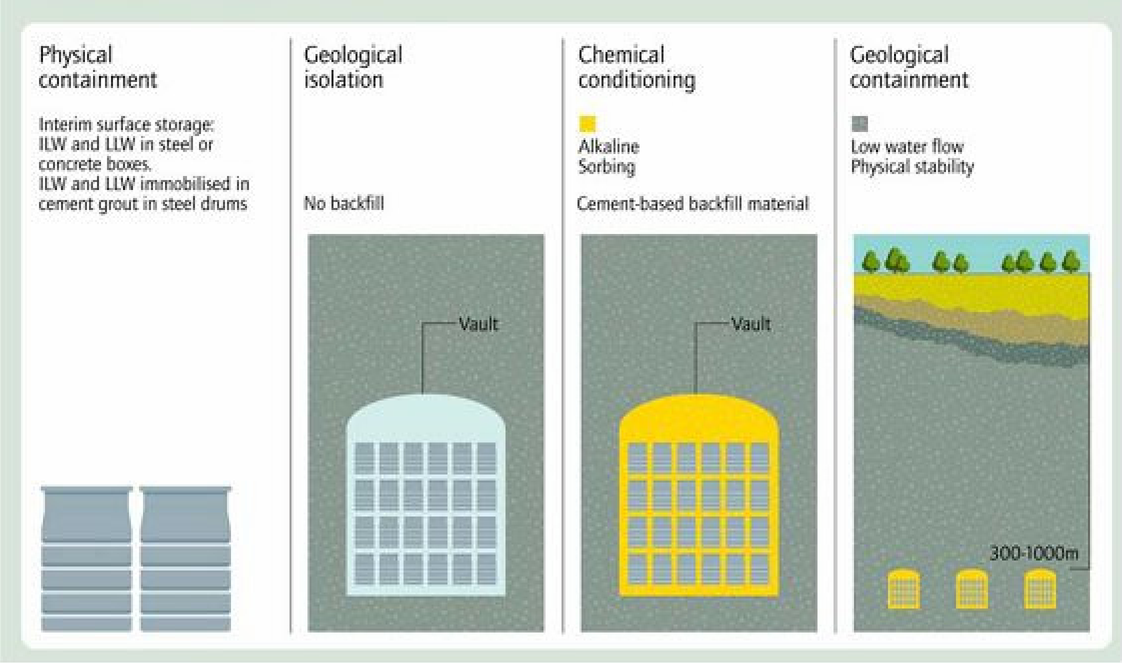

Figure 1.1 Schematic representation of the cement-based disposal concept for ILW and long-lived LLW [4]

The migration of radionuclides through the geosphere surrounding a GDF located in fractured crystalline rock is likely to be governed primarily by groundwater transport [10,11]. Two processes have been identified that may act to retard the migration of dissolved radionuclides advected with groundwater flow [11]: diffusion into the rock matrix surrounding fractures [12] and geochemical interactions between dissolved radionuclides and the rock including [13, 14] sorption, precipitation and mineralisation processes.

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[1] At the current stage of the programme, NDA are examining a wide range of potentially suitable disposal concepts so that a well-informed assessment of options can be carried out at appropriate decision points in the implementation programme, this includes work to review potential canister materials.

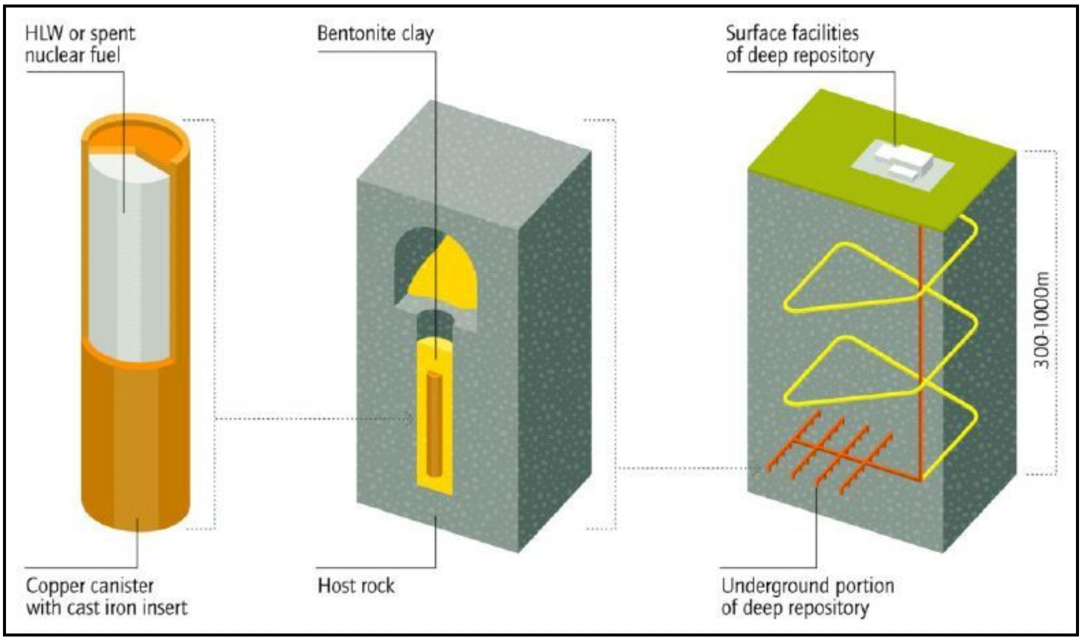

Figure 1.2 Schematic representation of the UK Reference HLW/SF concept (from [15]).

In the case of a repository located in a low permeability sedimentary rock, such as a mudrock (e.g. Opalinus Clay under consideration as the host rock in Switzerland), the principal mechanism of radionuclide migration is expected to be diffusion [e.g. 16]. In this case, geochemical interactions between dissolved radionuclides and the rock will provide the major retardation process.

Radionuclide behaviour in the geosphere may also be affected by an association with any colloidal particles that are present in the groundwater [17- 20]. If radionuclide-bearing colloidal particles are present and mobile along the groundwater pathway, the retardation of radionuclides may be reduced, with a potentially detrimental effect upon the containment performance of the geological barrier.

The potential mobility of colloidal particles through rock depends crucially on the rock type and the dimensions of the principal groundwater pathways through the rock porosity. Colloids are potentially mobile through fractures in crystalline rock and through permeable sedimentary rocks containing macroscale porosity such as sandstones, where the flow paths have dimensions significantly larger than colloid particle size. Only the smallest colloidal particles may be mobile through the finer-scale porosity of low permeability sedimentary rocks, however, which thus may act as an effective filter for most colloidal species [21].

There are numerous reports in the literature indicating that, in near-surface waters, mobile colloids may serve as carriers for strongly sorbed contaminants such as radionuclides [e.g. 22], toxic metals [e.g. 23- 25] and organic compounds [23,26,27]. Matshunaga *et al*. [28] have reported the association of radionuclides released during the Chernobyl accident with colloidal material in surface waters. There is a general recognition that colloid facilitated transport may occur in deep groundwaters that are of relevance to geological disposal of radioactive wastes [e.g. 18,19,29,30]. However, there is much less information available to assess the potential impact of colloid–facilitated radionuclide transport (CFRT) [2] in deep groundwaters; there are few, if any, field examples to demonstrate the operation of CFRT over significant

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[2] The term colloid-facilitated contaminant transport (CFCT) is used generally in the scientific literature and will be used, where appropriate, in this report.

distances. The reported observations of plutonium migration over a distance of kilometres from nuclear test areas at the Nevada Test Site, US [31-33], have been attributed to colloid transport, but this is for a highly disrupted site, where there is significant uncertainty about the nature of the transport processes (see also the critique by Honeyman [34]). Similarly, low concentrations of plutonium has been detected at a distance of 4 km after about 55 years from a surface source at Mayak in Russia, and their transport attributed to association with amorphous iron oxide colloids [35]. However, alternative explanations, including complexation by oxalate [36] or natural organic matter, have yet to be investigated. Nevertheless, colloidal particles are present in all natural waters, including deep groundwaters [37], and there is evidence that they may be generated in the repository near field [e.g. 38- 43] or at the interface of the bentonite buffer and host rock in some HLW/SF concepts [44]. Therefore, there is a need to evaluate the potential impact of colloids on the performance of a GDF. Consequently, many national programmes have undertaken research into colloids [e.g.,13, 45- 48]; this includes work undertaken by Nirex in the UK [e.g. 38,41,49- 54]. This research on colloids has considered the formation and presence of a range of colloid types (e.g. natural, cement, bentonite, metal, organics, etc), their stability, mobility and their uptake of radionuclides. In a number of cases, methods have been developed to quantify the potential impact of colloids in performance assessments (PA) [e.g. 55- 59].

Despite a significant body of research into the role of colloids in facilitating the transport of radionuclides in the environment over the last 25 years, there remain unanswered questions [60] and uncertainties concerning their potential impact. For example, HSK, the Swiss Nuclear Safety Inspectorate, stated [48] that "*...possible colloid associated transport of radionuclides remains an important open question*."

With the UK Government's decision to adopt geological disposal as the solution for the long-term management of higher activity wastes in the UK and the subsequent ramping–up of the NDA's research programme in support of geological disposal concepts for both HLW/SF and ILW, a critical review of the progress made in research into geosphere colloids, and identification of priorities for future research is timely.

The objective of this report is to review critically the international literature concerning the formation, stability, migration and capacity for radionuclide uptake of colloids in the geosphere, and to make recommendations for future research. No decision has yet been made concerning the site geology for a UK GDF. Six generic geological environments have been identified that may potentially be suitable for geological disposal in the UK [61]. Therefore, this review considers potential colloid behaviour in a range of geologies including fractured crystalline rock, porous sedimentary rock and low-permeability mudrock. The review is relevant to both HLW/SF and ILW (cementitious) disposal concepts, and a brief overview of current understanding of near-field colloids from each type of facility that may migrate into and through the geosphere is included in this review. A recent report provides a detailed compilation of research into the behaviour of colloids in the near field of a cementitious repository [62].

An important component of this report is an evaluation of approaches to the treatment of colloid-facilitated transport in the geosphere in performance assessments (PAs) (Section 11). Based on this and the findings of the recent near-field colloids report, a companion report will recommend a strategy for treating colloids in future UK PAs [63].

1.2 Structure of this report

This report is structured as follows. The types and sources of colloids that may arise in the geosphere and which have the potential to affect radionuclide migration are outlined in Section 2. Section 3 outlines the key processes that are relevant to colloid behaviour in the geosphere, based on the understanding of colloid behaviour built up over many years in the fields of colloid science, chemical and environmental engineering. Section 4 describes methods for sampling and characterisation of colloid populations from deep groundwaters and Section 5 summarises the findings of colloid characterisation studies undertaken worldwide. Section 6 provides an overview of the current understanding of colloid generation in a repository near field and at the near field to far field interface that may potentially migrate into and be mobile in the geosphere.

Section 7 provides an overview of colloid stability studies undertaken for key types of colloids of potential importance in the geosphere. The current understanding of radionuclide-colloid interactions is discussed in Sections 8. Experimental and modelling studies of colloid transport are reviewed in Sections 9 and 10, respectively. The treatment of colloids in the geosphere in recent performance assessments are discussed Section 11. Based on the outcome of the review, Section 12 provides a summary of the state of the science and recommendations are made for future approaches and strategy. Finally, conclusions are drawn in Section 13.

2 Colloids: definitions, types and sources

2.1 Definition of colloids

The term *colloid* (from the Greek for "glue") was coined by the Scottish chemist Thomas Graham in 1861 to describe certain solutions, known as Selmi's "pseudosolutions" or "sols" [64], that diffused only very slowly through a sheet of parchment. Graham deduced from the low rate of diffusion that the sols contained a dispersion of coarser aggregates than in ordinary solutions that were "glued" together. Despite being something of a misnomer, the name has stuck [65].

The terms colloid and colloidal refer to two-phase systems in which (usually) finely-divided particles of one phase, the dispersed phase, are distributed in a second phase, the dispersion medium. Colloidal systems vary widely in composition and some everyday examples include: oil-in-water emulsions such as milk and mayonnaise; liquid in gas aerosols such as mist and liquid sprays; and solid in liquid pastes such as toothpaste. Although strictly, the terms colloid and colloidal refer to the two-phase system as a whole, through common usage these terms have become synonymous with the dispersed particles themselves, particularly in the environmental field. This usage has been widely adopted and the terms colloid and colloidal will be used to refer to dispersed particles throughout this report.

The IUPAC definition of the term colloidal refers to a "*state of sub-division in which molecules or polymolecular particles dispersed in a medium have in at least one direction a dimension roughly between 1 nm and 1000 nm in size*[3]" [66]. Thus, colloids dispersed in water are intermediate in size between ionic solute species in true solution and suspended particles (which are typically larger than about 1000 nm). The size distinction between colloidal and suspended particles is not sharp, however. On a phenomenological basis, the distinguishing characteristic of a denser than water colloid is that it is sufficiently small to be maintained in stable dispersion for a prolonged period due to the thermal motion of the liquid (Brownian motion), whereas suspended particles will sediment in the absence of forces (e.g. hydrodynamic lift forces or fluid shear) that oppose gravity.

It is important to note that, in many studies, a colloidal size fraction may be operationally defined as being smaller than 450 nm (more usually quoted as 0.45 μm) as this is the 'standard' filter pore size used when sampling ground-, pore- and seawaters [e.g. 67- 70]. In colloid studies,

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[3] This terminology is designed to include system such as slurries of long needle-like particles and thin liquid films which are colloidal in one and two dimensions, respectively.

this standard pre-filter may then be followed by sequential filtration through a range of filters with increasingly smaller pore sizes [cf. 29, 45]. The lower size limit may also be operationally defined; in many solubility and sorption studies [e.g. 71, 72], material passing through either a 10,000 to 30,000 nominal molecular weight cut-off (NMWCO) filter, with pore size typically in the range 1.8-3 nm, is treated as the dissolved phase[4] .

In addition, in colloid population studies, the size range accessible to measurement may be limited by the resolution of the analytical technique. For example, the lower size limit for colloid size distributions by scanning electron microscopy (SEM) may be limited typically to 30 or 50 nm. Therefore, it is important that particle population data are quoted with the appropriate size range of the measurements.

Recently, the terms nanoparticle [75] and nanocolloid [e.g. 76] have started to appear in the literature, reflecting the recent nanotechnology boom. The terms are applied to particles at the smaller end of the colloidal size range and usually less than 100 nm in maximum dimension.

In the field of colloid-facilitated contaminant transport, two types of radionuclide-bearing colloids have been distinguished: type I (or intrinsic) colloids consist predominantly of radionuclide-containing phases, e.g. thoria, becquerellite, uranophane; type II (or carrier) colloids are particles of non-radioactive mineral phases (e.g. metal hydrous oxides, clays) or organic macromolecules to which radionuclides may be bound. Somewhat misleadingly, intrinsic and carrier colloids bearing actinide elements were widely referred to as ‘real colloids’ and ‘pseudo-colloids’ (after [18]), respectively, but this practice is becoming less common. Intrinsic colloids are sometimes referred to as eigencolloids in the literature (after the german eigen for own) [e.g. 77].

2.2 Types and sources of colloids in the geosphere

In considering the potential role of colloids in the transport of radioactivity through the geosphere from a GDF, three sources of colloids and their behaviour under geosphere conditions need to be considered:

- the colloid population in the groundwater (potential carrier colloids) which may be transported through the geosphere by groundwater flow (and which also may enter and be transported through the repository);
- colloids that may be generated in the repository (intrinsic and potential carrier colloids), *in situ*, from the degradation of wastes and near-field materials, i.e. near-field colloids, which may migrate into the geosphere; and
- potential carrier colloids that may be generated at the interface between the near field and the host rock, for example:
  - for a cementitious repository in the alkaline disturbed zone (ADZ) of the geosphere where the host rock is contacted by an alkaline plume; and
  - for a bentonite-buffered respository in a crystalline host rock, where erosion of the buffer may occur at the buffer-rock interface.

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[4] This definition of the dissolved phase has been adopted in recent data elicitation exercises for radioelement solubility and sorption distribution parameters for use in performance assessment undertaken for NDA RWMD [e.g. 73,74]

Colloid characterisation programmes for a wide range of groundwater systems, world-wide, have shown that colloids are present in all groundwaters [e.g. 37, 78, 79, 80, 81]. In 1993, McCarthy and Degueldre concluded that in deep, undisturbed groundwater systems (over 300m depth), with low organic contents, colloid populations, comprising predominantly inorganic mineral particles, have mass concentrations typically less than 1 mg dm^{-3} [37]. In general, the nature of the groundwater colloid population will be a site-specific issue and will be dependent on the mineralogy and geochemistry of the host rock/groundwater system.

Two principal types of carrier colloids can be distinguished in groundwater systems based on their chemical composition: inorganic (or mineral) colloids and organic macromolecular colloids (although it is probably truer to say that in natural systems a continuum exists between inorganic colloids (clay, oxides), inorganic colloids coated with organic material, organic colloids associated with inorganic phases and organic colloids [80]). Water-borne bacteria and viruses may also be classed as colloids and, indeed, bacteriophages have been used to conduct tracer experiments in deep groundwaters [e.g. 82].

Inorganic colloids in groundwater may comprise mineral fragments of the host rock (e.g. silica) or secondary minerals, (e.g. clays, iron oxides). In the ADZ of a cementitious repository, inorganic colloids may be formed as secondary phases from the interactions between the alkaline plume and the host rock. Depending on the repository concept and the types of waste disposed, inorganic carrier colloids may be generated in the near field from degradation of wasteform (e.g. cementitious, vitrified or ceramic) [83], by corrosion of the metal containers and constituents of the waste [84] and/or the degradation/erosion of backfill or buffer materials (e.g. cement or bentonite). Intrinsic radionuclide colloids may also be formed in the near field, particularly from spent fuel [60, 83]. If accessible to groundwater flow, these near-field colloids may be advected into the surrounding rock.

Organic macromolecules in deep groundwaters are thought to arise either due to percolation of organic-rich surface waters or from leaching of deep deposits of (fossil) organic material, such as the intercalated brown coal sands at the Gorleben site in Germany [85]. Although organic macromolecular colloids are present in groundwaters in true solution, they may be classified as colloids on the basis of their size. Organic colloids may comprise biomacromolecules (e.g. hydrocellulose, lignin, proteins) and humic substances. In simple terms, humic substances are polymeric compounds produced through microbial action, which are not synthesised directly to sustain the lifecycles of the biomass [86]. Humic substances are variable in chemical composition, molecular mass and structure. Three types of humic substances are classified on the basis of their solubility characteristics: insoluble humin; humic acids, which are soluble under alkaline conditions but precipitate when the solution is acidified; and fulvic acids, which are soluble in both acid and alkaline conditions.

Fulvic acids are low molecular weight polyelectrolytes (molecular weight typically less than 2000) [86] and should not be regarded as colloidal species. Typically, humic acids have a higher degree of polymerisation than fulvic acids (higher molecular weight) and a lower content of functional groups (e.g. carboxylate, phenolic). Humic acids are at a more advanced stage of humification [86]. Since most of the acidic functional groups of humic and fulvic acids are expected to dissociate between pH 5 and 7, the polyelectrolytes are expected to bear a net negative charge in groundwaters and may readily complex metal ions.

Organic macromolecules may act as carriers (i.e. complexants) of radionuclides in groundwater both as discrete colloidal species and as adsorbed species attached to inorganic colloids where the presence of organic coatings may modify colloid stability behaviour [e.g. 87] and their sorption capacity for radionuclides [e.g. 88].

This review is concerned with the nature and behaviour of colloids in deep groundwaters. In general, inorganic colloids are the predominant colloid types in deep groundwaters (see Section 5.2.4) and, in the absence of a deep source of fossil organic material, concentrations of natural organics can be expected to be low. Therefore, this report will focus on the behaviour of inorganic colloids, potentially affected by the presence of natural or repository-derived organics. Complexation and colloidal behaviour of natural organic compounds is considered beyond the scope of this review. For completeness, the review will also consider the general behaviour under far-field conditions of colloidal materials that may arise in the near field from the wastes and from engineered barrier materials in different disposal concepts. The nature of colloids that may be generated in the near field and migrate into the far field is discussed in more detail in Section 6.

3 Key processes affecting colloid behaviour

The work carried out on national waste disposal programmes to understand the potential significance of colloid facilitated-transport to repository performance has built on existing understanding of colloid behaviour, developed over many years and reported in the scientific literature. In the following sections, the key processes that are relevant to the behaviour of colloids in the geosphere are outlined.

3.1 Colloid formation and growth

Inorganic colloidal particles in groundwater are generated primarily by the physical disintegration and weathering of rock in contact with water [89]. Degueldre termed this process primary colloid generation [45]. Colloidal particles may also be formed under conditions where the groundwater chemistry is not in equilibrium with the primary mineral composition [45], and supersaturation is reached with respect to secondary minerals. As chemical processes alter to re-establish equilibrium conditions, changes in both groundwater chemistry and mineral phases will occur, which can lead to the precipitation of new crystalline or amorphous phases; colloidal particles may be produced by homogeneous nucleation and growth processes. These processes have been termed secondary colloid generation [45]. However, there will be competition between rock surface sites, nucleating colloids and existing colloids for secondary phase growth [90]. Modelling suggests that precipitating solids may attach predominantly to the rock surfaces if the relative colloid surface area is low [90]. In general, the formation of colloids by the above processes is associated with either local chemical and/or physical changes, or perturbations, of the groundwater system [e.g. 91].

Recently, Conrad and co-workers [76] have developed kinetic models for the homogeneous nucleation and precipitation of colloidal silica under "*geologically-relevant conditions*", based on previously reported experimental data [92]. Changes in the rate of formation of the silica colloids were dependent on the degree of supersaturation, ionic strength and pH of the experimental solutions. The primary particle size of the colloidal silica was observed to be about 3 nm and continued growth of the particles resulted in precipitation of particles larger than 100 nm in size. The highest rates of silicate polymerisation and colloid growth were found at neutral pH (studied range pH 3-7). However, such work needs to be put in broader context of heterogeneous natural systems if it is to provide insight into possible mechanisms of colloid formation in deep groundwater systems.

Colloidal particles may grow by aggregation processes (as a result of particle collisions) or may themselves break-up to form smaller particles by disaggregation (peptisation). The rate of colloid aggregation or peptisation depends on the interaction forces that control colloid stability during particle collisions (see subsection 3.2 below). If particles grow sufficiently large, generally >1 μm, then sedimentation may occur, removing colloids from the fluid.

The above processes will give rise to colloid-sized mineral particles in the groundwater system. This does not necessarily mean that the colloidal particles will form a stable dispersion in the groundwater and be transported with groundwater flow. Ryan and Elimelech have argued that the major source of colloids dispersed in groundwater is the mobilisation of existing colloid-sized mineral, which is promoted by perturbations of the chemical and physical conditions of the groundwater system [93]. This process is of major importance in shallow groundwater systems which are subject to periodic changes in chemical conditions and water flow (e.g. due to rain water infiltration), but should not be overlooked in the context of deep groundwaters, even though such rapid changes are much less likely. The release of bentonite colloids from the margins of a bentonite buffer in contact with flowing water (e.g. in a fracture at the bentonite-host rock interface) is an example of the potential mobilisation of existing colloidal particles that may arise by either a chemical (hydration, ion exchange, swelling and dispersion [94]) or a physical perturbation (hydrodynamic flow-induced release). In general, mobilisation is related to the strength of the interactions between colloidal particles and the surface of immobile solids, which may depend on the chemical conditions (ionic strength, pH, etc); it may depend also on the variations in lift forces arising from changes in flow velocity and fluid shear, for example. These aspects will be discussed further in section 3.3.

Geckeis [95] has pointed out that the presence of a GDF within a host rock will create hydraulic and geochemical gradients that may last for a very long time and that such perturbations may lead to possible generation of colloid populations and interactions of radioelements with colloids. Colloids may be generated in the near field by processes that are similar to those outlined above, e.g. by the disintegration and chemical “weathering” of the wasteform components and backfill, corrosion of metal waste containers and structural components or by secondary nucleation and growth processes in the near-field porewater. Some recent work has considered the potential for colloid formation and incorporation of radionuclides in the mixing zone between granite groundwater and bentonite porewater relevant to disposal concepts for SF [96].

3.1.1 Particle size distributions

In general the processes of colloid formation, growth and aggregation as well as loss by dissolution, sedimentation or attachment to surfaces, result in a colloid population containing particles with a distribution of size as well as composition and shape.

It has been found that the size distributions of suspended material in atmospheric aerosols, sea water and environmental samples follow a power law scaling behaviour with size [97]:

$$n(d_\mathrm{p}) = \left(\frac{\Delta N}{\Delta d_\mathrm{p}}\right) = A d_\mathrm{p}^{-\beta}, \tag{3.1}$$

where $n(d_\mathrm{p})$ is the distribution function for particle size, d_p, ΔN is the number of particles with a diameter in the size interval Δd_p; A and β are constants. This relationship appears to hold for particles in groundwater systems down to at least 15 nm in size (based on [98]) and up to 100 µm in surface waters [97], displaying a linear region in a log-log plot of ΔN versus size class with slope $-\beta$.

The value of β provides an insight into how the size distribution has evolved with time. When particles are produced by erosion, $\beta = 4$ [80]. However, when nucleation or aggregation occurs, the values of A and β will be modified. Aggregation will favour the formation of larger particles over smaller ones and will result in a reduction in β; nucleation of new particles will tend to increase β. In general, environmental samples are often found to have β in the range 2-5, and close to 4 in many cases [97].

Thus, determination of particle size distributions using appropriate size discriminating colloid analysis techniques (see section 4.3 below) can (in principle) provide additional insight into the nature of the colloid population.

3.2 Colloid stability

Colloid stability is a key aspect of colloid behaviour that will determine the magnitude of colloid populations dispersed in natural groundwater systems. Indeed, as will be discussed in sections 5.2.1 and 7.4 below, there is evidence for a correlation between water chemistry, colloid aggregation rates and colloid concentrations in natural groundwaters [80]. Colloid populations that are not stable in the groundwater will not be transported over large distances [99] and will not facilitate radionuclide transport although they may contribute to radionuclide retardation.

Two types of particle stability can be distinguished: chemical stability and physico-chemical stability. The former concerns the thermodynamic stability of individual particles towards chemical (or biochemical) reactions such as dissolution or oxidation. The latter, often referred to as *colloidal stability*, concerns the stability of the dispersion as a whole towards aggregation as a result of particle collisions in the fluid phase.

3.2.1 Chemical stability

Inorganic colloids are thermodynamically metastable with respect to bulk solid phases [100, 101]. Small particles have a higher surface free energy than larger particles and this is the thermodynamic basis of the particle growth process known as Ostwald ripening, whereby larger particles in a colloidal dispersion grow at the expense of the smallest particles, which dissolve. This lack of thermodynamic stability may not play a role over laboratory timescales but may become significant when geological timescales are considered. It follows that groundwater colloids must be composed of mineral phases with low solubility and which have slow dissolution kinetics, if they are to remain as colloids for long timescales. Thus groundwater colloid populations (see section 5.2.4) are frequently composed of primary silicate minerals (such as potassium feldspar, mica and quartz) or secondary minerals (clays, metal oxides), which dissolve very slowly in water. An individual colloid particle under steady state chemical conditions may have a finite lifetime [80] determined by its size, mineralogy and rate of dissolution. The last will also depend on the groundwater chemistry (pH, composition, presence of organic complexants, redox potential, etc).

Particles that are composed predominantly of redox sensitive elements (e.g. iron(III) or uranium(VI) oxides) may be reduced or oxidised if exposed to a change in redox conditions. The resulting surfaces may have a higher solubility than the original surface and dissolve more rapidly.

The dissolution (weathering) of minerals has been studied extensively in the field of earth sciences (e.g. [102] and references therein) but the potential effects of particle dissolution kinetics on colloid chemical stability have rarely been assessed or discussed in the literature of colloid-facilitated transport. An exception is provided by Voegelin and Kretzschmar [21], who have argued that amorphous silica colloids would be expected to dissolve in Opalinus Clay groundwaters where silicon concentrations are significantly lower than the solubility of amorphous silica.

In contrast, organic colloids such as humic acid are thermodynamically stable, comprising macromolecular material in true solution. In terms of their long-term stability, humic substances are considered to be the most stable fraction of organic matter in soils and may persist for tens, hundreds or even thousands of years based on ^{14}C-dating [103].

3.2.2 Physico-chemical stability

(a) Inorganic colloidal stability

The principal mechanism of inorganic colloid stabilisation against aggregation is electrostatic repulsion. Colloidal particles composed of oxide minerals will develop a surface charge on contact with water as a result of the dissociation of surface hydroxyl groups and/or the adsorption of charged species. Clay particles possess a structural negative charge due to isomorphous substitution in which silicon atoms may be replaced by aluminium atoms, for example. To preserve electroneutrality, the particle is surrounded by a diffuse layer of counterions. This spatial separation of charge is called an electrical double layer (EDL).

The thickness of the diffuse part of the EDL is characterised by the Debye-Hückel parameter κ which has units of reciprocal length. The value of κ is determined by the ionic strength of the solution, I, and κ can be written, in units of nm^{-1}, (in water at 25°C) as

$$\kappa = 3.288 \sqrt{I}, \tag{3.2}$$

Values of $1/\kappa$ range decrease from 30.4 nm at $I = 10^{-4}$ mol dm^{-3} to 0.96 nm at $I = 0.1$ mol dm^{-3}. Thus, at higher values of ionic strength, it is predicted that the diffuse layer of the EDL will be highly compressed.

According to the classical theory of Derjaguin and Landau [104], and Verwey and Overbeek [105] (DLVO theory) the stability of colloidal dispersions is controlled by the net interaction energy (Figure 3.1) composed of an attractive van der Waals interaction and a repulsive electrostatic interaction. The extended version of the theory also includes a repulsive Born interaction at close separations due to atomic overlap that prevents particle coalescence. As particles approach during a Brownian or advective collision, repulsive electrostatic interactions result from the overlap of the diffuse parts of the electrical double layers. If the resulting energy barrier (V_{max}) is higher than the kinetic energy of the particles, they will be prevented from coming into contact to form an aggregate. The extent of electrical double layers and the height of the energy barrier to aggregation in the primary minimum[5] is controlled by the solution ionic strength and particularly the valency of counterions. As the ionic strength is increased, a point is reached at which the net energy barrier is reduced to zero. At this point the system the rate of coagulation becomes purley diffusion-controlled with all particle collisions resulting in aggregation. This point is known as the critical coagulation concentration (CCC).

It has been recognised for over a century that for a given colloidal system, the CCC is determined almost completely by the valency of the counterions. Polyvalent ions coagulate colloidal dispersions at lower electrolyte concentrations than monovalent ions. This effect of ion valency on the CCC, illustrated by the data presented in Table 3.1is known as the Schultz-Hardy rule. The following approximate expression is commonly used for the CCC for a dispersion of uniform composition [106]:

$$CCC = \frac{3.84 \times 10^{-39} . \gamma^4}{A^2 z^6} \tag{3.3}$$

where A is the Hamaker constant for the colloidal phase in water and z is the valency of the counterion. At high potentials γ approaches unity, whereas at low potentials $\gamma = ze\Psi/4kT$, where e is the electronic charge, Ψ is the surface potential of the particle, k is the Boltzmann constant and T is the absolute temperature. Therefore, the CCC is predicted to be proportional to $1/z^6$ at high potentials and Ψ^4/z^2 at low potentials (typically < ±50 mV); the former relationship has

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[5] Under suitable conditions, secondary mimima may arise in particle interaction curves at larger separation distances, as shown in Figure 3.1. When secondary mimina are sufficiently deep and the energy barriers to coagulation in the primary minima are sufficiently high, reversible coagulation of particles in secondary minima can occur [106]. As a rule of thumb, secondary minimum coagulation is considered to be unimportant for particles less than 100 nm in size (see Swanton [107] and references therein).

been confirmed experimentally for a number of colloidal systems as illustrated in Table 3.2 [107].

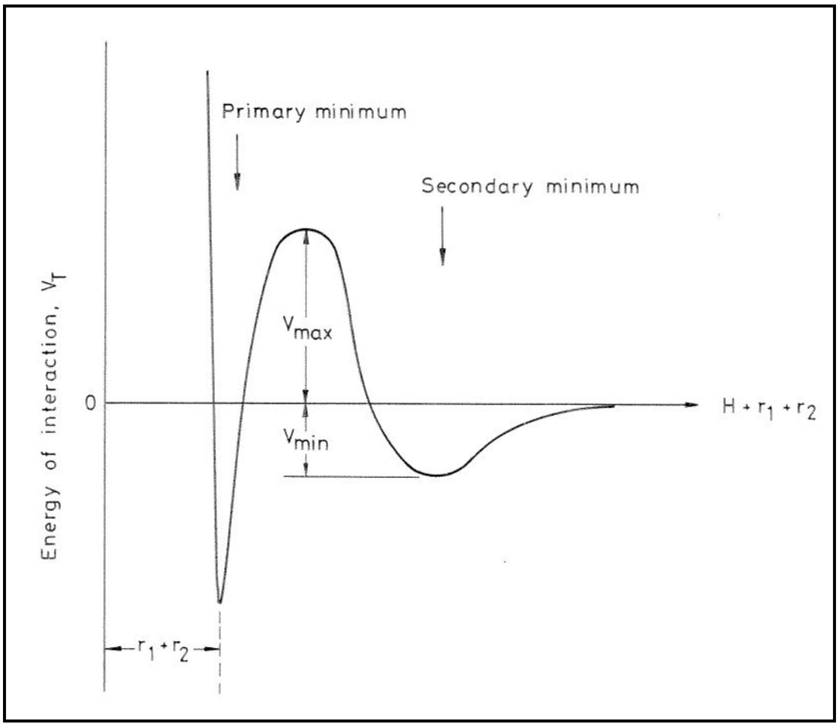

Figure 3.1 Schematic representation of the total interaction energy curve between two spherical particles of radii r_1 and r_2, as a function of their separation distance *H*, which shows both primary and secondary minima and an energy barrier to attachment in the primary minimum. The Born repulsion term is included in the total interaction energy to account for the excluded volume at contact (from Swanton [107])

The surface potential of colloidal particles depends on their composition and the protonation-deprotonation behaviour of hydroxyl groups on their surface as a function of solution pH. In general, at low pH values, where there are high concentrations of H^+ ions in solution, oxide surfaces will tend to be positively charged, whereas at higher pH, in the presence of excess OH^- ions, they will become negative. At some intermediate pH value, the net surface charge will become zero; this is known as the point of zero charge (PZC). In general, colloidal particle will tend to have a minimum in stability (as a function of pH) at pH values close to their PZC.

Examples of PZC values reported in the literature for a range of minerals are presented in Table 3.3 [108,109].

Table 3.1 **CCC values of negatively charged As_2S_3 and AgI dispersions and a positively charged Al_2O_3 dispersion with a variety of electrolyte containing counterions of different vacancy [106]**

As_2S_3 dispersion		AgI dispersion		Al_2O_3 dispersion	
Electrolyte	**CCC mmol dm^{-3}**	**Electrolyte**	**CCC mmol dm^{-3}**	**Electrolyte**	**CCC mmol dm^{-3}**
LiCl	58	$LiNO_3$	165	NaCl	43.5
NaCl	51	$NaNO_3$	140	KCl	46
KCl	49.5	KNO_3	136	NH_4Cl	43.5
HCl	31	$RbNO_3$	126	KCNS	67
				KNO_3	60
$MgCl_2$	0.72	$Mg(NO_3)_2$	2.60	K_2SO_4	0.30
$CaCl_2$	0.65	$Ca(NO_3)_2$	2.40	K_2CrO_4	0.95
$SrCl_2$	0.635	$Sr(NO_3)_2$	2.38	$K_2Cr_2O_7$	0.63
$BaCl_2$	0.69	$Ba(NO_3)_2$	2.26	$K_2C_2O_4$	0.69
		$Zn(NO_3)_2$	2.50		
		$Pb(NO_3)_2$	2.43		
$AlCl_3$	0.093	$Al(NO)_3$	0.067	$K_3Fe(CN)_6$	0.080
$Al(NO)_3$	0.095	$La(NO)_3$	0.069		
		$Ce(NO)_3$	0.069		
$Th(NO_3)_4$	0.090	$Th(NO_3)_4$	0.013	$K_4Fe(CN)_6$	0.053

Table 3.2 **Mean CCC values for the dispersions listed in Table 3.1**

Valence	**As_2S_3 dispersion**		**AgI dispersion**		**Al_2O_3 dispersion**		**Theory z^{-6}**
	Mean CCC (mmol dm^{-3})	**Ratio**	**Mean CCC (mmol dm^{-3})**	**Ratio**	**Mean CCC (mmol dm^{-3})**	**Ratio**	
M^{+}/A^{-}	55	1	142	1	52	1	1
M^{2+}/A^{2-}	0.69	0.013	2.43	0.017	0.63	0.012	0.016
M^{3+}/A^{3-}	0.091	0.0017	0.068	0.0005	0.080	0.0015	0.0013
M^{4+}/A^{4-}	0.090	0.0017	0.013	0.0001	0.0053	0.0010	0.00024

Table 3.3 Point of zero charge (pH value) for some oxide minerals, clay minerals and and calcite [21, 108, 109]

Mineral	Point of Zero Charge
Quartz, SiO_2	2-3.7
Cassiterite, SnO_2	4.5
Rutile, TiO_2	6.0
*Haematite (natural) Fe_2O_3	4.8
Haematite (synthetic)	8.6
Goethite, FeO(OH) (synthetic)	9.4
Corundum, Al_2O_3	9.0
Magnesia, MgO	12
Kaolinite	4.6
Montmorillonite	2.5
Albite	2.0
Calcite, $CaCO_3$	9.5

* Probably contaminated with SiO_2

The pH values of deep groundwater tend to be near-neutral, in the range 6-9, depending on the nature of the principal minerals comprising the rock surfaces, which control solution chemistry. Most primary silicate and secondary clay minerals bear a net negative surface charge in deep groundwaters, and potentially may form stable colloidal dispersions[6]. Iron oxide minerals, on the other hand, with PZC values in the near-neutral pH range, are less likely to form stable colloids.

In general, the potential at the surface of colloidal particles is not directly accessible to measurement. The potential that can be measured experimentally, known as the zeta potential, is the potential at the surface of shear, close to the particle surface and within which the fluid phase is stationary. The surface of shear is located within the diffuse part of the electrical double layer and (usually) the zeta potential is lower in magnitude than the surface potential due to the presence of chemically or physically adsorbed counter-ions close to the particle surface. Measurement of zeta potentials is discussed in more detail in section 7.2.2.

According to Hunter, there is a large body of experimental evidence showing that near the CCC, when rapid coagulation occurs in aqueous colloidal systems, the measured zeta potential is commonly in the range ±25-50 mV [111].

At electrolyte concentrations above the CCC, the rate of aggregation is diffusion-controlled and can be described by the classical equations of Smoluchowski [112]. At electrolyte

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[6] Secondary clay minerals bear both a permanent negative charge due to isomorphic substitution in the clay layers and pH-dependent charges from hydroxyl groups at the edges of the layers. The pH of the PZC of the edge hydroxyl groups is about 6.5 in the case of montmorillonite, for example [110]. However, the permanent negative charge of the clay layers tends to shield the poorly-charge edge surfaces at the pH values of deep groundwaters so that stable colloidal dispersions may be formed in low ionic strength systems.

concentrations below the CCC, where an energy barrier exists to particle attachment, particle aggregation may still occur, but at a significantly reduced rate. The rate will depend on the number of particle collisions with sufficient kinetic energy to overcome the energy barrier. The stability of a colloidal system is commonly described by a parameter known as the stability ratio, W, which is the reciprocal of the collision efficiency, α, the fraction of collisions resulting in attachment. For a given system, α is defined as the ratio of the rate of coagulation under a given set of conditions, k_c, to the rate of fast coagulation, k_f, when there is no energy barrier to coagulation (by definition, $\alpha \leq 1$). Thus:

$$W = \frac{1}{\alpha} = \frac{k_f}{k_c} \tag{3.4}$$

For the aggregation of similar particles, an approximate expression relating W to the height of the energy barrier, V_{max}, was derived by Reerink and Overbeek [113]:

$$W = \frac{1}{2\kappa r} \exp\left(\frac{V_{max}}{kT}\right). \tag{3.5}$$

Thus, DLVO theory predicts that at high electrolyte concentrations where there is no repulsive interaction between particles all collisions will lead to aggregation and $W = 1$. However, at electrolyte concentrations below the CCC, W rises rapidly.

Based on the approximate expressions for the van der Waals and electrostatic interations, a further was derived which predicts a linear relationship between log W and log C at concentrations below the CCC:

$$\log W = const. - 2.06 \times 10^{-9} \left(\frac{r\gamma^2}{z^2}\right) \log C$$

where

$$\gamma = \frac{\exp(ze\psi / 2kT) - 1}{\exp(ze\psi / 2kT) + 1}. \tag{3.6}$$

A plot of log W against log C is frequently referred to as a stability curve. It will be noted that the slope of stability curves is predicted to depend on particle size, the magnitude of the slope increasing for larger particles. In other words, large particles are predicted to be more stable at concentrations below the CCC than small particles.

In practice, however, a consistent finding of experimental coagulation studies using well-characterised mono-dispersed spherical particles, is that coagulation rates below the CCC are higher than predicted by DLVO theory, the predicted dependence of particle size is not observed [113- 116], and there appears to be no relationship between coagulation rate and counter-ion valency [113]. The possible reasons for this discrepancy, which have been reviewed by Swanton [107], include deposition in secondary minima (see Figure 3.1) [e.g. 117], surface roughness of real particles [113, 115] and the discreteness of surface charges [115].

It has become increasingly recognised that the interfacial structure of particles can significantly alter the interparticle forces and modify particle stability, effects that are not accounted for in the DLVO theory [107]. Structuring of water layers at surfaces may lead to additional short-range repulsive (hydration) forces between approaching particles, which may increase particle stability [118]. It has been reported that these forces may restabilise colloidal dispersions at electrolyte concentrations above the CCC [119].

The presence of adsorbed material on particle surfaces can modify surface properties and stability. The sorption of polyvalent cations can reduce the surface charge of (negatively charged) groundwater colloids, reducing their stability and even reversing their charge [e.g. 120]. There is extensive evidence from fresh waters, estuaries and oceans that the surface charge and colloidal stability of particles in natural (surface) waters are controlled by natural organic matter [121]. This has been attributed to the influence of sorbed humic substances on surface charge. Layers of natural organic macromolecules may also prevent particles approaching sufficiently closely to aggregate (steric stabilisation) [122]. Alternatively at low organic concentrations, macromolecules may sorb onto two separate particles and cause them to flocculate (this is known as bridging flocculation) [123].

Silica, commonly found as a component of groundwater colloid populations (see section 5.2.4), displays a particularly complex variation in aggregation behaviour, which appears to depend on particle size, pH, counter-ion type and surface treatment history. In particular, small particles of amorphous silica are found to show anomalously high stability that cannot be accounted for by the classical Smoluchowski [112] or DLVO theories [124]. The presence of a gel-like layer of protruding polysilicic acid groups at silica surfaces appears to provide at least a partial explanation [125] for this anomalous stability behaviour and other unusual surface properties of silica. Studies of silica aggregation will be discussed in more detail in section 7.3.1

Particle aggregation is not necessarily an irreversible process. In many cases particles can be disaggregated (or peptised) if the electrolyte concentration is decreased from a value above to one below the CCC, or by a change in pH or temperature that causes a shift in the CCC, or by the addition of excess polyvalent counter-ions that are adsorbed and cause charge-reversal [100].

In practice, the findings of colloid science outlined above mean that although there is a qualitative understanding of inorganic colloid stability behaviour (and a semi-quantitative understanding in terms of CCC values), coagulation rates for natural colloid populations in deep groundwaters cannot be estimated *a priori* but must be measured. Thus, to understand the stability behaviour in the groundwaters at any candidate site for a GDF, there is a need to characterise the stability behaviour of colloids that are representative of the natural groundwater population, and possibly of mobile near-field derived colloids, under the range of groundwater chemical compositions representative of the site.

(b) Organic colloidal stabiliy

Organic macromolecules are stabilised in solution by a combination of electrostatic and solvation forces. Even at their point of zero charge, organic macromolecules may exhibit stability due to strong interactions with the solvent. However, organic colloids may be precipitated by high concentrations of electrolytes. This salting-out effect is due to dehydration of the macromolecule by competition for its water of hydration by the added salts. Ions that more strongly hydrate are more effective as salting-out agents (i.e. $Mg^{2+} > Ca^{2+} > Li^{+} > Na^{+} > K^{+}$) [100].

3.3 Colloid mobilisation

As discussed above, it has been argued that the major source of colloids dispersed in groundwater is the mobilisation of existing colloid-sized mineral promoted by perturbations of the chemical and physical conditions of the groundwater system [93]. The process of colloid mobilisation has been studied in the context of shallow groundwaters that are susceptible to periodic perturbations of local chemical conditions, e.g. due to seasonal variations or due to infiltration of rain water [e.g. 126, 127]. The processes of colloidal fines release, plugging and permeability reduction are also of key technological importance in the oil industry in relation to formation damage during water-flooding operations for secondary oil recovery [e.g. 128].

Colloid release and mobilisation in natural porous media have been discussed in the reviews by Ryan and Elimelech [93], Kretschmar *et al.* [129] and more recently by Sen and Khilar [130]. Bergendahl and Grasso [131] have compiled the findings of a selection of particle release experiments in natural and model systems under different chemical and physical conditions. Particle release from collector surfaces has been studied extensively in the field of colloid science to further the understanding of interaction forces between surfaces (see for example the review by Kallay *et al*. [132]).

Colloid mobilisation involves two steps: first, detachment of colloid particles from the matrix by diffusional transport across an energy barrier and second, diffusion of the particles through the stationary water film, referred to as the diffusion boundary layer (DBL), that separates the matrix surface from the bulk liquid [129]. The thickness of the DBL depends on physical factors such as flow velocity, geometry of the flow field and fluid viscosity [133]. In general, it is considered that the dimensions of the DBL are larger than colloidal dimensions and that only for larger particles and high flow velocities (leading to very thin DBLs) are hydrodynamic drag and shear forces able to induce colloid particle mobilisation. For this reason a number of authors have suggested that hydrodynamic forces are unimportant for inducing particle release at flow velocities relevant to natural systems [e.g. 129, 133, 140]. However, this view is questionable for confined flow in fractured and porous media. Recent direct observations of particle deposition have identified the role of hydrodynamic forces in deposition and release behaviour in porous media (see section 3.5.3(c)). In addition, even if the DBL is larger than particle dimensions, this does not mean that particle release rates will be independent of flow velocity because flow velocity also influences the thickness of the DBL, as outlined below.

Numerous experimental studies have demonstrated that colloidal particles can be released from columns of soils or sands, sandstone cores or from model collector surfaces by a change in solution composition that results in a decrease in ionic strength [e.g. 134] and/or for certain colloid types (e.g. iron oxides), a change in pH away from a value close to the PZC [e.g. 133]. In particular, colloids are found to be more readily mobilised by lower ionic strength solutions containing monovalent rather than divalent counter-ions [e.g. 127, 134]. In common with the finding of a CCC for particle aggregation, a critical salt concentration or CSC or critical total ionic strength, CTIS, for mixed salts, has been proposed for rapid particle release [130]. Reducing the electrolyte concentration or ionic strength below this value is found to induce rapid release. Examples of CSCs for simple electrolyte systems are presented in Table 3.4.

The release of a colloidal particle attached to a surface is controlled by the same particle-surface interaction forces that control colloid stability, namely short-range attractive van der Waals forces, longer-range electrostatic forces, a very short-range Born repulsion force and short-range repulsive structural or hydration forces. Therefore, particle release is also understood qualitatively in the framework of the DLVO theory of colloid stability outlined in section 3.2.2. In common with the understanding of the CCC predicted by DLVO theory, the CSC is understood as being the concentration at which both the total interaction energy and the net force acting between a particle and surface of like surface charge are zero such that the particle is neither adhering to the matrix surface or immobilised by the presence of an energy barrier. If colloid and surface are of opposite charge, changes in ionic strength will have no effect on particle mobilisation, however. In this case, particle release may only be induced by changes in pH or the addition of polyvalent additives that lead to charge neutralisation or reversal of either the particle or medium surfaces.

Calculation of particle release rates from surfaces *a priori*, is very difficult due to a lack of understanding of the forces that arise at very short-range distances (i.e. less than 1 nm), which govern particle-surface interactions. At these small separations the solution phase can no longer be viewed as a continuum and intermolecular forces come into play. Nevertheless a range of theoretical treatments have been proposed. The interested reader is referred to the review by Kallay *et al*. for further information [132]

In the absence of an energy barrier to particle release, the rate of detachment from the surface is fast and diffusional transport through the DBL becomes the rate limiting step. The overall release rate, k_r, is then expected to be high and increase with increasing flow velocity, U, with $k_r \propto U^{2/3}$ [129].

Under conditions where there is a deep primary minimum and a barrier to release, the overall release rate will be slow and the rate of colloid detachment from the surface is expected to be the rate limiting step. Under these circumstances theoretical studies suggest that the colloid release process can be described by a first order rate law [e.g. 135]:

$$\frac{\partial S}{\partial t} = -k_r S(t)\,, \tag{3.7}$$

where S is the amount of mobilisable colloid attached to matrix surfaces.

However, non-exponential release behaviour has been observed commonly in studies of natural porous media (i.e. a reduction in k_r with time), which has been attributed to a distribution of colloidal particle populations and heterogeneities of the natural system [127].

Table 3.4 Examples of critical salt concentrations for particle release measured in experimental systems with simple electrolyte solutions (updated from [130]).

Reference	Porous Medium	Salt	CSC (mol dm^{-3})	pH
Quirk and Schofield [136]	Packed bed of soil. Clay content – 19% of which kaolin – 40% and Illite – 40%	NaCl KCl $MgCl_2$ $CaCl_2$	0.25 0.067 0.001 0.0003	5.2 5.2 5.4 5.4
Rowel *et al*. [137]	Packed bed of soil. Clay content – 22% of which kaolin – 10-15%, illite – 75-80% plus montmorillonite	NaCl	0.1	Not reported
Hardcastle and Mitchell [138]	Bed of compacted soil. Clay content – 15% of which illite – 100%	NaCl	0.05	Not reported
Kolakowski and Matijevic [139]	Packed bed of glass beads with deposited 280 nm chromium hydroxide particles	$NaNO_3$ $Ca(NO_3)_2$ $Co(dipyr)_3(ClO_4)_3$	0.2 0.0001 0.00001	11.5
Khilar and Fogler [140]	Berea sandstone Clay content – 8% of which kaolin – 88% and Illite – 12% Temperature -= 303K	NaCl LiCl KCl NH_4Cl CsCl $CaCl_2$	0.07 ± 0.002 0.068 ± 0.002 0.044 ± 0.003 0.013 ± 0.005 0.006 ± 0.002 <0.0001	~7
Kia *et al*. [141]	Berea sandstone as per Khilar and Fogler [140]	NaCl	0.03 to 0.004	8.5 to 9.5

Although hydrodynamically induced released is not always regarded as important for colloidal particles in groundwater systems, some authors have suggested that hydrodynamic effects may be more important in fractured media [127]; hydrodynamic effects may be important also during groundwater sampling and in laboratory or field experiments where the flow rates applied may be significantly higher than in natural systems.

Hydrodynamically-induced release (i.e. erosion) and transport of colloids has been studied, principally in the fields of soil science and sedimentology. Three types of forces are recognised that can act to mobilise a particle from a surface as a result of a physical perturbation:

- A lift force, due to the unsteady nature of the viscous layer in the turbulent boundary layer (turbulent flow is not expected in deep groundwater systems except under conditions of excessive groundwater pumping);
- A hydrodynamic force along the surface, which may cause the particle to slide; and
- A torque from the gradient in fluid velocity in the vicinity of the surface, which may cause the particle to roll along the surface.

Sen and Khilar [130] note that "*it has been observed that fines are released only beyond a certain threshold parameter…*", which in the case of hydrodynamically-induced release may be a critical shear stress or a critical flow velocity [140].

Studies by Arulandan *et al*. [142] found that the critical shear stress for the erosion of soil mass depends not only on the nature of the fine particles but also on the ionic strength, composition, pH and temperature of the flowing liquid phase, the same parameters that influence the CSC. Nevertheless, it was noted recently that: "*The influences of various parameters relating to the pore surfaces, fine particles, and permeating liquid on the magnitude of "critical shear stress" have not been systematically studied*" [130].

Arguably, such erosive production of colloids is of little relevance to the environment of a GDF (although this may not be the case for those at shallow depths or in relatively permeable host rocks such as the LLWR facility near Drigg in the UK or the Rokkasho L1 facility in Japan), but the process has to be kept in mind when examining groundwater colloid data due to some of the experimental methods employed (see section 4.2 below). The potential erosion of bentonite colloids from the backfill and buffer has already been highlighted as an example where colloid mobilisation may be important. This process has been under examination in the CRR (colloid and radionuclide retardation) and CFM (colloid formation and migration) experiments in the Grimsel Test Site in Switzerland (see [48,143] for details) and the Colloid Project in the Aspö URL in Sweden [144]. This will be further discussed in section 6.4.3.

3.4 Colloid transport

3.4.1 Advection and dispersion

Colloidal particles entrained in groundwater will be advected with the groundwater flow and will be subjected to processes of hydrodynamic dispersion similar to those that affect the water. However, it is frequently observed that colloidal particle transport is accelerated with respect to solute or water flow [145]. This process, which is referred to as hydrodynamic chromatography, is a size exclusion effect [146]. The velocity of water through a flowing feature (fracture or pore) has a velocity profile with zero velocity at the rock surface and a maximum velocity at the centre of the pore. Owing to its size, a colloid particle will be excluded from the near-surface volume and the slowest moving streamlines of the water velocity profile. Therefore, the colloids will have a mean velocity greater than that of the water, although the effect is usually relatively small; the ratio of colloid velocity to water velocity in a single pore or fracture is typically between 1 and 1.4 and usually not greater than 1.1 [146]. It should be noted that this factor is small in the context of other uncertainties considered in performance assessments.

The hydrodynamic dispersion of colloids may be different from that of water if the groundwater flow paths of water and colloid are different [147]. Grindrod [148,149] has argued that the dispersion of colloids that are excluded from slower moving steamlines of groundwater flow and from non-flowing porosity, due to size exclusion, will be less than the dispersion of tracers that may access a larger fluid volume.

3.4.2 Diffusion

Owing to their small size, colloidal particles are subject to Brownian motion and it is because colloidal particles diffuse sufficiently fast to overcome gravitational settling that stable dispersions may be formed in water. The free water diffusion coefficient, D, for a colloidal particle is inversely proportional to the particle size:

$$D = \frac{kT}{6\pi\eta r_{\mathrm{h}}}, \tag{3.8}$$

where η is the water viscosity and r_{h} the hydrodynamic radius of the particle.

Not all the porosity of a groundwater system will form part of the flowing porosity; some pores will contain stagnant or immobile water (these include dead end pores and stagnant regions of larger pores). Colloidal particles will diffuse into these stagnant regions of the water volume provided that they are not excluded on the basis of size or charge.

The diffusion of dissolved solutes into the accessible rock matrix porosity adjacent to fractues, a process known as rock matrix diffusion (or RMD), and potential sorption to matrix surfaces therein, provides an important retardation mechanism for solute transport in fractured rocks [12]. Therefore, the association of radionuclides with colloids that are excluded from the matrix porosity, provides a mechanism for accelerated radionuclide transport over longer distances in fractured systems.

Owing to the inverse relationship between particle size and the diffusion coefficient, where colloids can access stagnant porosity, the rate of diffusional transport for the colloidal particles will be significantly lower than for solutes.

3.4.3 Flotation

Flotation involves the adsorption of particles to the surface of gas bubbles. It is recognised that hydrogen and other gases may be generated within a GDF as a result of processes such as corrosion of metals or microbial activity [150]. Studies have shown that colloidal clay particles may attach strongly to gas bubbles and that their transport may be either accelerated or retarded compared to water flow depending upon bubble transport [151]. However, there is little information available concerning the transport of colloids by flotation in geological systems and further discussion is beyond the scope of this report.

3.4.4 Sedimentation

Sedimentation is usually considered to be of secondary importance for particles of colloidal size in a stable dispersion, and is frequently overlooked in the treatment of colloid transport processes. Nevertheless, all particles dispersed in water will be subject to gravitational forces with a sedimentation rate characterised by a sedimentation coefficient, s, such that the terminal velocity, v, is:

$$v = s \cdot g, \tag{3.9}$$

where g is the local acceleration due to gravity. For spherical particles, s is proportional to the square of the particle radius:

$$s = \frac{2(\rho - \rho_o)r^2}{9\eta}, \qquad (3.10)$$

where ρ is the density of the colloidal phase and ρ_o is the density of the solution. Alternative forms of equation 3.10 are available for oblate and prolate ellipsoids of revolution (after [152]).

Under stagnant conditions, a concentration gradient of colloids may be established in a water column as a result of equilibrium between diffusion and sedimentation – sedimentation equilibrium conditions[7] [153]. Particles of large size and mass will tend to sediment more and diffuse less than smaller particles, which may result in partial separation of a particle size distribution through the water column.

Sedimentation of mineral particles becomes particularly important under conditions that favour particle aggregation (or growth) when particles may grow to a size and mass that can no longer remain in dispersion and will deposit from the groundwater. Thus, aggregation and sedimentation may act as a retardation mechanism for colloids transported through a porous medium.

3.5 Colloid capture and retardation

3.5.1 Mechanisms of particle capture

The principle mechanism of colloid retardation will be particle capture by the rock surfaces. As a particle is advected with groundwater flow, four mechanisms of particle capture can be identified, as illustrated in Figure 3.2 and outlined in the sections below.

(a) Surface filtration

Surface filtration refers to filtration that occurs at the surface of a porous medium where particles are too large to enter the medium porosity, leading to the build up of a surface filter-cake. In this case, colloidal particles are excluded from the flowing porosity in a porous medium.

Surface filtration processes may operate in the geosphere at the interface between rock layers that differ in their porosity, for example at the interface between a fractured rock and a porous rock, where the flow regime changes from fracture flow to matrix flow. Particles that may have been advected through a fracture may be excluded from the porous rock due to their size, leading to the formation of a surface or interfacial filter-cake at the rock boundary.

(b) Straining filtration

Straining filtration refers to filtration that occurs within the rock porosity, where particles are small enough to migrate into the porosity but may be too large to pass through all the pore throats (or constrictions). Straining may operate within a porous matrix or at constrictions in a fracture. Particles that are too large to pass through a pore throat between grains may become trapped. The trapped particles may restrict the pore throat size further. Smaller particles may be captured by the bridging particles [154]. This can lead to the formation of an internal filter-cake, pore blockage and permeability reduction of the porous medium.

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[7] The same balance of gravitational forces and diffusion is responsible for the distribution of air in the Earth's atmosphere as a function of altitude; these processes form the basis for the sedimentation equilibrium ultracentrifugation technique for the molecular weight determination of biological macromolecules [153].

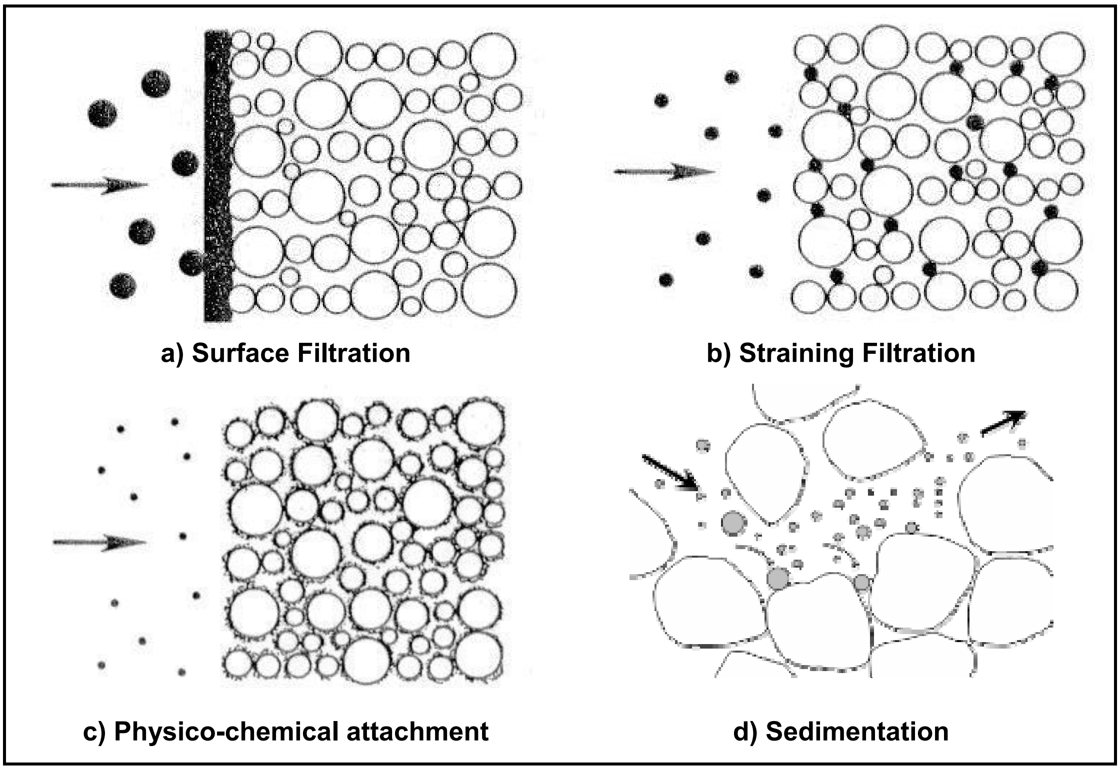

Figure 3.2 Mechanisms of colloid capture by the rock in a porous medium; notice the particle size dependence and the differences in deposit morphologies (after [155])

Mobilisation of the fine particle (clay-sized) fraction and subsequent pore blockage due to straining is now recognised as the process underlying the water sensitivity of sandstones, whereby replacement of the original saline water with fresh water can lead to severe permeability reductions known as formation damage. In general, an internal filter cake can only be displaced and permeability restored by a reversal in direction of flow through the porous medium with an ionic strength above the critical salt concentration (CSC, see section 3.3) for the colloid-matrix system that will prevent remobilisation of the filtered particles [140].

(c) Physico-chemical attachment

Particles that are sufficiently small to migrate through a porous matrix or fracture may be deposited (sorbed) onto the surface as a result of net attractive physico-chemical interactions with a surface site. This can either lead to the formation of a surface monolayer of particles or to particle multilayers, depending on the magnitude of particle-particle interactions [156]. For particles of colloidal size, particle mobility is dominated by physico-chemical interactions with the rock matrix [20, 155].

(d) Gravitational settling

As noted in section 3.4.4, sedimentation may be an important retardation mechanism under conditions that favour particle aggregation (or growth), depending on the size, density and shape of the aggregates formed. In general, mineral particles greater than 1 μm in size are not expected to remain in dispersion due to settling under gravity.

3.5.2 Particle mobility in porous systems

Table 3.5 outlines the ranges of the ratio of the size of particles to pore constrictions under which each particle capture mechanism outlined above may operate.

Owing to filtration and sedimentation effects [155], particles of micron-sized dimensions are not anticipated to be mobile in deep groundwaters in low-permeability rocks under natural flow rates. It is particles of colloidal dimensions that may form stable dispersions and may be mobile. However, the smaller the particle size, the faster the particles will diffuse in the groundwater and thus the more frequently they will collide with each other and with the pore or fracture wall, leading to potential attachment. Thus, smaller colloidal particles are expected to be less stable and less mobile than larger particles in a groundwater system. Overall, the combined effects of particle diffusion and sedimentation lead to the prediction of a maximum in colloid stability and mobility at an intermediate particle size [155]. It has been suggested by Degueldre that particles with a size of about 100 nm are likely to be the most stable and mobile in groundwater systems [80].

Table 3.5 Dependence of particle capture mechanism and resultant pore blocking on the ratio of particle size d_c to the size of pore constrictions, d_p (after [130])

d_c/d_p	Occurrence
≥1	Surface cake formation and pore blocking due to surface filtration (size exclusion)
0.1 to 0.6	Straining filtration may lead to pore blocking due to multi particle bridging
0.04 – 0.10	Surface deposit with potential for pore blocking due to multi-layer deposits and straining of larger particles
0.01 – 0.04	Surface deposition

The potential mobility of colloidal particles through a rock is ultimately controlled by the aperture dimensions of the flow paths through the rock porosity. In fractured rock, where the dimensions of flowing fractures may typically be between a few microns to hundreds of microns, the predominant mechanism for colloid particle capture will be physico-chemical attachment and mobility may be controlled by the particle-rock interactions. Straining filtration could occur at a fracture constriction and, if there is significant flow into an adjacent porous matrix, then surface filtration may occur at the interface. For transport within a porous hard rock, such as sandstone, both straining filtration and surface attachment may be important retention mechanisms.

In the case of low-permeability sedimentary rocks, such as mudrocks, and bentonite buffer materials, which have very fine-scale porosity, the principal mechanism of solute transport is by diffusion rather than by groundwater flow, and colloids may be largely excluded due to their size and charge. In addition, the inverse relationship between particle size and diffusion coefficient (Equation (3.8)) means that for colloidal particles, diffusional transport would be significantly slower than for solutes. For this reason, intact bentonite buffer is generally considered to provide a barrier to colloid transport either from the groundwater into the near field or *vice verse*.

Given that physico-chemical attachment is the dominant mechanism for colloid capture in deep groundwater systems in hard rocks, the current understanding of this process will be discussed in the following section.

3.5.3 Physico-chemical attachment to rock surfaces

(a) Deposition onto clean surfaces

The theoretical basis for the qualitative understanding colloid-surface interactions and the rate of particle attachment to surfaces is the DLVO theory of colloid stability discussed in section 3.2.2 above. In this case, DLVO theory considers the ideal case of Brownian collisions between spherical colloid particles and a smooth collector surface. In common with particle coagulation, the rate of particle deposition is predicted to be dependent on ionic strength, which controls the strength of repulsive electrostatic interactions under conditions where particle and surface have like surface charge, and the pH, which controls the surface potential of particle and collector surfaces.

In common with particle coagulation, the fraction of particle-surface collisions resulting in attachment may be described by a collision efficiency, α, defined as the ratio of a dimensionless capture rate, to a dimensionless transport rate, η_T, of particles to the collector surface. Expressions for η_T, have been derived for a variety of different collector geometries (including beds of spherical particles and parallel-walled channels) under a variety of flow conditions from mechanistic simulations of colloid transport (see the review by Adamczyk *et al*. [157] and references therein). These so-called correlation equations capture the mechanistic results in phenomenological expressions that allow prediction of colloid transport in the absence of electrostatic repulsion. An approximate analytical solution for α for particle collection by porous media in the presence of electrostatic repulsive forces (based on DLVO theory and taking account of electrostatic and van der Waals interactions) was derived by Spielman and Friedlander [158].

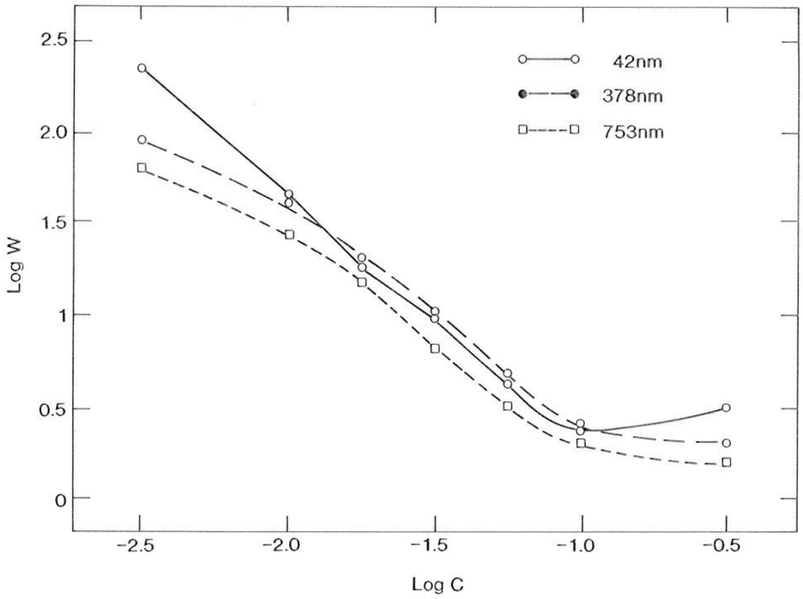

Figure 3.3 Stability curves for the deposition of latex particles of different particle size onto a packed bed of glass beads (from [107])

The interactions of particles with surfaces have been studied extensively as a function of ionic strength for a variety of collector geometries to understand particle deposition behaviour under both so-called "favourable" (i.e. α close to one) and unfavourable (i.e. $\alpha < 1$) attachment conditions [e.g. 157, 159, 160]. Experimental data on particle collection by clean media under conditions of high ionic strength, when electrostatic interactions are effectively screened, give deposition rates that agree with predictions to within a factor of two [161,162]. However, a consistent finding of experiments (in all geometries) has been that while observed deposition rates as a function of ionic strength are qualitatively in agreement with theoretical predictions, measured initial deposition rates are always orders of magnitude greater than those predicted [161, 163, 164, 165]. In fact, deposition onto clean media may be observed even under conditions where no deposition at all is predicted [161]. Furthermore, measured deposition rates under unfavourable conditions show little variation with particle size dependence, contrary to the predictions of DLVO theory [164, 165]. This is illustrated in Figure 3.3.

Possible reasons for the discrepancies between predicted and observed initial deposition rates were reviewed by Swanton [107] in the mid-1990s and include the non-smooth, non-uniform and chemically heterogeneous nature of surfaces, and the presence of additional forces, which may be repulsive or attractive, acting at short range, that arise from interactions between surfaces and water. Only it the last five years or so, has a clearer understanding of the processes involved emerged (and this will be discussed later in section 3.5.3(c)).

During the 1990s, one probable cause of higher than expected initial deposition rates in column experiments using packed beds of synthetic or cleaned natural materials, was identified to be the presence of chemical heterogeneities or impurities that provide patches on the surface with differing surface charge, that are locally favourable to deposition [107, 166]. These patches are envisaged as macroscopic features such as iron oxide coatings, different mineral phases or crystal planes exposed in natural materials. A patchwise charge heterogeneity model was developed by Elimelech and co-workers [167] that has been successfully applied to predict model deposition behaviour of silica colloids in packed beds containing varying proportions of quartz sand and sand coated with iron oxyhydroxide, where the fraction of the total surface area favourable to deposition was controlled directly [166].

Essentially this type of model treats deposition onto a portion of the available medium surface as being favourable. The advantage of such an approach is that deposition under favourable conditions is well understood, however, its predictive capacity relies on knowledge of the mineralogy of the medium and particularly of the medium surfaces. As Elimelech and his team found, for less well-defined systems, even when compositional information is available, this is not straightforward.

The model [167] was applied to fit experimental data for deposition onto glass beads that contained small amounts of Al and Fe oxides in their bulk composition [168]. Although the data could be successfully fitted with the model, the minimum percentage of favourable surface sites obtained (1.1%) was significantly higher than the percentage of Al_2O_3 and Fe_2O_3 in the glass (0.3% on a molar basis). It was concluded that "…*charge heterogeneities other than those arising from bulk chemical impurities are present on the collector surfaces*" [167].

(b) Surface blocking and filter ripening effects

The discussion above has focused on the initial stages of colloid deposition onto a clean surface. However, as a significant amount of colloidal particles becomes attached to the surface the rate of particle deposition can either decrease, stay the same or increase, depending on the magnitude and sign of the colloid-surface and colloid-colloid interactions. When colloid aggregation is unfavourable due to interparticle repulsion, the rate of colloid attachment to the matrix will decrease with time due to blocking of surface sites by already deposited particles [169]. Such deposition may eventually stop once a monolayer of particles has been formed on the surface. This type of deposition behaviour is associated with transport experiments where a constant colloid concentration is applied, colloid particle breakthrough is delayed relative to water flow but the effluent colloid concentration subsequently rises until it reaches the input concentration indicating that colloid deposition has stopped [e.g. 170].

Under conditions which are more favourable to colloid aggregation, the overall deposition rate may increase with time giving rise to a multi-layer deposit [156]. This phenomenon, called *filter* *ripening*, may arise when the collision efficiency between the colloidal particles is higher than between the colloids and the matrix.

Various models have been used to model deposition behaviour when blocking is important. In these models the colloid deposition rate, k_d becomes a function of the fractional surface coverage, θ:

$$k_d = k_{d,o} B(\theta), \tag{3.11}$$

where $B(\theta)$ is the so-called *dynamic blocking function* and $k_{d,o}$ is the initial deposition rate.

The $B(\theta)$ decreases from a value of one initially to zero at the maximum attainable surface coverage θ_{max}. The value of θ_{max} has been found to vary with ionic strength with the excluded area associated with deposited particles increasing, and θ_{max} decreasing, as the thickness of the diffuse part of the EDL increases at lower ionic strength giving rise to longer range electrostatic repulsive forces.

Expressions that have been applied to model $B(\theta)$ include the Langmuir adsorption model and a more sophisticated random sequential adsorption (RSA) model [166, 171]. The latter predicts more pronounced blocking effects than the Langmuir model and has proved to be superior in fitting experimental deposition results [166, 171]. A review by Talbot and co-workers [172] discusses how the RSA model may be applied more generally to treat experimental features including: non-spherical particles; polydisperse particle populations; desorption and multi-layer formation.

The application of these concepts to predicting colloid behaviour in groundwater systems is far from straightforward, but they nevertheless provide insight into some of the processes that may occur. The effects of blocking and filter ripening can be manifested in laboratory and field experiments and therefore an understanding of these concepts is important for experimental interpretation and modelling.

While the models described above have been successfully applied to predict colloid deposition behaviour in carefully designed experiments, the use of idealised packings and uniform geometries (i.e. mono-sized spherical colloid particles and bed materials) is very far for the complexity of real systems. A very significant amount of information is required concerning the experimental system to be able to make predictions, which is unlikely ever to be obtainable for natural systems. Thus quantitative prediction of particle deposition in real systems, *a priori*, in particular under unfavourable attachment conditions using this approach does not appear to be a realistic goal.

For this reason, most modelling of colloid transport in real systems has adopted a simpler approach [e.g. 50], in which colloid attachment and detachment processes are treated with empirical models, which may be parameterised by fitting to experimental data obtained under relevant ranges of conditions. This type of approach will be discussed in more detail in section 10.4.

It is possible, however, that the modelling of colloid deposition is on the verge of a major advance….

(c) New observations of colloid filtration behaviour

Recently, major new insights into the mechanisms of colloid retention in porous media under unfavourable conditions have been made through a combination of careful measurement of deposition behaviour onto media with different geometries and direct observation of particle deposition in optically transparent systems. These developments have been reviewed and are summarised by Johnson *et al*. [173]. In particular, the deposition and elution behaviour of colloids has been found to be dependent on the geometry of the system. Thus, deposition rates in packed beds have been found to be much greater than onto unbounded surfaces in impinging jet systems[8] with identical surface characteristics by factors of between 2 and 50. In addition, the colloids captured in the porous media can be eluted with a lower ionic strength solution, whereas release of equivalently loaded impinging jet systems is negligible with decreases in ionic strength or increases in fluid velocity.

Recent observations have implicated wedging in grain to grain contacts and retention in secondary minima at flow stagnation points as the principle mechanisms of colloid retention in the presence of an energy barrier between colloids and surfaces. The retention process is conceptualised as colloids translating across the collector surface until they become wedged within grain to grain contacts or retained via secondary minima (without attachment) in stagnant flow zones where the balance of fluid drag, colloid interaction, diffusion and gravitational forces allow retention. Thus it is the geometry at the pore scale, giving rise to grain-to-grain contacts and zones of relatively low fluid drag that governs colloid deposition behaviour under unfavourable attachment conditions. This contrasts with the approach based on the calculation of the attachment efficiency, α, where (originally) it had been assumed that deposition could occur at any position across the collector surface when collisions are sufficiently energetic to overcome the energy barrier to deposition in the primary minimum.

This new insight into colloid deposition behaviour is also applicable to deposition in fractures. However, suitable experimental studies to test and develop this new understanding in simulated fracture models, for example, have yet to be published.

This new understanding of retention behaviour is considered to be amenable to trajectory analysis by particle tracking methods and offers the potential for the development of correlation equations to describe particle deposition under unfavourable conditions, similar to those developed for modelling deposition under favourable conditions. This is expected to be an area of significant research activity over the next 5-10 years.

3.6 Colloid loss

As noted in subsection 3.2, inorganic colloidal particles are thermodynamically metastable with respect to bulk crystalline phases and, in general, will dissolve more rapidly than bulk phases [100,101], the rate of dissolution decreasing with increasing particle size. Therefore, over long times, colloidal particles may be lost due to dissolution. The lifetime of a colloidal particle may be determined by the extent of any chemical disequilibrium of the groundwater system and the (slow) rate of dissolution.

Colloids that are deposited onto a fracture surface may effectively be lost if they become incorporated into the surface as a result of interfacial dissolution/recrystallisation reactions or the deposition of secondary coatings (e.g. calcite or iron oxides).

The long-term fate of humic substances in the environment is not well understood [85].

3.7 Radionuclide-colloid interactions

A key aspect of colloid behaviour that will control whether or not colloid-facilitated transport is significant as a migration process for radionuclides in the geosphere is the interaction of colloids

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[8] In an impinging jet system the fluid is directed normal to a flat surface; on impinging the surface the flow spreads out radially across it.

with radionuclides. In the context of the geosphere, natural colloid populations may potentially sorb radioelements that migrate from the near field as solutes in the groundwater. Thus, the role of natural colloids as potential carriers is of principal interest. Potentially, radionuclide carrier and intrinsic colloids may be released from the near field, and therefore their stability and mobility under geosphere conditions needs to be considered.

Owing to the low concentrations of radioelements migrating from the near field, secondary generation of intrinsic radioelement colloids is not expected to occur in the far field. The only mechanism by which intrinsic colloid generation in the far field can be envisaged is through longer-term precipitation and mineralisation processes, for example, where deposits of radioelements build up on rock surfaces, become mineralised and subsequently the rock surfaces may be weathered to release mineral colloids. This type of process is only likely to be significant for radioelements present in bulk in a disposal facility, such as uranium.

Radionuclides may sorb onto the surfaces of inorganic colloidal particles by the same processes of surface complexation and/or ion exchange by which they may sorb onto the surfaces of the host rock [13, 14, 174]. Radionuclides may also complex to natural organic molecules that are present as colloids or attached to inorganic colloidal particles. Owing to the higher surface area to volume ratio of colloids compared to the rock, the specific sorption capacity of colloidal particles is expected to be higher than for the rock.

In general, radionuclides sorbed onto the surface of particles are anticipated to be in thermodynamic equilibrium with the solution phase. However, there are number of mechanisms, in addition to kinetic considerations, by which sorbed species can be removed from the sorption equilibrium so that sorption is effectively irreversible over a given timescale. Degueldre [80] identified the following:

(i) sorption followed by colloid aggregation (and particle fusion);

(ii) sorption followed by chemical masking (e.g. by coating);

(iii) sorption following by encrustation (i.e. crystallisation of new phases);

(iv) sorption into an internal site (e.g. clay interlayer).

Whether these processes should be regarded as irreversible over geological timescales (i.e. many thousands of years) that are typical of deep groundwater return times to surface is open to question. For example, radionuclides that may become incorporated into a surface (mineralisation) following sorption may be released at a later time due to mineral dissolution.

The nature of radionuclide-association of colloids and in particular the reversibility of these interactions and the timescales of desorption/release processes are key questions concerning the potential role of colloids in facilitating radionuclide transport from a GDF [49, 60, 95]. When there is fast exchange of radionuclides between dissolved species and sorbed species on both rock and colloid surfaces, a significant colloid population is required for radionuclide transport to be enhanced even for strongly sorbing radioelements [49, 56]. On the other hand, slow desorption kinetics or removal from thermodynamic equilibria of radionuclides sorbed to colloids over a period of time that is significant on timescales of groundwater migration in the geosphere (i.e. thousands of years) could provide a vector for accelerated transport at quite low colloid concentrations. This is also true for persistent intrinsic radioelement colloids that may migrate from the near field. In both cases, the long-term stability and mobility of the colloid population through the geosphere becomes a key determinant for the arising radiological risk.

It is important to note that, in the context of the safety of a GDF, the timescales of importance when considering the reversibility of radionuclide interactions with colloids are significantly longer than those accessible in laboratory experiments. Laboratory studies can give insight into the short-term reversibility of radionuclide-mineral interactions under a range of experimental conditions. However, processes working on longer timescales can only be investigated through the study of natural geochemical systems [175].

Studies of the radionuclide-colloid interactions are reviewed in Section 8 of this report.

4 Groundwater colloid sampling and characterisation

4.1 Introduction

The previous thematic colloids review [49] focused on the experience gained and techniques applied in the Nirex programme in the UK. This section will take a broader view, considering methodologies used across a range of national programmes where colloid populations in deep groundwater have been studied over the last 20 years (for shallower systems, see, for example [176, 177, 178]). In particular, limitations of the methods, the potential for artefacts and methods for mitigating these effects will be discussed. Work from the Finnish, German, Swedish, Swiss and US programmes (with emphasis on fractured host rocks) has been at the forefront of these developments. A number of important review articles that drew together the results from a range of studies were published in the 1990s [including: .80, 179, 180, 181, 182].

When evaluating far-field colloid populations at any site, it is necessary to measure the colloid concentration, particle size distribution, composition and morphology and ensure that the potential for artefact formation is fully understood. This may not be as simple as it sounds as some artefacts will be more significant at one site than at another, being dependent on a range of parameters such as the groundwater chemistry and the host rock lithology.

At certain sites (e.g. those of natural analogue studies – see section 9.5); information can also be provided on other areas of relevance such as the association of natural groundwater uranium or rare earth elements (REEs) with colloids. If sufficient material is available, it may also be possible to study surface charge/potential properties – all information of direct relevance to understanding the potential transport of radionuclides by far-field colloids.

In all the above cases, it is absolutely imperative to understand the hydrogeological and hydrochemical context of the colloid data – so adequate information on the groundwater chemistry, associated rock mineralogy, transport properties of the site, etc, is a prerequisite. As such, it is expected that colloid analysis is carried out as an integral part of a site characterisation, be it as a potential GDF site [e.g. 183] or as part of a natural analogue study [e.g. 46, 184]. In general, however, it is recommended that colloids are studied only after an adequate understanding of the site hydrochemistry and hydrogeology is available, otherwise much effort can be expended on analysing samples which are more than likely to be of low value due to artefacts.

4.1.1 Why is flow system information important?

Colloid transport is sensitive to the geometrical, hydrogeological, mineralogical and geochemical properties of a geological medium. In many rock types, water-conducting features provide the dominant pathways for radionuclide transport. These features may be structural or sedimentary and include joints, mineralised veins, complex shear zones, regional faults, sedimentary lenses and various forms of alluvial channels. As shown in Figure 4.1, advection and dispersion are usually the dominant transport processes in the flow systems of deep geological media, with retardation by matrix diffusion, filtration and physico-chemical attachment (colloid sorption).

The processes that dominate colloid transport often vary according to the flow system properties, which are typically heterogeneous over a range of spatial scales. Even if it is the transport of colloids over a scale of tens or hundreds of metres that is of interest to the long-term performance of a GDF, this does not necessarily mean that small scale structures and property variations can be neglected or "averaged over". Small-scale structures may, for example, provide relatively fast paths for advective transport, particularly if they are lined with minerals that prevent or limit colloid retardation by sorption and filtration. Alternatively, fracture infill material and altered zones adjacent to fractures may have porosities and mineralogical properties that favour colloid retardation (see also [48]).

In argillaceous sediments, the low hydraulic conductivity, lack of water-conducting features and immobility of colloids means that transport is dominated by diffusion of solutes, with retardation by sorption [16]. Coupled processes may also play a role where, for example, strong thermal gradients are present [185].

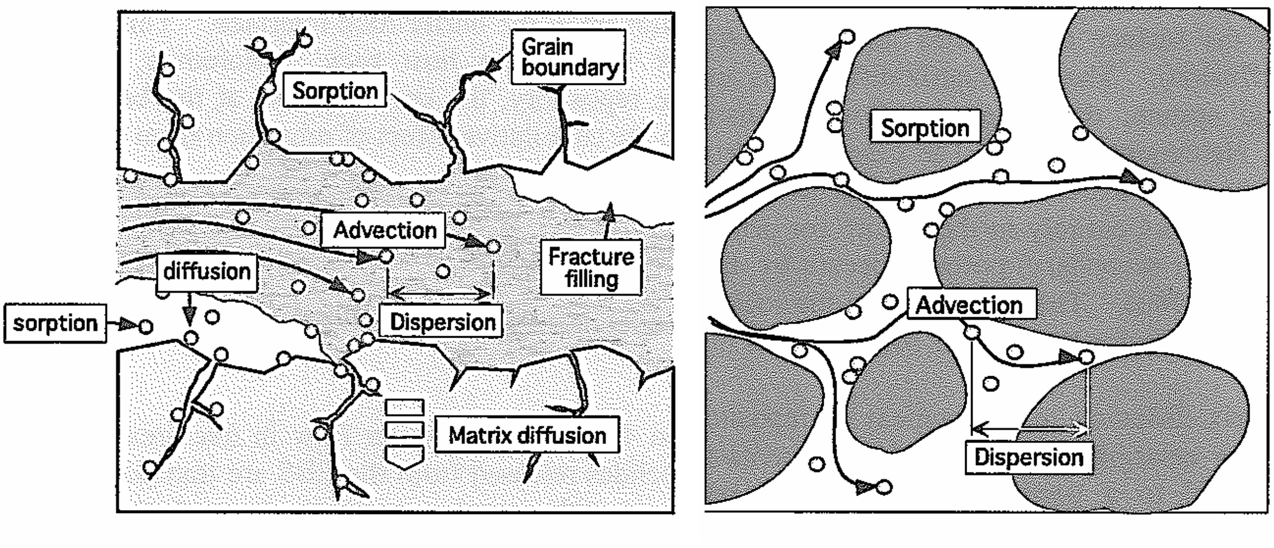

Figure 4.1 **Schematic illustration of transport processes in and around a flow system. Top, fractured rock, bottom, porous rock (from [186])**

4.2 Colloid sampling

Groundwater colloid sampling techniques have come a long way since the first experimental studies on colloids in the latter half of the 19th century when solutions were allowed to seep through sheets of parchment to assess particulate loads [64]. Nevertheless, colloid sampling is still a relatively simple affair, with colloids being separated from the solution and collected on some form of substrate for subsequent analysis.

In the field of radioactive waste disposal, understanding of far-field colloids is focused on the potential association of radionuclides released from a GDF with the natural colloids in the groundwater (note, as stated in [187], all waters contain colloids). Effort has consequently been expended on:

- assessing colloid stability
- studying colloid mobility (or transport properties in the groundwater) and the impact on their mobility by transient processes such as redox fronts

- measuring uptake of radionuclides on colloids – and the degree of reversibility of that uptake
- last, but perhaps most important, quantifying sampling (from the groundwater), storage (before analysis) and preparation (for analysis) induced artefacts, all of which can alter the original, *in situ*, properties of the groundwater colloids

This last point is crucial as, although detailed quality assurance (QA) criteria have been developed for bulk groundwater sampling [e.g. 188, 189 and discussions therein], nothing of comparable stringency yet exists for colloid sampling. Despite years of discussion [e.g. 183, 190, 191], only some general guidelines exist [e.g. 182, 192] which, while useful, offer few hard and fast rules. Historically, the constituent colloid separation steps can be broken down as:

- collection of bulk groundwater sample
- temporary sample storage on site
- transport of the sample to the laboratory
- colloid separation (e.g. for SEM analysis) or concentration (e.g. for PCS analysis) from the bulk groundwater

Collecting bulk groundwater samples from deep boreholes or URL (underground rock laboratory) tunnels potentially induces many forms of disturbance (see Table 4.1), all of which may produce a sample which is not representative of either the geological formation being studied or the sampling depth[9]. Traditionally (see references [193, 194] for a comprehensive description of standard well head practices), samples would be pumped from the sampling interval at depth, up to the surface and sub-samples would be taken at the well head. As noted in Table 4.1, this alone can induce significant changes to the original groundwater with, for example

- the pressure drop inducing de-gassing of the groundwater, so shifting existing pH and Eh conditions and inducing colloid precipitation
- gas seeping in through plastic sampling lines causing similar effects to the those above
- production of metal colloids from metal sampling lines
- colloid loss from attachment to the walls of the sampling lines.

Well head and tunnel conditions are also frequently less than pristine, although this has been addressed by utilising dedicated well head laboratories in shipping containers or purpose-built caravans [e.g.184, 195]. Arguably, more recent work [e.g. 196] has refined the methodologies used to sample groundwaters (and the associated colloids) from deep boreholes, for example using closed sampling systems which minimise atmospheric contamination both during and after filtration and maintaining downhole pressure and temperature conditions during well head sampling (see Figure 4.2, for example).

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[9] See [187] for a discussion on groundwater sample representivity.

Temporary storage on site is not always necessary, but when the boreholes are far from the analytical laboratories or when other downhole tests, for example, take priority, then the bulk water sample may have to be stored for hours to days on site. Clearly, as the bulk groundwater sample is no longer in the *in situ* environment, changes can occur which can impact the colloids [e.g. 197, 198, 199]. For example, unless stored in a high-integrity container, atmospheric gases

Table 4.1 Processes that may occur during deep groundwater sampling and which may influence the quality of hydrochemical data in general and colloid samples in particular - those of direct relevance to colloids are italicised in green [after 189]

Potential processes
Contamination of the groundwater by drilling fluids or additives and by the material of the drilling equipment: • *this will dilute/concentrate the groundwater solutes* • *drilling fluid (usually groundwater-based) will contain colloids* • *additives, such as bentonite, will change the major element chemistry and may add colloids themselves* • *metals from the drill bit and lines can change the perceived redox state* • *drilling fluid will contain oxygen that may induce redox gradients, potentially generating colloids*
Damage to the host rock by the physical and chemical process of drilling • *this can produce large colloid populations, for example, when weak rock is badly damaged by the drill bit. This can produce clay, silica, aluminium etc colloids*
Alteration of the *in situ* conditions during sampling • *by the introduction of contaminants such as oxygen (trapped in or on sampling equipment) which changes the in situ redox conditions. This can produce iron oxyhydroxide and sulphur colloids;* • *by degassing groundwater samples as they are brought to the surface due to pressure changes, so changing pH and Eh values. This can produce iron oxyhydroxide and calcite colloids;* • by pumping at too great a rate for the local groundwater 'reservoir' in the vicinity of the sampling point. This can induce draw-in of groundwater from further afield and mixing with the *in situ* groundwater to produce a sample which in non-characteristic of that horizon in the borehole. *It can also increase colloid populations due to erosion in surrounding fractures;* • *by pumping at too slow a rate, colloids can be produced by decompression during transport to the surface, etc.*
Introduction of surface microbes or additional nutrients • either will change the *in situ* microbial populations and, as a consequence, the redox state of the groundwater
Contamination during sample handling, transport and storage prior to analysis • *by the introduction of gases or other contaminants during well-head sampling and subsequent transport to off-site laboratories*

Physical and chemical changes induced during sample handling, transport and storage

- *changes in populations can arise during storage due to changes in temperature, agitation, interactions with container materials, etc. , e.g. particle adhesion to vessel walls, aggregation and sedimentation of particles, precipitation or dissolution of colloidal phases, microbial growth, change in the sample redox state, etc.*

will diffuse into the water, so changing the *in situ* Eh and pH conditions. The sample may also warm-up, so encouraging microbial growth which could induce coagulation (and potential sedimentation) of the colloids. The container walls are also unlike the surfaces of the rock fractures or pores and so may induce colloids to adhere to the walls.

Transport of samples to the laboratory. Some of the changes noted above may also occur during transportation, especially if the transport system is slow. In addition, although not examined directly, it seems likely that the agitation of the groundwater samples during transport may induce changes similar to those reported by [199] when examining laboratory agitation (by shaker table, stirrer etc), namely that orthokinetic coagulation[10] of the colloids may occur, so changing the measured colloid population and size distribution.

Over the last two decades of colloid study, numerous techniques for *colloid separation* have been developed, tested and improved (see, for example, the reviews [190, 191, 183]). In general, all methods look to separate the colloids from the groundwater with the minimum mechanical and chemical disturbance possible and then provide what is hoped to be an artefact-free sample to the analysts. Here, three representative methods of colloid separation which cross the spectrum of possibilities are briefly examined in Table 4.2.

Unfortunately, as noted in Table 4.2, each separation method can also induce artefacts in addition to those noted above. This only serves to magnify the problems with artefact formation when considering sampling the deep groundwaters of relevance to geological disposal (see discussion in [2]). It is also worth noting that the three methods examined here have produced differing estimates of colloid populations when sampling the same waters – a factor of 58 (colloid population assessed by direct filtration>inert filtration>ultracentrifugation) was noted by [192]. Unfortunately, because of differences in external factors (such as pumping rates) which are method-and organisation-dependent [cf. 189], it is not always possible to make a direct comparison between the different separation techniques [see also discussion in 192, 201].

In the three examples in Table 4.2, samples have to be collected in tunnels or from deep boreholes before handling. Although arguably less of a problem in tunnels, pumping samples up several hundred metres of sample line to the well head can still induce artefacts (as noted above). Ideally, this could be avoided by the use of a downhole system which would collect (i.e. separate) the colloids directly in the sampling interval. Downhole collection systems already exist for bulk groundwater samples [e.g. 194] as illustrated in Figure 4.2, but although much development work was carried out on systems for colloid separation in the Swedish, Swiss and UK programmes over the last decade, no downhole systems have been successfully deployed in the field. A downhole instrument, known as the the colloidal borescope [202], is effectively a downhole video monitor, which can observe colloids and particles in a borehole section in real time (see Figure 4.3). To date, it has only been utilised to measure flow velocities and directions [e.g. 203] and there is no indication that it has been employed to assess colloid populations *in situ*. Due to the commercial nature of the instrument, full technical specifications are not openly

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[10] Agitation increases the rate of coagulation of colloidal dispersions due to an increase in the particle flux and the frequency of particle collisions. The flux increases with the third power of the particle collision diameter. Thus, orthokinetic coagulation is of much greater importance for larger rather than smaller particles [200].

available (e.g. no data are currently available regarding limits of detection for the colloids (see comments in [204]), but there seems to be no fundamental reason why it could not be used in this rôle in the future.

Table 4.2 Examples of common groundwater colloid separation methods

Method [reference]	Short description	Advantages and disadvantages
Centrifugal deposition [e.g. 205]	Colloids deposited from a dispersion onto a carbon-coated copper grid using an ultracentrifuge. Particles above a certain minimum size (which is dependent on the centrifugal field, height of solution and duration of centrifugation) from a known volume of solution are deposited, essentially quantitatively, onto the activated top surface of the grid. In general, centrifugation conditions are selected so that all particles greater than about 15 nm are sedimented onto the carbon film.	Formation of salt particles from the original leachate solution on drying grid. Can be minimised by washing grids *in situ* in the centrifuge tubes using dilute electrolyte solution. Significant likelihood of colloid agglomeration (into larger particles) noted by [205]. Can be used on-site [e.g. 205], but requires sample handling which may perturb the original *in situ* conditions
Direct filtration [e.g. 37]. Filters can be coupled in series (in decreasing nominal pore size) or in parallel (also known as 'inert filtration' – see [205])	Directly filter solution through appropriate nominal pore size filters held in a range of different filter holders. The water is collected in a standard 50 ml (for example) capacity filtration cell, first being passed through a 1µm nominal pore size pre-filter (to remove any large particles). The cell can be evacuated either by the application of a vacuum to the cell or by gas overpressure.	Easy to set up as a closed system in the field (see, for example [46]) Repeated filter handling can easily cause sample contamination. In addition, the operator has to have enough experience to know when enough water has been filtered or a thick 'cake' of colloids can be produced, making examining individual colloid morphology, for example, difficult. Inert filtration avoids the build up of 'cake'.
Flow Field Flow Fractionation (FFFF) [e.g. 206]. Asymmetric FFFF (or AF4 as it is most commonly known) is being developed as the most promising of a whole range of FFF methods as it can separate (bio-)polymers, particles and colloids in the size range of 1 nm to 100 µm.	Separation occurs in a thin flow channel comparable to the separation column used in chromatography. Flow in the channel is laminar and a force is generated perpendicular to the flow – in AF4, this is a liquid cross flow. Colloids are separated in the laminar flow by the velocity gradient and are forced toward the lower membrane by the cross flow . The cross flow passes through the membrane while the colloids are bounced back into the laminar flow. Smaller colloids diffuse back into the channel further on and are caught in the faster parts of the laminar flow and so are eluted more rapidly than larger colloids.	Potential reaction of the colloids in the cross flow field. Not easily portable for well head and other site use. Many analytical methods can be effectively directly coupled to the sample stream [e.g. 207], so minimising potential sampling artefacts.

Recent advances in soil and atmospheric sciences do, however, hold some promise [e.g. 208]. Here, colloids are collected directly downhole onto Transmission Electron Microscope (TEM) grids and so minimise colloid separation artefacts. Although physical and chemical data can be obtained directly on the samples during subsequent laboratory analysis, information such as colloid populations will be absent (or at least difficult to justify statistically). Actually placing the TEM grids in the borehole sampling interval is unlikely to be simple, but this method offers the possibility of directly examining colloid samples separated *in situ* and brought to the surface in the systems developed for bulk groundwater samples (see Figure 4.2).

A similar scenario can be envisaged with Environmental Scanning Electron Microscopes (ESEM). Although this does not appear to have been utilised within geological disposal programmes to date, the size distribution, zeta potential, chemical composition, adsorption capacity and morphology of groundwater colloids have been studied before by this method (e.g. [209, 210] and Table 4.3). The advantage here is that the colloids do not need to be separated from the groundwater for analysis.

Regardless of the precise combination of groundwater sampling and colloid separation and analytical methods, it should be emphasised that it remains difficult to assess when is the ‘right time’ to sample a borehole for colloids. Generally, the drilling and hydrogeological, hydrochemical and geophysical testing associated with a new borehole will induce large colloid populations and it is necessary to wait months to years before truly representative samples can be collected. This can be assessed to a degree from the groundwater chemistry of the borehole interval to be sampled, but this is also far from foolproof. To be certain of the representivity of colloid samples, any deep borehole interval must be re-sampled repeatedly over several years, both for hydrochemical and colloid analysis, and an assessment made of the overall hydrochemical stability as well as the stability of the colloid population and size distribution.

For example, in the specific case of groundwaters from the fractured Fennoscandian Shield [192], it was recommended that the following steps be taken to minimise colloid separation artefacts:

- filtration of groundwaters should not be carried out under atmospheric conditions as the deep groundwater is almost certainly not in equilibrium with the atmosphere and changes in Eh and pH will induce colloid precipitation

- utilise ultrafiltration methods which contain several stages (e.g. decreasing filter nominal pore size) as this can increase both the amount of data collected on, for example, size fraction vs. colloid composition, and information on possible artefacts

- preferably avoid defining size fractions by means of cross-flow filtrations

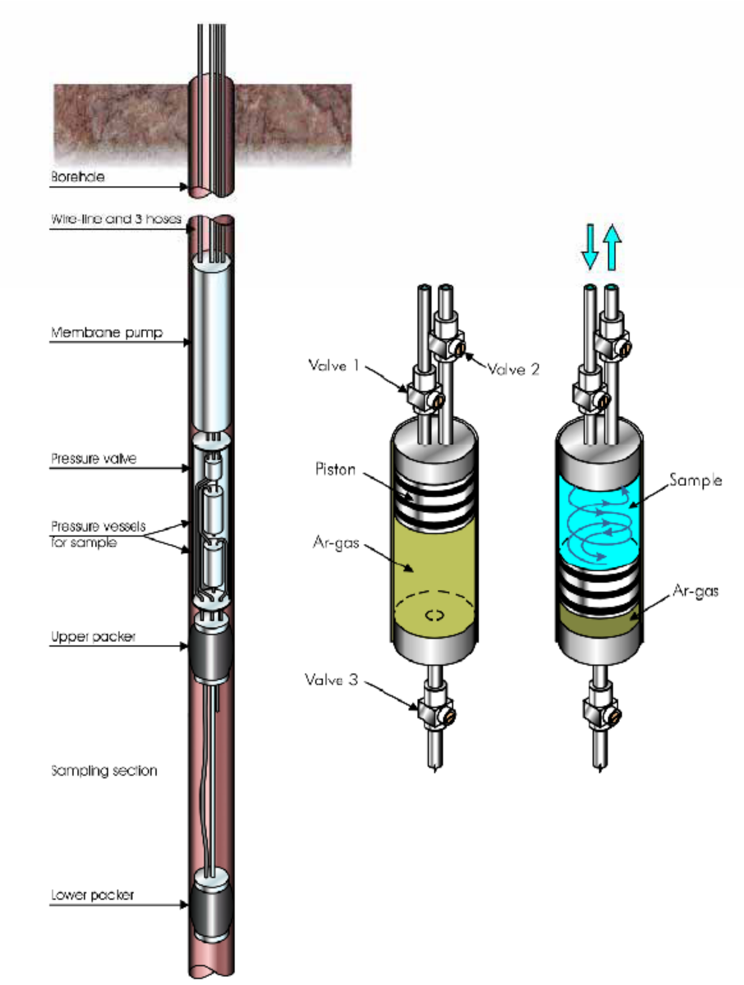

Figure 4.2 An example of a pressurised downhole sampling system – Posiva's PAVE unit [from 211]. The equipment consists of one or two inflatable rubber packers, a membrane pump and the PAVE-unit, which is a combination of two or three pressure vessels, valves and a pressure-regulated control valve. A membrane pump that pumps water up to the surface at *in situ* pressure is attached to the other instrumentation. The pump is driven either by nitrogen gas and water or just water

- use sample enrichment factors which are high enough to ensure that any increase in colloid concentrations can be observed above the normal uncertainties in colloid analysis

- avoid long sampling and handling times to minimise potential disturbances of the *in situ* conditions in the former (cf. comments in [188, 189]) and of the colloids themselves (see comments above)

- handle under inert gases and filter with gas over-pressure (rather than vacuum pump which may change the partial pressure of dissolved gases and so lead to the precipitation of, for example, calcite)

- if possible, use an inert gas mixed with CO_2 at *in situ* partial pressure to better simulate *in situ* conditions

- where possible, use methods which avoid filtration at all
- use *in situ* groundwater sampling and colloid separation methods where possible as these minimise artefacts (see comments above)

"*Otherwise, money and effort may be wasted on careful investigation of sampling artefacts.*"

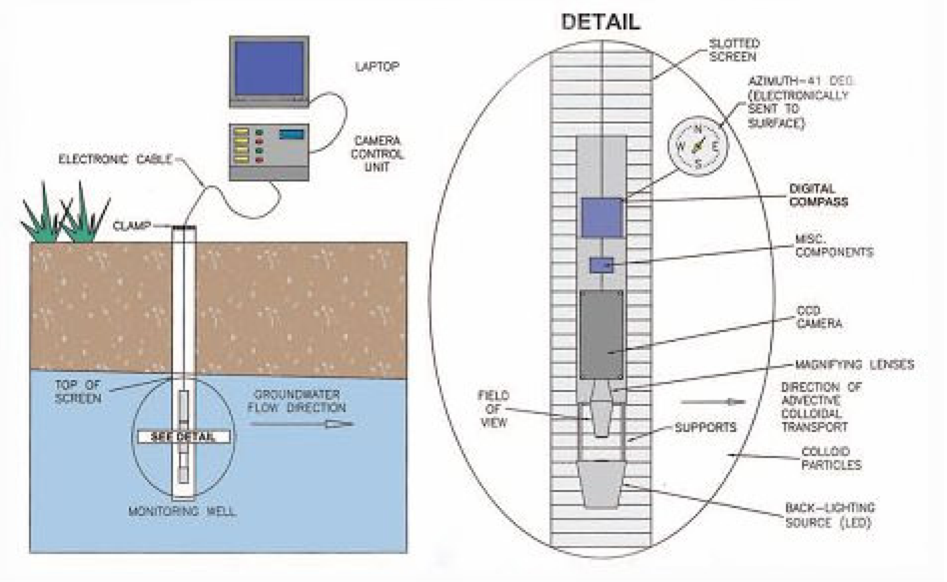

Figure 4.3 The colloidal borescope [from 212]. A video camera captures time-lag images of colloids and particles moving through the field of view and the software calculates the rate and direction of flow

Overall, it should be emphasised that [192] is currently an exception and that all deep borehole colloid data must be assumed to contain some form of artefacts, unless it can be directly shown otherwise.

Finally, two other areas of deep groundwater colloids still remain to be addressed on a regular basis:

- concurrent studies of groundwater colloidal and microbiological populations along with other groundwater organic species (e.g. dissolved inorganic carbon); and
- colloid populations in low permeability, non-fractured host rocks such as indurated mudstones (where colloid mobility is expected to be limited).

Both these areas have been briefly touched on, with the former most recently as part of SKB's currently ongoing site characterisation programme [see 183 for details] and the latter as part of the R&D (research and development) programme of the Mont Terri URL in Switzerland [see 213 for a discussion]. However, in neither case can it yet be claimed that studying the role of colloids in these situations is anything near routine and it is likely that significant R&D effort would be required to attain such a position.

4.3 Colloid characterisation techniques

Today, a range of characterisation techniques is available to study the concentration, composition and size distribution of colloids in water samples and many of these have been applied to study colloid populations in groundwaters of relevance to geological disposal in the UK and other national programmes. Here, this information is summarised in Table 4.3, with focus on those methods that are of direct relevance to groundwater colloids. The list of techniques in Table 4.3 is non-exhaustive because, as was noted in [207, 62], the current interest in nano-technology has sparked off a technology race in imaging and analytical techniques for nanoparticles (or colloids by another name) which shows no sign of slowing down. Consequently, the current rate-of-change in colloid analytical technology is greater than can adequately be addressed in a report in this form.

Despite the requirements of [192] being over fifteen years old now, perhaps of most note in Table 4.3 is that the majority of techniques still require invasive separation of colloids and sample pre-treatment. For other techniques, such as Focused Ion-Beam (FIB) registration [e.g. 214], imaging can be very time-consuming and this has probably mitigated against the widespread use of this technique in groundwater colloid studies to date. Equally, even those methods which can be employed on site (most notably LIBD – see Figure 4.4), still need samples pumped to the surface or to the tunnel in an URL. As such, the awareness of the likelihood of artefacts in any groundwater colloid data remains as essential as two decades ago.

Figure 4.4 The use of LIBD in the Grimsel URL's CRR (Colloid and Radionuclide Retardation) project. FZK's (Forschungzentrum Karlsruhe) white van is being transported directly to the URL tunnels by cablecar and the analytical equipment (Figure 4.5) is transported in the back of the van, is coupled directly to the sampling lines (image courtesy Nagra's Grimsel URL Programme)

Table 4.3 Examples of common groundwater colloid analytical techniques

Method	Short description	Parameters measured	Advantages	Disadvantages
Laser-induced breakdown detection (LIBD) [e.g. 215, 216]	A high-energy pulsed laser is used to selectively generate a plasma (dielectric breakdown) on the colloids. This breakdown is generated selectively as the threshold energy is lower for solids than for liquids and gases. The laser pulse energy is calibrated so that no breakdown of liquid occurs, but the breakdown threshold within the focal area of the beam exceeds that for colloids.	LIBD enables the concentration (ppt to ppm) and size (10-1000 nm) of colloids to be determined.	Method is non-invasive, sample preparation is not required, and measurement can take place on-line and on site (see Figure 4.4). The current instrumentation can detect colloids down to only a few nm in size in the ppt concentration range (10^{-12} gg^{-1}). Compared to light scattering techniques (e.g. PCS), the limits of detection are lower by several orders of magnitude [217].	Colloid populations are given relative to a calibration with polystyrene reference colloids and so 'non-standard' colloids will present a different signal, so increasing uncertainty in the signal. Although very small colloids can be detected, this is only the case at low concentrations, with higher concentrations inducing greater uncertainty.
Photon Correlation Spectroscopy (PCS) (also referred to as Dynamic Light Scattering) [e.g.##]	Groundwater sample is placed in a cuvette mounted in a thermostatted vat of liquid and illuminated with a focused laser. Brownian motion of the particles produces , fluctuations in the intensity with time, which are detected, usually with a photomultiplier.	PCS measures the diffusion coefficient of dispersed particles from which their size can be determined by applying Stokes Law. PCS can be used to study both the steady-state size distribution of particles in a water sample and the kinetics of aggregation through changes in the size distribution with time.	Generally, detection limit is 50 nm for 'normal' groundwater colloid cconcentrations, particularly in the presence of even small fractions of larger particles that may dominate the light scattering.	Pre-treatment is often required for groundwater samples – pre-filtration to remove larger particles and, often, pre-concentration of the colloids. Because the technique measures diffusive motions, it cannot be used for in-line measurements.
Scanning Electron Microscopy (SEM) [e.g. 46]	For quantitative analysis, colloids can be collected on a membrane filter and then sputter coated with gold or carbon (see Figure 2.5). With a flat substrate, image resolution is about 50nm.	Samples can be either backscattered electron (BSE) or secondary electron (SE) imaged. Former shows atomic number contrasts, the latter topographic contrast which can be used to highlight heavier elements against a background of lighter elements.	Direct collection of samples onto the matrix (followed by additional direct treatment) minimises artefacts.	Sample pre-treatment (coating with gold or carbon) can cause interference and examination under vacuum can destroy non-crystalline colloids
Environmental SEM (ESEM) [e.g.209]	ESEM is effectively a SEM which is capable of analysing colloids without any pre-treatment (i.e. no filtering or gold/carbon coating).	To date, ESEM has been used to better assess *in situ* colloid morphology, to directly study attachment of colloids to fracture faces and pore surfaces and to examine organic colloids [e.g. 218].	Major advantage over SEM is that no vacuum is required and therefore all forms of colloids can be analysed. Additional advantage is that samples can be effectively analysed without any handling.	There has been a hiatus in the use of ESEM because the company holding the original patent went out of business. Subsequent systems were not of an equivalent standard. A resurgence is expected now that the original system is available again.

Method	Short description	Parameters measured	Advantages	Disadvantages
Transmission Electron Microscopy (TEM) [e.g. 219]	Requires ultrathin samples in or on a matrix which is transparent to the electron beam.	Features down to a few nm (Figure 2.6) can be resolved (better than for SEM, see above). Imaging systems can evaluate colloid populations and size distributions on a quantitative level for low colloid populations [e.g. 38].	Now possible to run a SEM in STEM (Scanning Transmission Electron Microscopy) mode to integrate the best features of both systems [e.g. 220]. Digital cameras and image analsis tools allow recovery of colloid images at high resolution.	Requires significant handling (from production of a colloid dispersion to production of the analytical matrix) under clean conditions, so avoidance of artefacts is an issue (cf. SEM above).
Single Particle Counting (SPC) [e.g. 221]	Colloids transported in a fluid through a laser beam scatter light in direct proportion to its size and through an angle that is larger the smaller the particle. The pulses of scattered light are recorded by photodiode detectors positioned at 90° to the incident laser beam.	SPC can define the colloid size distribution in groundwaters. Systems currently capable of is counting and sizing colloids from 50 nm to 2 µm in diamter.	The system is small and easily transportable for on-site analysis. No filtration necessary.	Sample pre-treatment is necessary for groundwaters – normally dilution of the solution is required which could lead to the dissolution of certain colloids (e.g. calcite).
Single Particle Inductively Coupled Plasma-Mass Spectrometry (SP-ICPMS) [e.g. 222, 223]	The signal induced by the ionization of a colloid in the plasma torch can be measured by the mass spectrometer.	Size detection limit is around 25 nm and one colloid per mL may be detected during a 1 min time scan [e.g. 224].	The system is small and could easily be transported for on-site analysis. No filtration necessary.	Generally, samples are transported back to the laboratory. Sample pre-treatment is necessary for groundwaters – normally dilution of the solution is required which could lead to the dissolution of certain colloids (e.g. calcite).
Energy Dispersive X-ray Analysis (EDX)	Common accessories to both SEM and TEM instruments. The electron beam is focused to a spot on a colloid or group of colloids and the characteristic X-rays emitted by the elements are detected using an energy-discriminating X-ray detector.	Enable the composition of individual colloids or groups of colloids to be determined. Single particle analysis can be undertaken on particles greater than about 500 nm in size by SEM, somewhat smaller by TEM.	Strength of the technique lies in being able to quickly distinguish the compositions of particles with different appearance and morphologies. In combination with BSE-SEM, EDX can be used to identify the compositions of heavy-element rich particles that might be present at low proportions in colloid populations	There remains a gap between the size range of the imaging methods (e.g. a few nm for TEM) and that of the analytical methods such as this, meaning that direct interpretation is difficult.

Method	Short description	Parameters measured	Advantages	Disadvantages
Atomic Force Microscopy (AFM) [e.g. 225,]	Maps the morphology of surfaces. A piezo-electric scanner moves the surface to be investigated beneath a pyramid-shaped tip attached to a cantilever. In contact mode, Steps in the surface are identified by deflection of the tip, which is measured using a laser deflection system. Linescans of the surface build up a detailed map of its morphology. In addition, soft materials can be probed using a tapping mode.	Can be used to measures the size and size distribution of colloids in two-dimensions, attached to a surface. Can distinguish particle morphologies and with phase contrast imaging organic coatings on particles or surfaces can also be identified. Potentially, the technique can probe particle dimensions down to the 1nm level.	The AFM is able to image any type of surface including inorganic, organic polymeric and biological materials. The technique can be applied to surfaces submerged in solution allowing complex colloid structures to be investigated in their native hydrated state.	The resolutions is dependent on the quality (roughness) of the underlying surface [226]

It is important to note that many of the existing data sets for colloid populations are limited by the range of colloid size distributions that were readily accessible to measurement. In particular, it is difficult to measure quantitatively the smallest size fractions in the size distribution, that is, in the range 1-50 nm, by traditional techniques (e.g. transmission and scanning electron microscopy (TEM, SEM) and photon correlation spectroscopy (PCS)). The minimum particle sizes measurable quantitatively have been about 15 nm when applying TEM and about 30 nm when applying SEM due to constraints imposed by specimen preparation (and instrument resolution in the case of SEM). The recently-developed LIBD technique allows quantitative measurement of the size fraction down to at least 10 nm and the atomic force microscopy (AFM) technique potentially allows dimensions down to the 1nm-scale to be measured.

Many of the newer techniques, such as Surface Enhanced Raman Spectroscopy (SERS – [e.g. 227]) or X-ray Absorption Fine Structure (EXAFS – [e.g. 228], are currently focused on metal analysis and will require further development for the examination of inorganic (mineral) and organic colloids of relevance to deep groundwaters. Others, such as Diffusion Gradients in Thin films (DGT) [e.g. 229], Diffusion Equilibration in Thin films [e.g. 230], voltammetry [e.g. 231] and the permeation liquid membrane method (PLM) [e.g. 232] have the ability to indirectly quantifying the amount of metal bound to colloids, even in the very small fraction (<5–10 nm). In addition, these methods have the advantage of providing fundamental information on the colloids such as binding affinity, diffusion coefficients etc in a non-destructive manner.

While none of these techniques have yet been fully explored for deep groundwater colloid analysis, they certainly offer the promise of better understanding of, for example, the association of natural radionuclides with groundwater colloids. As such, this will be addressed further in sections 5, 8 and 9.

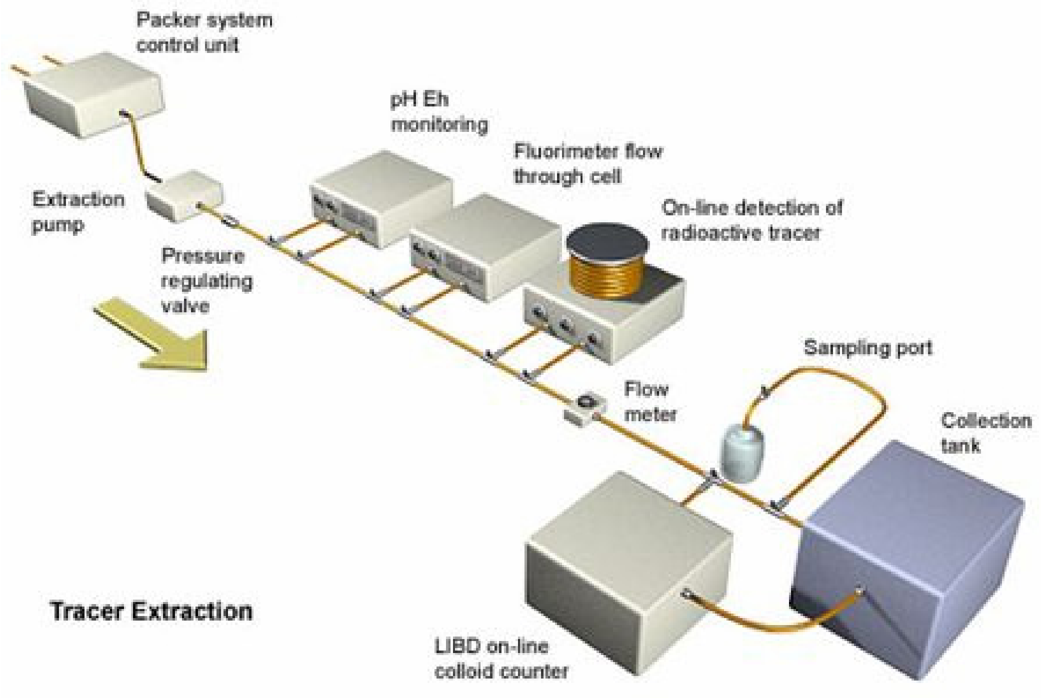

Figure 4.5 Schematic diagram of the LIBD analytical system: groundwater is pumped directly from the borehole sampling interval from the left of the image and flow can be diverted through a series of on-line analytical systems, including the LIBD (Image from [233])

4.4 Summary and conclusions

It is clear from the above presented examples that the greatest obstacles to a clear understanding of colloid populations in deep groundwaters are representative groundwater sampling, colloid separation (from the groundwater) and adequate (i.e. artefact-free) characterisation of the samples (see also comments in [234]). From a non-specialists viewpoint, the first point may seem strange as it is probably the simplest looking part of the entire procedure (it is certainly the least 'high-tech'), but this is to ignore the massive difficulties in obtaining pristine groundwater samples in deep boreholes (see the comments in [189, 195]).

Consequently, from the viewpoint of groundwater sampling and separation and characterisation of far-field colloids, it is recommended that future studies focus on:

- Establishment/adoption of standard groundwater sampling methodologies that enable collection of representative samples for colloid analysis. This should be agreed internationally to allow better comparison of different data sets from different national programmes (see also comments in section 5 and in [207]). The deep groundwater colloid research community could learn much from the novel practices being adopted in the field of surface water shallow groundwater research

- further investment of effort in developing improved *in situ* colloid separation techniques (see also comments in [192]).

- analysis of colloids by methods that minimise handling and avoid separation or dehydration steps that may introduce artefacts and change colloid structures or induce aggregation – for example, LIBD, ESEM, AFM, etc (see also comments in [192])

- integrated studies, which cover colloidal, microbial and organic populations at the same time, be carried out [see also comments in 183]

- dovetailing the above with any work focused on defining the redox state of the deep groundwater as both systems require careful and dedicated sampling approaches to achieve any great degree of success (see also comments in [189, 235])

- closing the gap between the minimum size range of traditional imaging methods (e.g. a few nm for TEM) and that of the compositional analysis methods (e.g. EDX at 500 nm), meaning that direct interpretation is difficult. This is especially important as there is significant uncertainty about the rôle that these very small colloids (with a high surface area to mass ratio) could have in radionuclide transport in deep groundwaters.

- closely tracking analytical developments in the field of nano-technology where commercial pressures are forcing a rate of change several times greater than in the field of environmental colloids (see also comments in [207, 62])

- accepting the fact that "...*the ranges in the measurable attributes of colloids in a single sample can be usually expected to be greater than the working range of any single technique*." [207] and so planning an integrated system of groundwater sampling, colloid separation and colloid analysis before beginning any analysis of deep groundwater colloids.

"*Otherwise, money and effort may be wasted on careful investigation of sampling artefacts*" [192].

5 Groundwater colloid populations

5.1 Introduction

Considering the number of deep, research-oriented boreholes that exist worldwide, there are, perhaps surprisingly, few datasets for groundwater colloids. Those which do exist come from three main sources:

- boreholes drilled for the purpose of GDF site characterisation;
- URL programmes, usually from the tunnels themselves (from drips at the tunnel walls or short boreholes from the tunnel) and occasionally from deep boreholes associated with the programme; and
- natural analogue studies.

In addition to the scarce data from deep groundwater colloids, much work has been focused on shallow groundwater colloids (see, for example, the reviews of [236, 237, 238]), but this area will not be addressed here as it is of little relevance to deep groundwater systems. This is due to the fact that the shallow systems studied:

- are much more dynamic than the deep systems;
- are more likely to be oxidised, for at least part of the year;
- are often unsaturated, for at least part of the year;
- are more greatly influenced by organic material and microbial processes; and
- will have redox and pH fronts that are far from representative of those that may arise in GDF host rocks post-closure.

With this in mind, the extensive literature on the colloids from the clean-up of the various nuclear research sites in the US [e.g. 239, 240] has been omitted as the work generally deals with the shallow (i.e. tens of metres deep) systems. Similarly, due to the massive differences between the environment of the Yucca Mountain site in the USA and any likely GDF site in the UK, information from here [e.g. 33] is also not included. Although the vast majority of the work done on the Gorleben site in Germany [e.g. 85, 241] is focused on the shallower groundwaters, some of the older work [e.g. 78, 242] on the deeper systems is included in Table 5.1.

5.2 Deep groundwater colloid parameters in detail

Most studies of deep groundwater colloids measure certain parameters (usually dictated by the sampling and measurement methods employed) and these are listed for 26 studies worldwide in Table 5.1. Although not exhaustive, this table provides an overview of colloid data for a wide range of rock and groundwater types. Certain things are immediately clear from the listing: fractured hard rocks dominate, in particular, fractured crystalline. This is partly a reflection of historical bias to such rock types in the earlier days of the radioactive waste programme (see discussion in [243]), but is also an indication that it is very difficult to sample groundwaters for colloid separation in deep geological formations other than hard, fractured rocks (see also comments in section 5.3.3).

Table 5.1 Examples of groundwater colloid populations in various host rocks and groundwaters (colloid number concentrations in green)

Site	Rock type and groundwater	Flow system	Colloid concentration (mgL^{-1}) or colloid number (L^{-1})	Size and form	Sampling and analytical methods	Colloid composition	Comments
1. Canadian Shield (Whiteshell Research Area), Canada [79]	Canadian Shield (crystalline) with deep saline (pH 6.1 – 7.7) or shallow Na-Ca-HCO_3 type (low ionic strength), pH 7.4 – 8.9 groundwaters	Fractures	Range 0.04 to 14 Mean 0.34 ± 0.34	10-450 nm	Sequential ultrafiltration (colloid concentrations calculated from compositions)	Iron oxides, aluminosilicates (probably clays) and carbonates.	URL and so flow conditions disturbed. No significant difference in populations between shallow and deep waters. No observable ionic strength effect
2. Canadian Shield (Atikokan), Canada [244]	Canadian Shield (crystalline) with deep saline or shallow Na-Ca-HCO_3 type (low ionic strength)	Fractures	Mean 2.4 ± 0.3		Sequential ultrafiltration		Suggested that highly fractured and altered rock has greater surface area to produce colloids than at Whiteshell URL
3. Fennoscandian Shield (Äspö), Sweden [144, 245]	Granitoids with basic sills and xenoliths and dykes of fine-grained granite.	Fractures and deformation zones	<0.1 [245] <0.3 [246] 0.01x10^{-3} to 1.00x10^{3} [247]	19-993 nm	PCS Ultrafiltration (SEM/EDS) LIBD	Organics, inorganic colloids (clay, calcite, ironoxohydroxide) and microbes.	URL and so flow conditions disturbed
4. Fennoscandian Shield (Forsmark), Sweden [196]	Granite with muscovite/ biotite, feldspar, quartz and clays (chlorite and illite). Groundwater Na-Ca-Cl type, pH=7.53 Eh=–203mV,	Fractures and deformation zones	0.14 to 1.8x10^{-3} (see Table 5.3)		Sequential ultrafiltration and SEM/EDS	Clay	From borehole KFM11A, at 391 m depth

Site	Rock type and groundwater	Flow system	Colloid concentration (mgL^{-1}) or colloid number (L^{-1})	Size and form	Sampling and analytical methods	Colloid composition	Comments
5. Fennoscandian Shield (Laxemar), Sweden [248]	Porphyritic granitoids and red/grey granites to quartz monzodiorite. Groundwater , pH 8.2-8.5, Eh -277 mV.	Fractures and deformation zones	6-12x10^{-3} 2-5x10^{-3}		Sequential ultrafiltration, with mass calculation from the filter chemistry. LIBD	Illite, calcite, iron and manganese hydroxide (colloid compositions calculated from the filtrate chemistry)	Very careful groundwater and colloid sampling.
6. Fennoscandian Shield (Olkiuoto), Finland [192]	Migmatite granite with tonalite and granodiorite with Na-Ca-Cl groundwater, anoxic, pH~8.5.	Fractures and deformation zones	0.020-0.450 0.028-0.142 0.039-0.091	20-450 nm 50-2500 nm 2-1000 nm	Ultracentrifugal deposition, ultrafiltration and AF4 (see Table 4.2) with SEM/EDS	Clays, silica, pyrite, goethite and magnesium oxide	URL so site is disturbed by tunnels. High salinity groundwater will induce colloid agglomeration.
7. Fennoscandian Shield (Palmottu), Finland [249]	Mica gneiss and granite, groundwater is split between shallow Ca-HCO_3 to Na-HCO_3 types and deep Na-SO_4 and Na-CL types. pH 7.0-8.5 (100 m) to 9.0-9.5 (300 m), anoxic. I=30 mmol L^{-1} at depth.	Fractures and deformation zones	0.05 0.89	290 nm 217-229 nm	Ultrafiltration for PCS and EDAX	Silica gel and organics	Although uranium ore is present at the site, the only disturbance is from sampling boreholes. In the deepest, stagnant water (>400 m), no colloids were detected.
8. Grimsel Test Site, Switzerland [250]	Granite and granodiorite, low salinity Na-Ca-HCO_3-F groundwater, sub-oxic, pH 9.6	Fractures filled with fault gouge (see Figure 5.3)	Range 0.13 to 13 4.2x10^{6} to 3.9x10^{10}	Angular to rounded, 20-450 nm	Suite of methods used	Silica, phyllosilicates (illite/muscovite/ biotite) and calcium silicates (probably plagioclase) .	Low salinity water induces colloid stability. URL and so flow conditions disturbed

Site	Rock type and groundwater	Flow system	Colloid concentration (mgL^{-1}) or colloid number (L^{-1})	Size and form	Sampling and analytical methods	Colloid composition	Comments
9. Transitgas Tunnel, Switzerland [80]	Granite and granodiorite, gneiss and mafic amphibolite, low salinity Na-Ca-SO_4-HCO_3 groundwater, oxic, pH 8-9.6	Fractures (no detailed description)	$<2x10^{-4}$ to $<2x10^{-3}$	10-1000 nm	Cross-filtration, bulk water for SPC and colloids on membrane for XRD	Clay (including illite), silica	Collected from seeps in a tunnel, therefore drawdown disturbance
10. Menzenschwand, Germany [179]	Granite intruded into gneiss and metasediment, $CaHCO_3$ water, oxic, pH 6.5	Large aperture fracture	$<4x10^{-4}$	10-1000 nm	Cross-filtration, bulk water for SPC and colloids on membrane for XRD	Clay, silica	Uranium prospect, heavy pumping of water (up to 2000 L min^{-1}) therefore significant disturbance of the local groundwater system. Evidence of long-distance (1-5 km) transport of colloids
11. Leuggern, Switzerland [80]	Mica-granite, Na-HCO_3-Cl-SO_4 water, strongly anoxic, pH 7.8	Not described, assumed to be fractures	<20	10-1000 nm	Cross-filtration, bulk water for SPC and colloids on membrane for XRD	Silica, clay	Water pumped 1700 m to the surface, so degassed
12. Fanay-Augères, France [251]	Granite with Na-Ca-HCO_3-SO_4-Cl groundwater	Fractures	$<0.1x10^{-3}$	100-1000 nm		Silica and organics	Former uranium mine, so significant disturbance to the system.

Site	Rock type and groundwater	Flow system	Colloid concentration (mgL^{-1}) or colloid number (L^{-1})	Size and form	Sampling and analytical methods	Colloid composition	Comments
13. El Berrocal, Spain [53]	Two-mica granite (with leucogranite and pegmoaplites), groundwater Na-Ca-HCO_3-Cl type to Ca-Na-HCO_3-Cl type, pH 6.2 to 7.3, oxic, I= 6-11 mmol L^{-1}.	Fractures	<0.1 10^{12} 10^{10} $10\text{-}10^{8}$	 down to 1 nm down to 50 nm 208 to 342 nm [252]	Tangential flow ultrafiltration with TEM and PCS/SEM	Quartz/silica, iron oxy-hydroxides and alumina gels Albite, apatite, clays, calcite, other carbonates and Al- and Fe-oxyhydroxides. Some organics too [252]	Shallow (S1 and S7) boreholes in a former uranium mine, so heavily disturbed site [252]. Boreholes were left open for a long time and "*...geochemical stabilisation....may not have been reached at all....sampled water may represent mixtures...*" . Majority of U and Th in solution.
14. Sellafield, UK [49]	Borrowdale Volcanic Group	Fractures			Tangential flow ultrafiltration and STEM/EDAX	Fe-oxyhydroxides	Borehole 9A, drilled specifically for geochemical sampling. No detailed analysis carried out due to interference from Fe-oxyhydroxides on filters.

Site	Rock type and groundwater	Flow system	Colloid concentration (mgL^{-1}) or colloid number (L^{-1})	Size and form	Sampling and analytical methods	Colloid composition	Comments
15. Cigar Lake, Canada [184, 253]	Zone of altered crystalline basement, Na-Ca-HCO3-Cl groundwater, oxic to anoxic, pH 6.1 to 7.8	Heavily damaged zone, crushed rock. Fracture in basement	7.78 ± 4.14 0.03 to 2.21		Tangential flow ultrafiltration and colloids on membrane for XRD and SEM/EDX	Clays (illite, chlorite, kaolinite), amorphous Fe-Si oxides, quartz and organics	U deposit has been explored with several hundred boreholes, so significant disturbance
16. Osamu Utsumi, Brazil [254]	Phonolite, K-Fe-SO_4, oxidising and weakly to strongly acidic groundwaters, oxic.	Fractures (with extensive redox front development near surface)	<0.5 (generally 0.1 to 0.2) by filtrate chemistry		Sequential (cascade) cross-flow ultrafiltration (filter size 450 to 1.5 nm) with ESCA, SEM, XRD	DOC (80-90%), Fe-oxyhydroxides (2-20%) and clay±chalcedony (<2%)	U deposit extensively mined, therefore highly disturbed site. Groundwater flow from depth to surface, the opposite of the state before mining.
17. Morro do Ferro, Brazil [254]	Phonolite, groundwater varies from the bottom of the hill, which resembles the water from Osamu Utsumi (above), to the ore body at the top of the hill which is similar but less mineralised and more oxidising, representing unsaturated conditions	Fractures in heavily weathered host rock	0.01 to 0.10 by SEM 0.26 by filtrate chemistry 3.4x10^7	Large (0.5-1.0 µm), irregular/angular shaped particles, agglomerates (5-10 µM) of these particles and long (humic) chains (2-3 µM)	Sequential (cascade) cross-flow ultrafiltration (filter size 450 to 1.5 nm) with ESCA, SEM and XRD	DOC (80%), Fe-oxyhydroxides (18%) and clay (2%)	Th, REE deposit has been explored with a drift and several boreholes, so some disturbance. Colloid concentration range represents the same borehole, but different samples.
18. Wellenberg, Switzerland [255]	Tectonised marl (clay-rich limestone)	Heavily tectonised fractures		Colloids are cylinders 30 – 100 nm diameter and 5-15 nm long. Mean diam. 72nm	Cross-filtration and colloids on membrane for AFM (atomic force microscopy) LIBD [217]	Clay	Pumped from depth, but borehole was supposedly hydrochemically 'stable'.

Site	Rock type and groundwater	Flow system	Colloid concentration (mgL^{-1}) or colloid number (L^{-1})	Size and form	Sampling and analytical methods	Colloid composition	Comments
19. Cigar Lake, Canada [184, 253]	Sandstone and ore (within clay halo), Na-Ca-HCO3-Cl groundwater, oxic to anoxic, pH 6.1 to 7.8	Porous matrix	Mean 0.6±0.09 to 1.52±0.29	10 nm to 20 µm, but most in 100-400 nm range	Tangential flow ultrafiltration and colloids on membrane for XRD and SEM/EDX	Clays (illite, chlorite, kaolinite), amorphous Fe-Si oxides, quartz and organics	No significant U association with the colloids found downflow of the ore body.
20. Sellafield, UK [51]	St Bees Sandstone Formations	Porous matrix	0.5 $8x10^{10}$	100-200 nm	Tangential flow ultrafiltration and STEM/EDAX	Silica, coated with iron oxyhydroxide associated with an illitic clay mineral. Significant amounts of Ca, S, Zn and As also associated with these colloids.	Borehole RCF3 (NB long-term pump test ongoing, so likely to be disturbed)
21. Oklo and Bangombé natural reactors The Gabon [256]	Sandstone, conglomerates and clays, Na-Mg-Ca-HCO_3 groundwater, pH 6-7, slightly negative Eh	Porous matrix	0.03 to 0.92 $2x10^5$ to $2x10^7$	>100 nm	Colloids on membranes for SEM/EDEX and ICP-MS, bulk water samples for SPC	Silica, clay and iron oxyhydroxides	Sampled from 4 shallow (<105 m) boreholes below the reactor zone. Bacteria and organics examined in parallel, but no attempt to link the results.
22. Zurzach, Switzerland	Sandstones and marls directly above crystalline basement, $Na- HCO_3-Cl-SO_4$ water, strongly anoxic, pH 8.0	Not defined, possibly fractures in sediments	<10	10-1000 nm	Cross-filtration, bulk water for SPC and colloids on membrane for XRD	Silica, clay	Pumped from 470 m deep so disturbed. Note similarity of water type to Leuggern; likely that groundwater from the crystalline basement is being drawn in.

Site	Rock type and groundwater	Flow system	Colloid concentration (mgL^{-1}) or colloid number (L^{-1})	Size and form	Sampling and analytical methods	Colloid composition	Comments
23. Ruprechtov, Czech Republic [257]	Clays (altered tuff), lignite and altered granite, Ca-HCO_3 groundwater, I=0.003 to 0.02 mol L^{-1}, oxic to anoxic, pH 6.2 - 8.0	Zones of higher hydraulic conductivity in the clay lignite [258]	0.003 to 0.744	Most >45nm	LIBD	No data	Samples from shallow boreholes (max. depth 37 m), some questions regarding Eh status of system (varies with time).
24. Alligator Rivers, Australia [259]	Quaternary sands over clay-rich zone of intensely-weathered schist grading into weathered schist. Mg-Ca-Si-HCO type groundwater, pH~7, oxic, I=1-1.5 mol L^{-1}.	Not described in detail, seems to be permeable zones in the sands and clays.	<0.05 10^2 to 10^5	Platelets, spheres, crystals (quartz, Fe-oxide) up to 1 µm diameter	Hollow-fibre ultrafiltration and direct ultrafiltration for ICPMS and SEM/TEM/EDS	Quartz, Fe-rich colloids and clays. In highly weathered zone, colloidal clay is kaolinite, in less weathered zones, chlorite. Also uranyl silicate and lead.	Uranium ore not mined, but over 100 exploration boreholes drilled. Site also experiences significant seasonal fluctuation of the water table
25. Gorleben, Germany [242, 78]	150-300 m of glacial sand, silt, marl and clay over the Gorleben salt dome. Two water types: GoHy 2227. Na-Ca-Cl-HCO_3, high organics, low salinity type, pH 7.7-7.9, Eh, -66 mV. GoHy 1231. Na-Ca-Cl-SO_4-HCO_3, low organics, high salinity type pH 6.8-7.1, Eh +205-273 mV.	No information, permeable zones in the sediments.	2227: 158 mgL^{-1} humic colloids in total $6.5x10^9$ $10.x10^9$ $4x10^9$ $5x10^9$ $0.1x10^9$ 1231: total~$3x10^9$	<1000 nm <400 nm <100 nm <30 nm <15 nm	Tangential flow ultrafiltration (field) and flat-bed, permeable membrane filtration (lab). Colloid analysis by α–spec., T-R LFS & neutron activation analysis. ICP-AES, TOCSIN (for DOC). and LPAS also used.	Humics (2227), fulvics (1231) and quartz and feldspar	No information on the boreholes (packers?), but 3 volumes pumped before sampling. Natural U and Th strongly associated (85-95% of total) with the humic colloids in sample 2227, mainly is solution in 1231.
26. Tsukinuno, Japan [45]	Bentonite beds intercalated with shales,	Not described, but fractures likely.	None detected, presumed to be due to groundwater chemistry (Table 5.5)		Ultrafiltration and ICP-AES (colloid concentrations calculated from [Si, Mg and Al]	Assumed to be bentonite, but not presented.	Bentonite deposit is mined, so highly disturbed site. Colloid detection limit is not presented.

5.2.1 Colloid concentration

As can be seen from Table 5.1, the range in measured colloid concentrations is rather large, covering from $1x10^{-5}$ mgL^{-1} (example 3, Äspö URL [247]) to 158 mgL^{-1} (example 25, Gorleben groundwater [78, 242])[11]. As noted in section 4, it is difficult to compare these two most extreme data sets due to:

- different methods of groundwater sampling – sampling in tunnels and sampling in crystalline rock;
- differences in colloid separation methods – same equipment and approach used in both cases;
- operator differences;

and all can play a role in producing artefacts. In addition, the colloid compositions are quite different, with those from Gorleben being almost entirely humic acids while those from Äspö are predominantly inorganic (clay, calcite, iron oxyhydroxide). Even if the Gorleben humic acids are excluded, the maximum population of (predominantly) inorganic colloids is still 20 mgL^{-1} (example 9, Transitgas Tunnel) i.e. a factor of 6 orders of magnitude across the various groundwater types and host rocks examined.

Previously, a clear correlation between colloid populations and ionic composition of the groundwater was reported [180] for a range of groundwater systems (and this will be discussed further in section 7.4). This analysis has been updated recently [257] and when colloid concentrations in mass terms are plotted against ionic strength, as in Figure 5.1, a simple relationship does not always hold. More recent data for the Grimsel Test Site (red hatched zone), the Ruprechtov natural analogue site (blue hatched zone) and the Äspö URL show little relationship between ionic strength and groundwater colloid populations; the authors of [257] comment "*....that different parameters besides ionic strength as e.g. pH and/or ground water velocity may control the actual colloid concentrations*." The composition of the particles will also be important. The authors tentatively suggest that above a groundwater ionic strength of 0.1 mol dm^{-3}, colloid stability is effectively decreased. Further natural colloid data for higher ionic strength groundwaters are required to fully test this hypothesis.

That the pH at the Äspö and Grimsel URLs varies little between individual sites (Figure 5.1), suggests that something as mundane as (sampling) flow rates may be more significant in controlling colloid populations and this is supported by the data from Table 5.2 for the Äspö URL. Here, the variability of colloid populations with the flow rate can be clearly seen, although, confusingly, the relationship is not a simple 'more flow, more colloids', rather the population appears to vary randomly with flow. This is discussed further in section 5.2.4.

Groundwater sampling artefacts aside, it is clear from Table 5.1 that there is no clear and simple relationship between colloid populations and rock or groundwater type. Unfortunately, little is ever reported about the flow systems (see section 4.1.1) in which the groundwater samples are collected and it is strongly recommended that this be a focus of future effort as the route to developing a mechanistic understanding of colloid transport.

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[11] It was originally thought that the highest reported colloid concentrations was 400 mgL^{-1} in the Menzenschwand groundwaters in [179], but re-examination of the raw data [260] show that this was probably a transcription error, with the actual value being $4x10^{-4}$ mgL^{-1} (see Table 5.1).

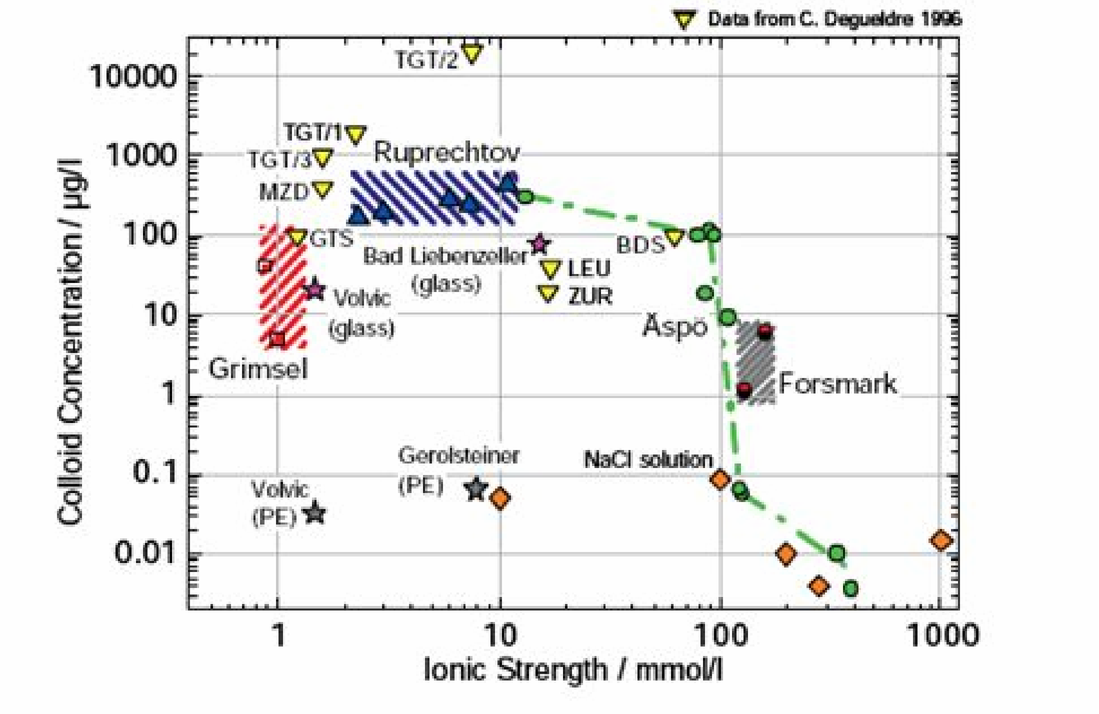

Figure 5.1 **Comparison of colloid concentration in different types of natural groundwater, mineral water and synthetic NaCl-solution versus ionic strength (blue hatch - Ruprechtov; red hatch- Grimsel CRR tunnel; grey hatch Äspö tunnel); data shown from [180] includes TGT: transit gas tunnel, MZD: Menzenschwand, GTS: Grimsel test site, BDS: Bad Säckingen, LEU: Leuggern, ZUR: Zurzach (from [257])**

5.2.2 Size and form

Few data are reported on the size and form of the colloids and, in general, the size discrimination is method dependent, usually reflecting the nominal pore size of the filter membrane. In those cases where detailed SEM investigations have been carried out, there is a greater likelihood that a more detailed description of the colloids is available. A good example is shown in Table 5.3 from a deep borehole at Forsmark in Sweden (example 4, Table 5.1) where, with certain assumptions, the colloid concentration can also be calculated. Plotted in Figure 5.2, these data show a strong log-log relationship between colloid diameter and colloid number, with the number falling quickly with increased diameter, a not unusual situation in groundwaters [e.g. 80, 261] and surface waters [e.g. 262].

Although information on colloid form is often lacking, it can be very useful for checking conceptual models. For example, in the case of the Morro do Ferro data (example 17, Table 5.1), samples were collected at the top of the hill, half way down and at the bottom. The data indicate the presence of rather large colloids and/or agglomerates of these large colloids, suggesting that filtration/sedimentation in the flow system would be likely. Most are reported to be irregular/angular shaped, which also implies little transport in the groundwater system [cf. 263]. As a rule of thumb, the more rounded a particle is, the more it has been transported – more specifically, a ‘roundness index’ may be used to infer the nature of the transport and deposition process. Although never applied mechanistically to colloids, this applies at all scales from clay grains to large boulders and is unlikely to be significantly different for colloids. Obviously, softer mineral grains/rock clasts are rounded more quickly than harder mineral grains/rock clasts and this has to be taken into account in any assessment. See also discussion in [264]. – something which analysis of the trace element signatures of the colloids supports, with no indication of the thorium- and rare earth element- (REE) rich colloids from the ore body at the top of the hill being seen at the bottom.

Table 5.2 Summary of FZK's LIBD analysis of groundwater colloids at Aspö versus bulk groundwater flow rate [247]

Borehole ID	Elevation (m)	Tubing Length	Flow Rate ml/min	Visual Inspection		LIBD Data Evaluation		Colloid Conc (ppb)
				Gas-Gen	Colrd Disp	Bd Prob (%)	Colloid Diameter (nm)	
1 KR0012B	-69	0	4 222	No	Yes	100 100	~404[2] ~600[2]	~300[2] ~600[2]
2 SA1229A	-168	40	4 930	No	Yes	92 100	~600[2] ~300[2]	~190[2] ~110[2]
3 HA1330B	-182	55	4 125	No	Yes	100 100	~993[2] ~404[2]	~1000[2] ~100[2]
4 KA1755A	-235	100	4 550	Yes	No	69.5 3	631[3] 281[3]	630[3] 4.1[3]
		0	12 1400			0.2 0.4	<19[2], 57[3] 129[3]	<0.01[2], 0.014[3] 0.15[3]
5 SA2074A	-282	0	4 190	No	Yes	100 38.8	~600[2] 354[3]	~600[2] 99[3]
6 SA2273A	-306	75	4 900	No	Yes	14.5-26.0 46	175[3]-263[3] 218[3]	9.2[3]-35.5[3] 53[3]
7 HA2780A	-370	70	4 11 20 920 1100	Yes	No	2.3-18.0 28.5 63.1 14.5 17.2	165[3]-296[3] 456[3] 627[3] 244[3] 245[3]	1.2[3]-19[3] 102[3] 525[3] 16.5[3] 19.6[3]
8 KA3110A	-416	0.5	4 2400	No	Yes	9.9 9.4	365[3] 333[3]	22[3] 18[3]

Key:

1 Flow rate adjusted at bypass valve
2 Data s-curve evaluated[†]
3 Data evaluated with constant laser pulse energy

Bd Prob = Breakdown Probability
Gas Gen = Gas Generation
Colrd Disp = Coloured Dispersion

[†] The s-curve is the curve of breakdown probability as a function of laser pulse energy. The shape of the curve is particle-size dependent and can de analysed to obtained particle size (see for example reference [98]).

Table 5.3 Colloid size distribution and concentration at Forsmark [196]. For the colloid size *d* on the basis of the number of colloids *N* on the micrograph, the colloid number N_{col} is calculated on the basis of the active membrane size and the filtered volume. For the average colloid size d_{av}, of volume V_{av} or mass m_{av} (estimated for a an assumed density of 2 g cm^{-3} and for $d_{max} \equiv\approx 2\times d_{min}$) the colloid concentration C_{col} is calculated.

Parameters	Values for each membrane size (nm)			Total
	50	100	200	50-500
N	30	3	(0.3)	33.3
N_{col} (L^{-1})	36 × 10^{8}	3 × 10^{8}	0.3 × 10^{8}	33.3 × 10^{8}
d_{av} (nm)	60	120	240	
v_{av} (cm^{3})	0.2 × 10^{-15}	1.7 × 10^{-15}	1.4 × 10^{-14}	
m_{av} (g)	0.4 × 10^{-15}	3.4 × 10^{-15}	2.8 × 10^{-14}	
c_{col} (mg.L^{-1})	0.00014	0.00090	(0.0008)	0.0018

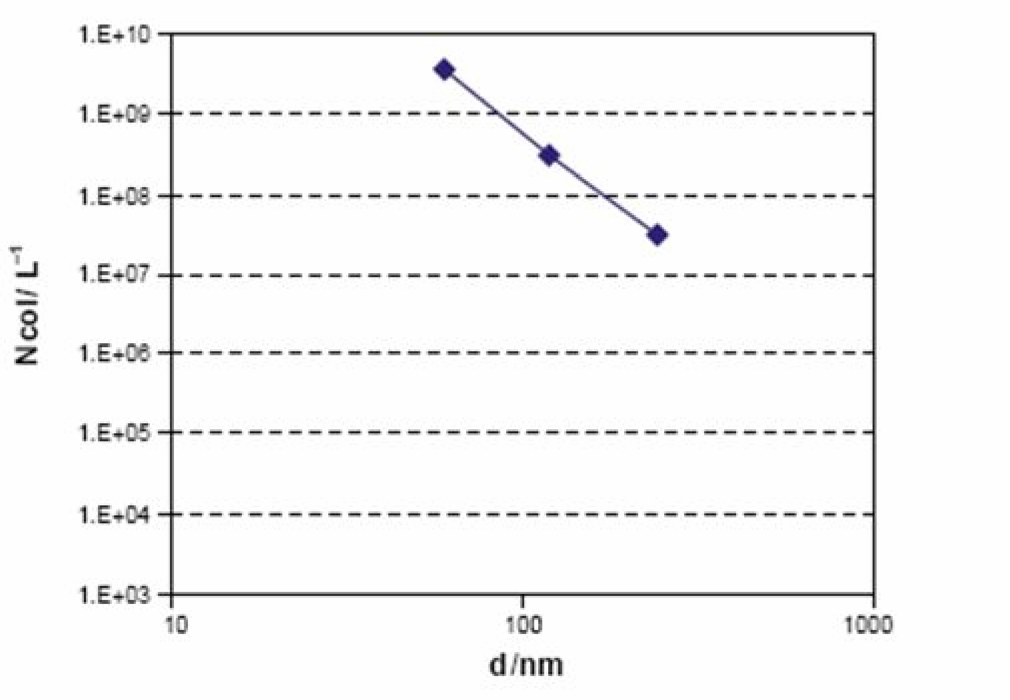

Figure 5.2 Colloid size distribution for the Forsmark groundwater (calculated from Table 5.3 [196])

5.2.3 Sampling and analytical methods

As noted in section 4, one of the greatest difficulties in comparing data from different sites is that the methods employed to separate and then analyse the colloids vary significantly; this can be seen from inspection of Table 5.1. This is not going to change and, indeed, the current pace of change in nano-scale analytical techniques due to the push from the nano-technology industry means that intercomparison of data may effectively become more problematic.

The disturbances inherent to groundwater sampling and colloid separation have been covered in section 4, but it is worth emphasising here that every sample noted in Table 5.1 has been disturbed to some degree. Many samples have been collected at sites which are intrinsically disturbed, such as uranium mines (see section 5.3.2 below) or, less so, in URL tunnels. But even under the relatively controlled conditions of an URL, the simple presence of the tunnels and shafts will induce draw-in to the tunnel of groundwater (and even porewater – see [265]) from the host rock and this acceleration of groundwater flow in the vicinity of the tunnel can be seen to have an impact on the water-conducting features. For example, in Nagra's Grimsel Test Site [266], erosion of the fault gouge in the part of the fractures (see Figure 5.3) in the immediate vicinity of the tunnels has been observed [267]. Crucially, experimental conditions in any URL can also induce erosion in the flow paths and production of colloids under standard experimental conditions which usually utilise flow rates which are several orders of magnitude greater than in a typical GDF host rock (see also comments in references [268, 269]). This is discussed further in section 9.4.1.

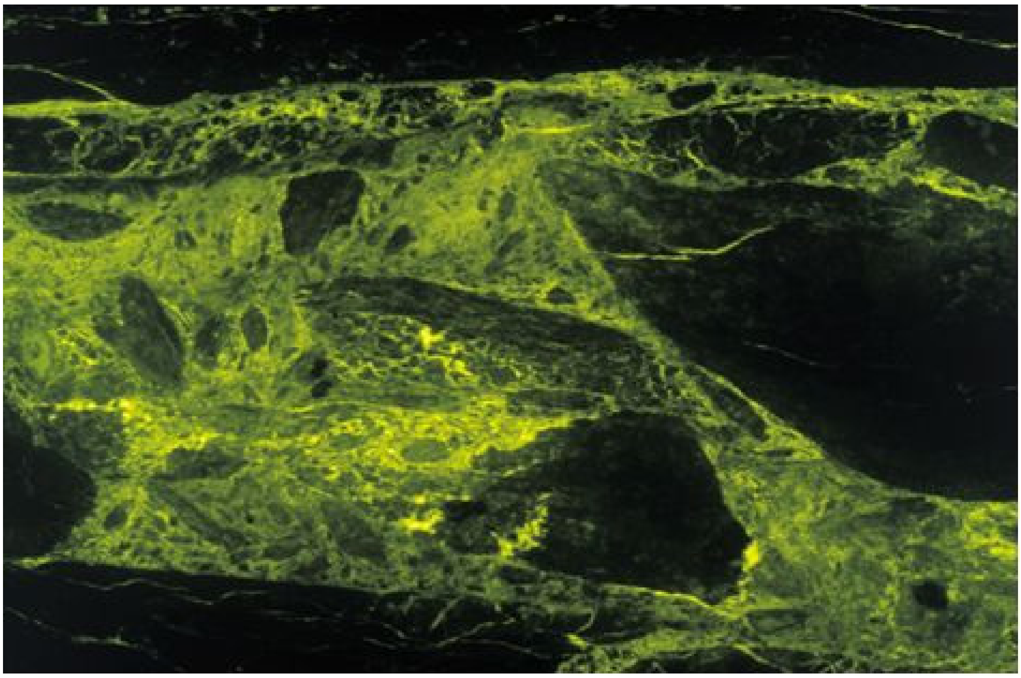

Figure 5.3 Thin section across a fracture from Nagra's Grimsel Test Site (field of view 4 mm). The black material is granodiorite, the green an epoxy resin with a fluorescent dye. The brighter the green, the more open porosity is present – where it is slightly darker, this means more fault gouge is present. This very fine (clay-sized) material is easily eroded by increased water flow, so producing colloids (from [267])

5.2.4 Colloid composition

Generally speaking, colloids in any groundwater system reflect the host rock from which they originate and most examples in Table 5.1 follow this rule. For example, in the groundwaters from the Grimsel granodiorite (example 8, Table 5.1), the colloids present reflect the host rock mineralogy very well:

Colloids [80]	Host rock [267]
silica	quartz
muscovite/biotite	biotite/muscovite
calcium silicates	plagioclase (anorthite)
illite	secondary illite in altered plagioclase

Exceptions include instances where organics are present and these can come from sources of hydrocarbons at depth [e.g. 189] or from soils, etc, from the surface [e.g. 188]. Where alteration to the host rock (for example, from hydrothermal fluids) is limited to the groundwater flow path and a volume of rock very close to this path, then the colloids may also be representative of only the flow path.

Obviously, this will change as the groundwater moves, for example, from a granitic basement rock, upwards into a clay, but even then the differences may not be so great. For example, in the only case of long distance colloid migration reported, in the Krunkelbach uranium prospect at Menzenschwand in the Black Forest of southern Germany (example 10, Table 5.1), the difference in mineralogy was completely unremarkable. The signature from the 1 to 5 km distant Feldberg gneiss/metasediment was only noticeable in the trace element chemistry of the colloids, with Mg, Ti, Nd and some of the REE being most indicative.

Although present naturally, Fe-oxyhydroxide, sulphur and calcite colloids can often be indicators of groundwater sampling problems. The Fe-oxyhydroxides and the sulphur colloids can be produced by the oxidation of pyrite in the host rock (from oxidants in the drilling water or air introduced with the sampling equipment), whereas calcite can be due to degassing the groundwater sample as it is pumped to the surface. Fe-oxyhydroxide colloids are discussed further in section 5.3.3.

5.3 Case studies

5.3.1 Forsmark (Sweden)

One point, which was briefly discussed in section 4, concerns how representative any groundwater sample is of its surroundings, i.e. the local rock, groundwater, specific depth, etc? This is often a difficult quality to assess and, at least for bulk groundwater samples, often requires building up a statistically relevant database. Unfortunately, this can be a problem for colloid studies as either sampling possibilities are limited (e.g. the Maqarin natural analogue site in Jordan is in a military-controlled zone and access is by restricted permit only [270]) or the variability in the site is too large to cover adequately. For example, the borehole SKB used for the initial colloid study at Forsmark, KFM11A (see Figure 5.3), is one of eleven deep boreholes at the site. However, only one set of samples, from a packed-off section between 447.5–454.6 m deep, was collected for colloid separation from this borehole. Subsequently, studies of colloid populations in two intervals in a second borehole at Forsmark have been reported (see Appendix 7 in [271].

Not only is this a small sub-sample of the overall number of groundwater samples taken at the site, the highly complex nature of the geology and structure (Figure 5.4) of the site allied to the equally complex hydrochemistry mean that the dataset is not statistically meaningful. Thus great care must be taken not to place too much weight on only one or two examples from the globally limited dataset for deep groundwater colloids.

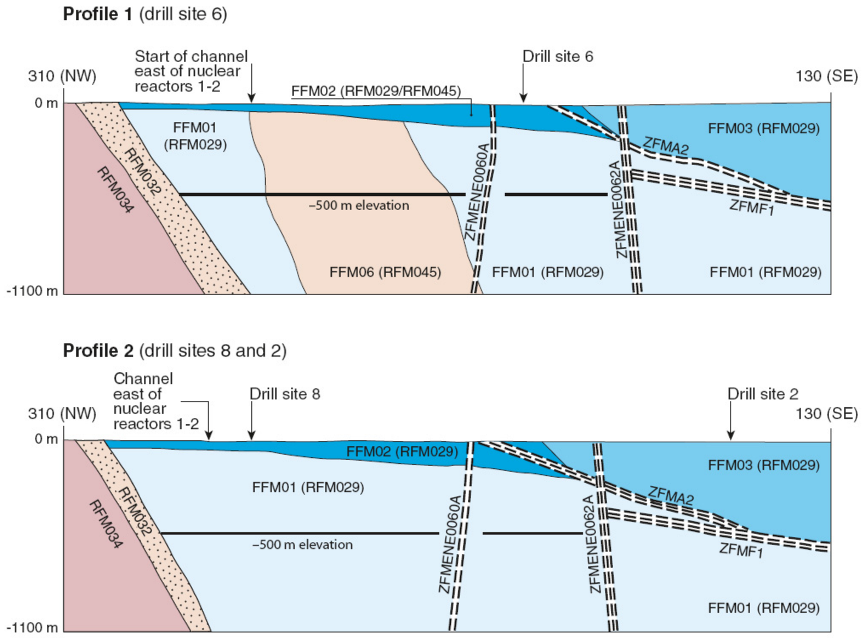

Figure 5.4 Simplified NW-SE profiles across the Forsmark candidate site showing the highly complex structural nature of the site. The different colours represent different structural domains and the hatched lines represent deformation zones – all of which have different hydrogeological environments (from [235)].

5.3.2 Laxemar (Sweden)

Several organisations (including Nirex in the UK) have drilled deep exploratory boreholes which were dedicated to hydrochemical studies, rather than piggy-backing such studies on hydrological and geophysical studies. For dedicated hydrochemical boreholes, great effort was expended in minimising the groundwater disturbance from drilling and the associated testing which can gravely impact the quality of the subsequent groundwater samples [188]. In non-dedicated boreholes, the time required for testing between borehole completion and installation of long-term sampling equipment can be rather prolonged. For example, in Nagra's Weiach exploration borehole in northern Switzerland, the drilling ceased (at a depth of 2482 m) on 12th November, 1983 (started on 10th January,1983) and the preparation to install groundwater sampling systems began at the end of February, 1985 [272]. Thus the extra effort required for a dedicated hydrochemistry borehole can be seen to make sense because the effects of prolonged testing, such as that at Weiach, which increase disturbances to the groundwater system by extended pumping and leaving the borehole open to the atmosphere, for example, are minimised.

The Laxemar site is considered here as it represents a good example of very careful groundwater sampling and colloid separation and, as such, the data are deemed to be of a high quality. This particular borehole (KLX13A) was drilled specifically for hydro- and geochemical purposes and, as such, "*Only activities that are necessary in order to select borehole sections are carried out in the borehole prior to the chemistry campaign*" [248]. These are listed in Table 5.4 and it is interesting to compare the timescales here with those noted above for the Weiach borehole (which was focused on areas other than hydrochemistry). In addition, contamination of the borehole was deemed to be low as a mass balance of the drilling fluid showed minimal loss to the host rock.

Table 5.4 Borehole activities performed in borehole KLX13A prior to and in connection with groundwater sampling (from [248])

Activity	Date of Completion	Length of section (m)
Percussion drilling	30-06-2006	0.15-99.86
Core drilling	16-08-2006	99.86-595.85
Hydrochemical logging	19-09-2006	0.-585
BIPS-logging	10-08-1006	380-545.15
Nitrogen lift of water	07-09-2007	0-595.85
Geophysical logging	08-09-2008	101.2-592.8
Differential flow logging	26-09-2006	95-585

In addition to being careful with the borehole, care was taken with the groundwater sampling and colloid separation, including the use of a mobile chemistry laboratory on-site (Figure 5.5) with in-line colloid separation under *in situ* pressure to minimise sampling and transport problems. That two different colloid analytical methods produce very similar results ($6\text{-}12 \times 10^{-3}$ and $2\text{-}5 \times 10^{-3}$ mgL^{-1}) is further indication of the high quality of these samples. As such, it is proposed that these values are some of the few realistic deep groundwater colloid data currently available.

Figure 5.5 The mobile units used at borehole KLX13A, Oskarshamm, Laxemar. From left, container for collecting the water from the borehole, laboratory unit, hose unit with downhole equipment and a unit for computer work (from [248])

5.3.3 Osamu Utsumi (Brazil)

Much has been made here and in section 4 about the many and varied routes to produce a colloid separate which owes more to artefacts than to nature, for the very good reason that colloid science, at least in the field, remains very much on the cutting edge of sampling procedures (see also Table 4.1). Here, then, is a good example (16, Table 5.1) of a site which, although an excellent natural analogue for other processes of relevance to a GDF (see discussion in [273], is less than satisfactory as a site to study colloids.

First, the site was a recently abandoned uranium mine (see Figure 5.6) where so much overburden had been removed that the groundwater flow had reversed and so was now moving upwards, from depth, to the surface. Second, the significant volumes of pyrite at the site effectively acidified much of the groundwater following oxidation after overburden removal. This not only significantly altered the groundwater speciation, but also released large quantities of Fe in the form of Fe-oxyhydroxides which swamped the inorganic colloid signal. Finally, the high organic load of the groundwaters dominates the colloidal fraction and this is of little relevance to a deep groundwater system.

At the time, the focus of the study was on the behaviour of trace elements in the vicinity of the redox fronts as these were thought to be analogous to such fronts developed in the engineered barrier systems (especially of spent fuel repositories) as a result of radiolytic decomposition of water [e.g. 274]. However, this is probably of no concern in those designs with a massive steel canister (or copper with a steel insert) as the steel will mop-up all oxygen likely to be released in this process [275, 276].

As such, this dataset should be consigned a low degree of relevance to deep groundwater colloid studies.

Figure 5.6 Osamu Utsumi open cast uranium mine, Poços de Caldas, Brazil. Removal of the overburden reversed the groundwater flow direction (from [277])

5.3.4 Low permeability sediments

For lower permeability rock types such as the Callovo-Oxfordian argillaceaous rocks of France, the Opalinus Clay of Switzerland and the Boom Clay of Belgium where transport is essentially diffusion-dominated, it is generally assumed that colloid transport will not be an issue (see discussion in [62, 278]). This has been checked experimentally [21] and appears to be verified by the study in the Tsukinuno bentonite mine (Figure 5.7) in Japan (example 26, Table 5.1). The authors note [45] that the absence of colloids is consistent with the groundwater chemistry (Table 5.5) encouraging colloid agglomeration, but this is slightly at odds with the work at Ruprechtov (Czech Republic) [257] discussed in section 5.2.1. However, new work on bentonite at natural analogue sites in the Philippines and Cyprus suggest that the absence of colloids could have more to do with sealing of groundwater flow paths in the bentonite due to the presence of swelling clays than groundwater ionic strength [cf. 279, 280, 281].

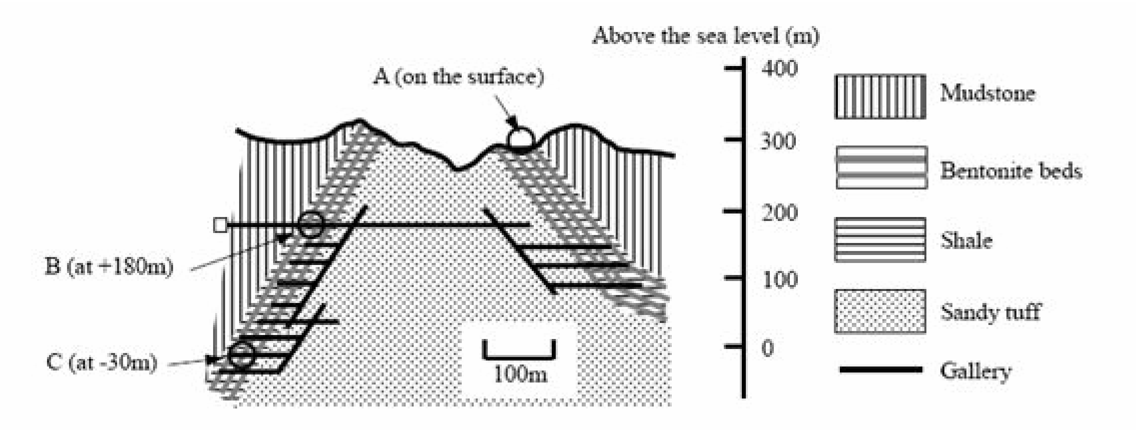

Figure 5.7 **Schematic cross-section through the Tsukinuno bentonite mine, northern Japan (example 26, Table 5.1), showing the sampling points A, B and C (from [45])**

Table 5.5 **Chemical composition of the water at the three sampling points in the Tsukinuno mine shown in Figure 5.7 (from [45])**

Samples:	**A**	**B**	**C**
Sampling depth (above sea level)	About 300m (On the surface)	180m	-30m
pH	7.0	4.0†	8.7
Analyte	**Concentration ($mol.dm^{-3}$)**		
Na^+	4.5×10^{-4}	3.9×10^{-3}	4.3×10^{-2}
K^+	4.4×10^{-5}	1.1×10^{-4}	9.5×10^{-5}
Ca^{2+}	5.2×10^{-5}	4.9×10^{-4}	1.1×10^{-4}
Mg^{2+}	9.9×10^{-6}	3.4×10^{-4}	3.4×10^{-5}
HCO_3^-	8.2×10^{-5}	0	1.7×10^{-2}
Cl^-	1.6×10^{-4}	1.6×10^{-4}	2.3×10^{-3}
SO_4^{2-}	1.8×10^{-4}	2.5×10^{-3}	1.0×10^{-2}

† Oxidation of pyrite, naturally present in the bentonite (0.6 vol%), is suspected as the cause of this very low pH at the sampling point where the bentonite is exposed to air [282].

5.4 Conclusions

Several datasets for deep groundwater colloids now exist worldwide and they cover a respectable range of environments, both of rock and groundwater types (although there is a obvious bias to fractured hard rocks: Table 5.1). A wide range of colloid populations, covering six orders of magnitude, have been reported in the literature, but there is, as yet, no comprehensive mechanistic understanding to explain this range.

Throughout this and the proceeding section, reference has been made to artefacts induced by disturbances to:

- the *in situ* rock-groundwater system (e.g. by the presence of a mine)
- the bulk groundwater during collection
- the colloids during transport and separation

The artefacts clearly need to be addressed "*Otherwise, money and effort may be wasted on careful investigation of sampling artefacts*." [192].

There remains a general lack of information about the flow systems in which most far-field colloids have been studied. Often this is a reflection of the background of the research teams involved, but also indicates a lack of integration of the colloid studies in other aspects of the site characterisation. Even in those larger scale studies which show a high degree of vertical and horizontal integration [e.g. 235], colloids (and microbes) tend to be 'added on' and are not fully integrated with the rest of the project. This is then often reflected in systems which are underdefined from the viewpoint of the transport and PA modellers. This is discussed further in section 12.

It should already be clear that certain datasets should have less weight placed on them, certainly in those cases where either excessively disturbed systems have been studied (e.g. Osamu Utsumi) or where clear groundwater sampling problems still exist (e.g. most boreholes and URLs). For the other datasets noted in Table 5.1, this does not mean that they are artefact-free, rather, from a PA perspective, the colloid populations should be viewed as representing maximum concentrations (while accepting that some artefacts will reduce colloid numbers). The example of the Laxemar study shows that high quality samples can be collected and colloids separated from the bulk water with a minimum of artefacts, but it should not be forgotten that, first, such datasets only come at the cost of much expensive effort and, second, that they usually do not provide a statistically significant understanding of a given GDF site.

As was noted in section 4, some form of quality assurance systems for bulk groundwater analyses now exist [e.g. 188, 189,195] and it is now time to move to a similar 'categorisation' scheme for colloid data. This will be discussed further in section 12.

6 Experimental studies of colloid generation in the near field

In addition to colloid populations that will be present naturally within the groundwater that may act as carriers for radionuclides in the geosphere, radionuclide-bearing colloids may be generated in and migrate from the engineered barrier system. The potential formation of colloids from wasteform materials has been studied for each type of disposal concept under consideration in national and international research programmes. This includes: cement-based concepts for L/ILW (recently reviewed by Swanton and Alexander [62]); vitrified HLW and SF disposal with a bentonite buffer or under unsaturated conditions [e.g. 283, 284, 285, 286]; disposal in salt mines [e.g. 77, 287], and surplus plutonium and uranium disposal in ceramic wasteforms [e.g. 288]. The potential for colloids to be generated at the interface between the near field and the far field (e.g. within the alkaline disturbed zone [62] or the bentonite/host rock interface [44]) has also been recognised.

It is beyond the scope of this study to provide a detailed review of colloidal processes in the near field. Nevertheless, a general overview of work in this area is of value to indicate the potential contribution of colloids to the near field source term and identify where near-field derived colloids may need to be considered in the far field. As part of this study, a brief overview is given of colloids in a cementitious near field (based on [62]); a summary of the principal results is given in Appendix 1. A review has been undertaken of colloid generation from borosilicate glass wasteforms (Appendix 2); and of recent work on colloid generation from spent fuel (Appendix 3). Also included is a summary of a paper by Geckeis and co-workers [284] which considers in a generic way colloid generation from a vitrified HLW/SF near field.

6.1 Colloids in a cementitious near field

Current understanding of colloid populations that may be formed in the near field of a cementitious repository for ILW/LLW was reviewed recently [62]. The main sources of information come from laboratory experimental programmes that have been concerned with colloid generation from cementitious materials under consideration as either backfill materials or waste encapsulation grouts [38,39,40, 289,290, 291]. These will be the predominant materials in a cementitious repository in terms of volume and mass and were identified from early review studies as potentially important sources of near-field colloids [e.g. 19]. Most of these experimental programmes have involved batch leaching tests in which cured cementitious materials in the form of granules or intact samples have been leached in a solution of selected initial composition (ranging from demineralised water to simulated saline groundwaters) for periods ranging from days to several years. In one dynamic leaching test, leachate samples were taken from a column of crushed mortar through which a mortar-equilibration water was flowing [39,40]. Further information is available from the results of colloid analyses of leachates from a number of equilibrium leach tests (ELTs) undertaken by Nirex [41, 292, 293] and Nagra [294,295,296], which combined waste and cementitious materials and in each case ran for about 7 years, and from studies of the cementitious natural analogue site at Maqarin in Jordan [46].

Appendix 1 provides a summary of the principal results. The picture emerging consistently from these studies is that cementitious colloid concentrations generated under simulated near-field conditions are low with number concentrations typically less than 10^{12} particles dm^{-3} for the size range larger than 15 nm, with maximum mass concentrations of less than 1 mg dm^{-3}.

The formation of colloid-like artefacts during specimen preparation from the cementitious waters in a number of the studies (particularly by TEM) has been found to complicate the characterisation of the cement colloid populations; in these cases maximum concentrations have been reported.

Owing to limitations of the conventional colloid characterisation techniques that have been used for quantifying the smallest size fraction of the colloid populations (smallest quantifiable sizes have varied between 15 nm and 100 nm depending on the specimen preparation/analysis method used in a study), there is uncertainty concerning the contribution of the smallest particle size fraction. Attempts have been made to extrapolate measured particle size distributions to smaller size to estimate this contribution assuming power law behaviour of the number concentration with size class [40]. On this basis, maximum colloid concentrations could be increased by three to four orders of magnitude compared to measured values. However, it is not clear whether such an extrapolation is justified and, therefore, should be treated as a cautious assumption. Owing to the small mass of the smallest particles, this has minimal effect on estimated colloid mass concentrations. However, the smallest particles are likely to have the largest surface area to mass ratio and therefore may be particularly significant with regard to available surface sites for radioelement sorption. There is very little data available concerning radionuclide association with cementitious colloids.

It was concluded in [62] that overall, colloid populations generated in laboratory experiments may be enhanced compared to repository conditions due to aspects of the experimental methods employed (such as the use of crushed cements, high liquid to solid ratios, etc) Despite these limitations there is no indication of significantly high colloid populations being generated from near-field cementitious materials as a result of the procedures used.

The colloid concentrations measured in short-term, small-scale laboratory examples are supported by low colloid concentrations (1-5 10^{10} particles dm^{-3}) measured in the long-term, large-scale Maqarin cementitious natural analogue system. The Maqarin results build confidence in the laboratory data, in particular, because the Maqarin site represents a shallow, high energy system, the findings add weight to the view that the laboratory data are cautious.

In general, the compositions of colloid particles leached from cured backfill materials reflect the mineralogical composition of the materials. For NRVB, colloid particle types identified include CSH gel, calcium carbonate, ettringite-like and hydrotalcite-like particles. Spallation from the cement surface appears to be dominant colloid generation mechanism from the bulk material in the longer-term in leaching experiments.

6.2 Colloid generation from vitrified wastes

In the UK, high level waste arising from the reprocessing of nuclear fuel (principally Magnox but also oxide fuel) is being incorporated into borosilicate glass for long-term immobilisation, a process termed vitrification. The use of borosilicate glass formulations for HLW immobilisation is widespread internationally due to their good durability and their ability to incorporate a wide range of elements found in typical process waste streams [297]. Ojovan and Lee [298] provide a useful introductory text on the application of glassy wasteforms. A review of the development of the UK HLW vitrified product was undertaken for Nirex in 2006 [299].

The disposal concept under consideration for UK HLW is similar to those under consideration in a range of other countries (e.g. France [300], Japan [301]) in which steel containers containing HLW would be surrounded with a bentonite buffer at depth in a suitable geological formation. The exception to this approach internationally is in the USA, for the proposed facility at Yucca Mountain, where disposal of HLW canisters is envisaged in tunnels above the water table without a surrounding buffer or backfill [302].

A review of colloid generation from borosilicate glass wasteforms was undertaken as part of this study and is provided in Appendix 2, the principal findings are summarised here.

Studies of the aqueous durability of vitrified wastes have been undertaken on all national programmes in which vitrified wasteforms have been under consideration for waste immobilisation. Some of the studies have included an element of colloid characterisation, as outlined in Appendix 2. What is apparent from the literature is that, with the notable exception of the US, work on colloid release and characterisation from glass wasteforms petered out in the late 1990s. This is believed to coincide with recognition that a bentonite buffer may act as an effective filter for near field colloids due to its fine-scale porosity and that although colloidal particles may arise in the near field, they were unlikely to migrate into the geosphere. In the US, where no buffer is envisaged, such a screening argument cannot be deployed and therefore estimates of waste-glass source terms have been required for the Yucca Mountain assessment.

A review of the literature found very little quantitative information on colloid populations released from waste forms and owing to the nature of the accelerated tests used (often at elevated temperatures) it is not clear how applicable such data would be to geological disposal. Indeed, even on the US programme quantitative data appears to be scant. No studies of colloid release from UK HLW have been identified in the open literature.

The principal mechanism of colloid generation from borosilicate wasteforms is the formation of secondary phases from alteration of the glass surface. The principal alteration products are phylosilicates (clays) such as smectite, binessite, saponite, nontrite, etc [303]. However, a wide variety of other mineral phases have also been identified as colloids depending on the glass composition, the leachant and the presence of other solid phases (such as metals or bentonite). The minerals have included weeksite, a uranium silicate [304]. Uranium has been identified associated with clay particles and tetravalent actinides have been identified with phosphate phases from phosphate containing glasses [305, 306].

The mechanisms by which colloidal particles may be generated from glass surfaces are similar to the weathering processes by which mineral colloids may be generated from rock surfaces in contact with water; the principal secondary minerals are broadly similar. The major difference is the likelihood for the direct incorporation of radioelements into the core of colloidal particles, and the formation of intrinsic radioelement colloids.

The potential significance of colloids to the source term from a UK GDF containing vitrified wastes will need to be evaluated depending on the disposal concept(s) adopted.

6.3 Colloid generation in a non-cementitious near field

Geckeis and co-workers have analysed colloid formation and stability data from a range of near-field experiments to elucidate the key processes and trends controlling colloid generation and stability as a function of simulated (non-cementitious) near-field conditions [284]. Data were obtained from leaching studies of LWR SF and HLW, container corrosion tests and precipitation experiments from oversaturated solutions [284 and references therein]. The experiments, which were all static tests, were carried out for a range of SA/V values in solutions of both high and low ionic strength, covering a range of pH values (from 2-11 in some cases), with durations between 10 and 720 days. Most experiments were undertaken at 25°C, with the exception of glass leaching and sorption experiments onto glass corrosion products, which were undertaken at 90-190°C and 80°C, respectively. A common feature of the experiments was the separation of leachate samples by sequential filtration and determination of the colloid fraction of actinide or rare earth elements (REE) in the size range 1.8-450 nm.

Geckeis *et al*., comment on the difficulty in making quantitative assessment of colloid formation and stability under near-field conditions: "*Major problems… arise from the multiply coupled processes controlled by various degrees of supersaturation, such as co-dissolution of waste matrix, container materials and repository rock, [and] co-precipitation of radionuclides with the main components of the system. Furthermore strong thermal and chemical gradients (e.g. redox fronts sustained by radiolysis) may persist for long periods of time.*" However, from examination of experimental data under a wide range of conditions, three parameters were identified with a significant influence: pH; ionic strength and dissolution kinetics.

The principal colloid types in the experiments were polyuranates or schoepite (from SF), smectite (from HLW) or magnetite (from container corrosion). The tendency for colloidal formation/association was greatest for the tetravalent elements, with the following general trend:

$$\mathrm{Np(V)} < \mathrm{U(VI)} \leq \mathrm{REE/Am/Cm(III)} < \mathrm{Th(IV)}.$$

Pu colloid formation was more variable, which was attributed to variability of the principal oxidation state between different studies. Generally, colloid-associated radionuclide concentrations tended to decrease with time.

In general, colloid formation was found to be less in experiments at lower pH (i.e. <7), which was attributed to the higher solubility limits for actinide and REEs, and thus a lower tendency towards nucleation, and weaker sorption onto mineral colloids. As expected on the basis of theoretical considerations (see section 3.2.2), colloid concentrations were also lower in solutions of higher ionic strength. Nevertheless, measurable colloidal radionuclide fractions were found in some concentrated brine solutions. This was attributed by Geckeis *et al*. to higher rates of colloid formation than rates of coagulation and sedimentation or attachment to surfaces.

6.4 Colloid generation at the near field/far field interface

In addition to the possibility of colloid generation within the repository near field, colloid generation may also occur due to changes in chemical and physical conditions associated with the interface between the near field and the surrounding host rock. Depending on the type of near field under consideration, two very different situations may arise.

In the case of cementitious repository, a chemically-reactive, alkaline plume will migrate from the near field, which will react with the host rock immediately adjacent to the repository to produce a disturbed or reacted zone, referred to in the UK as the alkaline disturbed zone or ADZ. The presence of chemical gradients between the alkaline, high calcium conditions of the near field and the near-neutral pH conditions of the undisturbed geosphere will have an impact on colloid chemical stability, physico-chemical stability and may provide conditions in which new types of colloidal particles may be formed by primary and secondary generation processes.

In the case of an HLW/SF repository surrounded by bentonite buffer and located in hard rock, there is the potential for colloids to be generated at the host rock interface due to erosion of the bentonite.

Current understanding of colloid generation under these conditions is outlined below.

6.4.1 ADZ in hard rock

Little information is available concerning colloid populations generated at the margins of an alkaline plume in hard rock where geochemical gradients are high and alumino-silicate colloids could form. In a recent survey of laboratory experiments focused on host rock/cement leachate interactions [307], it was noticeable that none had considered studying colloids in this zone. The margins of the alkaline plume have not, as yet, been accessed for colloid studies in the Maqarin natural analogue study.

Arguably, the most appropriate approach to study such a zone would be in a large-scale, *in situ* experiment in a URL (such as the international Hyperalkaline Plume in Fractured Rock (HPF) experiment in Nagra’s Grimsel Test Site – see [308] for details). Unfortunately, this was not included in HPF[12] but may be part of the ongoing Long-term Cement Studies (LCS) experiment at the same site (see [309] for details), so providing input in the foreseeable future.

Unfortunately, no other recent large-scale URL experiments, such as those at Mont Terri in Switzerland [310] or international collaboration projects [e.g. 311, 312] have focused on the issues of ADZ-derived colloids.

6.4.2 ADZ in bentonite/argillaceous rock

Several of the disposal concepts for HLW/SF include a bentonite buffer and bentonite-containing backfill [e.g. 8]. Although the cement-based disposal concept for ILW developed previously in the UK [4,6] has not included bentonite backfill, several others do, citing requirements for improved barrier function [e.g. 313] or for simplifying modelling of the near-field source term. Some concepts envisage disposal in a low permeability argillaceous rock, such as

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[12] An attempt was made to sample for colloids in the latter stages of the project, but it was thwarted by equipment failure.

the Boom Clay in Belgium [314] or Opalinus Clay in Switzerland [315]. In all of these concepts, there are interfaces at which alkaline cementitious porewaters can come into contact and react with clay materials.

Some work has been undertaken on the alteration of bentonite in alkaline leachates [e.g. 316] and in low alkali cement leachates [e.g. 317] and the effect this has on colloid filtration by the bentonite, but only one reported study [318] has looked at the potential production of bentonite colloids during alkaline reaction. That study focused on colloid production due to erosion at the bentonite-host rock interface, and as such, will be discussed below.

6.4.3 Colloid generation from bentonite-host rock interface

Bentonite by its nature is composed of colloidal material (clay particles) that is essentially immobilized as a solid matrix. For clay colloids to be released from the bentonite and migrate into the geosphere they must be dispersed into mobile groundwater. This may occur at the margins of the clay buffer, where the bentonite may contact groundwater flowing in fractures in the host rock, for example. Therefore, work on colloid generation from bentonite [e.g. 44, 319, 320] has focused on bentonite as a source of colloids in the geosphere at the bentonite-host rock interface.

Grindrod and co-workers provide a useful summary of the underlying processes [94]:

> "*Once saturated, the clay extrudes into the available rock fractures, behaving as a compressible non-Newtonian fluid…. Extrusion is halted either when the advancing clay front reaches a narrow enough aperture along the fracture (relative to the yield stress of the gel-like front), or when enough of the clay mass has extruded so as to reduce the density back in the buffer, and hence the swelling pressure (which is exponentially dependent upon density). In the latter case a relatively small reduction in density may be sufficient. As the clay extrudes, the gel-like front may be a source of clay colloids, being sufficiently hydrated so as to allow clay platelets to escape the matrix and diffuse away*."

They demonstrated that such mass loss is limited as a mechanism for leaching away the emplaced barrier, yet may still be significant in mobilising otherwise highly sorbing radionuclides within the buffer.

Some work on bentonite release has been carried out in the CRR (colloid and radionuclide retardation) experiment and new work is ongoing in the CFM (colloid formation and migration) and NF-Pro experiments in the Grimsel Test Site in Switzerland [48,143] and the Colloid Project at the Aspö URL [95].

Recent laboratory evaluations [320, 321], indicate that significant concentrations of colloids (Figure 6.1) can be mobilised at relatively low flow rates. However, it is difficult to compare the results of these two studies directly as the two methods employed are substantially different. Indeed, the results are, to a degree, counter-intuitive insofar that the static experiment (i.e. extrusion of bentonite into a water-conducting feature, but with no flow in the feature) reported a greater mass 'loss' of bentonite than did the erosive experiment (i.e. extrusion of bentonite into a water-conducting feature with water flow to simulate an active groundwater system).

One reported study [48] has looked at the potential production of bentonite colloids during hyperalkaline reaction. In this case, the authors reported the erosion of bentonite gels in NaCl solutions (0.01 to 0.5 $molL^{-1}$) at pH 12 at flow rates of 6.4 to $8.9x10^{-5}$ ms^{-1} and in $Ca(OH)_2$ saturated solution at $2.1x10^{-5}$ ms^{-1}, somewhat higher flow rates than in [321] which estimated that the critical flow rate for erosion to occur and produce bentonite colloids is between $2x10^{-6}$ ms^{-1} (fresh water) and $8x10^{-6}$ ms^{-1} (seawater). Interestingly, in [48], erosion flow rates for bentonite gel in NaCl solutions (again, 0.01 to 0.5 $molL^{-1}$) at pH 6 and 9 are higher still, at 2.1 to $4.4x10^{-4}$ ms^{-1}. Unfortunately, not enough information is presented on the methods employed to ascertain why the differences exist. In any case, the flow conditions necessary to induce erosion are of little relevance to GDFs, where groundwater flow rates will be much lower, but are arguably applicable to surface and shallow repositories such as Drigg (UK) and Rokkasho L1 (Japan).

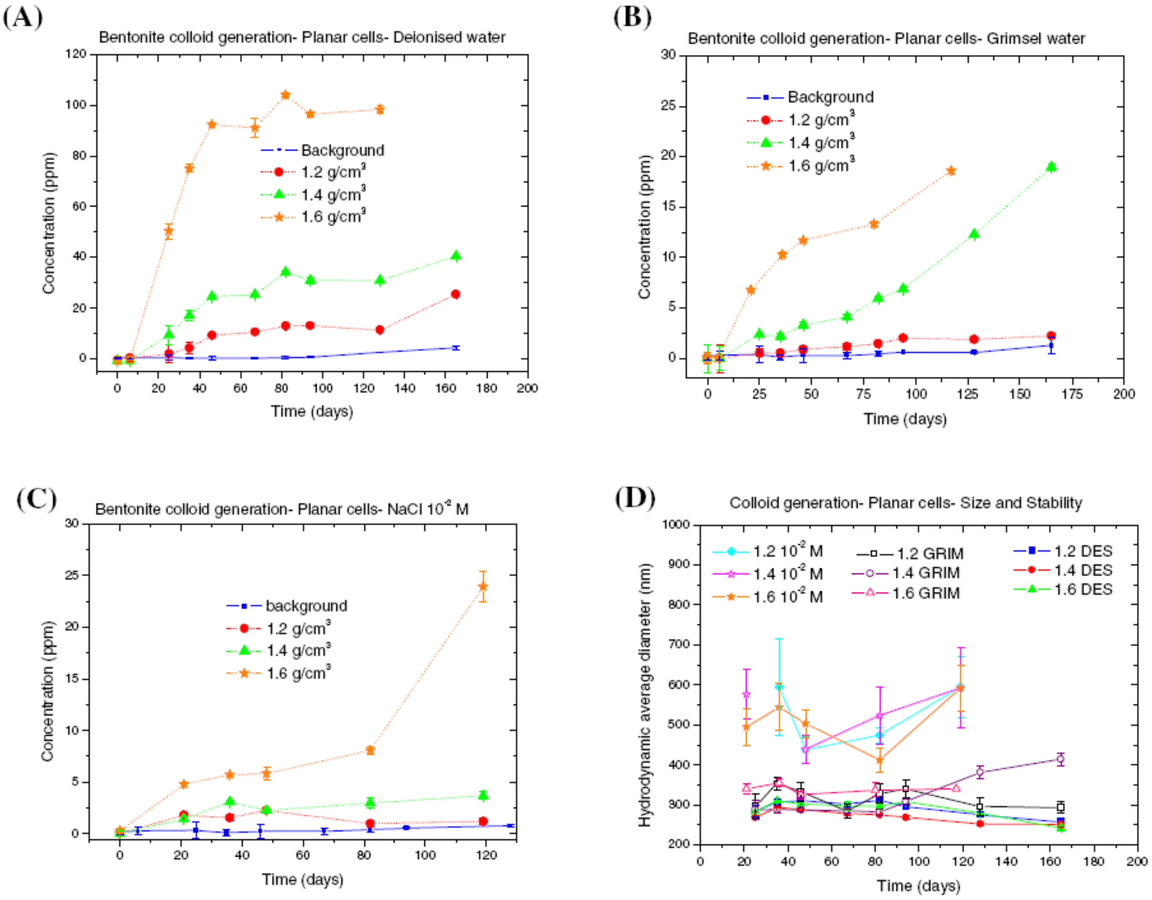

Figure 6.1 **Concentration of bentonite colloids generated in the laboratory under static conditions as a function of time and at different compaction densities [320]: (A) de-ionised water; (B) Grimsel water; (C) 10^{-2} mol dm^{-3} NaCl solution; (D) mean hydrodynamic diameter measured for the colloids generated at different compacted densities and as a function of time, for each water type.**

7 Stability of colloids in the geosphere

7.1 Introduction

In section 3.2, the factors underlying the stability of colloidal dispersions were introduced and the basic theoretical understanding of colloid stability behaviour built up over many years in the colloid science literature was outlined. In this section, the current understanding of the stability of colloids in the geosphere is reviewed. There are two key questions of interest:

- how stable are colloid populations that may be generated in the geosphere?
- are colloids released from the near field potentially stable in the geosphere?

In this section, the focus will be on the phenomenological understanding of colloidal stability in groundwater. However, the potential stability, both chemical and colloidal, of near-field colloids in the geosphere is considered in section 7.6.

7.2 Experimental methods

7.2.1 Aggregation studies

The principal method for studying the physico-chemical stability of colloidal systems is through studies of aggregation as a function of time. Such studies involve following changes in particle size in response to the addition of electrolytes or organic compounds that may potentially interact with the particle surfaces. Commonly used methods include studying changes in turbidity [e.g. 113, 114], scattered light intensity [e.g. 115, 124], or measuring changes in particle size distribution by PCS [e.g. 322, 323, 324]. These techniques are most commonly used to study changes over relatively short timescales of a few hours or days; generally only a small sample volume is required (a few cm^3) contained in a light scattering cell or cuvette. Longer timescales may be investigated through periodic sampling of larger batches of dispersion.

In general, these methods require concentrations of colloidal particles that are significantly higher than have been measured in deep groundwaters. Therefore, they have usually been applied to simulant or model colloidal systems that are chosen to be representative of the types of colloids under consideration. Such simulant systems may be obtained from commercial sources (e.g. colloidal silicas), prepared in the laboratory from standard recipes (e.g. haematite colloids [325]) or prepared by crushing/disaggregation and dispersion (e.g. with ultrasound) from bulk materials. The first two sources have the particular advantage that dispersions can be obtained or prepared with known shape and with relatively uniform particle size. In particular, monodispersed spherical latex particles, which have been widely used in studies of colloid stability (and deposition behaviour), have been available since the 1960s. Standard clay minerals are available from the Source Clay Repository of the Clay Minerals Society [326]; colloidal sized clay fractions can be separated by re-dispersion and progressive centrifugal sedimentation of larger sized fractions. On the Nirex programme, stability studies were undertaken on samples prepared by redispersion of fracture in-fill materials that were composed predominantly of iron oxides and illite clays [50].

Aggregation studies on model monodisperse systems are particularly useful for measuring aggregation rates because the analysis of the early stages of aggregation is relatively straightforward.

The lower the sample concentration, the longer the timescales over which aggregation will occur (see Table 7.1 below). Studying colloid stability at more representative groundwater concentrations, for example, generally requires periodic sampling and examination by more sensitive characterisation techniques such as single particle counting or TEM/SEM (see Table 4.3).

A number of aggregation studies have been undertaken using model colloidal systems as simulants of groundwater or near-field generated colloids to investigate their stability in the presence of varying amounts of calcium to simulate the transition from a low calcium groundwater to a high calcium cementitious near-field porewater [84, 327].

7.2.2 Studies of surface charging properties

Given the importance of the surface charging properties of particles in determining their stability, measurements of surface charge are commonly used to assess the stability of colloidal dispersions [328]. These measurements are most commonly made by electrophoresis techniques, which measure the electrophoretic mobility of dispersed particles in an applied electric field. The electrophoretic mobility can be related directly to the zeta potential of the colloidal particles in the liquid medium, which (as noted previously) is the potential at the surface of shear close to the particle surface and within which the fluid phase is stationary. In the case of a particle undergoing electrophoresis, the kinetic unit consists of the particle plus associated water and entrained ions within the volume bounded by the surface of shear. Thus the electrophoretic mobility (defined as the particle velocity per unit applied field) gives a measure of the net charge of the solid particle.

Up until the early 1990s, the electrophoretic mobilities of colloidal particles were often measured using labour-intensive microelectrophoresis techniques [329], requiring observation of the electrophoretic migration of individual particles. Since the late 1980s, these manual measurements have been largely superseded by laser-based electrophoretic light-scattering techniques. The electrophoretic mobility is determined from the Doppler shift of scattered light (measured with a photomultiplier) arising from particles migrating in an oscillating electric field (see the reviews in [330, 331] for further information). Electroacoustic techniques have also been developed [332, 333], which can be applied to more concentrated samples that are not transparent to light, such as cement pastes.

In a typical stability study [50], the electrophoretic mobility of the colloidal material is measured as a function of pH at different concentrations of varying electrolytes and/or additives (such as natural organic materials) to determine the PZC of the particles, identify which species may be indifferent (i.e. have no effect on the PZC) and which specifically-adsorbed (shift the PZC) and capable of modifying charge characteristics. An example of such a study is presented in Figure 7.1 which shows the effect of natural humic acid at varying concentrations on the electrophoretic mobility of synthetic hematite particles. Here the adsorption of humic acid is found to shift the surface charge of the hematite to more negative values across the whole pH range. As a result, the hematite colloids are stabilised towards aggregation at near-neutral pH, particular at higher humic acid concentrations. This is recognised as an important stabilisation mechanism for iron oxide particles in natural waters [121].

7.2.3 Studies of surface forces

A number of techniques have been developed that allow the forces between two surfaces or between a particle and a surface as a function of separation distance to be measured directly. These methods include the force balance [334] and the atomic force microscope (AFM) [e.g. 335, 336]. These techniques have been used to measure intersurface forces using model systems with well-defined geometries.

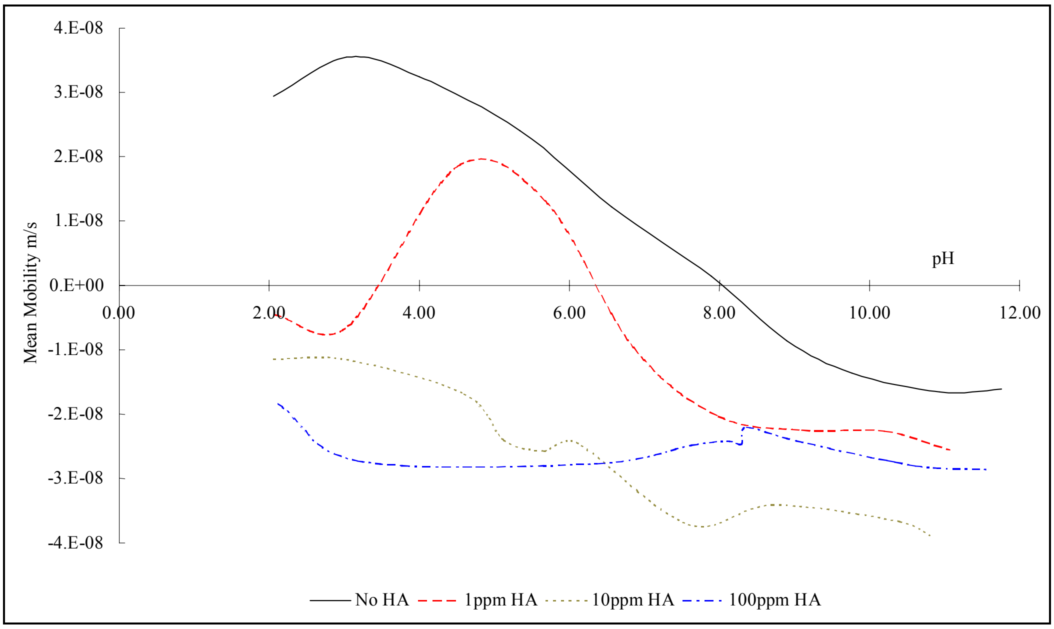

Figure 7.1 Electrophoretic mobility as a function of pH for a synthetic hematite colloid (~130 nm diameter) in contact with different concentrations of Aldrich humic acid (HA) solution measured by micro-electrophoresis

7.3 Results of colloid stability studies

A large number of studies of colloid stability are reported in the literature. For the purpose of this review we shall focus on current understanding of the stability behaviour of two types of inorganic colloids that are particularly important in the context of geological disposal: silica, which is commonly identified as a component of geosphere colloid populations (see section 5.2.4 and Table 5.1); and bentonite. A discussion of stability behaviour of colloids derived from fracture in-fill materials studied on the Nirex programme [50] is given in the previous thematic report [49].

7.3.1 Silica colloids

The ready-availability of synthetic monodisperse colloidal silicas of varying but small particle size (8-120 nm) from commercial sources and suitable methods for making larger-sized particles in the laboratory [e.g. 337] have meant that amorphous silica sols have been widely used as model systems in colloid science and their coagulation behaviour has been studied extensively [e.g. 50,124, 322, 338]. However, as noted in section 3.2.2, silica is something of a special case in terms of its colloidal stability, because it displays complex and often anomalous behaviour compared to the predictions of DLVO theory. There is a significant variation in behaviour with particle size, pH, surface treatment and the nature of the coagulating ion [124, 339, 340]. Recent work has started to distinguish different aspects of the silica colloid stability behaviour and provide an understanding of the underlying processes [341].

Small particles of colloidal silica show anomolously high stability at low pH and a decrease in CCC values with pH for a given electrolyte that is contrary to expectations of DLVO theory. This is illustrated in Figure 7.2, which shows the CCC values for 15 nm-sized silica colloids as a function of pH with NaCl as the coagulant, one and twenty four hours after mixing [124].

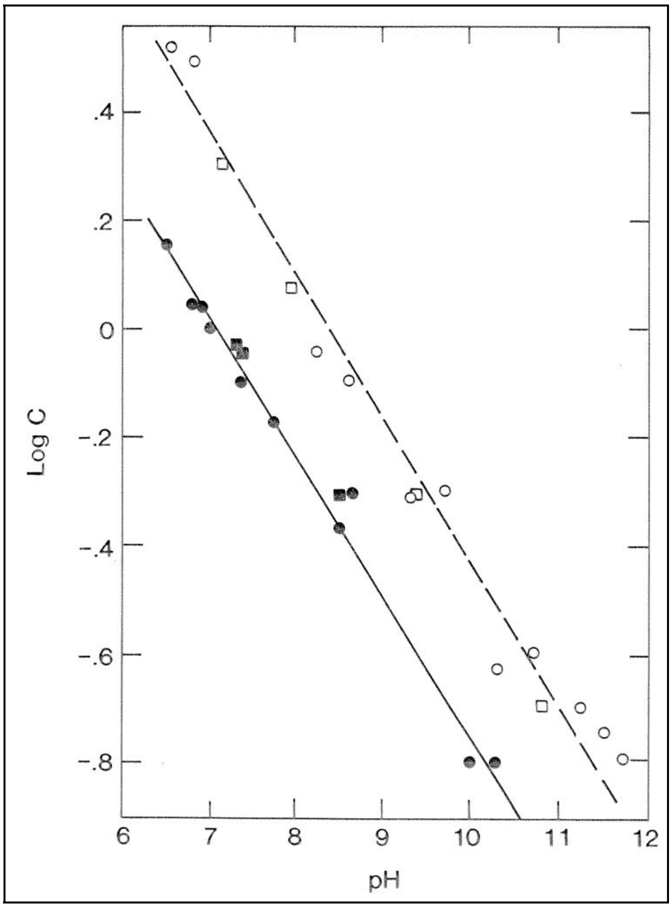

Figure 7.2 Critical coagulation concentrations as a function of pH for colloidal silicas measured 1 hour (open symbols, dashed curve) and 24 hours (closed symbols, full curve) after mixing. Results are for a constant silica concentration of 0.2% w/v (redrawn from [124])

In fact, over the whole pH range from 6-10, the CCC values in NaCl solutions are greater than 0.1 mol dm^{-3}, significantly higher than those expected on the basis of DLVO theory [338].

Silica has a PZC at a pH value of ~2 to 3 and possesses a negative charge at higher pH. Thus, EDL interactions are expected to be low at the PZC and DLVO theory would predict coagulation under these conditions with increasing stability at higher pH contrary to the results in Figure 7.2.

Electrophoretic mobility measurements found that above pH 6 the potential of the silica particles is negative, virtually constant and independent of pH in the absence of added salt [124]. Addition of electrolyte causes a reduction in the electrophoretic mobility that is independent of pH. However, the CCC is strongly dependent on pH and so there is no correlation between the electrokinetic properties of the particles and the stability of the silica dispersion. In other words, the stability of the sol is not determined by the variation of EDL interactions as expected by DLVO theory. Additional repulsive forces must act to stabilise the silica particles.

In the same study [124], different coagulation behaviour was observed when KCl or CsCl were used as the electrolyte in place of NaCl (or LiCl). In particular CCC values were about an order of magnitude lower at pH 7, a minimum in CCC was observed at pH 9 and greater stability at higher pH. Similar variations in behaviour with cation type have been observed subsequently for small particles [339, 341], however, the extent of anomalous stabilisation appears to be less for larger particles [340, 341].

A particularly illuminating study was published in 1991, which looked at the effect of particle size on the aggregation of silica and polystyrene latex particles, by measuring the initial rate of coagulation as a function of pH and electrolyte concentration [342]. It was found that under conditions of fast aggregation, particles larger than 100 nm had a rate constant consistent with that expected for diffusion-limited aggregation. However, for particles of less than 100 nm (silica or latex) measured rate constants for fast concentration were significantly lower than predicted and were constant over a range of pH. These findings indicated the presence of either additional short-range forces between the particles that prevented attachment and/or that primary minima for particle attachment were shallow such that attachment was reversible. It was suggested that these effects became important for the smaller particles due to their size.

Various explanations have been proposed in the literature for this unusual behaviour of silica, including the presence of viscous layers of structured water associated with the silica surface or with adsorbed cations. Some clarification of the underlying processes was provided during the 1990s, when it was shown from force balance measurements between silica surfaces that a gel-like layer of protruding polysilicic acid chains may be formed, which provides an additional short range repulsive interaction [343]. Kobayashi and co-workers [341] have suggested that this steric mechanism is more important at low pH, whereas at higher pH, electrostatic repulsive forces dominate and aggregation is more "DLVO-like".

In the presence of calcium, CCC values for silica are lower than in the presence of monovalent ions, but for small particles still show the anomalous CCC-pH trend, decreasing from nearly 0.1 mol dm^{-3} at pH 8 to less than 10^{-3} mol dm^{-3} over the pH range 10 to 12 (1 hour after mixing) [124]. Baranay *et al*. [340] report a ratio of 50 between the CCCs in the presence of K and Ca for 265 nm particles at pH 7-11 and suggest that the "…*'so-called' structural forces are much less important for large silica particles*".

Silica is frequently used as a model system in experiments, but its stability behaviour is anything but simple. The above discussion illustrates the potential difficulty in predicting the stability behaviour of a colloid population in groundwaters based on DLVO theory given the potentially complex interplay between pH, solution composition, particle compositition and size. For characterising potential colloid behaviour at a potential site, it is important that the stabilities of suitably representative colloids and preferably natural colloid populations are studied under a range of conditions that are representative of those in deep groundwater.

7.3.2 Bentonite colloids

Owing to their proposed use as buffer materials, the colloidal dimensions of the constituent particles and potential for colloid generation at the interface between the buffer and the host rock, the stability of bentonite and montmorillonite (the principal clay mineral component) colloids has been of significant interest. Numerous studies of bentonite or montmorillonite colloid stability have been reported over the last 25 years [e.g. 80, 327, 344]; work carried out on the Swedish programme has been reported recently [,345, 346, 347, 348]. Lagaly and Zeismer [349] have reviewed the coagulation of sodium montmorillonite by inorganic and organic cations and the influence of a range of compounds of practical interest including phosphates, cationic and anionic surfactants, betaine-like molecules and carboxy methylcellulose.

Degueldre [80] presents the results of batch aggregation tests carried out with montmorillonite colloids to determine attachment factors as a function of the monovalent and divalent cation concentrations in solution but at a constant pH of 8. Experimental details are not provided in [80], but it is stated that the colloid concentration for a given size (which was 100 nm) was measured as a function of time; larger particles resulting from aggregation were not counted. Attachment factors, α, were calculated by model fitting to the decay in the concentration of the

100 nm size fraction with time. The resulting attachment factors as a function of solution composition are presented schematically in Figure 7.3.

Similar to the results of Ramsay *et al*. [327], the montmorillonite colloids were found to be very sensitive to divalent metal ion (Mg, Ca) concentration at values of the order of 10^{-4} mol dm^{-3}. In the absence of calcium, in line with the Schulze-Hardy rule, a significantly higher concentration of monovalent cations (Na, K), $>10^{-2}$ mol dm^{-3} was required to induce aggregation .

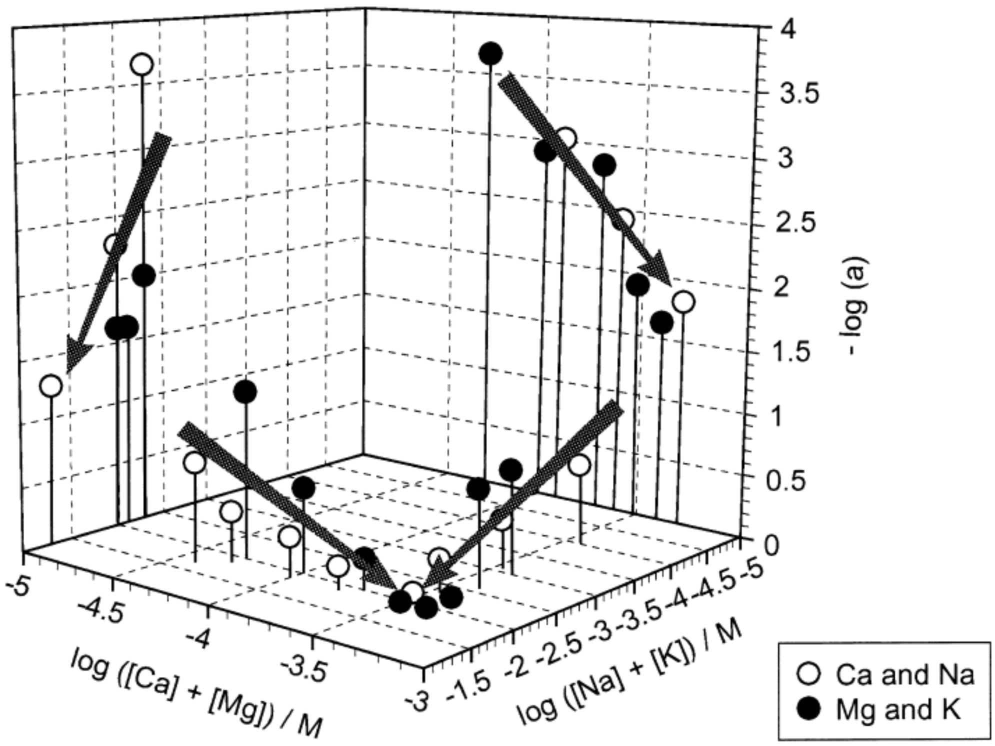

Figure 7.3 The effect of monovalent (Na, K) and divalent (Mg, Ca) cation concentrations on the attachment factor, *α*, for montmorillonite colloids; the arrows denote decreasing stability [80]. Experimental conditions: colloid size ≥100 nm, initial colloid concentration 10 mg dm^{-3} with pTOC <4.3 and pH 8.0, precision ±20%

An upshot of the low CCC for montmorillonite in the presence of calcium at near-neutral pH values is that dispersion of montmorillonite into the colloidal state requires that the bentonite is in a sodium (or potassium) form [349], Ca-montmorillonite being resistant to dispersion.

In a recently published study [348], increased stability of Na-montmorillonite dispersions was found following exposure to γ-irradiation (doses of 0-53.2 kGy ^{137}Cs). This finding was ascribed to an increase in surface potential of the particles as a result of interaction with aqueous radiolysis products. Similar increases in stability of montmorillonite dispersions were found on treatment with ozone [344], which was also found to increase the surface charge and leach ions from the crystal structure. Ozonation was found to have the largest effect on coagulation behaviour in the presence of sodium ions, less effect in the presence of divalent calcium ions and minimal impact in the presence of trivalent lanthanum ions.

7.4 Understanding of colloid populations in terms of colloid stability

7.4.1 Correlation between colloid populations and water composition

Examining the colloid populations measured in a range of groundwaters worldwide, Degueldre and co-workers found evidence for a correlation between measured colloid number concentrations and the groundwater composition, in particular the concentrations of mono- and divalent cations [80, 180]. This is illustrated in Figure 7.4 which shows colloid populations varying over about four orders of magnitude depending, in particular on the calcium (and/or magnesium) concentration[13]. The shape of this 3-D population/composition surface is remarkably similar to the surface of attachment factors measured for montmorillonite dispersions and illustrated in Figure 7.3.

These results presented in Figure 7.3 and Figure 7.4 have been interpreted as showing a strong correlation between colloid stability (in terms of the aggregation rate) and concentrations, in terms of particle number, in natural groundwaters.

To understand this relationship, Degueldre considered from a theoretical viewpoint the effect of colloid aggregation kinetics on colloid population [80]. Given that colloid aggregation is a second order process, for an initially monodisperse population of spherical particles, the variation in monodisperse fraction concentration, C_{col}, with time can be expressed as [350]:

$$\frac{dc_{col}}{dt} = -\frac{4\alpha k_b T}{3\eta} c_{col}^{\ 2}, \tag{7.1}$$

where η is the solution viscosity, T is the temperature (in Kelvin) and k_b is Boltzmann's constant.

Solving Equation (7.1), a colloid population "half-life" for an aggregating dispersion with an initial concentration $c_{col,o}$, can be expressed as a function of the attachment factor, α, as follows:

$$t_{1/2} = \frac{3\eta}{4\alpha K_b T c_{col,o}}. \tag{7.2}$$

Degueldre [80] has used equation (7.2) to calculate half lives for various sizes and concentrations of colloidal particles as a function of the attachment factor. The calculations assumed monodispersed spherical particles in water with a density of 2 g cm^{-3}. The results are reproduced in Table 7.1.

Equation (7.2) indicates that the population "half-life" is inversely proportional to the colloid number concentration (n.b. aggregation is a second order process); as a result, the lower the concentration, the longer the lifetime of a dispersed particle against aggregation.

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[13] The recent analysis presented in Figure 5.1 and discussed in section 5.2.1, confuses the picture somewhat. This is partly because the populations are presented in mass terms in relation to ionic strength and the concentrations of divalent and monovalent ions are not distinguished. Thus the key features of the correlation between number concentration and solution composition have been obscured. A more useful analysis would be to co-plot the new data onto a 3-D chart such as Figure 7.4.

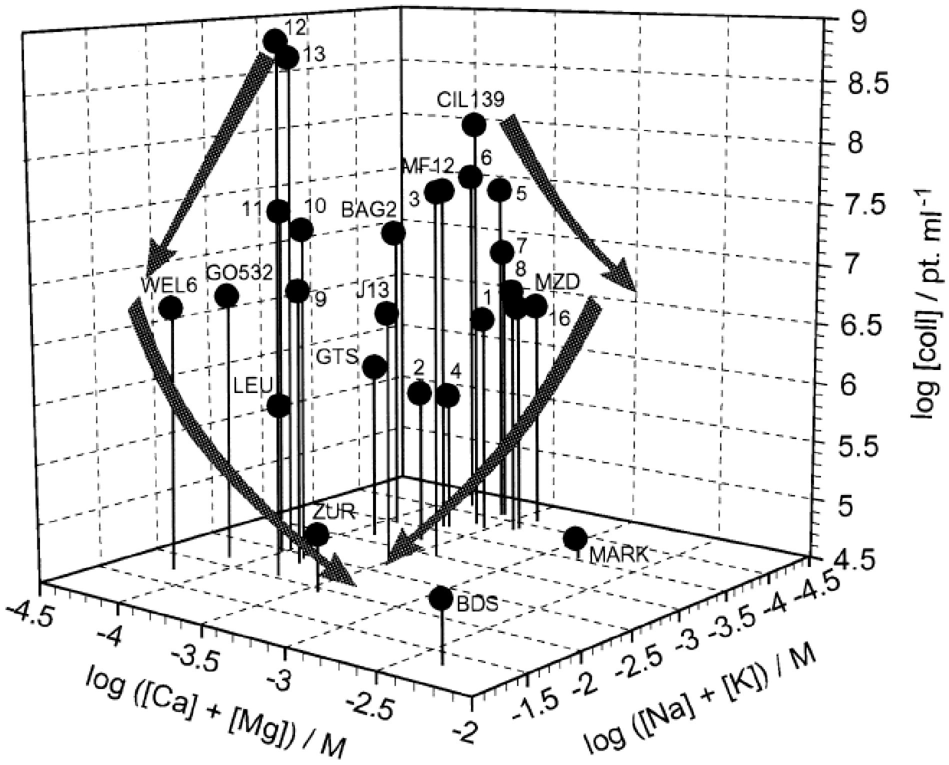

Figure 7.4 The effect of groundwater compositions on natural colloid (>100 nm nominal size) concentrations; the arrows denote decreasing stability [80]. Locations: Switzerland - Transitgas tunnel (1±16), Grimsel Test Site (GTS), Leuggern (LEU), Zurzach (ZUR), Wellenberg (WEL6); Canada - Cigar Lake (CIL139); Nevada, USA (J13); Germany - Gorleben (GO532), Menzenschwand (MZD), Bad Sackingen (BDS); UK - Markham (MARK); Brazil - Morro do Ferro (MF12); Gabon - BagombeÂ (BAG2). Precision on colloid concentration about 10%

Table 7.1 Calculated half-lives of colloid populations for monodispersed colloids of different size and concentration as a function of attachment factor, *α* (after [80])

Particle size	Colloid concentration		Population half-life		
(nm)	Mass (mg dm^{-3})	Number (dm^{-3})	$\alpha = 10^{-6}$	$\alpha = 10^{-4}$	$\alpha = 1$
100	0.1	$7.5\ 10^{10}$	80 y	300 d	40 min
100	1.0	$7.5\ 10^{11}$	8 y	30 d	4 min
100	10	$7.5\ 10^{12}$	0.8 y	3 d	0.4 min
10	0.1	$7.5\ 10^{13}$	700 h	400 min	2 s
10	1.0	$7.5\ 10^{14}$	70 h	40 min	<1 s
10	10	$7.5\ 10^{15}$	7 h	4 min	<1 s

7.4.2 Contribution of the smallest particle size fraction

The results of prediction of population half-lives in Table 7.1 have potential implications for the particle size distribution of natural colloid populations. If colloid concentrations are compared on a mass basis, it will be noted that populations of smaller particles will aggregate more rapidly than populations of larger ones of similar initial mass concentration. This has been illustrated more clearly in simulations carried out by Filella and Buffle [97].

Filella and Buffle simulated the development of particle size distributions with time based on a classical coagulation/sedimentation model in which coagulations kinetics were described by Smoluchowski's equations [112] and sedimentation by Stokes' Law. For the simulations, an initial particle size distribution with $\beta = 4$ (Equation (3.1)) was used, which contains equal particle volume (or mass) in logarithmically increasing size grades, over the size range from 1 nm to 100 µm. The total mass of the size distribution was chosen to be 3 mg dm^{-3} initially and a uniform colloid attachment factor was assumed for all particle sizes with a value, $\alpha = 0.05$, a value that was typical of those measured for surface waters. Figure 7.5 illustrates the evolution with time for the initially continuous size distribution.

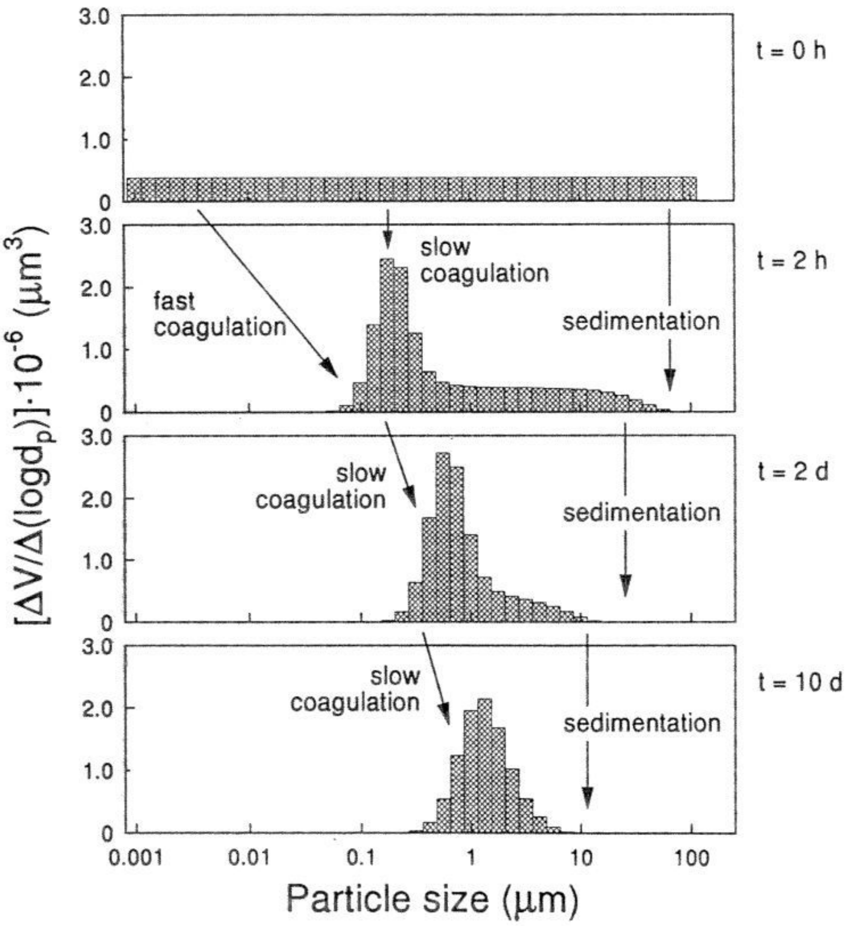

Figure 7.5 Simulation of evolution of a particle size distribution with time by aggregation and sedimentation for an initially continuous distribution, with $\beta = 4$ and size ranges from 1 nm to 100 µm, (from [97]); other parameters: initial total mass 3 mg dm^{-3}, $\alpha = 0.05$, particle density 1.5 g cm^{-3}, mean velocity gradient 10 s^{-1}, temperature 15°C. The terms fast and slow coagulation are used here to provide a qualitative description of the kinetics of the process.

Filella and Buffle identified three different coagulation/sedimentation regimes [97]:

(i) initially small particles that coagulate rapidly to form more stable agglomerates of about 100 nm with the near-disappearance of the smallest size fraction (in mass terms);

(ii) particles with intermediate size (100-700 nm) that coagulate slowly to agglomerates hardly larger than the initial particles; and

(iii) initially larger particles (>700 nm) that are mainly affected by sedimentation.

In number terms, the number of particles in the smaller size classes decrease to similar concentrations as the larger particles at the front of the peak (i.e. on the low size side). Essentially, for the smallest size classes, the particle size function becomes a constant, which decreases with time.

The predicted behaviour was found to agree "*reasonably well*" with natural distributions obtained for surface waters that showed peaks in size distributions at sizes greater than 100 nm.

Examination of the effect of initial particle concentration on the evolving distribution found that a three-fold increase in colloid concentration, from 0.01 to 10 mg dm^{-3} had a greater effect on the larger particles than the smaller ones, the latter disappearing rapidly under all conditions. In all cases log-log plots of particle number concentrations against size showed a drop in gradient towards a flat line at the lowest particle size with coagulation time.

As discussed in section 4.3, the measurement of the smallest particle sizes in colloid populations is difficult due to the limiting size resolution of many colloid analysis techniques, and this is a potential source of uncertainty concerning the potential impact of colloids. The analysis by Filella and Buffle suggests that, on theoretical grounds, significant populations of very small particles (i.e. <100 nm) are unlikely to be present in groundwater colloid populations due to rapid coagulation. However, in the case of silica colloids at least, as discussed above, significantly enhanced stability has been found for the smallest sized particles and k_f values (Equation 3.4) have been found to be significantly lower than predicted by Smoluchowski kinetics[14]. Thus for silica, the assumption of a uniform coagulation rate for all values of particle size, does not hold. A key question then is whether the behaviour observed for silica and also for latex particles is general or a special case?

Studies that have considered the effects of particle size on colloid stability with materials other than silica and latex are rare. However, a recent study considered the possible effect of particle size on the aggregation of 3 different sizes of hematite 'nanoparticles' (mean size 12, 32 and 65 nm) between pH 5 and 9 in NaCl solutions [75]. These authors saw rapid aggregation of hematite at pH values close to the PZC (at pH 7.7-9 for 12 nm particles, pH >8.5 for 65 nm) and increasing stability at lower pH values broadly in agreement with DLVO theory. At a fixed pH of 5.7, they also noted a decrease in CCC with decreasing particle size in line with theoretical predictions (from 70 mmol dm^{-3} for 65 nm to 45 mmol dm^{-3} for 12 nm), although this is also related to a shift in measured PZC to lower values for the smaller-sized particles. Overall, there is no evidence to suggest increased stability for the hematite particles with smaller size in contrast to results with silica. The results are qualitatively in agreement with DLVO theory.

The above set of results suggests that the anomalous increase in stability of small silica and latex particles is not a general phenomenon and is probably related to the properties of the solid phase in each case. In the case of a silica-rich colloid population, it would appear possible that

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[14] Colloidal dispersions of small silica particles are readily produced and are stable as concentrated dispersions (up to 50% w/v), usually at high pH (>10), for periods of years.

small particles, <100 nm in size, may form a significant proportion of the colloid fraction. Whether or not this may be the case for other colloid types appears to remain something of an open question? However, in natural systems, other factors such as chemical stability determined by mineral phase solubility may also be significant.

It is interesting to note that the stability ratios for the hematite particles at pH 5.7 reported in the study above [75] increase by 4 orders of magnitude as the electrolyte concentration is reduced by a factor of 10 below the CCC; $W = 10^6$ for 12 nm particles in 10^{-3} mol dm^{-3} NaCl solution. The results indicate a relatively sharp transition between stable and unstable regimes as a function of a change in either pH or ionic strength close to the PZC and CCC respectively.

7.5 Conclusions concerning geosphere colloidal stability

Although Smoluchowski kinetics and DLVO theory provide a qualitative understanding of colloid stability behaviour, a range of factors not accounted for in the simple theory (variations in particle shape, surface roughness, inhomogeneities of surface charge, etc) become important in controlling aggregation rates [107]. Since theory does not allow reliable calculation of attachment factors under less favourable conditions, for prediction of colloid behaviour in the field, aggregation rates may need to be measured.

To characterise potential colloid behaviour at any candidate site for a GDF, it may be necessary to study the stabilities of suitably representative colloids under a range of conditions that are fully representative of those in deep groundwaters at the site. Although studies of natural colloid populations would be preferable, owing to the low number concentrations measured in deep groundwaters, and difficulties associated with groundwater handling, the practical challenges would be significant. An approach which has been used on the Swedish and Nirex programmes has been to generate colloids from appropriate buffer or fracture in-fill materials and use these in aggregation studies.

A reasonable understanding has been obtained of the physico-chemical stability behaviour of some of the principal colloid types present in deep groundwater, including silica, smectite clays and iron oxides over the range of chemical conditions that is typical of deep groundwaters. In the absence of significant concentrations of natural organics, there appears to be a correlation between colloid populations in number terms and groundwater composition, in particular the concentrations of mono- and di-valent cations (in qualitative agreement with DLVO theory). However, for any given groundwater system, stability will be dependent on the mineralogy of the principal colloid types and pH (in particular where the PZC is in the near-neutral pH range) and, for certain colloid types (iron oxides) the presence of organic materials that may sorb onto and alter colloid surface charge and stability. The significance of particle size on colloid stability and the potential importance of the smallest size fraction remains something of an open question.

When the ionic strength is high, it is expected that colloids will be destabilised and populations will be very small. This is borne out by the very low colloid concentrations that have been measured recently in the deeper, more saline, groundwaters at Äspö (example 3 in Table 5.1) [144].

7.6 Stability of near-field colloids in the geosphere

7.6.1 Colloids from a cementitious near field

As noted in sections 3.2.1 and 3.6, colloidal particles are thermodynamic metastable with respect to bulk solid phases owing to their higher surface free energy, which increases with decreasing particle size. Thus, colloidal particles of all types have a tendency to dissolve at some rate, with preferential growth of larger particles and bulk solids at the expense of smaller particles. The dissolution rate of particles will depend on their mineral composition and solubility at the pH at which they are dispersed, the solution composition and the extent of undersaturation with respect to the colloid mineral phase(s), particle size and temperature. The rate of dissolution will tend to accelerate when colloids migrate from their source into groundwater that is undersaturated with respect to colloid mineral phases.

In the case of colloids generated in a cementitious near field, transport into the geosphere would be accompanied by a significant change in chemical conditions, e.g. from the high pH, CSH-dominated environment of a cementitious near-field to the near-neutral pH primary silicate-dominated environment of a hard rock geosphere. Thus any cementitious phase colloids that were sufficiently mobile to reach the geosphere would be expected to dissolve there. For this reason, in the last Nirex assessment to include a treatment of colloid-facilitated transport, Nirex 97 [55], near-field colloids were assumed to dissolve and release their radionuclide burden on migration into the far field.

Some attempts have been made to study the stability of cementitious colloids on changing chemical conditions from those of the near field to those of the far field by means of diafiltration (i.e. by washing colloids retained above an ultrafiltration membrane with simulated groundwater), but details have not been published. Such studies have been hampered by the very low concentrations of near-field colloids produced in leachates and high colloid losses during the diafiltration procedure under control conditions (i.e. without changing the water composition). Thus, to date, the above hypothesis has not been tested experimentally.

The physicochemical stability of colloids generated from high fused silica content (HFSC) cement backfill, under consideration in Japan, was studied by as a function of calcium concentration by aggregation studies by PCS [291]. The CCC for these colloids at near-field pH was found to be about 5 × 10-4 mol dm^{-3} calcium. This concentration was expected to be significantly less than near-field calcium concentrations and therefore HFSC-colloids are not expected to be stable in the near field.

Studies of colloids from the cementitious M1 mortar backfill under consideration in Switzerland included measurements of particle concentrations as a function of settling time after end-over-end shaking [39]. The observed decline in particle concentrations with time was attributed to an aggregation-sedimentation process controlling the colloid inventory to low levels.

The surface potentials of a range of cementitious materials including ordinary portland cement (OPC), 9:1 BFS (Blast furnace slag):OPC grout and CSH gels have been studied at alkaline pH [291]. In general, these materials have positive zeta potentials at high pH owing to the presence of calcium surface sites. If present as colloids, migration from high pH and high calcium conditions to lower pH and low calcium concentrations, is expected to lead to preferential leaching of calcium from the surface of these materials and a lowering of the surface potential. At some point during migration, such colloids would be destabilised at their PZC.

Thus near-field colloids derived from cementitious materials are not expected to be thermodynamically stable in the geosphere, have limited stability iin the near field and are expected to be destabilised by changes in surface charge on migration from the near field to the far field.

7.6.2 Colloids from a HLW/SF near field

In the presence of a bentonite buffer, colloids generated in the near-field of a GDF for HLW or SF would not be expected to be mobile into the far field due to the barrier properties of the bentonite buffer. If a bentonite buffer was not present in the chosen disposal concept (as in the US programme) or its barrier function was potentially compromised (e.g. by erosion), then colloids generated from the near field could potentially migrate into the geosphere. In these cases, the potential impact of near field colloids would need to be considered in more detail.

The principal colloid types generated would be uranium minerals (from SF), smectites (from vitrified wastes) and iron oxides (from container corrosion). As noted previously, iron oxide colloids, which have a PZC typically of about pH 9 and are positively charged at lower pH are not expected to be mobile in a geosphere comprised of primary silicates or secondary clay minerals owing to favourable electrostatic attachment to rock surfaces. On the other hand, should they be able to migrate into the far field, smectite-like colloids derived from HLW degradation would be expected to be exhibit similar stability to geosphere colloids due to their similar mineral composition to natural clay mineral colloids. It was noted on the US programme that the critical ionic strength for colloids derived from HLW glass corrosion was about 0.05 mol dm^{-3}, above which colloids were unstable [351]].

The PZC of uranium(VI) oxide hydrates are typically around pH 4 [352]. Colloidal suspensions of meta-schoepite [$(UO_2)_4O(OH)_6.5H_2O$] and uranium dioxide (UO_{2+x}) that are typical of colloids released from spent fuels were found to be stable at pH values greater than 5.5 exhibiting zeta potentials of -30 to -60 mV [353]. Thus, uranium mineral SF-derived colloids are also potentially colloidally stable under geosphere conditions and would be expected to exhibit similar stability behaviour to natural colloids. However, given that uranium-based intrinsic colloids moving into the geosphere would be moving from source into water unsaturated with respect to uranium minerals, dissolution of the particles would be expected at some rate. Dissolution kinetics will be a key factor, therefore, in determining particle lifetimes, if such colloids are able to migrate into the geosphere.

8 Radionuclide uptake onto colloids

8.1 Introduction to sorption onto colloids

This section deals with radionuclide sorption onto carrier colloids present in groundwater. The focus is mainly on inorganic colloids. Naturally-occurring organic colloids such as humic acids may be present, although most probably not in large quantities in a deep geosphere scenario. In addition, the subject of humic acids and similar organic materials is a very extensive one and is largely outside the scope of this report. A brief discussion on naturally-occurring and near-field derived organic colloids is included however.

Some long-lived radionuclides will eventually migrate away from the near field of a GDF in solution in the porewater and enter the surrounding geosphere. Here they will come into contact with rock surfaces and mobile colloidal particles dispersed in the groundwater. Disposal concepts are such, however, that the quantity of radionuclides migrating away will be minimised. One of the principal mechanisms for retarding radionuclide migration from such a waste repository is through sorption onto the surfaces of the surrounding rock. Many performance assessments use an assumption of reversible radionuclide sorption onto solid surfaces in the geosphere and adsorption isotherm models. Irreversible sorption or slow desorption from the rock would lead to an under-estimate of radionuclide retardation. Some elements demonstrate significant differences between their sorption and desorption behaviour, even those with ‘simple’ chemistry such as caesium. This effect has been shown, for example, for caesium sorption onto smectite [354].

In principle, radionuclides can sorb onto the surfaces of colloids by the same processes by which they can sorb onto the solid surfaces of the host rocks (i.e. surface complexation and ion exchange). Radionuclides can also complex to natural organic molecules that are present as colloids or attached to inorganic colloidal particles. However such sorption behaviour onto colloids presents the opposite position to that onto the geosphere if the colloids are both stable and mobile [49]. There is therefore the potential for colloids, if present in sufficient quantities and radionuclides are strongly sorbed, to impact on radiological risk through providing an additional migration mechanism. This is especially the case if the radionuclide becomes part of the 'core' of the colloid rather than on the surface, and is therefore not available for desorption.

Since the ratio of surface area to volume is higher for colloidal material than for host rock surfaces, the sorptive capacity per unit mass of colloidal material is expected to be higher. Such a 'scaling approach' has been employed previously in performance assessments to estimate the sorption capacity of mobile colloids [55]. Therefore, assuming reversible sorption for each radionuclide, this could be expressed by:

$$K_{nc} = F.K_{nr} \tag{8.1}$$

where K_{nc} is the sorption distribution coefficient for partitioning between the solution phase and the colloidal material, F is a scaling factor taking account of surface area to volume ratio, and K_{nr} is the 'conventional' distribution coefficient for sorption onto the host rock (often reported as an Rd value).

Laboratory sorption measurements of Rd values onto rock surfaces or colloids typically give values for the degree of sorption but do not provide information on sorption mechanisms. Methods for measuring Rd values are summarised in reference [355]. Values generated are usually regarded as conservative. However it should be recognised that care should be exercised in using the Rd concept, especially in describing sorption onto colloids. This is because the Rd value is dependent on available surface sites for sorption which are in turn dependent on pH, particle size, mineralogy and morphology. It is a macroscopic parameter that gives only limited understanding of radionuclide-solid phase interactions.

As stated earlier, if irreversible sorption or slow desorption were to occur to rock surfaces, it would tend to be favourable for safety assessment considerations. The significance of any such irreversible sorption processes to colloids and their impact on radiological risk is perhaps the most difficult question to answer experimentally. This is due, in part, to the relatively short timescales over which sorption processes are amenable to study in laboratory experiments. Processes that may appear to be very slow or irreversible over short timescales in the laboratory may nevertheless be fully reversible over the longer timescales relevant to transport in deep groundwater. Studies of natural analogue sites provide a means of studying chemical equilibria in natural groundwater systems [e.g. 53, 253] . Information regarding whether uranium or thorium bound to natural colloid populations are in thermodynamic equilibrium with dissolved species can, in principle, be obtained from studies of isotope distributions (uranium series disequilibrium studies). However, natural uranium or thorium concentrations in groundwaters are frequently too low for such information to be obtained.

In general, radionuclides sorbed onto the surface of particles are expected to be in thermodynamic equilibrium with the solution phase. The treatment of radionuclide sorption onto host rock surfaces is therefore usually based on the assumption of reversible linear sorption described by a distribution coefficient for each radionuclide [e.g. 55, 356, 357]. However, as noted in section 3.7, there are number of mechanisms, in addition to kinetic considerations, by which sorbed species can be removed from thermodynamic equilibria so that the radionuclide-colloid interaction effectively becomes irreversible over a given timescale [80].

In a recent review [60], it is pointed out that laboratory experiments are needed to elucidate the underlying sorption mechanisms. A quantitative description of solid-liquid interface reactions based on surface complexation models (e.g. in [358]) can only be applied if sorption mechanisms are fully understood and the sorption reaction can be described by dynamic equilibrium complexation constants. Without such knowledge, the development of surface complexation models is hampered by uncertainties over the relevant surface species. In addition, surface complexation models do not account for sorption / desorption kinetics – a main source of concern [60].

8.2 Methods

8.2.1 Batch sorption studies

The most common method for studying the sorption of radioelements onto either geological or cementitious materials is the batch sorption method [355]. This technique measures the distribution of an element between the solution phase and the surface of a crushed solid such as a cement or rock. The radioelement should be added to the solution phase to give a concentration that is below its solubility limit under the experimental conditions. The solution phase is analysed at the outset of the experiments (before contact with the solid) to determine the initial radioelement concentration. The solution is then added to the solid and equilibrated for the required time which may vary from a few hours to many months. The experiment may be undertaken in air, but frequently inert-atmosphere gloveboxes are used. After the equilibration period, a portion of the solution phase is removed and passed through a pre-treated filter to separate the solution phase from any suspended solids. The final concentration of radioelement is solution is then measured by a suitable analytical technique. The experimental container can also be washed to remove the bulk solid and leached with acid (or alkali, if appropriate) to measure any radioelement sorbed to the container walls. The amount of radioelement sorbed to the solid phase can then be calculated from the depletion in the solution phase concentration. The distribution is usually expressed in terms of a sorption distribution ratio or R_d value, calculated from:

$$Rd = \frac{(C_o - C_t)}{C_t} \cdot \frac{V}{m}, \qquad (8.2)$$

Where C_o and C_t are the initial and final concentrations, V is the volume of solution and m is the mass of solid.

The batch sorption method can also be used to measure radioelement sorption onto colloidal particles, the crushed solid phase being replaced with a dispersion of the colloids of interest [e.g. 48, 354]. However, for sorption onto the colloidal phase to be clearly distinguished, the concentration of the colloid dispersion may be required before use in the experiments. Desorption experiments can be carried out in a similar manner [354], allowing for measurement of the low concentrations of desorbing radionuclides.

8.2.2 Uranium-series disequilibrium studies

Studies of uranium series isotope distributions in groundwaters have been carried out alongside colloid sampling programmes at a range of sites world-wide. Colloid studies at natural analogue sites such as El Berrocal in Spain [53, 359] and Cigar Lake in Canada [253] have provided particular opportunities to investigate radiocolloid formation and migration in natural systems. The association of natural uranium and thorium with a range of natural colloid types and under a variety of groundwater chemistries has been studied.

During field collection of groundwater colloids, the existing geochemical equilibrium in the groundwater/particulate/rock system must not be significantly altered if a realistic analysis is to be obtained [49]. Colloid concentrations in groundwaters are often low, and therefore, contamination of the samples must be kept to a minimum at all stages, from collection and storage through to handling and analysis, as discussed in section 4.

The volume of colloid sample required for physical and chemical characterisation is small (10-10^2 cm^3), but measurement of actinide activities by isotope dilution/alpha spectrometry techniques requires much larger volumes (10^2-10^3 litres). Therefore, both large and small volume samples are normally collected. The precision of colloid and actinide activity analysis can be improved by concentrating the colloids contained in a large volume of groundwater using tangential flow ultrafiltration [360]. Measurements of thorium and uranium concentrations in colloid concentrates and ultrafiltrates can be used to determine the distribution of these elements between solution, colloidal and suspended particle phases.

8.2.3 Mechanistic studies

Work has been done to investigate the mechanisms of sorption of radionuclides to colloids under geosphere conditions by investigating radionuclide interactions with mineral surfaces.

Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) has been used in a number of studies. Spectra were recorded for a series of natural uranium-silicate minerals and four uranium(VI)-contaminated Hanford vadose zone sediments [362]. The major spectral characteristics indicated that the sediment uranium(VI) was a uranophane-type solid. The chemical interaction of trivalent actinides, americium(III) and curium(III) in the process of hydroxy aluminosilicate (HAS) colloid formation has been investigated [363]. Speciation studies made by TRLFS showed two colloid-borne Cm species, which have seven and six hydration water molecules, respectively. Curium interaction with calcite was also investigated by TRLFS [364]. Two different Cm(III)-calcite sorption species were found. The first sorption species consisted of a curium ion bonded onto the calcite surface. The second species had lost its complete hydration sphere and was incorporated into the calcite bulk structure. TRLFS has also been used to look at curium sorption onto silica colloids and two different inner-sphere complexes were characterised [365]. TRLFS was also used to look at the sorption of curium onto colloidal γ-alumina over the pH range 3.5 – 13 [366]. Three different surface-sorbed curium species appearing at different pH values were identified.

Complementary X-ray absorption fine structure (EXAFS) experiments were undertaken with gadolinium and lutetium as analogues of trivalent actinides. Nickel sorption onto montmorillonite was also investigated [367]. The authors found strong evidence for the formation of a nickel phyllosilicate having its layers parallel to the montmorillonite layers. EXAFS has also been used to investigate uranium(VI) sorption onto amorphous silica, montmorillonite and alumina [368], but at pH values below 7.

Nuclear magnetic resonance (NMR) spectrometry has also been used. The sorption of caesium onto clay minerals and silica gel was shown to occur in primarily two ways: at sites relatively tightly bonded to the surface, at more loosely bonded sites in the diffuse layer [369, 370].

8.3 Sorption of radionuclides onto colloids

8.3.1 Inorganic groundwater colloids

(a) Naturally-occurring colloids

Naturally-occurring inorganic colloids in groundwater generally comprise mineral fragments of the host rock (e.g. silica) or secondary minerals such as clays or iron oxides [e.g.354]. Typical sorption coefficients from measurements made of sorption onto natural colloids [80] are compared with data used in a performance assessment [55] and scaling factors derived. These are shown in Table 8.1.

The K_{nc} values are all larger than the corresponding rock K_{nr} values. The scaling factors range from 6 to 940, with a mean value of ~100 (calculated excluding these two extreme measurements). The largest ratio was found for the sample with the smallest mean colloid size - 20 nm amorphous silica particles.

Table 8.1 Experimental distribution coefficients for radionuclide sorption onto colloidal materials derived from natural materials compared with Nirex 97 central case values for sorption onto rock [49]

Colloid type & conditions	Element	Concentration (mol dm^{-3})	K_{nc} (Rd) [80] (cm^{3}g^{-1})	K_{nr}(50%) [a] (cm^{3}g^{-1})	Scaling factor [b]
Grimsel colloids 0.1 mg dm^{-3}, clay & silica pH 9.6, P$_{(CO_2)}$ $10^{-5.5}$ atm.	Sr Cs Am	1.6-16 × 10^{-6} 7-140 × 10^{-7} 4 × 10^{-10}	6 × 10^{2} 2 × 10^{3} 1 × 10^{6}	2.7 × 10^{1} 1.6 × 10^{2} 3.2 × 10^{3}	2.2 × 10^{1} 1.25 × 10^{1} 3.1 × 10^{2}
Zurzach colloids 0.02 mg dm^{-3}, clay and silica pH 8.0, P$_{(CO2)}$ $10^{-3.5}$ atm	Pb Ni	2.8 × 10^{-9} 2. × 10^{-10}	5 × 10^{5} <10^{4}	3.2 × 10^{3} 1.7 × 10^{2}	1.6 × 10^{2} <6 × 10^{1}
SiO_2 (quartz) colloids 1 mg dm^{-3}, pH 8	Am	8 × 10^{-10}	2 × 10^{4}	3.2 × 10^{3}	6.25 × 10^{0}
SiO_2 (amorphous) colloids 1 mg dm^{-3}, pH 8, 20 nm size	Am	8 × 10^{-10}	3 × 10^{6}	3.2 × 10^{3}	9.4 × 10^{2}
Montmorillonite colloids pH 8	Pb Ni Am	2.8 × 10^{-9} 2. × 10^{-10} 8 × 10^{-10}	5 × 10^{5} 5 × 10^{3} 3 × 10^{5}	3.2 × 10^{3} 1.7 × 10^{2} 3.2 × 10^{3}	1.6 × 10^{2} 2.9 × 10^{1} 9.4 × 10^{1}
Illite colloids pH 8	Am	8 × 10^{-10}	3 × 10^{5}	3.2 × 10^{3}	9.4 × 10^{1}

Notes:

a Central case value used in Nirex 97 [55]

b The ratio of K_{nc} values from [80], to K_{nr}(50%) values used in [55].

A study of americium sorption onto colloids from marl [371] (high concentration of 1.7 ± 1.3 mg dm^{-3}) obtained Rd values of 1 – 3 × 10^{6} cm^{3}g^{1}, by comparison with values of 1 × 10^{4} to 5 × 10^{5} cm^{3}g^{-1} for corresponding larger particle-sized samples (> 1μm) of illite, montmorillonite and chlorite.

At the El Berrocal natural analogue site, trace elements including isotopes of uranium and thorium were found predominantly in solution (passing through 1 nm pore size ultrafilters) and there was little association of uranium or thorium with colloidal particles. However, in groundwater samples from one borehole system at the site (S17), colloidal particles of uranophane were observed by transmission electron microscopy. Thus intrinsic uranium colloids may be generated in the groundwater. However, given uncertainties concerning the groundwater sampling conditions, there is insufficient evidence to conclude that they play a part in uranium transport through the batholith.

At the Canadian Whiteshell Research Area, between 0.5 and 15% of the total groundwater uranium concentration was associated with the colloidal phase [79]. 0 to 68% of groundwater thorium (which is less soluble than uranium) and 0 to 20% of radium-226 in the groundwater were associated with the colloidal fraction. At Grimsel in Switzerland, only 10% of groundwater uranium and radium-226 was found associated with colloids [250].

The uranium ore body at Cigar Lake contains up to 55 wt% uranium surrounded by a clay-rich boundary zone consisting of 30 to 80% illite and kaolinite. Significant colloidal uranium was determined in some groundwaters from the ore zone, the clay-rich zone and the basement zone [253]. The concentration of uranium associated with the particles from the ore zone (0.06% U) is significantly lower than the average uranium content of the ore (12%), suggesting that within the ore, particles originate mainly from the clay rather than from uranium-containing minerals. Outside the clay-rich zone, the groundwaters were found to contain mainly dissolved uranium, suggesting that the clay may be an effective barrier to particle migration. Suspended particulates (including colloids) differed widely in measured *R*d values for incorporated uranium, thorium and radium. These results, combined with USD data, provided evidence that the sorbed actinides were not in equilibrium with the groundwater. It was suggested that some particles could have retained their uranium for as long as 8000 years.

However, USD measurements on groundwaters extracted from slate, granite and sand formations in the UK, provided evidence that uranium bound to colloids was in chemical equilibrium with the solution solid phase (although actinide concentrations were low so that activity ratios were poorly determined) [52].

By contrast, at Gorleben, Germany, over 70% of uranium and 99% of total thorium is associated with high concentrations of organic colloids (5.3×10^{17} dm^{-3}) measured in the humic-rich groundwater extracted from Borehole GoHy-2227 [242]. The isotopic ratios for the ^{238}U, ^{235}U and ^{232}Th decay series differed significantly between the colloidal fraction and the ultrafiltered groundwater, indicating a lack of chemical equilibrium. Evidence for thorium isotope disequilibrium due to complexation with humic acid fractions has also been found in waters from Volo Bog, a small glaciated bog located in Illinois, USA [372]. It has been suggested that irreversible sorption to humic substances may be associated with conformational changes of humic acid molecules, which effectively shield the bound radionuclides from the solution phase [79].

These examples reinforce the view that the fraction of colloid-bound uranium becomes important only in systems where the groundwaters have significant colloidal loading, whether organic or inorganic. It has also been shown that in groundwaters containing organic colloids, the apparent solubility of thorium is related to organic colloid concentration [373]. There is evidence for the incorporation (irreversible sorption) of radionuclides into colloids. However, the nature of the radionuclide-colloid association appears to be dependent on the geochemical conditions and the types of colloids that may be found at any given site.

(b) Bentonite colloids

In a typical HLW repository scenario, the vitrified waste, encased in steel or copper, is disposed of surrounded by a compacted bentonite backfill. It is generally considered that the bentonite barrier will act as a filter to colloids generated within the near field [318], although studies have suggested that lignosulphonate colloids may diffuse through compacted bentonite if the ionic strength is high enough for the colloids to appear as small ‘uncharged’ colloids[15] [374].

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[15] Unfortunately, the possibilities either that the lignosulphonate colloids may have degraded during the experiments or that it was no-colloidal (low molecular weight) components of the additive solutions that migrated through the bentonite cannot be ruled out from the data presented.

However, colloids may be generated at the bentonite / host-rock interface [375]. At this interface, groundwater contacting the bentonite causes swelling of the clay, promoting both the clay intrusion into the host-rock pores and the formation of colloidal phases [376].

The potential contribution to radionuclide migration from inorganic colloids in general and bentonite colloids in particular has recently been reviewed [60]. Rd values are cited for sorption onto bentonite colloids at different contact times (Table 8.2).

Table 8.2 Rd values (cm^3g^{-1}) for sorption onto bentonite colloids after different contact times [60, 377]]

Element species and C_o (mol dm^{-3})	1 week	2 weeks	4 weeks	12 weeks	18 weeks
Cs 1.10×10^{-7} M	8750 ± 900	6400 ± 600	6850 ± 250	8500 ± 250	not determined
U(VI) 4.04×10^{-7} M	820 ± 50	1050 ± 50	1420 ± 50	1500 ± 50	1630 ± 50
Tc(VII) 5.33×10^{-7} M	0	0	0	6 ± 2	45 ± 15
Tc(IV) 4.5×10^{-9} M	360 ± 50	480 ± 50	470 ± 70	450 ± 50	not determined
Se(IV) 1.36×10^{-7} M	7 ± 3	14 ± 1	11 ± 3	45 ± 9	27 ± 9

Values have been rounded off by present authors.

Table 8.3 Rd values (cm^3g^{-1}) for sorption onto bentonite after ultrafiltration [378, 379]

Element species and C_o (mol dm^{-3})	Water:bentonite ratio	Rd (cm^3g^{-1})
U(VI) 1.5×10^{-7} M	20:1 100:1	20 – 40 140 - 230
Tc(VII) 1.0×10^{-10} M	20:1 100:1	30 – 50 50 - 60
Tc(IV) 4.0×10^{-11} M	20:1 100:1	1400 – 1800 570 - 640

For comparison, data for sorption onto bentonite after 4 months contact time are shown in Table 8.3 [378, 379]. uranium(VI) sorption can be seen to be much stronger onto the bentonite colloids , whereas with both Tc(IV) and Tc(VII), sorption is comparable.

A study of the sorption of caesium and uranium(VI) onto bentonite colloids in a reducing granitic groundwater showed several trends including non-linear behaviour [354]. Sorption of caesium involved two reactions, a rapid exchange (hours) and a slower component (days). The latter was believed to be responsible for the partial irreversibility of sorption and occurred at low concentrations of caesium ($<10^{-9}$M). Rd values from desorption experiments increased significantly with the age of the sorption complex. Sorption of uranium(VI) showed a rapid increase in Rd with time over the first four weeks, then a slower increase possibly due to the reduction of uranium(VI) to uranium(IV). Desorption experiments with uranium showed no change in Rd with age of the sorption complex, but a sorption/desorption hysteresis was observed, possibly because of the surface complexation nature of the sorption mechanism and sorption was not completely reversible.

The influence of smectite colloids on the migration behaviour of uranium(VI), thorium, americium, neptunium(V), strontium and caesium was studied in both in-situ and batch experiments [380]. The authors conclude that these colloids can exhibit a considerable mobility in a granitic shear zone. They were found to act as carriers notably for the tri and tetravalent actinides. Interaction between the colloids and uranium(VI) and neptunium(V) was found to be negligible. Combining the field and laboratory studies showed the importance of kinetic effects in radionuclide interactions at groundwater-mineral and groundwater-colloid interfaces. Kinetic effects were also found to be important in the bentonite colloid transport of thorium and europium in fractures [381]. Again, uranium(VI) did not interact with the colloids. Eu was also used in a study of sorption onto montmorillonite to develop further a cation exchange / surface complexation model [358].

The sorption/desorption of lead, bismuth and polonium onto montmorillonite has been reported [382]. At pH values above 7, behaviour was independent of ionic strength. Distribution ratios for sorption and desorption were similar for lead, but with bismuth and polonium, values were much larger for desorption. ‘Quasi-irreversible sorption’ was invoked and discussed.

(c) Synthetic colloids

Permeation grouting with synthetic colloidal silica gel is a potentially effective technique for creating hydraulic barriers to prevent the advective migration of radioactive contaminants in shallow permeable sediments. However the effectiveness of silica gel grouted barriers in controlling radionuclide transport through sorption and diffusion is unknown [383]. Sorption of caesium and strontium with silica gel and two kaolinitic sediments were conducted to evaluate the effectiveness of silica gel grouted barriers. Experiments were performed in the presence and absence of silica gel. The sorption and desorption of strontium onto Ca-montmorillonite and silica colloids has also been studied [384]. Solution ionic strength and calcium concentration significantly affected sorption onto silica colloids whereas sorption onto Ca-montmorillonite colloids was strong in all cases. Desorption from Ca-montmorillonite colloids was slower than from silica colloids. Another study looked into the effect on the sorption onto granite of the presence of silica sol [385]. Technetium(VII), neptunium(V) and (VI) were unaffected by the presence of silica sol, sorption being minimal in all cases, but its presence reduced the sorption of plutonium and americium significantly.

(d) Modelling studies

Several of the studies discussed above have included the modelling of the sorption of radionuclides onto inorganic colloids. Two recent studies have featured modelling of the sorption of thorium [386] and plutonium [387] onto colloids of (or coated with) functional groups containing iron, aluminium, silica and titanium oxyhydroxides. A surface complexation model was developed to simulate thorium sorption on colloids and precipitation by polymerisation at their surface. Calculations were performed comparing the effect of various polymer chain lengths, pH, radius of colloids and concentrations of colloids and thorium. Calculated Rd values were comparable to literature measured values. Plutonium sorption was modelled as a function of pH, redox potential and the presence of ligands and carbonate. The model predicted that oxidation of plutonium(III) to plutonium(IV) increased sorption. Again, calculated Rd values were comparable to literature measured values. The model is apparently equally applicable to other redox sensitive elements.

The potential impact of colloid-facilitated transport of plutonium through fractured rock at the Äspö site has been modelled using a kinetic sorption model [388]. It was found that if the filtration rate was low and maximum concentration of plutonium on colloids and irreversible sorption rates were relatively large, then the colloid-facilitated transport was significant, provided that advective transport was rapid (short water residence times). Transport was two orders of magnitude greater than predicted in an earlier study that used an equilibrium sorption model [389]. The kinetic sorption modelling work was subsequently developed to aid in the experimental planning for an experimental study of transport through a single fracture [390].

8.3.2 Organic groundwater colloids

While the dominant organic complexants in the near field are the products from the anaerobic degradation of cellulose and as-disposed complexants, naturally occurring humic and fulvic substances tend to dominate in the far field. Humic and fulvic acids form a major area of study in their own right and their colloids are known to be potentially strong complexing agents for radionuclides. Organic materials such as humic substances in solution may also enhance the stability of colloids. In one study [391], the authors looked at americium sorption onto sediments in the presence of haematite and ferrihydrite colloids as a function of humic substance concentration. They state that the results demonstrated the crucial importance of humic colloids to the stabilisation of colloidal metal oxides on one hand and to counter-balancing charge heterogeneities on the other. The sediment charge heterogeneities led to high colloid attachment. Am sorption onto the sediment was enhanced by the presence of the colloids. Equilibrium was not reached after 30 days, showing the importance of kinetic effects. In column experiments, humic-colloid borne americium travelled 3% faster than HTO tracer.

The mobility of organic colloids through compacted bentonite and their effect on diffusing strontium has been studied [392, 393]. The organic colloids had higher diffusivities than the authors had first expected. Humic acid had no effect on diffusing strontium under the experimental conditions. However there was a significant effect on cobalt and europium, diffusivities being increased.

The effect of humic acid on the sorption behaviour of caesium on silica colloids was studied over a pH range of 3-10 [394]. The sorption of caesium on bare silica colloids was negligible up to pH7, above which it was found to increase sharply with pH. In the presence of humic acid significant enhancement in the sorption was observed at lower pH values with no effect at pH >7. Zeta potential of the colloidal suspension of humic acid, silica and their binary mixture were investigated to explain the observations. The results could only be explained through a surface complexation model rather than a simple ion exchange mechanism.

8.3.3 Near field-derived colloids

Colloids that are formed in the near field have the potential to migrate by diffusion or advection into the geosphere [62, 284]. In the case of a cementitious ILW repository, there will be a significant chemical transition, especially the drop in pH (and also probably ionic strength) which may cause desorption of sorbed radionuclides. However, if near-field colloids are stable in the chemical conditions of the geosphere, they may potentially be mobile and act as radionuclide carriers and therefore need to be considered in the far-field transport model.

(a) Cementitious colloids

A typical scenario for an ILW repository features a cement backfill to produce both a physical and chemical barrier to radionuclide migration. Such a backfill will give rise to colloids and the situation regarding cementitious colloids has recently been reviewed in detail [62]. Little information is available concerning colloid populations generated at the margins of an alkaline plume where geochemical gradients are high and alumino-silicate colloids could form.

(b) Corrosion product colloids

A significant quantity of metals will be present in a repository either as construction materials, waste containers or as waste constituents. Corrosion will form metal oxides or hydroxides which may have a large capacity for radionuclide sorption. It is possible that some corrosion products will form mobile colloidal phases, adding to the natural population and hence providing a transport mechanism. The possible effects of colloidal corrosion products on the transport of actinides from the near field of radioactive waste repositories have been studied [395].

Plutonium was found to sorb very strongly onto haematite colloids (Rd = $2\text{-}9 \times 10^6$ cm^3g^{-1}) under near-field conditions. Upon altering the conditions to neutral pH to simulate transition to the geosphere, little desorption was observed after 6 days. Slightly weaker sorption was noted for magnetite but overall results were similar. In other experiments, the authors studied the sorption of plutonium and americium onto, and desorption from, colloidal corrosion products of iron and zirconium (haematite, magnetite and zirconium hydroxide) under conditions again simulating a transition from near-field to far-field environmental conditions. Experimental timescales for the desorption experiments were longer (1 month). Desorption of the actinides occurred very slowly from the colloids under far-field conditions, was not dependent on pH change alone, but did occur. Desorption occurred more rapidly at high actinide loadings.

Thorium has also been found to sorb strongly onto haematite colloids [396], with sorption increasing with pH, but being little affected by ionic strength between 0.1 M and 0.01 M. Two surface complexation models were considered.

8.3.4 The effects of organic complexants on sorption to colloids

In general, significant concentrations of organic materials in solution may compete with solid surfaces for the uptake of radioelements and reduce the effective sorption distribution coefficients for the solid. The magnitude of the effect depends on a number of factors including the mineralogy, the chemistry of the radioelement and the strength of complexation. There may be some circumstances, in which sorption of organic complexants to a solid surface enhances the radioelement uptake onto the solid. This type of effect may also arise on the surfaces of colloid particles as a result of competition or co-operative effects with organic complexants.

Much work has been undertaken on the UK and on overseas programmes to understand the potential effects of organic complexants on radioelement sorption both in the near field and the far field of a geological repository. The effects of complexants on sorption and the treatment of these effects in performance assessments were reviewed in 2004 by Heath and Williams [397].

8.3.5 Nevada Test Site

The Nevada Test Site (NTS) situated in south-western USA provides a field laboratory to study the mobility of radionuclides in an underground environment. Approximately 300 of more than 800 underground nuclear tests were conducted below the water table, depositing a radionuclide source term in excess of 3.7×10^6 TBq since testing began in 1951 [398]. Transport of the actinides appears to be controlled by sorption to mineral colloids, including clays, zeolites, and cristobalite. Colloids may move radionuclides at near ambient groundwater velocities through permeable fractured rock. Isotope ratios of plutonium measured on colloids filtered from water samples taken down-gradient of a nuclear test cavity have been used to fingerprint their source and indicate minimum transport distances of more than 1 kilometre [33]. However, it must be borne in mind that the extreme violence of the implantation of the radionuclides at the NTS coupled with instant access to groundwater could not be further from the concepts for the carefully conceived engineered barrier system of a waste repository (a 100 kton test in 1962 displaced 12 million tons of earth, leaving a crater 100m deep and 390m across, by comparison with the much-studied migration from the 'Benham' test which was 1.15 Mton [399]). The study of these colloid-radionuclide interactions has been recently summarised [58,400].

8.3.6 Effects of chemical conditions

The sorption behaviour of americium at pH values of up to 12 onto silica colloids was studied as a function of americium concentration, colloid concentration, ionic strength, temperature and silica allotropic species [401]. The distribution ratio for amorphous silica increased from ~10^2 cm^3g^{-1} at pH 6 to ~10^5 cm^3g^{-1} at pH 9. For quartz, the distribution ratio increased from ~ 5 10^3 cm^3g^{-1} at pH 5 to ~5 10^5 cm^3g^{-1} at pH 12. There was minimal difference in sorption between americium at 10^{-10} mol dm^{-3} and 10^{-11} mol dm^{-3}. Sorption onto amorphous silica decreased with increasing colloid concentration (10^3 to 10^2 cm^3g^{-1}) while with quartz there was no effect. There was also only a minimal effect with varying the ionic strength from 0.1 to 0.001 mol dm^{-3}. The sorption mechanisms for amorphous silica and quartz appeared to be different, but no mechanisms were discussed. In another study [402], the sorption of uranium, neptunium, plutonium and americium onto colloids of haematite, montmorillonite and silica was investigated as a function of time, ionic strength, temperature and colloid concentration. Different behaviour was seen for both the actinides and the colloid types. Sorption was fastest and greatest for plutonium and americium. Temperature affected plutonium sorption onto montmorillonite and uranium and neptunium sorption onto all three colloid types. Increasing ionic strength decreased sorption of all four actinides onto montmorillonite and silica colloids.

The sorption of technetium, caesium, strontium and promethium has been measured as a function of pH and particle size [403]. The sorption of promethium on silica colloids was found to be strongly dependent on colloid concentration; the higher the colloid concentration, the lower the distribution ratio (1.2 10^4 cm^3g^{-1} at 0.1 gdm^{-3} to ~500 cm^3g^{-1} at 10 gdm^{-3}). Sorption also increased at pH values above 8. No such effect was seen for caesium or strontium. Distribution ratios for the fission products on granitic colloids were at least a factor of ten higher than with crushed granite. No measurable sorption was observed with technetium (presumably technetium(VII)).

8.3.7 Reversibility of sorption

The significance of far-field colloids in the transport of radionuclides is highly dependent on the reversibility of the sorption process because, if radionuclides readily desorb when chemical changes occur along the flowpath (e.g. due to dilution), colloids would have little effect on radionuclide migration through the far field.

Sorption and desorption rates of ion exchange reactions are often considered to be similar, generally because the ion exchange process is fast and reversible. However, sorption and desorption rates of surface complexation reactions may show considerable hysteresis. In the laboratory, most sorption processes are studied over timescales of minutes to weeks, but in natural environments it has been observed that desorption processes can take much longer. It is noted that the term "irreversible sorption" is used rather loosely in the literature, and that the apparent lack of reversibility observed in some sorption studies is due to the short duration of desorption experiments compared to the slow desorption kinetics found. For example, thorium was described as sorbing irreversibly onto natural organic matter over a 5-day time period, but reversibly onto silica [404]. In contrast, Comans [405] found that at low ionic strength, cadmium sorption onto illite was reversible, but long equilibration times (7-8 weeks) were required due to the slow desorption kinetics.

There is a growing body of work concerned with studies of the reversibility of sorption and the mechanisms of sorption to mineral phases [e.g. 406, 407, 408] and rock lithologies [e.g. 409]. A number of studies have been concerned with sorption reversibility onto colloids.

Sorption of plutonium(IV) onto a range of mineral colloids was found to occur at a fast rate [410]. Desorption rates varied however and were frequently slow. Plutonium(V) sorption varied and appeared to depend on the rate of reduction to plutonium(IV).

Other studies looked at the rates of sorption and de-sorption of plutonium(IV) and plutonium(V) onto haematite, goethite, smectite and silica colloids [411, 412]. Rd values ranged from ~10^3 cm^3g^{-1} for silica to >10^5 cm^3g^{-1} for haematite and goethite. Rd values from desorption experiments were similar or lower showing significant desorption albeit slower, except that there was very little from haematite or goethite. Unfortunately important details are omitted from the report. There is no description of how oxidation states were measured or maintained either in stock solutions or when added to groundwaters; no details are given concerning pre-treatment of filters, vessel wall sorption and no explanation of the statement "*…corrected with results obtained from blank samples"*, etc. A later study by the same group [402] looked at desorption of uranium, neptunium, plutonium and americium from colloids of haematite, montmorillonite and silica. Desorption of plutonium and americium was observed, but not of uranium or neptunium.

The desorption of caesium from bentonite has been found to depend on the age of the sorption complex, Rd values increasing with age [354]. In the same study, Rd values for uranium (VI) however were found to be independent of age but there was sorption/desorption hysteresis. Neither caesium nor uranium sorption were completely reversible [377]. In the case of caesium, this may be due to selective sorption on frayed edge sites or fixation at the hexagonal cavity of the tetrahedral surface. However, the authors believe that it is probable that only the caesium fraction 'fixed' in the high affinity sites was able to move in these tests. At low uranium concentrations and above-neutral pH values, sorption is by surface complexation on edge sites with the formation of inner-sphere complexes. It has been stated however that although there is a large amount of literature covering uranium sorption mechanisms on smectite, information about the irreversibility of sorption is very scarce [377].

The sorption/desorption of strontium onto/from silica and montmorillonite colloids has been studied [384]. Sorption behaviour was very dependent on groundwater solution composition, especially calcium concentration. Desorption from montmorillonite was slow with between 1% and 16% desorbed after 90 days. Desorption from silica colloids was faster, with between 7% and 100% desorbed after 90 days again depending on the groundwater.

The sorption/desorption of lead, bismuth and polonium onto montmorillonite has been reported [382]. At pH values above 7, behaviour was independent of ionic strength. Distribution ratios for sorption and desorption were similar for lead, but with bismuth and polonium, values were much larger for desorption. 'Quasi-irreversible sorption' was invoked and discussed. Sorption/desorption experiments have also been performed using natural colloidal minerals and plutonium (IV) and (V), with EXAFS techniques being used to characterise the speciation of the sorbed plutonium [410, 413]. Sorbed species were found to be dominated by plutonium(IV).

8.4 Summary of current understanding

There are many similarities between the current fundamental understanding of sorption onto colloids and of that onto larger particles and surfaces. As has been noted earlier in this report, much work has been undertaken world-wide to measure distribution ratios and also obtain isotherm data for sorption onto both colloids and larger surfaces. Current understanding of the principal mechanisms and identification of species involved has improved following recent studies as outlined in Section 8.2.3, but there remain major uncertainties. The study of radioelement speciation, for example, is hindered by the low solubility of many radioelements under geosphere conditions, especially the actinides. The precise role of coatings, both organic and inorganic, on mineral surfaces is not as well understood as would be wished.

Uncertainties also exist around the types of interaction involved between radioelement and colloid. There is additionally a lack of knowledge concerning sorption kinetics, especially the frequently-observed slow kinetics of de-sorption processes.

The limitations of current understanding of sorption onto colloids will be highlighted, or mitigated, by the site-specific nature of groundwater colloids, including their populations. The whole position regarding groundwater colloids is extremely site-specific and includes the colloid size distribution, their surface-volume ratios, mineralogy, morphology and presence or otherwise or organic materials. The adequacy of our current understanding could therefore also be regarded as being site-specific.

9 Transport of colloids in the geosphere - experiments

9.1 Introduction

This section focuses on experimental studies of colloid transport undertaken over a range of lengthscales, from a few centimetres in the laboratory to many metres in field and URL experiments and kilometres at natural analogue sites. The main objective of experimental studies has been to gain understanding of colloid transport behaviour in natural systems and the effects of key variables such as ionic strength, particle size and flow rate on colloid mobility. In addition, a range of colloid-facilitated transport experiments, involving both sorbing solutes and colloids have been reported over the last 15-20 years.

One of the major problems with laboratory experiments is the relatively high flow rates and short timescales of the experiments, which are very different from low flow rates and long timescales of relevance to transport processes in deep groundwater. For this reason, studies of natural analogue sites are particularly useful for studying transport processes under conditions that are more directly relevant to the safety of a GDF. A number of colloid studies have also been undertaken, or are in progress, in URLs that have attempted to study colloid and colloid-facilitated transport in flow systems that are more relevant to geological disposal. Examples of all of these different types of study are discussed in the following sections.

9.2 Laboratory studies

Laboratory experiments studying colloid transport in shallow groundwater systems have been carried out for many years, looking at both saturated and unsaturated conditions (see, for example, the reviews in [173] and [414] respectively). These have the same drawbacks as the shallow field studies discussed in section 5, but at least provide a mechanistic understanding of likely colloid-colloid and colloid-surface interactions in porous and fractured media. More recently, some attempt has been made to look at flow systems more relevant to a GDF and these few studies will also be examined.

Two main types of laboratory experiment have been carried out:

- *colloid transport (CT):* is primarily concerned with understanding colloid velocity compared to solute tracer transport and the interactions of colloids with solid matrices (e.g. fracture faces, pore surfaces, etc);
- *colloid-facilitated contaminant transport (CFCT):* is where both colloids and sorbing solutes are added together to look at colloid-facilitated transport and to assess whether solute

transport is faster in the presence of colloids. In the context of radioactive waste disposal, this usually referred to as *colloid-facilitated radionuclide transport (CFRT).*

These are studied with two main solid phase geometries, namely:

- column experiments with beds of crushed porous material
- columns or blocks (sometimes very large) with artificial or natural fractures

Although column experiments are not necessarily representative of geological disposal conditions, they do provide useful information on transport processes and provide a basis for the development of understanding and testing of models. They can be designed to provide model systems to test various aspects of colloid transport and provide idealised geometries for modelling. For example, studies of the effect of surface heterogeneity on particle deposition have used mixtures of clean quartz grains and grains that have been previously coated with iron hydroxides in differing ratios as column packing [166]. Effects of ionic strength, pH, flow rate, etc., can be systematically varied and assessed in turn and in combination in a way which is obviously more difficult in a field experiment and generally impossible in a natural analogue study.

One of the biggest problems with all laboratory experiments is applying sufficiently low flow rates typical of deep groundwater. The effect of high flow rates is that (particularly in fracture systems) some entrained colloids are transported through the fracture without ever approaching the matrix surfaces. Thus transmission is often a function of flow rate, may appear artificially high and actual analysis of the data yields very little useful information concerning colloid-colloid and colloid-surface (fracture face or pore surface) interactions. Of course, as noted in section 5, high flow rates can also be a problem for field experiments.

An overview of some of the available data is presented in Table 9.1 and two case studies are picked out for discussion below. In the following sections, a few specific aspects of experimental methodology are discussed.

9.2.1 Porous media studies - overview

Several representative examples are presented in Table 9.1 and a further 20 are listed in the review by Sen and Khilar [130]. Most have taken an admirably simple approach and have tried to focus on specific mechanisms in a clear and logical manner [e.g. 171]. This is undoubtedly worthwhile as specific mechanisms have been identified (for an overview, see section 3.4) and studied in detail, but from the viewpoint of deep groundwater colloids, they generally suffer from several drawbacks:

- the current experimental studies are almost exclusively focused on shallow systems, either examining processes in the vadose zone (e.g. of the 20 studies reviewed in [130], only the colloid and radionuclide retardation (CRR) experiment at Grimsel was not dealing with soils, shallow sands or gravels, etc), mine tailings [e.g. 415] or similar systems
- they tend to consider uncemented systems of simple or monomineralic make-up and/or monodimensional form [e.g. 416]
- many reflect the much greater importance of microbiological processes in shallow systems compared to deeper groundwaters – in some cases, microbial processes completely dominate the system [see, for example, the reviews in 417, 418]
- many look at unsaturated systems and these have been excluded here (although they are of interest to the Yucca Mountain site [e.g. 419])

Table 9.1 Examples of colloid migration experiments of relevance to a GDF: laboratory studies

Study	Rock type and groundwater	Flow system type and experimental duration	Form of tracer employed	Sample handling and flow system data	Observed colloid behaviour	Comments
1. CT, fractured column [420]	Chalk	Natural single fracture, with equivalent hydraulic apertures of 183 and 380 mm. Solution of degassed artificial rainwater, pH 7.3 I=0.0023 M. Duration of 384 and 183 min for cores 1 and 2 respectively.	Negatively charged fluorescent latex microspheres (0.02, 0.1, 0.2, and 1.0 µm diameter) and Li$^+$ and Br$^-$ as the soluble tracers.	Core separated, fracture faces cleaned and then placed back together. Core horizontal, flow rate 1 mL min^{-1}. No head data. Calculated equivalent fracture apertures were 380(±4) and 183(±7) µm for cores 1 and 2.	Colloids had earlier arrival times than solutes and complete lack of tails in their breakthrough curves (BTC), proving that their transport is advection-dominant. Recovery: 0.2>1.0>0.02 µm High diffusion coefficient of 0.02 µm colloids leads to irreversible (on the experimental timescales) matrix diffusion.	Recovery rates observed (90%, 95%, 75% for the 1.0, 0.2, and 0.02 µm colloids) are extremely high. No attempt to re-stress the core with simulated overburden pressures.
2. CT, fractured block [421, 422]	Fractured granite block with distilled water and Äspö Synthetic Water - 1.70 g/L Na, 0.66 g/L Ca, 0.08 g/L Mg, 0.01 g/L K, 3.80 g/L Cl and 0.30 g/L SO4. Ionic strength of 0.14 mol/L and a pH = 7.7.	Fracture flow - The main fracture is associated with a number of intersecting sub-parallel fractures, which form splays from the main.	Injected tracer concentrations (Co) were 31–41 mgL^{-1} for bentonite, 63–79 mgL^{-1} for latex and 31–99 mgL^{-1} for NaI.	Block was opened to examine fracture - and closed again for the experiment.	At low ionic strength (0.001 M), bentonite colloid recovery dropped from 60-70% at 0.4 mh^{-1} to ~20% at 0.005 mh^{-1}. At high ionic strength (0.14 M), recovery dropped to ~0.5% (flow velocity of 0.034 mh^{-1}). At lowest flow velocity, only smallest bentonite colloids (4-15 nm range) were transported.	Different granite from Äspö (Whiteshell sample). Solutions used are different to original groundwater. Changes to the fracture are to be expected – but not discussed. Lack of discussion on differences between experimental fracture and that found *in situ* at Äspö.

Study	Rock type and groundwater	Flow system type and experimental duration	Form of tracer employed	Sample handling and flow system data	Observed colloid behaviour	Comments
3. CFCT, fractured column [423]	Fractured tuff from the Topopah Spring Formation	Fractures run length of cores of between 12.6 and 21.9 cm long. Effective half apertures, matrix diffusion coefficients, and solute dispersivity parameters all calculated from the 3-T breakthrough curves.	Pu(V) (~10^{-8} M) sorbed onto inorganic montmorillonite and silica colloids, and Pu(IV) sorbed onto inorganic clinoptilolite colloids. Colloid concentration of ~140 to 200 mgL^{-1}. 3-T also included as non-reactive tracer.	No information	Plots of Pu-colloid with ‘high’ and ‘low’ flow are shown plotted against model fits, but no data provided on the non-reactive tracer for comparison.	Experimental system is so underdefined as to be ill-defined. Sweeping conclusions made with no supporting data (and none offered in the references).
4. CFCT, fractured block [424]	Fractured granite block (0.83x0.90x0.60 m) immersed in groundwater of Na-Ca-HCO_3 type, no information on pH or Eh.	Fracture flow in dipole	Natural colloids of clay, quartz, calcite and unidentified micro-organisms isolated from Whiteshell groundwaters along with bentonite colloids. ^{241}Am and ^{85}Sr sorbed on natural colloids, only ^{85}Sr on bentonite. Br as non-reactive tracer. 19.3 mgL^{-1} natural colloids injected, included 15.8 mgL^{-1} of 1–10 nm colloids and 3.5 mgL^{-1} of 10–450 nm colloids. 3164 mgL^{-1} of bentonite colloids injected.	Block cut from quarry, no information on handling of block (but cf. 421). Water flow rate of 15 mLh^{-1}, tracers injected for 5 hours. No head information.	Natural colloids produced a measurable migration of ^{241}Am, but not of ^{85}Sr. Bentonite colloids sorbed significant amounts of ^{85}Sr and were retarded in the fracture.	Br breakthrough curve showed that the flow system was unstable and changing during/between experiments. Repeated tests run on the same flow system, so colloids retarded in previous tests could influence subsequent experiments.

Study	Rock type and groundwater	Flow system type and experimental duration	Form of tracer employed	Sample handling and flow system data	Observed colloid behaviour	Comments
5. CT, porous column [166]	Packed column of quartz sand (reported sieve size of 50-70 mesh). Sand grains prolate spheroidal in shape, with surfaces having a subangular to subrounded appearance. Solution is KCl. Expt 1: 10^{-5} to 10^{-2} M. Expt 2: 10^{-3} M.	Two experiments: 1. porous flow , duration of 1.5 to 6.3 h for ionic strength variations and	Monodispersed silica spheres (mean diameter 0.30 μm) in variable ionic strength KCl. Expt. 1: Colloid concentration of 72.4 ~140 to 200 mgL^{-1}, (colloid number of $2.246x10^{6}$ L^{-1} (again, no uncertainty on this value). Expt. 2: Colloid concentration of 18 mgL^{-1} ($5.584x10^{5}$ L^{-1} colloid number.	Sand is cleaned then part coated with Fe-oxyhydroxide, column is then wet-packed to a standard porosity of 0.392 (with no definition of uncertainty on this figure) Expt 1: column depth of 2 cm, flow velocity of $1.02x10^{-4}$ ms^{-1}. Expt 2: column depth of 10.1 cm, flow velocity of $1.02x10^{-4}$ ms^{-1}.	Colloids transported at 1.01 x non-reactive tracer velocity (NO_3^-), dispersivity parameter of 0.692 mm calculated from breakthrough curves. Kinetic deposition rates, excluded area (of the column) parameters and blocking rates.	Expt 1: Data from the experiment were used to test the RSA (random sequential adsorption) mechanism vs Langmuirian blocking function – RSA produced poor fits to the data, presumably due to non-ideal nature of the sand grains. Expt 2: minor changes in the amount of 'favourably charged surfaces' (i.e. Fe-oxyhydroxide coated sand grains) causes a significant increase in colloid retardation. Generally, the system appears to be underdefined and the modelling would appear to have too many free parameters to approach anything near an unique solution for most of the parameters studied, despite this being a relatively simple system.

Study	Rock type and groundwater	Flow system type and experimental duration	Form of tracer employed	Sample handling and flow system data	Observed colloid behaviour	Comments
6. CFCT, fractured core [381]	Fractured granite core with a Na-Ca-HCO-SO type groundwater with pH=9.6, Eh=-300 mV and I=0.001 M [425]	Fracture flow, see Figure 9.1 for a detailed image of the fracture. Flow velocity was varied between 46 ma^{-1}, 94 ma^{-1} and 187 ma^{-1}	Two experiments. I: 10^{-6} mol L^{-1} U(VI), 10^{-8} mol L^{-1} Th(IV) and 10^{-8} mol L^{-1} Eu(III) without colloids II: same with 2 mgL^{-1} bentonite colloids Natural groundwater colloids also present (0.13 to 13 mgL^{-1}, see Table 5.1 site 8)	Core removed from experimental fracture using triple-packer corer to minimise damage to flow system. Core isolated in resin and placed in argon glovebox	U(VI) is not colloid borne, whereas Th(IV) and Eu(III) are associated with both bentonite and groundwater colloids. Some colloid-facilitated transport of Th(IV) and Eu(III) by both colloid types at high flow rates, at medium rate only with bentonite (27% and 37% recovery respectively) and at low rate, no colloid-mediated transport. Reference colloid experiments using dye labeled latex microspheres (25 nm, 50 nm and 100 nm) revealed in general a higher recovery of smaller colloid size classes increasing with groundwater velocity	It is assumed that the low flow rate is repository relevant, but this is still too high (see section 0) – nevertheless, colloid retardation is observed. Note, however, that the colloid recoveries found in the laboratory core experiments are lower than those obtained in the field studies (section 9.4.1).
7. CT fractured block [54]	Fratured slate block from Reskajeage Quarry, Cornwall. Saturation with 10^{-1}, 10^{-2} or 10^{-3} mol dm^{-3} NaCl solutions	Fracture 1.05 × 1.25m. Flow velocity between 5 × 10^{-5} and 1 × 10^{-3} ms^{-1}	Monodispersed silica colloids of 30, 120 and 800 nm diameter plus HTO as non-sorbing tracer	Fracture block was restressed to simulate 10m burial depth. Inlet and exit ports were attached at each end. Outer surface sealed.	Transmission of silica colloids through the fracture decreased with increasing ionic strength, residence time and particle size. Colloid breaks through ahead of HTO tracer and the effect increases with particle size.	Water flow best interpreted using a two-channel model. No modelling of colloid retention behaviour.

The biggest single question which remains then is how representative are these simple systems (with ideal colloid sizes and shapes and ideal sand grain forms, etc) to the shallow systems they attempt to represent? Currently, this is difficult to assess as no true 'blind test' of any colloid transport model has been attempted. Many attempts to fit mechanistic models to colloid breakthrough curves, for example, have been reported [e.g. 423, 426, 427,, but these do not represent true model testing in the manner normally accepted in a repository PA.

9.2.2 Column characteristics

Obviously any column experiments are already some way from reality, but it is worth considering other aspects of the column and how the experimental set up could influence the data produced.

(a) Porous media – pre-treatment

When studying colloid transport in porous media, most research is performed in laboratory column experiments using model systems, such as glass beads [e.g. 428] or well-sorted quartz sand [e.g. 429]. Such column experiments have the advantage of allowing control of the experimental conditions and isolation of the variables of interest from the rest of the system, but with the clear disadvantage that the column is not representative of the complexity of natural processes. In an attempt to further simplify the system, many researchers opt to sieve and/or clean the sand [e.g. 430], aiming for a more uniform substrate which will (hopefully) allow more reproducible experiments.

In one study [431], the authors focused on the sieving procedure and noted that:

- sieving with stainless-steel sieves may contaminate the sand because of the abrasion of the brass mesh;

- sieving causes inadequate sizing of the sand grains because of sieve clogging, rather than uniformity of the sand batches;

and reproducibility is therefore highly questionable. Additionally, many researchers choose to wash the substrate before the experiment, either to clean the sand of functional surface groups (rinsing with acidic or basic solutions) [e.g. 432] or colloids (flushing with distilled water or solutions of differing ionic strengths) [e.g. 433]. However, as noted by [434], washing can have a variety of effects on the substrate, including:

- the grain size distribution is changed as fine particles are washed away and the relative mass of grain sizes with larger diameters is increased in the sand batch

- this impacts filtration processes - bacterial filtration is dominated by the smaller grain sizes whereas colloid retention decreases with increased grain size

Indeed, they noted that observed differences in colloid breakthrough curves cannot be attributed to changes of surface chemistry alone, but rather to a combination of changes in grain size distribution and differences in surface properties of the sand grains. In conclusion, they stated that their "...*findings place a question mark over experiments with natural porous media which employ washing procedures, thereby unintentionally changing a critical retention mechanism the researchers may have indirectly wanted to investigate. Further efforts must be made to prove and quantify the influence of changes in grain size distribution on colloid retention.*"

(b) Fractured media – column handling

To simplify laboratory experiments in fractured media, researchers often work with clean, simple fractures, even going so far as to open the core, clean the fracture face and then to close it again [e.g. 420]. Unfortunately, such handling can change the nature of the original fracture completely – one study [435] which attempted to quantify the influence of such treatment on matrix diffusion values, estimated that the laboratory data probably overestimated *in situ* diffusion coefficients by a factor of 2 to 5. These factors should be treated as minimum values, however, as the study was conceptually simple, assuming that re-stressing the core with simulated overburden pressures would return to core to undisturbed, *in situ* conditions.

Looking at Figure 9.1, a close-up of the experimental fracture used in the CRR and CFM experiments (see section 9.4.1) clearly illustrates that a system of this complexity cannot be reconstituted in the laboratory (see also comments in [48]). In general, it would appear that the results of any such study should be questioned as they have almost certainly induced significant alteration of the *in situ* system.

The above two sections really call into question the validity of any laboratory experiments which simply assume that disturbances to the system are minimal when, if anything, they could be dominating the entire measurement process.

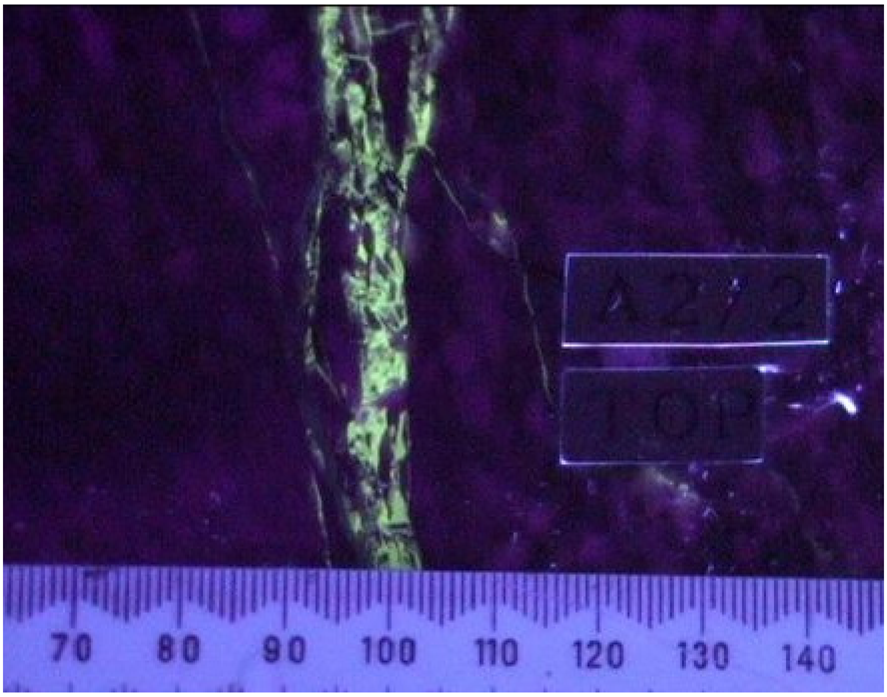

Figure 9.1 **An example of the complexity of experimental fracture used in the CRR and CFM experiments in Grimsel. Scale bar in mm, image taken under UV light. Light green material in the fracture is a fluorescent resin used to highlight pore space – bright green is open porosity, black areas within the green are rock clasts, grey areas are high porosity (up to 40%), resin-filled fault gouge. Note secondary fractures splaying off the main system into the rock matrix (from [436])**

(c) Flow conditions

It was previously noted in section 3.2.3 that high flow conditions can induce erosion and cause other experimental problems. Further, it is clear that such conditions, although often used in laboratory, field and URL experiments (see Table 9.1 and section 9.4) are of little relevance to

GDF host rocks. Chamindu *et al*. [437] report that, at low flow rates, soil colloids (diameter <1 μm) showed complete retention in packed sand columns, but showed significant recovery at higher flow rates. A recent experiment [268] further emphasises the importance of using repository-relevant flow conditions; here bentonite colloid recovery from a CT-fractured block experiment decreased from from 60-70% at a flow velocity of 0.4 mh^{-1} to ~20% at 0.005 mh^{-1}, clear evidence of the significance of this artefact. However, this is a flow velocity of nearly 44 ma^{-1}, still much more than the 0.1 ma^{-1} assumed by Nagra[16] [57, 438] for a previous HLW disposal concept in the fractured crystalline rock of northern Switzerland.

(d) Flow system

In general, there is a lack of information on the detailed flow system in most laboratory experiments carried out to date. Not only does this weaken the value of the data to transport modellers, but it makes it impossible to ascertain if the laboratory produced data can be directly compared with that produced in the field or, indeed, if it is at all possible to upscale the laboratory-derived data for use in the field. In general, data transferability between systems is difficult, but is often essential. As noted by [439], there are the several major motivations for the transfer of information among sites and experimental systems:

- Information from other sites is taken to fill current gaps in a specific national programme, in order to provide data for a preliminary safety case. For example, the basis for extrapolating laboratory measurements to *in situ* conditions can be justified if both laboratory and *in situ* data are available in other programmes

- Information from other sites is taken to highlight that the investigated site does not represent an exceptional situation but has relevant features in line with other sites. If independent programmes converge towards consistent data sets and conclusions, confidence is built in the national programme

- Conceptual models on different levels (individual features and processes, their coupling and safety relevance) can be transferred from other, similar sites or URLs

However, these arguments can be fatally weakened when even the most basic experimental assumptions are not checked – for example in a recent study [422] where a laboratory experiment using a fracture in one host rock was used to support field work in another host rock, there was no attempt to check the compatability of the fractures, the very thing at the root of both experiments.

(e) Matrix diffusion

Matrix diffusion is the process by which solute, flowing in distinct fractures, penetrates into the surrounding rock and may diffuse, through the connected system of pores or micro-fractures that make up the matrix porosity. The importance of matrix diffusion in the context of radionuclide migration is that it increases the pore volume and surface area of rock in contact with migrating radionuclides compared to the flow paths alone. . It is referred to as a retardation process, because it results in slower transport than would be the case if only advection, mechanical dispersion and diffusion along water-conducting features operated. In some media, matrix pores may be accessible to solutes by diffusion, but larger molecules, ions and colloids may be excluded due to size and/or charge effects. The retarding effect of matrix diffusion may thus apply to dissolved radionuclides (e.g. ^{36}Cl), but not necessarily to those associated with colloids (e.g. actinides).

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[16] Calculated from the normalised fluxes in transmissive elements (Table 10.1 of [26]) and the porosity of the flow systems (e.g. Figure 10.7 same report) for an average flux of 10^{-11} and porosity of 3%, provides an estimated velocity of $3x10^{-9}$ ms^{-1} or about 0.1 ma^{-1}.

Example 1 in Table 9.1 points out that the high diffusion coefficient of the 0.02 μm diameter colloids leads to irreversible matrix diffusion – but fails to add the crucial information 'on the experimental timescales'. As the two experiments reported lasted only 384 and 183 min for cores 1 and 2 respectively, it really is not possible to make any firm statement on colloidal matrix diffusion.

In another study, Rutherford Backscattering Spectrometry (RBS) was used to assess whether bentonite colloids are able to diffuse into the rock matrix [440]. The apparent diffusion coefficients calculated, $D \approx 7.5 \times 10^{-17}\ m^2s^{-1}$, were slower than those measured in parallel for Eu in solution ($10^{-14}\ m^2s^{-1}$) [60]. In a further experiment [441], similar diffusion coefficients ($10^{-18}\ m^2s^{-1}$) were obtained for the diffusion of model gold colloids of different sizes (2 nm to 250 nm) into granite. It was noted that the colloid uptake decreased with time, suggesting that the pore throats block as colloids accumulate, thus hindering the access of other colloids and restricting diffusion.

In the Grimsel CRR experiment (section 9.4.1), it was originally intended to excavate the flow field after the experiment (cf. section 0(e)) and assess the retardation sites of the colloids and radionuclides (as this had been shown to work well for radionuclides in the experimental fracture [442]). Unfortunately, preliminary experiments showed that a realistic bentonite colloid suspension (of 20 mgL^{-1}) for the expected conditions at the near-field/far-field boundary of the EBS, would provide too low a colloid loading on the fracture walls and rock matrix for analysis. It remains to be seen if this can be overcome in CFM (Grimsel) or Colloid (Äspö – see section 9.4.2), but it seems unlikely that *in situ* experiments can successfully measure this parameter.

9.3 Case Studies

9.3.1 Example study I: Reskajeage Farm Quarry Research Project, UK

(a) Background

The laboratory-based experiments examined a fracture through a large slate block (1.02 X 1.5 X 0.8m) from Reskajeage Farm Quarry, Cornwall, UK (see section 9.4.4 for a description of the associated field study) [54]. The methods used were based on previous work on an artificial fracture (in perspex) and fractured granite [443]. The boundary conditions here were:

- flow rates of 0.2 ml min^{-1} to 4 ml min^{-1}
- groundwater ionic strength of 10^{-3} M to 10^{-1} M
- monodispersed silica colloids (30nm, 120nm and 800nm diameter) and rhodamine dye added to the flow

The main results were that:

- rhodamine and silica colloids breakthrough at more-or-less the same time (larger colloids before smaller due to size exclusion), with colloid losses of 2% (30 nm), 35% (120 nm) and 78% (800 nm)
- greater flow rate (for same colloid diameter and groundwater ionic strength) means greater degree of colloid recovery
- increasing colloid retardation was observed with increasing ionic strength (see Figure 9.2)

(b) Input to modelling studies

Fitting of conservative tracer breakthrough curves with a two channel solute transport model (and with no matrix diffusion) was successful and this same model was applied to the colloid data. A range of parameters (including dispersion coefficients, velocity, mixing length for both channels, splitting of flow between the channels) were varied. The results show that there is a 50% variability in the fitted parameters for the colloids which was claimed to be due to slight changes in the channelling through the fracture from experiment to experiment. Although there is no information on the details of the flow system, this implies that fault gouge was present and was moving as in the GTS fracture described in section 5.2.3. Alternatively, no gouge is present and the differences are simply artefacts of the flow field set up in each experiment – either way, both represent significant experimental artefacts.

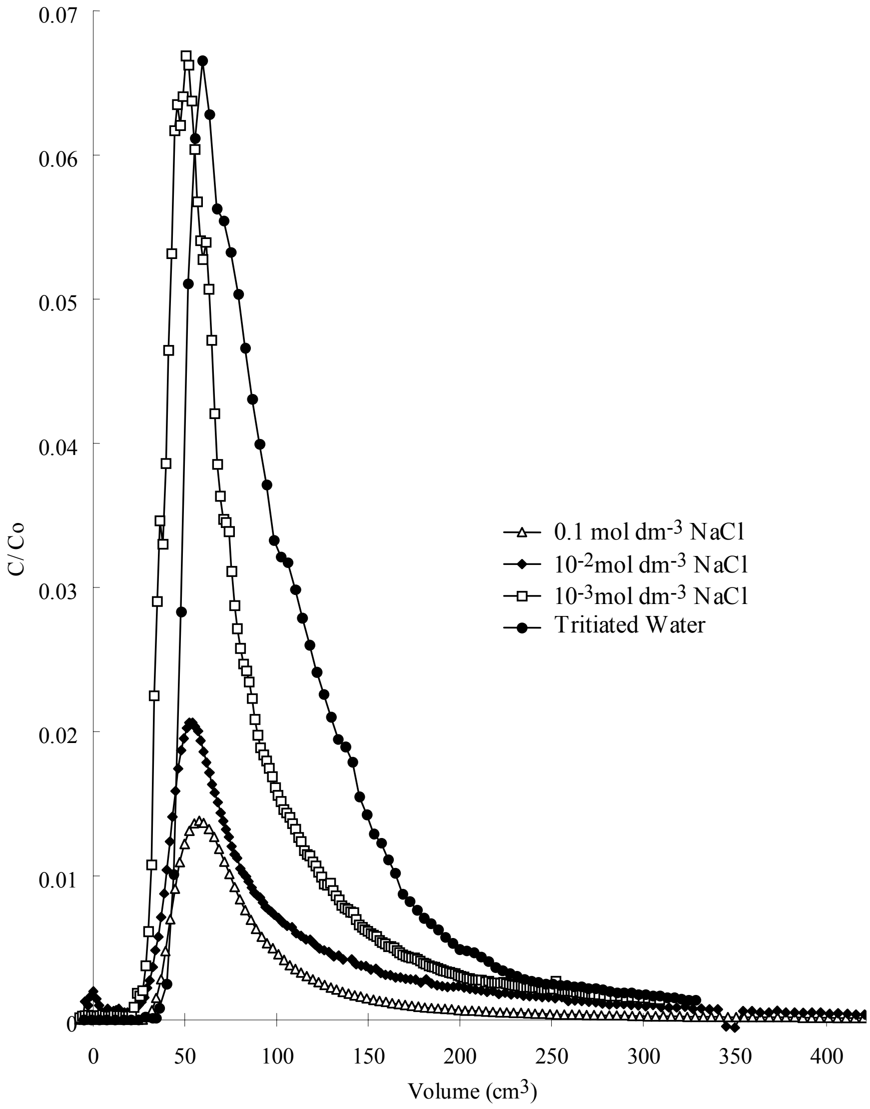

Figure 9.2 Pulse transmission of 120 nm silica colloids through a single fracture compared to tritiated water at constant flow rate of 2.0 cm^{3}min^{-1}; note the slightly earlier breakthrough of colloids and that increasing ionic strength leads to greater colloid loss in the fracture (from [54])

9.3.2 Example study II: Whiteshell fractured block experiment

(a) Background

As noted in Table 9.1, several fractured block experiments have been conducted with materials from the Whiteshell URL over the last decade. This example [444] used a 1 m^3 block which had been cut from the tunnel wall and included a fracture running through the middle of the block. The fracture trace on the block surface was sealed and the entire mass immersed in a tank of groundwater (a Na-Ca-HCO_3-Cl type with pH=8.5 and Eh=-220 to -160 mV) pumped directly from the fracture at the tunnel wall. Over 180 hydraulic tests were carried out before the colloid experiments, so the fracture is likely to be disturbed from *in situ* conditions, with both destressing following quarrying from the tunnel wall and with movement of any fault gouge during the hydraulic testing. The boundary conditions here were:

- flow rates of 5 ml min^{-1}
- experimental duration of 20 hours
- fluorescent dye labelled carboxylate-modified polystyrene microspheres (mean diameters of 34, 190, 560 and 1000 nm) and sorbing (strontium, neptunium(V), plutonium and technetium(VII)) and non-sorbing (bromide and tritium) tracers used serially in the migration experiments
- after completion of the experiments, the block was opened and the distribution of the colloids and radionuclides ascertained

The main results were that:

- 10% of the neptunium passed through without retardation and it is assumed that the neptunium (V) was only weakly reduced in the fracture to neptunium (IV)
- no plutonium was eluted,
- no strontium was retarded
- ~50% of technetium was retarded during the short experimental duration
- colloid arrival times were 190 nm>34 nm>560 nm>1000 nm
- degree of colloid retardation during the short experimental duration was 190 nm>560 nm>34 nm>1000 nm

Post-experiment examination of the fracture face showed:

- two main flow paths existed across the fracture face;
- a large amount of the total activity was concentrated within 10-20 cm of the flow inlet;
- colloid deposition was concentrated approximately half way across the flow system.

(b) Input to modelling studies

There have been none to date other than the authors note that:

- “*Strontium....elution curves are expected to lend themselves to a validation of transport models that incorporate sorption and matrix diffusion*.”

And speculate that:

- "*Colloid transport exhibited a complicated process that may include sedimentation and diffusion into stagnant zones*."

9.4 Field and URL studies

Field experiments studying colloid transport in shallow systems have been carried out for many years (see review by McCarthy and McKay [261]), for example] but, as these are of little relevance to GDFs, they will be discussed no further here.

9.4.1 CRR and CFM Experiments, Grimsel, Switzerland

(a) Background

Focused study of colloids in the Grimsel URL groundwaters goes back to the late 1980s and much development work on colloid separation methods was carried out there [e.g. 80, 250]. Despite a decade-long radionuclide migration programme in the URL (see [425, 445] for details), colloids were not considered again until the CRR (colloid and radionuclide retardation) project began in the late 1990s. However, the focus of the work was the behaviour of bentonite colloids produced from the EBS (engineered barrier system – see Figure 9.3) in the groundwaters [48] and little attention was paid to natural groundwater colloids.

In most HLW (high-level radioactive waste) repository designs, the waste is packaged in massive metal canisters which are surrounded by a large volume of bentonite backfill. The canister will slowly degrade and eventually fail, releasing small quantities of radionuclides, most of which are expected to be trapped and to decay within the bentonite. However, it is conceivable that

- erosion and gas pressure might build potential flow paths for radionuclide transport; and that
- erosion of the bentonite at the bentonite/host rock interface could produce colloids (see Figure 9.3) and this combination was the focus of the CRR experiment.

The main areas of interest were [268, 446]:

- the generation of bentonite colloids from the surface of the bentonite backfill;
- the stability and mobility of bentonite colloids in the groundwater;
- the sorption behaviour of a suite of radionuclides on the bentonite colloids;
- the sorption behaviour of bentonite colloids on different solids; and
- the degree of irreversibility of the sorption.

Although the transport distances were short (only 1-4 m), the colloids were relatively large (Figure 9.4) and the residence times in the fracture were only in the order of a few hours, it was nevertheless planned to look at potential colloid retardation mechanisms by excavating the flow field after the *in situ* experiments were complete. Unfortunately, as noted in section 9.2.2(e), the colloid loading in the flow path was deemed too low to analyse and so this part of the *in situ* experiment was cancelled and dropped from the supporting studies.

The CRR project is now completed but, to date, only the field report [268] and one modelling paper and report [47, 447] have been completed, so a full analysis of the results is not yet feasible. A follow-up project, CFM (colloid formation and migration), has now started with the aim of carrying out the experiment in a flow field that is much more relevant to a repository host rock (see discussion in section 5.2.3). In CFM, it is argued that process and mechanism understanding has now progressed to the stage where such unrealistic experiments can provide little more relevant information and that future work must consider significantly longer time scales than has been the case so far and focus on, for example, semi-stagnant groundwater systems, to better match the conditions in and around a waste repository. As such, the experimental fracture is isolated with a massive steel liner (a ‘Mega-packer’ - see Figure 9.5) in the tunnel to effectively return the hydrogeological conditions in the fracture to pre-tunnel conditions. This has the advantage of minimising the experimental artefacts discussed in section 5.2.3 and allows the experiment to be conducted under hydrogeological conditions of relevance to the near-stagnant conditions expected around a GDF.

The conceptual layout for the field experiment (see Figure 9.5) is:

- A bentonite emplacement borehole (shown above in grey) supplies the access for the colloid source (shown above in blue) to a water conducting feature in the host rock, outside the influence of the GTS tunnel system
- Sealing of the shear zone at the tunnel surface (shown above in brown) with a tunnel mega-packer (top right corner of Figure 9.5) to create a no-flow boundary and to reduce the gradient in the groundwater heads from the rock towards the tunnel
- Seal the upper and lower boundaries of the flow field with two resin impregnated boreholes in order to cut off the natural groundwater flow (shown above in green)
- Drilling of a small diameter borehole close to the tunnel surface in order to apply a monopole flow field (shown above in red)

As with CRR, the bentonite colloids will be introduced in the flow system with a suite of safety-relevant radionuclides and their combined retardation will be studied over a 5-10 year period.

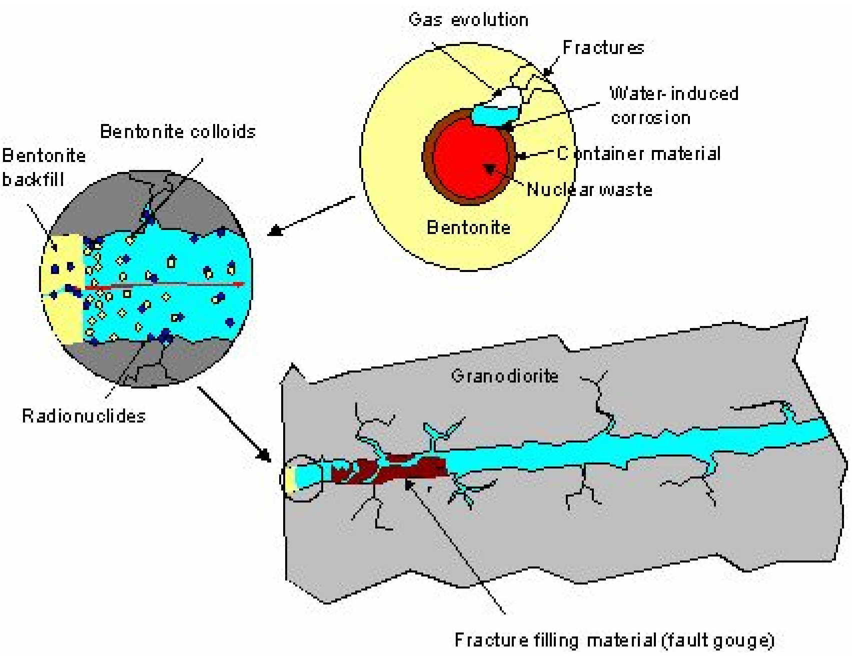

Figure 9.3 The scenario for radionuclide release and bentonite colloid formation considered in CRR (from [268])

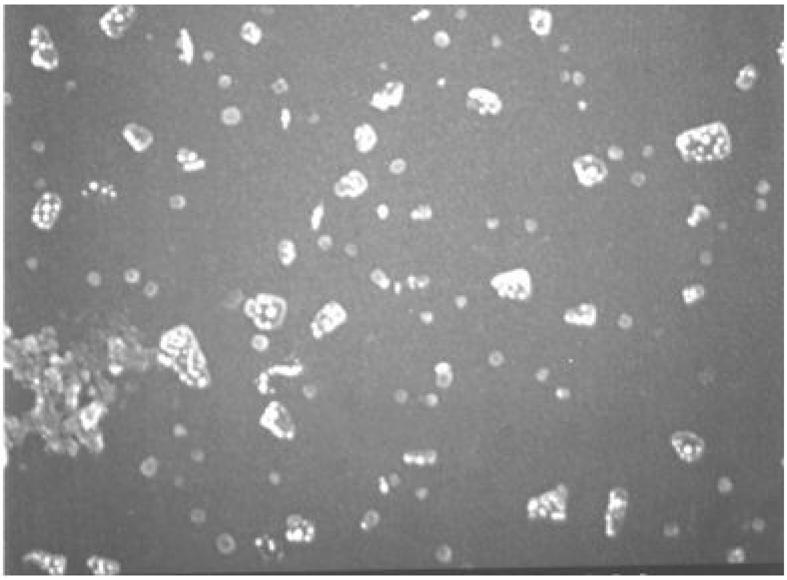

Figure 9.4 SEM image of bentonite colloids generated at a model granite/bentonite interface in the CRR experiment; the field of view is approximately 5 µm (from [446])

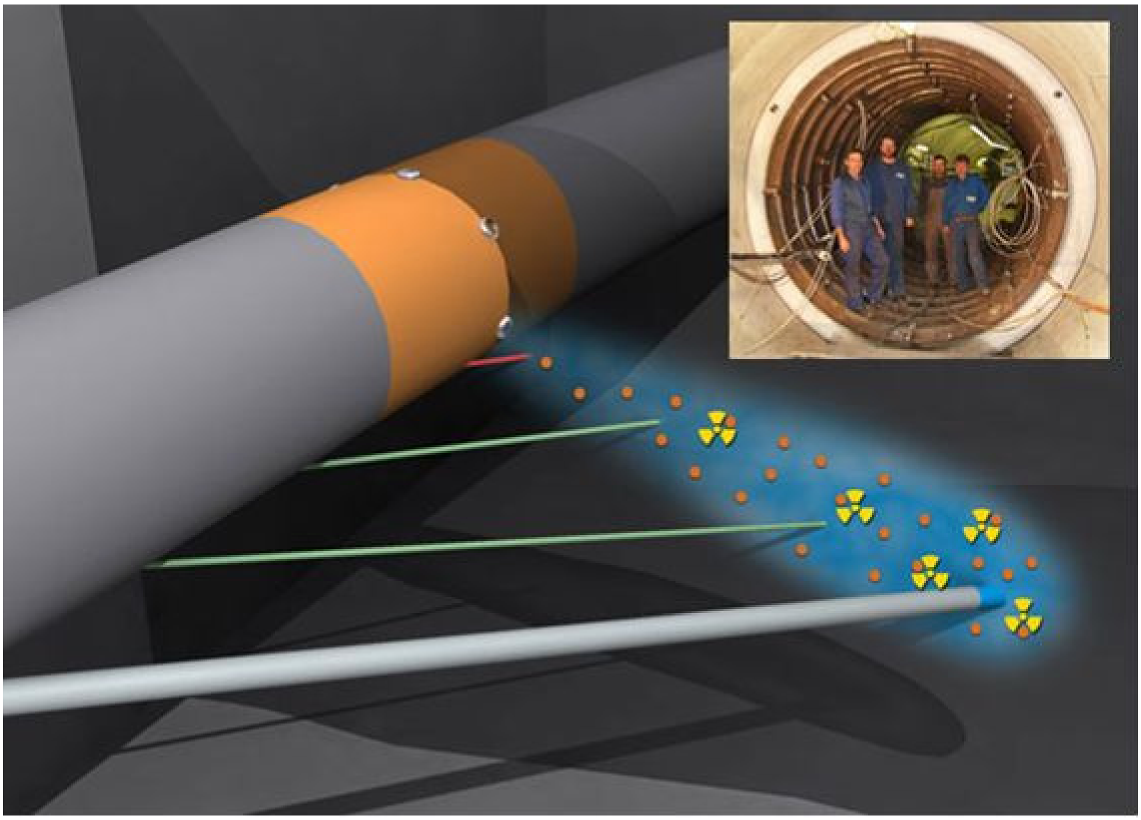

Figure 9.5 Conceptual layout of the CFM field experiment, explained in text below (from [448])

(b) Input to modelling studies

Although bentonite colloids are studied here, the data collected in CRR and to be collected in CFM will be just as applicable to the deep groundwater colloid transport processes. The current input from CRR is discussed below, whereas the CFM modelling work is just beginning and currently has two main aims:

- Supporting the *in situ* tests

- Initiating PA relevant studies on colloid generation and on colloid-facilitated radionuclide transport (including irreversibility of sorption and matrix diffusion/filtration effects)

The area focused on colloid-facilitated radionuclide transport is clearly of direct relevance to deep groundwater colloids and this is discussed further in section 12.

9.4.2 Äspö Colloid Project, Sweden

(a) Background

The overall goal of the project is to determine in what conditions colloid transport is significant in the bedrock of a Swedish facility for spent nuclear fuel. The two main questions posed are:

- when should colloid transport be taken into account in the safety assessment

- how can colloid transport be included in safety assessment modelling.

More specific aims and objectives are to:

- Investigate under what conditions the bentonite barrier can release colloids

- Study stability and transport of bentonite colloids in dilute to saline groundwater

- Study actinide and bentonite colloid transport in dilute (to represent intrusion of dilute glacial melt water to repository depth), to more saline (to represent more ‘normal’ conditions) groundwater

- Study stability and transport of other types of natural inorganic and organic colloids in dilute to saline groundwater

- Monitor background concentrations of colloids in granitic groundwaters

- Study radionuclide-colloid interactions in dilute to saline groundwaters.

The Äspö Colloid Project started with Phase I in 2000 and ran to 2004 before continuing as the Colloid Dipole project. After confirming the relatively low-level of natural groundwater colloids in the Äspö groundwaters (see Table 5.1, site 3), this moved on to look at bentonite colloid behaviour in the groundwaters as this was of greater interest to SKB’s PA modellers (cf. section 9.4.1). The bentonite colloids were shown to be unstable in the high ionic strength deep Äspö (and Olkilouto) groundwaters [450] and so the populations were also as low as the groundwater colloids.

The current focus is on:

- Stability of bentonite colloids as a function of groundwater composition, pH ionic strength, cation composition, presence of organic or other natural colloids, temperature and γ irradiation [347, 348, 449].

- Bentonite colloid transport in water bearing fractures is studied on different scales – looking at flow rates, aperture distribution, surface roughness, physical filtration and sorption onto fracture walls [e.g. 422] both *in situ* and in a completely unrelated fracture in a large block at the Whiteshell URL (see Table 9.1)

- Transport modelling is performed on the colloid transport experiments. The vision is to be able to model colloid transport in any fracture with different apertures, roughness and minerals with colloids of different size, shape and origin.

The Colloid Dipole project finished in 2007 and reporting is ongoing. A new phase, called Colloid, is due to run from 2008 to 2010 [449].

(b) Input to modelling studies

As noted in [450], the results from the project were planned to "...*be used mainly in future development of safety assessment modelling of radionuclide migration*." and this has been going on in the Colloid Dipole project. Unfortunately, as with the Grimsel CRR project, little has been published to date on the modelling apart from some scoping calculations [390] which have been used to guide the design of the field experiment. This is a pity as the higher ionic strength groundwaters of Äspö offer a perfect counterpoint to the very low ionic strength groundwaters at Grimsel which, although useful for conducting *in situ* colloid experiments, are much less representative of GDF host rock groundwaters than those at Äspö.

9.4.3 Mol URL, Belgium

(a) Background

Here, the migration of uranium, selenium, plutonium and Am was studied in the Boom Clay of the Mol URL in Belgium [451]. In case of selenium and uranium the transport was shown to be independent of NOM (natural organic material). The dominant effect of NOM on uranium was the formation of colloids and the formation of organic complexes could not be demonstrated. These colloids (> 2 nm) did not increase the uranium mobility as they were immobilised in the Boom Clay by ultrafiltration. Am and plutonium become immobilised upon interaction with the Boom Clay solid phase, although plutonium is also associated with colloids. These are either unstable in the Boom Clay porewaters or are filtered in the pores. Upon reduction of SeO_3^{2-}, part of the selenium in solution is found to be associated with NOM as colloids but with no pronounced effect on the selenium(0) solubility. Once again, the colloids are unstable or filtered in the clay pores [452].

(b) Input to modelling studies

To date, no mechanistic understanding of colloid removal by Boom Clay (i.e. is it filtration or instability in the porewater or both?) is available and neither is any detailed description of the likely flow paths. As such, the work currently offers little to colloid transport models, but is a useful qualitative indicator of colloid retardation for PA.

9.4.4 Reskajeage Farm Quarry Research Site, UK

(a) Background

The field experiments, undertaken at Reskageage Quarry, Cornwall, UK were an extension of an earlier laboratory programme (section 9.3.1). The site geology and hydrogeology were investigated [453, 454] and a fracture network model was developed [455]. The field site gave access to a longer pathway through a more complex fracture network than experienced in the laboratory. Two colloid types were investigated along with rhodamine as a non-reactive tracer [456]:

- monodisperse silica particles (30nm, 65nm, 800nm) – PCS analysis
- monodisperse haematite(130nm) – ICP-OES analysis

Eight migration experiments (six silica colloid and two haematite colloid) were performed on length scales of 5m, 9.4m or 15.4m by the use of appropriate pairs of boreholes. Groundwater was abstracted from a borehole to achieve a radially-convergent flow field. The results showed:

- the transport velocities of the silica colloids and rhodamine were similar
- retardation of 30nm silica colloids ranges from -20% to 50%
- haematite aggregates readily, but flocks are transported in the rapidly flowing water
- retardation of hematite colloids is ~90%
- size exclusion was not observed (cf. laboratory experiment)
- clear trends are, however, difficult to define

Some of the differences are probably due to a more heterogeneous fracture system *in situ* than in the laboratory along with more complex hydrogeological situation.

(b) Input to modelling studies

Here, the normalised breakthrough curves were fitted with a semi-analytical method (inversion of the closed form Laplace transform solution) and, while invoking molecular diffusion could explain the long tails of the breakthrough curves, the solution required that a higher number of fractures were involved in the transport than seemed reasonable [456].

9.4.5 Whiteshell URL, Canada

(a) Background

The Whiteshell URL in Manitoba Province, Canada, has many similarities with the Äspö URL in Sweden insofar that it is also in a crystalline shield environment. Colloid research began at Whiteshell in the mid-1980s [e.g. 79, 457] and, more recently, much effort has focused on so-called ‘*in situ* fractured block experiments’ (see Table 9.1), including one which is running in parallel with the Äspö Colloid project *in situ* studies. The data from the actual groundwater are noted in Table 5.1 (site 1) and indicate rather low colloid populations, especially in the high ionic strength deeper groundwaters.

(b) Input to modelling studies

Although the data produced in the ‘*in situ* fractured block experiments’ has been the subject of colloid transport modelling effort [e.g. 458], nothing has been done on the actual groundwater data. Although this is a good site for fractured host rock transport studies and it has a huge background database on colloids, groundwater hydrochemistry and flow systems descriptions built up over the several decades of operation of the URL, the current uncertainty over the site’s future suggests that it is currently not an option for future model testing.

9.5 Natural analogue studies

The combination of laboratory studies, which show radionuclide uptake on colloids, and field experiments, which show colloid transport in shallow systems, have highlighted the need to try and assess colloidal transport of radionuclides in deep groundwaters, i.e. under repository-relevant conditions. Several field studies have measured sizeable colloidal populations in deep groundwaters, but this information alone is not sufficient. What is required is an unambiguous demonstration of colloid transport in an appropriate geological formation over repository relevant distances, and this can only be obtained by natural analogue studies. The ideal location for such a demonstration would be a deep ore body (a point source) from which any mobile colloids could be followed downstream.

This has been attempted in several studies (e.g. Cigar Lake, Morro do Ferro) and these will be discussed below. As in the preceding sections, shallow systems will not be considered and so studies such as Broubster and Needles Eye (details in Boxes 12 and 13 of [459]) are not included here.

9.5.1 Morro do Ferro

(a) Background

The Morro do Ferro site in Brazil has a long record of investigations [e.g. 460], mainly because it is the most naturally radioactive place on the Earth's surface [461]. The advantage of Morro do Ferro is that the Th-REE ore body sits at the top of a hill, about 140 m above a local stream and flow from the ore to the stream was thought easy to intercept (Figure 7.8), providing a clear-cut case of colloid mobility or retardation. In fact, no colloids from the ore body were found in the lower boreholes nor in the stream at the base of the hill and no clay colloids were observed in the lowest borehole (MF12, Figure 9.6), despite being observed in the groundwaters sampled in the upper boreholes. As noted in section 5, the colloids analysed also showed little evidence of prolonged transport, all of which suggests efficient colloid retardation in the groundwater flow system at the site.

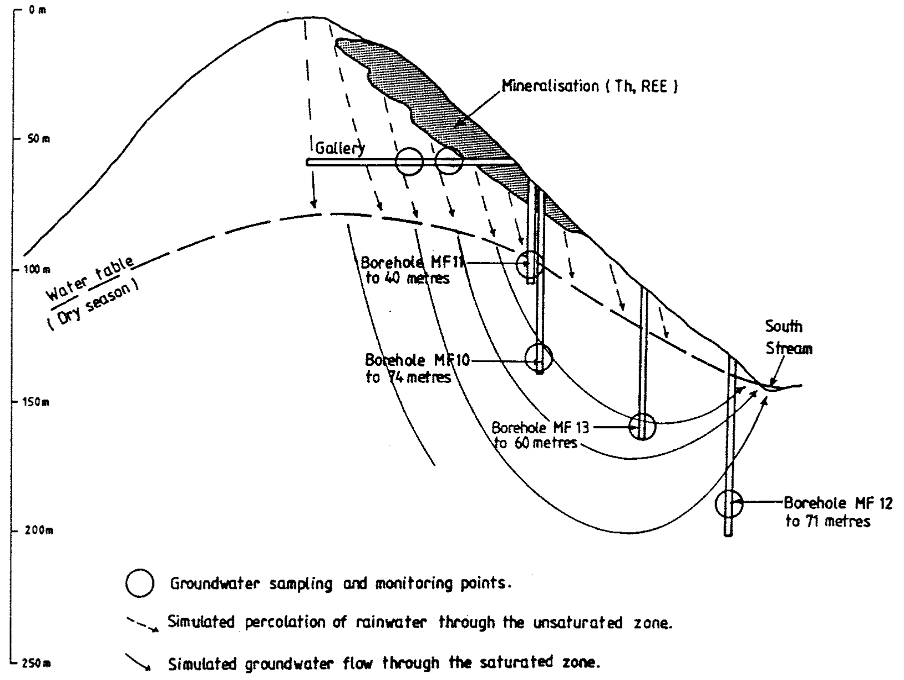

Figure 9.6 A cross-section through the Morro do Ferro showing the ore body, gallery and the boreholes (from [254])

(b) Input to modelling studies

No modelling work was carried out on the data, probably because the site was underdefined – no information was collected on potential flow path characteristics, for example. It was also realised early in the study that the ore body is in the unsaturated zone (Figure 9.6) for more than half the year and it is suspected that any colloidal material mobilised from the ore body is efficiently filtered before reaching the saturated zone [459]. This suggests that the site is not appropriate for colloid transport modelling studies, but offers a qualitative example of colloid retardation for PA.

9.5.2 Menzenschwand

(a) Background

As noted in section 5.2.1, the Menzenschwand study was carried out in a highly disturbed environment and, as such, the data must be treated with caution. While there was evidence of transport of colloids from the nearby Feldberg gneiss/metasediment formation, it must be remembered that:

- the Krunkelbach uranium prospect seriously disturbed the local groundwater flow system, drawing in up to 2000 L min^{-1}, equivalent to 14% of the precipitation in the mine's surficial catchment area

- the main fracture sampled is ~10 cm wide and contains no fault gouge – such a wide-open fracture is likely to be unusual in most repository host rocks

- as only four samples were analysed, the results are statistically weak

(b) Input to modelling studies

No modelling work in support of the data was carried out due to the paucity of data. The German government suspended the mine's operating licence and closed it down before a planned follow-up study could take place. As such, the data offer no more than a weak, qualitative example of colloid migration over long distances, but the unique approach is worth repeating (discussed further in section 12).

9.5.3 Alligator Rivers

(a) Background

The Alligator Rivers Natural Analogue Project (ARAP) investigated of a secondary enriched uranium deposit in the Northern Territory of Australia. Four large uranium deposits are located in the region: Nabarlek, Jabiluka, Ranger and Koongarra, the last being the focus of the project (Figure 9.7). The first colloid study in the area [462] showed an association between the colloids and natural thorium and this was followed up [259, 463] as one of the main areas of focus of the study. This concluded that colloids were a "....*relatively unimportant mechanism for radionuclide transport in Koongara groundwaters*...." [259] and that the colloid populations were relatively low (Table 9.2).

(b) Input to modelling studies

The results from the ARAP have been widely published (see, for example, 464 and the MRS Symposium Proceedings from the early 1990s] and discussed in detail in a series of 16 project reports, the first of which [465] is a summary of the project findings. However, as the groundwaters at Koongara are all oxidising (Eh of 100 to 400 mV) and mildly acidic and the upper 15 m of the rock and soil is unsaturated in the dry season, the results of the work are generally of little relevance to deep groundwater systems. Although the dataset from ARAP has been used in several modelling studies such as the international INTRAVAL study [466] and the USNRC has applied coupled codes developed in the project to estimate the impact of uranium and other pollutants in near surface contaminated sites (Cape Cod, Naturita) [467], little use has been made of the colloid data.

However, in the TSPA for Yucca Mountain, the Alligator Rivers Analogue was used to exemplify uranium transport in the saturated zone and it is mentioned as a site where colloidal transport has had little impact on uranium transport [468].

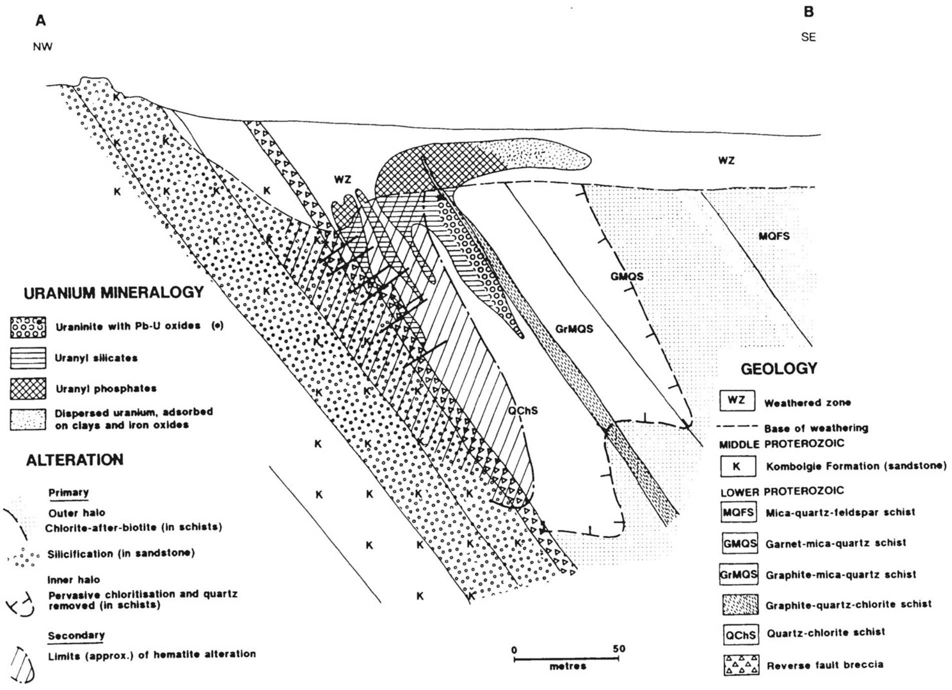

Figure 9.7 Simplified cross-section through the Koongara number 12 ore body, showing the primary and secondary mineralisation and the dispersion fan of tertiary uranium sorbed on clays and iron oxides (from [259])

Table 9.2 Mass of colloids and particles in 3 size ranges from boreholes PH14, PH49 and PH55 (from [259])

Size range (µm)	Colloid/particle mass (mgL^{-1})
1.5×10^{-3} to 1	$<5 \times 10^{-2}$
1 to 5	1 to 10
>5	5 to 35

9.5.4 Cigar Lake

(a) Background

The Cigar Lake uranium deposit is a sandstone-hosted ore body located in the Athabasca Basin of northern Saskatchewan, Canada. The ore lies at a depth of 432 m below the surface and is located at the contact between the sandstone and altered basement rock and is separated from the sandstone host by zones of clay-rich altered sandstone (Figure 9.8). There is no surface expression of its existence and it was discovered by a systematic drilling campaign through promising geological strata. Natural analogue studies were initiated by AECL in 1982 and continued through various phases until 1993.

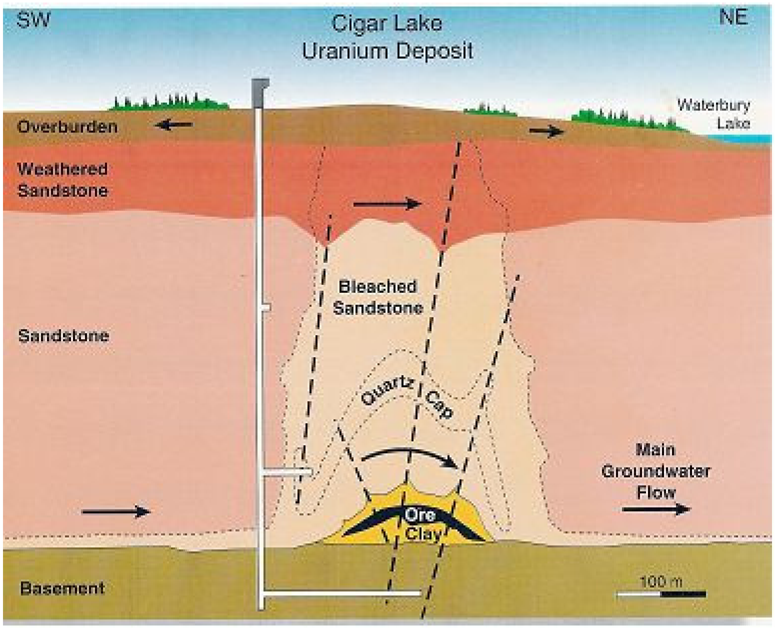

Figure 9.8 Schematic cross section through the Cigar Lake uranium deposit showing major lithological types, groundwater flow pathways, main fractures and some of the mine shafts and tunnels (from [468])

The deposit is hydrothermal in origin and consists of an irregularly-shaped lens about 2150 m long, 25 to 105 m wide and 1 to 20 m thick. The average grade of the ore is around 12 wt% uranium with maximum concentrations up to 55 wt%. Alteration of the host sandstone resulted in clay (illite) formation around the ore zone which has been taken to represent the bentonite buffer around a waste package in a HLW or SF repository.

Colloid concentrations are low (0.03 to 2.21 mgL^{-1}, see Table 5.1 (site 19)) and consist primarily of clay minerals (illite, chlorite and kaolinite), amorphous Fe-Si precipitates, quartz and organic material and were found to be fairly uniform throughout the deposit. The uranium concentration of colloids down-flow of the ore body (see Figure 9.8) were no greater than those upstream, indicating the absence of any uranium 'plume' in the sandstone. The colloids collected within the clay hola, in contact with the ore body, were of a similar composition to those collected in the sandstone, but had higher uranium concentrations, providing further support for the thesis that the clay halo provides an efficient barrier to colloid transport.

(b) Input to modelling studies

The Cigar Lake study has been quoted many times [e.g.469] as an excellent example of the barrier role of the clay halo around the ore (as an analogue of the bentonite buffer) and was used in SR-97 [470] as support for insignificant colloid concentrations at repository depths. Despite this, no attempt has been made to model the colloid data and, in fact, in a post-project reappraisal of the study from the PA viewpoint [471], colloids were not even mentioned. Although the sandstones are highly porous and hydraulically transmissive and so would be considered unsuitable for a HLW/SF disposal facility, such rock types could still be part of the far-field for any future GDF in the UK. This, allied with the fact that a significant project database still exists and the site is still accessible, suggests that it may be worth consideration for any future tests of colloid transport models. Although the mine remains closed due to flooding, limited information is available on the groundwater flow system [e.g. 184] and more could be collected with new boreholes, so allowing detailed testing of colloid transport in a real, deep groundwater system.

9.5.5 Oklo and Bangombé

(a) Background

The natural fission reactor of Bangombe is one of a number of reactor zones found in the Franceville sedimentary basin of the Gabon and is about 30 km south from the main Oklo uranium deposit. The reactor zone is shallow (~12 m deep), has undergone intense tropical weathering and is oxidising and so is similar to the ARAP site regarding relevance to GDF groundwater systems. Studies at Bangombé (see Table 5.1 (site 21)) showed low colloid contents and also underlined the lack of evidence for enhanced radionuclide transport by colloidal material. Only 2% of the uranium in the groundwater (predominantly uranium(VI) was found to be associated with colloids [472].

(b) Input to modelling studies

Due to the long and complex history of the site, it is difficult to isolate simple subsystems that have not been influenced by the variations of boundary conditions. Colloid studies performed in Bangombe indicate that, even in a superficial, oxidising, dynamic groundwater system subjected to a subtropical climate, the contribution of colloids to uranium transport is very low.

10 Transport of colloids in the geosphere - modelling

10.1 Types of transport models

Since the early 1980’s a significant literature has been produced on the modelling of colloid transport and colloid-facilitated contaminant transport with groundwater flow through porous media and fractured systems. The modelling of colloid transport has built on the extensive chemical engineering literature on modelling of the deep-bed filtration process (porous medium filtration) [e.g. 473, 474, 475, 476], in addition to developments in the modelling of fluid flow and solute transport in porous and fractured systems.

Although as part of this study, we have found a number of reviews that have dealt with various aspects of the modelling of CT or CFCT, we have not identified any comprehensive reviews that give a clear overview of the state of development of transport models, outline the various modelling approaches, analyse their strengths and weakness, and consider their effectiveness as predictive tools, etc. Here we shall attempt to give a broad overview, focussing on the extent to which the models are effective in modelling experimental data and observed behaviour and their potential for predicting behaviour in real systems.

The modelling work in the scientific literature can be divided between models of colloid transport and those of CFCT that couple colloid and solute transport. The work can be further divided between porous medium and fractured medium models, although the approaches adopted and the processes considered in each case are largely the same.

CFCT models can also be further differentiated broadly between research-type or interpretative models and assessment-type models. In research-type models, the parameters describing colloid and solute behaviour are included explicitly in the models and can be used as variable parameters to fit and interpret experimental data. In assessment-type models the effect of colloids on solute behaviour are incorporated into effective parameters, such as effective sorption distribution coefficients, flow velocities or hydrodynamic dispersion parameters, which are applied in solute transport codes. Assessment codes are used for predicting the impact of colloids under various scenarios for chosen parameter values.

There is a significant amount of experimental data available concerning colloid transport behaviour in porous media, including laboratory and field data, and in other flow geometries including parallel-plate flow channels for the testing of models of colloid transport (see section 3.5). It should be noted, however, that most of this data has been collected under flow conditions and timescales that are very different from those of transport processes in deep groundwater (c.f. section 9.1).

There is far less data available for testing CFCT models in general. While there has been some data for CFCT in porous media since the early 1990s [e.g. 477, 478, 479], data for fractured media has only become available in the last ten years through laboratory and URL studies [e.g. 47, 423, 424, 480]. A number of these studies will be discussed below.

Given the paucity of data sets, it is perhaps not surprising that there are numerous CFCT models described in the literature, some highly sophisticated (in complicated flow geometries such as spatially variable aperture fractures, for example), that do not appear to have ever been tested against experimental data.

Predictive modelling of CT and CFCT in natural systems even in small-scale laboratory experiments appears to be very difficult owing to the inherent complexity of real systems and the amount of characterisation data that is required to support the modelling effort. As a result, most of the approaches that have been used to model behaviour in real systems have remained relatively simple in conceptual terms. While more data sets have become available in the last 10 years, it is probably fair to say that there have been few significant developments in CT or CFRT modelling over the same period. The exception to this has been the recent development in understanding and modelling of colloid transport in the unsaturated zone, in the context of the Yucca Mountain repository programme in the US [e.g. 237]. However, such developments are beyond the scope of this report. The interested reader is referred to recent publications and model reports from the Yucca Mountain programme (available online at [481]).

10.2 Processes considered

The following features and processes will arise in real systems and need to be accounted for in a model of solute (radionuclide) transport through a porous medium or a fractured medium.

Those related to the flow zone:

1) Nature (geometry) of the water-saturated pore space;

2) Fluid flow through the flowing porosity of the medium;

Those related to solute transport:

3) Solute flux into the flow system
4) Advection and dispersion of solutes transported by water flow through the flowing porosity;
5) Diffusion of solutes into accessible non-flowing matrix porosity
6) Exclusion of solutes from part of the water-accessible porosity
7) Interaction of solutes with the rock matrix surfaces (e.g. by sorption)
8) Radioactive decay

For transport of colloidal particles, the list of features and processes is more extensive and in addition includes:

9) Colloid flux into the flow system
10) Existing colloid population immobilised within the flow system;
11) Advection and dispersion of colloids transported by water flow through the flowing porosity;
12) Diffusion of colloids into accessible non-flowing matrix porosity;
13) Exclusion of colloids from parts of the solute-accessible porosity (which will include parts of both the flowing and non-flowing porosity);
14) Interactions of colloids with rock matrix surfaces;
15) Physical filtration of colloids in pore throats or fracture constrictions;
16) Birth of colloids *in situ* arising from erosion of the rock surfaces or precipitation processes
17) Death of colloids *in situ* due to their dissolution or incorporation into the rock matrix
18) Growth of colloids arising from precipitation and/or aggregation processes
19) Shrinkage of colloids due to dissolution and/or disaggregation processes
20) Sedimentation of particles under the influence of gravity

Many of the above processes are dependent on the size and shape of the colloid population, which also needs to be accounted for (either implicitly or explicitly) in a model description. Some processes will also be dependent on solution chemistry, in particular the ionic strength.

In addition, for cases where concentrations of mobilised colloids are high, it may be necessary to consider effects of particle filtration on permeability reduction of the porous medium due to blockage of pore throats or fracture restrictions [e.g. 130].

Models for CFRT also need to consider:

21) Interactions of solutes with colloids, freely mobile in fluid flow, attached to rock surfaces or captured in pore throats/restrictions

In general, not all of the above processes will be included in any particular model where various simplifying assumptions will be made (either implicitly or explicitly). For example, colloid populations may be assumed to remain invariant (i.e. balance between growth, shrinkage, birth and death) and colloids may be assumed to be excluded from all matrix porosity in fractured systems.

For ease of computation, transport models have tended to be based on idealised models for porous media or fracture geometry, considering regular packing of uniformly-sized spherical particles for porous media or parallel-sided fractures[17]. More sophisticated models may account for variability of flow paths through natural fractures and porous media, these may include:

- spatial variability in fracture apertures
- variability of pore throat dimensions in porous media; or
- channel models which add together flow through pipes or slots of different dimensions to represent variable flow paths through porous or fractured media;
- discrete fracture networks (for modelling at larger scales).

For fractured systems, so called “dual porosity” models have been developed that account for the presence of non-flowing porosity in the rock matrix that is accessible by diffusion from the fracture porosity. Diffusion of solutes into the matrix porosity (rock matrix diffusion or RMD) and sorption onto the matrix surfaces therein provides an important retardation mechanism for radionuclides transported by groundwater flow in fractures [12]. Not all of the water-accessible porosity will be accessible to all solute species, however, due to anion exclusion [482] and colloids may be excluded from fine-scale matrix porosity on the basis of both charge and size.

Most colloid transport and CFRT modelling studies have assumed uniform spherical particles although, occasionally polydisperse size distributions have been considered [e.g. 483]. The effect of particle shape on colloid transport has been largely neglected (on pragmatic grounds) despite the importance of layered clays as common groundwater colloid components. The size and shape of particles are potentially important because these will affect the volume of porosity accessible to colloids, the strength of particle-particle and particle-surface interactions and particle filtration in flow constrictions.

Given the inherent difficulties in characterising the complexity of real systems, in general, the models that have been used to predict and interpret CT and CFRT experiments, though complex, have tended to assume simple geometries and include simplifying assumptions concerning processes that are unlikely to vary significantly over experimental timescales.

It needs to be borne in mind, however, that even for migration experiments performed in idealised geometries, transport and mixing through both inlet and outlet systems will also contribute to the observed migration behaviour (cf. discussion in [484]). Additional dispersion will occur in the dead volumes of both inlet/outlet pipework and manifolds, and sorption of colloids and solutes can occur to the surfaces there-in. These additional effects due to the

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[17] For this reason, many of the experiments designed to study colloid filtration and deposition behaviour have been undertaken in packed beds containing regular spherical packings or in flow cells with well-defined collector surface geometries (such as rotating discs, parallel plate flow channels, etc).

injection and collection system, often referred to as the injection function, need to be understood to allow a correct interpretation of colloid migration processes and to avoid over-interpretation of experimental breakthrough curves.

10.2.1 Data requirements for CFRT modelling

Clearly, the modelling of CFRT processes requires a significant amount of input data for simulations of experiments and even more for predictive use. Depending on the complexity of the experimental system under consideration, the parameters required for model fitting are likely to include:

- flow characteristics of the system including water flow velocity and dispersion coefficient;
- fracture aperture distribution of flowing porosity plus matrix porosity (for dual-porosity systems);
- solute partitioning parameters for sorption to the matrix surfaces; this may involve sorption distribution coefficients for linear reversible sorption or other types of sorption isotherms (e.g. Langmuir) and adsorption and desorption rate coefficients in kinetic models;
- solute diffusion coefficients and accessible porosity in the matrix
- colloid velocity and dispersion coefficient for transport with water flow.
- colloid interaction parameters with the matrix; this may include rate constants for deposition and detachment to the surface and surface capacity (if deposition is limited)
- colloid diffusion coefficients and accessible porosity in flowing porosity and matrix;
- solute partitioning parameters between solution and colloid surfaces, etc.

Colloid and solute fluxes are usually defined experimentally. Some of the above parameters will be sensitive to ionic strength including the colloid-surface interactions and, for some radionuclides, sorption parameters (e.g. where the predominant process is ion exchange).

Given the data demand, it is usually necessary to undertake a range of supporting experiments to characterise the flow system and the contributing chemical and physico-chemical processes as part of a programme to study CFRT [e.g. 477, 479]. Solute sorption onto the colloid and solid phases may be measured by means of batch sorption experiments. Colloid and sorbing solute transport experiments may be undertaken independently and it is standard practice to use non-sorbing tracers to characterise the water flow through the porous system.

The importance of using a consistent approach to model the transport of non-sorbing tracers and colloid transport in the interpretation of any given set of transport experiments needs to be emphasised [149]. Modelling non-sorbing tracer transport and sorbing solute transport in the absence and presence of colloids all need to go hand-in-hand. Parameters obtained from fitting non-sorbing tracer and sorbing tracer migration data provide an important basis for fitting and interpreting observed colloid transport and CFCT data.

10.3 Modelling approaches

Two principal approaches to the modelling of transport in flowing systems can be distinguished [93, 485]: Lagrangian methods and Eulerian methods. Lagrangian methods consider the trajectory of individual particles moving under the influence of hydrodynamic and other forces (e,g. electrostatic, gravitational) through a porous system. In the field of fluid transport, this approach is often referred to as particle tracking. In Lagrangian approaches, diffusion may be incorporated using random walk methods.

Eulerian methods describe particle concentrations in time and space. The Eulerian description of particle motion is by means of a probability density in fluid space described by a set of coupled ordinary differential equations termed the Fokker-Plank (F-P) equations. For dilute dispersions of particles where interparticle interactions can be neglected, the F-P equations reduce to a continuity equation, commonly referred to as the advective-diffusion equation (ADE). Eulerian methods have the advantage that diffusive effects are readily taken into account.

In general, the Eulerian approach has been the more widely used for modelling solute, colloid and colloid-facilitated transport. Lagrangian methods are suitable for estimating transport behaviour of solutes or colloids but are less well suited for studying coupled transport, although recently Lagrangian CFCT models have been described [390, 486].

10.3.1 The Advective Diffusion Equation

Most models of colloid transport and CFCT are based on application of the advective diffusion equation to describe either or both colloid particle transport and contaminant transport.

The general mass balance equation for particle transport is given by:

$$\frac{\partial C}{\partial t} + \nabla . J = Q \qquad [10.1]$$

Where C is the particle number concentration, t is time, J is the particle flux vector and Q is a source term.

In the advective-diffusion equation, the particle flux vector, J, is made up of components arising from particle diffusion, advection and the action of additional interactions which affect particle distribution. In the case of solutes, these interactions include solute-matrix electrostatic interactions. In the case of colloidal particles these including gravity and those arising from colloid-surface interactions; a local, pore-scale form of the ADE can be written as [93]:

$$J = -D . \nabla C + uC + \frac{D . F}{k_B T} C \qquad (10.2)$$

Where D is the particle diffusion tensor, u is the particle velocity induced by fluid flow, k_B is the Boltzmann constant and T is the temperature. The right hand term in equation (10.2) represents the mobility of the particle under the action of external forces where, F is the external force vector. For particle transport in flowing systems, F is composed of gravitational (F_G) and colloid-surface interaction (F_{cs}) components:

$$F = F_G + F_{cs} \qquad (10.3)$$

The colloidal interaction forces can be obtained from the total interaction potential between a particle and a surface, φ_T:

$$F_{cs} = -\nabla \phi_T \qquad (10.4)$$

At larger lengthscales (ie. over a larger volume of the porous medium), the diffusion tensor is replaced by the dispersion tensor which has components of both diffusion and dispersion; the latter arises from variations in flow path and flow velocity through the porous medium.

In most applications of the ADE to colloid transport and colloid-facilitated contaminant transport (CFCT) processes, various simplifications are made to the mathematical description for ease of computation. For example, many models consider fluid transport in only one dimension, and the interaction between particles and the pore walls may be treated in terms of rate constants for particle deposition and release by the solid matrix [e.g. 50, 487] (where colloid-surface interactions potential are not known). In most cases, gravitational effects are neglected. Although in some cases (with appropriate approximations) analytical solutions to the ADE can be obtained [e.g. 488], in most cases transport is calculated by numerical methods.

10.3.2 Particle tracking methods

The particle tracking method applied to solute or colloid transport can be broken down into the following four steps:

1) define the aperture distribution in each flowing feature (porous medium or fracture) within the model;

2) predict the flow field in the porous medium;

3) identify and define the additional processes and associated forces acting upon the particles (e.g. gravity, electrostatic forces)

4) predict tracer transport for an ensemble of particles, using random walk methods to account for diffusion.

A particular advantage of particle tracking methods is the capability to consider more complex flow distributions than is possible using the averaged description of flow applied in Eulerian models. Non-uniform aperture distributions are usually treated by assuming that each cell within the model has uniform aperture and that fluid flow within each cell can be treated as flow between two parallel plates [e.g. 489].

For either colloids or solutes the boundary conditions at the wall of the porous medium are used to define the interactions of the particles with the matrix surface. These may be non-sticking, irreversible sticking or a reversible interaction with associated kinetic terms for sorption and desorption.

10.3.3 An example of the Lagrangian approach

Reimus and co-workers [490] used particle tracking methods to model tracer experiments with monodisperse latex colloids (0.3 and 1.0 µm in size) and non-sorbing solute, iodide, in three saturated natural fractures. The experiments were of the continuous feed rather than pulse feed type.

The aperture distributions of the fractures were determined using surface profiling techniques and used to construct an aperture distribution grid for the simulations. The flow field in the fractures assumed localised parallel-plate flow. Fracture walls were treated as reflective walls for colloids (i.e. no deposition was assumed to occur), with hydrodynamic corrections included to account for a gradient in diffusivity and differences in advective velocity compared to the free fluid adjacent to the fracture wall. Solute RMD was modelled by assuming that when a solute hit the wall it had a probability of entering a pore equal to the matrix porosity. If so, a pre-determined distribution of diffusion times was randomly sampled to assign the time it takes before the solute returns to the fracture.

In the experiments, hydrodynamic chromatography of the colloids was observed with an earlier breakthrough compared to iodide. In addition, the colloid breakthrough curves rose to feed concentration levels more rapidly than iodide. The approach of iodide concentration levels was faster at higher flow rates which was consistent with retardation by RMD.

The particle tracking approach accounted for hydrodynamic chromatography of the colloidal particles and matrix diffusion of the solute. As shown in Figure 10.1, the approach was successful in predicting initial breakthrough times of solute and colloid tracers, and qualitatively in predicting the shapes of the experimental breakthrough curves, although in general, solute concentrations were overpredicted and colloid concentrations underpredicted. The authors speculated that the discrepancies could have resulted from roughness of the fracture surfaces such that the colloid-excluded volumes were larger than estimated in the model. However, uncertainties in the aperture distributions and other assumptions in the modelling approach could have contributed.

The above results probably illustrate about the best that can be achieved in terms of quantitatively modelling colloid behaviour in simple, small-scale transport experiments in natural fracture systems. This example benefits from (apparently) negligible colloid deposition to the fracture surfaces and a well-characterised fracture aperture distribution as a model input. Reducing the experimental uncertainties to improve the model predictions would not be straightforward.

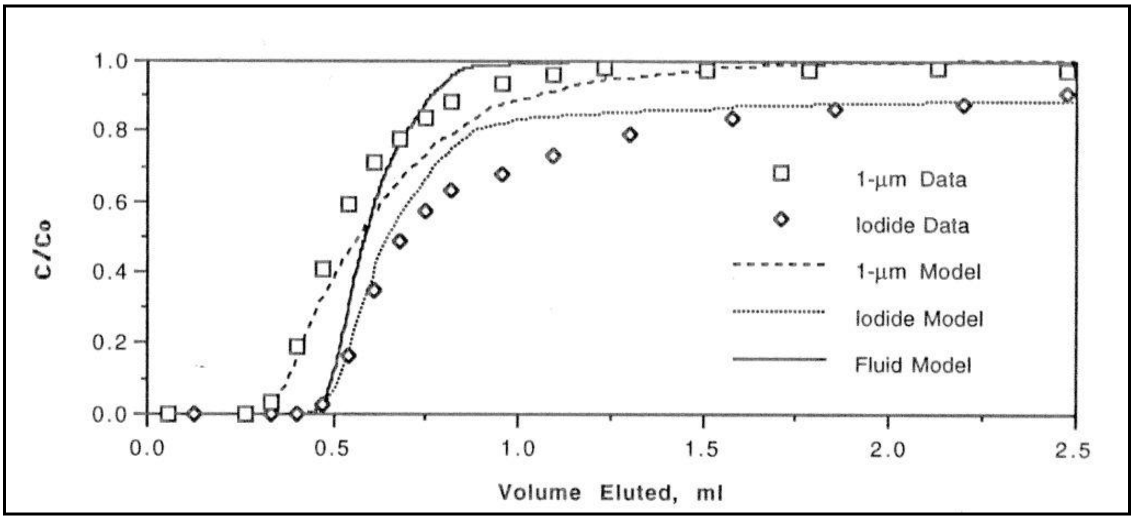

Figure 10.1 Experimental and predicted breakthrough curves for 1.0 µm latex particles and non-sorbing iodide tracer applied simultaneously to a natural fracture in Bandelier tuff at a flow rate of 8.28 cm^3 hr^{-1}; the "fluid model" refers to calculations for point-like particles excluded from the matrix (from [490]).

10.4 Models of colloid transport

Some aspects of colloid transport behaviour and its modelling have been covered in section 3.5.3. Here the emphasis is on the design of models and their potential application to predict colloid transport behaviour in the laboratory and in the field. The coupling of colloid and solute transport in colloid-facilitated transport models will be discussed in the section 10.5.

10.4.1 Modelling colloid-surface interactions

The modelling of colloid transport through porous and fractured media has its roots in the modelling of deep bed filtration processes for water treatment and fundamental studies of colloid deposition and particle adhesion undertaken in the colloid science. The application of these models to the sub-surface aquatic environment dates from the 1980s. Development and application of models of particle transport in porous media up until the mid-1980s are summarised by McDowell-Boyer *et al*. [155] and up until 1996 by Ryan and Elimelech [93].

Filtration theories tend to assume that deposition of colloids to the filter media is essentially irreversible. Clean bed removal kinetics can be modelled empirically as being first order in particle concentration, C_c [491]:

$$\frac{dC_c}{dx} = -\lambda_o C_c , \tag{10.5}$$

where λ_o is the clean bed filter coefficient. An approximate analytical expression for λ_o in a packed bed of uniform spherical particles (and for deposition in other uniform geometries) accounting for Brownian motion, interception and gravitational sedimentation was obtained from particle trajectory simulations (as summarised in [475]). These expressions also include corrections to account for hydrodynamic effects (after Honig *et al*. [492]). These arise from the viscous resistance of the fluid that must be displaced from the narrowing gap between two bodies as they collide.

As discussed in section 3.5.3, experimental data on particle collection by clean media give filter coefficients that agree with predictions to within a factor 2 under conditions of high ionic strength when electrostatic interactions are effectively screened [155]. However, at low ionic strength where attachment is unfavourable, attempts to predict particle deposition on the basis of DLVO theory have been largely unsuccessful, even when applied to well-characterised uniform laboratory systems.

Given the difficulties in modelling colloid-surface interactions *a priori*, the modelling of colloid transport in real systems has tended to adopt a simpler empirical approach [e.g. 50, 423]. Given that the goal is to develop a predictive capability for modelling CT and CFRT behaviour in the field, the approach is based on the assumption that by modelling colloid behaviour under a range of relevant conditions, ranges of parameter values can be obtained that may be used to predict behaviour at larger scales.

The approaches used have been to treat colloid-surface interactions as either reversible and/or irreversible with (usually) first order kinetics for both particle deposition and release. Most models have assumed linear isotherms for particle deposition. However, alternative, non-linear isotherms such as the Langmuir isotherm that account for finite (i.e. monolayer) surface coverage or the Freundlich isotherm may be used.

Experimental evidence that colloid deposition onto surfaces may be reversible has been obtained by direct observation of experiments in transparent flow chambers, such as the parallel flow cell of Meinders *et al*. [159, 493]. Harvey and Garabedian [494] included both reversible and irreversible particle capture in their model for bacteria transport in small-scale injection tests.

This type of empirical approach was adopted on the Nirex programme to fit colloid transport data for natural fractures obtained in laboratory experiments [49, 50]. The model and its fitting to laboratory data are discussed in some detail in the previous thematic report [49], but will outlined here to illustrate the approach.

Essentially, the advection-dispersion model for flow through a parallel-side fracture included reversible colloid sorption to the fracture walls with adsorption and desorption rate constants k_a and k_d respectively. The model was applied to data from a series of pulse migration tests through a small slate block undertaken with rhodamine-WT as a non-sorbing tracer and synthetic (hematite and silica) and fracture infill-derived colloid tracers.

The breakthrough curves for the rhodamine-WT were found to be best fitted using a two-channel advection-dispersion model in which about 40% of the rhodamine travelled rapidly through fast flow paths while the remainder travelled by slower paths at about one half of the average velocity through the fast channel. As a result, the single channel implementation of the colloid sorption model applied was inevitably limited in its ability to represent the data for colloid transport in the fracture. Nevertheless, the results are informative. An example of a model fit to colloid breakthrough data is shown in Figure 10.2.

A number of parameters can be obtained by fitting experimental data from pulse experiments such as that shown in Figure 10.2. As pointed out by Grindrod *et al*. [149], the initial part of the breakthrough curve arises from colloids that pass through the experiment without attachment to the solid phase and which have moved freely with fluid flow. This unfiltered fraction provides information on the advection and dispersion of the colloidal particles through the experiment. Attachment of particles to the solid phase causes attenuation of the colloid pulse from which the rate coefficient for particle deposition can be obtained. Provided that the attenuation is significant and data quality is good, the attachment rate coefficient can be fitted with relatively low uncertainty. The tail of the breakthrough curve provides information on colloid release from the medium. However, owing to low concentrations in the tail and the relatively greater contribution of experimental noise, k_d values tends to be less well-defined and there is significant uncertainty concerning fitted values.

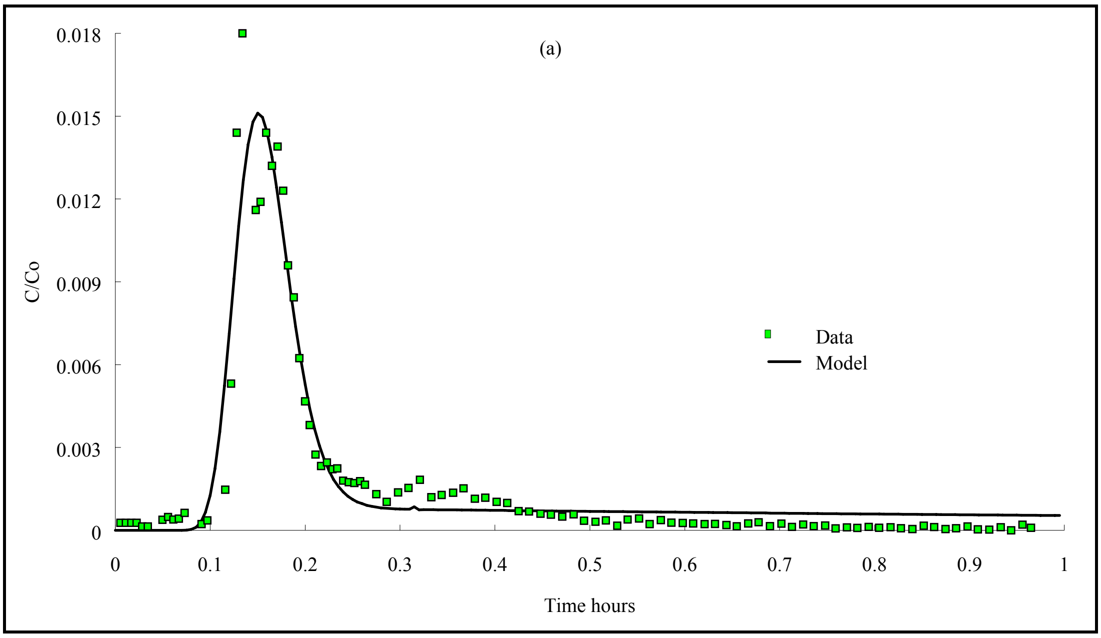

Figure 10.2 Colloid sorption advection-dispersion model fits to haematite fracture infill colloid breakthrough data from fracture flow experiments (from [49])

In all cases modelled there was a good fit to the initial peak, but fits to the secondary shoulder and tail were poor. The secondary shoulder would account for colloid transport through slower flow paths (as for rhodamine-WT) and clearly a two-channel model would better represent the data. Simulations showed [50] that when the single-channel colloid transport model is applied to these data, the desorption rate parameter, k_d, is varied to fit (poorly) the secondary shoulder and the tail of the data. However, the model does not distinguish between retardation of colloid breakthrough (compared to transport through the fast channel) that arises because a proportion of colloids are advected through slower flow paths and retardation that arises due to sorption in the fracture. For this reason, it is not clear whether the assumption of reversible colloid sorption is valid for the infill-derived colloids.

As a result of the modelling results described above, a two-channel implementation of the colloid sorption model was incorporated into TALBOT. However, due to the increased number of fitting parameters required, it was found to be very difficult to constrain the model fit with a consistent set of parameters; a situation that was not helped by the noise on the data. Therefore, the approach was not pursued further.

One factor that was not considered in the above analysis concerns the potential impact of the injection function (see section 10.2) which may also contribute to the shape of the observed breakthrough curve.

The results of the Nirex study illustrate the difficulty in interpreting and modelling colloid transport in real systems using simple models and the difficulties in applying more complicated models where the system becomes under-defined.

10.5 Models of colloid-facilitated transport

Models to simulate and predict the facilitated transport of contaminant species by mobile colloidal particles were first developed in the late 1980s [e.g. 27, 495] and significant progress has been made over the last twenty years, as outlined recently by Sen and Khilar [130]. A key aspect of these models is the coupling of solute-colloid and solute-matrix interactions with advective transport of both colloids and sorbing solutes.

Some of the earliest approaches incorporated a mobile sorbent colloidal phase into a one-dimensional solute transport model (e.g. CML/COMET [495], CHEMTARD [477,496]). The COMET model implemented in the US EPA's CML code was one of the first assessment-type models developed specifically to assess the potential significant of CFCT. In this model, the effects of an equilibrium distribution between the dissolved phase and the surfaces of both mobile colloids and immobile matrix were incorporated in terms of an effective solute sorption distribution coefficient to the solid phase. The COMET model did allow different types of colloidal species to be included in the model, for example to reflect different particle size and solute partitioning coefficient, and for a different colloid velocity accounting for hydrodynamic chromatography.

CHEMTARD, a solute transport code developed by the UK Department of the Environment in the early 1990s, was extended to include mobile colloids. In CHEMTARD, the advection and diffusion of colloids and dissolved solutes through the porous medium were modelled independently. Simultaneous sorption of a solute species onto both mobile colloids and the solid matrix was assumed with reversible linear sorption. This also required an additional transport equation for solution species sorbed to colloids. In common with COMET, the models also assumed that there was no interaction between the colloids and the porous medium.

CHEMTARD was tested using data from column experiments to study the migration of thorium through a bed of fused silica in the presence or absence of silica colloids. In the absence of colloids, no thorium was eluted over the timescale of the experiments, as predicted by the solute transport model. However, CHEMTARD could not model the delayed breakthrough of a continuous feed of thorium-loaded colloids (this could only be achieved by fitting a lower colloid velocity), which was indicative of transient particle filtration, and thorium was found to remain attached to the colloids. Over the timescale of the experiment (3 hours travel time) thorium desorption from the colloids was negligible and clearly thorium behaviour could not be represented by an equilibrium sorption process.

The testing of CHEMTARD illustrates the importance of including colloid-matrix interactions in transport models and the limitations of laboratory experiments for studying the distribution of solutes between dissolved, colloid and matrix sorbed species owing to the relatively short timescales involved compared to sorption (in particular desorption) kinetics.

More sophisticated Eulerian models appeared in the mid-1990s which attempted to incorporate colloid-surface interaction processes into the transport models. These included the equilibrium partitioning model of Corapcioglu and Jiang [487, 497] and a model by Saiers and Hornberger [479] (with two different treatments of solute sorption) for porous media, and a range of fracture medium models of both assessment-type [e.g. 498, 499, 500] and research type [e.g. 501, 502, 503]. Most of the fractured medium models considered flow through parallel-walled fractures; Abdel-Salam and Chrysikopoulos simulated CFCT in a fracture with spatially variable aperture [504]

The model of Saiers and Hornberger [479] warrants more detailed discussion as it was developed in parallel with a well-designed suite of laboratory experiments to investigate the effect of kaolinite colloids on the migration of caesium through columns of mineralogically pure quartz sand [478, 479]. Caesium transport experiments were undertaken with and without colloids plus batch sorption experiments to study caesium-kaolinite and caesium-sand interactions. The effect of ionic strength on these processes was also investigated [479].

The processes included in the model were kaolinite transport and rate-limited deposition onto the quartz grains, kinetically controlled caesium sorption and desorption to the quartz and equilibrium sorption of caesium to mobile kaolinite colloids (with no sorption to deposited kaolinite). Variant models that included: 1) sorption to deposited colloids; and 2) kinetic sorption model for caesium sorption to both mobile and deposited colloids; were also considered but were less successful in modelling data. Caesium sorption was modelled as an ion exchange process which was sensitive to ionic strength and competition from sodium ions in the bulk electrolyte. Although the colloid breakthrough curves displayed evidence of surface blocking by deposited particles at low ionic strength and filter ripening at high ionic strength, for simplicity, these effects were not accounted for in the models.

The solute transport model with no colloids was used to fit the experimental breakthrough curves for caesium in the absence of kaolinite as a function of ionic strength. This took account of the ionic strength dependence of kaolinite sorption. The parameters determined by fitting the solute transport and batch experiments were used to predict behaviour in the CFCT experiments. The FTM was found to give a significantly better prediction of the CFCT experiments than solute transport alone and the difference was most pronounced at low ionic strength, where caesium was strongly sorbed to the kaolinite. At higher ionic strength little enhancement in caesium transport by the colloids was predicted due to weak caesium sorption, in agreement with experiments.

The authors observed that the model predictions of CFCT were very sensitive to the values of the mass transfer parameters that were evaluated from the supporting batch sorption and solute transport experiments and were thus sensitive to uncertainties in the parameter values. For this reason, they did not consider that their attempt to transfer parameters from the supporting experiments to the CFCT experiments was a complete success. They concluded that:"*This extreme sensitivity of the model calculations to parameter variability indicates that caution should be exercised when transferring mass transfer parameters from one set of experiments to another*."

All of the fracture transport models were used to simulate CFCT and consider effect of various parameter values on potential impact of colloids. No suitable data was available for testing these models at the time and it is unclear from the literature whether any experimental testing has been undertaken subsequently. The assessment type models of Smith [498, 499] and Baek and Pitt [500] are dual-porosity models that coupled transport in two orthogonal one-dimensional systems advection-dispersion of colloids and solute in the fracture and diffusion of solutes into the matrix porosity. The model of Ibaraki and Sudicky [502] accounted for aqueous phase contaminant transport by advection and dispersion in both parallel-sided fractures and the matrix porosity, from which colloids were excluded. Abdel-Salem and Chrystikopoulos [504] considered transport in two dimensions in a spatially variable fracture with or without colloid size exclusion from small aperture constrictions in the aperture model. The model also accounted for matrix diffusion of solute but colloid exclusion from the matrix.

The major variations between the various fracture models concern the treatment of solute sorption and desorption kinetics and isotherms onto matrix and colloids surfaces and in the treatment of colloid-surface reactions as reversible or irreversible with first order kinetics.

Baek and Pitt [500] used a full linear equilibrium model for solute sorption, and a kinetic sorption/desorption model for colloid interaction with fracture surfaces. The model of Smith [498, 499] accounted for two types of adsorption site on the surface of the colloids: irreversible and reversible. Sorption (and desorption from the reversible site) were treated with first order kinetics. The model of Ibaraki and Sudicky [502] considered irreversible deposition of colloids onto the fracture surfaces, and accounted for solute sorption onto the mobile and filtered colloids, the fracture walls and the porous matrix surfaces. The numerical formulation allowed for either equilibrium or kinetic sorption of the solute according to either a Langmuir or Freundlich isotherm.

The simulations undertaken by Ibaraki and Sudicky [502] give typical results. They explored the importance of a range of parameters on the potential influence of colloids in enhancing solute migration. These included: the solute sorption kinetics; the colloid filtration coefficient; the matrix porosity; the sorption capacity of the colloids and the effect of a Langmuir isotherm. Significant enhancement of solute transport was predicted when desorption of solutes from colloids was slow; rapid sorption kinetics could facilitate transport if the sorption capacity of the colloids is large. When colloids were strongly filtered there was little enhancement of solute transport due to low colloid mobility. In addition, colloids had a greater effect in enhancing solute transport when the matrix porosity was high rather than low, owing to the greater capacity of the matrix for the solute in the former case. The model was subsequently used for more extensive simulations in discrete fracture network models [503].

In general, CFCT models do not incorporate the effects of particle entrapment and pore plugging. Sen *et al*. [505, 506 ,507], recently developed a 1-D transport model for porous media which incorporated: 1) changes to the medium porosity due to plugging phenomena; 2) the release of fines occuring due to hydrodynamic forces; and 3) the coefficient of particle capture is negligibly small until the colloid concentration reaches the critical particle concentration (CPC); beyond the CPC, the porous medium becomes plugged due to advective jamming and the flow stops.

The model was tested using data from nickel transport experiments through sand beds containing up to 6% added kaolinite, from which colloids were mobilised under the experimental conditions. The model predicted additional retardation of nickel migration under "*plugging conditions*", as seen in the experiments; quanlitative agreement to the shape of breakthrough curves was obtained on fitting. These types of modelling and experiments are more appropriate for shallow sand/soil systems than to deep porous rock.

More recently, models have been applied to experimental data for CFCT in fractures, with the purpose of obtaining data that might be applied in predictive modelling at the larger scale. An example is outlined below.

10.5.1 Modelling colloid-faciitated plutonium transport

As part of the work on the Yucca Mountain Project, Viswanthan *et al*. [423] have developed a reactive transport model for colloid-facilitated plutonium transport in saturated fractures. The model has been applied to a series CFRT experiments through natural fractures with the simultaneous application of natural colloids, plutonium and tritium (as non-sorbing tracer). The objective of the study was to identify the physical and chemical processes and parameters that affect CFRT of plutonium transport in fractured rocks.

A series of 12 CFRT experiments with plutonium were conducted in 4 naturally fractured tuff cores from the Nevada Test Site. The injected feed solutions contained plutonium that had been pre-equilibrated with inorganic colloids: plutonium(V) equilibrated with two types of montmorillonite or silica colloids, or plutonium(IV) sorbed onto inorganic clinoptilolite (zeolite) colloids. For each colloid type, experiments were undertaken in two fractured cores at two flow rates.

The principal results of the tests were that:

- No free aqueous plutonium exits the fractures;
- The desorption rate of colloids effectively determines the extent of CFRT over the experimental timescale:
    - plutonium(IV) sorbs strongly to zeolite colloids and all the plutonium originating on the colloids breaks through on the colloids (i.e. no desorption on the timescale of the experiments);
    - Silica and montmorillonite are less sorbent for plutonium(V) and appear to facilitate plutonium transport only for small residence times (i.e. at high flow rates);

The CFRT model assumes a parallel-walled fracture and includes:

- plutonium aqueous speciation,
- plutonium sorption and desorption on colloids with first order rate constants;
- reversible attachment of colloids to the fracture walls with first order attachment and detachment rate constants;
- solute diffusion into the matrix; and
- equilibrium sorption by surface complexation and ion exchange of plutonium with fracture and matrix minerals

The conceptual scheme is illustrated in Figure 10.3.

Data fitting was carried out to identify the optimal set of transport parameters for multiple experiments with the same type of plutonium-colloid mix. Typical results are illustrated in Figure 10.4. It is stated that first-order kinetic parameters for colloid attachment and detachment obtained provided "*very good matches between simulated and observed data*".

The colloid transport parameters were then fixed to estimate the plutonium sorption parameters to colloids and immobile minerals. Model fits to the plutonium(IV)-zeolite colloid breakthrough data, where no plutonium desorption occurred appear reasonable. However, in the experiments with silica where some plutonium(V) desorption from colloids occurred, there was difficulty in fitting a consistent set of parameters to the data. Neither the colloid breakthrough data nor fitted parameters have been presented, but it is evident from the presented plutonium breakthrough curves that significant colloid loss occurred during the experiments. It is not entirely clear whether CFRT of plutonium(V) is limited owing to desorption from the colloids or because the carrier colloids are removed.

We also note that, in general, the tails of the breakthrough curves, which are dependent on k_d, seem to be poorly fitted (c.f. Figure 10.4). Thus there would appear to be significant uncertainty concerning the suitability of upscaling the fitted parameters to the field scale.

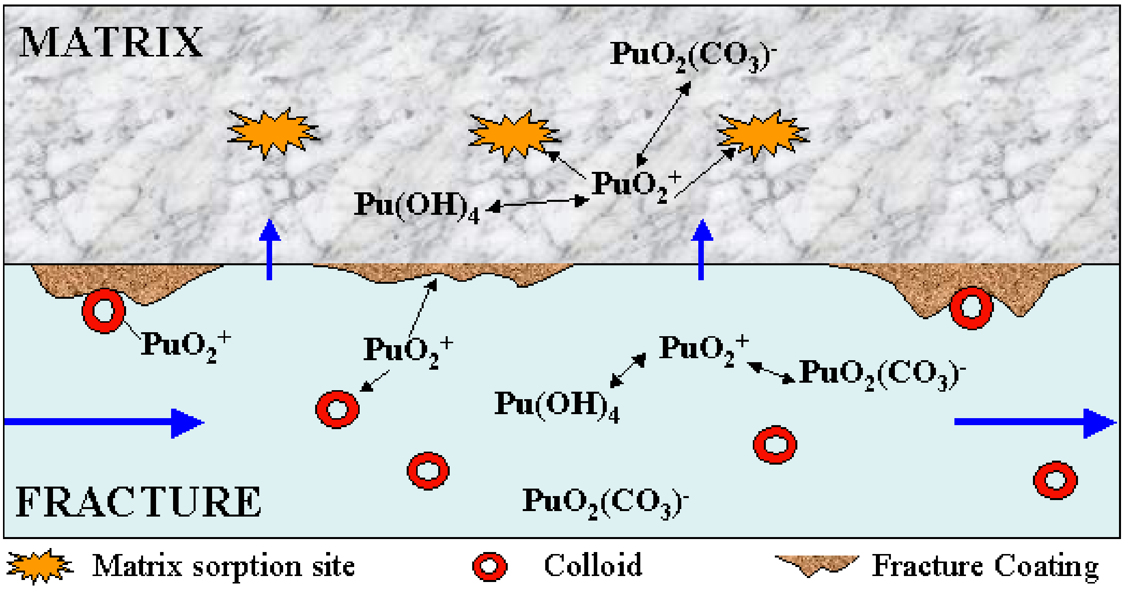

Figure 10.3 Schematic of conceptual model for plutonium and colloid transport in fractures (from [423])

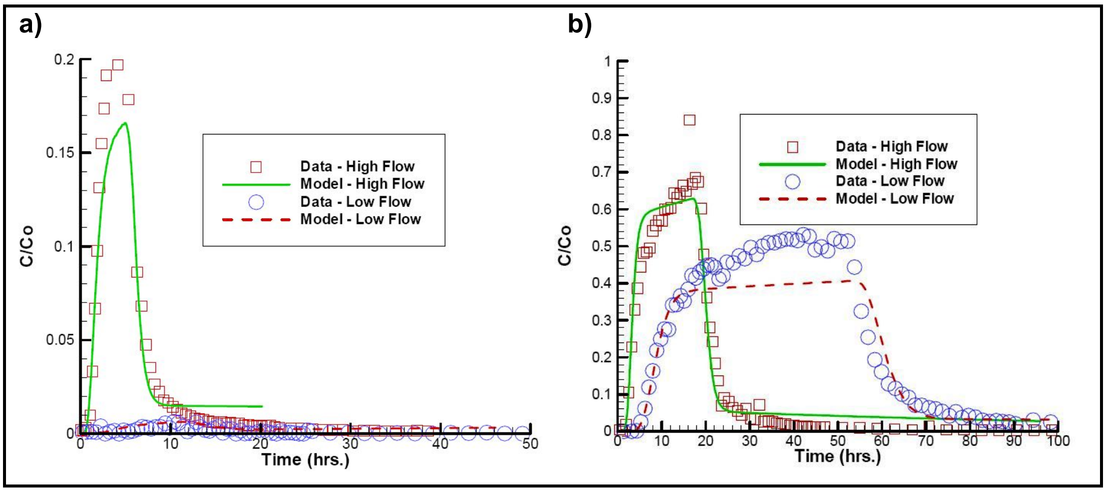

Figure 10.4 Comparison of experimental and modelled breakthrough curves for: a) plutonium(V) in the presence of Otay-montmorillonite colloids; and b) plutonium(IV) in the presence of clinoptilolite (zeolite) colloids (from [423])

10.6 Recent developments in modelling colloid transport and colloid-facilitated transport on waste disposal programmes

In this Section, we will briefly outline the state of development and application of colloid transport and CFCT models on two international URL collaboration projects (CRR, Äspö).

10.6.1 Colloid and radionuclide retardation (CRR) experiment

Kosakowski and Smith [447] applied three different approaches to model the results of the CRR experiments outlined in section 9.4.1.

- a 1-D advection-dispersion dual porosity model;
- a 2-D advection-dispersion dual porosity model; and
- a non-Fickian dispersion or continuous time random walk (CTRW) model.

The first model is essentially the same as that developed by Heer and Hadermann [508, 509] and applied in the GTS Migration Experiment (MI). Both Eulerian models treat dispersion as a diffusion-like process that obeys Fick's laws. Rock matrix diffusion (RMD) of solutes and solute sorption on matrix pore surfaces were included. Colloids were excluded from matrix pores in all three approaches. The CTRW model allows a more general treatment of dispersion, but does not currently include RMD, and so was only applied to the transport of colloids.

None of these models was a coupled CFCT model, however. The assumption was made that the transport of all components of the tracer cocktails could be modelled independently. In particular: "*Colloids are stable* [i.e. do not interact with fracture surfaces] *, and do not interact with each other or with tracers in aqueous solution – radionuclide tracers may be associated with colloids at the time of injection, but no further interaction takes place, i.e. the colloid-bound fraction of each tracer remains constant during migration*." No attempt was made to include colloid filtration or interactions with the fracture walls in the models and the observed attenuation of colloid concentrations in the breakthrough curves was treated by merely applying an appropriate scaling factor.

10.6.2 Äspö TRUE

Cvetkovic [390], using a Lagrangian approach, undertook scoping calculations of colloid-facilitated transport of two sorbing tracers (Sr, Cs) as part of the preparation for planned tracer experiments in the TRUE block at Äspö (see section 9.4.2). The model considered flow through a single fracture with flowpath conceptualised as many streamlines or tubes. The flow velocity was assumed to vary along a streamline, such that the advective travel time associated with a streamline is a random variable sampled from a probability density function (PDF), which contains the information on advection and dispersion along the flow path. The key assumptions concerning the treatment of CFCT were:

- Radionuclide diffusion/sorption into the water-saturated rock matrix porosity is the major retention mechanism;
- Colloids can be filtered (i.e. sieved); but it is assumed that their concentration is approximately constant, either because colloids are also generated and/or because the filtration rate is relatively small;
- Colloid-solution tracer exchange described by first order, linear and reversible sorption model (with colloids and tracers only mixing on injection to the fracture).
- Colloid and tracer retardation by reversible deposition or sorption to the fracture surface were ignored.

Simulations were carried out of tracer discharges for water residence times of 10 and 100 hours for different values of the tracer-colloid forward rate constant and colloid filtration (i.e sieving) coefficient.

As noted in section 9.4.2, the results from the Colloid Dipole project, completed in 2007 have yet to be published.

11 Treatment of geosphere colloids in PA

11.1 Introduction

Colloids have the potential to affect the transport of radionuclides in the geosphere, if they are sufficiently mobile and there is significant sorption of radionuclides to those colloids. In some circumstances, therefore, it will be necessary to take account of colloid-facilitated transport of radionuclides in performance assessments (PAs). It is important to note that the treatments of CFRT in PA codes are rather different from the research-type interpretive modelling activities discussed in section 10.

In this section, the treatments of geosphere colloids in a number of PAs are examined. For each PA, the following questions have been considered:

- Is colloid transport taken into account in the PA? If not, what is the justification for excluding colloid transport?
- If colloid transport is included, which processes and transport mechanisms are considered?
- What key assumptions were made in developing an assessment model of colloid transport?
- How were the PA models of colloid transport implemented and evaluated?
- What conclusions about the importance of colloid transport were drawn?

A summary of the answers to these questions are provided in Table 11.1 and Table 11.2. A more detailed discussion is provided in the following sections.

11.2 Studies undertaken by Nirex

11.2.1 Nirex 97

The potential impact of colloids on radionuclide transport (and hence doses and risks) was considered in two variant calculations undertaken as part of the Nirex 97 assessment [55]. This assessment considered the safety afforded by a cement-based GDF in a low permeability, fractured host rock located at Sellafield. The rationale for considering colloids in the geosphere, in the Nirex 97 study, was that sorption of radionuclides onto mobile colloids could lead to a lower effective retardation of the radionuclides as they travel through the geosphere.

The assessment methodology is described in detail in the supporting report by Swanton *et al*. [56], which also details the results of a wider ranging sensitivity study (see below).

The variant calculations for Nirex 97 were based on an overall system model with two different descriptions of the near field, with the effects of colloids added. The two variants consider different loadings of organic complexants in the near field. The “base case” geosphere was assumed to be present in both cases.

In developing an approach for treating colloids in Nirex 97, the following assumptions were made in respect of geosphere colloids:

- Spatially and temporally constant colloid concentrations were assumed.
- Near-field and far-field colloid populations were assumed to be independent.
- Colloids were assumed to travel at the same velocity as the groundwater.
- In the backfill and the hydrogeological units represented as Porous Geosphere submodels, colloids were assumed to be subject to exclusion from a fraction of the porosity, the exclusion factor specified being that appropriate to anions.
- In the Fractured Geosphere submodels, the colloids were totally excluded from the matrix porosity.
- The colloids in groundwater were assumed not to interact with the rock surfaces in the geosphere, so that the sorption distribution coefficient for the colloids in the geosphere was zero.
- Radionuclides were assumed to sorb reversibly onto the surfaces of colloids, with linear sorption distribution coefficients that were 300 times larger than the central case values in the assessment for sorption to the rock.
- If organic complexants were taken to be present, the distribution coefficients specifying sorption onto colloids were assumed to be subject to the same reduction factor as those specifying the sorption onto backfill in the near field and rock in the far field.

The approach adopted for including colloids in the geosphere was based on the use of effective sorption coefficients for each radionuclide. This enabled the approach to be implemented in existing MASCOT submodels without the need to make changes to the underlying methodology.

The results obtained in Nirex 97 can be summarised as follows:

- The risk contribution from Cl-36 (the dominant radionuclide at early times) is unaffected by colloids, because Cl-36 does not sorb to colloids;
- In the reference assessment model, there is a negligible increase in the risk contribution from U-238 and its daughters;
- In the second variant (in which it was assumed that organic complexants have no effect), the risk contribution U-238 and its daughters increases by a factor of three.

The results indicate that (at least for the parameter values adopted in Nirex 97), the effect of organic complexants exceeds that of colloids, and hence neglecting colloids is only likely to be significant when the effects of organic complexants are limited or zero.

11.2.2 Supporting sensitivity studies

The supporting studies to the Nirex 97 assessment undertaken by Swanton *et al*. [56] considered the impact of a wider range of colloid concentrations in both the near field and far field and included the effects of additional processes namely colloid sorption to rock and the effects of irreversible sorption to colloids, which were not considered in Nirex 97.

It is worth noting that, in this current review of treatments in PA, the study by Swanton et al. [56] was found to provide the most detailed coverage of the various processes and interactions between colloids and radionuclides. In addition, the study provides methodologies for transport in both porous and fractured media.

Table 11.1 Summary of Key Aspects of the Treatment of Colloids in Various Performance Assessments

Assessment	Is colloidal transport included in the performance assessment?	What are the key assumptions that were made in the assessment studies?	How were the colloid models implemented and evaluated?	What were the key conclusions about the importance of transport on colloids?
Nirex 97	Colloids are considered in the Nirex 97 assessment as a variant scenario.	Reversible sorption to colloids considered, no colloid sorption to rock, no velocity profile in fractures.	The formalism of the equations was such that existing MASCOT submodels could be used with effective parameters.	Very little impact on overall risk. Factor of 3 increase in risk from the U-238 chain when effects of organics are negligible.
Other Nirex Studies	More detailed studies considering aspects of colloid transport not considered in Nirex 97.	Irreversible sorption to colloids taken into account, colloid sorption to rock taken into account, no velocity profile in fractures.	The formalism of the equations was such that existing MASCOT submodels could be used with effective parameters.	Very little impact on overall risk. Increased colloid concentrations in the geosphere were found to give rise to more significant increases in risk.
Yucca Mountain	Colloids are considered as an integral component of the saturated transport in the TSPA-LA assessment.	Reversible and irreversible sorption to colloids, no matrix diffusion of colloids with irreversibly sorbed RNs, no velocity profile in fractures	The formalism of the equations was such that they could be implemented in a GoldSim pipe element with effective parameters.	No analyses seem to be undertaken in TSPA-LA to identify the specific impact of colloids on risk.
SKI	Quantitative assessment undertaken to investigate the potential impact of colloids on the KBS-3 concept.	Considers reversible sorption to mobile and immobile colloids. No velocity profile in fractures.	The model was implemented in a bespoke code called COLLAGE.	Concluded that colloids could be more important than previously acknowledged, especially for transport of Pu isotopes.
Japan	Considered a variant scenario with colloid transport in producing the Second Progress Report	Reversible sorption, no sorption of colloids to fracture surfaces, no diffusion of colloids into rock matrix, no velocity profile	Not clear. However, governing equation is standard transport equation with effective parameters.	The variant with colloids gave a peak dose about twice that obtained without colloids. main contributor was Cs-135.

Assessment	Is colloidal transport included in the performance assessment?	What are the key assumptions that were made in the assessment studies?	How were the colloid models implemented and evaluated?	What were the key conclusions about the importance of transport on colloids?
NAGRA	Not considered in formal performance assessment, but supporting studies undertaken	Key assumption is that colloids are immobile, and hence do not present a transport mechanism.	N/A	Supporting studies show that colloids could potentially affect transport of some radionuclides.
ONDRAF	Not considered in formal performance assessment, e.g. SAFIR-2.	Boom clay acts as a micro-filter for colloids.	N/A	N/A
SKB	Not included in consequence calculations, but note that could be relevant in glacial conditions	Colloid concentrations in Swedish deep groundwaters expected to be low	FARF31 module of PROPER has been developed to deal with colloid transport	N/A
ANDRA	Not considered in the Dossier Argile assessment	Callovo-Oxfordian clays assumed to act as an effective colloid filter	N/A	N/A
POSIVA	Not considered in any performance assessment calculations	Naturally occurring colloids are not expected to be stable in high ionic strength groundwaters found at Olkiluoto	N/A	N/A

Table 11.2 Summary of key colloid transport processes considered in various performance assessments

Assessment	Reversible Sorption	Irreversible Sorption	Colloid Sorption to Rock	Transport in Porous Media	Transport in Fractured Media	Matrix Diffusion of Colloids	Exclusion Effects	Velocity Profile in Fractures
Nirex 97	Y	N	N	Y	Y	Y (a)	Y	N
Other Nirex Studies	Y	Y	Y	Y	Y	Y	Y	N
Yucca Mountain	Y	Y	Y (b)	Y	Y	Y (c)	N	N
SKI	Y	N (d)	Y	N	Y	N	N	N
Japan	Y	N	N	N	Y	N	N	N
NAGRA								
ONDRAF								
SKB								
ANDRA								
POSIVA								

(a) But only for some hydrological units where pore-throat data indicated this was appropriate.
(b) Only for colloids with irreversibly sorbed radionuclides.
(c) Not for colloids with irreversibly sorbed radionuclides.
(d) Colloids can be either mobile or immobile in the SKI model.

The following processes were considered:

- Reversible sorption of radionuclides to colloids;
- Irreversible sorption of radionuclides to colloids;
- Sorption of colloids to rock;
- Exclusion of colloids from rock porosity;
- Matrix diffusion of colloids (in fractured media);

Irreversible sorption was modelled by considering a proportion of radionuclides to be irreversibly sorbed, and then setting the velocity, dispersion and retardation of those radionuclides equal to those of the colloids to which they are sorbed.

For the case of reversible sorption of radionuclides to colloids, the presence of 0.5 ppm mobile, unretarded colloidal particles in the geosphere (based on limited data for colloid populations in Sellafield groundwaters) was found to have a negligible effect on the calculated risk. However, increasing the mobile unretarded colloid concentration to 50 ppm throughout the geosphere (which was considered to be a cautious upper limit for geosphere colloids in hard rock) may increase the risk due to ^{238}U decay chain daughters by up to an order of magnitude.

Including sorption of colloids to rock was found to produce a decrease in risk, compared with the results obtained in Nirex 97. This is because the additional colloid sorption process further delays the arrival of radionuclides such as Tc-99 and the actinides into the biosphere. The study notes that this decrease will only be significant for radionuclides that sorb strongly to colloidal species.

In the case of irreversible sorption, it was found that substantial increases in risk could arise if a proportion of radionuclides are irreversibly sorbed to colloids. However, the report goes on to note that there are significant uncertainties relating to irreversible sorption to colloids, in particular the proportion of radionuclides that will be sorbed in this way. Thus, the significance of irreversible sorption remained to be determined.

11.3 Studies undertaken in Japan

In Japan, a substantial programme of work is underway to consider the disposal of HLW in fractured rock. A very useful summary of the treatment of colloidal transport in the Japanese programme is provided in [400].

The following assumptions are made in the treatment of colloids in the geosphere in the Japanese programme:

- The colloid concentration is constant in space and time;
- The sorption of radionuclides to colloids is linear, instantaneous and reversible;
- Sorption of colloids to fracture surfaces is ignored;
- Diffusion of colloids in to rock matrix is ignored.
- The transport velocity of the colloids was taken to be the same as the groundwater flow velocity;

As with the other concepts considered so far, the sorption of radionuclides to colloids is treated through the use of a sorption coefficient. This results in a transport equation very similar to that for the case with no colloids, but with effective retardation factors and dispersion coefficients. The sorption coefficients for radionuclides to colloids were based on the sorption properties of radionuclides to bentonite.

It is not clear how the results presented in [400] were obtained. However the presence of effective parameters in the approach ensures that the approach with colloids can be implemented in the code that was used for transport without colloids.

It is difficult to determine the impact of colloids on calculated doses compared with a case in which no colloids are present from the results presented in [400]. This is because the two sets of results appear to have differing groundwater flow rates through the repository. The authors of [400] note that some increases in calculated doses occur because of the assumption that colloids do not undergo matrix diffusion, and hence radionuclides sorbed to colloids are not as effectively retarded as in the case with no colloid transport.

11.4 Studies undertaken in Sweden

11.4.1 SR-CAN assessment, SKB

The treatment of colloids in the SR-CAN assessment of the disposal of spent nuclear fuel is described in [510]. In that study, it was concluded that colloids are unlikely to provide a significant transport mechanism, except possibly under glacial conditions. The principal reason for this is that measured concentrations of colloids in deep Swedish waters are found to be very low (less than 10^{-4} kg m^{-3}), and the high ionic strength of the waters (due to its salinity and the presence of ions such as Ca^{2+}) will tend to destabilise any colloids that are present.

During glacial periods it is noted in [510] that groundwaters may be more dilute, and hence the destabilising effect of the groundwaters would be less. However, it is concluded that even under these conditions, colloid concentrations are unlikely to be high enough to present a significant transport mechanism for radionuclides sorbed to them. Calculations have been undertaken in SR-CAN to investigate the consequences of reduced sorption in the geosphere. It is considered that these calculations provide a suitable bound on the likely impact of colloids on radionuclide transport in Swedish waters.

11.4.2 SKI

SKI have also undertaken studies to investigate the potential impact of colloids on the Swedish KBS-3 concept [58]. These have been based on the progressive development of a code known as COLLAGE-II, designed specifically for modelling the transport of colloids [511]. It is worth noting that this work precedes the SR-CAN assessment discussed above.

The conceptual model of colloid transport in the geosphere in COLLAGE-II is shown in Figure 11.1.

The COLLAGE-II model considers the possibility for radionuclides to sorb to colloidal particles, and for those colloidal particles to sorb to the wall of a fracture in which transport is taking place. Matrix diffusion of colloidal particles is not considered. An interesting feature of the model is that it allows for both mobile and immobile colloids to be present.

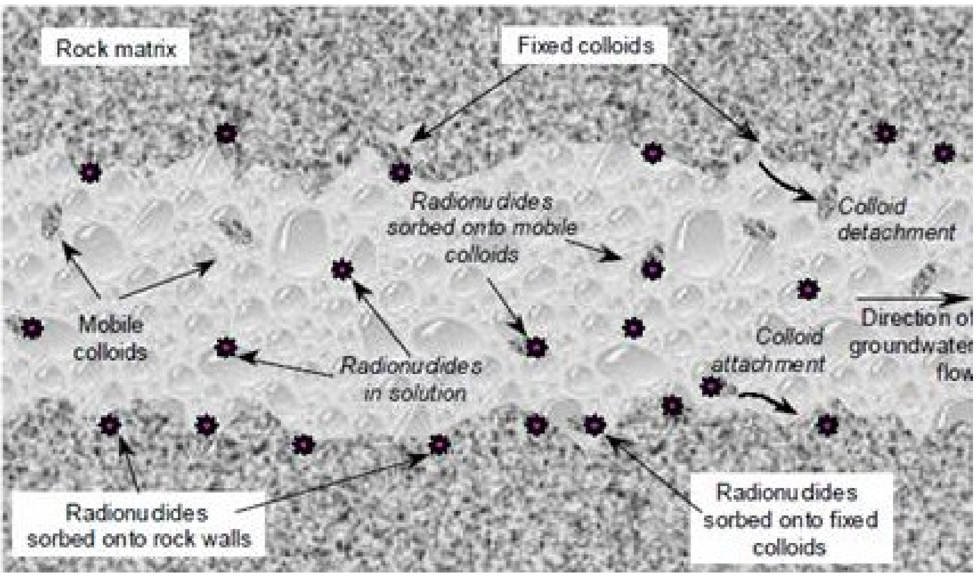

Figure 11.1 Conceptual Model of Colloid Transport in COLLAGE-II

In the concepts considered previously, the aim of the transport modelling has been to compute an absolute value of radionuclide flux. That is, a flux that takes account of the radionuclide flux in solution combined with that for radionuclides bound to colloids. In the COLLAGE-II approach, these two fluxes are considered separately, so that the model can be used to investigate how important they are relative to each other. It is argued that this provides a suitable means for determining the significance of colloid-facilitated transport.

SKI has applied the COLLAGE-II model to the transport of plutonium in conditions that might be expected in deep Swedish groundwaters. The aim of this modelling study was to identify any regions of parameter space where transport of plutonium through interaction with colloids could be significant.

These calculations involved two major assumptions, namely that there are no immobile colloids present, and that the colloids travel through the centre of the fracture, which implies a flow velocity higher than the mean groundwater flow velocity averaged across the fracture.

The calculations indicated that there could be regions of parameter space where colloidal transport in deep Swedish waters is significant. These relate to the presence of significant colloid concentrations, strong sorption of plutonium to colloids, and they identified a “critical” range of colloid sorption / desorption rates.

11.4.3 Recent code developments by SKB

Recently, SKB has developed a code called FVFARF [512] for colloid-facilitated radionuclide transport modelling in fractured rock. The model takes advection-dispersion transport of a number of radionuclides in solute and colloidal phases along a stream line into account, including retention by transversal diffusion into the rock matrix and chain decay. The authors state that it would be easy to extend the model to allow for physical parameters that vary in space.

FVFARF has been verified by comparisons with results obtained by the FARF31 code [513] and the COLLAGE II Plus code [511], using the standard set of FARF31 test cases [514]. The models behind FARF31 and COLLAGE II Plus are roughly equivalent. The differences are exclusive, where FARF31 handles chain decay and that COLLAGE II Plus handles radionuclides sorbed onto colloids.

FVFARF is intended to be used in the safety assessment project SR Site, which was initiated 2008 and will be completed during 2009 prior to SKB's site selection and subsequent application for underground investigations at one of the two sites that have been investigated from the surface between 2002-2007 (Forsmark and Laxemar).

(a) Verification of colloid facilitated migration in a KBS-3 repository

Vahlund and Hermanson [512] compared the effects of colloid facilitated migration in a KBS-3 repository using FVFARF with the results using COLLAGE II Plus as reported in Chapter 4 of Klos [58]. These simulations were based on the parameters used in the SR 97 far-field simulations [470], but colloids were added to the model. In the simulations all colloids were assumed to be fully mobile, i.e. no filtering occurs. All radionuclides enter the flow path in the solute phase. The downstream boundary condition has been applied right at the end of the flow path.

Vahlund and Hermanson [512] conclude that the results are similar but not identical. One remaining difference between the FVFARF and the Collage II Plus programs is that FVFARF uses extrapolation of concentration as boundary condition at the downstream boundary, while Collage II Plus sets the concentration to zero. This model difference probably accounts for the remaining differences in results between the Collage II Plus and the FVFARF programs according to [512].

11.5 Other UK-relevant international studies

11.5.1 NAGRA

In considering the transport of radionuclides through an Opalinus Clay host, NAGRA has considered that colloid-facilitated transport is unlikely to be a significant mechanism [21]. However, studies undertaken at the Grimsel Test Site indicate that colloids could potentially have some significance for radionuclide transport [447].

The rationale for eliminating colloids from consideration in Opalinus Clay is as follows [21]. In Opalinus Clay, colloids are present and radionuclides might be associated with them. However, because of the high ionic strength of the Opalinus Clay groundwater, colloids are expected to have a low colloidal stability. In addition, because of the low permeability of Opalinus Clay and the size of the pores, colloids are also expected to be immobile. Therefore, in present hydrological and geochemical conditions, colloid-facilitated radionuclide transport in Opalinus Clay is unlikely to be a relevant transport mechanism.

Reference [21] does, however, note that chemical or mechanical perturbations might lead to an increase of colloid generation and mobility. If such perturbations were to be expected, the implications for colloid-facilitated radionuclide transport would have to be evaluated.

11.5.2 ONDRAF

Colloidal transport of radionuclides is not taken into account in the SAFIR-2 assessment of the disposal of HLW and/or long-lived waste in a repository in Boom Clay [515]. The argument for this is that the properties of the Boom Clay, in particular the size of the pores (around 5 nm), are such that colloids would be almost immobile, and as such their impact on the transport of radionuclides will be limited.

11.5.3 ANDRA

The Dossier 2005 Argile [300] considers the feasibility of the disposal of HLW and long-lived wastes in the Callovo-Oxfordian clay host. Colloids are not considered to be relevant for this host rock, for two reasons:

- Transport in the Callovo-Oxfordian clay is diffusion-dominated, and therefore the rate of transport of colloids will be considerably smaller than in other hosts where advection is dominant;

- The Callovo-Oxfordian clay acts as a very effective “filter” for colloids, rendering them almost immobile and therefore reducing their effectiveness as carriers of radionuclides.

11.5.4 POSIVA

POSIVA is currently engaged in the production of a safety case for a spent fuel repository at the Olkiluoto site. Within this safety case, colloidal transport in the geosphere is neglected in all scenarios considered [516]. The rationale for neglecting colloid transport is similar to that adopted by SKB (section 11.4.1) in the SR-CAN assessment, namely that the deep groundwaters at Olkiluoto are of very high ionic strength, and as such any colloids present in those waters would not be stable. However, it is acknowledged in [516] that during a glacial period, infiltration of glacial melt water (and hence dilution of the ionic strength of the deep waters) could enhance the stability of the colloids and increase the relevance of colloid-facilitated transport.

11.6 Studies Undertaken for Yucca Mountain

The HLW/SF disposal concept under development in the US for a geological facility at Yucca Mountain is very different from those under consideration in most other international programmes, with disposal of wastes in tunnels above the water table in the heart of the mountain. The host geological environment is very different from those under consideration in the UK. Nevertheless, CFRT is being addressed in the system models. This includes colloidal releases from the engineered barrier system, transport in the unsaturated zone and transport through the saturated zone comprising fractured tuff and alluvium (treated as a porous medium).

The treatment of colloids in the TSPA-LA assessment for Yucca Mountain is described at a broad level in the TSPA AMR documentation [517], and in detail in the description of radionuclide transport in the saturated zone [59]. The assessment models in the TSPA-LA assessment are implemented in the GoldSim computer code [518], and so one of the requirements of the approach to colloids was that it should be possible to implement it within the framework of GoldSim.

Figure 11.2 illustrates the conceptual model of saturated zone radionuclide transport in TSPA-LA which includes colloid-facilitated transport.

The model captures the possibility that radionuclides could be sorbed reversibly or irreversibly to colloids. For those colloids to which radionuclides are reversibly sorbed, it is assumed that there is no sorption interaction between colloids and geosphere materials. For colloids to which radionuclides are irreversibly attached, it is assumed that the colloids are subject to retardation in the geosphere through attachment and detachment processes. It is also assumed that these colloids are not subject to the effects of matrix diffusion.

As with the Nirex studies considered above, reversible sorption to colloids is treated by defining an effective sorption coefficient for radionuclides to colloids. This results in the introduction of modified retardation and diffusion coefficients into the “colloid-free” transport equations. An effective retardation factor is also used to describe the delay in transport of colloids with irreversibly sorbed radionuclides.

In the TSPA-LA assessment, transport by colloids is an intrinsic part of the overall saturated zone transport model. This model is implemented in GoldSim, and a view of the model is shown in Figure 11.3.

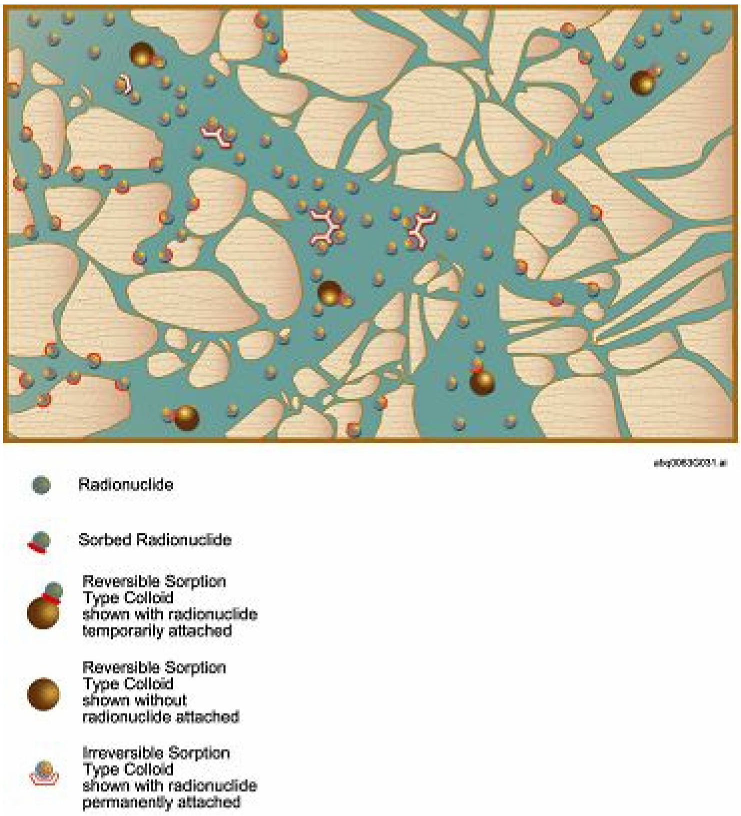

Figure 11.2 Conceptual model of saturated zone radionuclide transport in TSPA-LA (from [59])

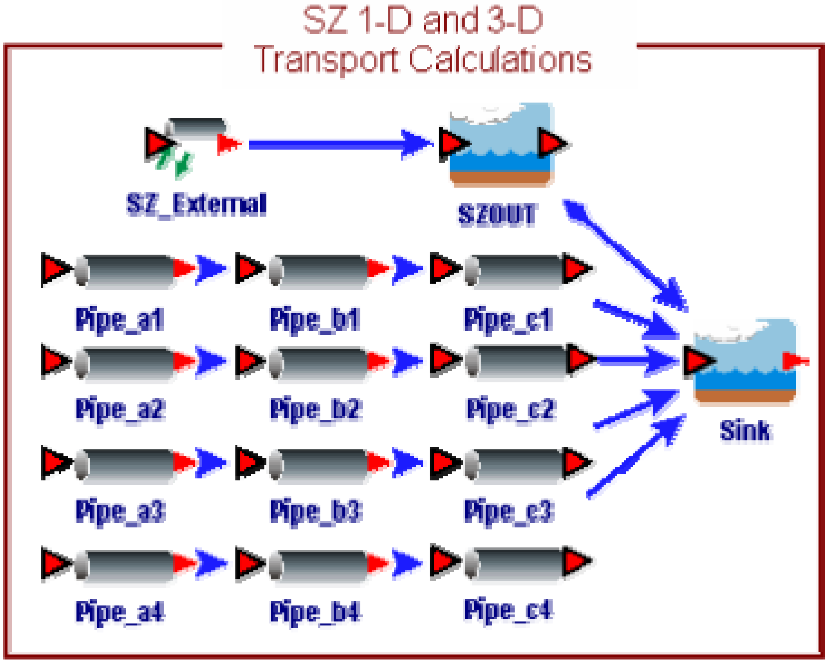

Figure 11.3 The Saturated Zone Transport Model in TSPA-LA.

Each of the “pipes” in this model represents a distinct region of the geosphere, in which saturated transport is assumed to take place. It is interesting to note that the treatment of colloids in TSPA-LA does not require any of the special facilities of GoldSim, such as the ability to model the transport of suspended solids in groundwater. Note also that the results presented for the TSPA-LA assessment in [517] do not enable the impact of colloidal transport on dose to be deduced, because there appear to be no variant calculations in which the effects of transport of colloids are neglected.

11.7 Conclusions

The following conclusions can be drawn from this review of the treatment of colloids in national and international performance assessments.

1. In a number of assessments the effects of colloids are argued to be negligible, either through qualitative arguments or limited quantitative scoping calculations. Examples of qualitative screening arguments include the presence of high ionic strength groundwaters (SKB, POSIVA) or the limited mobility of colloids in clay host rocks (ANDRA, ONDRAF).

2. With the exception of studies at Yucca Mountain, those assessments that do consider the potential impact of colloids do so by defining a variant scenario. In the Yucca Mountain studies, transport of colloids is an intrinsic part of the main saturated zone flow model.

3. In the assessments that do take account of colloids, the range of processes and phenomena included vary between the assessments. However, all of the concepts take account of reversible sorption of radionuclides to colloids, and many take account of colloid sorption to rock and matrix diffusion of colloids. Neglect of the latter two processes is a cautious assumption.

4. Only Nirex studies and studies for Yucca Mountain take account of irreversible sorption of radionuclides to colloids. The SKI studies take account of sorption of radionuclides to both mobile and immobile colloids.

5. In all concepts, reversible sorption of radionuclides to colloids is taken into account through a radionuclide-colloid equilibrium sorption coefficient. This enables a combined transport equation to be derived that takes into account the combined effects of radionuclide transport in solution and transport attached to colloids. This equation takes the same form as the transport equation without colloids, albeit with effective parameters. The exception is the SKI study, in which the COLLAGE-II code keeps transport in solution and transport attached to colloids as separate quantities.

6. With the exception of the SKI study, the approaches adopted to colloid transport can be implemented in existing transport codes, albeit with effective parameters. In the SKI study, a specialised code was developed to evaluate colloid transport.

7. In general, the various assessments found that the effects of colloids on geosphere transport, and hence dose or risk, were limited. Increases in risk by a factor of two or three could occur under some circumstances, for example in the Nirex 97 assessment in variants where the effects of organic complexants are limited. For certain radionuclides that would normally be sorbed in the geosphere, colloid transport can also be significant.

From the perspective of deriving an approach to colloid transport suitable for use in future NDA assessments, the conclusions of this review suggest that the approach should be developed on the basis of the following considerations:

a) Determine if colloids can be ruled out by qualitative or simple screening arguments;

b) If not, determine if colloids should be treated as a variant scenario, or as part of the main radionuclide transport methodology (e.g. as in studies at Yucca Mountain);

c) Determine the transport processes to be included;

d) Determine the mathematical representation of those processes (e.g. whether equilibrium sorption coefficients can be used as in the studies considered in this review).

e) Define the appropriate transport equations, either to give the combined effects of transport in solution and on colloids, or keeping these separate as in COLLAGE-II.

f) Determine how the methodology could be implemented in the GoldSim radionuclide transport code.

12 State of the science

12.1 Current understanding of key questions concerning colloids in the geosphere

The previous thematic report on Nirex research on colloids in the geosphere [49], written in 1998 and published in 2002, summarised the current understanding of the key questions concerning colloids in a geosphere comprised of hard rock up to the late 1990s. Ten years on, it is appropriate to ask what progress has been made internationally in that time? In addition given uncertainty about the geology of a future UK disposal site, what is the current understanding of colloid behaviour in other rock types, in particular in low permeability sedimentary rock (e.g. mudrocks)?

Current understanding of each of the main topic areas covered in sections 5 to 11 can be summarised as follows.

12.1.1 Colloid presence

(a) Mobile colloid populations in the geosphere

A number of datasets for mobile deep groundwater colloid populations now exist worldwide (Table 5.1) and they cover a range of environments, both of rock and groundwater types although there is a bias towards fractured hard rocks. A wide range of colloid populations, covering seven orders of magnitude in mass terms (from 10^{-5} to >100 mg dm^{-3}), has been reported in the literature, including a six orders of magnitude range in crystalline rocks. Thus, there is no straightforward discrimination of datasets in terms of rock type.

In general, the composition of colloids reflects the local composition of the rock (predominantly primary siliciates) and rock weathering products (principally clay minerals); common colloid types include silica, feldspars and phylosilicates (smectites, illite, micas, etc). High concentrations of principally organic colloids were measured in Gorleben groundwaters, which may be regarded as something of a special case in terms of deep groundwaters owing to the presence of nearby coal sands. In 1993, McCarthy and Degueldre [37] suggested that mobile colloid concentrations in natural, undisturbed groundwater systems where organic concentrations are low, are less than 1 mg dm^{-3}; in general, more recent studies have been consistent with this view.

Given the inherent difficulties in groundwater colloid sampling, the reported populations (e.g. those presented in Table 5.1) should not be viewed as being free from artefacts but rather as representing maximum concentrations (accepting that some artefacts may reduce rather than increase colloid numbers). The example of the Laxemar study shows that high quality samples can be collected and colloids separated from the bulk water with a minimum of artefacts. However, even in that case the data are insufficient to provide a statistically meaningful understanding of colloid populations at the site. The same criticism can also be made of previous sampling of colloids by Nirex at the Sellafield site where only a few datapoints were obtained.

The wide range of colloid concentrations measured in deep groundwaters reflects the significant variations in salinity between systems studied, varying from low ionic strength waters in alpine regions to higher ionic strength coastal groundwaters, where colloids are destabilised and measured populations are very low. An inverse correlation has been observed between the composition of the groundwater, particularly in terms of the concentration of divalent ions, and the colloid number populations, with lower populations at higher ionic strength. Other factors that may also play a role including pH, the mineralogy of the colloids, local flow rate and rate of weathering of the rock (i.e. the rate of *in situ* colloid generation) and, in some cases, the presence of natural organic materials that may sorb onto and stabilise colloids.

In general, particle size distributions of groundwater colloid populations show inverse power law scaling behaviour with size over the size range accessible to measurement, generally down to about 10-100 nm depending on analysis method. However, there is uncertainty concerning the potential contribution of the smallest particle sizes to colloid populations owing to analytical difficulties in their quantification.

It is important to recognise that the colloid populations measured in groundwater sampling campaigns are the mobile colloid populations. These mobile populations do not exist in isolation, however, but represent a fraction of the total colloid population of the groundwater system, the majority of which is immobile under steady-state conditions. This is illustrated by the observations of formation damage in sandstones that result from the flooding of saline saturated rocks with fresh water; the observed permeability reductions are attributed to the mobilisation of part of the clay particle fraction in the rock and internal pore blocking as a result of the reduction in ionic strength. What is of interest here is not so much the effect of water flooding itself (an example of an extreme chemical shock that is not appropriate to deep groundwaters relevant to a geological disposal) but what it reveals about the colloid population in the sandstones. Thus, there is a significant colloid population (the clay fraction) within the sandstones that under steady-state saline conditions is predominantly immobile.

Sandstones often have a significant clay fraction but the presence of a fine, clay-size fraction is common to all rock types in the flowing porosity. The amount of colloidal material will vary significantly between rock types, depending on the extent of rock weathering, etc. Thus all types of rock can be expected to contain colloidal material that is predominantly immobile, but which potentially can be mobilised as a result of physical or chemical perturbations of the groundwater system. The importance of colloid mobilisation processes as the major source of colloidally dispersed particles in natural systems is recognised in discussion of CFCT in shallow groundwater systems [e.g. 93, 129, 130], but is not always appreciated in the context of deep groundwaters. The mobilisation of otherwise immobile colloids by high flow rates on groundwater extraction is one of the potential artefacts that may arise during groundwater sampling.

(b) Near-field colloids in the far field

As discussed in the companion cementitious near-field colloids review [62], due to the limited stability of colloids in a cementitious near field, colloid mobility in the near field is expected to be limited. Therefore, migration of near-field colloids into the geosphere with groundwater flow is not expected to be a significant issue.

In the case of HLW/SF near-field concepts incorporating a bentonite buffer, although colloidal material will be generated in the near field due to degradation of the wasteforms, the buffer is expected to act as an effective barrier for colloid migration into the far field (except possibly for the very smallest colloid particle sizes) provided that the bentonite barrier remains intact and there is no cracking or fracturing of the buffer that may provide pathways for transport by groundwater flow, or chemical changes (such as silification or illitisation) that will alter the porosity and degrade the filter efficiency.

(c) ADZ-derived colloids

At present there is limited understanding of the potential for colloid formation in the ADZ of the host rock surrounding a cementitious repository. It is anticipated that the pH will decrease gradually across the ADZ [519], i.e. there will be a non-steady state, and this may lead to increased rates of colloid generation and/or loss. A generic conceptual model has been developed for the chemical evolution of a crystalline host rock in contact with an alkaline plume, which provides a basis for developing a conceptual understanding of colloid formation and loss processes under the non-steady state conditions in this part of the geosphere [62]. However, the nature of colloids formed in this region will be dependent, at least in part, on the nature of the host rock and as such will also be a site-specific issue.

(d) Colloids generated at a bentonite buffer-host rock boundary

Although a number of studies have been reported concerning the potential for colloid generation from the surface of a bentonite buffer as a result of contact with groundwater (e.g. in a fracture) at the interface between the buffer and a crystalline host rock, results obtained appear to be contradictory. While in dynamic tests the colloid generation rate was determined primarily by water flow rate rather than by solution composition [320], in quasi-static tests, colloids were generated from the bentonite surface when there was a sufficiently high degree of hydration [321]. Thus different processes may dominate under the differing conditions. Although the underlying processes have been described [e.g. 94], it is unclear whether such conceptual understanding has always been applied to underpin the experimental design to discriminate release processes.

To date there is little clear data concerning colloid generation rates at the bentonite/host rock boundary, and no clear assessment has yet been made concerning the potential significance of this process. A recent review by Alonso *et al*. [60], concluded that the "*quantification of colloid generation rates under low groundwater flow and the elucidation of geochemical processes at the bentonite/host rock boundary under in situ conditions are open questions…*". In the recent SR-Can assessment by SKB [510] it was concluded that: "*The long-term performance of the buffer depends critically on the extent to which colloid release will occur*" and that: "*…colloid release from the buffer is one of the research areas which requires the greatest attention in* [a] *future RD&D program*." Currently, such a study is in progress in the CFM experiment at Grimsel.

12.1.2 Colloid stability

(a) Geosphere colloids

The principal colloid types in groundwaters reflect the principal minerals of the rock formation in which they are found, which have low solubility and a relatively low rate of dissolution in natural waters. These minerals, comprising primary silicates, secondary clays, etc, predominantly have PZCs at low pH and are negatively charged at the near-neutral pH of natural waters. Mineral colloids are stabilised towards aggregation and surface attachment primarily by repulsive electrostatic interactions between particles and between particles and rock surfaces. The magnitude of these interactions varies with pH and the ionic strength of the groundwater. At pH values close to the PZC where net surface charges are close to zero, and above a critical electrolyte concentration, colloids are readily destabilised and will aggregate rapidly. In general, CCC values are very sensitive to the valence of the counterion (varying with sixth power) and colloids are destabilised at significantly lower concentrations in the presence of divalent cations.

Iron oxide minerals and calcite are not expected to form stable colloids in deep groundwater systems owing to the PZCs being close to pH 8 and 9.5, respectively and their net positive charge at lower pH. Thus particles of these minerals are expected to attach rapidly onto negatively-charged rock surfaces. However, in the presence of significant concentrations of organic materials, sorption of negatively-charged species and charge reversal of the colloids can enable stabilisation of iron oxide colloids. This is an important mechanism for iron oxide particle stabilisation in surface waters. The observation of significant iron oxide or calcite populations in deep groundwater samples may be an indicator of sampling problems, associated with atmospheric contamination or degassing, for example.

In general, most of the principal colloid types found in deep groundwaters have similar charge characteristics and broadly similar stability behaviour at near-neutral pH. As noted above, for inorganic colloid populations in a wide range of groundwater systems (where natural organic concentrations are very low) there is an inverse correlation between divalent cation concentrations and colloid number concentrations; the higher the calcium and/or magnesium concentration, the lower the mean colloid number concentration. In general, the colloid populations in deep groundwaters are controlled by the water composition (including pH and the presence of organic compounds) which controls the rates of particle aggregation. Other factors that play a role include the local flow rate and the rate of colloid generation by weathering processes. Measured populations are considered to represent an equilibrium between colloid generation and loss (due to aggregation and sedimentation).

The stability behaviour of a number of important colloid types, including silica, smectites and iron oxides, have been studied quite extensively and their stability behaviour in groundwaters is reasonably well understood.

On the basis of aggregation theory, the smallest-sized particles in a colloidal dispersion are expected to aggregate more rapidly and be removed from dispersion faster than larger-sized colloids. However, in the case of silica, small-sized particles display anomalously high stability, which has been identified as resulting from additional repulsive forces that arise from the formation of a gel layer at the particle surface. It is suggested that the effects of such additional forces become more important for small particles than for larger ones. It is not clear whether silica may be a special case or whether this behaviour may be observed more generally for a range of minerals. This may have implications for the importance of the smallest-sized particle fractions to CFRT.

(b) Effect of organic materials

The sorption of organic compounds onto the surfaces of colloidal particles provides an important stabilisation mechanism for inorganic colloid particles in natural waters due to enhanced repulsive electrostatic interactions and repulsive steric interactions between adsorbed layers on colliding particles. This mechanism becomes less significant when organic concentrations are low, which is more typical of deep groundwaters.

In the case of an ILW disposal facility, uncertainty exists as to whether organic compounds derived from waste (as-disposed or from degradation of solid organic materials), cement additives (e.g. superplasticisers) or the degradation of polymeric encapsulant materials may be present in sufficient quantities and be sufficiently persistent to migrate into the geosphere and influence the stability of natural colloid populations. Further work on the potential impact of organic degradation products on geosphere colloid populations would build confidence in the understanding of this issue. It should be noted, however, that stabilisation of geosphere colloids by organic wasteform-derived components is considered to be of secondary importance compared to the impact of organic complexants on radionuclide sorption behaviour in the far field.

(c) Stability of near-field derived colloids in the far field

Colloidal particles are thermodynamic metastable with respect to bulk solid phases owing to their higher surface free energy, which increases with decreasing particle size. Therefore, it is expected that near-field colloids of all types would have a tendency to dissolve on migration from the near field into the geosphere. The rate of colloid dissolution may be enhanced by the changes in chemical conditions experienced on migration, e.g. from the high pH, CSH-dominated environment of a cementitious near-field to the low pH primary silicate-dominated environment of a hard rock geosphere. The persistence of colloids that migrate through a change of chemical conditions will depend on their solubility in the solution in which they are dispersed, their size and rate of dissolution. Owing to the solubility of cement phase minerals in general, cementitious colloids are expected to dissolve relatively rapidly under geosphere conditions. However, this process has yet to be demonstrated experimentally.

The colloidal stability of chemically persistent near-field derived colloids will be subject to the same processes that control physicochemical stability as geosphere colloids, with PZC dependent on their mineral composition. Should they be able to migrate into the far field, smectite-like colloids derived from HLW degradation would be expected to be exhibit similar stability to geosphere colloids due to their similar mineral composition to natural clay colloids.

Iron oxide colloids derived from degradation of steel wastes, waste containers or repository structural components would not be expected to be stable in the geosphere unless associated with organic material.

The stability of uranium mineral colloids derived from spent fuel degradation has not been reviewed in this report.

(d) Colloid stability in the ADZ

At present there is limited understanding of the potential for colloid stability and mobility in the ADZ of the host rock surrounding a cementitious near field. However, the processes that may control colloid chemical and physico-chemical stability will be the same as those that operate in the near and far fields, their influence being subject to the changing chemical conditions (e.g. in pH and calcium concentration) through the ADZ. To a large extent, the potential for colloid stability will be dependent on the host rock groundwater salinity, with a low ionic strength being required to favour colloid stability. Therefore, colloid stability in the ADZ will be a site-specific issue.

12.1.3 Colloid transport

(a) Transport in fractured rock

There is evidence from field experiments that silica colloids may be mobile over distances of many metres in fractured rocks [54, 457]. However, this tends to be at significantly higher flow rates than would arise in deep groundwaters; erosional effects may be important and the applied colloids may have relatively little interaction with fracture surfaces due to the limited residence time in the fracture system. In laboratory experiments there is a clear reduction in mobility of silica colloids with increasing residence time [269], increasing particle size and ionic strength of the groundwater [54].

Similar results have been obtained with bentonite colloids in URL and laboratory experiments in terms of residence time in the fracture [48, 380, 480], particle size and ionic strength [421, 422]. Bentonite colloids were found to be essentially immobile through a granite block at the high ionic strength of Äspö groundwater (0.14 mol dm^{-3}) [421, 422].

At present a clear mechanistic understanding of the interactions between these colloid types and the natural fractures has yet to be obtained; it is not yet clear whether colloid capture is associated with straining at constrictions, attachment to mineral heterogeneities or particular physical features of the fracture surfaces (such as wedging at grain contacts or steps/dislocations).

(b) Transport in porous media

Few, if any studies of advective colloid transport in intact porous media have been reported in the radioactive waste management literature, although particle migration in sandstones has been studied for many years in the oil industry in the context of formation damage. Studies of colloid transport in unconsolidated media (e.g. in packed sand columns), which are of more direct relevance to shallow systems, have been widely used to understand colloid transport behaviour and assist model development.

Many experiments in packed columns with natural materials show transient deposition of colloids onto the porous medium (i.e. colloid breakthrough is initially retarded and concentrations rise slowly to feed levels). This behaviour suggest that a limited number of sites are available on the solid surfaces for colloid deposition and that once filled, deposited particles block further deposition. This behaviour can be accounted for (at least in part) by the presence of surface chemical heterogeneities in natural systems.

Recent research has further clarified the nature of retention mechanisms by which colloids may be captured in porous media under unfavourable chemical conditions. In particular, visual observation of colloid deposition behaviour has revealed the importance of particle capture by wedging at grain contacts and in secondary minima at stagnation points in the flow field around particles. The development of models that incorporate this aspect of colloid transport behaviour is expected to be an area of significant research activity over the next 5-10 years.

Colloid mobility through porous media with water flow is ultimately controlled by the ratio of particle size to pore throat size; larger particles may be excluded from porous media altogether or may by sieved in narrow pore throats on the basis of their size. Thus it is the smaller size fractions of colloid populations that are more likely to be mobile over significant distances in consolidated porous media. This is not to overlook the predictions of classical filtration theory that the highest stability and mobility is found for particles of the order of 100 nm in size.

(c) Field evidence for long-distance transport and CFRT

Although the potential for CFRT has been recognised and a very significant body of research has been undertaken over the last 25 years, clear examples demonstrating CFRT in the environment are relatively scarce. As Honeyman commented in 1999 "*Colloid-facilitated transport of contaminant has become something of a Gordian knot for environmental scientists… few studies have unequivocally demonstrated its significance in the field*." Attempts to quantify colloid facilitated transport of uranium and thorium from ore bodies have to date been largely unsuccessful in demonstrating long-range transport of the radioelements in colloidal form.

The association of radioelements including plutonium with colloid fractions has been established in groundwaters sampled from depth at the Nevada Test Site [33], and which based on isotopic signatures had originated from the Benham Test conducted some 1.3 km distant. This is an often cited example of CFRT. However, owing to the mode of dispersal of the radioelements into the groundwater – explosive injection – and the significant disruption of the environment (a smaller test than Benham left a 300 m wide crater at the surface) it is far from being an appropriate analogue for an undisturbed deep host rock. While the association of plutonium and other low solubility radioelements with colloidal material in the sampled groundwaters is not in doubt, there is significant uncertainty concerning the mode of radioelement migration [34].

Likewise, given the number of colloid sampling and natural analogue studies that have been undertaken, remarkably little evidence appears to have been collected that has demonstrated long-distance transport of colloids in groundwaters in fractured rock. Only one clear example has been found, at the Menzenschwand uranium prospect in Germany. In that case, colloids originating from a different rock type, 1-5 km away, were identified by different trace element signatures. However, as groundwater was extracted at high flow through relatively wide fractures (1-10cm) and the local ionic strength was rather low, promoting colloid stability, conditions were rather far from those expected in a deep groundwater. As Degueldre has commented [80] "…*the results should not be over-interpreted*". "*The colloids are likely to be transported over a distance of several kilometres without having the opportunity to attach to the surfaces of the rock or to lose their chemical signature* [80]"

The position with inorganic colloids contrasts with that for natural organic (humic) materials. The fact that humic materials are found to be present in deep groundwaters and their mobilisation from brown coal sands at Gorleben, for example, provide clear evidence for the stability and mobility of humic-type colloidal material in the geosphere.

(d) Transport in mudrock

Mudrocks are expected to provide an effective barrier to colloid-facilitated transport, provided that fracture flow does not occur [21].

Although mudrocks contain a colloid population (indeed, the rock itself will be composed of a significant fraction of smectite particles of colloidal dimsensions), the mobility of these particles is expected to be extremely low due to both chemical and physical factors [21]. In mudrocks, solute migration is controlled by diffusion, however, the rate of diffusive transport of particles of colloidal dimensions is significantly lower than for dissolved species owing to the inverse relationship between particle size and translational diffusion coefficient. In addition, owing to the fine-scale of the porosity and relatively high ionic strengths of clay porewaters, colloidal particles are anticipated to have limited mobility owing to a combination of physical straining, low stability and tendency to deposit on matrix surfaces.

There is some evidence for the mobility of very small organic colloidal species through bentonite [374, 392, 393], which suggests that there is the potential for the very smallest size fraction of inorganic colloids to have some mobility. This remains a possibility that has yet to be addressed experimentally.

12.1.4 Radionuclide uptake

A range of studies are reported in the literature in which sorption of radionuclides onto colloids has been investigated. These include studies onto both synthetic (model) colloids and natural colloids. In general, sorption onto geosphere colloids is stronger than sorption onto crushed rock (Table 8.1), which reflects the higher surface area expected to be available for sorption onto colloid surfaces compared to bulk solids.

The relationship between the available surface area (i.e. available concentration of sorption sites per unit mass) to particle size of colloids has yet to be clearly established. In the case of minerals which have significant accessible intra-granular (micro-) porosity, such as zeolites (which are of interest in the US programme), Rd values (which may be large) would not be expected to vary significantly with particle size (when radionuclides were able to access the micro-porosity). For particles with no internal porosity, Rd would be expected to scale with geometrical surface area. A cautious assumption is often made that particles can be approximated by hard spheres and that the surface area scales with the square of the particle radius. In practice, however, colloidal particles have been observed in a variety of shapes (spheroids, needles, platelets), may be composed of aggregates and possess some intergranular porosity. Thus the hard-sphere model may be an over-simplification. There is also uncertainty concerning how the high surface energy of very small colloidal particles may affect their sorbent behaviour.

Some of the processes by which radioelements may be incorporated into colloidal particles (i.e. removed from sorption equilibrium with the solid phase) have been described conceptually. However, there is only very limited understanding of the operation of such processes in practice. With regard to de-sorption / sorption reversibility, the following points may be made. There is strong evidence for irreversibility of sorption from both laboratory and natural analogue studies, but not in all cases. Parameters that reversibility of sorption appears to depend upon include:

- sorption mechanism;
- radioelement;
- substrate;
- groundwater;
- redox conditions;
- colloid concentration; and
- age of sorption complex.

Sorption kinetics play a most important role here, and there is generally a lack of knowledge concerning sorption kinetics, especially the frequently-observed slow kinetics of de-sorption processes.

12.2 Current understanding of potential impact of colloids in the geosphere

The potential importance of CFRT in the geosphere remains an open question in disposal concepts in a hard rock geosphere due to significant gaps in the understanding of colloid behaviour in deep groundwater systems and at particular sites under investigation. Due to these gaps in understanding, colloids have rarely been included in reference case scenarios for PA, but have tended to be treated in alternative scenarios. The exception to this is in the recent Yucca Mountain TSPA-LA undertaken in the US [517] (see section 11.6), although in that case the host geological environment is very different to those under consideration in the UK..

Where geosphere colloids have been treated in PAs or assessment-type calculations, a consistent picture has emerged concerning their potential impact, which depends crucially on the reversibility of the association of radionuclides with colloids.

If sorption is assumed to be reversible and that colloid uptake by carrier colloids is not more than about 3 orders of magnitude higher than onto rock surfaces, even if colloids are assumed to be mobile and unretarded by interactions with the rock matrix, CFRT will not have a significant impact on radiological risk (compared to dissolved transport) at colloid concentrations typically measured in deep groundwaters (up to 1 mg L^{-1}).

Colloids may have an impact on risk if some radionuclide-colloid associations are irreversible. In this case, the potential impact depends on the amounts of radionuclides irreversibly associated with colloids, the mobility of those colloids in groundwater (e.g. are they removed or retarded by filtration or attachment to the rock) and the lifetime of such colloids as a distinct entity. It is expected that any one colloidal particle will have a distinct lifetime before its dissolution or growth/aggregation with other particles, subsequent sedimentation or filtration by the rock and potential incorporation into the solid matrix.

Clearly, the impact under an “irreversible-sorption to colloid” scenario is difficult to quantify due to lack of knowledge concerning the extent of sorption irreversibility, for which radionuclides it is important, colloid mobility and particle lifetimes. Thus, where this scenario is considered, it has been necessary to make cautious assumptions concerning colloid behaviour [e.g. 499, 520] It should be noted, however, that the same processes that may lead to irreversible incorporation of radionuclides onto colloids will also occur onto the rock matrix, and (in the absence of colloids) this would have a significant effect in retarding the transport of radionuclides compared to a reversible sorption dissolved transport case. Given the importance of the reversibility of sorption behaviour to the potential impact of colloids, some further sensitivity analyses would help to bound the problem and identify the key factors that may impact on risk.

In summary, for colloids to have a significant impact on risk compared to dissolved transport for a hard rock geosphere, it is necessary to make cautious assumptions concerning colloid behaviour. Given our current knowledge, it is not possible to rule out these cautious scenarios and thus the potential impact of colloids remains an open issue.

In the case of a geosphere comprising low-permeability sedimentary rocks, where transport is diffusion-controlled, colloids are expected to have very limited mobility through the fine-scale porosity of the host rock. On the grounds of the effective barrier function of these rock types to colloid transport [e.g. 21], geosphere colloids have been screened out from further consideration in a number of PAs/disposal concepts (e.g. Project Opalinus Clay [279] and SAFIR-II [515]) at an early stage of the assessment. Should further hydrogeological investigations indicate regions of fracture flow, however, the treatment of colloids would need to be re-evaluated [21].

12.3 State of development of data gathering

12.3.1 Introduction

In the field of deep groundwater colloid studies, the attitude of ‘do what we can do’ rather than ‘do what is required of us by the PA modellers’ appears to remain dominant, some two to three decades after the relevant questions were asked. Thus it is often seen to be enough in a site characterisation or field or natural analogue study to simply define the colloid concentrations and make-up, rather than taking the next step and assessing the actual relevance of these colloids in overall transport processes. As such, it is recommended that PA programmes more directly drive data collection efforts in deep research boreholes and influence moves towards integrated studies of colloidal sized material (i.e. including microbes/viruses/organics) in deep groundwaters.

Currently, there is a lack of integration of colloid studies in the overall site characterisation process and this is often reflected in the fact that the host rock, and more specifically the flow system, is underdefined from the viewpoint of the (colloid) transport modeller. Appropriate flow system data are also missing from the vast majority of all laboratory (and many field) experiments. This is especially critical if transferability of the data (from laboratory to field, for example) is to be assessed – and even more so if a claim for transferability is to be made.

12.3.2 State of development of colloid sampling methodologies and characterisation techniques

As noted in section 4, the primary obstacles to quantification of far-field colloids populations in the geosphere of a GDF are:

- appropriate groundwater sampling techniques;
- effective (i.e. artefact-free) colloid separation (from the groundwater); and
- adequate characterisation of the samples.

To some extent, the first point may seem strange, considering that, as an industry, we have been collecting groundwater samples from research-oriented boreholes for several decades. Unfortunately, this is to ignore the massive difficulties which still exist in obtaining pristine groundwater samples in deep boreholes. Routinely sampling groundwaters for major elements and stable isotopes is generally achievable, but moving on to trace elements and certainly to redox-sensitive species is much more problematic. Added to this is the fact that sampling for colloids (and microbes) is often seen to be of low priority and, consequently, are often added almost as an afterthought.

To improve this situation, the following are recommended.

- Standardised groundwater sampling methodologies that enable collection of representative groundwater samples for colloid analysis should be established. This should be agreed internationally to allow better comparison of colloid data sets from different host rock/groundwater types within different national programmes. In the first instance, this will require another benchmarking exercise, some two decades after the last one in the Grimsel URL, but this time a deep borehole would be a more appropriate site (see comments below).

- Effort be invested in the further development of *in situ* colloid separation techniques. Although there has been a significant improvement in colloid separation techniques in the last decade, there is no doubt that transporting groundwater to the place of analysis, even if that is only by pumping from depth to the borehole wellhead, greatly increases the chances of inducing artefacts.

- Effort be invested in the further development of *in situ* colloid analytical methods. Here, attention could be focused on four areas:

    - greater awareness of environmental issues has meant the investment of more funding in the field of surface water/shallow groundwater colloid research and the novel practices being adopted here should be followed more closely by the deep groundwater colloid research community with an eye to transferring the more relevant methods to the deep groundwater systems of interest;

    - closely tracking analytical developments in the field of nano-technology where commercial pressures are forcing a rate of change in analytical methodology several times greater than in the field of environmental colloids;

    - more investment in analysis of colloids by methods which avoid (or at least minimise) any handling and separation steps – for example, LIBD, ESEM, etc;

    - planning an integrated system of groundwater sampling, colloid separation and colloid analysis before beginning any analysis of deep groundwater colloids because the ranges in the measurable attributes of colloids in a single sample can be usually expected to be greater than the working range of any single technique.

- Better integration of colloid studies with other aspects of deep groundwater hydrochemistry, in particular definition of the flow system's redox state and microbial/viral/organic populations. In too many national programmes, these themes are assessed in parallel, but separate, working areas, so missing the direct connections which exist between them

12.3.3 Field and URL studies

While laboratory studies are obviously necessary to gain a mechanistic understanding of the various processes involved in colloid transport in deep groundwaters, the lack of clear evidence of transferability of these data to the *in situ* environment means that any overall understanding of colloid transport properties still depends on data from full-scale studies, be they in field or natural analogue programmes.

Numerous data sets for deep groundwater colloids now exist worldwide and they cover a respectable range of environments, both of rock and groundwater types. However, although a wide range of colloid populations, covering six orders of magnitude, have been reported in the literature, there is, as yet, no comprehensive mechanistic understanding to explain this range. For example, it has been evident for some time that the groundwater ionic strength plays a significant role in colloid stability (and, hence, concentrations), but newer data suggest that this relationship is probably only part of the overall picture. Unfortunately, the general lack of the appropriate information on the flow system means that the wider understanding necessary for PA is still absent.

In the case of URL studies, it is recommended that repository host rock-relevant studies be carried out. For example, while experiments such as CFM are a move in the right direction, they are still looking at systems which are much more dynamic than in a repository system - as noted in section 9, more appropriate flow velocities of 0.1 to 1 m yr^{-1} are required. Obviously, this implies very long experimental time scales, needing decades before anything of worth could be measured. This would require novel experimental set-ups, with ‘install and walk away’ systems being the order of the day.

For example, to study radionuclide transport including CFRT in fractured rock, a borehole could be drilled in a suitably quasi-stagnant fracture, a contaminant source containing non-sorbing, sorbing and colloid tracers (preferably non-radioactive to minimise safety procedures) emplaced downhole and the borehole sealed and left in peace for several decades. After a suitably long period of time, the site could be immobilised (e.g. by the injection of resin) and over-cored to examine colloid-associated transport. This is the simplest form and variants could include a series of sources which could be extracted for analysis every decade or so or another with observation boreholes downstream from the emplacement borehole where very small samples of groundwater could be taken every few years to assess colloid transport.

Indeed, a perfect model already exists in the UK with the Rothamsted Research Centre in Harpenden. Founded in 1843, Rothamsted started the first of a series of long-term field experiments almost immediately, some of which continue to this day. These so-called "*Classical Field Experiments*" [521] were begun with the main objective of measuring the effect on crop yields of inorganic and organic fertilisers and are an increasingly valuable experimental resource for today's researchers.

Unfortunately, although proposed in the past for radioactive waste programmes, similar long-term experiments have not proven easy to implement, being eroded by experimenters’ (and funders’) desires to see something for their effort more immediately. While this is perhaps understandable, it remains fundamentally flawed as the requirement to obtain repository-relevant data also requires repository-relevant scales, both temporal and spatial (see also comments in sub-section 9.2.2(c))

As no URLs are currently available in the UK, collaboration with other national programmes’ facilities or, perhaps more appropriately, to develop experimental ‘niches’ in existing tunnels in the UK – salt mines, transport tunnels in granite, clay workings etc etc could all be utilised for a minimum of cost. In both cases, no massive infrastructure is required and, after the initial outlay of effort and funding, the nature of the experiment will require very little care and maintenance if properly designed. More importantly, they will deliver data on colloid-associated contaminant transport in relevant systems over relevant timescales and within the implementation phase of any likely future repository. Clearly any such experiment will be, to a degree, site specific (if not host rock and groundwater type specific), but collaboration on similar experiments in other national programmes would ensure a spread in rock types examined.

12.3.4 Natural analogue studies

That natural analogue studies promise much but often deliver less is not a novel observation. However, natural analogues remain the only likely source of a full test of both colloid transport models *per se* and PA models of colloid-associated transport of radionuclides. For example, it seems likely that, in more recent site characterisations, enough data exist to fully define both the flow system and the deep groundwater chemistry in sufficient detail to test part of the models. Unfortunately, any colloid data tend to be little more than spot values, both in the spatial and temporal sense and so do not easily lend themselves to model testing. It requires a good analogue site to make all the data on:

- colloid mobility;
- colloid stability;
- radionuclide uptake; and
- irreversibility of that uptake;

fully available for the modellers.

Several examples have been presented in sections 5 and 9, but most extant colloid data sets are more like those collected in a site characterisation than in a truly appropriate natural analogue. The one striking exception is that of the Morro do Ferro where an unique site provided the chance for researchers to follow colloid-associated radionuclides (and REEs) from a point source (the ore body – see Figure 9.6) along the flow system to the surface. The results clearly indicated that colloid-associated transport of radionuclide does not take place, but the seasonal nature of the ore body saturation means that this is not a wholly relevant test of colloid transport models (although it does add qualitative support to the PA).

Nevertheless, the study did show that the approach is fundamentally sound and that it only requires an appropriate natural analogue to work. Several potential sites exist in the UK, but it should be emphasised that, to ensure that the system is studied in a relevant manner, input from colloid transport modellers is required from the beginning.

12.4 State of development of modelling approaches and treatment in PA

12.4.1 Modelling of colloid behaviour in the geosphere

Interpretative modelling activities reviewed in this report have concerned the treatment of colloid stability, colloid mobilisation, colloid transport behaviour in fractured and porous media and the modelling of CFRT.

The long-standing DLVO theory of colloid stability provides a sound basis for the semi-quantitative understanding of colloid stability behaviour and also provides a framework for understanding colloid attachment and detachment behaviour from solid surfaces. It also provides an explanation for understanding the role of colloid stability in controlling colloid populations in a wide range of groundwater systems, and in particular the role of the divalent cation concentration in controlling the rate of colloid aggregation. The theory does have limitations for predicting rates of colloid aggregation, particularly when these are low, based as it is on simple models of uniform regular particles interacting in simple electrolyte systems. In practice, where required, colloid aggregation rates need to be measured.

The DLVO approach also provides a quantitative understanding of the transition between conditions of unfavourable and favourable attachment to surfaces in natural systems at high ionic strength due to suppression of repulsive electrostatic interactions between like-charged particles and surfaces. However, the failure of the DLVO theory to predict non-negligible particle attachment rates to surfaces under unfavourable conditions has been a long-standing question in colloid science. Progress was made during the mid-1990s in recognising the potential importance of surface chemical heterogeneities in natural systems on deposition behaviour which provides an explanation for some of the transient deposition behaviour observed in experiments.

As noted above, recent research has clarified the nature of retention mechanisms by which colloids may be captured in porous media under unfavourable conditions, which helps to explain the reasons for the failure of “classical” modelling approaches. In particular, visual observation of colloid deposition behaviour has revealed the importance of particle capture by wedging at grain contacts and in secondary minima at stagnation points in the flow field around particles under unfavourable attachment conditions [173]. This new understanding of retention behaviour is considered to be amenable to trajectory analysis by particle tracking methods and offers the potential for the development of correlation equations to describe particle deposition under unfavourable conditions, similar to those developed for modelling deposition under favourable conditions. This is expected to be an area of significant research activity over the next 5-10 years.

At present, there is a significant gap between the predictive modelling capability of colloid transport and CFRT behaviour and the results of experiments. Owing to the difficulties in modelling colloid deposition behaviour *a priori*, the approach that has been followed on a number of programmes has been to develop simple filtration models to fit experimental data with a view to developing understanding, obtaining parameters under a range of conditions and if possible developing a predictive capability. However, even relatively simple models have often been found to be difficult to apply in a consistent manner to colloid transport data (let alone CFRT data which adds an extra layer of complexity). One of the major obstacles has been a lack of knowledge of the flow systems in most experiments; such knowledge is essential if fitted parameters are to be transferred and upscaled for predicting colloid behaviour in the field. The quality of the data (signal to noise levels) has also been an issue on some occasions. In addition, the actual mechanisms of particle capture have not been known.

At the present time, it is not envisaged that a predictive modelling capability for CFRT will be required. Rather, simpler tools to enable an assessment of the potential implications of colloids are considered to be appropriate at this stage. If such assessment calculations indicate that a more detailed understanding of CT and CFRT behaviour in the geosphere and an interpretative modelling capability are required, then there will be a requirement to design and undertake well-characterised experiments to provide suitable data for model testing. Ideally, such experiments should cover a range of length-scales and flow geometries as well as flow rates, colloid types and chemical conditions.

12.4.2 Treatment of geosphere colloids in PA

The treatment of geosphere colloids in a number of recent assessments has been reviewed as part of this study. The principal conclusions concerning these PA treatments can be summarised as follows.

In a number of assessments the effects of colloids are argued to be negligible, either through qualitative arguments or limited quantitative scoping calculations. Examples of qualitative screening arguments include the presence of high ionic strength groundwaters (SKB, POSIVA) or the limited mobility of colloids in clay host rocks (ANDRA, ONDRAF).

With the exception of studies at Yucca Mountain, those assessments that do consider the potential impact of colloids do so by defining a variant scenario. In the Yucca Mountain TSPA-LA, transport of colloids is an intrinsic part of the main saturated zone flow model.

In general, quantitative treatment of geosphere colloids in PA remains rudimentary. The effects of colloids are commonly incorporated into effective sorption coefficients (and other parameters, where appropriate) that treat both solute and colloid transport in combination. This approach enables a treatment of colloid transport to be implemented in existing transport codes, albeit with effective parameters. The exception to this approach was in the SKI study using the COLLAGE-II code, which separates transport in solution and transport attached to colloids.

Of the PAs considered, only supporting studies for Nirex 97 and the recent Yucca Mountain TSPA –LA have taken account of irreversible sorption of radionuclides to colloids. The SKI studies took account of sorption of radionuclides to both mobile and immobile colloids.

In general, the effects of geosphere colloids on radiological risk are considered to be negligible when association of radionuclides with colloids is assumed to be reversibile. However, if sorption to colloids is irreversible, then there may be an impact on risk.

As discussed in section 12.2, the current gaps in knowledge concerning the reversibility of sorption to colloids, colloid mobility and colloid particle lifetimes mean that it is very difficult to quantify the potential impact of colloids when accounting for the possibility of irreversible sorption, without making highly cautious assumptions concerning likely colloid behaviour. To help bound the problem and identify the key parameters and parameter ranges that are significant, a sensitivity study of the impact of irreversible sorption under various conceptual scenarios for scenarios would be timely. This might consider the effect of varying sorption/desorption kinetics (to colloids and rock), colloid retardation and particle lifetimes on radiological risk. One approach may be to develop insight models to compare potential risks arising under different situations. The results of such a study would help to direct research on the key areas of uncertainty and the timescales which are most important.

A general strategy for treating colloids in future PAs undertaken by NDA is proposed in a separate report [63].

12.5 Outstanding questions, priorities and approaches to study

The potential impact of colloids in the geosphere on the safety of a GDF will be dependent on the geology of the site selected. Colloids will need to be considered in PA for a facility located in a fractured hard rock where the fractured rock extends to the surface or is overlain by hard rock sedimentary cover, where transport is dominated by advection with groundwater flow. In the case of a GDF located in a low permeability sedimentary rock, where transport is predominantly diffusion controlled, the rock itself is likely to provide an effective barrier to colloid migration provided that there is no significant groundwater flow in fractures.

Thus, the principal outstanding questions and priorities for future study are concerned with the understanding and treatment of colloids and colloid-facilitated radionuclide transport in a hard rock geosphere.

The principal uncertainty concerning the potential impact of geosphere colloids is the reversibility of radionuclide-colloid interactions. Geosphere colloids may have an impact on risk if some radionuclide-colloid associations are irreversibile. In this case, the potential impact depends on the amounts of radionuclides irreversibly associated with colloids, the mobility of those colloids in groundwater (e.g. are they removed or retarded by filtration or attachment to the rock) and the lifetime of such colloids as a distinct entity. It is expected that any one colloidal particle will have a distinct lifetime before its dissolution or growth/aggregation with other particles, subsequent sedimentation or filtration by the rock and potential incorporation into the solid matrix. The finite lifetimes of colloid particles and interactions of colloids with rock surfaces are expected to mitigate the transport of colloids bearing irreversibly-associated radionuclides. However, given the gaps in current understanding concerning these processes, a cautious approach is required and the potential impact of colloids remains something of an open question.

The priority for a future programme to investigate the role of colloid-facilitated transport in the geosphere is to address the lack of understanding concerning the reversibility of radionuclide-colloid interactions. We propose the following approach to address this question initially:

- Undertake a review of the reversibility of radioelement-mineral interactions that will consider the question of the reversibility of sorption, co-precipitation and other processes by which radioelements may associate with mineral phases, including colloids, that will consider the topic in greater depth than has been possible in this review or the previous review of colloids in a cementitious near field.
- Undertake sensitivity calculations of the effect of key parameters on risk associated with irreversible or time-dependent sorption processes; this might be accomplished by incorporating the effects of colloids and time-dependent processes (sorption, dissolution, surface attachment and detachment) into insight models.
- From the results of these activities, key radioelements for which time-dependent sorption processes may be important and key aspects of colloid behaviour will be identified for more detailed study in an experimental programme.

In general, slow desorption kinetics tend to be observed with some of the most strongly sorbing radioelements such as plutonium (as plutonium(IV)) [e.g. 411] for which measured Rd values onto colloids typically are large. Studying desorption kinetics for these systems is difficult because radioelement concentrations in solution even at equilibrium are always low and may be significantly lower than the amount sorbed. One possible approach to study desorption would be to investigate sorptive partitioning in three-phase systems, e.g. with colloids, solution and a solid phase that would act as a sink for the sorptive that was pre-loaded onto the colloids (or vice verse). Such an approach would more closely resemble possible behaviour in real systems and would also assist the design and interpretation of CFRT experiments.

If one or more sites in the UK with a fractured host rock and/or hard rock cover sequences are investigated as part of a site selection/characterisation process, it is anticipated that characterisation of groundwater colloid populations will be necessary to demonstrate understanding of the possible contribution of geosphere colloids to radiological risk. For other potential site lithologies, it may not be necessary to study groundwater colloids if it can be demonstrated that transport is diffusion-dominated and that advection with groundwater flow would not be a significant process. The following recommendations are made concerning future site-specific colloid studies:

- There is a need to establish standardised groundwater sampling methodologies that enable collection of representative groundwater samples for colloid analysis. Ideally, this should be agreed internationally to allow better comparison of colloid data sets from different host rock/groundwater types within different national programmes. It is envisaged that this would require another benchmarking exercise, some two decades after the last one in the Grimsel URL, but this time a deep borehole would be a more appropriate site.
- There is a need for better integration of colloid studies with other aspects of deep groundwater hydrochemistry, in particular definition of the flow system's redox state and microbial/viral/organic populations. It is recommended that plans for colloid characterisation studies are built into the design of the site characterisation programme at the outset and are not treated as an optional add-on to be considered later.
- Future studies should utilise analysis methods that avoid or at least minimise handling and separation steps that may introduce artefacts – for example LIBD, SPC, ESEM and AFM. In addition, effort should be invested in the further development of *in situ* colloid separation techniques.
- An integrated process of groundwater sampling, colloid separation and colloid analysis should be designed before beginning any analysis of deep groundwater colloids because the ranges in the measurable attributes of colloids in a single sample can be usually expected to be greater than the working range of any single technique.

A key topic for further research identified in other programmes concerns release of colloids from the bentonite buffer and potential for severe erosion of the bentonite, that would compromise its key safety related features. This key area of uncertainty is being addressed in a number of URL studies worldwide. It is recommened that NDA RWMD should collaborate with these international studies if the use of bentonite buffer is adopted in the concepts for HLW and SF disposal.

13 Conclusions

13.1 Current understanding of the potential impact of colloids in the geosphere

There is general recognition that colloid facilitated radionuclide transport (CFRT) by inorganic colloidal particles may potentially occur in deep groundwaters in hard (fractured or porous) rocks of relevance to the geological disposal of radioactive wastes, where transport is dominated by advection with flowing groundwater. CFRT is potentially important for radioelements of low solubility that will also sorb strongly to mineral surfaces (such as thorium, americium or plutonium (as plutonium(IV)) whose retardation through the geosphere may be reduced by association with mobile colloids.

In the case of a low-permeability sedimentary rock (such as mudrocks), where transport is predominantly diffusion controlled, the rock itself is expected to provide an effective barrier to colloid migration and CFRT is not anticipated to be an issue, provided that there is no significant groundwater flow in fractures.

To date, there is little concrete evidence for the long-distance transport of inorganic colloids or for CFRT in deep groundwater systems. However, due to significant gaps in the understanding of colloid behaviour in deep groundwater systems and the interactions of radioelements with colloids, the potential importance of CFRT in the geosphere comprising hard rocks remains an open question. Thus, at the present time, colloids need to be considered in performance assessments for disposal concepts in a hard rock geosphere, and key uncertainties need to be addressed.

This review has focused on the behaviour of inorganic colloids in the geosphere because mineral colloids are expected to be the predominant colloid types in deep groundwaters in hard rocks where concentrations of natural organic species are expected to be low. Detailed discussion of the behaviour of natural organic colloids has been beyond the scope of this report, although the interactions of organic material with inorganic colloids have been included where these are potentially important to the behaviour of inorganic colloids in the geosphere. It should be noted, however, that natural organic colloids (predominantly humic materials) are chemically persistent and mobile in the geosphere and may potentially be more significant than inorganic colloids as vectors for facilitating radionuclide transport in deep groundwaters if there is a deep source of fossil organic material (such as the brown coal sands found at Gorleben in Germany).

The current understanding of the potential impact of inorganic colloids on the safety of a GDF is that at the levels of mobile colloids measured in deep groundwaters in hard rocks (< 1mg dm^{-3}), assuming cautious values for sorption distribution coefficients onto colloids and cautiously assuming that colloids are mobile and advected with groundwater flow, without retardation, the impact of colloids will be negligible if radionuclide sorption onto colloids can be treated as reversible.

The principal uncertainty concerning the potential impact of geosphere colloids is the reversibility of radionuclide-colloid interactions. Geosphere colloids may have an impact on risk if some radionuclide-colloid associations are irreversibile. In this case, the potential impact depends on the amounts of radionuclides irreversibly associated with colloids, the mobility of those colloids in groundwater (e.g. are they removed or retarded by filtration or attachment to the rock) and the lifetime of such colloids as a distinct entity. The finite lifetimes of individual particles and the interactions of colloids with rock surfaces are expected to mitigate the transport of colloids bearing irreversibly-associated radionuclides. However, given the gaps in current understanding concerning these processes, a cautious approach is appropriate.

The processes by which radioelements may associate with colloids include physical and chemical adsorption processes (ion exchange and surface complexation) at particle surfaces, which are expected to be in thermodynamic equilibrium over transport timescales, and processes such as co-precipitation by which radionuclides may be absorbed into colloidal particles and removed from thermodynamic equilibria for a prolonged period. In the context of the post-closure performance of a GDF, the timescales of importance when considering the reversibility of radionuclide interactions with colloids are significantly longer than those accessible in laboratory experiments. Laboratory studies can give insight into the short-term reversibility of radionuclide-mineral interactions under a range of experimental conditions. However, processes working on longer timescales can only be investigated through the study of natural geochemical systems, and this is not straightforward.

The priority for a future research is to address the current limited understanding of the reversibility of radionuclide-colloid interactions. A combination of a more detailed review of the reversibility of radioelement-mineral interactions and sensitivity analysis of key parameters that may impact on risk for various ‘irreversible sorption to colloids’ scenarios (using scoping models, for example) is suggested as an initial step to address this issue. It is envisaged that the results of these activities would help to design an experimental programme to address sorption reversibility for key radioelements and other key areas of uncertainty in colloid behaviour.

For a GDF located in a hard rock, characterisation of groundwater colloid populations (alongside organic, viral and microbial populations) will be necessary to demonstrate understanding of the possible contribution of geosphere colloids to radiological risk. Such colloid characterisation studies will need to be properly integrated into the site characterisation programme and this will require significant effort to install dedicated geochemistry boreholes suitable for groundwater colloid sampling and analysis. It is clear from review of current practices, that there is a need to standardise groundwater sampling methodologies internationally that will enable collection of representative groundwater samples for colloid analysis and provide good quality colloid data. This would allow better comparison of colloid data sets from different host rock/groundwater types from different national programmes. It is envisaged that this would benefit from another benchmarking exercise, some two decades after the last one in the Grimsel URL, but this time a deep borehole would be a more appropriate site.

Future groundwater colloid studies should utilise analysis methods that avoid or at least minimise handling and separation steps that may introduce artefacts – for example LIBD, SPC and ESEM. The further development of *in situ* colloid separation techniques should be considered. It is recommended that an integrated process of groundwater sampling, colloid separation and colloid analysis should be designed before beginning any analysis of deep groundwater colloids because the ranges in the measurable attributes of colloids in a single sample can be usually expected to be greater than the working range of any single technique.

It is not yet possible to model colloid transport and CFRT behaviour predictively in small-scale laboratory experiments. Even relatively simple models have been found to be difficult to apply in a consistent manner to colloid transport data, let alone CFRT experiments which add another layer of complexity. One of the major obstacles has been a lack of knowledge of the flow systems in most experiments. A predictive modelling capability would demand significant effort to design and undertake well-characterised experiments to provide suitable data for model testing. Overall, this represents a significant experimental challenge However, it is not envisaged that a predictive modelling capability is required, rather simpler tools to enable an assessment of the potential implications of CFRT are considered to be appropriate. A number of experimental approaches to investigate radionuclide transport and the significance of CFRT in long term and natural analogue experiments have been proposed in this report to support such an assessment approach.

A key topic for further research identified in other national programmes concerns release of colloids from the bentonite buffer in HLW/SF concepts. Not only may released colloids act as carriers for radionuclides released from waste packages but also there is the potential for long-term erosion of the buffer that might eventually compromise its key safety-related features. To date, there is limited data concerning colloid release rates from bentonite in contact with flowing groundwater and no clear assessment has been made concerning the potential significance of the process. This key area of uncertainty is being addressed in a number of URL studies worldwide. It is recommended that NDA RWMD should consider collaborating with these international studies if the use of a bentonite buffer is adopted in the UK concepts for HLW and SF disposal.

A number of URL experiments and supporting studies concerned with colloids are in progress worldwide (e.g. at Äspö) and it is recommended that NDA RWMD should keep a watching brief on these studies.

13.2 Current understanding of colloid behaviour in the geosphere

Current understanding of colloid behaviour in the geosphere can be summarised as follows:

- A wide range of colloid concentrations in crystalline rocks, covering over six orders of magnitude in mass terms (from $<10^{-5}$ to 10 mg dm^{-3}), has been reported in the literature. In general, mobile colloid concentrations in natural, undisturbed deep groundwater systems with low organic content are quite low and less than 1 mg dm^{-3}.

- The composition of colloids reflects the local composition of the rock (predominantly silica, primary silicates and secondary alteration phases (clay minerals)), which display low solubility in groundwater.

- The wide range of colloid concentrations measured in deep groundwaters reflects the significant variations in salinity between systems studied, varying from low ionic strength waters in high alpine regions to higher ionic strength coastal groundwaters, where colloids are destabilised and measured populations are very low. The latter is likely to be more typical of a potential disposal site in the UK. An inverse correlation has been observed between the composition of the groundwater, particularly in terms of the concentration of divalent ions, and the colloid number populations, with lower populations at higher ionic strength. Other factors that may also play a role in determining colloid stability and dispersed colloid concentrations include pH, the mineralogy of the colloids, local flow rate and rate of weathering of the rock (i.e. the rate of *in situ* colloid generation) and the presence of natural organic materials that may sorb onto and stabilise colloids.

- Due to the large amount of organic materials in the UK waste inventory, organic materials leached from an ILW disposal facility could, if sufficiently persistent and present in significant concentration, stabilise and enhance colloid populations in the far field. However, any effect is likely to be of secondary importance to the effect of these materials on radioelement sorption due to complexation, but this remains an uncertainty.

- On thermodynamic grounds, cementitious colloids leached from an ILW part of a facility are not expected to be chemically stable but are expected to dissolve on migration from the high pH near field to the lower pH far field, however, this process has yet to be demonstrated experimentally. In addition, there is uncertainty concerning the formation, nature, stability and mobility of colloids in the ADZ of the host rock adjacent to the repository.

- Near-field colloids are expected to be generated by the degradation of spent fuel and vitrified HLW. However, they are not expected to migrate into the geosphere in the presence of an intact bentonite buffer, if this is included in the disposal concept. The bentonite buffer will act as an effective filter for all but the smallest sized particles of the colloid population. This possibility has yet to be fully investigated experimentally.

- There is evidence for slow desorption kinetics of radioelements associated with colloids from both laboratory and natural analogue studies, but not in all cases. Evidence to date appears to indicate that the reversibility of sorption interactions depends on a range of factors including the mechanism of the interaction, the radioelement, the mineral phase, the composition of the groundwater, redox conditions, colloid concentration and the age of the sorbed species. Generally, there is a lack of data concerning sorption and desorption kinetics.

- There is evidence from field and URL experiments that silica colloids may be mobile over distances of up to 17m in fractured rocks. However, this tends to be at significantly higher flow rates than would arise in deep groundwaters. Both silica and bentonite colloids show a clear reduction in mobility with increasing residence time (lower flow rate), increasing particle size and ionic strength of the groundwater. Bentonite colloids were found to be essentially immobile through a granite block at the high ionic strength of Äspö groundwater (0.14 mol dm^{-3}).

- A clear understanding of the nature of the interactions between groundwater colloid types and natural fracture surfaces has yet to be obtained; it is not yet clear whether colloid capture is associated with straining at constrictions, attachment to mineral heterogeneities or particular physical features of the fracture surfaces (such as wedging at grain contacts, steps or dislocations).

- To date only one clear example of long-distance transport of inorganic colloids in deep groundwater has been reported in the literature, at the Menzenschwand uranium prospect in Germany. In that case, colloids originating from a different rock type 1-5 km away were identified by their trace metal signature. However, as groundwater was extracted at high flow rate through relatively wide fractures (1-10 cm) and the groundwater ionic strength was low promoting colloid stability, conditions were far from those expected in a deep groundwater.

- Definitive examples of CFRT are also scarce. A number of field examples from US nuclear sites have been reported in which low solubility radioelements have been found associated with colloidal fractions in groundwaters, but where the actual mechanisms of transport cannot be unambiguously identified (alternatives include explosive injection in nuclear tests and association with complexants). In addition, these observations have been made either in shallow systems or, at the Nevada Test Site, in a highly disturbed system, under conditions which are far removed from those expected in a deep groundwater.

- Natural analogue studies of uranium and thorium transport from ore bodies have to date been largely unsuccessful in demonstrating long-range transport of the radioelements in inorganic colloidal form.

13.3 Key recommendations

The key recommendations of this review can be summarised as follows:

- Characterisation of groundwater colloid (along with natural organic) populations will be necessary to demonstrate understanding of the possible contribution of geosphere colloids to radiological risk. Such colloid characterisation studies need to be properly integrated into a site characterisation programme from an early stage.

- In preparation for future site characterisation studies, NDA RWMD should work with other waste management organisations internationally to develop standardised groundwater colloid sampling protocols to enable collection of representative groundwater samples for colloid analysis.

- In addition, NDA RWMD should consider investing in the development and application of improved colloid analysis techniques, in particular in the use of *in situ* techniques for colloid separation.

- The priority for future research is to address the current limited understanding of the reversibility of radionuclide-colloid interactions. A combination of a more detailed review of radioelement-mineral interactions and a sensitivity analysis of key parameters in assessment-type calculations is suggested as an initial step. The results of these activities would help to design a focused experimental programme.

- NDA RWMD should consider collaborating with international studies concerned with colloid release from a bentonite buffer, if its use is adopted in UK disposal concepts.

- NDA RWMD should keep a watching brief on the outcome of colloid studies on other national and international programmes. This would enable NDA RWMD to optimise its research activities cost-effectively and maintain a consistency of approach internationally.

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Appendix I
Colloid generation from cementitious materials

Contents

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A1.1 Colloids in a cementitious near field

Current understanding of colloid populations that may be formed in the near-field of a cementitious repository for ILW/LLW was reviewed recently [A1.1]. Table A1.1 provides a summary of the principal results from experimental studies of colloid generation identified in that review.

The main sources of information come from laboratory experimental programmes that have been concerned with colloid generation from cementitious materials under consideration as either backfill materials or waste encapsulation grouts [A1.2-A1.8]. These will be the predominant materials in a cementitious repository in terms of volume and mass and were identified from early review studies as potentially important sources of near-field colloids. Most of these experimental programmes have involved batch leaching tests in which cured cementitious materials in the form of granules or intact samples have been leached in a solution of selected initial composition (ranging from demineralised water to simulated saline groundwaters) for periods ranging from days to several years. In one dynamic leaching test, leachate samples were taken from a column of crushed mortar through which a mortar-equilibration water was flowing [A1.7,A1.8]. Further information is available from the results of colloid analyses of leachates from a number of equilibrium leach tests (ELTs) undertaken by Nirex [A1.12-A1.14] and Nagra [A1.9-A1.11], which combined waste and cementitious materials and in each case ran for about 7 years, and from studies of the cementitious natural analogue site at Maqarin in Jordan [A1.15].

Table A1.1 Comparison of existing data on near-field cementitious colloids

Material/Study	Methodology	Population Size Range Studied (nm)	Colloid Population Ranges (dm^{-3})	Comments
3:1 PFA/OPC granule leaching experiments [A1.2] plus see discussion in [A1.3]	Leaching of crushed PFA/OPC in NRVB- and simulated saline NRVB-equilibrated water at solid to liquid ratios (g cm^{-3}) of 1:5 and 1:50 for 1 week	15-1000	10^{10} -2 × 10^{11}	Particles predominantly silica, 300-500 nm in size, appeared to be agglomerates of smaller particles.
NRVB granule leaching experiments [A1.3]	Leaching of crushed NRVB in demineralised water at solid to liquid ratios (g cm^{-3}) of 1:5, 1:10 and 1:50 for 41 days at ambient	15-1000	4 - 5 × 10^{10} (all three S/L ratios)	Colloids sampled from leachate with minimal agitation of sample. Results for lowest S/L ratio considered to be overestimated due to counting bias from high magnification prints.
NRVB monolith leaching experiments [A1.3, A1.4]	Leaching of cut square-faced sticks of cured NRVB in demineralised water at initial solid to liquid ratios (g cm^{-3}) of 1: 5.25, 1:10 and 1:42.5	15-1000	36 days $<10^{11}$ 12 mths $<7 \times 10^{10}$ 18 mths $<1.1 \times 10^{11}$	Estimated populations are upper limits that include very small (<50 nm) artefact particles on TEM grids. The NRVB-derived colloid populations were estimated to be < 10^{10} dm^{-3}.
Continuation of NRVB monolith leaching [A1.5]	After 24 months S/L ratios were 1:4.4, 1:8.8, 1:34.8 g cm^{-3}	>50	S/L 4.4 $3.6 \pm 1.4 \times 10^{10}$ 8.8 $8.8 \pm 2.8 \times 10^{10}$ 34.8 $5.6 \pm 5.0 \times 10^{10}$	Analysis by SEM reduced problems with artefact particle formation. Artefact particle levels reduced to values equivalent 10^{10} dm^{-3} or less depending on sample volume used.
NRVB monolith leaching (continued) [A1.5]	After 31 months S/L ratios were 1:2.8, 1:6.5, 1:23.9 g cm^{-3}	>50	S/L 2.8 $5.1 \pm 0.5\ 10^{10}$ 6.5 $1.6 \pm 0.3\ 10^{10}$ 23.9 $1.0 \pm 0.3\ 10^{10}$	Results after 31 months potentially enhanced due to sampling by decanting. Results are for 5 μm pre-filtered samples.

Material/Study	Methodology	Population Size Range Studied (nm)	Colloid Population Ranges (dm^{-3})	Comments
NRVB monolith leaching (continued)	After 34 months S/L of initially 1:5.25 experiment was 1.7 g cm^{-3}		1.7 3.2 10^9	
CRIEPI batch leaching studies [A1.6]	Pulverized samples of High Flyash and Silica fume-content Cement (HFSC) hydrate were leached in low-salinity groundwater at three S/L (1:5, 1:50 and 1:100 g cm^{-3}), at 20 and 60 °C for durations of ~2 and 8 months.	15-1000	10^{11} – 10^{12} (for 1:50 and 1:100 S/L ratios)	Analysis by TEM. Colloids have same composition as HFSC.
PSI batch leaching experiments [A1.7, A1.8]	Leaching of crushed PZHS monocorn mortar (2-4mm diameter) or quartz aggregate with cement pore waters, solid:liquid ratio of 1:10 g cm^{-3}	$\geq$ 100 100-1000 100-1000	0.7 – 3.4x10^{11} 0.2 – 6.2x10^{10} 2.0 – 8.0x10^{8}	‘Total colloid’ concentration measured 1 minute after end-over-end mixing of a batch system. ‘Undisturbed colloid’ concentration measured after leaving batch system undisturbed for 24 hours. Steady state colloid’ concentration measured after leaving batch system undisturbed for 150 - 200 days (following agitation for 180 – 330 days). No significant differences between M1 and quartz aggregate or leachate.

Material/Study	Methodology	Population Size Range Studied (nm)	Colloid Population Ranges (dm^{-3})	Comments
PSI batch leaching experiments in presence of ISA [A1.7]	Leaching of crushed PZHS M1 monocorn mortar (2-4mm diameter) or quartz aggregate with cement pore waters and Na-isosaccharinic acid (ISA), solid:liquid ratio of 1:10 g cm^{-3}	50-1000	M1 2.2 (+/-0.3)x10^{11} Quartz 3.4 (+/-0.2)x10^{11} M1 6.2 (+/-0.2)x10^{10} Quartz 1.4 (+/-0.2)x10^{10} M1 8.0 (+/-3.5)x10^{8} Quartz 4.5 (+/-2.6)x10^{8}	'Total colloid' 'Undisturbed colloid' 'Steady state colloid' No significant differences with ISA present.
PSI column experiments [A1.7]	Leaching of crushed M1 mortar in a column with cement pore waters (populations measured at the top of the column are above those at the bottom (*in italics*))	50-1000	Week 1 7.1×10^{9} *1.8×10^{10}* Week 4 4.4×10^{9} *5.5×10^{9}* Week 12 2.4×10^{9} *2.2×10^{9}*	Colloids sampled at the top and bottom of the column. High flow rate of 10 mL min^{-1} means complete column porewater replacement approximately every 36 hours. *NB Background colloid mass in stock leachate of 0.002 mg dm^{-3} (very close to analytical limit)*
Nagra/BGS microcosm experiments [A1.9, A1.10, A1.11]]	Incubation cells containing simulated waste, containment and backfill materials in synthetic groundwater. S/L = 1:330 g cm^{-3}	15-	average 5x10^{9}	Constantly stirred system. Colloid populations collected on 15 nm pore size ultrafiltration membrane.
Nirex combined waste ELTs [A1.12, A1.13, A1.14]	Two 30 dm^{3}-scale experiments using representative proportions of real ILW, encapsulation grouts and NRVB operated for 6 years at 50°C and then 9 months at ambient.	100-5000	< 2 10^{9}	Estimated upper limit in equilibrium leachates after 3 months storage following completion of the tests (based on low resolution SEM).

Material/Study	Methodology	Population Size Range Studied (nm)	Colloid Population Ranges (dm^{-3})	Comments
	ELT1 S/L ratio = ~1:1 g cm^{-3} at start Solids 53% NRVB, 36% grout by weight	100-5000	ELT1 8 10^8 ELT2 4 10^8	Measured populations in equilibrium leachate after 15 months storage
	ELT2 S/L ratio = ~1:2 g cm^{-3} at start Solids ~8% NRVB, 69% grout by weight	100-5000	<10^{10}	Estimated upper limit in equilibrium leachates at the end of tests based on recovery of deposited material from containers after 15 months storage
Maqarin natural analogue study [A1.15]	Collection of groundwater at the cement/host rock interface	N/R-1000	1.0-5.0 x 10^{10}	Cement leachate travels through fractures in the cement, so data representative of fractured EBS (and may include erosion-derived colloids).

Notes:

ELT = Equilibrium leach test
HFSC = High Flyash and Silica fume-content Cement
NRVB = Nirex Reference Vault Backfill
N/R = Not recorded
OPC = Ordinary Portland Cement
PFA = Pulverised Fuel Ash
PZHS = High Sulphate Resistance Portland Cement (NAGRA M1 monocorn mortar)
S/L = Solid to liquid ratio (g cm^{-3})

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Appendix 2
Colloid generation from vitrified waste

Contents

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A2.1 Introduction

In the UK, high level waste arising from the reprocessing of nuclear fuel (principally Magnox but also oxide fuel) is being incorporated into borosilicate glass for long-term immobilisation, a process termed vitrification. Reprocessing involves the dissolution of spent nuclear fuel in concentrated hot nitric acid and the extraction of the remaining uranium and plutonium. The arising highly-active waste liquor (HAL) is stored in stainless steel tanks prior to treatment. The HAL requires conversion to a solid form for interim storage and long-term disposal.

Vitrification involves melting of waste materials with glass-forming additives so that the waste is incorporated into the micro- and macro-structure of the glass [A2.1]. The waste constituents are immobilised either directly by incorporation into the glass structure or by encapsulation. The Magnox vitrification process involves first calcining the waste to produce a granular product in a rotary calciner. The waste is then mixed with crushed glass in a furnace to produce a molten product incorporating up to 25% waste by weight. The molten glass is then poured into 150 litre stainless steel canisters and allowed to cool before a stainless steel lid is welded on. To date nearly 650 cubic metres of vitrified HLW (HLW) have been produced, and the resulting 4,300 canisters placed in an air-cooled store [A2.2].

One of the illustrative disposal concepts under consideration for the disposal of UK HLW [A2.3] is similar to that under consideration in a range of other countries (e.g. France [A2.4], Japan [A2.5]) in which steel containers containing HLW would be surrounded with a bentonite buffer at depth in a suitable geological formation. The exception to this approach internationally is in the USA, for the proposed facility at Yucca Mountain, where disposal of HLW canisters is envisaged in tunnels above the water table without a surrounding buffer or backfill [A2.6].

The use of borosilicate glass formulations for HLW immobilisation is widespread internationally due to their good durability and their ability to incorporate a wide range of elements found in typical process waste streams [A2.7]. Some examples of borosilicate glass compositions are given in Table 2.1. Ojovan and Lee [A2.1] provide a useful introductory text on the application of glassy wastforms. A review of the development of the UK HLW vitrified product was undertaken for Nirex in 2006 [A2.8].

Table 2.1 Typical compositions of borosilicate HLW glasses examined worldwide (adapted from [A2.1])

Component	Percentage by weight				
	UK Magnox	France R7/T7	USA, DWPF	Germany-Belgium PAMELA	Russia LILW K26
B_2O_3	16.9	14.9	8.0	13.2	6.6
Na_2O	8.4	10.6	8.7	5.9	23.9
MgO	5.3	-	1.4	2.2	-
Al_2O_3	4.8	4.4	4.0	2.7	3.0
SiO_2	47.2	47.2	49.8	52.7	43
CaO	-	4.1	1.0	4.6	13.7
Misc	17.4	18.8	27.1	18.7	9.8
Waste Loading	≤25	≤28	≤33	≤30	≤35

A2.2 Mechanism of glass leaching and colloid generation

The determining factor for the performance of glass wasteforms is their long-term alteration behaviour in contact with water [A2.9], which controls the kinetics of radioelement release from the wasteform. The general understanding of glass alteration in contact with water can be summarised as follows [A2.1, A2.9, A2.,10].

Initially on contact with water, incongruent dissolution of the glass surface occurs leading to a depletion of the surface layer in more soluble glass components such as alkali metals. This process is controlled by the diffusion of protons (and water) into the glass surface which ion exchange with the soluble cations. Penetration of water molecules into the glass surface also leads to the hydrolysis of the glass network itself and congruent dissolution of the glass. The hydrolysis reactions lead to cleavage of oxygen bridges between the network-forming cations of the glass (principally Si but also Al, B, Zr, etc) and the release of silicate and other metal species into solution. This process leads to the formation of an amorphous gel layer on the glass surface.

As dissolved species diffuse out of the gel layer, supersaturation with respect to mineral phases can arise at the glass-water interface. This leads to reprecipitation of solid phases (often clay minerals) on the glass surface and the formation of an altered precipitation (or alteration product) layer. The composition and properties of the alteration product layer will vary with the compositions of the glass and groundwater, and the temperature. For nuclear waste glasses, the alteration layer may incorporate poorly soluble radioelements leached from the bulk glass either by co-precipitation or adsorption onto the surface of the precipitated mineral phases, which may be retained at higher concentration than in the bulk glass.

In general, the rate of ion exchange decreases rapidly as the surface layers become depleted in soluble cations; the network-hydrolysis process controls glass degradation behaviour in the longer term. The longer-term alteration rate will also diminish with time as the density of the gel layer increases and its porosity decreases. This is thought to create a barrier to the out-diffusion of glass components.

The precipitation processes occurring at the altered glass surface may also lead to the nucleation of colloidal particles in adjacent bulk solution [A2.11] and this process has been observed experimentally [.e.g A2.12, A2.13]. In addition, the mineral phase particles forming the altered surface layer may be spalled into solution [A2.14] leading to the presence of a dispersed colloid population. These colloid particles may incorporate or sorb radionuclides dissolved from the wasteform.

A principal objective of research into the durability of HLW is to understand and predict the long term (or residual) dissolution rate of the glass matrix and the associated leaching rate for immobilised radioelements [A2.10]. For soluble matrix elements (e.g. B) and encapsulated radionuclides (e.g. ^{99}Tc as Tc(VII)), the rate of elemental release is expected to be the same as the matrix dissolution rate [A2.15]]. However, radioelements of lower solubility and that are more strongly sorbing onto surfaces (such as Pu and Am) will incorporate into or sorb onto glass alteration products and their release rates will be significantly lower [A2.15]. Colloid transport may play a role, therefore, in enhancing the release rate of these radioelements from glass wasteforms over long timescales.

A2.3 General procedures for vitrified waste leaching and colloid analysis

Standard tests for determining the aqueous durability of vitrified waste (and other wasteforms) were developed at the Materials Characterisation Centre (MCC) of the Pacific Northwest Laboratory (PNNL), USA [A2.16, A2.17]. These tests have been adopted as the internationally-approved standards. For durability testing, the IAEA has recommended the ISO standard

ISO 6961-1982, which is similar to MCC-1 at room temperature [A2.18]. The most important of these standard tests are outlined in Table 2.2.

Table 2.2 Standard tests for determining the durability of vitrified wasteforms (adapted from [A2.1])

Test	Conditions	Application
ISO 6961, MCC-1	Static leaching of monolithic specimen in deionised water. Sample surface area to volume (SA/V) usually 10 m^{-1}. Open to atmosphere, temperature 25°C (IAEA), 40, 70 and 90°C (MCC-1).	For comparison of wastforms.
MCC-2	Deionised water, temperature 90°C in a closed system.	Same as MCC-1 but at high temperatures.
PCT (MCC-3)	Glass powder stirred in deionised water in a closed system at various temperatures and values of SA/V.	Product consistency test. For durable wasteforms to accelerate leaching.
SPFT (MCC-4)	Single pass flow test in deionised water. Open to atmosphere.	The most informative test giving kinetic leaching parameters for performance assessment.
VHT	Vapour phase hydration test. Monolithic specimen at high temperatures in aclosed system.	Accelerates alteration product formation.

Most laboratory studies of vitrified waste colloid characterisation in the literature have been based on either one of the standard test methodologies outlined in Table 2.2 or modified forms of these tests using more representative water compositions [e.g. A2.19] or in the presence of other near-field components (such as steel corrosion products [e.g. A2.20]). On the US programme, a “drip test” method was designed to simulate the flow of small amounts of water that enter and trickle through a breached waste glass container in an unsaturated repository [A2.14]. Tests have been undertaken on both inactive and radionuclide-doped glasses to study the mechanisms of glass alteration and release rates of radioelements, respectively. It should be noted, that many of the tests (similar to PCT in Table 2.2) are undertaken at elevated temperatures and use crushed glass to provide high surface area to leachant volume ratios (SA/V) to accelerate ageing of the glass surface, and represent conditions far removed from a deep geological repository.

In many of the studies of radionuclide-doped glasses identified in this review that have included an element of colloid characterisation, this has been limited, frequently, to sequential filtration of leachates coupled with chemical/radiochemical analysis [e.g. A2.19, A2.20, A2.21] to measure colloid-associated radionuclide concentrations; relatively little work has been undertaken to identify the colloid species with which radionuclides are associated. More detailed studies of colloid characterisation have been undertaken on the US programme, where the colloids leached from actinide doped-glasses have been studied by TEM [e.g. A2.14, A2. 22]. Nevertheless, despite a significant body of work, next to no quantitative data for colloid populations in terms of mass or number concentrations or particle size distributions has been produced. It is notable that, near-field colloid population data for use in the Yucca Mountain assessment have been characterised in terms of an enhanced plutonium solubility rather than in terms of colloid number concentrations or size distributions [A2.23].

Many of the leaching tests described in the literature is that they are undertaken at elevated temperatures and samples are allowed to cool to room temperature before filtration/colloid analysis. Changes in temperature can lead to supersaturation of solutions with respect to solid phases and induce colloid formation and/or particle growth artificially, thus affecting the results. Though noted by Pirlet [A2.15], this aspect of the methodology does not appear to have been discussed in the literature, and it is difficult to assess its potential significance.

No studies of colloid release from UK HLW have been identified in the open literature for discussion in this review.

A2.4 Results

Table 2.3 summarises the findings of a range of laboratory glass wasteform colloid characterisation studies presented in the literature. There appears to be general agreement that the principal alteration products of borosilicate glasses are phylosilicates (clays) such as smectite, birnessite, saponite, nontrite, etc, [A2.10]; clay particles have been identified as the main colloid types released from waste glasses. However, a wide variety of other mineral phases have also been identified as colloids depending on the composition of the glass, the leachant and the presence of other solid phases (e.g. metals or clay buffer). Mineral phases identified include [A2.24]: weeksite (a uranium(VI) silicate), clay particles with brockite inclusions, aluminium oxides, sodium silicates, absalone ($Si0_{0.2}Ca_{0.2}K_{0.05}MnO_x$), calcite, dolomite, apatite (a calcium phosphate) and zeolites [A2.19]. Uranium has been identified associated with clay particles [A2. 25] in addition to weeksite, and tetravalent actinides have been identified with phosphate phases (brockite, rhadophane) from phosphate containing glasses [A2.14, A2.22]. There is some evidence for the potential formation of actinide polymer colloids under certain conditions [A2.20].

The predominant mode of colloid formation observed depends on the nature of the test [A2.26]. There is clear evidence for the release of particles by spallation from the surface of corroded waste glass in drip tests undertaken to simulate the unsaturated conditions of a US repository in the unsaturated zone at Yucca Mountain [A2.14, A2.26, A2.27]. It has been suggested that this occurs primarily due to erosive forces associated with intermittent flowing water. There is evidence also that the mechanism may operate in static leach tests after prolonged leaching times. For example, Buck and co-workers [A2.25] report weeksite particle release after prolonged leaching times with SRL glasses.

The principal mechanism of colloid formation in static tests is considered to be homogeneous nucleation [A2.12, A2.27]. The variations in colloid concentrations (observed qualitatively) as a function of leaching time [e.g. A2.25] can be ascribed to a combination of glass dissolution, colloid nucleation and colloid aggregation (leading to sedimentation) kinetics. Thus colloid formation is delayed until solution concentrations of leached glass components become supersaturated with respect to secondary phase minerals. There then follows a period of particle nucleation and growth. The stability of the resulting colloidal population is dependent on the ionic strength of the leachate. Continued dissolution of soluble glass components will result in a gradual increase in solution ion strength; this will act, increasingly, to destabilise the colloid population. The greater extent of glass dissolution in high SA/V experiments and faster rise in ionic strength would explain the more rapid disappearance of colloid populations in these experiments than at lower SA/Vs.

In static leaching experiments on lanthanide- and actinide-doped glasses [A2.28], there is clear evidence that trivalent and tetravalent lanthanides and actinides (e.g. La, Ce,Am, Th and Pu) in the leachate are associated with colloidal particles. There is also significant retention of these radioelements in the alteration products on the glass surface. In contrast, pentavalent and hexavalent actinides (e.g. Np(V) and U(VI)) are found as dissolved species with significantly less retention. Association of Np with colloids is enhanced in the presence of magnetite due to the reduction of Np to Np(IV) [A2.20].

Table 2.3 Summary of examples of colloid characterisation studies from leaching of vitrified waste materials

Study	Type of test	Colloid analysis	Results
Bates *et al.* [A2.14] 1992	50-month drip test onto actinide-containing glass (not identified).	Sequential filtration of leachates; filtrate and filter alpha spectrometry analysis; alpha radiography and TEM analysis of filter-deposited material.	>99% of Pu and Am in leachate was retained on filters as colloidal solids; principally with particles on 1 µm pore-size filter. Colloids comprise Na-rich smectite with brockite $(Ca,Th)PO_4.H_2O$ inclusions. Pu and Am was associated primarily with the brockite.
Buck *et al.* [A2.25] 1993 (see also [A2.27]	MCC-1 and PCT type leaching of crushed SRL 200R, 200S and 202U glasses. PCTs at various SA/V in J-13 and DIW for up to >500 days at 90°C in steel vessels.	TEM study of leachate colloids	Leachates of 200R at SA/V 340 m^{-1} after 182 and 364 days contained smectite-like colloids which were not present initially (56 days) or at long reaction times (>500 days). 202U leachates showed lower amounts of colloid at higher SA/V. In general, amount of colloid increased initially but then decreased at longer times. Drop off occurred earlier for higher SA/V. U detected with particles at SA/V ≥ $2000m^{-1}$ in both J-13 and DIW. After >360 days uranyl silicate (weeksite) appeared.
Feng *et al.* [A2.29] 1994	Modified PCT test. Static leaching of SRL 131S and actinide-doped SRL 131A glass in J13 water at 90°C at various SA/V in a closed system. For SA/V 11,400 after 80 days at 90°C, pH 9.1.	PCS, zeta potential and TEM of leachate colloids	Silica-rich clay colloids and needle-like crystals of weeksite (uranium silicate) observed in leachates by TEM. Particle zeta potentials negative at pH > 1, and minimum at pH 6. Colloidal agglomeration and sedimentation observed at room temperature by PCS over 5 days leaving 600-700nm colloids in stable dispersion.

Study	Type of test	Colloid analysis	Results
Fortner *et al*. [A2.26] 1996	Drip tests with J-13 (tuff-equilibrated) groundwater onto DWPF glass (N2 tests) and ATM-10 glass (N3 tests) in 304L stainless steel holder at 90°C in a closed system. Results of periodic sampling after 6-9 years.	Sequential filtration of leachate samples, with filter and filtrate analysis by alpha spectroscopy. TEM coupled with EDS	Examination of top surface of N2 and N3 glasses show cracking and spalling from thick clay alteration layer. Pu and Am releases suggested to jump in association with spallation of the clay. TEM showed smectite-type clay particles with brockite inclusions in N3 tests (but not N2). In both N2 and N3 tests both clay and iron silicates (latter from enhanced corrosion at steel-glass interface) observed, which often contain uranium.
Wei and Van Iseghem [A2.19] 1997	Static leaching of Eu-doped powdered PAMELA glass (SM527) at 40, 90 & 150°C for SA/V = 4000 to 11,500. Leachants included Boom clay water, synthetic interstitial clay water and humic acid-free interstitial clay water. Leaching from 30-180 days in Ar atmosphere (except 150°C). Average leachate pH ~9.3.	Sequential filtration of leachate and analysis of filtrates by ICP-MS for metals and humic acid by spectrophotometry.	Eu leached from glass predominantly as Eu-humate complex (at 40, 90°C). Inorganic colloids composed of Si, Al and Ca also released as zeolite-like phase. Inorganic colloid inventories comprised up to 50% of the total leachate Si and Al at 150°C. Amount of colloids decreases with increased leaching time and at lower temperatures. After 73 days at 90°C the 1.5-450 nm colloid fraction amounts to 36 gL^{-1} of $SiO_2 + Al_2O_3$ which decreased to 19gL^{-1}.after 180 days.
Kohara *et al*. [A2.21] 1997	Static leaching of crushed, waste-doped glass in double distilled water (s/l = 1:10) at 90°C under aerobic conditions for periods of 14, 28 and 775 days. pH 9.3, 9.4 and 9.9 respectively.	Sequential filtration followed by major element and radionuclide analysis of filtrates.	Between 33% and 48% of the Pu, Am, Cm, Eu and Al in the leachates were associated with particles retained on filters between 0.8 µm and 1.5 nm in pore size. Sb, Cs, Li, Na, B, Si and Np showed no significant variation in concentration with filter pore size.

Study	Type of test	Colloid analysis	Results
Inagaki *et al.* [A2.20] 1998	Static leaching of crushed Pu- and Np-doped R7T7-like glass in deionised water at SA/V = 2600 at 90°C for up to 91 days in air or reducing atmosphere with or without magnetite. pH ~9.5.	Sequential filtration followed by major element and radionuclide analysis of filtrates.	Released Pu (up to 5 10^{-8} M) was predominantly associated with fraction of small colloids (1.8-5 nm in size) under all conditions. The presence of magnetite enhances formation of colloids containing Pu and Np.
Buck and Bates [A2.22] 1999.	Static leaching of crushed SRL glasses at 90°C for SA/V = 340, 2000 and 20,000m^{-1} from 3 to 1456 days. pH values (after 100 days): 340m^{-1} pH 9.6 2000m^{-1} pH 10.1 20,000m^{-1} pH 11.5	SEM and TEM coupled with EDX analysis.	The major colloidal phase was a partially crystalline dioctahedral smectite clay. Weeksite (a uranium(VI) silicate), a U-Ti phase, calcite, dolomite and transition metal oxides were also present. Partially crystalline rare-earth bearing calcium phosphate colloids (structurally related to rhabdophane) were found. The clay particles disappeared from solution in SA/V = 20,000m^{-1} tests when the ionic strength reached 0.3-0.5 M, but were stable at lower SA/V.

DIW = Deionised water

DWPF = Defence Waste Production Facility

J-13 water = tuff-equilibrated

SA/V = Surface area to volume ratio

SRL = Savannah River Laboratory

However, the presence of concentrated clay is found to alter significantly glass dissolution behaviour [A2.15]. In particular, bentonite may act as a sink for silicon released from the glass and this has been found to accelerate glass leaching. The clay also acts as a strong sorbent for leached actinides and this leads to reduced actinide retention on the glass compared to pure water. It has been noted that [A2.9]: "*Because of the specific effects of clay (or other Si sinks), glass dissolution in concentrated clay seems fundamentally different from glass dissolution in water or in dilute clay suspensions*." The presence of a low-permeability clay buffer will also tend to act as a barrier to colloid transport..

It is notable that the recent CORALUS II project [A2.30], which has studied the *in situ* alteration of alpha-doped glass samples for up to 10 years in the Mol underground research facility in Belgium, evidence was found for Am and Pu migration in colloidal form in two candidate buffer materials (dried boom clay and bentonite/sand/graphite) surrounding the R7T7 glass matrix. However, this was ascribed to the attachment of Am and Pu to organic (e.g. humate) colloids present in the buffer material. The potential migration of alteration product colloids into the matrix has not been discussed. The position isn't entirely clear, but it is noted that difficulties arose in separating the glass from the buffer for analysis which led to the partial loss of alteration layers in many of the samples.

A2.5 Vitrification of ILW

In addition to HLW vitrification, high temperature processing to a vitrified or slag wasteform is currently of great interest in the UK as an alternative method for immobilising L/ILW for disposal, due to potentially significant volume reductions compared to traditional cement grouting methods. Currently, the disposability of vitrified ILW in a cementitious repository is under consideration and recently NDA RWMD has funded experimental work to study the interactions of vitrified waste simulants with a cementitious environment. This study will include an analysis of colloid generation during glass alteration under alkaline conditions. Results from this work are expected to be published in 2011.

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Appendix 3
Colloid Generation and Migration from Spent Fuel

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A3.1 Colloid Generation and Migration from Spent Fuel

A literature survey using the INIS database with the query: ‘colloid* And spent And fuel’[1], yielded 105 references, of which 12 were considered relevant to the present topic. A further four that had not included these keywords in their abstracts are also included. These are summarised below.

A recent study [A3.1] determined how far the properties of clay influenced the dissolution of spent fuel. Experiments were carried out with UO_2 in the presence of either compacted dry Ca-bentonite or compacted dry Boom Clay with Boom Clay groundwater. The uranium concentration after 0.45 µm filtration was 50 times higher in the Boom Clay with Boom Clay water than in Ca-bentonite with Boom Clay water. The authors believe that this difference was probably due to colloid formation in the Boom Clay system.

An analysis has been made of available colloidal data from waste form corrosion tests at Argonne National Laboratory [A3.2], extracting characteristics of these colloids that can be used in modelling their contribution to the source term for sparingly soluble radioelements. Specifically, the focus was on developing a useful description of the following waste form colloid characteristics: (1) composition, (2) size distribution, and (3) quantification of the rate of waste form colloid generation. This information was intended to support analysis of the potential transport of the sparingly soluble radionuclides associated with the waste form colloids and their concentrations. Data were interpreted to address mechanisms controlling colloid formation and stability. The data analyses and conclusions that are presented in this report were based on small-scale laboratory tests conducted on a limited number of waste glass compositions and spent fuel types.

Studies have included the nature of colloidal materials produced during corrosion of metallic uranium fuel in simulated groundwater at elevated temperature in an unsaturated environment [A3.3]. Colloidal analyses of the leachates from these corrosion tests were performed using dynamic light scattering and transmission electron microscopy. Results from both techniques indicated a bimodal distribution of small discrete particles and aggregates of the small particles. The average diameters of the small, discrete colloids were approximately 3-12 nm, and the larger aggregates had average diameters of approximately 100-200 nm. X-ray diffraction of the solids from these tests indicated a mineral composition of uranium oxide or uranium oxyhydroxide. A later programme [A3.4] found spherical UO_2 and nickel-rich montmorillonite colloids from the corrosion of uranium metal fuel at 90ºC. Eventually the uranium colloids were oxidised forming filaments that settled, leaving predominantly clay colloids.

Laboratory studies have also shown that the corrosion of metallic uranium fuel with groundwater generates significant quantities of stable colloids [A3.5]. The authors believed that this observation is important in the light of the finding of rapid subsurface transport of radionuclides at the Nevada Test Site via colloids [A3.6]. Accordingly, they believe that characterization of colloids generated by fuel corrosion is necessary for assessing the long-term fate and transport of radionuclides in a repository environment. In an earlier study [A3.7], two well-characterized types of spent fuel were subjected to testing with simulated groundwater at 90ºC. The actinides present in the leachate were determined at the end of two successive periods of approximately 60 days. Both colloidal and soluble actinide species were detected in the leachate. The uranium phases identified in the colloids by transmission electron microscopy were schoepite and soddyite. The actinide release behaviour of the two fuels appeared to vary. Both the total amount of material released and the relative amount of each isotope released were found to be different for the two fuels.Similar studies [A3.8] testing UO_2 pellets with simulated groundwater

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[1] The * character is used as a wildcard in INIS searches to represent all permutations of letters. In this case it will return all references with the root colloid- (i.e. colloid, colloids, colloidal, etc).

at 90ºC over time periods of up to 10 years have been undertaken. Only a very small quantity of released uranium was present in a colloidal form.

The characterisation of colloids from the corrosion of aluminium-based fuels has been reported [A3.9]. The colloids were predominantly clays >100nm, carrying 99% of released uranium but whose concentration never exceeded a value well within the range of values used in the repository release models.

The formation and stability of colloids has been analysed in spent-fuel and HLW-glass leaching studies, in container corrosion tests and in precipitation experiments [A3.10]. The amounts of colloidal species determined by ultrafiltration were highest for tetravalent elements. They were high in solutions of low ionic strength such as simulated granitic groundwaters and at pH-values higher than 7. Experiments carried out in saturated brines showed much lower concentrations of colloids. Corrosion of container material also contributed to the formation of colloidal material consisting mainly of Fe(II/III) species. Their stability in brines has been found to be very low. At high ratios of the waste surface area to the solution volume, higher colloid concentration fractions were detected, indicating a dependency of colloid formation on dissolution kinetics. Considerable concentrations of ultra-filterable fractions were found for some actinides also in solutions of very high ionic strength. These were unstable as the total concentration of dissolved and colloidal fractions in general decreased with time. From all these findings, colloid formation from waste forms in rock salt near-field conditions is not expected to be relevant.

A report evaluated continuous dissolution and colloid formation during spent-fuel performance under repository conditions in high-level waste disposal [A3.11]. Various observations suggested that re-precipitated layers formed on spent-fuel surfaces may not be protective. This situation could lead to continuous dissolution of highly soluble radionuclides. For low-solubility actinides, processes regarding colloid formation have been analysed, including condensation, dispersion, and sorption. At the time of writing (1996), the author believed that because there were only limited data available on matrix dissolution, colloid formation, and solubility limits, many uncertainties still existed and that these uncertainties had to be addressed before the significance of radionuclide releases could be determined.

The effects of carbonate concentration in aqueous media on UO_2 oxidation/dissolution rates under an alpha beam irradiation in a cyclotron have been studied [A3.12]. Nanometre-sized UO_2 particles were used and were shown to be well crystallized UO_2. In the absence of carbonate, dissolution rates of UO_2 were found to be much lower than the rate of consumption of H_2O_2, produced by water radiolysis. In the presence of carbonate, the rates were similar. In the latter case, after oxidation, the uranium was complexed with carbonate. UO_2 oxidation and dissolution were connected as sequential reactions. At low carbonate concentrations, dissolution was found to be slower than oxidation, whereas at high carbonate levels, dissolution was immediate.

Dissolution rates of unirradiated UO_2, UO_2 doped with ^{233}U, and spent fuel under normal atmospheric conditions and under reducing conditions have also been studied [A3.13]. Batch tests conducted under reducing conditions showed evidence of colloidal material in the early solution samples. Early testing of the ^{233}U-doped materials under reducing conditions showed relatively rapid (30 minute) dissolution of small amounts of U. Results of analyses of an acidified fraction of the same solutions after 1 or 2 weeks holding indicated that the solutions were inhomogeneous, indicating the presence of colloidal material or small grains of solid.

An ‘in-package’ chemistry model has been developed to predict the bulk chemistry inside breached waste package and to provide simplified expressions of that chemistry as a function of time after breach [A3.14]. The packages include both spent fuel and vitrified HLW. The model outputs are linked to principal factors such as dissolved concentrations of radionuclides and colloid generation. The ability of models to predict the impact of colloid-facilitated transport has been discussed in detail [A3.15]. The authors concluded that by establishing the extreme conditions that result in colloid immobilisation from altered spent fuel, it will be possible to bound the impact of colloids in the case of the proposed US spent fuel / HLW repository.

The overall role of the actinides arising from spent fuel in the long-term safety of waste disposal has recently been reviewed [A3.16]. Specific topics discussed include colloid generation and colloid-facilitated migration.

In Sweden, SKB plans to submit a licence application for the construction of a repository for the disposal of spent nuclear fuel. The relevant Swedish authorities commissioned a team of independent experts to assess and provide comments on SKB's safety reports [A3.17]. SKB identified colloid generation in the buffer and backfill as a process that could have significant effects on the practicality of engineered barrier emplacement and on the long-term performance of the disposal system. SKB has suggested that the uncertainties associated with colloid generation are large. The review group considered that significant uncertainties remained in the understanding of both of these processes and that SKB needed to conduct further work to improve assessments of their effects and plans for their mitigation.

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